Synthesis and transformations of metallacycles
31.* Catalysts based on cobalt complexes in reactions of trialkyl- and alkylhaloalanes with olefins, allenes, and acetylenes

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Cobalt-containing complexes capable of catalyzing reactions of trialkyl- and alkylhaloalanes (R_nAlCl_{3-n}) with olefins, allenes, and acetylenes were synthesized. The reactions afford cyclic and acyclic organoaluminum compounds.

Key words: catalysis; hydro-, cyclo-, carbo-, and dialumination; organoaluminum compounds; olefins; cobalt complexes; deuterolysis.

Reactions of hydro-, carbo-, and cycloalumination of unsaturated compounds by trialkyl- and alkylhaloalanes are known[2,3] to occur in the presence of Ti- or Zr-containing catalysts. The use of metal complexes of other transition metals as catalysts has not been described.

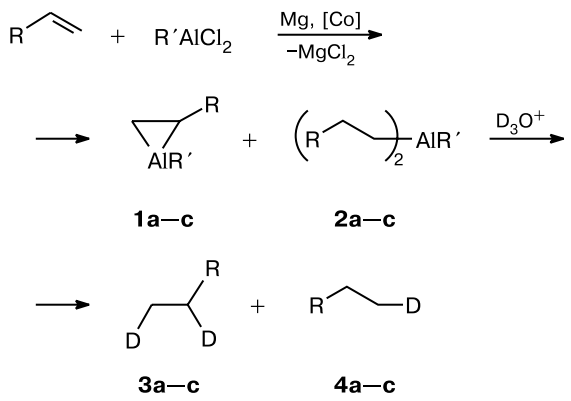
In this work, with the purpose of searching for new catalytic systems for these reactions and reactions of organoaluminum compounds (OAC) with olefins, dienes, and acetylenes, we studied the reactions of trialkyl- and alkylhaloalanes with unsaturated compounds in the presence of the Fe, Co, Ni, Pd, Rh, Ir, and rare-earth metal (Pr, Ho, Gd) complexes, which are most widely used in reactions of olefins and dienes.

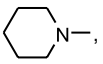
Results and Discussion

It has been established for the reaction of styrene with $EtAlCl_2$ that in the presence of metallic magnesium, which acts as an acceptor of chloride ions, cobalt phosphine complexes ([Co]) catalyze cyclo- and hydroalumination ($CoCl_2$: Ph_3P = 1 : 2, 10 mol.%, 20—21 °C, 8—10 h, THF) to form OAC **1a** and **2a** in a ratio of ~1 : 3 in an overall yield of ~70% (Scheme 1). The structures of the products of deuterolysis **3a** and **4a** were proved by spectroscopic methods and comparison with authentic compounds.[4,5]

For studying the catalytic activity and structural selectivity of the cobalt phosphine complex, we investigated the reactions of $EtAlCl_2$ with *o*- and *p*-methylstyrene. Under the chosen conditions, we obtained OAC **1b,c** and **2b,c** in a ratio of ~1 : 3 in an overall yield of ~65%. In addition to OAC **1** and **2**, regioisomeric 2,4- and 2,5-diarylalumacyclopentanes are formed,[6] whose overall yield does not exceed 15%.

Scheme 1



R = Ph (**a**), *o*-Tol (**b**), *p*-Tol (**c**); R´ = Et, Et_2N,  , MeO, Bu^nO

[Co] = $CoCl_2$ + 2 Ph_3P, $Co(acac)_2$ + 2 Ph_3P

It is assumed that the precursors of 2-aryl-1-ethylalumacyclopropanes **1** in these reactions are cobaltacyclopropane intermediates, which were previously identified in the cyclodimerization of acetylenes with nitriles.[7] The intermediate cobalt hydride complexes can be responsible for the formation of acyclic OAC **2**. These intermediates are formed under the reaction conditions *via* the mechanism analogous to that proposed previously[8] for the synthesis of titanium hydride complexes.

When $EtAlCl_2$ is replaced by $R´AlCl_2$ (R´ = Et_2N, 1-piperidyl, MeO, Bu^nO) in the reaction with styrene

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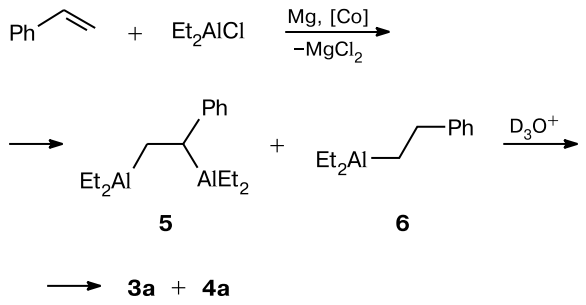
(10 mol.% $CoCl_2$+Ph_3P, THF, 20—21 °C, 8—10 h), heterocyclic and acyclic OAC **1a** and **2a** are formed in a ratio of ~1 : 4 in an overall yield of 60—65%.

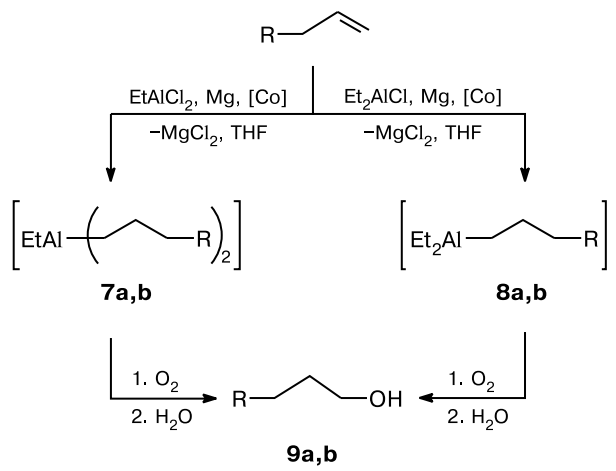
The reaction of styrene with a twofold excess of Et_2AlCl in the presence of Mg and 10 mol.% of the cobalt phosphine complex $CoCl_2$+Ph_3P (THF, ~20 °C, 8 h) afforded 1-phenyl-1,2-bis(diethylaluminio)ethane (**5**) and 1-phenyl-2-(diethylaluminio)ethane (**6**) in a ratio of ~2 : 3 in an overall yield of ~75%. The structures of these compounds were established by the deuterolysis products (Scheme 2). Regioisomeric diphenyl-1,4-dideuteriobutanes (5—12%) were identified along with 1-phenyl-1,2-dideuterioethane (**3a**) and 1-phenyl-2-deuterioethane (**4a**).

Scheme 2



Unlike aryl-substituted α-olefins, the reactions of α-alkenes with $EtAlCl_2$ or Et_2AlCl in the presence of 10 mol.% $CoCl_2$+Ph_3P and metallic magnesium proceed *via* hydroalumination to form dialkylethylalanes **7a,b** and alkyldiethylalanes **8a,b** (Scheme 3). The structures of compounds **7** and **8** were proved by the identification of their hydrolysis and deuterolysis products and by oxidation to the corresponding primary alcohols **9**.[5]

Scheme 3

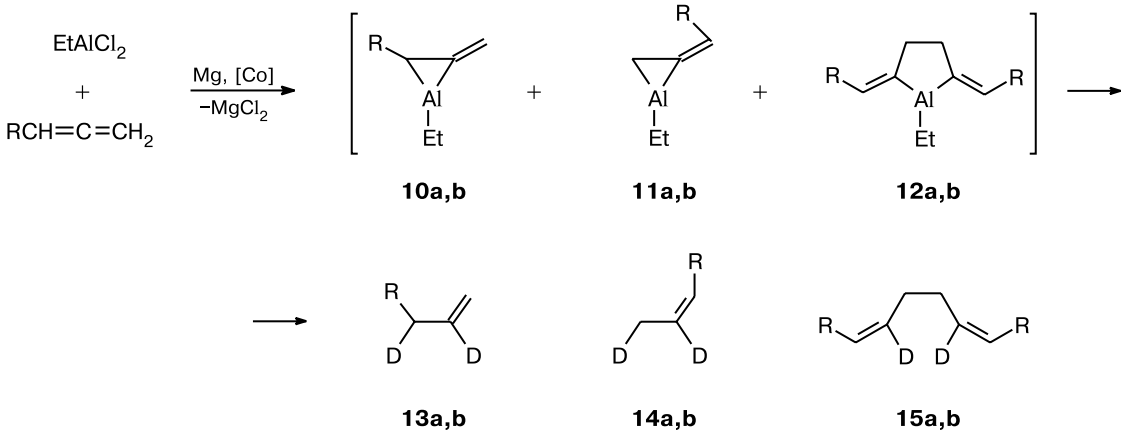


R = Pr^n (**a**), n-C_5H_{11} (**b**)

The reactions of alka-1,2-dienes with $EtAlCl_2$ in THF at 20 °C for 8 h in the presence of activated magnesium and cobalt phosphine complexes taken in the molar ratio $RCH{=}C{=}CH_2$: $EtAlCl_2$: Mg : [Co] = 10 : 13 : 12 : 1 afford a mixture of unsaturated cyclic OAC **10—12** in an overall yield of 60—65% (**10** : **11** : **12** ≈ 4 : 1 : 15) (Scheme 4). Monodeuterioolefins were identified (8—12%) by mass spectrometry of the deuterolysis products of OAC **10—12** along with dideuterioolefins **13—15**, indicating that the competitive hydroalumination of allenes with the cobalt phosphine complexes occurs, most likely, along with cycloalumination.

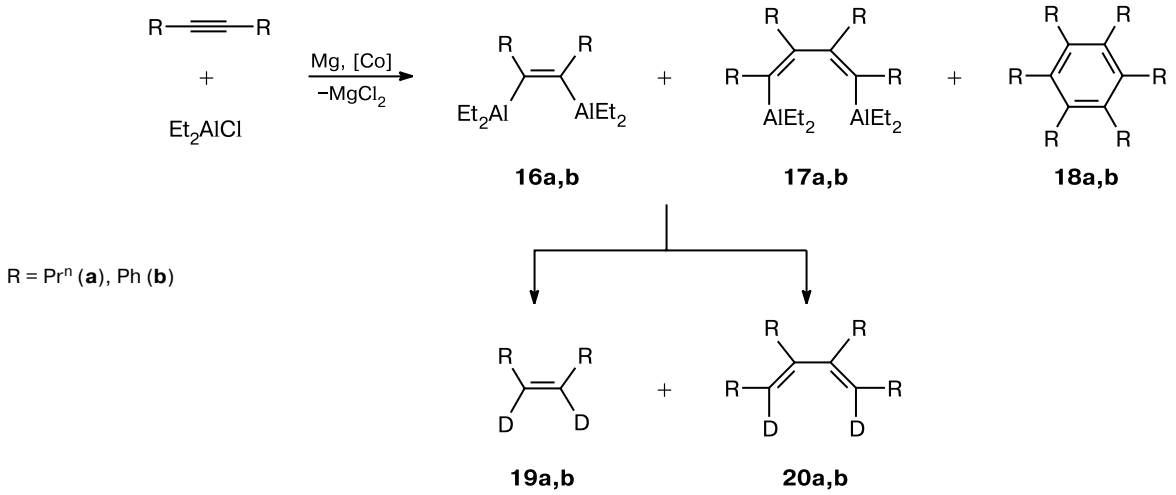
The reaction of Et_2AlCl with oct-4-yne or styrene in THF at ~20 °C in the presence of the $CoCl_2$+Ph_3P catalyst and activated metallic magnesium ([Al]:RC≡CR : Mg : [Co] = 22 : 10 : 22 : 1) affords unsat-

Scheme 4



R = n-C_6H_{13} (**a**), n-C_8H_{17} (**b**)

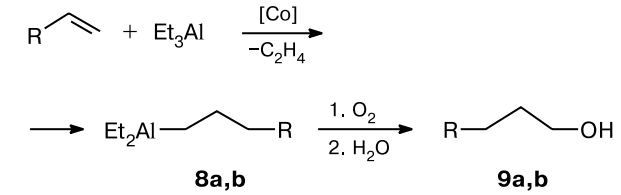
Scheme 5



urated acyclic OAC **16**, **17**, and hexasubstituted benzene (**18**) in a ratio of ~3 : 1 : 1 in an overall yield of ~65%. The deuterolysis of OAC **16** and **17** produces partially deuterated olefins **19** and **20** (Scheme 5).

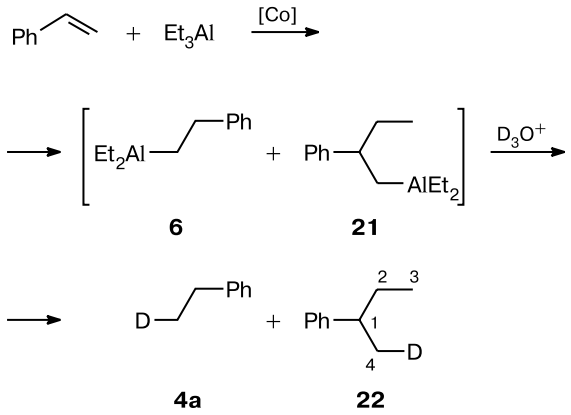
The cobalt phosphine complexes were found to catalyze reactions of unsaturated compounds with $EtAlCl_2$ or Et_2AlCl and also with Et_3Al. The reactions of α-alkenes with Et_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 afford 3-alkyl-substituted alumacyclopentanes.[9] In the case of aryl-substituted α-olefins[10] and norbornene and its derivatives,[11] the reaction proceeds *via* cycloalumination. However, in the presence of the two-component $CoCl_2$+Ph_3P catalyst, depending on the structure of the starting olefin, the reaction proceeds *via* hydroalumination or as hydro- and carboalumination. For example, α-alkenes react with $AlEt_3$ in the presence of 10 mol.% $CoCl_2$+Ph_3P to form hydroalumination products **8a,b** in a 90—95% yield (Scheme 6).

Scheme 6



Under the same conditions, aryl-substituted α-olefins form the products of both hydroalumination of **6** and carboalumination of **21** in a ratio of ~1 : 2 in an overall yield of ~50%. This reaction was studied for styrene (Scheme 7).

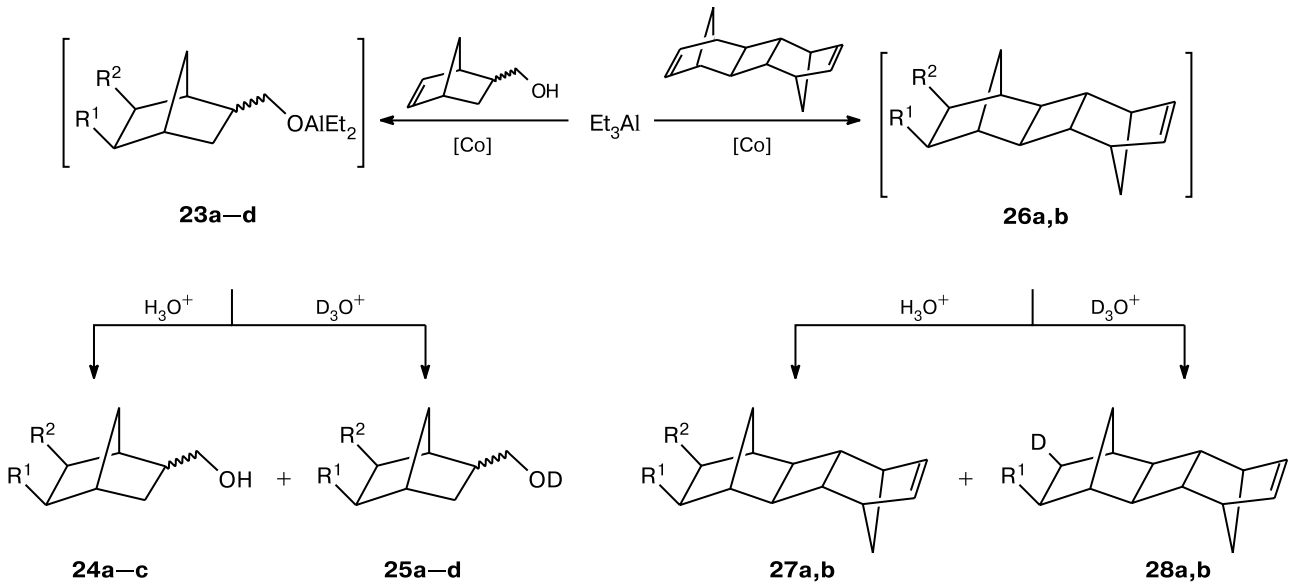
Scheme 7



The compounds of the norbornene series form the hydro- and carboalumination products in a ratio of ~3 : 1 in an overall yield of 70—75% (Scheme 8).

Based on the results obtained, we can conclude that the cobalt phosphine complexes catalyze the reactions of trialkyl- and alkylhaloalanes with olefins, 1,2-dienes, and acetylenes to form both cyclic (alumacyclopropanes, alumacyclopentanes) and acyclic (1,2-dialuminioethylenes, 1,4-dialuminiobuta-1,3-dienes) OAC in high yields. The cobalt phosphine complexes are analogous, to a great extent, to the titanium- and zirconium-containing catalysts by the catalytic properties and structural selectivity. Therefore, they can successfully be used in the hydro-, carbo-, and cycloalumination of olefins and acetylenes.

Схема 8



23	R^1	R^2	**24**	R^1	R^2	**25**	R^1	R^2		R^1	R^2
a	H	$AlEt_2$	**a**	H	H	**a**	H	D	**26a**	H	$AlEt_2$
b	Et	$AlEt_2$	**b**	Et	H	**b**	D	H	**26b**	Et	$AlEt_2$
c	$AlEt_2$	H	**c**	H	Et	**c**	Et	D	**27a**	H	H
d	$AlEt_2$	Et				**d**	D	Et	**27b**	Et	H

R^1 = H (**28a**), Et (**28b**)

Experimental

Reactions with organoaluminum compounds were carried out in a dry argon flow. Solvents were distilled over $LiAlH_4$ prior to use. Commercial Et_3Al (95%), $EtAlCl_2$ (86%), and Et_2AlCl (86%) (Redkinskii Opytnyi Zavod Joint-Stock Company) were used. The hydrolysis and deuterolysis products were analyzed by GLC on a Chrom-5 chromatograph (He, columns 1200×3 mm, 5% SE-30 or 15% PEG-6000 on Chromaton N-AW). IR spectra were measured on an IR-75 spectrometer (in films). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on JEOL FX-90 Q spectrometers (89.55 MHz (H^1) and 22.5 MHz (C^{13}), respectively). Starting aluminum amides and alkoxides were synthesized by known procedures.[12,13] Compounds **3a—c**, **4a—c**, **9a,b**, **13a,b**, **14a,b**, **15a,b**, **18**, **19a,b**, and **20a,b** were identified by comparison with authentic samples.[1,4—6,14,15] It was difficult to obtain the ^1H and ^{13}C NMR spectra of the synthesized OAC because of strong signal broadening due to admixtures of the intermediate paramagnetic Co^{2+} complexes ($I = 7/2$).

Reactions of olefins with $EtAlCl_2$—Mg—[Co] and Et_2AlCl—Mg—[Co]. ***A.*** The $CoCl_2$+Ph_3P catalyst (1 mmol), Mg powder (12 mmol), THF (10 mL), olefin (10 mmol), and $EtAlCl_2$ (12 mmol) were placed in a glass reactor in a dry argon atmosphere at −5 °C. The solution was heated to ~20 °C and stirred for 8 h. The reaction mixture was treated with 10% HCl or 10% DCl in D_2O. The products were extracted with ether or hexane and isolated by distillation.

B. Under the same conditions, the $CoCl_2$+Ph_3P catalyst (1 mmol), Mg powder (22 mmol), THF (10 mL), olefin (10 mmol), and Et_2AlCl (22 mmol) were placed in a reactor. Then the reaction was carried out similarly to variant ***A***.

Reactions of allenes with $EtAlCl_2$—Mg—[Co]. ***C.*** Under the conditions of method ***A***, the $CoCl_2$+$2Ph_3P$ catalyst (1 mmol), Mg powder (12 mmol), THF (10 mL), allene (10 mmol), and $EtAlCl_2$ (12 mmol) were placed in a glass reactor. The solution was heated to ~20 °C and stirred for 8 h. Then the reaction mixture was treated as described in method ***A***. The products were extracted with ether or hexane and isolated by distillation.

Reactions of acetylenes with Et_2AlCl—Mg—[Co]. ***D.*** Under the conditions of method ***A***, the $CoCl_2$+Ph_3P catalyst (1 mmol), Mg powder (22 mmol), THF (10 mL), acetylene (10 mmol), and Et_2AlCl (22 mmol) were placed in a glass reactor. The solution was heated to ~20 °C and stirred for 8 h. The reaction mixture was treated as described in method ***A***. The products were extracted with ether or hexane and isolated by distillation.

Reactions of olefins and norbornenes with Et_3Al. ***E.*** Under the conditions of method ***A***, $CoCl_2$+Ph_3P (1 mmol), hexane (10 mL), olefin or the corresponding norbornene (10 mmol), and Et_3Al (12 mmol) were placed in a glass reactor. The solution was heated to ~20 °C and stirred for 8 h. The reaction mixture was treated as described in method ***A***. The products were extracted with ether or hexane and isolated by distillation.

1-Deuteriomethylpropylbenzene (22), b.p. 59—60 °C (10 Torr) (see Ref. 16). IR, ν/cm^{-1}: 710, 800, 1010, 1050, 1350, 1450, 1500, 1600, 2165 (ν_{CD}), 2420, 2860, 2940, 3050. ^1H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, Me, J = 7.5 Hz); 1.20 (d, 2 H, CH_2D, J = 7.0 Hz); 2.60—2.78 (m, H, CH); 6.80—7.20 (m, 5 H, CH arom.). ^{13}C NMR ($CDCl_3$), δ: 12.49 (q, C(3)); 22.54 (t,

C(4), J = 19.5 Hz); 32.56 (t, C(2)); 42.15 (d, C(3)); 125.61 (d, C(4)); 127.54 (d, C(2), C(6)); 128.25 (d, C(3), C(5)); 141.10 (d, C(1)).

***endo*-2-Hydroxymethylbicyclo[2.2.1]heptane (*endo*-24a) and *exo*-2-hydroxymethylbicyclo[2.2.1]heptane (*exo*-24a)** (~5 : 1), b.p. 74—75 °C (5 Torr) (see Ref. 17). IR, ν/cm^{-1}: 710, 1005, 1050, 1450, 2850, 2340, 3310. ^{1}H NMR ($CDCl_3$), δ: 0.38—2.09 (m, 11 H, CH, CH_2); 3.11—3.44 (m, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$), δ, ***endo*-24a**: 22.47 (t, C(6)); 29.82 (t, C(5)); 33.60 (d, C(3)); 36.59 (t, C(4)); 37.82 (d, C(1)); 39.71 (t, C(7)); 42.31 (d, C(2)); 64.48 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-24a**: 28.85 (t, C(5)); 29.82 (t, C (6)); 33.99 (t, C(7)); 35.03 (d, C(4)); 36.07 (t, C(3)); 38.02 (d, C(2)); 44.65 (d, C(1)); 66.37 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-5-ethylbicyclo[2.2.1]heptane (*endo*-24b) and *exo*-2-hydroxymethyl-*exo*-5-ethylbicyclo[2.2.1]heptane (*exo*-24b)** (~5 : 1), b.p. 83—84 °C (1 Torr). IR, ν/cm^{-1}: 710, 960, 1010, 1050, 1450, 2850, 2930, 3310. ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, Me, J = 7.0 Hz); 1.06—1.99 (m, 11 H, CH, CH_2); 3.10—3.45 (m, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$), δ, ***endo*-24b**: 12.89 (q, C(5″)); 29.61 (t, C(5′)); 32.83 (t, C(3)); 35.81 (t, C(6)); 39.60 (d, C(4)); 39.77 (t, C(7)); 40.02 (d, C(1)); 42.86 (d, C(5)); 44.17 (d, C(2)); 63.81 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-24b**: 12.89 (q, (5″)); 29.61 (t, C(5′)); 33.96 (t, C(7)); 36.11 (t, C(3)); 36.15 (d, C(6)); 38.04 (d, C(4)); 40.10 (d, C(2)); 40.92 (d, C(5)); 45.63 (d, C(1)); 66.35 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-6-ethylbicyclo[2.2.1]heptane (*endo*-24c) and *exo*-2-hydroxymethyl-*exo*-6-ethylbicyclo[2.2.1]heptane (*exo*-24c)** (~5 : 1). ^{13}C NMR ($CDCl_3$), δ, ***endo*-24c**: 12.68 (q, C(6″)); 27.52 (t, C(6′)); 32.14 (t, C(7)); 34.62 (t, C(3)); 38.57 (d, C(4)); 38.96 (t, C(6)); 41.24 (d, C(5)); 42.18 (d, C(2)); 44.02 (d, C(1)); 63.20 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-24c**: 12.68 (q, C(6″)); 27.52 (t, C(6′)); 31.90 (t, C(7)); 36.54 (t, C(3)); 38.57 (d, C(4)); 39.05 (t, C(2)); 39.18 (d, C(6)); 40.84 (t, C(5)); 46.12 (d, C(1)); 66.35 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-6-deuteriobicyclo[2.2.1]heptane (*endo*-25a) and *exo*-2-hydroxymethyl-*exo*-6-deuteriobicyclo[2.2.1]heptane (*exo*-25a)** (~5 : 1), b.p. 74—75 °C (5 Torr) (see Ref. 17). IR, ν/cm^{-1}: 710, 1005, 1050, 1450, 2170 (ν_{CD}), 2850, 2930, 3310. ^{1}H NMR ($CDCl_3$), δ: 0.32—2.03 (m, 10 H, CH, CHD, CH_2); 3.11—3.44 (m, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$), δ, ***endo*-25a**: 22.17 (d, C(6), J = 19.5 Hz); 29.78 (t, C(5)); 33.56 (d, C(3)); 36.57 (t, C(4)); 37.79 (d, C(1)); 39.68 (t, C(7)); 42.30 (d, C(2)); 64.48 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-25a**: 28.83 (t, C(5)); 29.57 (t, C(6), J = 19.5 Hz); 33.86 (t, C(7)); 34.93 (d, C(4)); 36.00 (t, C(3)); 37.96 (d, C(2)); 44.39 (d, C(1)); 66.34 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-5-deuteriobicyclo[2.2.1]heptane (*endo*-25b) and *exo*-2-hydroxymethyl-*exo*-5-deuteriobicyclo[2.2.1]heptane (*exo*-25b)** (~5 : 1). ^{13}C NMR ($CDCl_3$), δ, ***endo*-25b**: 22.47 (t, C(6)); 29.36 (t, C(5)); 33.56 (d, C(3)); 36.57 (t, C(4)); 37.79 (d, C(1)); 39.68 (t, C(7)); 42.30 (d, C(2)); 64.48 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-25b**: 28.51 (d, C(5), J = 19.5 Hz); 29.80 (t, C(6)); 33.86 (t, C(7)); 34.93 (d, C(4)); 36.00 (t, C(3)); 37.96 (d, C(2)); 44.39 (d, C(1)); 66.34 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-5-ethyl-*exo*-6-deuteriobicyclo[2.2.1]heptane (*endo*-25c) and *exo*-2-hydroxymethyl-*exo*-5-ethyl-*exo*-6-deuteriobicyclo[2.2.1]heptane (*exo*-25c)**, b.p. 83—84 °C (1 Torr). IR, ν/cm^{-1}: 710, 960, 1010, 1050, 1450, 2165 (ν_{CD}), 2850, 2930, 3315. ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, Me, J = 7.0 Hz); 1.05—1.98 (m, 10 H, CH, CHD, CH_2); 3.10—3.45 (m, 2 H, CH_2OH). ^{13}C NMR ($CDCl_3$), δ, ***endo*-25c**: 12.86 (q, C(5″)); 29.64 (t, C(5′)); 32.86 (d, C(3)); 35.54 (d, C(6), J = 19.5 Hz); 39.58 (d, C(4)); 39.96 (t, C(7)); 40.00 (d, C(1)); 42.85 (d, C(5)); 44.15 (d, C(2)); 63.80 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-25c**: 12.85 (q, C(5″)); 29.60 (t, C(5′)); 33.95 (t, C(7)); 35.79 (d, C(6), J = 19.5 Hz); 36.10 (t, C(3)); 38.02 (d, C(4)); 40.10 (d, C(2)); 45.61 (d, C(1)); 66.32 (t, C(2′)).

***endo*-2-Hydroxymethyl-*exo*-6-ethyl-*exo*-5-deuteriobicyclo[2.2.1]heptane (*endo*-25d) and *exo*-2-hydroxymethyl-*exo*-6-ethyl-*exo*-5-deuteriobicyclo[2.2.1]heptane (*exo*-25d).** ^{13}C NMR ($CDCl_3$), δ, ***endo*-25d**: 12.68 (q, C(6″)); 27.52 (t, C(6′)); 32.11 (t, C(7)); 34.60 (t, C(3)); 38.57 (d, C(4)); 38.94 (d, C(6)); 40.92 (d, C(5), J = 19.5 Hz); 42.20 (t, C(2)); 44.00 (d, C(1)); 63.18 (t, C(2′)). ^{13}C NMR ($CDCl_3$), δ, ***exo*-25d**: 12.70 (q, C(6″)); 27.61 (t, C(6′)); 32.03 (t, C(7)); 36.56 (t, C(3)); 38.58 (d, C(4)); 39.20 (d, C(6)); 39.81 (d, C(2)); 40.52 (d, C(5), J = 19.5 Hz); 46.15 (d, C(1)); 66.30 (t, C(2′)).

Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradec-11-ene (27a). IR, ν/cm^{-1}: 720, 750, 920, 2870, 2940, 3060. ^{1}H NMR ($CDCl_3$), δ: 0.94—1.98 (m, 14 H, CH_2, CH); 2.54—2.57 (m, 2 H, CH); 5.88—5.97 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 27.82 (t, C(5), C(6)); 33.73 (t, C(14)); 38.92 (t, C(13)); 41.52 (d, C(3), C(8)); 43.16 (d, C(2), C(9)); 44.26 (d, C(7), C(11)); 45.43 (d, C(1), C(10)); 135.28 (d, C(11), C(12)).

***exo*-5-Ethylpentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradec-11-ene (27b).** IR, ν/cm^{-1}: 710, 1345, 1475, 2930, 2950, 3070. ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, Me, J = 7.0 Hz); 1.06—1.97 (m, 15 H, CH, CH_2); 5.53—5.96 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 12.53 (q, C(5″)); 29.30 (t, C(5′)); 30.73 (t, C(14)); 36.26 (t, C(6)); 39.51 (d, C(2), C(9)); 39.90 (t, C(13)); 40.49 (d, C(8)); 41.53 (d, C(3)); 42.31 (d, C(5)); 43.55 (d, C(1), C(10)); 43.81 (d, C(4)); 44.26 (d, C(11), C(12)).

***exo*-6-Deuteriopentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradec-11-ene (28a).** IR, ν/cm^{-1}: 720, 750, 920, 2165 (ν_{CD}), 2870, 2940, 3060. ^{1}H NMR ($CDCl_3$), δ: 0.94—1.98 (m, 13 H, CH_2, CH_2D, CH); 2.54—2.57 (m, 2 H, CH); 5.88—5.97 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 27.61 (d, C(6), J = 19.5 Hz); 27.81 (t, C(5)); 33.73 (t, C(14)); 38.93 (t, C(13)); 41.53 (d, C(3), C(8)); 43.16 (d, C(2), C(9)); 44.26 (d, C(7), C(11)); 45.43 (d, C(1), C(10)); 135.30 (d, C(11), C(12)).

***exo*-5-Ethyl-*exo*-6-deuteriopentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradec-11-ene (28b).** IR, ν/cm^{-1}: 705, 1345, 1470, 2165 (ν_{CD}), 2930, 2950, 3070. ^{1}H NMR ($CDCl_3$), δ: 0.86 (t, 3 H, Me); 1.06—1.97 (m, 14 H, CH, CH_2, CHD); 5.53—5.96 (m, 2 H, CH=CH). ^{13}C NMR ($CDCl_3$), δ: 12.59 (q, C(5″)); 29.30 (t, C(5′)); 30.73 (t, C(14)); 35.94 (d, C(6), $J_{C,D}$ = 19.5 Hz); 39.38 (t, C(13)); 39.97 (d, C(3)); 40.49 (d, C(2), C(9)); 41.59 (d, C(8)); 42.70 (d, C(5)); 43.55 (d, C(1), C(10)); 43.81 (d, C(4)); 44.26 (d, C(6)); 135.37 (d, C(11), C(12)).

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