2336 *Russian Chemical Bulletin, International Edition, Vol. 50, No. 12, pp. 2336—2345, December, 2001*

Synthesis and transformations of metallacycles
27.* Quantum-chemical study of the mechanism of styrene catalytic cyclometallation with triethylaluminum in the presence of Cp_2ZrCl_2

S. V. Rusakov, L. M. Khalilov,* L. V. Parfenova, A. G. Ibragimov, O. A. Ponomarev, 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

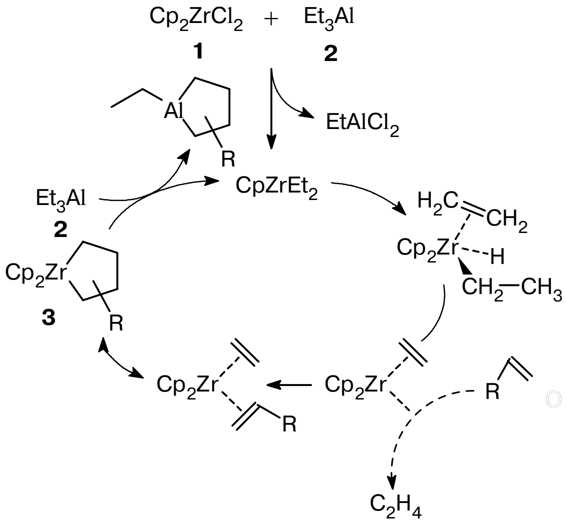
Cyclometallation of olefins with $AlEt_3$ in the presence of Cp_2ZrCl_2 affording five-membered monosubstituted cyclic organoaluminum compounds, was studied by the semiempirical quantum-chemical PM3 method. The proposed model of catalytic cycloalumination of styrene catalyzed by Cp_2ZrCl_2 is in a good accordance with experimental data obtained by dynamic NMR spectroscopy.

Key words: reaction mechanism, cycloalumination, bis-zirconacenedichloride, catalysis, organoaluminium compounds, bimetallic complexes, quantum-chemical calculations, PM3.

The discovery of the catalytic cycloalumination[2] of olefins and acetylenes by trialkyl- and alkylhaloalanes to form the corresponding tri-, penta-, and macrocyclic organoaluminum compounds (OAC) initiated a new, intensely developed field of organometallic synthesis.[3—6]

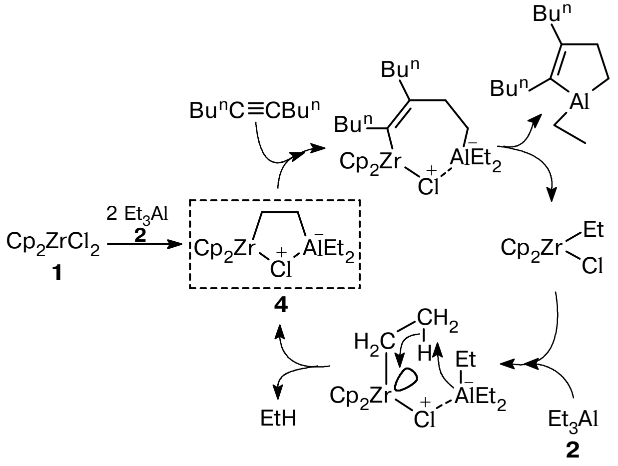
In several works,[2,7] various cyclometallation mechanisms based on experimental data are discussed. The first proposed scheme[2] included the formation, under the reaction conditions, of zirconacyclopropane and zirconacyclopentane intermediates, whose transmetallation with excess OAC results in the corresponding alumacyclopentanes (Scheme 1).

Scheme 1



Later,[7] based on experimental data for the $Cp_2ZrCl_2—Et_3Al$ [8] and $Cp_2ZrCl_2—Et_3Al$—5-decine system, the mechanism of acetylene cycloalumination was proposed, which took into account the formation of intermediate bimetallic Zr—Al complexes (Scheme 2). Analysis of Scheme 2 shows that this process is also possible in the cycloaalumination of olefins.

Scheme 2



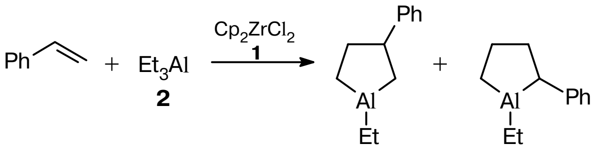
Therefore, we attempted to study the mechanism of catalytic cycloalumination of unsaturated hydrocarbons by quantum-chemical methods using the reaction of styrene with Et_3Al in the presence of the Cp_2ZrCl_2 complex as an example (Scheme 3). This reaction occurs at room temperature and, in the absence of a solvent, affords preliminarily a mixture of 2- and 3-phenyl-substituted alumacyclopentanes.[9]

---

* For Part 26, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2229—2238, December, 2001.

Scheme 3



The purpose of this work was to reveal the sequence and nature of transformations of intermediate complexes formed in styrene cyclometallation.[9,10]

Calculation procedure

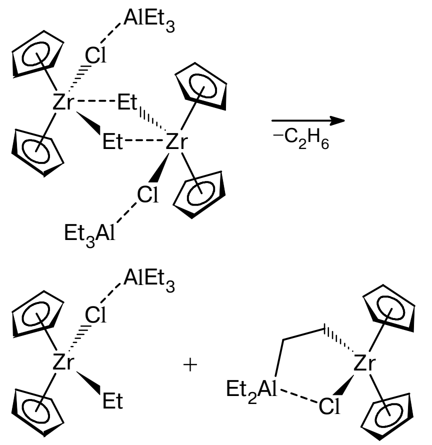
The geometric and energetic parameters of reactants, intermediates, transition states (TS), and products of the model considered for catalytic cycloalumination were calculated by the semiempirical PM3 method[11] accomplished in the HyperChem v.5.1 program package. In all cases, the restricted Hartree—Fock approximation was used. No limitation was imposed on changes in the geometric parameters of the subsystems studied. The types of points localized on the potential energy surface of the system were identified by the analysis of the second derivatives of its energy. The transition state was preliminarily estimated by the method of synchronous transition.[12] The convergence interval for the self-consistency procedure was 0.007 kcal Å^{-1} mol^{-1}.

Results and Discussion

It is known[13] that the semiempirical PM3 method satisfactorily reproduces the geometric parameters of complexes containing Zr and Al atoms. Adequacy of the description of the energy characteristics of the intermediate complexes was verified by test calculations for the Cp_2ZrCl_2 (**1**)—Et_3Al (**2**) system, for which the energy parameters of individual stages were obtained by dynamic ^{1}H NMR spectroscopy studying the kinetic dependences of the interaction of the Cp_2ZrCl_2—Et_3Al reactants.[8] Transformation of the dimeric $[Cp_2(Et)ZrCl \cdot Et_3Al]_2$ system into the $Cp_2(Cl)Zr—CH_2CH_2—AlEt_2$ and $Cp_2(Et)ZrCl \cdot Et_3Al$ complexes (Scheme 4) was chosen as a standard simple reaction. According to experimental data,[10] the activation energy of this process is 15.3 kcal mol^{-1}, whereas the analysis of calculated energy characteristics showed that the highest energy barrier surmounted during this transformation was 15.0 kcal mol^{-1}.

Thus, the test calculations showed the possibility of using the PM3 method for the satisfactory qualitative description of the energy characteristics of the model system including the Cp_2ZrCl_2 and Et_3Al reactants.

Scheme 4



As shown in experimental works,[7,8,10] at the initial stage of olefin cyclometallation the molecules of catalyst **1** vigorously react with Et_3Al (**2**). Indeed, the calculated data for complex **5a** (Fig. 1) indicate a high exothermicity of the initial complexation stage, *viz.*, 53.4 kcal mol^{-1} (Table 1). This fact further determines all main processes, which need surmounting of energy barriers. The exchange of the ethyl group and Cl atom (stage *Ia*) between the Zr and Al complexes to form compound **7a** has an energy barrier of 18.4 kcal mol^{-1} (TS **6a**). Also note the endothermicity of ligand exchange (accord-

Table 1. Relative energies (Δ*E*) of structures*

Routes	Structure	$-\Delta E$/kcal mol^{-1}
	Interligand exchange Et—Cl	
Ia	**5a**	53.4
	TS **6a**	34.9
	7a	37.1
Ib	**5b**	87.6
	TS **6b**	74.1
	7b	75.7
	β-Hydride transfer	
IIa	**8a**	130.96
	TS **9a**	97.64
	10a	113.08
IIb	**8b**	139.20
	TS **9b**	121.45
	10a	129.08
	Styrene insertion	
IIIc	**11a**	133.39
	TS **12a**	113.04
	13a	139.18
IIIc'	**11b**	132.96
	TS **12b**	117.64
	13b	141.46
	Formation of monosubstituted alumacyclopentanes	
IVa	**14a**	143.4
	TS **15a**	135.8
	16a	152.3
	17a + **8b**	162.3
IVa'	**14b**	150.1
	TS **15b**	145.8
	16b	153.0
	17b + **8b**	158.8

* The total energy of the system of non-interacting molecules (energy counting out level) is −163961.8 kcal mol^{-1}.

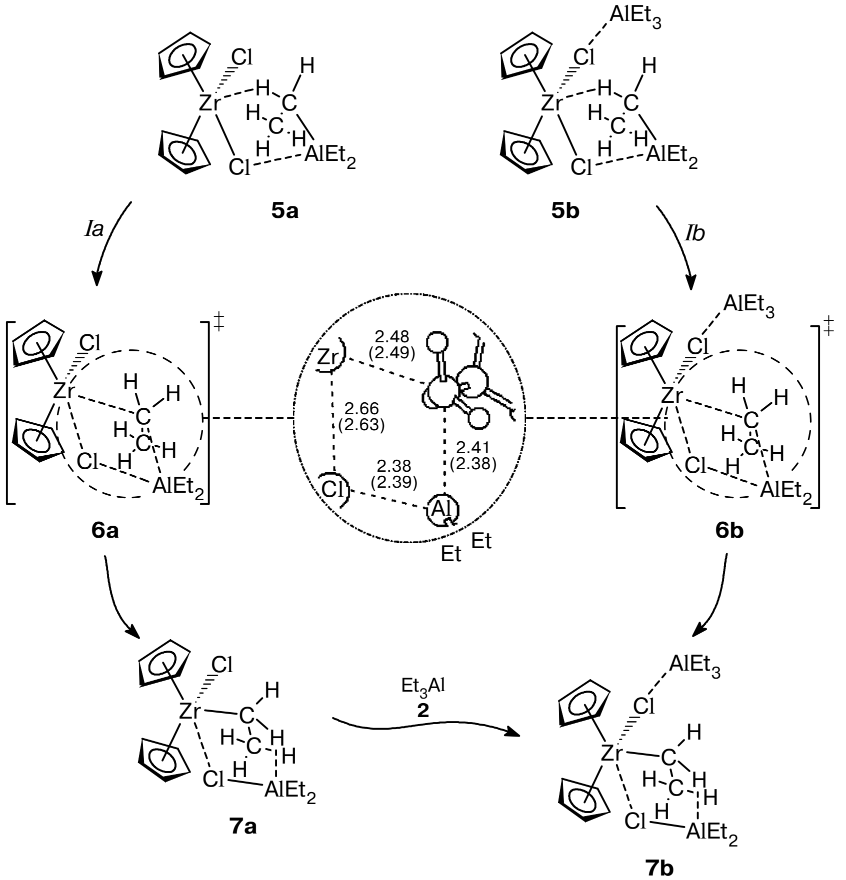


Fig. 1. Scheme of ligand exchange in complexes **5a** (route *Ia*) and **5b** (route *Ib*). Bond lengths in Å are presented for TS **6a** (for **6b**, in parentheses).

ing to calculated data, the energy absorption is 16.3 kcal mol^{-1}).

In the case of a twofold excess of molecules **2**, complex **5b** is formed (see Fig. 1, route *Ib*). Exchange process *via* route *Ib* (**5b** → **7b**) requires surmounting of an energy barrier of 13.5 kcal mol^{-1} (TS **6b**), *i.e.*, by 4.9 kcal mol^{-1} lower (Fig. 2) that in the case of route *Ia*. It follows from this that in the catalytic reaction with a high excess of Et_3Al (**2**) exchange processes of the type *Ib* are more preferential. Experimental data[7,10] confirm the conclusion that the **1**—**2** equimolar system is more inert.

The removal of the Et_2AlCl molecule that formed from the coordination sphere of the Zr atom (complex **7b**) produces complex **8** (Fig. 3). In the gas phase the evolution of Et_2AlCl requires an expense of 16.8 kcal mol^{-1}; however, subsequent dimerization[14] decreases considerably the total energy of the system (TES). As calculations show, the formation of the $(Et_2AlCl)_2$ dimer is a barrier-free reaction with a decrease in TES by 68.0 kcal mol^{-1}. Conformational analysis made it possible to localize two minima to which structures **8a** and **8b** correspond (see Fig. 3). Complex **8a** has an agostic interaction of the Zr and H atoms at the C_β ethyl group at Zr, and **8b** exhibits the agostic interaction of the Zr and H atoms due to the insertion of the ethyl group of molecule **2** between the Zr—Cl and Zr—C(1) (Et—Zr) bonds.

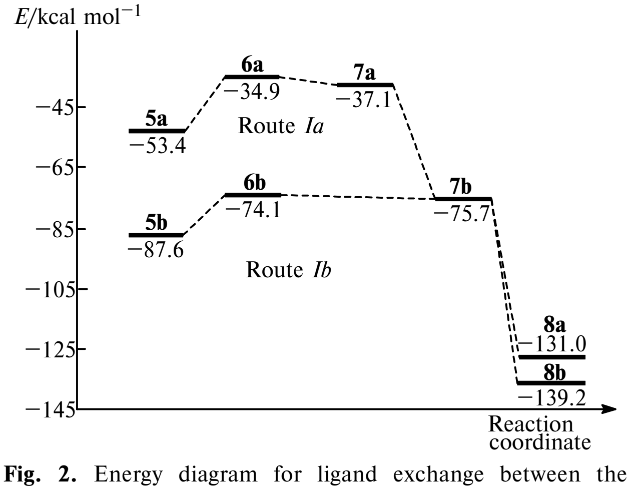


Fig. 2. Energy diagram for ligand exchange between the interacting molecules Cp_2ZrCl_2 and Et_3Al. The energy of non-interacting molecules are taken as initial level; *E* is the relative energy of the structure.

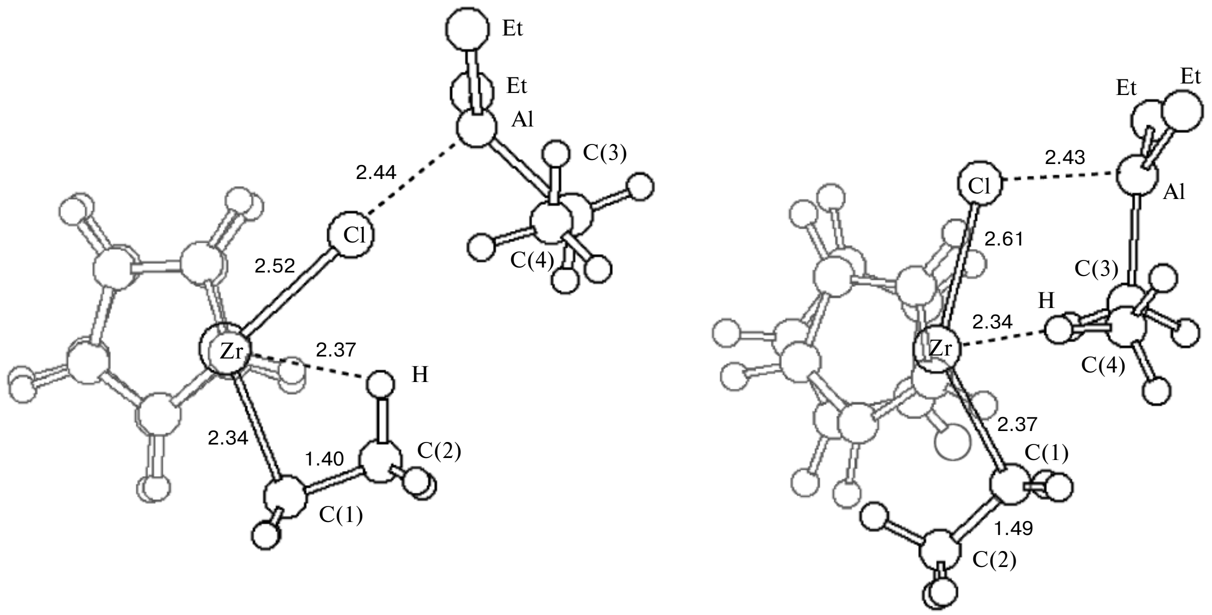
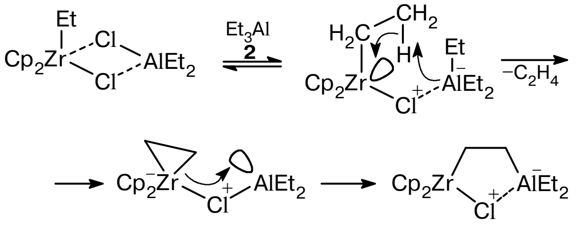


Fig. 3. Structures **8a,b** illustrating mutual transformations of the $Cp_2Zr(Et)Cl \cdot Et_3Al$ complex; bond lengths in Å are presented.

The further evolution of the reacting system results in β-hydride transfer producing the active form of the catalyst (**4**), which can react with olefin fragments, and the ethane molecule, whose evolution was experimentally detected.[7,8,10]

According to previously published data,[7] complex **4** can be formed due to the hydride transfer (Scheme 5) because of the postulated preliminary activation of the C—H bond of the Me fragment of the Et group, which is directly adjacent to the Zr atom, to form zirconacyclopropane **4′** followed by its transformation into complex **4**. A study of route *IIa* (Fig. 4) showed that this reaction has an activation barrier of 33.2 kcal mol^{-1} (TS **9a**). The occurrence of intermolecular hydride transfer in this process is responsible for a sufficiently high activation energy. The subsequent transformation **4′** → **4** has an energy barrier of 6.8 kcal mol^{-1}, and the barrier to the inverse reaction **4** → **4′** is 2.1 kcal mol^{-1}. A comparison of the energy characteristics shows that π-complex **4′** is by 6.5 kcal mol^{-1} more stable than complex **4**. However, taking into account low activation barriers to mutual transformations **4** ↔ **4′**, we can assume that these complexes are at thermodynamic equilibrium.

Scheme 5



Using published data[15—17] on the activation of saturated hydrocarbons by transition metal complexes, we also considered the possibility of the activation of the C—H bond of the Me fragment of the Et group at the Al atoms (see Fig. 4, route *IIb*) to form a five-membered complexes without involvement of zirconacyclopropane intermediates. A study of route *IIb* showed that this activation pathway is energetically more favorable for the transfer of the H atom to the methylene group of the Et group at the Zr atom than that for route *IIa*. According to calculations, the **8b** → **10b** transition is possible through TS **9b** with a barrier of 17.7 kcal mol^{-1} and an increase in TES by 10.1 kcal mol^{-1} (Fig. 5).

The interaction of molecules by route *IIc* [8] can also create favorable conditions for β-C—H activation due to the coordination of the Et group at the Zr atom of one of the $Cp_2(Cl)ZrEt \cdot Et_3Al$ associates, forming complex **18** (Fig. 6). β-Hydride transfer through TS **19** resulting in complex **20** is characterized by an increase in TES by 8.9 kcal mol^{-1} and an activation energy of 14.9 kcal mol^{-1}. The subsequent coordination of the Et group (structure **21**) creates necessary conditions for repeated β-hydride transfer to form complexes **8** and **4**. Analysis of results of quantum-chemical calculations shows that this process should be endothermic by 3.2 kcal mol^{-1} with an energy barrier of 15.0 kcal mol^{-1}.

A comparison of the energy characteristics of the considered routes *IIa—c* indicates that the formation of the bimetallic Zr—Al complex **4** is preferential when β-C—H activation occurs *via* route *IIc* (resulting in the free ethane molecule), *i.e.*, when two zirconium sites interact. However, the concentration of the catalyst used in the catalytic reaction is low (Cp_2ZrCl_2, Et_3Al, and styrene molar ratio is[9] 1 : 60 : 50), and such interactions are highly improbable when the molecules are uniformly

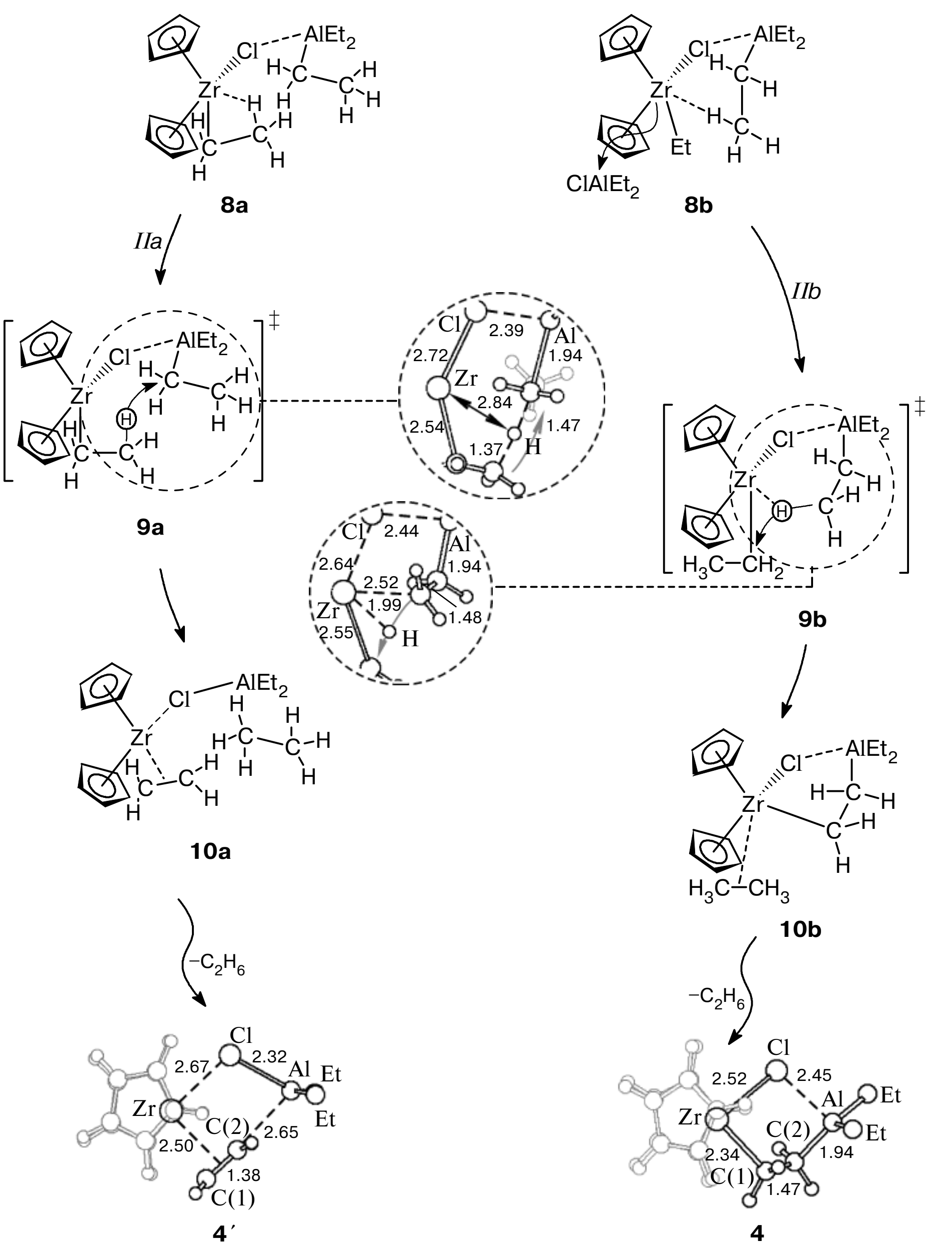


Fig. 4. Scheme of β-hydride transfer (routes *IIa,b*); bond lengths in Å are presented.

distributed over the reaction volume. Thus, hydride transfer in the one-centered system seems preferential under these conditions. Therefore, route *IIb* is more probable for the catalytic reaction, although the channel of formation of the dimeric [Zr—Zr] system is not excluded and is more preferential, most likely, under stoichiometric conditions.

We considered the variant of interaction of terminal olefin with the dicyclopentadienylzirconacyclopropane complex according to the previously proposed[2] scheme (see Scheme 1), which takes into account the formation of the target reaction products by the route zirconacyclopropane → zirconacyclopentane → alumacyclopentane. Preliminary calculations did not clarify unambiguously a possibility of coordination of the styrene molecule with the transition metal atom. Therefore, two possible variants were considered for the chosen hereinafter subsystems: the *syn*-conformation in which the substituent is arranged more closely to the Zr atom and *anti*-conformation with the substituent remote from the Zr atom (Fig. 7). Simulation by route *IIIa* showed a high barrier to the reaction *via* this pathway (at R^1 = Ph E_a = 40.7 kcal mol^{-1} and at R^2 = Ph E_a = 41.6 kcal mol^{-1}, see Fig. 7). Therefore, the cyclometallation of terminal olefins through intermediate ethylene- or cyclopropanezirconacene and its transformation into zirconacyclopentane followed by transmetallation can be considered improbable.[2]

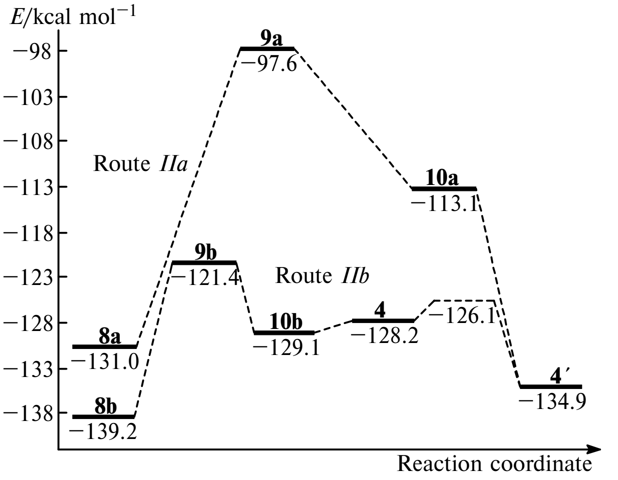


Fig. 5. Energy diagram for β-hydride transfer in the system of interacting molecules Cp_2ZrCl_2 and Et_3Al. The energies of non-interacting molecules are taken as initial level; *E* is the relative energy of the structure.

Previously[10] we studied the interaction of complexes of the type **4** with olefins found by dynamic NMR spectroscopy. Taking into account data on the thermodynamic equilibrium between **4** and **4′** (see above), we can conclude about the interaction of olefins with complexes **4′** and **4**. Analysis of the calculated results showed that the olefin complexes possess the lowest energy when the ethylene fragment of the styrene molecule is arranged near the Zr atom from the side of the Zr—C bond in complex **4**. We imposed these conditions when determined the geometry of the initial complexes of the subsystems under study.

We studied the interaction of styrene with complex **4′** similarly to route *IIIa* at different arrangements of the Ph group of the olefin molecule. The results of calculations showed that the interaction of styrene with complex **4′** (route *IIIb*) results in the formation of zirconacyclopnetane complexes **28** (see Fig. 7) and the energy barrier for this process is comparable with the those of formation of zirconacyclopentane intermediates

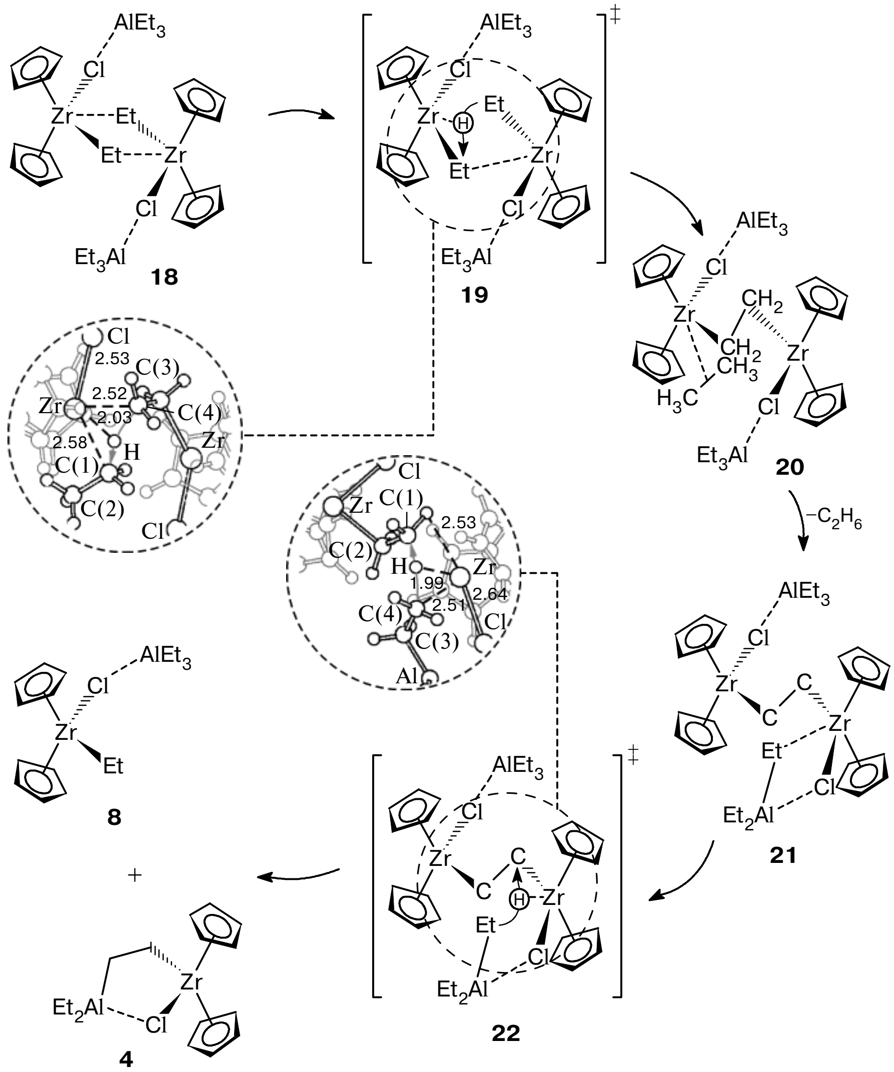


Fig. 6. Scheme of β-hydride transfer (route *IIc*); bond lengths in Å are presented.

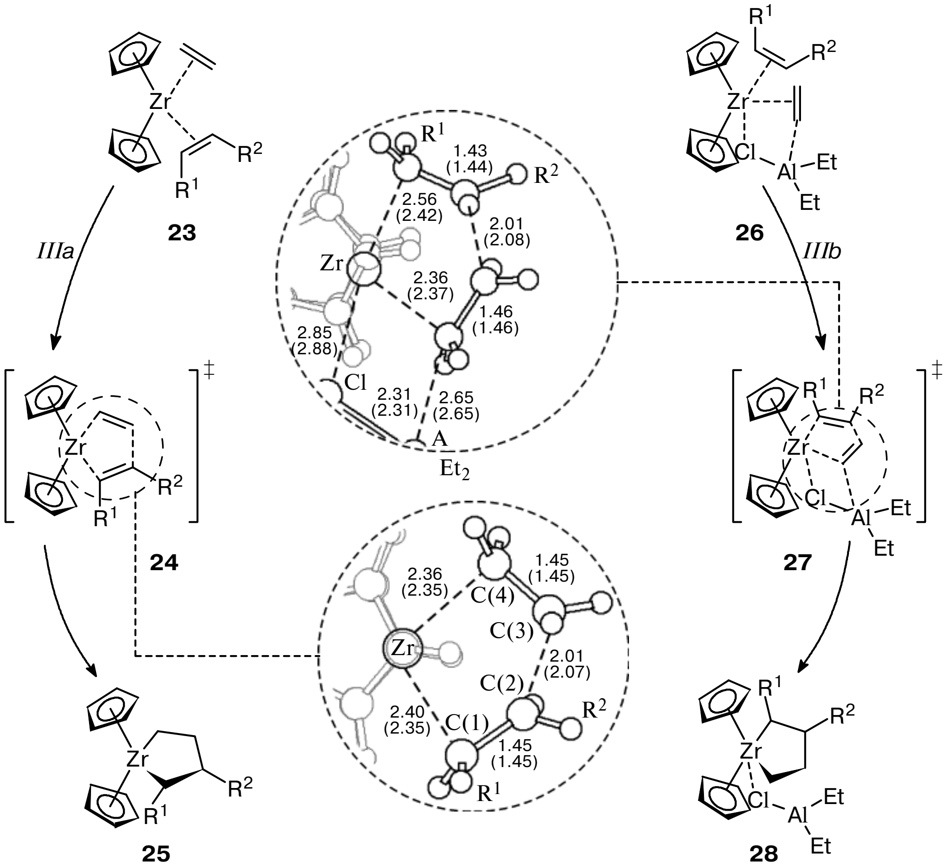


Fig. 7. Scheme of styrene insertion (routes *IIIa,b*). Bond lengths in Å are presented for TS **24** and **27** (for R^1 = H and R^2 = Ph, in parentheses).

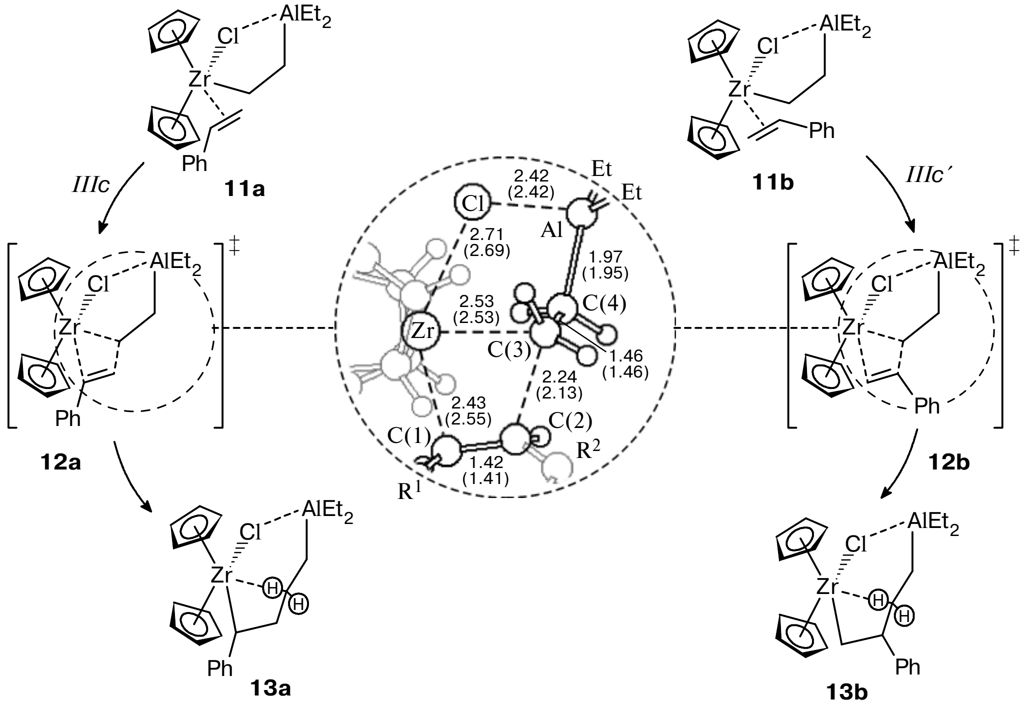


Fig. 8. Scheme of styrene insertion (route *IIIc*). Bond lengths in Å are presented for TS **12a** (for **12b**, in parentheses).

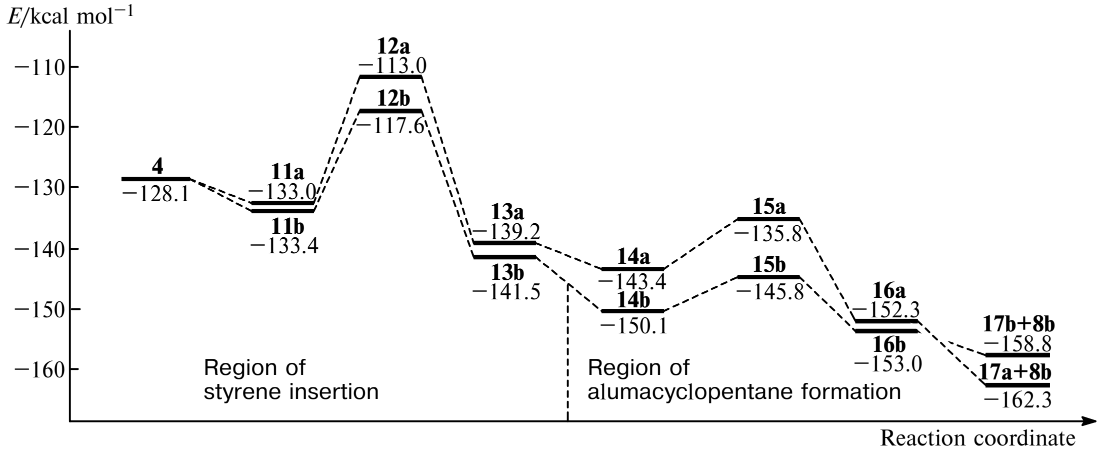


Fig. 9. Energy diagram for the simple reaction between complex **4** and styrene. The energies of non-interacting molecules are taken as the counting out level; *E* is the relative energy of the structure.

via route *IIIa*. For the *syn*-conformation, the reaction has an energy barrier of 39.8 kcal mol^{-1}, and for the *anti*-conformation it is 41.8 kcal mol^{-1}. As in the case of route *IIIa*, the barrier is rather high and, hence, this process is improbable.

Complexes **11** are formed by the possible interaction of styrene with bimetallic Zr—Al complex **4** (Fig. 8). Two variants of olefin coordination were also considered for them: the *syn*-conformation (**11a**) and *anti*-conformation (**11b**), which transform into complexes **13a,b**

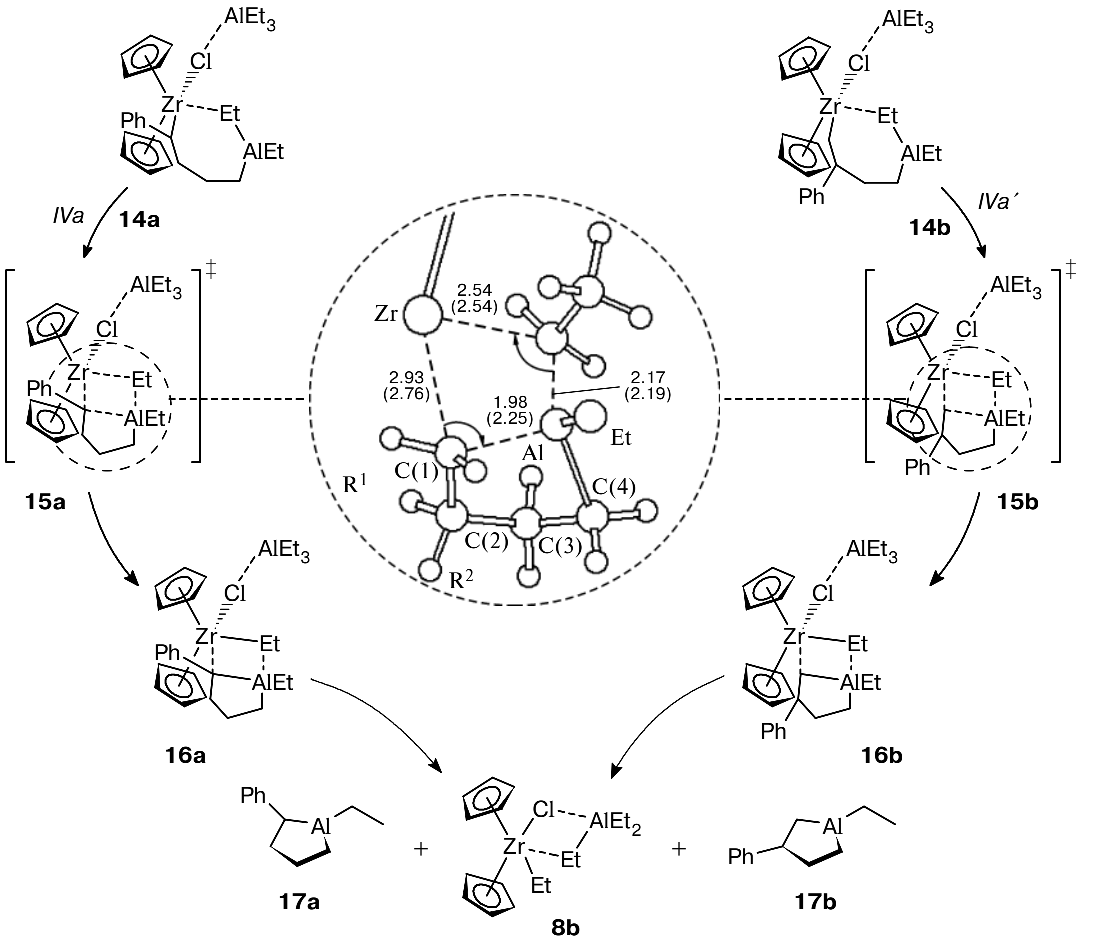


Fig. 10. Scheme of formation of the target product of reactions of 2- and 3-substituted alumacyclopentanes (routes *IVa* and *IVa′*). Bond lengths in Å are presented for TS **15a** (for **15b**, in parentheses).

through the corresponding TS **12a** (route *IIIc*) and **12b** (route *IIIc′*).

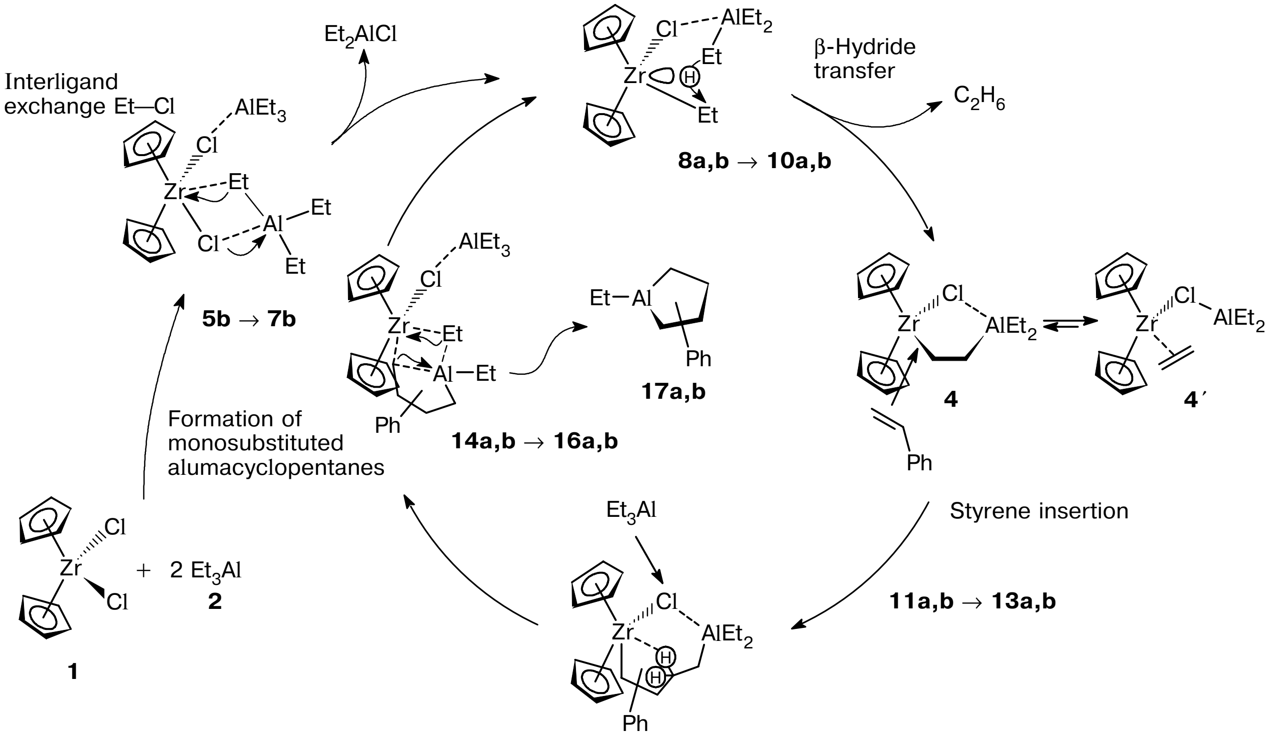
Analysis of the geometric characteristics of TS **12a** shows an increase in the Zr—Cl bond length by 0.07 Å and a decrease in the Al—Cl bond length by 0.03 Å compared to similar parameters of complex **4**, *i.e.*, its bimetallic cycle opens. According to the results of quantum-chemical calculations, the insertion process *via* route *IIIc* should be exothermic (energy gain is 5.8 kcal mol^{-1}, energy barrier is 20.4 kcal mol^{-1}, Fig. 9). When the reaction proceeds *via* route *IIIc′*, the characteristic Zr—Cl and Al—Cl bond lengths in TS **12b** change relatively to the geometric parameters of five-membered cycle **4**, being 0.07 Å and −0.03 Å, respectively. Estimation of the energy parameters of these transformations showed that the process should be exothermic (energy gain is 8.5 kcal mol^{-1}, activation energy is 15.3 kcal mol^{-1}). A comparison of the energy barriers to styrene insertion demonstrates that *anti*-conformation **11b** is preferential, which indicates a definite selectivity of the process and corresponds to experimental data.[10] Analysis of the geometric characteristics of complexes **13a,b** indicates a weak agostic interaction of the Zr and H atoms at the C(3) atom.

Thus, a comparison of the energy characteristics of the processes of terminal olefin insertion in the described subsystems suggests favorable conditions for its occurrence by the interaction of styrene with bimetallic five-membered complex **4**. The catalytic cycle, *viz.*, the formation of the catalytically active site and its interaction with terminal olefin, should be described, according to the lowest energy principle, by the chain of transformations **4′** → **4** → **4** + styrene → **13**. However, taking into account the possibility of the concerted formation of active site **4** by passing the stage of **4′** formation (route *IIb*), the pathway **4** + styrene → **13** can be preferred.

The formation of the final reaction products, *viz.*, 2-phenyl- (**17a**) and 3-phenyl- (**17b**) monosubstituted alumacyclopentanes, is accompanied by the transformation of complexes **13a,b** involving the third Et_3Al molecule (**2**) into complexes **14a** and **14b** (Fig. 10) and exchange processes (**14** → **16**), which occur through TS **15a** (route *IVa*) and **15b** (route *IVa′*). According to the data of calculation, when the process proceeds *via* route *IVa*, the simple reaction **14a** → **16a** should be exothermic (energy gain is 8.9 kcal mol^{-1}, energy barrier is 7.6 kcal mol^{-1}). Process **14b** → **16b** occurs *via* route *IVa′* with a decrease in the TES by 2.9 kcal mol^{-1} and energy barrier of 4.3 kcal mol^{-1}. Thus, the target reaction products, *viz.*, 1-ethyl-2-phenylalumacyclopentane (**17a**) and 1-ethyl-3-phenylalumacyclopentane (**17b**), form at this stage. The removal of the molecule of monosubstituted alumacyclopentane that formed from the catalytic center completes the catalytic cycle of the reaction with the regeneration of the $Cp_2(Et)ZrCl \cdot Et_3Al$ complex (**8**).

Thus, based on the estimations of the energy parameters of individual stages of styrene cycloalumination by triethylaluminum (**2**) in the presence of Cp_2ZrCl_2 (**1**) by

Scheme 6



the PM3 method, we determined the preferential reaction routes, which are generalized in Scheme 6 and consistent with experimental results**[10]**: (1) initiation of the reaction by the interaction of the catalyst molecule **1** with two molecules **2** and Et—Cl ligand metathesis in this subsystem; (2) transformation of the $Cp_2(Et)ZrCl$ complex by the second molecule **2**, affording bimetallic Zr—Al complex **4**, with the parallel evolution of the ethane molecule due to β-hydride transfer from the Et fragment at the Al atom to the Et group at the Zr atom; (3) insertion of the styrene molecule into complex **4** at the Zr—C bond preferentially with the *anti*-orientation of the Ph group of the styrene molecule in the TS; and (4) formation of the target reaction products **17a** and **17b**, which completes the catalytic cycle.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-32912a and 98-03-32913a).

References

1. L. O. Khafizova, A. G. Ibragimov, G. N. Gil′fanova, L. M. Khalilov, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2089 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2188].
2. U. M. Dzhemilev, A. G. Ibragimov, A. P. Zolotarev, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 207 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 194 (Engl. Transl.)].
3. U. M. Dzhemilev and A. G. Ibragimov, *J. Organomet. Chem.*, 1994, **1**, 466.
4. U. M. Dzhemilev, *Tetrahedron*, 1995, **15**, 4333.
5. U. M. Dzhemilev and A. G. Ibragimov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 816 [*Russ. Chem. Bull.*, 1998, **47**, 786 (Engl. Transl.)].
6. U. M. Dzhemilev and A. G. Ibragimov, *Usp. Khim.*, 2000, **69**, 134 [*Russ. Chem. Rev.*, 2000, **69** (Engl. Transl.)].
7. E. Negishi, D. Y. Kondakov, D. Chouiry, K. Kasai, and T. Takahashi, *J. Am. Chem. Soc.*, 1996, **118**, 9577.
8. W. Kaminsky and H. Sinn, *Liebigs Ann. Chem.*, 1975, 424.
9. A. G. Ibragimov, L. O. Khafizova, K. G. Satenov, L. M. Khalilov, L. G. Yakovleva, S. V. Rusakov, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1594 [*Russ. Chem. Bull.*, 1999, **48**, 1574 (Engl. Transl.)].
10. L. M. Khalilov, L. V. Parfenova, S. V. Rusakov, A. G. Ibragimov, and U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 2086 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 2051].
11. J. J. P. Stewart, *J. Comp. Chem.*, 1989, **10**, 209.
12. C. Peng and H. B. Shlegel, *Israel J. Chem.*, 1993, **33**, 449.
13. K. J. Borve, V. R. Jensen, T. Karlsen, J. A. Stovneng, and O. Swang, *J. Mol. Model.*, 1997, **3**, 193.
14. G. A. Tolstikov and V. P. Yur′ev, *Alyuminiiorganicheskii sintez* [*Organoaluminum Synthesis*], Nauka, Moscow, 1979, 254 pp. (in Russian).
15. M.-D. Su and S.-Y. Chu, *Organometallics*, 1997, **16**, 1621.
16. M.-D. Su and S.-Y. Chu, *Chem. Eur. J.*, 1999, **5**, 198.
17. Yu. A. Ustynyuk, L. Yu. Ustynyuk, D. N. Laikov, and V. V. Lunin, *J. Organomet. Chem.*, 2000, **597**, 182.

Received October 31, 2000;
in revised form May 28, 2001