Reactions of dysprosium diiodide with phenyl- and pentafluorophenylgermanium compounds

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Reactions of DyI_2 with $(C_6F_5)_3GeH$, $(C_6F_5)_3GeBr$, and $(C_6F_5)_2GeBr_2$ gave rise to the hyperbranched polymer $[(C_6F_5)_2Ge(C_6F_4)]_n$ (**4**) in 22% to 65.7 yields. The major product of the reaction with $(C_6F_5)_3GeBr$ was perfluorinated hexaphenyldigermane in 61% yield. Under the same conditions, the germylmercury compound $[(C_6F_5)_3Ge]_2Hg$ yielded the ionic complex $\{[(C_6F_5)_3Ge]_3Hg\}^-[DyI_2]^+$. Hexaphenyldigermane slowly reacted with DyI_2 even at elevated temperature to give polymer **4** in 8% yield. Perfluorinated tetraphenylgermane and nonfluorinated phenylgermanes Ph_3GeH, $Ph_3GeGePh_3$, and $(Ph_3Ge)_2O$ did not react with DyI_2 but they initiated its reaction with THF.

Key words: diiodide, dysprosium, phenylgermanes, hyperbranched polymer.

Recent investigations of the chemical properties of neodymium(II), dysprosium(II), and thulium(II) diiodides have shown that these salts, especially neodymium and dysprosium iodides, are highly reactive toward various organic and organometallic substrates.[1] In particular, the iodides LnI_2 (Nd and Dy) in THF easily reduce aryl and alkyl halides to the corresponding hydrocarbons, while in benzene, they give rise to alkylation products of the solvent. In cross-coupling reactions of alkyl halides with ketones, the same iodides are much more reactive than SmI_2.[2] Neodymium and dysprosium diiodides can be successfully used in the synthesis of vanadocene, cobaltocene, bis(benzene)vanadium, nitrogen-containing cyclic and acyclic hydrocarbons, and other compounds.[3] In further investigations of lanthanide iodides as synthons of a novel type, it was of interest to study their reactions with organogermanium compounds containing various functional groups. Earlier,[4] we have discovered that tris(pentafluorophenyl)germane reacts with some rare-earth metal compounds such as $C_{10}H_8Ln(THF)_3$ (Ln = Eu, and Yb), $(Pr^iO)_3Ln$, $Ln(acac)_3$ (Ln = La and Gd), $(PhC{\equiv}C)_2Eu$, $La(bipy)_4$ (bipy is 2,2-bipyridyl), and $(Bu^tO)_2Eu$ to give a hyperbranched polymer, namely, polyphenylenegermane $[(C_6F_5)_2Ge(C_6F_4)]_n$ with the molecular mass $M = (4—7) \cdot 10^4$.

In the present work, we report on the reactions of DyI_2 with phenyl- and pentafluorophenylgermanium compounds $(C_6F_5)_3GeH$ (**1**), $(C_6F_5)_3GeBr$ (**2**), and $(C_6F_5)_2GeBr_2$ (**3**) containing the Ge—H, Ge—Br, or Ge—metal groups.

Results and Discussion

A few minutes after Ph_3GeH, $Ph_3GeGePh_3$, or $(Ph_3Ge)_2O$ were added to a green solution of DyI_2 in THF at room temperature, the solution turned brown and a precipitate of $DyI_3(THF)_3$ formed. Upon hydrolysis of the reaction mixture with dilute HCl, the starting organogermanium compounds were recovered in virtually quantitative yields. Similar transformations have been observed earlier upon addition of aromatic compounds Ph_4Sn or Ph_2Hg to solutions of NdI_2 or DyI_2 in THF or DME.[5] Supposedly, these additives initiate disproportionation of LnI_2 into LnI_3 and very reactive iodide Ln(I)I, which attacks the solvent to form a mixture of complexes of the type LnIRR´ (where R and R´ are the hydrogen atoms and the fragments of the cleaved solvent molecule). The formation of typical brown solutions and the triiodide DyI_3 in nearly 50% yield from DyI_2, as well as the recovery of the unreacted starting compounds, leads us to a conclusion that phenylgermanes, like benzene and Ph_4Sn, favor the disproportionation of DyI_2 and subsequent transformations.

Pentafluorophenylgermanium compounds proved to be substantially more reactive, except for $(C_6F_5)_4Ge$, which exerted the same effect on a solution of DyI_2 as nonfluorinated phenylgermanes. Germane **1** was consumed as fast as the reagents were mixed, which was evident from decoloration of the mixture. After the precipitate of DyI_2F that formed was filtered off, hyperbranched polymer **4** was isolated from the solution in 65% yield

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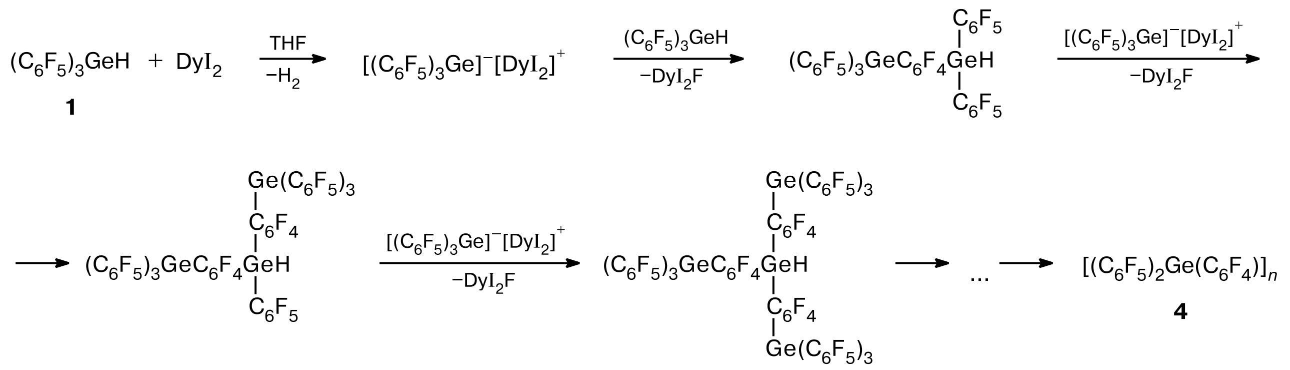
Scheme 1



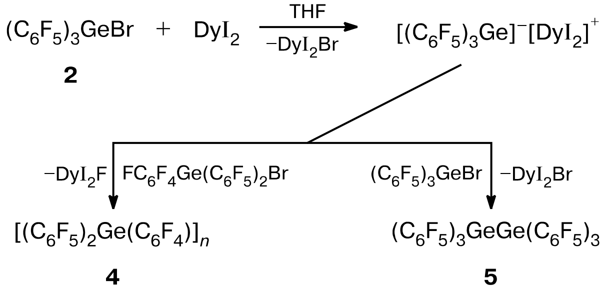
(Scheme 1). The strong electron-withdrawing effect of the C_6F_5 group imparts the acid character to the Ge—H group in hydride **1** and, consequently, makes the hydrogen atom easily replaceable by dysprosium(II) diiodide. Earlier,[6] generated anions $[(C_6F_5)_3Ge]^-$ have been found to easily replace the fluorine atoms in the *para*-position of the C_6F_5 rings of adjacent germane molecules, forming hyperbranched polymer **4**.

Scheme 1 represents a divergent pathway of the formation of product **4**; however, in reality, the real reaction, like the synthesis of other hyperbranched polymers,[7] follows both the divergent and convergent pathways. The molecular weight of polymer **4** ($1.5 \cdot 10^4$, $M_w/M_n = 1.37$) and its other properties are close to the corresponding characteristics of polyphenylenegermane obtained earlier by a reaction of germane **1** with Et_3N,[6] $(Pr^iO)_3Ln$, or Ln(acac) (Ln = La and Gd).[4] Polymer **4** is an air-stable white powder, which is soluble in most organic solvents, except for alcohols and alkanes. The IR spectrum of polymer **4** contains a set of bands for the C_6F_5Ge (1630, 1510, 1450, 1370, 1270, 1165, 1135, 1070, 1010, 940, 900, 850, 815, 750, 715, 615, 585, and 490 cm^{-1}) and C_6F_4Ge fragments (1230, 940, and 430 cm^{-1}).

The reaction of DyI_2 with bromogermane **2** under the same conditions was also rapid, giving digermane **5** as the major product (61%) rather than polymer **4**, whose yield did not exceed 7%. It is reasonable to assume that the first step of this reaction involves the formation of the trihalide DyI_2Br and the same ionic intermediate $[(C_6F_5)_3Ge]^-[DyI_2]^+$ as in the aforesaid reaction with germane **1**. However, at the second step, two reactions can compete a nucleophilic substitution of the $[(C_6F_5)_3Ge]^-$ anions for the F atoms in the C_6F_5 rings and a reaction of the intermediate $[(C_6F_5)_3Ge]^-[DyI_2]^+$ with the second molecule of compound **2** with cleavage of the Ge—Br bond to give digermane **5** (Scheme 2). According to the yields of products **4** and **5**, the second pathway is dominant.

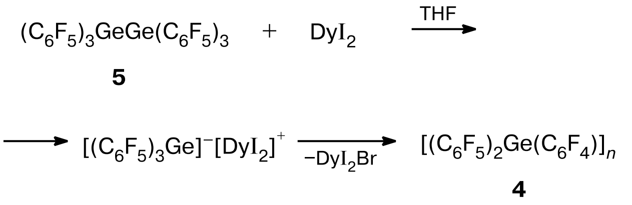
The C_6F_5 rings in fast-formed digermane **5** can also participate in polycondensation with the $[(C_6F_5)_3Ge]^-$ anions. In this case, a dendrite molecule of polyphenylenegermane is augmented exclusively along the divergent pathway and contains a Ge—Ge fragment. However, the content of the Ge—Ge fragments in polymer **4** cannot be considerable since digermane **5**, which is negligibly soluble in THF, goes out of the reaction solution immediately upon its formation.

Scheme 2



Another pathway is possible in the reaction with bromogermane **2**: cleavage of the Ge—Ge bond in the resulting digermane **5** by dysprosium diiodide. As has been found earlier,[8] the Ge—Ge fragment in digermanes containing pentafluorophenyl substituents are highly labile, as distinct from that in nonfluorinated analogs. For instance, digermanes **5** and $(C_6F_5)_3GeGeEt_3$ in THF, DME, or acetone easily react with water, alcohols, HCl, sulfur, and other reagents. In all cases, the Ge—Ge bond is cleft and the corresponding derivatives $(C_6F_5)_3Ge—X$ are obtained. Reactions with such reducing agents as Li and EtLi gave, instead of the expected product $(C_6F_5)_3Ge—Li$, a white organogermanium compound,[8b] which was identified much later as hyperbranched polyphenylenegermane. Insofar as DyI_2 is also a strong reducing agent, its reaction with digermane **5** was highly probable. We found that such a reaction occurs in fact but under substantially more drastic conditions than the reaction with bromogermane **2**. On heating of a mixture of DyI_2 and compound **5** in THF at 70 °C for 1 h, the conversion of digermane **5** into polymer **4** was only 8% (Scheme 3).

Scheme 3



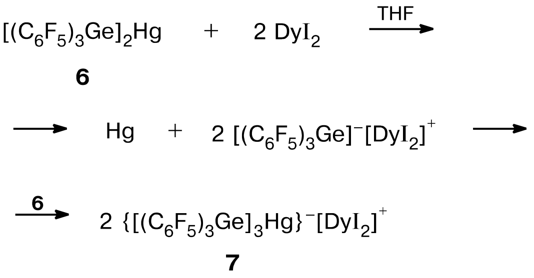
$$\underset{\mathbf{5}}{(C_6F_5)_3GeGe(C_6F_5)_3} + DyI_2 \xrightarrow{THF} [(C_6F_5)_3Ge]^-[DyI_2]^+ \xrightarrow[-DyI_2Br]{} \underset{\mathbf{4}}{[(C_6F_5)_2Ge(C_6F_4)]_n}$$

An unexpected result was obtained in the reaction of DyI_2 with dibromogermane **3**. Having two Ge—Br bonds in its molecule, compound **3** could be expected to yield either germylene $(C_6F_5)_2Ge$: (or its derivative $[(C_6F_5)_2Ge]_n$) or cross-linked network polyphenylenegermane $[(C_6F_4)_2Ge]_n$. Such a polymer was isolated as an insoluble light yellow solid upon treatment of the dihydride $(C_6F_5)_2GeH_2$ with triethylamine.[9]

The reaction of DyI_2 with dibromide **3** in THF at 0 °C was completed in a few minutes and really yielded a polymeric product together with dysprosium trihalide. However, like hyperbranched polymer **4**, this polymer proved to be well soluble in THF and most other organic solvents. The elemental analysis data and IR spectrum of the product were also identical with the corresponding characteristics of polymer **4**. The molecular weight of the polymer determined by gel permeation chromatography (GPC) was $1.6 \cdot 10^4$. The reaction mechanism leading to polymer **4** remains unclear; yet, its relatively low yield (22%) and the presence in the reaction solution before and after hydrolysis of a considerable amount of pentafluorobenzene (19% of the total C_6F_5 groups) suggest cleavage of the Ge—C_6F_5 bond by dysprosium iodide. Plausible products of this cleavage (unstable intermediates of the type C_6F_5—DyI_2) subsequently interact with the Ge—Br groups in the starting dibromide **3** or in a growing polymer, thus blocking cross-linking of the macromolecule. A small amount of C_6F_5H (1—9%) was also detected among products of the reactions of DyI_2 with germanes **1** and **2**.

When studying redox transmetalation reactions of bis[tris(pentafluorophenyl)germyl]mercury (**6**) with rare-earth metals, we discovered that generated anions $[(C_6F_5)_3Ge]^-$ are not involved in polycondensation but they are scavenged by the starting mercury compound to give less reactive mercurate anions $\{[(C_6F_5)_3Ge]_3Hg\}^-$ or $\{[(C_6F_5)_3Ge]_4Hg\}^{2-}$, which cannot displace the fluorine atoms from the C_6F_5 rings.[10] The same scheme is valid for the reaction of compound **6** with DyI_2, yielding metallic mercury and dysprosium(III) diiodide mercurate (Scheme 4).

Scheme 4



$$\underset{\mathbf{6}}{[(C_6F_5)_3Ge]_2Hg} + 2\,DyI_2 \xrightarrow{THF} Hg + 2\,[(C_6F_5)_3Ge]^-[DyI_2]^+ \xrightarrow{\mathbf{6}} 2\,\underset{\mathbf{7}}{\{[(C_6F_5)_3Ge]_3Hg\}^-[DyI_2]^+}$$

Compound **7** was isolated in 75% yield as a colorless fine-crystalline substance and characterized by elemental analysis and IR spectroscopy. The poor quality of its crystals precluded X-ray diffraction analysis; however, it is reasonable to assume that the anionic part $\{[(C_6F_5)_3Ge]_3Hg\}^-$ is structurally identical with the same fragment in the complex $\{[(C_6F_5)_3Ge]_3Hg\}^-[Cp_2Co]^+$ with known crystallographic data.[10]

Recently,[11] we have found that some reactions of iodides LnI_2 (Ln = Nd, Dy, and Tm) can occur in benzene, although these compounds are completely insoluble in nonsolvating media. However, attempted reactions of DyI_2 with organogermanes **1**, **2**, **3**, and **6** in benzene failed. No changes in the reaction mixtures were observed even upon prolonged heating at 80 °C.

Thus, this study showed that dysprosium(II) diiodide is inert toward phenylgermanium compounds, but it acts as a reducing agent in reactions with pentafluorophenylgermanium derivatives. In all cases, hyperbranched organogermanium polymer **4** forms as the result of polycondensation of generated anions $[(C_6F_5)_3Ge]^-$. The exception is the reaction with compound **6**, which acts as a scavenger for germanium anions. The resulting mercurate anion $\{[(C_6F_5)_3Ge]_3Hg\}^-$ can be isolated as complex **7**. We found that the reactions of DyI_2 with compounds **1** and **2** are accompanied by partial cleavage of the C_6F_5—Ge bonds. This pathway becomes dominant in the reactions with digermane **3**. In all the reactions studied, the solvent nature is substantial: transformations easily occur in THF but not in benzene.

Experimental

All reactions were carried out *in vacuo* according to the Schlenk standard method. After hydrolysis of the reaction mixtures, products were isolated and identified in air. Tetrahydrofuran was distilled over NaOH and finally dried with NdI_2 immediately before use. Commercial benzene was dried with NdI_2 and transferred to a reaction vessel by condensation *in vacuo*. Commercial diiodides DyI_2 and NdI_2 (Sinor, Nizhnii Novgorod) and phenylgermanium compounds $Ph_3GeGePh_3$ and $(Ph_3Ge)_2O$ (Aldrich) were used. Pentafluorophenyl derivatives **1**—**3**, **5**, and **6** and Ph_3GeH were prepared according to known procedures.[12—15]

The dysprosium content was determined by complexometric titration. IR spectra were recorded on a Specord M-80 instrument (Nujol). Chromatographic analysis was carried out on a Knauer liquid—liquid chromatograph (column 150×3 mm) equipped with a UV-absorption detector (λ = 254 nm). The columns were packed with Separon SGX C18 (particle size 5 μm) and methanol—water (9 : 1) was used as an eluent. The molecular masses and their distributions were determined by gel permeation chromatography on a Knauer instrument with a set of five styrogel columns 10^5, $3 \cdot 10^4$, 10^4, 10^3, and 250 Å in pore diameter and THF as an eluent. A Waters λ-403 differential refractometer was used as a detector. In addition, an LCD 2563 photometer (λ = 254 nm) was used.

Reaction of dysprosium(II) diiodide with $(C_6F_5)_3$GeH (1). A solution of compound **1** (1.463 g, 2.55 mmol) in THF (10 mL) was added to a stirred green solution of DyI_2 (1.06 g, 2.55 mmol) in THF (10 mL) at 0 °C. The mixture immediately turned light yellow and a gray precipitate of DyI_2F formed. After centrifuging, the precipitate was separated from the solution by decantation, washed with benzene, and dried. The yield of dysprosium trihalide $DyI_2F(THF)_3$ was 1.2 g (62%). Found (%): Dy, 24.62. $C_{12}H_{24}DyFI_2O_3$. Calculated (%): Dy, 24.95. The solution was concentrated to 3 mL and methanol (10 mL) was added. The yellowish precipitate of polymer **4** that formed was filtered off on a glass filter, washed with methanol, reprecipitated with hexane from a solution in acetone, and dried in air. The yield of the product was 0.91 g (65%). IR (Nujol), ν/cm^{-1}: 620 w, 715 w, 730 w, 820 m, 940 m, 960 vs, 1080 vs, 1230 m, 1280 m, 1450 vs, 1500 s, 1640 m. The molecular weight was $1.5 \cdot 10^4$; M_w/M_n = 1.37. The IR spectrum and retention time (in GPC) of polymer **4** are identical with the corresponding characteristics of the polymer obtained earlier.[6]

Reaction of dysprosium(II) diiodide with $(C_6F_5)_3$GeBr (2). Compound **2** (1.873 g, 2.87 mmol) in THF (10 mL) was added to DyI_2 (1.18 g, 2.83 mmol) in THF (10 mL) under the conditions of the above experiment. The mixture immediately turned colorless and a gray precipitate formed gradually. After one hour, the mixture was centrifuged and the precipitate was separated from the solution by decantation, washed with water (3×5 mL), and sublimed *in vacuo* (200—220 °C (0.08 Torr)). The yield of digermane **5** was 0.777 g (47%), m.p. 312 °C (*cf.* Ref. 15: T_{subl} = 210—230 °C (0.02 Torr); m.p. 312—318 °C). The still bottoms (0.205 g, 31%) were identified by complexometric titration as DyI_2F. Dysprosium (0.385 g, 77%) was detected in the wash water by titration. The solution in tetrahydrofuran was concentrated to 3 mL and methanol (10 mL) was added. The yellowish precipitate that formed was isolated as described above. The yield of polymer **4** was 1.1 g (7%). The molecular weight was $7 \cdot 10^4$; M_w/M_n = 2.59. The IR spectra of this product and polymer **4** obtained above were identical. Pentafluorobenzene (0.13 g, 9%) was detected in distilled THF by HPLC.

Reaction of dysprosium(II) diiodide with $(C_6F_5)_2GeBr_2$ (3). Compound **3** (0.868 g, 1.53 mmol) was added at 0 °C to a solution of DyI_2 (1.219 g, 2.93 mmol) in THF (15 mL). The mixture was immediately decolorized and then gradually turned brown; a precipitate of DyI_2Br (1.31 g, 90%) formed. After one hour, the precipitate was filtered off and the solution was concentrated to 3 mL. Addition of methanol (10 mL) to the residue caused a white substance to precipitate. The mixture was centrifuged and the precipitate was separated by decantation and reprecipitated with hexane from a solution in THF. The yield of polymer **4** was 0.137 g (22%). The IR spectrum of this product was identical with the spectrum of the polymer obtained in the preceding experiments. The molecular weight was $1.6 \cdot 10^4$; M_w/M_n = 1.38. Elemental analysis detected no bromine in the product. Pentafluorobenzene (0.1 g, 19%) was detected in distilled THF and the THF—methanol mixture by HPLC.

Reaction of dysprosium(II) diiodide with $(C_6F_5)_3GeGe(C_6F_5)_3$ (5). Tetrahydrofuran (20 mL) was added at room temperature to a mixture of solid DyI_2 (0.45 g, 1.08 mmol) and solid compound **5** (1.175 g, 1.02 mmol). The mixture was decolorized and then turned light brown. The mixture was stirred at 70 °C for 1 h and the precipitate was filtered off on a glass filter. Sublimation *in vacuo* recovered the starting digermane **5** (0.952 g, 81%). The larger part of THF was removed from the filtrate and methanol (10 mL) was added to the residue. The amorphous white precipitate that formed was separated by decantation upon the centrifuging of the mixture, washed with methanol, and dried. The yield of polymer **4** was 79 mg (8%). The molecular weight was $2 \cdot 10^4$; M_w/M_n = 1.44. The IR spectrum of the product was identical with the spectrum of the polymer obtained by the aforementioned reactions with compounds **1**—**3**.

Reaction of dysprosium(II) diiodide with $[(C_6F_5)_3Ge]_2Hg$ (6). A solution of compound **6** (0.16 g, 0.12 mmol) in THF (5 mL) was added at 0 °C to a solution of DyI_2 (33 mg, 0.08 mmol) in THF (10 mL). The initial green color of the solution immediately vanished and a gray precipitate of metallic mercury (7 mg, 89%) formed. After the mercury was separated by decantation, the solution was slowly concentrated to 1 mL *in vacuo* to form a finely crystalline colorless precipitate. The yield of compound **7** was 0.14 g (75%), m.p. 168 °C (decomp.). Found (%): Dy, 5.84; I, 10.88. $C_{54}DyF_{45}Ge_3HgI_2$. Calculated (%): Dy, 5.43; I, 10.86. IR (Nujol), ν/cm^{-1}: 620 w, 715 w, 730 w, 820 m, 960 vs, 1080 vs, 1280 m, 1450 vs, 1500 s, 1640 m.

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References

1. M. N. Bochkarev, *Coord. Chem. Rev.*, 2004, **248**, 835.
2. (a) W. J. Evans, N. A. Allen, P. S. Workman, and J. C. Meyer, *Inorg. Chem.*, 2003, **42**, 3097; (b) W. J. Evans and N. T. Allen, *J. Am. Chem. Soc.*, 2000, **122**, 2118.
3. T. V. Balashova, G. V. Khoroshen´kov, D. M. Kuzyaev, I. L. Eremenko, G. G. Aleksandrov, G. K. Fukin, and M. N. Bochkarev, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 789 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 825]; M. N. Bochkarev, G. V. Khoroshenkov, H. Schumann, and S. Dechert, *J. Am. Chem. Soc.*, 2003, **125**, 2894; M. N. Bochkarev and M. E. Burin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2086 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2091]; M. N. Bochkarev, M. E. Burin, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 447 [*Russ. Chem. Bull.., Int. Ed.*, 2004, **53**, 481].

4. M. N. Bochkarev, I. I. Brezhneva, M. A. Katkova, Yu. D. Semchikov, G. A. Maksimov, Yu. Yu. Gushchina, A. G. Vitukhnovskii, and L. S. Lepnev, *Vysokomol. Soedin., Ser. A*, 2002, **44**, 104 [*Polym. Sci., Ser. A*, 2002, **44**, 89 (Engl. Transl.)].
5. M. N. Bochkarev, A. A. Fagin, and G. V. Khoroshen´kov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1757 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1909].
6. M. N. Bochkarev, V. B. Silkin, L. P. Maiorova, G. A. Razuvaev, Yu. D. Semchikov, and V. I. Sherstyanykh, *Metalloorg. Khim.*, 1988, **1**, 196 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
7. G. R. Newkome, C. N. Moorefield, and F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, 2001, 635 pp.
8. (a) G. A. Razuvaev, N. S. Vyazankin, and M. N. Bochkarev, *J. Organomet. Chem.*, 1974, **74**, C4; (b) M. N. Bochkarev, N. S. Vyazankin, L. N. Bochkarev, and G. A. Razuvaev, *J. Organomet. Chem.*, 1976, **110**, 149; (c) M. N. Bochkarev, G. A. Razuvaev, and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1220 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28** (Engl. Transl.)].
9. M. N. Bochkarev, V. B. Silkin, and L. P. Maiorova, *Metalloorg. Khim.*, 1988, **1**, 1338 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
10. L. V. Pankratov, M. N. Bochkarev, G. A. Razuvaev, L. N. Zakharov, Yu. T. Struchkov, Yu. K. Grishin, and Yu. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2548 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **37** (Engl. Transl.)].
11. M. N. Bochkarev, M. E. Burin, and V. K. Cherkasov, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 447 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 481]; M. N. Bochkarev and M. E. Burin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2086 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2179].
12. O. H. Johnson, W. H. Nebergall, and D. M. Harris, *Inorg. Syntheses*, 1957, **5**, 76.
13. M. N. Bochkarev, L. P. Maiorova, and N. S. Vyazankin, *J. Organomet. Chem.*, 1973, **55**, 89.
14. D. E. Fenton, A. G. Massey, and D. S. Urch, *J. Organomet. Chem.*, 1966, **6**, 352.
15. M. N. Bochkarev, G. A. Razuvaev, and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1820 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].

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