Russian Chemical Bulletin, International Edition, Vol. 54, No. 1, pp. 247—251, January, 2005 247

Synthesis and reactivity of metal-containing monomers.
Part 59. Preparation and polymerization transformations of vinyl and isopropenyl derivatives of hafnocene dichloride*

D. P. Krut´ko,[a]* M. V. Borzov,[a] D. A. Lemenovskii,[a] G. I. Dzhardimalieva,[b] and A. D. Pomogailo[b]

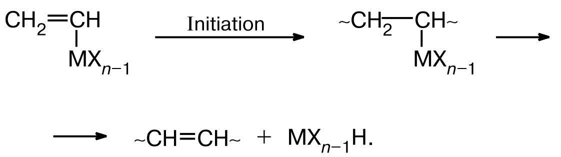
[a]Department of Chemistry, M. V. Lomonosov Moscow State University,
1, Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: kdp@org.chem.msu.su
[b]Institute of Chemical Physics Problems, Russian Academy of Sciences,
1, prosp. akad. N. N. Semenova, Chernogolovka, Moscow region, 142432, Russian Federation.
Fax: +7 (096) 515 5420. E-mail: adpomog@icp.ac.ru

Novel vinyl- and isopropenyl-substituted cyclopentadienyl complexes of hafnium(IV), $[C_5H_4(CR{=}CH_2)]_2HfCl_2$ [R = H (**5**), CH_3 (**6**)], were prepared and characterized. The organometallic monomers obtained were shown to undergo radical or anionic homopolymerization. Copolymerization of these metallocenes with styrene was performed. The potential applications of the metal polymers in question were considered.

Key words: hafnium, vinylcyclopentadiene, isopropenylcyclopentadiene, organometallic monomers, polymerization, copolymerization.

Organometallic polymers obtained by polymerization or copolymerization of appropriate monomers are of considerable interest as immobilized catalysts for various reactions and as precursors for the preparation of nanocomposite materials, ceramics, and so on.

However, the range of organometallic monomers in which the group capable of polymerization is directly bound to a transition metal atom through a metal—carbon bond is very limited, as these molecules are unstable. On the one hand, the average dissociation energy of a metal—carbon bond D(M—C) is comparable[2,3] with the average metal—halogen bond energy, D(M—Cl) or D(M—Br), even for the least stable alkyl derivatives of transition metals, but on the other hand, this bond is much more reactive than the M—O, M—N, M—Hal, *etc.* bonds. This is especially clear in the polymerization of such monomers because in the majority of cases, the synthesis of metal-containing polymers is accompanied by elimination of metal hydride:[4]



$$\underset{MX_{n-1}}{CH_2{=}CH} \xrightarrow{\text{Initiation}} {\sim}\underset{MX_{n-1}}{CH_2{-}CH}{\sim} \longrightarrow {\sim}CH{=}CH{\sim} + MX_{n-1}H.$$

The undesirable β-hydride transfer can be prevented by using organometallic compounds devoid of hydrogen at the β-carbon atom. For this purpose, Me or another group is introduced instead of the H atom.

Procedures for the synthesis of organometallic monomers in which the Cp rings contain a vinyl or an isopropenyl group have been developed in sufficient detail for a number of metals. This is a rather well-studied field of chemistry of polymers based on vinylferrocene, which is among the first monomers containing a chemically bound metal. The polymerization of metal monomers of this type can be initiated by any type of initiation (radical, cationic, anionic, Ziegler—Natta catalysts). Their susceptibility to a particular initiation type can be changed crucially by introducing appropriate substituents into the vinyl group. As an example, one can mention cyclopentadienyl complexes containing the isopropenyl group instead of vinyl, which are potential monomers for cationic polymerization.[5]

The purpose of this study is to prepare bis(vinylcyclopentadienyl)- and bis(isopropenylcyclopentadienyl)dichlorohafnium as potential metal monomers and to attempt the synthesis of polymers and copolymers based on these monomers.

Results and Discussion

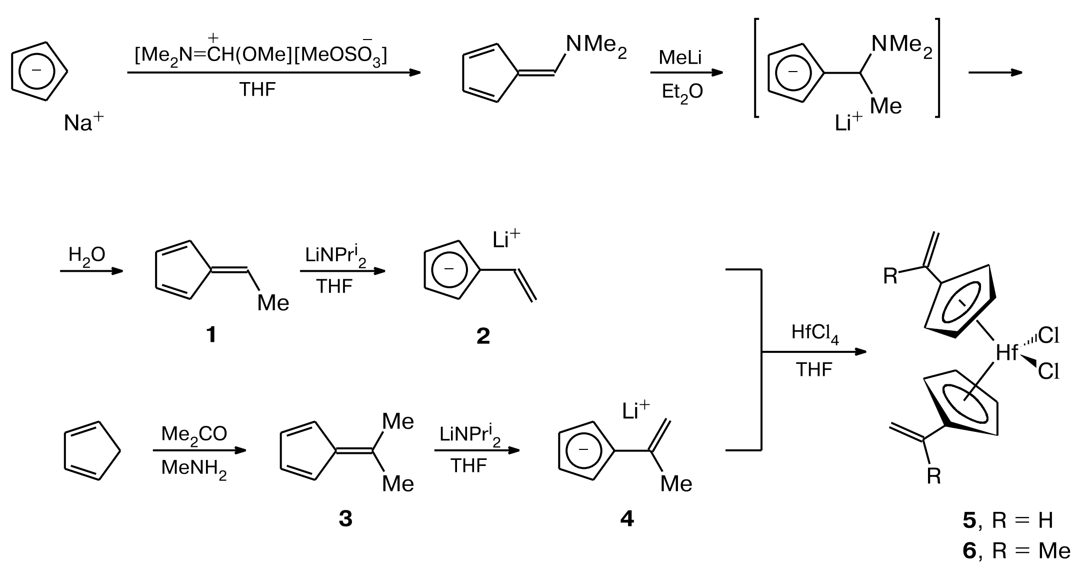
Synthesis of Hf^{IV}-containing monomers. As the starting monomers for the subsequent polymerization, we prepared two new hafnocene dichlorides,

---

* For Part 58, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 242—246, January, 2005.

Scheme 1



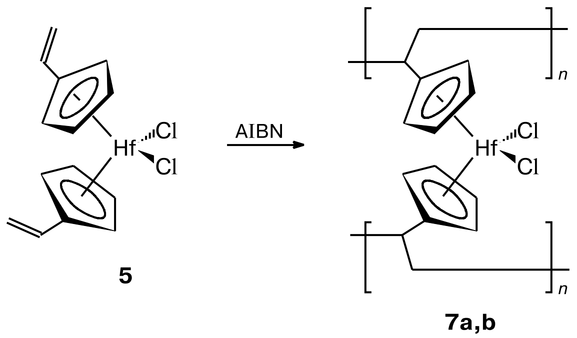
$[C_5H_4(CR=CH_2)]_2HfCl_2$ (R = H, Me), by the route shown in Scheme 1.

The sandwich complex **6** is rather readily available due to the fact that the initial 6,6-dimethylfulvene (**3**) can be easily prepared in one step from acetone and cyclopentadiene.[6] Conversely, the synthesis of the vinyl-substituted sandwich complex **5** is a more complicated task. We did not succeed in reproducing the procedure of synthesis of 6-methylfulvene (**1**) from acetaldehyde and cyclopentadiene,[6] similarly to fulvene **3**. The dicyclopentadiene whose boiling point was very close to that reported in a patent[6] for fulvene **1** (in reality, it is much lower) was the only product isolated after this reaction. Therefore, we prepared methylfulvene **1** by an alternative procedure[7,8] through 6-(*N*,*N*-dimethylamino)fulvene. Deprotonation of fulvenes **1** and **3** with lithium diisopropylamide gave lithium vinyl-[9] and isopropenylcyclopentadienides **2** and **4**, which were isolated and characterized by ^1H and ^{13}C NMR spectroscopy.

The sandwich complexes **5** and **6** were prepared by the reaction of lithium derivatives **2** and **4** with $HfCl_4$ in THF. Hafnocene dichlorides **5** and **6** are white crystalline solids readily soluble in THF, CH_2Cl_2, and $CHCl_3$. Complex **5**, unlike **6**, is also easily soluble in Et_2O and toluene and moderately soluble in hexane. Unlike unsubstituted hafnocene dichloride, compounds **5** and **6** are exceptionally sensitive to atmospheric oxygen. Even in the crystalline state, a short-term (~1 min) exposure to air is sufficient for initiation of polymerization processes. The subsequent dissolution in a high vacuum results in dark-colored polymeric products that precipitated from the solution within 24 h at room temperature. Therefore, all operations with monomers **5** and **6** should be carried out strictly in an inert atmosphere or in a high vacuum.

Polymerization of hafnium-containing monomers and some properties of polymers. Complexes **5** and **6** were studied as monomers in the liquid-phase (in a toluene solution) radical homopolymerization initiated by 0.5—2.0% azobisisobutyronitrile (AIBN). Monomer **5** was converted in a yield of up to 30% into a product, representing a mixture of cross-linked fraction **7a** insoluble in organic solvents and linear oligomer ($\bar{M}_n \approx 6000$) **7b** (Scheme 2).

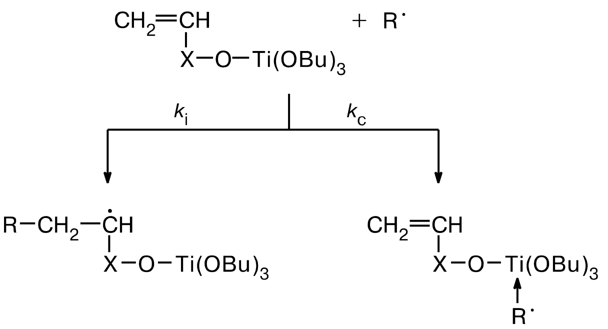
Scheme 2



The IR spectrum of the polymer exhibits stretching vibrations of the residual double bonds (1636 cm^{-1}) and vibrations of the substituted Cp ring. The relatively low yields of polymer **7** may be due to the same reasons as in the case of polymerization of Ti^{IV} monomers,[10] namely, the competing coordination of both the primary radicals and the macroradicals to metal ions and their participation in the initiation of polymerization (Scheme 3):

This assumption is supported by a number of known facts.[11] For example, even the stable di-*tert*-butyliminoxyl

Scheme 3



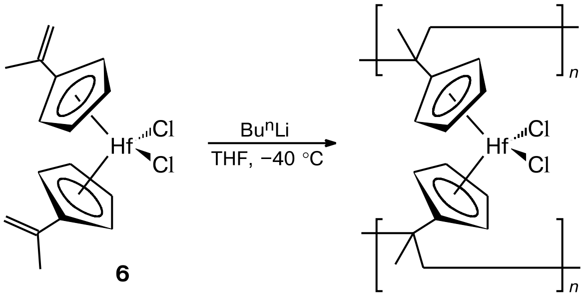
radicals easily replace the alkyl fragments in Cp_2HfR_2 to give *O*-alkyl-*N*,*N*-di-*tert*-butylhydroxylamine and $Cp_2M(R)O—N\text{-}Bu^t_2$.

The formation of the coordination radical complexes is often observed in the polymerization of metal-containing monomers,[12] the metal ion acting as a sort of radical trap. The metal-coordinated radicals participate in both the chain propagation and (mainly) in the chain termination. In the case of Ti^{IV} monomers, these processes were studied quantitatively.[10]

Note that the attempts to obtain the polymer from complex **5** using γ-radiation from ^{60}Co for initiation (THF, dose 20 Mrad) have not met with success, apparently, due to monomer decomposition under conditions of radiolysis.

Complex **6** could be converted into the polymer only by anionic polymerization (Bu^nLi, –40 °C, THF solution) (Scheme 4).

Scheme 4



Product **8** is also composed of two fractions; the DMF-soluble fraction has $\bar{M}_n$ ~4000, *i.e.*, only 10—12 monomer units are included in the oligomer chain.

Copolymerization of 5 and 6 with styrene. The monomers proved to be capable of copolymerization with styrene, although the yields of the polymeric products are relatively low. The number-average molecular mass of the copolymer formed by complex **5** with styrene was $\bar{M}_n$ = 25000 after three reprecipitations from benzene into ethanol. Note for comparison that the radical polymerization of styrene under the same conditions (benzene, 2% AIBN) results in the formation of polystyrene with the following molecular-weight characteristics: $\bar{M}_n$ = 29000, $\bar{M}_w$ = 47000, $\bar{M}_w/\bar{M}_n$ = 1.62. It is also possible to carry out radical copolymerization of complex **6** with styrene, unlike homopolymerization. The yields of the copolymer are also relatively low, and the number-average molecular mass is equal to ~10000.

Thus, we demonstrated the possibility of involvement of the Hf-containing monomers synthesized into radical or ionic polymerization. Presumably, optimization of the reaction conditions (initiation type, temperature, reaction medium, *etc.*) would allow one to increase the yields of the reaction products and increase the molecular weights.

In conclusion, note some prospects of this study. Metal-containing polymers combine the key properties of the polymers and metals contained in the polymer. Of particular interest are the variants where such systems exhibit synergism, *i.e.*, the properties are enhanced or new properties appear.

Recent years have seen increased attention to metal polymer nanocomposites, which find application as catalysts, magnetic and optical materials, sensors, *etc.*[13] It can be expected that the polymeric hafnocene dichlorides would be efficient catalysts for olefin polymerization (in combination with polymethylalumosiloxane). This follows from the search for polymer-immobilized metallocene catalysts developed intensively in recent years (see Ref. 14). We found that copolymers of complexes **5** and **6** with styrene in combination with polymethylalumoxane exhibit activity in ethylene and propylene polymerization; however, their catalytic properties are much lower (the highest activity in ethylene polymerization reaches 50 kg of PE $(g\ Hf)^{-1}MPa^{-1}h^{-1}$) than that of Zr compounds.

Organometallic polymers of this type also present interest for the preparation of thermally stable coatings based on hafnium carbide by controlled pyrolysis of Hf-containing polymers and their copolymers. The advantages of this approach may include the use of oxygen-free precursors (in other words, exclusion of HfO_2 from the pyrolysis products), relatively high contents of hafnium, and a uniform phase composition of the products. Preliminary studies have shown that the synthesis of Hf-containing polymers followed by their pyrolysis results in the formation of HfC_x. The products of pyrolysis (1300 °C) of metal polymers based on compounds **5** and **6** contain up to 80—85% (w/w) hafnium carbide.

Experimental

All synthetic procedures, preparation of NMR samples, and polymerization of metal monomers were carried out either in an inert atmosphere or in all-sealed evacuated apparatus such as Schlenk vessels. The solvents (including deuterated ones) were dehydrated by standard procedures.[15] Cyclopentadiene was prepared from dicyclopentadiene (Merck), dried over Na_2SO_4, and distilled under argon directly prior to use. Commercially available $HfCl_4$ (Merck) was used; 6-(*N*,*N*-dimethylamino)fulvene,[7] 6-methylfulvene,[8] and 6,6-dimethylfulvene[6] were synthesized by known procedures.

The ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian VXR-400 instrument (400 and 100 MHz, respectively). The ^{1}H and ^{13}C NMR spectra were referred to the signals of the deuterated solvents (δ 5.32 and 53.8 for CD_2Cl_2, δ 1.73 and 25.3 for THF-d_8). The elemental analysis of metal monomers was performed on a Carlo-Erba automated analyzer. IR spectra were recorded on Perkin-Elmer 1720-X and UR-20 spectrometers. The content of hafnium in the polymers was determined by spectrophotometry on a FEK-56 instrument. The molecular masses of the polymers were determined on a Hewlett-Packard-502 membrane osmometer.

Lithium ethenylcyclopentadienide (2) was synthesized by modification of a known procedure.[9] A hexane solution of *n*-BuLi (1.82 mol L^{-1}, 165 mL) was added at −78 °C over a period of 2 h to a mixture of diisopropylamine (42.1 mL, 30.36 g, 0.300 mol) and 100 mL of THF. The reaction mixture was warmed-up to room temperature and stirred for 3 h. The resulting solution of lithium diisopropylamide was cooled to −30 °C and a solution of fulvene **1** (27.64 g, 0.300 mol) in 50 mL of THF was added dropwise under stirring over a period of 3 h. The reaction mixture was warmed-up to room temperature and left for 16 h. The solvents and $HNPr^i_2$ were removed *in vacuo*, Et_2O (30 mL) and hexane (200 mL) were added to the residue, and the resulting precipitate was filtered off, washed on the filter with 150 mL of hexane, and dried in a high vacuum. Yield 16.73 g (0.170 mol, 56.9%, white crystalline powder). ^{1}H NMR (THF-d_8, δ, *J*/Hz): 4.29 (dd, 1 H, $=C\underline{H}H$, $^2J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 11.6 Hz); 4.89 (dd, 1 H, $=CH\underline{H}$, $^2J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 17.8 Hz); 5.59, 5.80 (both virt. t, 2 H each, C_5H_4, $^{3+4}J_{H,H}$ = 5.6 Hz); 6.52 (dd, 1 H, =CH Hz, $^3J_{H,H}$ = 17.8 Hz, $^3J_{H,H}$ = 11.6 Hz). ^{13}C NMR, δ: 98.76 (=CH_2); 103.76, 104.99 (CH in C_5H_4); 119.84 (C, C_5H_4); 136.87 (=CH).

Lithium (1-methylethenyl)cyclopentadienide (4) was prepared similarly to lithium salt **2** from fulvene **3** (31.85 g, 0.300 mol) in 50 mL of THF. After completion of the reaction and removal of the solvents and $HNPr^i_2$, ether (150 mL) was added to the residue, and the resulting precipitate of filtered off, washed on the filter with 150 mL of hexane, and dried in a high vacuum. On the subsequent workup of the ether mother liquor, the total yield of the product (a white crystalline solid) was 26.50 g (0.238 mol, 79.3%). ^{1}H NMR (THF-d_8), δ: 1.98 (s, 3 H, Me); 4.20, 4.80 (both m, 1 H each, =CH_2); 5.57, 5.84 (both virt t, 2 H each, C_5H_4, $^{3+4}J_{H,H}$ = 4.8 Hz). ^{13}C NMR, δ: 23.04 (Me); 98.61 (=CH_2); 102.48, 104.66 (CH, C_5H_4); 121.88 (C, C_5H_4); 142.89 [$=\underline{C}(CH_3)$].

Bis(η^5-ethenylcyclopentadienyl)dichlorohafnium (5). A solution of cyclopentadienide **2** (4.45 g, 45.4 mmol) in 20 mL of THF was added at −20 °C under vigorous stirring to a solution of $HfCl_4$ (7.27 g, 22.7 mmol) in 30 mL of THF. The homogeneous solution was kept for 4 h at 20 °C and for 2 h at 70 °C. The solvent was removed *in vacuo*, the residue was extracted with 75 mL of CH_2Cl_2, and the LiCl precipitate was filtered off. The extract was concentrated to a volume of ~15 mL, and 70 mL of ether was added. After slow evaporation of the solvents, the crystals of the complex were filtered off, washed on the filter with a minimum amount of cold pentane, and dried in a high vacuum (compound **5** is markedly soluble in warm pentane). Yield 5.19 g (12.0 mmol, 53.0%) (white crystalline powder). Found (%): C, 38.91; H, 3.30. $C_{14}H_{14}Cl_2Hf$. Calculated (%): C, 38.96; H, 3.27. ^{1}H NMR (CD_2Cl_2), δ: 5.31 (dd, 2 H, $=C\underline{H}H$, $^2J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 10.8 Hz); 5.55 (dd, 2 H, $=CH\underline{H}$, $^2J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 17.6 Hz); 6.25, 6.38 (both virt t, 4 H each, C_5H_4, $^{3+4}J_{H,H}$ = 5.6 Hz); 6.58 (dd, 2 H, =CH, $^3J_{H,H}$ = 17.6 Hz, $^3J_{H,H}$ = 10.8 Hz). ^{13}C NMR, δ: 113.55, 114.62 (CH, C_5H_4); 116.33 (=CH_2); 126.19 (C, C_5H_4); 129.96 (=CH).

IR, (CCl_4), ν/cm^{-1}: 827 (s, out-of-plane δ CH(Cp)); 890 (out-of-plane δ CH(=CH_2)); 1045 (m., δ CH(Cp) in-plane); 1407, 1459, 1494 (Cp-ring vibrations); 1634 (ν(C=C)); 3103 (ν(CH(Cp))).

Bis[(η^5-(1-methylethenyl)cyclopentadienyl]dichlorohafnium (6). The reaction was carried out in a similar way using $HfCl_4$ (7.40 g, 23.1 mmol) and salt **4** (5.18 g, 46.2 mmol). After the addition of CH_2Cl_2 and separation of LiCl, the extract was concentrated until the main bulk of the product crystallized. An equal volume of ether was added and the product was crystallized from this solvent mixture. The precipitated crystals were filtered off, washed on the filter with ether and pentane, and dried in a high vacuum. Yield 6.03 g (13.1 mmol, 56.8%) (white crystalline powder). Found (%): C, 41.73; H, 3.97. $C_{16}H_{18}Cl_2Hf$. Calculated (%): C, 41.80; H, 3.95. ^{1}H NMR (CD_2Cl_2), δ: 2.03 (dd, 6 H, CH_3, $^4J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 0.8 Hz); 5.12, 5.34 (both m, 2 H each, =CH_2); 6.22, 6.41 (both virt t, 4 H each, C_5H_4, $^{3+4}J_{H,H}$ = 5.4 Hz). ^{13}C NMR, δ: 21.52 (Me); 113.17, 113.87 (CH, C_5H_4); 113.42 (=CH_2); 129.53 (C, C_5H_4); 136.90 ($=\underline{C}(CH_3)$).

IR (CCl_4), ν/cm^{-1}: 838 (s, out-of-plane δ CH(Cp)); 860, (out-of-plane, δ CH(=CH_2) out-of-plane); 1058, 1408, 1440, 1452 (Cp-ring vibrations); 1628 (ν(C=C)); 3116 (ν(CH(Cp))).

Polymerization of complex 5. Complex **5** (0.71 g) and AIBN (0.013 g) were placed in a glass ampule in an inert atmosphere, the ampule was evacuated, toluene (50 mL) was added by recondensation, and the ampule was sealed off. Polymerization was carried out at 60 °C for 12 h. The polymer precipitate was filtered off in an inert atmosphere, washed with toluene, and dried *in vacuo*. The yield of **7** was 0.2 g, the Hf content was 41.3% (w/w). IR (KBr), ν/cm^{-1}: 810 (m, out-of-plane δ CH(Cp)); 1038 (m, in-plane δ CH(Cp)); 3100, 1636 (w, ν(C=C)).

Polymerization of complex 6. A 1.8 *M* heptane solution of Bu^nLi (1 mL) was added at −40 °C in an inert atmosphere to complex **6** (0.23 g) in THF. The reaction mixture was gradually heated to room temperature and left for 16 h. Polymer **8** (0.15 g) was reprecipitated with toluene, washed, and dried *in vacuo*. The hafnium content in the product was 40.0% (w/w). IR (KBr), ν/cm^{-1}: 838, 1058, 3100, 1628 (w).

Copolymerization of complex 5 with styrene. Complex **5** (0.66 g), styrene (1 g), and AIBN (0.0184 g) were placed in a glass ampule in an inert atmosphere and evacuated. Toluene (20 mL) was added by condensation and the ampule was sealed-off. Polymerization was carried out at 60 °C for 12 h. The copolymer was isolated by reprecipitation with methanol. The polymer yield was 22% and the hafnium content was 6.8% (w/w).

Copolymerization of complex 6 with styrene. Complex **6** (0.36 g), styrene (1 g), and AIBN (0.0129 g) were placed in a glass ampule in an inert atmosphere and evacuated. THF (20 mL) was added by condensation and the ampule was sealed-off. Polymerization was carried out at 60 °C for 12 h. The copolymer was isolated by reprecipitation with methanol. The polymer yield was 10% and the hafnium content was 3.6% (w/w).

Pyrolysis of hafnium copolymers was carried out *in vacuo* at 1300 °C, and powder X-ray diffraction analysis was carried out on a DRON UM-2 diffractometer using Cu*K*α radiation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32634).

References

1. N. D. Golubeva, O. A. Adamenko, G. N. Boiko, L. A. Petrova, Yu. A. Ol´khov, and A. D. Pomogailo, *Neorgan. mater.*, 2004, **45**, No. 3.
2. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* [*Dissociation Energy of Chemical Bonds. Ionization Potentsials and Electron Affinity*], Ed. V. N. Kondrat´eva, Nauka, Moscow, 1974, 351 pp. (in Russian).
3. V. E. L´vovskii, E. A. Fushman, and F. S. D´yachkovskii. *Zh. Fiz. Khim.*, 1982, **56**, 1864 [*J. Phyz. Chem. USSR*, 1982, **56** (Engl. Transl.)].
4. C. U. Pittman, Jr., *Organometallic Reactions*, Marcel Decker, New York, 1977, **6**, 1.
5. *Metal-containing Polymer Systems*, Eds J. E. Sheats, C. E. Carraher, Jr., and C. U. Pittman, Jr., Plenum Press, New York, 1985, p. 43.
6. W. Freiesleben, *Ger. Pat.* 1 146 050, (1963); *Chem. Abstr.*, 1963, **59**, 9914.
7. K. Hafner, K. H. Vopel, G. Ploss, and C. Konig, *Org. Synth.*, 1967, **47**, 52.
8. D. W. Macomber, W. C. Spink, and M. D. Rausch, *J. Organomet. Chem.*, 1983, **250**, 311.
9. M. Ogasa, D. T. Mallin, D. W. Macomber, and M. D. Rausch, *J. Organomet. Chem.*, 1991, **405**, 41.
10. G. I. Dzhardimalieva, A. O. Tonoyan, A. D. Pomogailo, and S. P. Davtyan, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1987, 1744 [*Bull. Acad. Sci. USSR. Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].
11. P. B. Brindley and M. J. Scotton, *J. Organomet. Chem.*, 1981, **222**, 89.
12. A. D. Pomogailo, and G. I. Dzhardimalieva, *Izv. Akad. Nauk. Ser. Khim.*, 1998, 2403 [*Russ. Chem. Bull.*, 1998, **47**, 2319 (Engl. Transl.)].
13. A. D. Pomogailo, A. S. Rozenberg, and I. E. Uflyand, *Nanochastitsy metallov v polimerakh* [*Metal Nanoparticles in Polymers*], Khimiya, Moscow, 2000, 672 pp. (in Russian).
14. H. G. Alt and A. Köppl, *Chem. Rev.*, 2000, **100**, 1205.
15. D. D. Perrin, W. L. F. Armarego, and D. N. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966, 362 pp.

Received March 30, 2004
in revised form October 6, 2004