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Synthesis and transformations of metallacycles

30.* Aluminacyclopentanes in the synthesis of secondary and tertiary alcohols

L. O. Khafizova, A. G. Ibragimov, D. F. Yalalova, A. L. Borisova,*
L. M. Khalilov, and U. M. Dzhemilev

Institute of Petrochemistry and Catalysis, Bashkortostan Republic Academy of Sciences
and Ufa Research Center of the Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru

A method for the synthesis of secondary and tertiary alcohols was developed. The method is based on cycloalumination of olefins with trialkylalanes in the presence of Zr-containing catalysts followed by the CuCl-catalyzed *in situ* reaction of the corresponding aluminacyclopentanes with aldehydes or ketones.

Key words: olefins, cycloalumination, trialkylalanes, aluminacyclopentanes, catalysis by CuCl, aldehydes, ketones, secondary and tertiary alcohols.

According to the published data,[2—4] cycloalumination of olefins with trialkyl- or alkylhaloalanes in the presence of Zr-containing catalysts (Cp_2ZrCl_2, $ZrCl_4$) affords substituted aluminacyclopentanes (ACP) in high yields (80—95%).

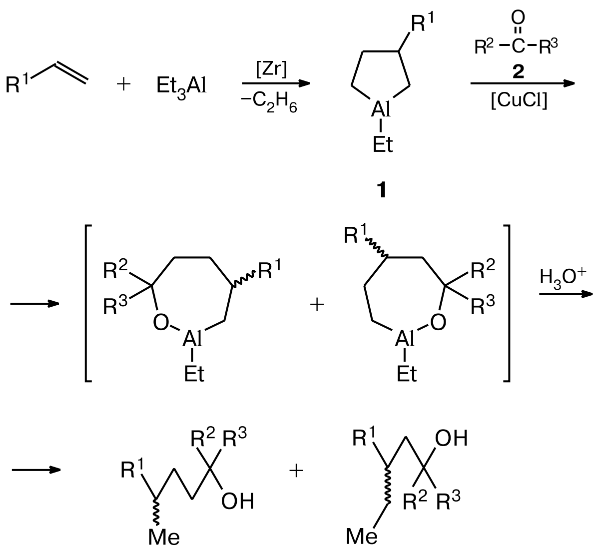
The synthetic value of the proposed reaction substantially increased after the resulting ACP had been found to be easily convertible into practically important thiophanes,[5] selenophanes,[6] cyclopropanes,[7] cyclobutanes,[8,9] 2-vinylalkanes,[10,11] and 2- or 1,2-substituted 1,3-dienes.[3]

In this work, with the aim of developing a new method for the synthesis of secondary and tertiary alcohols from olefins and trialkylalanes, *in situ* catalytic reactions of ACP **1** with aldehydes and ketones **2** in the presence of transition metal salts and complexes were studied.

Results and Discussion

It was found that hydrolysis of the reaction mixture obtained by the reaction of 1-ethyl-3-(*n*-hexyl)aluminacyclopentane[12] with butyraldehyde in the presence of 10 mol.% CuCl at 20—22 °C affords a mixture of four secondary alcohols. These are diastereomeric 7-methyltridecan-4-ols (**3a**) and 6-ethyldodecan-4-ols (**4a**) in a ratio of 55 : 45 (GLC data); the total yield was ~80% (Scheme 1). In both cases, the ratio between diastereomers **3a** and **4a** is ~1 : 1, which follows from the nearly equal integral intensities of the corresponding separate signals in the ^{13}C NMR spectrum.

Scheme 1



3a—f **4a—f**

3, 4	**a**	**b**	**c**	**d**	**e**	**f**
R^1	n-C_6H_{13}	n-C_6H_{13}	Bu^n	Bu^n	n-C_6H_{13}	n-C_6H_{13}
R^2	Pr^n	Ph	Pr^i	n-C_5H_{11}	Et	Me
R^3	H	H	H	H	Bu^n	Ph

In the above reaction, CuCl is most active among the studied complexes and salts of transition metals and rare-earth elements (Cu, Mn, Fe, Co, Ni, Pd, Zr, and Rh), which agrees with the data on addition of zirconacyclopentanes to a carbonyl group in the presence of copper salts.[13] For instance, the use of $PdCl_2$ or $NiCl_2$ instead of

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* For Part 29, see Ref. 1.

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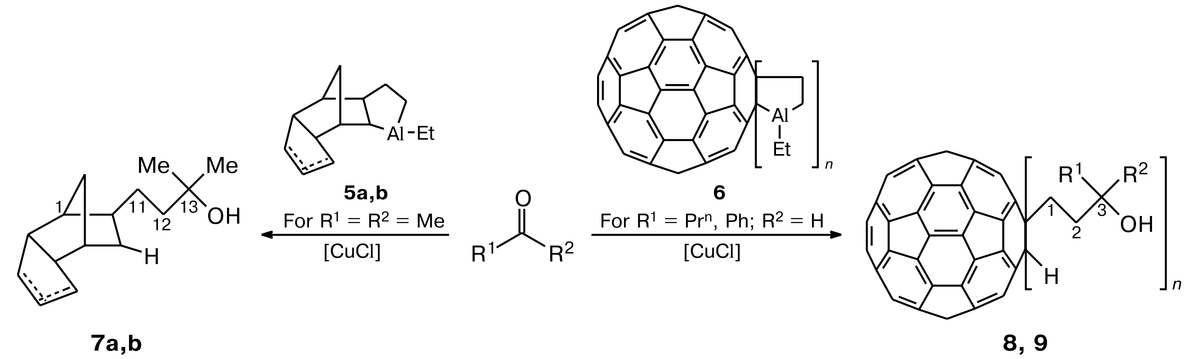
Scheme 2



5, **7**: Δ^4 (**a**), Δ^3 (**b**); **8**: $R^1 = Pr^n$, $R^2 = H$; **9**: $R^1 = Ph$, $R^2 = H$; $n = 1—3$

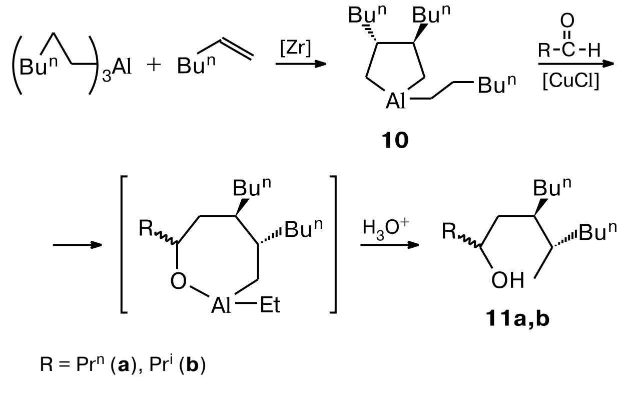
CuCl reduces the total yield of regioisomers **3a** and **4a** to 61 and 40%, respectively. The reaction did not occur at all without a catalyst.

The synthesis of secondary alcohols **3a** and **4a** involving the intermediacy of ACP is of general character. For example, 3-(*n*-alkyl)-1-ethylaluminacyclopentanes react with aldehydes containing alkyl, isoalkyl, and aryl substituents to give alcohols **3b—d** and **4b—d** in 75—85% yields (see Scheme 1). The R^2COR^3 : ACP ratio was 12 : 10 (10 mol.% CuCl).

It was found that ACP are also very reactive toward structurally various ketones, giving the corresponding tertiary alcohols. For instance, the reaction of alkyl and phenyl ketones with 1-ethyl-3-(*n*-hexyl)aluminacyclopentane in the presence of 10 mol.% CuCl (20—22 °C, 8 h) affords mixtures of tertiary alcohols **3e,f** and **4e,f** in the ~3 : 2 ratio; the total yield was ~80% (see Scheme 1).

Addition to a carbonyl group predominantly involves the Al—C bond, which is most distant from the alkyl substituent in ACP. This suggests that the reaction regioselectivity can be significantly enhanced when ACP contains bulky substituents at one of the Al-bonded carbon atoms. This assumption was experimentally confirmed by the reaction of 2,3-disubstituted ACP **5** [14] and **6** [15] with acetone, butyraldehyde, and benzaldehyde (Scheme 2).

Scheme 3



R = Pr^n (**a**), Pr^i (**b**)

Aluminacyclopentanes bearing symmetrically arranged substituents react with aldehydes. For instance, the reaction of *trans*-3,4-di(*n*-butyl)aluminacyclopentane **10** [16] with butyraldehyde or isobutyraldehyde affords a mixture of diastereomeric secondary alcohols **11a** or **11b**, respectively (Scheme 3).

Thus, starting from olefins and aldehydes or ketones, one can obtain various secondary and tertiary alcohols through the *in situ* formation of ACP.

Experimental

The catalyst Cp_2ZrCl_2 was prepared according to a known procedure.[17] Commercial CuCl was used. Solvents were dried immediately before use (over $LiAlH_4$ for hexane and over Na metal for toluene) and distilled. Reactions with organometallic compounds were carried out under dry argon. Commercially available 95% Et_3Al and 88.6% $Bu^i{}_3Al$ (OAO "Redkino pilot plant") were used. Hydrolysis products were analyzed by GLC on a Chrom-5 chromatograph in a helium flow (column 1200×3 mm, 5% SE-30 or 15% PEG-6000 on Chromaton N-AW). HPLC analysis of fullerene-containing alcohols was performed on a Hewlett Packard instrument (model 1050) (column 250×4 mm, Silasorb-600 (8 μm), toluene as the mobile phase; UV detection was at λ = 333 nm). IR spectra were recorded on a UR75 spectrometer (thin film). Mass spectra were recorded on an MX-1306 spectrometer (70 eV, 200 °C). ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90 Q (90 (^1H) and 22.5 MHz (^{13}C)) and Bruker AM-300 instruments (300.13 (^1H) and 75 MHz (^{13}C)) in $CDCl_3$; the spectra were edited with the JMOD procedure. Chemical shifts are given on the δ scale with Me_4Si as the internal standard. The yields of organoaluminum compounds were determined by GLC analysis of hydrolysis products. The mixtures of regioisomers (**3** and **4**) were separated on a Carlo Erba Fractovap Mod. GW preparative gas chromatograph in a helium flow (column 4000×6 mm, stationary phase SE-30). Compounds **7** and **11** were isolated by column chromatography on silica gel L (100—250 μm) in hexane—Et_2O (4 : 1). Compounds **8** and **9** were chromatographed on Al_2O_3 (successive elution with toluene and methanol).

CuCl-catalyzed reactions of 3-alkyl-1-ethyl-ACP with aldehydes and ketones (general procedure). The catalyst Cp_2ZrCl_2 (0.5 mmol), hexane (3 mL), an olefin (10 mmol), and Et_3Al (12 mmol) were placed in a glass reaction vessel under dry argon at 0 °C. The solution was stirred at ~20 °C for 12 h. Hexane (3 mL) and, at –15 °C, CuCl (1 mmol) were added. Then an aldehyde or ketone (12 mmol) was slowly added dropwise. The reaction mixture was stirred at ~20 °C for 8 h and treated with aqueous 8—10% HCl or 15% DCl in D_2O. Products **3** and **4** were extracted with ether or hexane.

7-Methyltridecan-4-ols* (3a). The yield was 44%, R_f 0.48. Found (%): C, 78.02; H, 13.86. $C_{14}H_{30}O$. Calculated (%): C, 78.43; H, 14.10. IR, ν/cm^{-1}: 3380, 2945, 2900, 2850, 1100, 1255, 750. ^{1}H NMR, δ: 0.84—0.93 (m, 9 H, Me); 1.26—1.63 (m, 19 H, CH$_2$, CH); 3.45—3.68 (m, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 14.06 (q, C(13)); 14.09 (q, C(1)); 18.80, 18.84 (t, C(2)); 19.60, 19.72 (q, C(14)); 22.66 (t, C(12)); 26.98, 27.02 (t, C(9)); 29.65 (t, C(10)); 31.92 (t, C(11)); 32.81 (t, C(6)); 32.90, 32.95 (d, C(7)); 34.95, 35.01 (t, C(5)); 36.92, 37.10 (t, C(8)); 39.63, 39.71 (t, C(3)); 72.04, 72.16 (d, C(4)). MS, *m/z*: 196 [M – 18]$^+$.

4-Methyl-1-phenyldecan-1-ols* (3b). The yield was 42%, R_f 0.28. Found (%): C, 81.67; H, 11.08. $C_{17}H_{28}O$. Calculated (%): C, 82.20; H, 11.36. IR, ν/cm^{-1}: 3380, 3050, 3015, 2910, 2840, 1450, 1275, 1085, 1020, 700. ^{1}H NMR, δ: 0.88 (t, 6 H, Me, *J* = 5.9 Hz); 1.24—1.47 (m, 14 H, CH$_2$); 1.65—2.17 (m, 1 H, CH); 4.63 (t, 1 H, C$\underline{\text{H}}$—Ph, *J* = 6.3 Hz); 7.21—7.51 (m, 5 H, Ph). ^{13}C NMR, δ: 14.15, 14.22 (q, C(10)); 19.68 (q, C(11)); 22.74 (t, C(9)); 27.03 (t, C(6)); 29.69 (t, C(7)); 31.97 (t, C(8)); 32.82 (t, C(3)); 33.08 (d, C(4)); 36.46, 36.78 (t, C(2)); 36.91 (t, C(5)); 75.21 (d, C(1)); 125.94 (d, C(15)); 127.50 (d, C(13)); 128.47 (d, C(14)); 144.99 (s, C(12)). MS, *m/z*: 230 [M – 18]$^+$.

2,6-Dimethyldecan-3-ols* (3c). The yield was 43%, R_f 0.50. Found (%): C, 77.05; H, 13.77. $C_{12}H_{26}O$. Calculated (%): C, 77.34; H, 14.07. IR, ν/cm^{-1}: 3350, 2940, 2905, 2840, 1455, 1380, 1020, 715. ^{1}H NMR, δ: 0.83—0.96 (m, 12 H, Me); 1.12—1.58 (m, 13 H, CH$_2$, CH); 3.24—3.52 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 13.96 (q, C(10)); 17.52 (q, C(1), C(12)); 19.66 (q, C(11)); 22.61 (t, C(9)); 30.62 (t, C(8)); 33.28 (d, C(6)); 34.09, 34.33 (t, C(5)); 35.14 (t, C(2)); 36.82, 36.99 (t, C(7)); 38.58 (t, C(4)); 73.26 (s, C(3)). MS, *m/z*: 168 [M – 18]$^+$.

9-Methyltridecan-6-ols* (3d). The yield was 42%, R_f 0.51. Found (%): C, 77.90; H, 13.82. $C_{14}H_{30}O$. Calculated (%): C, 78.43; H, 14.10. IR, ν/cm^{-1}: 3350, 2940, 2905, 2840, 1455, 1380, 1020, 715. ^{1}H NMR, δ: 0.83—0.96 (m, 9 H, Me); 1.12—1.58 (m, 19 H, CH$_2$, CH); 3.36—3.59 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 13.96 (q, C(1), C(13)); 19.55 (q, C(14)); 22.61 (t, C(12)); 23.00 (t, C(2)); 25.34 (t, C(4)); 28.78 (t, C(8)); 29.30 (t, C(11)); 31.97 (t, C(3)); 32.88 (t, C(9)); 33.27 (t, C(7)); 35.29 (t, C(10)); 37.30 (t, C(5)); 71.96 (d, C(6)). MS, *m/z*: 196 [M – 18]$^+$.

5-Ethyl-8-methyltetradecan-5-ols* (3e). The yield was 48%, R_f 0.25. Found (%): C, 79.26; H, 13.86. $C_{17}H_{36}O$. Calculated (%): C, 79.61; H, 14.15. IR, ν/cm^{-1}: 3370, 2950, 2915, 2850, 1470, 1385, 1110, 1065, 680. ^{1}H NMR, δ: 0.79—0.91 (m, 12 H, Me); 1.09—1.31 (m, 22 H, CH$_2$); 1.52—2.01 (m, 1 H, CH); 3.25—3.68 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 10.84 (q, C(16)); 14.22 (q, C(14)); 14.22 (q, C(1), C(14)); 19.81 (q, C(16)); 22.80 (t, C(2)); 23.45 (t, C(13)); 27.16 (t, C(10)); 29.76 (t, C(11)); 32.04 (t, C(12)); 32.10 (t, C(3)); 33.40 (d, C(8)); 34.83, 35.03 (t, C(15)); 37.11 (t, C(4), C(9)); 39.25 (t, C(7)); 41.66 (t, C(6)); 72.94 (s, C(5)). MS, *m/z*: 238 [M – 18]$^+$.

5-Methyl-2-phenylundecan-2-ols* (3f). The yield was 47%, R_f 0.23. Found (%): C, 81.96; H, 11.22. $C_{18}H_{30}O$. Calculated (%): C, 82.38; H, 11.52. IR, ν/cm^{-1}: 3380, 3050, 3010, 2920, 2850, 1445, 1375, 1025, 1065, 765. ^{1}H NMR, δ: 0.68—1.08 (m, 9 H, Me); 1.21—1.47 (m, 14 H, CH$_2$); 1.60—1.79 (m, 1 H, CH); 7.10—7.71 (m, 5 H, CH—Ph). ^{13}C NMR, δ: 14.09 (q, C(11)); 19.61 (q, C(12)); 22.61 (t, C(10)); 27.16 (t, C(7)); 29.56 (t, C(8)); 30.85 (q, C(1)); 31.84 (t, C(9)); 32.95 (t, C(4)); 34.64 (d, C(5)); 36.72 (t, C(6)); 41.46 (t, C(3)); 74.64 (s, C(2)); 124.77 (d, C(14), C(18)); 126.26 (d, C(16)); 127.95 (d, C(15), C(17)); 148.11, 148.31 (s, C(13)). MS, *m/z*: 244 [M – 18]$^+$.

6-Ethyldodecan-4-ols* (4a). The yield was 36%, R_f 0.54. Found (%): C, 78.06; H, 13.92. $C_{14}H_{30}O$. Calculated (%): C, 78.43; H, 14.10. IR, ν/cm^{-1}: 3380, 2945, 2900, 2850, 1100, 1255, 750. ^{1}H NMR, δ: 0.86—0.92 (m, 9 H, Me); 1.26—1.58 (m, 19 H, CH$_2$, CH); 3.48—3.68 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 10.74 (q, C(14)); 14.06 (q, C(12)); 14.10 (q, C(1)); 22.66 (t, C(11)); 22.83 (t, C(2)); 25.54, 26.35 (t, C(13)); 26.58 (t, C(8)); 29.74, 29.80 (t, C(9)); 31.91 (t, C(10)); 33.69 (t, C(7)); 35.53, 35.32 (d, C(6)); 40.39 (t, C(3)); 41.81, 41.89 (t, C(5)); 69.70 (d, C(4)). MS, *m/z*: 196 [M – 18]$^+$.

3-Ethyl-1-phenylnonan-1-ols* (4b). The yield was 35%, R_f 0.36. Found (%): C, 81.96; H, 11.06. $C_{17}H_{28}O$. Calculated (%): C, 82.20; H, 11.36. IR, ν/cm^{-1}: 3380, 3050, 3015, 2910, 2840, 1450, 1275, 1085, 1020, 700. ^{1}H NMR, δ: 0.73—0.84 (m, 6 H, Me); 1.19—1.70 (m, 14 H, CH$_2$); 2.38—2.51 (m, 1 H, CH); 4.47—4.74 (m, 1 H, CH—O$\underline{\text{H}}$); 7.13—7.48 (m, 5 H, Ph). ^{13}C NMR, δ: 10.84 (q, C(11)); 14.15, 14.22 (q, C(9)); 22.74 (t, C(8)); 25.47 (t, C(10)); 26.96 (t, C(5)); 29.82 (t, C(6)); 31.97 (t, C(7)); 33.40 (t, C(4)); 35.35 (d, C(3)); 43.35, 43.42 (t, C(2)); 72.48 (d, C(1)); 125.87 (d, C(13)); 127.24 (d, C(14)); 128.21 (d, C(15)); 145.38 (s, C(12)). MS, *m/z*: 230 [M – 18]$^+$.

5-Ethyl-2-methylnonan-3-ols* (4c). The yield was 35%, R_f 0.57. Found (%): C, 76.96; H, 13.83. $C_{12}H_{26}O$. Calculated (%): C, 77.34; H, 14.07. IR, ν/cm^{-1}: 3350, 2940, 2905, 2840, 1455, 1380, 1020, 715. ^{1}H NMR, δ: 0.83—0.96 (m, 12 H, Me); 1.12—1.58 (m, 13 H, CH$_2$, CH); 3.24—3.52 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 10.70 (q, C(12)); 13.96 (q, C(9)); 17.52 (q, C(1), C(10)); 22.61 (t, C(8)); 26.39, 26.52 (t, C(6)); 26.39, 26.52 (q, C(11)); 29.35 (t, C(7)); 34.75, 34.96 (d, C(5)); 35.09 (t, C(2)); 45.31 (t, C(4)); 71.89 (s, C(3)). MS, *m/z*: 168 [M – 18]$^+$.

8-Ethyldodecan-6-ols* (4d). The yield was 35%, R_f 0.57. Found (%): C, 78.00; H, 13.81. $C_{14}H_{30}O$. Calculated (%): C, 78.43; H, 14.11. IR, ν/cm^{-1}: 3350, 2940, 2905, 2840, 1455, 1380, 1020, 715. ^{1}H NMR, δ: 0.83—0.96 (m, 9 H, Me); 1.12—1.58 (m, 19 H, CH$_2$, CH); 3.36—3.58 (m, 1 H, C$\underline{\text{H}}$—OH). ^{13}C NMR, δ: 10.19, 10.58 (q, C(14)); 13.96 (q, C(1), C(12)); 22.61 (t, C(11)); 23.00 (t, C(2)); 25.34 (t, C(4)); 26.44 (t, C(13)); 29.30 (t, C(10)); 31.97 (t, C(3)); 34.90 (t, C(9)); 36.65, 36.78 (d, C(8)); 38.08 (t, C(5)); 41.66 (t, C(7)); 69.58 (d, C(6)). MS, *m/z*: 196 [M – 18]$^+$.

5,7-Diethyltridecan-5-ols* (4e). The yield was 32%, R_f 0.31. Found (%): C, 79.11; H, 13.85. $C_{17}H_{36}O$. Calculated (%): C, 79.61; H, 14.15. IR, ν/cm^{-1}: 3370, 2950, 2915, 2850, 1470, 1385, 1110, 1065, 680. ^{1}H NMR, δ: 0.76—0.91 (m, 12 H, Me);

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* A 1 : 1 mixture of diastereomers.

1.10—1.32 (m, 22 H, CH_2); 1.52—1.94 (m, 1 H, CH); 3.25—3.65 (m, 1 H, C$\underline{H}$—OH). ^{13}C NMR, δ: 10.84 (q, C(15), C(17)); 14.22 (q, C(1), C(13)); 22.80 (t, C(2)); 23.45 (t, C(12)); 26.34, 26.70 (t, C(14)); 27.22 (t, C(9)); 29.89 (t, C(10)); 32.04 (t, C(11)); 32.04 (t, C(3)); 32.29 (t, C(16)); 33.01 (t, C(8)); 34.84, 35.03 (d, C(7)); 39.25 (t, C(4)); 45.76 (t, C(6)); 73.52 (s, C(5)). MS, *m/z*: 238 [M – 18]$^+$.

4-Ethyl-2-phenyldecan-2-ols* (4f). The yield was 33%, R_f 0.29. Found (%): C, 81.92; H, 11.26. $C_{18}H_{30}O$. Calculated (%): C, 82.38; H, 11.52. IR, ν/cm^{-1}: 3380, 3050, 3010, 2920, 2850, 1445, 1375, 1025, 1065, 765. ^{1}H NMR, δ: 0.76—0.91 (m, 9 H, Me); 1.08—1.40 (m, 14 H, CH_2); 1.62—1.76 (m, 1 H, CH); 7.15—7.51 (m, 5 H, CH—$\underline{Ph}$). ^{13}C NMR, δ: 10.51 (q, C(12)); 14.09 (q, C(10)); 22.61 (t, C(9)); 26.90 (t, C(11)); 26.90 (t, C(6)); 29.56 (t, C(7)); 29.89 (q, C(1)); 31.84 (t, C(8)); 34.12 (d, C(4)); 36.72 (t, C(5)); 48.03 (t, C(3)); 75.67 (s, C(2)); 124.77 (d, C(14), C(18)); 126.26 (d, C(16)); 127.95 (d, C(15), C(17)); 148.11, 148.31 (s, C(13)). MS, *m/z*: 244 [M – 18]$^+$.

CuCl-catalyzed reactions of ACP 5a,b with acetone. The catalyst Cp_2ZrCl_2 (0.5 mmol), hexane (3 mL), *endo*-dicyclopentadiene (10 mmol), and Et_3Al (12 mmol) were placed in a glass reaction vessel under dry argon at 0 °C. The reactions were carried out according to the general procedure.

2-Methyl-4-(tricyclo[5.2.1.0^{2,6}]dec-4-en-8-yl)butan-2-ol (7a) and 2-methyl-4-(tricyclo[5.2.1.0^{2,6}]dec-3-en-8-yl)butan-2-ol (7b). The total yield was 75% (in the ratio ~3 : 1), R_f 0.19. Found (%): C, 81.35; H, 10.73. $C_{15}H_{24}O$. Calculated (%): C, 81.76; H, 10.93. IR, ν/cm^{-1}: 3395, 3030, 1930, 1450, 1380, 900, 720. ^{1}H NMR, δ: 0.66—0.95 (m, 6 H, Me); 1.08—2.48 (m, 15 H, CH_2, CH); 5.48—5.66 (m, 2 H, CH=CH). **$\underline{7a}$**: ^{13}C NMR, δ: 29.24 (q, C(14), C(15)); 31.58 (t, C(3)); 31.97 (t, C(8)); 34.04 (t, C(11)); 34.08 (d, C(9)); 38.41 (t, C(10)); 40.03 (d, C(7)); 42.37 (t, C(12)); 42.51 (d, C(2)); 46.02 (d, C(1)); 52.32 (d, C(6)); 70.99 (s, C(13)); 130.43 (d, C(4)); 132.57 (d, C(5)). **$\underline{7b}$**: ^{13}C NMR, δ: 29.24 (q, C(14), C(15)); 30.67 (t, C(8)); 32.36 (t, C(5)); 34.04 (d, C(9)); 34.08 (t, C(11)); 38.41 (t, C(10)); 41.72 (d, C(7)); 42.37 (t, C(12)); 42.46 (d, C(6)); 44.46 (d, C(1)); 53.69 (d, C(2)); 70.99 (s, C(13)); 130.43 (d, C(4)); 132.57 (d, C(3)). MS, *m/z*: 212 [M – 18]$^+$.

CuCl-catalyzed reactions of ACP 6 with aldehydes. Fullerene[60] (0.025 mmol) in 30 mL of toluene was placed in a glass reaction vessel under dry argon and stirred until C_{60} was completely dissolved. The catalyst Cp_2ZrCl_2 (0.0025 mmol) and Et_3Al (0.75 mmol) were added, and the reaction mixture was stirred for 12 h. Copper(I) chloride (0.01 mmol) was added at –15 °C, and then an aldehyde (0.75 mmol) was slowly added dropwise. The reaction mixture was stirred at ~20 °C for 8 h and treated with a saturated solution of HCl in ether. The products were extracted with toluene, and the extract was chromatographed on Al_2O_3. The products were isolated by successive elution with toluene and methanol.

1-(3-Hydroxyhexyl)-2-hydrofullerene[60] (8). The yield was 78%. Found (%): C, 92.07; H, 3.96. $C_{60}C_{18}H_{42}O_3$. For $n = 3$ calculated (%): C, 91.21; H, 4.12. IR, ν/cm^{-1}: 3350, 2950, 2880, 1570, 1520, 1460, 1520, 1460, 1380, 1280, 1245, 1090, 1030, 720, 530 (fullerene). ^{1}H NMR, δ: 0.89 (m, 3 H, Me); 1.21—1.58 (m, 6 H, CH_2); 3.38 (m, 1 H, C$\underline{H}$—OH); 2.22—2.36 (m, 2 H, C_{60}—CH_2); 6.40 (s, 1 H, C_{60}—H). ^{13}C NMR ($CDCl_3$, CS_2), δ: 14.10 (q, C(6)); 21.14 (t, C(5)); 33.22 (t, C(4)); 36.39 (t, C(2)); 37.04 (t, C(1)); 71.73 (d, C(3)); 120.21—157.65 (m, C_{60}).

1-(3-Hydroxy-3-phenylpropyl)-2-hydrofullerene[60] (9). The yield was 70%. Found (%): C, 91.65; H, 3.03. $C_{60}C_{18}H_{42}O_3$. For $n = 3$ calculated (%): C, 92.54; H, 3.21. ^{1}H NMR, δ: 2.22—2.31 (m, 2 H, CH_2); 2.89 (m, 2 H, C_{60}—CH_2); 4.38 (m, 1 H, C$\underline{H}$—OH); 6.09 (s, 1 H, C_{60}—H); 7.09—7.59 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, CS_2), δ: 31.12 (t, C(2)); 41.01 (t, C(1)); 66.24 (d, C(3)); 126.26 (d, C(6), C(8)); 127.76 (d, C(7)); 128.21 (d, C(5), C(9)); 140.57 (s, C(4)); 121.88—156.20 (m, C_{60}).

CuCl-catalyzed reactions of ACP 10 with aldehydes. Tris(*n*-hexyl)aluminum[18] synthesized from $Bu^i{}_3Al$ (12 mmol) and hex-1-ene (36 mmol) was placed in a glass reaction vessel under dry argon at 0 °C. Then, hex-1-ene (10 mmol) and Cp_2ZrCl_2 (0.5 mmol) were added, and the reaction mixture was stirred at ~20 °C for 12 h. The reactions were carried out according to the general procedure.

6-Butyl-7-methylundecan-4-ols* (11a). The yield was 78%, R_f 0.36. Found (%): C, 79.02; H, 13.88. $C_{16}H_{34}O$. Calculated (%): C, 79.26; H, 14.14. IR, ν/cm^{-1}: 3385, 2950, 2915, 2865, 2840, 1475, 1385, 1155, 1020, 910, 720, 690. ^{1}H NMR, δ: 0.72—1.02 (m, 12 H, Me); 1.21—1.53 (m, 18 H, CH_2); 1.76—2.15 (m, 2 H, CH); 3.48—4.01 (m, 1 H, C$\underline{H}$—OH). ^{13}C NMR, δ: 14.02 (q, C(1), C(11), C(15)); 18.77, 18.96 (q, C(16)); 22.61 (t, C(2)); 23.00 (t, C(10), C(14)); 29.89 (t, C(9)); 30.02, 30.15 (t, C(12)); 31.71, 31.85 (t, C(13)); 33.01, 33.73 (t, C(8)); 36.13, 36.33 (t, C(3)); 37.50, 38.02 (d, C(6)); 38.47, 38.99 (d, C(7)); 39.77, 40.62 (t, C(5)); 69.49, 70.14 (d, C(4)). MS, *m/z*: 224 [M – 18]$^+$.

5-Butyl-2,6-dimethyldecan-3-ols* (11b). The yield was 76%, R_f 0.33. Found (%): C, 78.89; H, 13.86. $C_{16}H_{34}O$. Calculated (%): C, 79.26; H, 14.14. IR, ν/cm^{-1}: 3380, 2950, 2920, 2870, 2845, 1480, 1385, 1150, 1020, 900, 720, 680. ^{1}H NMR, δ: 0.72—0.94 (m, 15 H, Me); 1.12—1.47 (m, 14 H, CH_2); 1.87—2.11 (m, 2 H, CH); 3.28—3.53 (m, 1 H, C$\underline{H}$—OH). ^{13}C NMR, δ: 14.02 (q, C(10), C(14)); 16.49, 17.27 (q, C(1), C(15)); 18.83, 19.03 (q, C(16)); 23.00 (t, C(9), C(13)); 29.89 (t, C(8)); 30.08 (t, C(12)); 31.12 (t, C(11)); 33.34, 33.92 (t, C(7)); 34.05, 34.25 (d, C(2)); 34.51, 35.09 (d, C(5)); 38.15 (d, C(6)); 39.45 (t, C(4)); 74.43, 75.02 (d, C(3)). MS, *m/z*: 224 [M – 18]$^+$.

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* A 1 : 1 mixture of diastereomers.

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