Oligodienyl compounds of d- and f-transition metals: synthesis and stability

E. I. Tinyakova,* G. N. Bondarenko, O. K. Sharaev, V. A. Yakovlev, and B. A. Dolgoplosk†

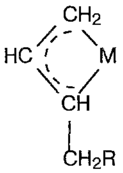
A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: +7 (095) 230 2224

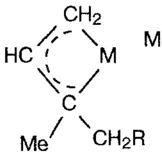
The results of investigations performed in the Laboratory of Organometallic Catalysis of the A. V. Topchiev Institute of Petrochemical Synthesis of the RAS are reviewed. The oligodienyl compounds of a series of transition metals, $R_n{}^{ol}M$ and $R_n{}^{ol}MX_m$ (R^{ol} = $R'(\text{diene})_{3-10}$, where R′ is an alkyl, allyl, alkenyl, or H; $(\text{diene})_{3-10}$ is an oligodienyl group with 3—10 monomeric diene units; M = Ti^{3+}, Cr^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Nd^{3+}, Pr^{3+}, Sm^{3+}, and Gd^{3+}; X is a halogen or an electronegative group), have been synthesized for the first time and some of their properties have been studied. The stability of oligodienyl compounds is much higher than that of the corresponding π-alkenyl derivatives. The IR spectra of the compounds synthesized allowed us to conclude that their stability and some peculiarities of the reactions of these compounds can be explained by π-coordination of the isolated double bond of the oligodienyl chain to the transition metal.

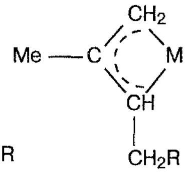
Key words: oligodienyl chain; transition metals; synthesis; stability; π-coordination; IR spectra.

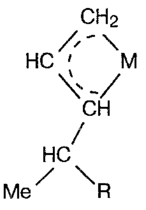
The majority of alkyl- and arylorganometallic compounds of the first transition row and rare-earth metals of the types R_nM and R_nMX_m containing carbon—metal σ-bonds are metastable and decompose when stored.[1] The π-allyl compounds are somewhat more stable, but many of them exist only at low temperatures.[2]

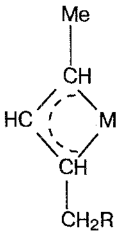
However, polymerization of conjugated dienes in the presence of the thermally unstable π-allyl and σ-alkyl (aryl) derivatives of transition metals occurs with high efficiency at 50—70 °C, which indicates the considerable stability of the corresponding active centers.[3] A study of the polymerization of dienes in the presence of a series of organometallic compounds (π-R_3Ti, $(PhCH_2)_3Ti$, π-R_3Cr, $(PhCH_2)_3Nd$, *etc.*) has shown that the process involves all of the C—M bonds. It has been concluded on this basis that polymeric analogs of the corresponding π-alkenyl complexes, namely, those of butadiene (**1**), isoprene (**2**, **3**), and piperylene (**4**, **5**), act as active centers for polymerization.


1


2


3


4


5

The active centers of diene polymerization in the presence of RMX_n-type compounds are also polymeric analogs of π-alkenyl compounds of transition metals.

One of the factors determining the stability of active centers during polymerization is the coordination of a monomer to the transition metal of an active center.[4] In recent years, our laboratory has been studying the synthesis and properties of oligodienyl compounds of transition metals of the types $R_n{}^{ol}M$ and $R_n{}^{ol}MX_m$ (where R^{ol} is an oligodienyl group containing 3—10 monomeric diene units). It has been shown that these compounds are also stable in the absence of dienes and that π-coordination of the isolated double bond of the oligodienyl chain to a transition metal atom additionally contributes to the stability of these compounds.[5—13]

The $R_n{}^{ol}M$ compounds

Oligodienyl compounds (butadienyl-, isoprenyl-, and pentadienyl-based) of the general formula $R_n{}^{ol}M$

---

† Deceased in 1994.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 15—23, January, 1995.

($M = Ti^{3+}$, Cr^{2+}, Co^{2+}, Mn^{2+}, Ln^{3+}) were obtained by two methods.

1. By reactions of π-R_nM (where R is allyl, crotyl, or pentenyl) with dienes, *e.g.*

$$(\pi\text{-}C_3H_5)_3Ti + n\ C_4H_6 \longrightarrow [C_3H_5(C_4H_6)_{3-10}]_3Ti\ .$$

The reactions were carried out in hydrocarbon solvents at temperatures from −70 to 20—50 °C at molar ratios diene/M—R = 3 to 10 or higher.* This method is unsuitable for the synthesis of oligodienyl compounds from π-R_nM compounds, which are catalysts of linear or cyclic dimerization (trimerization) of dienes; in particular, this relates to π-R_2Ni and π-R_3Co and to the reaction of R_3Ti with isoprene.

2. The more general method involves reactions of metal halides with oligodienyllithium ($R^{ol}Li$):**

$$MHal_n + n\ R^{ol}Li \longrightarrow R^{ol}{}_nM + n\ LiHal\ .$$

To obtain $R_3{}^{ol}Ln$, tricyclopentadienyl derivatives of lanthanides were used instead of $MHal_3$.

Oligodienyl compounds of titanium, $R_3{}^{ol}Ti$ (see Refs. 5 and 6). Tris-oligobutadienyltitanium was synthesized both by methods 1 and 2. The reaction of $(\pi\text{-}C_3H_5)_3Ti$*** with butadiene was studied by ESR. The ESR spectrum of the starting tris-π-allyltitanium at −196 °C consists of four lines (Fig. 1): $g_1 = 2.034\pm0.001$, $g_2 = 1.983\pm0.001$, $g_3 = 1.972\pm0.001$, $g_4 = 1.955\pm0.001$. In the temperature range from −196 to −50 °C, the concentration of paramagnetic species (PMS) in the solution**** corresponds to the overall concentration of titanium, which indicates that tris-π-allyltitanium is in the monomeric state. The intensity of the ESR signal after the solution of $(\pi\text{-}C_3H_5)_3Ti$ is kept for a short time at 20 °C is about 0.1 % of the starting value, which indicates that quantitative decomposition of the starting tris-π-allyltitanium occurs. The ESR spectra of the $(\pi\text{-}C_3H_5)_3Ti + C_4H_6$ (C_4H_6/Ti = 2000 : 1, mol/mol) reaction mixture at 20 °C change sharply: first, the components with *g*-factors of 2.034 and 1.955 disappear, then the signal transforms into a single line with $g = 1.991\pm0.001$ and $\Delta H = 8.5\pm0.05$ Oe (see Fig. 1, curves *2* and *3*). The intensity of this signal indicates that the concentration of PMS remains constant during the reaction of $(\pi\text{-}C_3H_5)_3Ti$ with butadiene under the conditions of this experiment. The changes in the ESR spectrum imply that the first step of the reaction between the components involves coordination of butadiene with a $(\pi\text{-}C_3H_5)_3Ti$ molecule. Subsequent insertion of the monomer into the Ti—C bond results in the thermally stable tris-oligobutadienyltitanium (see Fig. 1, curve *4*). Similar changes in the ESR spectrum are observed at the molar ratio C_4H_6/Ti = (10—100) : 1 normally used for obtaining $R_3{}^{ol}Ti$.

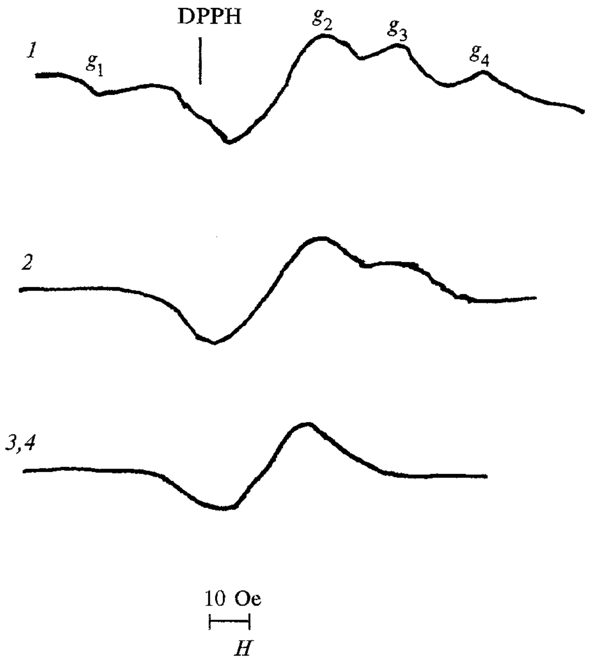


Fig. 1. ESR spectra of $(\pi\text{-}C_3H_5)_3Ti$ (*1*) and of the products of its reaction with butadiene (*2—4*): *2*, after storage for 2 min at 20 °C; *3*, after storage for 24 h at 20 °C; *4*, $R_3{}^{ol}Ti$, stored for 1 to 500 h at 20 °C.

Tris-oligobutadienyltitanium is stable at room temperature; the concentration of PMS determined by ESR agrees with the overall concentration of Ti in the solution. The ESR spectrum of $R_3{}^{ol}Ti$ obtained from $TiCl_4$ ($TiCl_3$) and $R^{ol}Li$ has the same parameters as the spectrum of the products of the reaction of π-R_3Ti with butadiene (see Fig. 1, curve *4*).

Tris-oligobutadienyltitanium synthesized both by methods 1 and 2 quantitatively reacts with molecular iodine in hexane at −78 °C. The consumption of I_2 is 3.0±0.05 mol per one g-at. Ti. However, when $R_3{}^{ol}Ti$ reacts with iodine at higher temperatures (>—30 °C), 5 mol I_2 per one mol $R_3{}^{ol}Ti$ is consumed. Special experiments showed that Ti^{III} is not oxidized by iodine into Ti^{IV} under these reaction conditions. Furthermore, the low-molecular polybutadiene obtained by methanolysis of $R_3{}^{ol}Ti$ does not add I_2. These data allow us to conclude that the increased consumption of iodine in the reaction of $R_3{}^{ol}Ti$ with I_2 at temperatures above −30 °C results from addition of the latter to the double bonds activated due to coordination with the Ti atom.

Tris-oligoisoprenyltitanium obtained by reacting β-$TiCl_3$ with oligoisoprenyllithium was also found to be

---

* Under the reaction conditions, the resulting $R_n{}^{ol}M$ compounds contained no free diene.

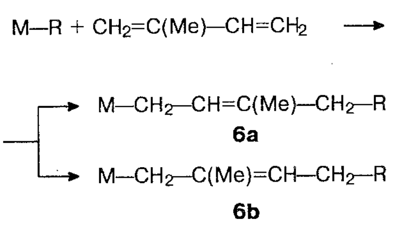
** $R^{ol}Li$ were obtained from Bu^sLi and the corresponding diene (molar ratio diene/Bu^sLi = 4 to 10) according to the reported procedure.[14]

*** $(\pi\text{-}C_3H_5)_3Ti$ was obtained from C_3H_5MgBr and $TiCl_4$ (or β-$TiCl_3$) in diethyl ether at temperatures from −75 to −60 °C. The yield was 35 %.

**** The intensity of the signal was determined by double graphical integration compared to the standard DPPH sample (see Fig. 1).

sufficiently stable at room temperature. This compound could not be synthesized by a reaction of $(\pi\text{-}C_3H_5)_3Ti$ with isoprene under conditions analogous to those used for tris-oligobutadienyltitanium because, as shown previously,[15] Ti^{III} derivatives catalyze the linear dimerization of isoprene. The insertion of isoprene into a C—M bond can occur both at the 1,4- and 4,1-positions (Scheme 1).

Scheme 1



Oligoisoprenyllithium contains a more stable **6a**-type compound as the major component (*cf.* Ref. 16). This probably makes it possible to obtain tris-oligodienyltitanium from $R^{ol}Li$ and $\beta\text{-}TiCl_3$ $(TiCl_4)$. The reaction directed to compound **6b** (see Scheme 1) gives less stable compounds that decompose to yield dimethyloctatrienes. The products of the reaction between $(\pi\text{-}C_3H_5)_3Ti$ and isoprene at −20 °C contain[15] isoprene dimers, mostly 2,6-dimethyl-1,3,6-octatriene.

Oligodienyl compounds of chromuim, $R_2^{ol}Cr$ (*cf.* Ref. 7). Tris-π-allylchromium is an unstable compound decomposing at temperatures above 0 °C. The initial product of its decomposition is tetraallyldichromium,[17] a derivative of bivalent chromium containing a Cr—Cr bond. Oligodienyl compounds of chromium that we obtained from $(\pi\text{-}C_3H_5)_3Cr$ and dienes (butadiene, isoprene, piperylene) were found to be stable at room temperature in the absence of moisture and oxygen. An analysis of Cr^{2+} and total Cr content showed that all of the oligodienyl compounds obtained are derivatives of Cr^{2+}. The $Cr^{3+} \rightarrow Cr^{2+}$ transformation found to occur during the synthesis of oligodienyl compounds of chromium also proceeds during the polymerization of dienes under the action of tris-π-allylchromium and is accompanied by a decrease in the reaction rate. Figure 2 demonstrates the accumulation of Cr^{2+} during the polymerization of butadiene, isoprene, and piperylene. One can see that the maximum rate of the process is observed in the case of piperylene, while the minimum rate is found in the case of butadiene. It should be noted that the rate of polymerization in the presence of bis-oligodienylchromuim is much higher than that in the presence of tetraallyldichromium. Obviously, this results from the fact that bis-oligodienylchromuim is a monomeric compound, which does not contain a Cr—Cr bond, unlike tetraallyldichromium, which exists as the $(\pi\text{-}C_3H_5)_2Cr—Cr(\pi\text{-}C_3H_5)_2$ dimer.

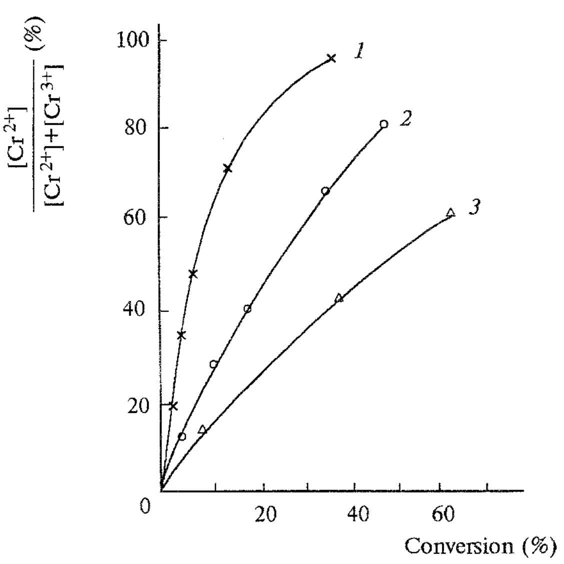


Fig. 2. Kinetics of the formation of Cr^{2+} compounds during the polymerization of piperylene (*1*), isoprene (*2*), and butadiene (*3*) in the presence of $CrAll_3$.

Bis-oligodienylmanganese, $R_2^{ol}Mn$ (see Ref. 6). To date, π-allyl (crotyl) derivatives of manganese have not been reported, probably due to their exceedingly low thermal stability. Tris-π-pentenylmanganese is more stable.[18] The reaction of $MnCl_2$ with oligobutadienyllithium results in an organic compound of two-valent manganese in a virtually quantitative yield; according to iodometry and complexometry data, the solution contains only Mn^{2+}, while Mn^{3+} compounds are not present.

$$MnCl_2 + 2\ R^{ol}Li \longrightarrow R_2^{ol}Mn + 2\ RLi$$

Bis-oligodienylmanganese is highly stable: the content of Mn in solution at room temperature does not change for at least 20 days.

Bis-oligodienylcobalt, $R_2^{ol}Co$ (see Ref. 6). It is known that the reactions of $CoCl_2$ with alkenylmagnesium chlorides in ether result in compounds of trivalent cobalt of the general formula $\pi\text{-}R_3Co$ (R is allyl, crotyl, or pentenyl).[2,18] The reaction of $CoCl_2$ with oligodienyllithium in a hydrocarbon solvent at −30 °C results in bis-oligodienylcobalt; this is indicated by the data of complexometric and iodometric titration.[6] Unlike the $\pi\text{-}R_3Co$ compounds, which are stable only at low temperatures, bis-oligodienylcobalt is stable in hydrocarbon media for a long time at room temperature.

Previously,[19] the synthesis and structure of a monovalent cobalt complex, $C_8H_{13}CoC_4H_6$ (where C_8H_{13} is 3-methylheptatrienyl), have been reported. This complex was obtained by the reaction of $CoCl_2$ with $NaBH_4$ in ethanol at −35 °C in the presence of butadiene. The 3-methylheptatrienyl ligand of the complex is π-coordinated to the Co atom through the terminal allyl and vinyl groups, while the butadiene molecule in the *cis* conformation is also coordinated to the metal. The same compound has been obtained by the reaction of $Co(acac)_3$ with $AlEt_3$ in the presence of butadiene.[20]

π-Allyloligodienylnickel, $C_3H_5NiR^{ol}$ (see Ref. 6). Bis-π-allyl(crotyl)nickel is a catalyst of cyclic trimerization of butadiene and isoprene. Hence, bis-oligodienylnickel cannot be synthesized by method 1. Attempts to obtain $R_2^{ol}Ni$ from $NiCl_2$ and oligobutadienyllithium also failed. Oligobutadienyllithium is consumed almost completely during the reaction, but the resulting organonickel compound decomposes to give metallic Ni. In all of the cases, the organonickel compound, formed under these conditions in a minor yield, is contaminated with oligobutadienyllithium. Allyloligobutadienylnickel, synthesized by the reaction of C_3H_5NiI with $R^{ol}Li$ in toluene or hexane at −78 °C in a nearly quantitative yield, was found to be stable. Its acidolysis affords one mol propylene per one mol $C_3H_5NiR^{ol}$. The compound synthesized is stable for a long time at room temperature and can be recondensed *in vacuo* without decomposition.

Tris-oligobutadienyllanthanides, $R_3^{ol}Ln$ (see Ref. 8). Compounds of the general formula $R_3^{ol}Ln$ were obtained from Cp_3Ln (Ln = Nd, Pr, Sm, or Gd) and oligobutadienyllithium.

$$Cp_3Ln + 3\ R^{ol}Li \longrightarrow R_3^{ol}Ln + 3\ CpLi$$

This exchange reaction is effective due to the formation of lithium cyclopentadienide, which is insoluble in hydrocarbons, and in which the C—Li bond is more polar than that in Cp_3Ln. The yield of tris-oligodienyllanthanides under the conditions of this synthesis is 90—100 % of the theoretical value, but the C—M/Ln ratios in the compounds obtained ($R_3^{ol}Ln$) are somewhat higher than the calculated ones and are up to 3.3. The increased C—M/Ln ratio with a nearly quantitative yield of $R_3^{ol}Ln$ suggests that CpLi is partially transferred into solution, probably due to the formation of the $Li[LnR_3^{ol}Cp]$ complex. The tris-oligodienyllanthanides synthesized are stable at room temperature in hydrocarbon solvents in the absence of oxygen and moisture. It has been shown for $R_3^{ol}Nd$ and $R_3^{ol}Sm$, for example, that, like tribenzylneodymium,[21] they catalyze the *trans*-polymerization of dienes: the resulting polymers contain 94—96 % *trans*-units. These data suggest that lithium cyclopentadienide, which accompanies the oligobutadienyl derivatives of lanthanides, does not participate in the initiation of polymerization.

Study of the vibrational spectra of $R_n^{ol}M$ (see Refs. 5—7). We have studied the IR spectra* of oligodienyl derivatives of Ti, Cr, Co, Mn, and Ni in the 200—4000 cm^{-1} region. In the spectra of oligobutadienyl compounds of Ti, Co, Mn, and Cr (Fig. 3), the most intense bands at 740, 910, 970, 1000, 1460, and 1640 cm^{-1} correspond to bending and stretching vibrations of the polybutadiene chain. The isoprene chain in the corresponding oligoisoprenyl compounds is characterized by bands at 840—850, 888, 910, 1000, 1380, 1460, and 1645 cm^{-1}. The high intensities of the $\delta_{\perp}[-C(Me)=CH_2]$ band at 888 cm^{-1} and the $\delta_{\perp}[-CH=CH_2]$ band at 910 cm^{-1} suggest that the content of 3,4- and 1,2-units is high, in accordance with the microstructures of polyisoprene and polybutadiene obtained in the presence of these systems. The difference between the spectra of oligopentadienyl and oligobutadienyl derivatives is the presence of an intense band at 1380 cm^{-1} in the former, which is typical of the methyl group. None of the above bands found in the spectra of the oligodienyl derivatives of transition metals change when the samples are oxidized by air oxygen.

In addition to bands characterizing polymer fragments, the spectra of oligodienyl derivatives contain a complete set of bands corresponding to a π-alkenyl group at a metal[22] (530, 1030, 1250, 1500—1510, and 3000—3100 cm^{-1}) and weak bands in the region of 350—460 cm^{-1} attributable to vibrations of the M—C bonds in π-alkenyl complexes of transition metals. These bands disappear after the samples are exposed to air for 15—30 s. The above set of frequencies and the rapid disappearance of the bands after oxidation of the samples suggest unambiguously that the oligodienyl complexes studied contain π-alkenyl groups.

In addition to the bands of π-alkenyl ligands linked to a metal, the medium-intensity bands at 1590—1620 cm^{-1} and the strong bands at 670 cm^{-1} in the spectra of oligobutadienyl and oligopentadienyl derivatives and the bands at 780 cm^{-1} in the spectra of oligoisoprenyl derivatives were also found to be sensitive to oxidation. The presence of these bands, which do not correspond to the set of frequencies of π-alkenyl ligands, may be due to two independent factors. They may be absorption bands of the valence and deformation vibrations, respectively, of the double bond of the oligodienyl chain coordinated to the metal. On the other hand, the presence of these bands may be explained by the presence of π-alkenyl groups asymmetrically linked to the metal. Previously,[17] it was concluded from X-ray diffraction data for $[(\pi\text{-}C_3H_5)_2Cr]_2$ and $[(\pi\text{-}C_3H_5)_2Mo]_2$ crystals that one of the allyl groups contains π—σ-bonded moieties. However, a theoretical analysis performed by us[7] for the normal vibrations of these molecules showed that the presence of one π-allyl group asymmetrically linked to a metal atom does not lead to the appearance of the above bands, but only causes splitting of the bands of the stretching and bending vibrations of the π-allyl groups. Furthermore, the spectra of oligodienyl derivatives of chromium do not contain bands in the 200—230 cm^{-1} region corresponding to the valence vibrations of the Cr—Cr bond.

---

* IR spectra were recorded on UR-20 and Perkin Elmer-457 spectrophotometers. The samples were prepared in a dry inert atmosphere and had the form of thin films fastened between KBr or CsI plates in sealed cuvettes.

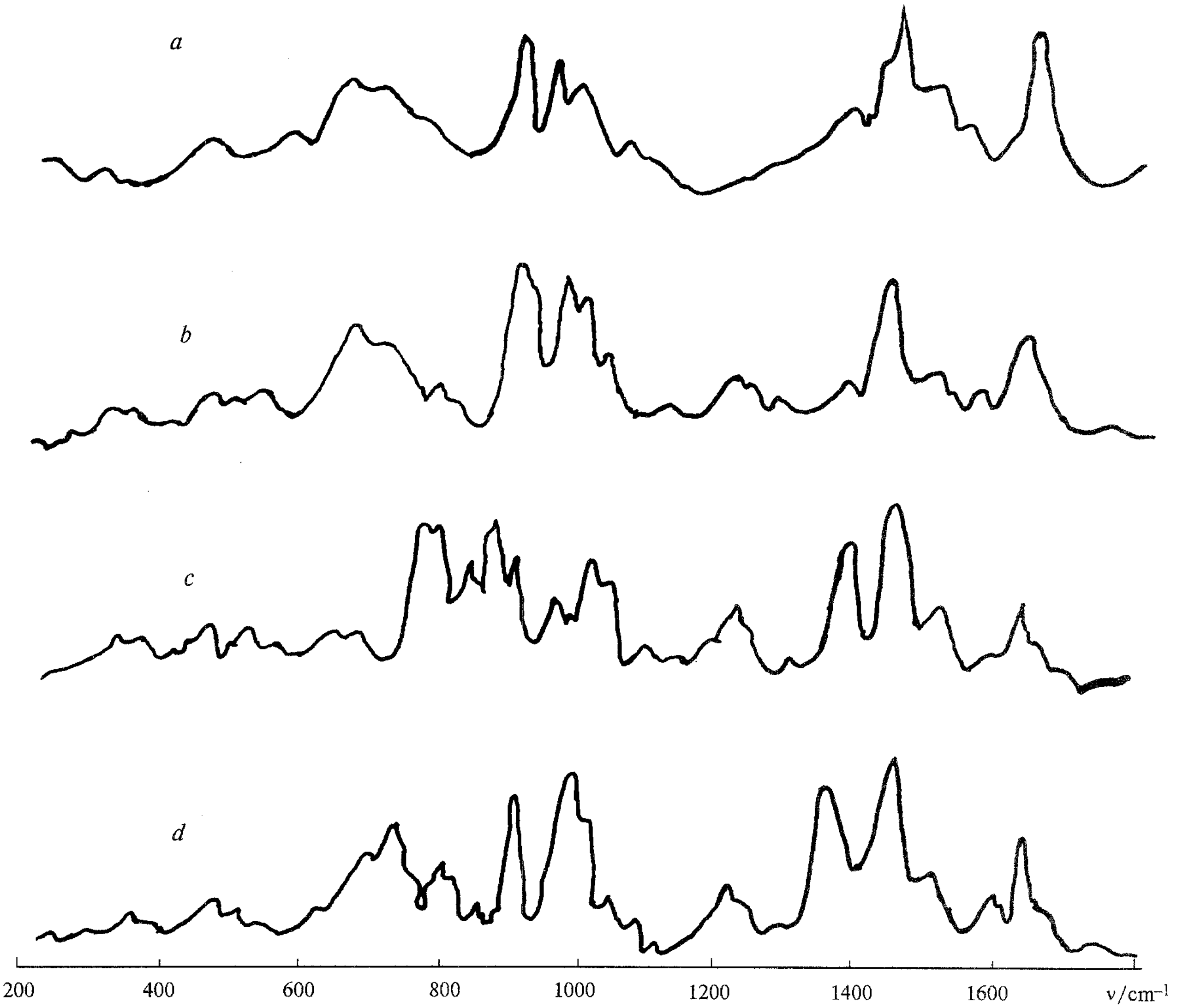


Fig. 3. IR spectra of tris-oligobutadienyltitanium (*a*), bis-oligobutadienylchromium (*b*), bis-oligoisoprenylchromium (*c*), and bis-oligopentadienylchromium (*d*).

Thus, it is reasonable to conclude that the bands at 1590—1620 cm^{-1} and 670 cm^{-1} refer to the stretching and bending vibrations of the CH=CH bonds of an oligodienyl chain coordinated to a metal. A theoretical calculation of the vibrational spectrum of a model fragment (Fig. 4, *b*; M = Ti), in which the double bond coordinated to the metal is at the second position from the M atom of the oligobutadienyl chain, showed that the antisymmetric vibrations of this double bond have a frequency of 1624 cm^{-1}, which is in good agreement with the experimentally observed band at 1620 cm^{-1}. The calculated frequency of the bending out plane vibrations of —CH=CH in this fragment (658 cm^{-1}) is comparable to the experimental band at 670 cm^{-1} that disappears during the oxidation of the sample.

The IR spectra of oligodienyl derivatives of Mn and Co contain the whole set of frequencies typical of metal-linked π-alkenyl groups and of the π-coordinated double bond of the oligodienyl chain. It should be noted that the intensity ratio of the bands of the π-alkenyl groups and the π-coordinated CH=CH bonds in the spectra of oligobutadienyl derivatives of Cr is the same as that in the spectra of similar compounds of Mn and Co, and this allows us to consider them as isostructural. The assumed structure of these compounds is shown in Fig. 4, *a*.

The intensities of bands caused by the absorption of the π-alkenyl ligands in the spectra of oligobutadienyltitanium are considerably lower than those in the spectra of oligobutadienyl derivatives of Cr, Co, and Mn; however, the relative intensities of the bands typical of π-alkenyl ligands and double bonds of oligodienyl chains π-coordinated to the metal changes. This suggests the structure of the complex shown in Fig. 4, *b*.

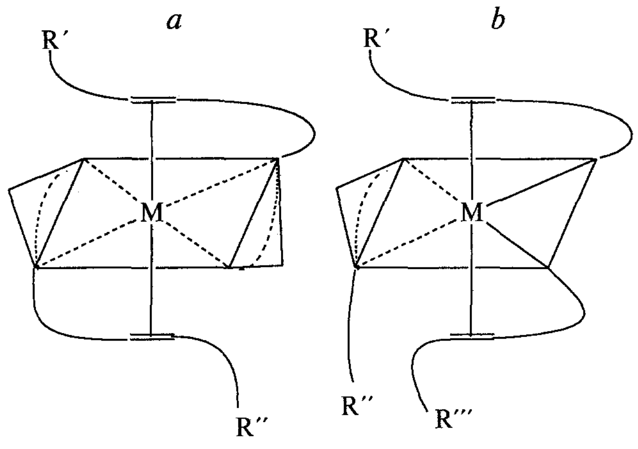


Fig. 4. Assumed structures of $R_2^{ol}Cr$, $R_2^{ol}Co$, $R_2^{ol}Mn$ (*a*) and $R_3^{ol}Ti$ (*b*) (R′, R″, and R‴ are oligodienyl chains).

The good agreement between the theoretical spectra that we obtained from an analysis of the normal vibrations of geometrical models (see Fig. 4) and the experimentally obtained IR spectra of oligodienyl derivatives of chromium and titanium suggests that the models chosen well describe the structures of these compounds.

Thus, the presence of an olefinic π-bond coordinated to a metal makes the stability of oligodienyl compounds of transition metals higher than that of their π-allyl derivatives. This is supported by the stability of tris-π-allyltitanium in the presence of a mixture of β-butenes at room temperature. The latter follows from the fact that the concentration of PMS in the reaction mixture of $(\pi\text{-}C_3H_5)_3Ti$ with $\beta\text{-}C_4H_8$ remains constant for at least 0.5 h at 20 °C, whereas in the absence of butene, tris-allyltitanium quantitatively decomposes at this temperature in 3—5 min (Fig. 5).

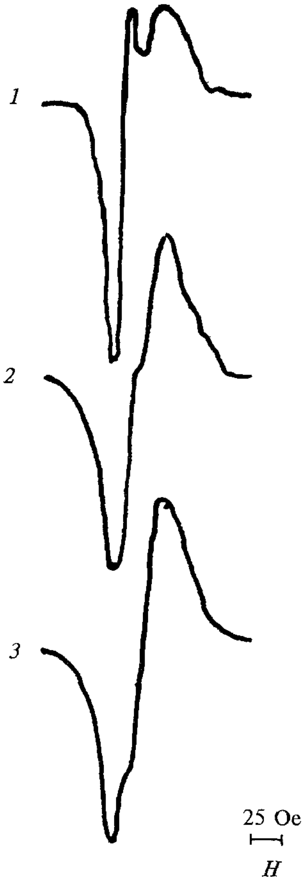


Fig. 5. ESR spectra of a mixture of $(\pi\text{-}C_3H_5)_3Ti$ + $\beta\text{-}C_4H_8$ (1 : 500, mol/mol) in a solution in toluene at −196 °C: *1*, $(\pi\text{-}C_3H_5)_3Ti$; *2*, $(\pi\text{-}C_3H_5)_3Ti$ + $\beta\text{-}C_4H_8$, after storage for 2 min at 20 °C; *3*, $(\pi\text{-}C_3H_5)_3Ti$ + $\beta\text{-}C_4H_8$, after storage for 30 min at 20 °C.

Oligodienyl compounds $R_n^{ol}MX_m$

The second group of oligodienyl derivatives includes compounds of the general formula $R_n^{ol}MX_m$ (M = Ni, Co, and Ln; X is a halogen or other electronegative group). These compounds were also obtained in two ways.

1. By the reaction of metal halides with trialkylaluminum in the presence of small amounts of a diene, *e.g.*

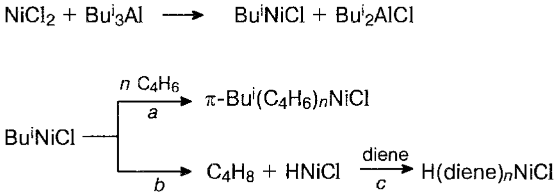
$$NiCl_2 + Bu^i{}_3Al + n\ C_4H_6 \rightarrow Bu^i(C_4H_6)_nNiCl + R_2AlCl.$$

2. By oxidative addition of RHal to zero-valent metals.

Oligodienylnickel chlorides $R^{ol}NiCl$ (see Ref. 9) In essence, these compounds provide the first example of stable oligodienyl derivatives of transition metals.[9] They were obtained by the reaction of $NiCl_2$ with $Bu^i{}_3Al$ in the presence of a diene. As a rule, the reaction was conducted at 0 to 20 °C and at a molar ratio of the components Ni/Al/diene = 1 : 2 : (10 to 30) in an aromatic hydrocarbon. Oligodienylnickel chloride was found to be sufficiently stable toward deoxygenated aqueous solutions of HCl and H_2SO_4 but was decomposed by dilute HNO_3. Therefore, $R^{ol}NiCl$ free from organoaluminum compounds and unreacted $NiCl_2$ were obtained by treating the reaction mixtures with deoxygenated aqueous HCl or H_2SO_4. The hydrocarbon solution was separated from the aqueous solution, dried by azeotropic distillation, and the content of Cl, Ni, and Al was analyzed. The analytical data suggested that the resulting solution did not contain aluminum ions, and the Cl/Ni ratio equaled 1. The yield of $R^{ol}NiCl$ was 90—95 % of the theoretical value. Increasing the starting Al/Ni ratio to 5 : 1 did not affect the yield of $R^{ol}NiCl$. This indicates that $R^{ol}NiCl$ does not undergo alkylation with excess triisobutylaluminum at 0 to 20 °C under the reaction conditions. Conversely, triethylaluminum can alkylate $R^{ol}NiCl$ under these conditions, since some amount of cyclic dimers and trimers of butadiene, whose formation is catalyzed by Ni^0, appear in the $NiCl_2$ + $AlEt_3$ + C_4H_6 system. According to a mass spectrometric analysis, the products of the hydrogenolysis of oligobutadienylnickel chloride contain hydrocarbons of two basic types, $[(C_4H_6)_n{+}2H]$

(n = 3 to 8) and $[(C_4H_6)_n+4H]$ (n = 4 to 5), while those of oligopentadienylnickel chloride contain only one type of hydrocarbons, namely, $[(C_5H_8)_n+2H]$ (n = 3 to 9). It can be assumed that hydrocarbons of the $[(C_4H_6)_n+2H]$ and $[(C_5H_8)_n+2H]$ types are formed due to hydrogenolysis of the complexes formed when the first diene molecule is inserted into the Ni—H bond (Scheme 2, pathway *b*), while the $[(C_4H_6)_n+4H]$ hydrocarbons are formed by hydrogenolysis of the complex formed when butadiene is inserted into the Ni—Bu bond (Scheme 2, pathway *a*).

Scheme 2



Thus, oligodienylnickel chlorides formed during the interaction of $NiCl_2$ with Bu^i_3Al in the presence of dienes are mixtures of oligomers that differ in the number of monomeric units. In these processes the first molecule of butadiene is inserted either into the Ni—Bu^i bond or into the Ni—H bond, whereas the first molecule of pentadiene is inserted only into the Ni—H bond.

Oligodienylnickel chlorides are sufficiently stable. When a solution of oligopentadienylnickel chloride in toluene is stored at 25 °C, the concentration of $R^{ol}NiCl$ remains constant for one month. The stability of oligobutadienylnickel chloride is somewhat lower than that of pentadienyl derivatives as the concentration of the compounds decreases by 10 % aftert 10 days of storage at 25 °C. The higher stability of oligopentadienylnickel chloride in comparison with oligobutadienylnickel chloride is consistent with the higher stability of π-pentenylnickel chloride relative to π-crotylnickel chloride. The IR spectrum of $R^{ol}NiCl$ contains all of the bands characterizing a π-alkenyl ligand linked to the metal.[9]

Compounds of the general formula $C_{12}H_{19}NiX$ (X = Cl, PF_6, SbF_6, BF_4, *etc.*) obtained by reactions of $C_{12}H_{18}Ni$* with one equivalent of the corresponding acids in ether at −50 to −78 °C have been reported in the literature.[23,24] The $C_{12}H_{19}NiX$ compounds (with X = PF_6 or SbF_6) are stable at −20 °C but decompose when stored at room temperature for a long time. Their solutions in dichloromethane are stable at +5 °C for several hours. An analysis of the ^{13}C NMR spectra of the $C_{12}H_{19}NiX$ complexes made it possible to conclude that the dodecatrienyl chain, $C_{12}H_{19}$, is coordinated to nickel through the π-allyl group, C(1, 2, 3), and two double bonds, C(6, 7) and C(10, 11). It has been noted[24] that the chemical shifts of the C(1, 2, 3), C(6, 7), and C(10, 11) atoms depend on the coordinating ability of the anion linked to Ni.

Oligodienylcobalt chlorides, $R^{ol}CoCl$ (see Ref. 9). When $CoCl_2$ reacts with Bu^i_3Al in the presence of dienes under the conditions of the synthesis of $R^{ol}NiCl$, 60—70 % of the starting amount of cobalt passes into solution and cobalt remains in the divalent state. However, when the reaction mixture is treated with a deoxygenated aqueous solution of HCl, 20—40 % of the cobalt remains in the hydrocarbon solution, and the molar ratio Co/Cl becomes 1 : (0.1 to 0.3). The addition of dry gaseous HCl to this solution yields $R^{ol}CoCl$.

Oligodienillanthanide halides, $R_n{}^{ol}LnX_{3-n}$ (see Refs. 11—13). Compounds of the general formula $R_n{}^{ol}LnX_{3-n}$ were synthesized by the oxidative addition of RX ($PhCH_2Cl$, PhBr) to Ln^0 (Nd, Pr, Gd, *etc.*) in the presence of small amounts of a diene (isoprene or piperylene) in THF*, as a rule, at molar ratios RX/Ln = (1 to 1.5) : 1 and diene/Ln = 10 : 1 at 20—70 °C. Under these conditions, benzyl chloride and phenyl bromide are consumed completely to give oligodienyllanthanide halides, $R_n{}^{ol}LnX_{3-n}$. Typical experimental results are presented in Table 1.

In general, the synthesis of oligodienyllanthanide halides can be represented by Scheme 3.

Scheme 3

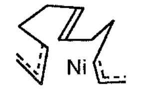
$$RX + Ln \longrightarrow [RLnX] \xrightarrow[a]{RX} RLnX_2 + R^{\cdot}$$

$$[RLnX] + R^{\cdot} \xrightarrow[b]{} R_2LnX$$

$$R_nLnX_{3-n} + C_5H_8 \xrightarrow[c]{} [R(C_5H_8)_m]_nLnX_{3-n}$$

In stage *a*, benzyl or phenyl free radicals with different activities appear. The main direction of the reaction involving the phenyl radical is probably interaction with an intermediate compound, [RLnBr], to give R_2LnBr, which subsequently reacts with $RLnBr_2$ to yield the corresponding oligodienyllanthanide sesquibromide. As shown previously,[13] the main reaction of the weakly reactive benzyl radical in the absence of isoprene is recombination into dibenzyl, whose yield is 40—50 % with respect to the reacted benzyl chloride. In the presence of isoprene, the yield of dibenzyl decreases abruptly and is as low as 2—5 % of the theoretical value,

---

* The starting compound  was obtained from bis-cyclooctadiennickel and butadiene.[23]

* In the absence of THF, oxidative addition of RX to Ln does not occur.[11—13]

Table 1. Composition of the products of the interaction of RHal with Ln^0 in THF in the presence of isoprene. Conditions: RHal/Ln = 1.5 (runs *1—5*) and 1.0 (runs *6*, *7*), C_5H_8/Ln = 8 to 10 (mol/mol), 20 °C (BzCl) and 70 °C (PhBr)

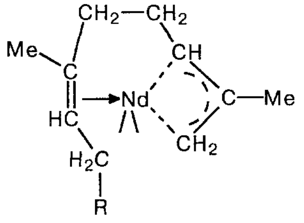
Run	Ln^0	RHal[a]	Found (mmol) in a solution in THF		Molar ratio		Yield of $R_n^{ol}LnX_{3-n}$ (% of the theoretical value)[b]
			Ln	Hal	$\frac{C—Ln}{Ln}$	$\frac{Cl}{Ln}$	
1	Nd	BzCl (4.0)	1.80	3.5	1.00	1.95	90
2	Nd	BzCl (2.0)	10.20	19.5	0.90	1.90	100
3	Nd	BzCl (7.4)	3.70	7.5	0.95	2.00	100
4	Pr	BzCl (8.4)	4.60	7.7	1.05	1.70	100
5	Gd	BzCl (5.6)	2.50	4.5	1.05	1.80	89
6	Nd	PhBr (12.0)	7.40	11.7	1.21	1.58	98
7	Nd	PhBr (13.0)	7.75	12.7	1.50	1.65	98

[a] The amount of RHal (in mmoles) is indicated in parentheses. [b] The amount of organolanthanide compounds (calculated from the Ln content in a solution in THF) according to the equation RHal + Ln + diene = $[R(diene)_m]_nLnHal_{3-n}$.

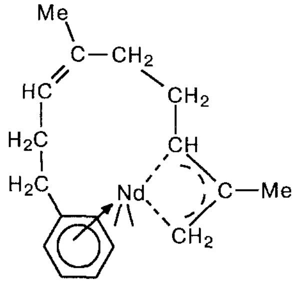
which probably suggests that benzyl radicals predominantly react with isoprene.

The IR spectra of oligoisoprenyl complexes obtained from benzyl chloride and phenyl bromide contain bands at 500—650, 970, 1010—1040, 1245—1340, and 1510 cm^{-1} that characterize a π-alkenyl ligand linked to the metal. These bands disappear when the samples are oxidized in air. A calculation of the vibrational spectra of π-C_4H_7MCl (M = Ni, Pd)[25] showed that the bands at 530 and 1270 cm^{-1} are characteristic of *syn*-crotyl complexes, whereas the corresponding bands in *anti*-crotyl complexes appear at 613 and 1340 cm^{-1}. The IR spectra of the oligodienyl complexes synthesized by us from benzyl chloride contain bands at 525 and 1245 cm^{-1}, while similar complexes based on phenyl bromide have bands at 620 and 1300 cm^{-1}. These differences may arise from the fact that the former complexes have a *syn*-configuration of the π-alkenyl ligand at the metal, while the ligand in the latter complex has an *anti*-configuration.

The IR spectra of the complexes obtained from phenyl bromide, whose oligodienyl chains contain 10 isoprene units, display weak bands at 750—770 and 1615 cm^{-1}, which characterize the π-coordination of the isolated double bond of the oligodienyl chain to the metal. The spectra of the product of the reaction between benzyl chloride and Nd in the presence of isoprene, which incorporates 1 to 3 isoprene units, do not contain bands characterizing π-coordination of the double bond. Instead, splitting of all bands of the monosubstituted phenyl ring is pronounced (690—710, 730—750, 1495—1500, and 1595—1600 cm^{-1}). This splitting disappears when the sample is oxidized by air oxygen. It may be concluded that stabilization of oligodienyllanthanide halides can occur not only through coordination of a double bond of the oligodienyl chain to a metal, but also through coordination of the metal with the phenyl ring linked to a short oligodienyl ligand. The combined IR spectroscopic data allow us to represent the structures of the oligodienyl complexes obtained as **A** and **B**.



A



B

The oligodienyllanthanide halides synthesized always contain THF molecules coordinated to a metal atom, which follows from the results obtained by chromatographic analysis of the products of the acidolysis of these complexes and by IR spectroscopy. The spectra of the complexes contain rather intense bands at 890 and 1040 cm^{-1} that correspond to the stretching vibrations of the C—O bonds in THF. The long-wave shift of these bands in comparison with those of free THF (920 and 1085 cm^{-1}) in the spectra of the $R_n^{ol}NdX_{3-n}$ complexes suggests that the THF molecules are coordinated to the metal atoms. These bands disappear after storage of the samples in air.

The $R_n^{ol}LnX_{3-n} \cdot m$THF complexes are virtually insoluble in hydrocarbons. In order to obtain efficient catalysts of *cis*-polymerization from these complexes, a small amount of AlR_3 and a diene was added to a suspension of $R_n^{ol}LnX_{3-n} \cdot m$THF (molar ratio Al/Ln = 3 : 1, diene/Ln = (5 to 10) : 1) in toluene maximally purified from THF *in vacuo*. After prolonged stirring, the resulting complex completely dissolves in toluene, has high stability in storage, and displays activity in the polymerization of dienes.

Thus, investigations showed that the oligodienyl compounds $R_n^{ol}M$ and $R_n^{ol}MX_m$ of a series of transition metals (Ti, Cr, Ni, Co, Mn, and Ln) are very stable, and are significantly more stable than the corresponding π-alkenyl derivatives. This stability results from additional π-coordination of isolated double bonds of the oligodienyl chain to the metal. It can be assumed that stabilization of this kind should also take place in oligodienyl compounds of other transition metals.

References

1. V. A. Yakovlev, I. A. Oreshkin, and B. A. Dolgoplosk, *Metalloorg. Khim.*, 1989, **2**, 93 [*Organomet. Chem. USSR*, 1989, **2**, 46 (Engl. Transl.)].
2. G. Wilke, B. Bogdanović, and P. Hard, *Angew. Chem.*, 1966, **78**, 157.
3. B. A. Dolgoplosk and E. I. Tinyakova, *Metalloorganicheskii kataliz v protsessakh polimerizatsii* [*Organometallic Catalysis in Polymerization Processes*], Nauka, Moscow, 1985 (in Russian).
4. L. J. Andrews and R. M. Keefer, *Molecular Complexes of Organic Chemistry*, Holden-Day, San Francisco, 1964.
5. B. A. Dolgoplosk, E. I. Tinyakova, I. Sh. Guzman, S. P. Smerkin, and G. N. Bondarenko, *Dokl. Akad. Nauk SSSR*, 1983, **272**, 394 [*Dokl. Chem.*, 1983, **272** (Engl. Transl.)].
6. S. P. Smerkin, I. Sh. Guzman, G. N. Bondarenko, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1986, **289**, 1171 [*Dokl. Chem.*, 1986, **289** (Engl. Transl.)].
7. I. F. Gavrilenko, G. N. Bondarenko, S. B. Sverchinskaya, E. I. Tinyakova, and B. A. Dolgoplosk, *Metalloorg. Khim.*, 1988, **1**, 309 [*Organomet. Chem. USSR*, 1988, **1**, 171 (Engl. Transl.)].
8. E. N. Zavadovskaya, O. K. Sharaev, G. K. Borisov, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1984, **274**, 333 [*Dokl. Chem.*, 1984, **274** (Engl. Transl.)].
9. A. I. Yashin, E. I. Tinyakova, Yu. V. Bryantseva, K. G. Miesserov, V. Makhdi, and B. A. Dolgoplosk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1608 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1978, **27**, 1404 (Engl. Transl.)].
10. S. P. Smerkin, Ph. D. Thesis (Chem.), Inst. of Petrochem. Synthesis, Acad. Sci. USSR, Moscow, 1990 (in Russian).
11. B. A. Dolgoplosk, E. I. Tinyakova, I. N. Markevich, T. V. Soboleva, G. M. Chernenko, O. K. Sharaev, and V. A. Yakovlev, *J. Organomet. Chem.*, 1983, **255**, 71.
12. I. N. Markevich, O. K. Sharaev, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1983, **268**, 892 [*Dokl. Chem.*, 1983, **268** (Engl. Transl.)].
13. V. A. Yakovlev, E. L. Vollershtein, L. S. Cherezova, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1983, **268**, 1422 [*Dokl. Chem.*, 1983, **268** (Engl. Transl.)].
14. V. N. Zgonnik, K. K. Kalnin'sh, Kh. B. Tsvetanov, and N. I. Nikolaev, *Vysokomolek. Soedin. A*, 1973, **15**, 900 [*Polym. Sci. USSR*, 1973, **15** (Engl. Transl.)].
15. I. V. Sal'nikova, O. I. Adrov, I. Sh. Guzman, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1986, **289**, 629; 1987, **296**, 355 [*Dokl. Chem.*, 1986, **289**; 1987, **296** (Engl. Transl.)].
16. W. Gerbert, J. Hinz, and H. Sinn, *Makromol. Chem.*, 1971, **144**, 97.
17. Takao Aoko, Akio Furusaki, Jugira Tomiie, *et al.*, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 545.
18. S. I. Beilin, I. N. Markevich, S. B. Gol'shtein, G. N. Bondarenko, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1974, **218**, 837 [*Dokl. Chem.*, 1974, **218** (Engl. Transl.)].
19. G. Allegra, Lo Giudice, and G. Natta, *Chem. Comm.*, 1967, 1263.
20. H. Ashitaka, K. Jinda, and H. Uena, *J. Pol. Sci. Chem. Ed.*, 1983, **21**, 1957.
21. N. N. Chigir, I. Sh. Guzman, O. K. Sharaev, E. I. Tinyakova, and B. A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 1982, **263**, 375 [*Dokl. Chem.*, 1982, **263** (Engl. Transl.)].
22. G. N. Bondarenko and A. V. Kotov, *Dokl. Akad. Nauk SSSR*, 1974, **219**, 1150 [*Dokl. Chem.*, 1974, **219** (Engl. Transl.)].
23. B. Bogdanović, P. Heimbach, G. Wilke, *et al.*, *Liebigs Ann. Chem.*, 1965, **727**, 143.
24. R. Taube, P. Bohme, and J. P. Gehrke, *J. Organomet. Chem.*, 1990, **399**, 327; 1991, **410**, 403.
25. G. N. Bondarenko and A. V. Kotov, *Dokl. Akad. Nauk SSSR*, 1977, **237**, 840 [*Dokl. Chem.*, 1977, **237** (Engl. Transl.)].

Received June 22, 1994;
in revised form September 19, 1994