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[13] For the effect of the hydroxyamino moiety of imines and for deprotection of this moiety of the product to form the free amino group, see ref. [8a].

[14] In NMR spectroscopic experiments, we were able to show that an allyl alcohol, as a model compound, was bonded to the zirconium center of the catalyst. From this observation, it is assumed that bonding of allylstannnane **2c** to the zirconium leads to a better-organized transition state and, therefore, to higher enantioselectivities and even accelerated reaction rates. When equimolar amounts of **4** and **2d** were mixed and imine **1a** was then added after 1 h, no formation of the product was observed. An allyltransfer from tin to zirconium is likely to be the reason for this observation (A. L. Costa, M. G. Piazza, E. Tagliavini, C. Trombini, A. Umani-Ronchi, *J. Am. Chem. Soc.* **1993**, *115*, 7001–7002). Also from the product formed when **2d** is the substrate, we can rule out the idea that an allyltransfer from zirconium to imine is the actual reaction pathway.

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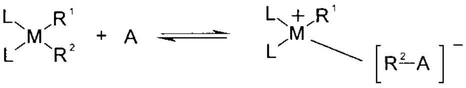
Noncoordinating Dendrimer Polyanions: Cocatalysts for the Metallocene-Catalyzed Olefin Polymerization

Michael Mager,* Sigurd Becke, Heike Windisch, and Uwe Denninger

The metallocene-catalyzed polymerization of nonpolar monomers (in particular α olefins) allows the production of polymers with new architectures and properties.[1] In addition, because of their high activity, metallocene catalyst systems are used in very small amounts and can be left in the product, simplifying the polymer work up. During the polymerization the activated metallocene complex is present as a cation $[L_2MR^1]^+$ that is stabilized by an noncoordinating anion $[R^2A]^-$.[2, 3] This contact ion pair can be formed by treating a neutral metallocene with an activating cocatalyst that can abstract a ligand from the metallocene [Eq. (1)]. To date the most important industrial examples of such cocatalysts have been methylaluminoxane (MAO),[4, 5] a condensation product prepared from $AlMe_3$ and water, which has a complex structure, and the perfluorphenylborane $B(C_6F_5)_3$.[3g, 6, 7] The interaction within the ion pair $[L_2MR^1]^+[R^2A]^-$ for a given ligand system L has an important influence on the catalytic properties such as activity, life time of the active species, chain-termination and chain-transfer reactions, and regio- and stereoregularity.[3w,x, 8] Thus there is increased interest in the synthesis of new, noncoordinating anions that are less nucleophilic; this can be achieved by the extensive delocalization of the negative charge[9] or steric shielding[3x, 10]. Tris(perfluorobiphenyl)alkylborates,[11] (perfluoroaryl)fluoroaluminates,[12] and triorganosilyl-substituted tetrakis(perfluorophenyl)borates[13] are examples of anions which, in addition to a delocalization of the charge, are sterically more demanding than $[R^2B(C_6F_5)_3]^-$. We wished to study the polymerization properties of metallocene–cation–anion pairs in which the anion is extremely sterically demanding; dendrimers, defined, highly branched, and highly functionalized, space-filling molecules have not been used in this context before.[14] Carbosilane dendrimers appeared to be particularly suitable in that the Si–C bond is basically chemically inert and thus side reactions (such as degradation of the dendrimer) during synthesis or the polymerization are unlikely.[15] The new polyanionic carbosilanes **IVa–c** are the first noncoordinating polyanions to be based on dendrimers. The construction of the Si–C framework was by means of alternating hydrosilation and Grignard reactions starting from tetravinylsilane, followed by hydroboration of the resulting allylsilyl dendrimer



$$L_2MR^1R^2 + A \rightleftharpoons [L_2MR^1]^+ \; [R^2\text{–}A]^- \qquad (1)$$

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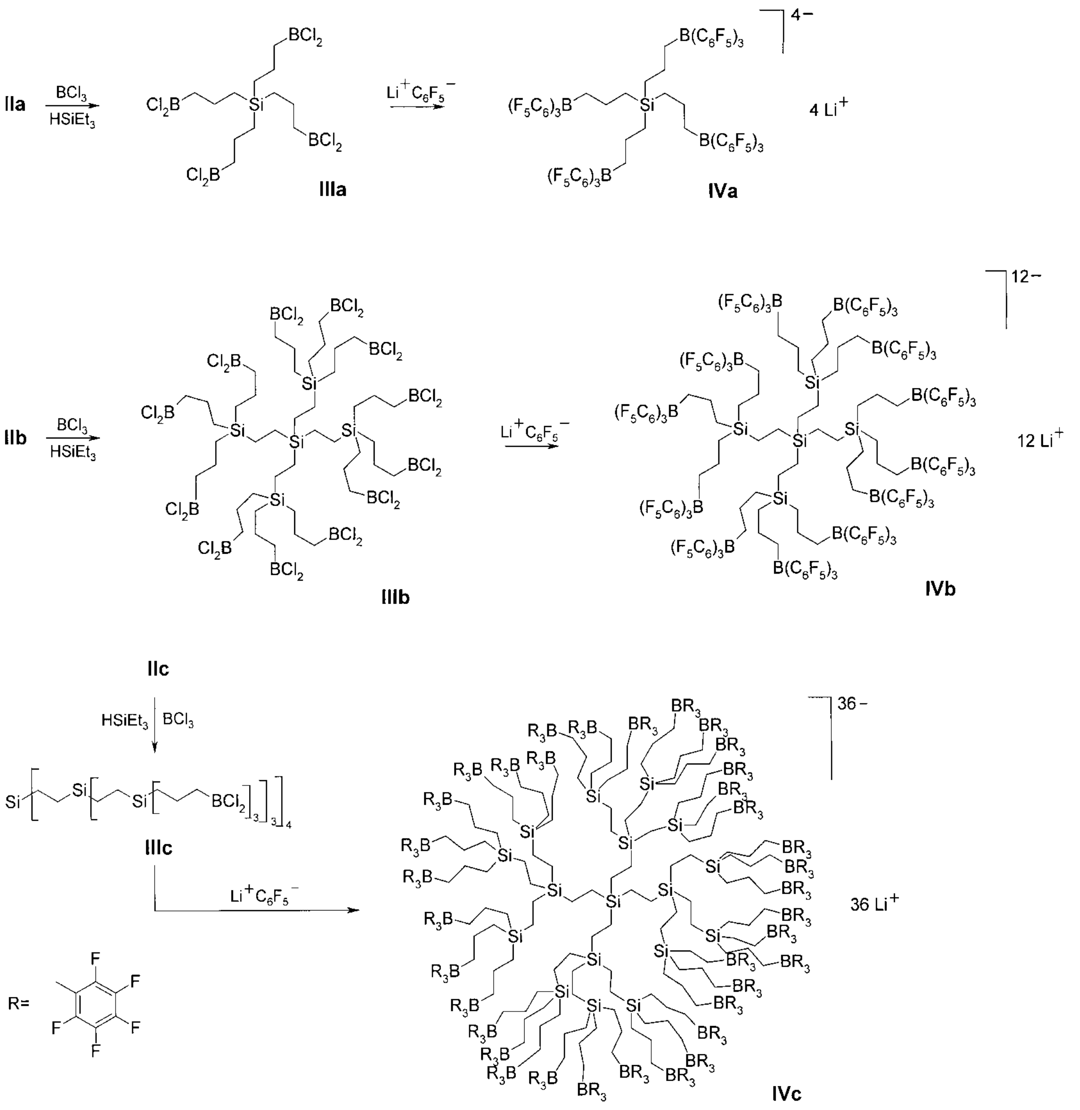
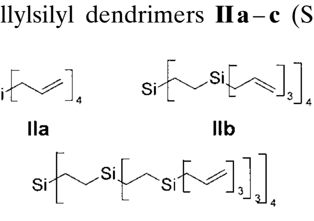


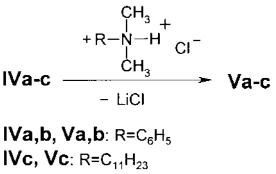
Scheme 1. The synthesis of the polyanionic carbosilane dendrimers **IVa–c**.

with dichloroborane and arylation with pentafluorophenyllithium (Scheme 1). The divergent synthesis of the carbosilane skeleton has been described many times before and gives the allylsilyl dendrimers **IIa–c** (Scheme 2) in high yield.[15] By



Scheme 2. The carbosilane dendrimers **IIa–c** with 4, 12, and 36 allyl groups, respectively.

hydroboration with $HBCl_2$, prepared in situ from BCl_3 and $HSiEt_3$, at –60 °C[16] the polyalkyldichloroboranes **IIIa–c** are produced as colorless oils or waxes (Scheme 1). These products hydrolyze rapidly in air. The hydroboration is quantitative and regioselective (because of the influence of the silicon atom the hydroboration of the corresponding vinylsilyl dendrimers is no longer regioselective and a large amount of the α-addition product $SiCH(BCl_2)CH_3$ is formed). In the $^{11}B\{^1H\}$ NMR spectrum resonance signals corresponding to **IIIa–c** are found at $\delta = 63.1$, 63.1, and. 62.2, respectively, which corresponds well to the expected value ($C_3H_7BCl_2$, $\delta = 62.3$[17]). Through the reaction of **IIIa–c** with pentafluorophenyllithium, the lithium salts of the anionic polyborates **IVa–c** are formed (Scheme 1). For this reaction a suspension of pentafluorophenyllithium is prepared in situ by transmetallation of bromopentafluorobenzene with *n*BuLi at –70 °C[18] and the polyalkyldichloroborane **III** was then added at a temperature below –65 °C (exothermic reaction). At higher temperature the pentafluorophenyllithium formed can decompose. The lithium salts **IVa–c** are only sparingly soluble in standard solvents. Treatment of the lithium salts with *N*,*N*-dimethylaniliniumhydrochloride (**IVa**, **b**) or *N*,*N*-dimethylundecylammoniumchloride (**IVc**) affords the soluble ammonium salts **Va–c** (Scheme 3), which can be isolated from the reaction mixture by extraction with CH_2Cl_2 and characterized by NMR spectroscopy. In the $^{11}B\{^1H\}$ NMR



Scheme 3. Reactions of **IVa**, **b** with *N*,*N*-dimethylanilinumhydrochloride and of **IVc** with *N*,*N*-dimethylundecylammoniumchloride to give **Va**, **b**, and **Vc**, respectively.

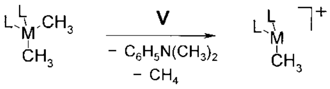
spectra of each of **Va–c** a singlet is found at $\delta = -13.4$, -13.2, and -13.9, respectively; as is characteristic for tetraorganoborates these resonance signals are very sharp (Table 1). The high field shift compared to the corresponding signal of $[C_6H_5N(CH_3)_2H]^+[B(C_6F_5)_4]^-$ can be explained through the presence of the electron-donating silylpropyl group. The structure of the polyborates **Va–c** is further confirmed by $^{19}F\{^1H\}$ NMR spectroscopy: these spectra show resonance signals for the aromatic *o*-, *m*-, and *p* fluorine atoms in the expected region and in the ratio of 2:2:1 (Table 1).

Table 1. $^{11}B\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopic data for **Va–c**.

Compound	$\delta(^{11}B\{^1H\})$[a]	$\delta(^{19}F\{^1H\})$[b]		
Va	−13.4 (s)	−133.0	−165.4	−168.4
Vb	−13.2 (s)	−132.5	−165.4	−168.2
Vc	−13.9 (s)	−127.5	−160.6	−163.0
$[C_6H_5N(CH_3)_2H]^+[B(C_6F_5)_4]^-$[c]	−16.3 (s)			
$Li^+[B(C_6F_5)_4]^-$[d]		−131.6	−164.2	−167.9
$B(C_6F_5)_3$[d]		−128.7	−144.3	−160.6

[a] Measurements in CD_2Cl_2; external standard BF_3OEt_2. [b] Measurement of **Va** and **Vb** in CD_2Cl_2, **Vc** in $CDCl_3$; results for $Li^+[B(C_6F_5)_4]^-$ in Et_2O and for $B(C_6F_5)_3$ in pentane from ref. [27]; external standard $CFCl_3$. [c] For preparation see ref. [26]. [d] For preparation see ref. [18].

The stable ammonium salts **Va–c** were prepared for the first time and tested in catalysis. **Va** and **Vb** are among the most active cocatalysts of the type $[RB(C_6F_5)_3]^-$ (R = alkyl), described so far.[6, 9b] The dimethylzirconocenes bis(indenyl)dimethylzirconium (**Ia**), bis(cyclopentadienyl)dimethylzirconium (**Ib**), and *rac*-ethylenebis(1-indenyl)dimethylzirconium (**Id**) react with **Va–c** by abstracting a methyl group thus generating catalytically active metallocene cations (Scheme 4). These reactions do not lead to degradation of the polyborates and thus no deactivation of the catalyst is observed.[3d, 19, 20] The metallocene dichloride *rac*-dimethylsilylbis(1-indenyl)dichlorozirconium (**Ic**) and *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dichlorozirconium (**Ie**) were alkylated in situ with aluminumalkyl compounds then activated with **Va** or **Vb**. To investigate the cocatalytic properties of the polyborates **Va–c** ethene, propene, as well as ethene/propene and ethene/1-hexene mixtures were polymerized in the presence of the metallocenes **Ia–e** (Table 2). Al*i*Bu$_3$ was added as a scavenger to remove disruptive impurities (e.g., traces of water). All the catalyst systems tested showed high activity that could be increased significantly further by increasing the (ethene) pressure from 1.1 bar to 4 or 6 bar.[3x, 9a, 10] Although polymerization experiments with cationic metallocenes are usually carried out in toluene,[3g–x] this solvent is in fact unsuitable for industrial polymerizations.[21] With **Va** and **Vb** however, high polymerization activities are achieved in aliphatic solvents such as *n*-hexane. A further advantage of the new catalysts based on dendrimer anions is their high stability during the polymerization.[22] In the copolymerization of ethene and propene no decrease in activity was observed after 40 mins. The new polyborates could prove to be particularly interesting if employed for bulk and gas-phase polymerization.[23] The dendrimers described here are the first examples of effective polyanionic cocatalysts for the metallocene-catalyzed polymerization of olefins.



Scheme 4. Activation of metallocenes with **Va–c**.

Experimental Section

All procedures were carried out under argon or in vacuum, the solvents were dried by standard methods and distilled under argon before use. Tetraallylsilane **IIa** was prepared from $SiCl_4$ and allylmagnesiumchloride,[24] $Si[(CH_2)_2SiCl_3]_4$ from the hydrosilylation of tetravinylsilane with $HSiCl_3$ and $Si\{(CH_2)_2Si[(CH_2)_2SiCl_3]_3\}_4$ followed by further treatment with vinylmagnesiumbromide and $HSiCl_3$.[25] The preparation of carbosilane dendrimers with allyl end groups is known,[24] and $Si[(CH_2)_2Si(C_3H_5)_3]_4$ (**IIb**) and $Si\{(CH_2)_2Si[(CH_2)_2Si(C_3H_5)_3]_3\}_4$ (**IIc**) were obtained by the corresponding reaction with allylmagnesiumchloride.

IIIa: At −65 °C BCl_3 (23.5 g, 0.2 mol) was condensed into a flask with a gas inlet, reflux condenser, and internal thermometer, and a mixture of $HSiEt_3$ (23.3 g, 0.2 mol) and **IIa** (9.6 g, 0.05 mol) was slowly added dropwise. After the end of the addition the reaction mixture was warmed to room temperature and the volatiles (mainly $ClSiEt_3$) were removed under vacuum, first at room temperature and then at a bath temperature of 40 °C. The product was obtained as a colorless runny oil. ^1H NMR ($CDCl_3$): $\delta = 0.5$ (m, 2H, $SiCH_2$), 1.6 (m, 4H, $(CH_2)_2BCl_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$

Table 2. Polymerization of ethene (E), propene (P), ethene/propene (E/P) and ethene/1-hexene (E/H) with **Ia–e** and **Va–c**.

Entry	Metallocene/cocatalyst	Monomer	Metallocene [μmol]	Zr:B	t [min]	T [°C]	p [bar]	Yield [g]	Activity[a] [g mol^{-1} h^{-1}]
1	$[(Ind)_2ZrMe_2]$ **Ia/Va**	E	5.0	1:1	15	40	1.1	2.0	1.6×10^6
2	$[(Ind)_2ZrMe_2]$ **Ia/Vb**[b]	E	5.0	5:6	15	40	1.1	2.1	1.7×10^6
3	$[(Ind)_2ZrMe_2]$ **Ia/Vc**	E	10.0	1:2	10	40	1.1	1.6	9.6×10^5
4	$[Cp_2ZrMe_2]$ **Ib/Va**	E	1.0	1:2	20	60	6.0	36.6	1.1×10^8
5	$[Me_2Si(Ind)_2ZrCl_2]$ **Ic**[c]**/Va**	P	5.0	1:2	30	40	1.1	4.4[d]	1.8×10^6[e]
6	$[Et(Ind)_2ZrMe_2]$ **Id/Va**	E/H	1.0	1:2	30	20	1.1	5.4	1.1×10^7
7	$[Et(H_4\text{-}Ind)_2ZrCl_2]$ **Ie**[f]**/Vb**	E/P	1.0	1:3	40	40	4.0	70.1	1.1×10^8[e]

[a] Activity = mass(polymer) [g] × 6 × 10^7 mol (metallocene) [μmol^{-1}] × time [min^{-1}]; solvent: toluene. [b] Standard solution in CH_2Cl_2. [c] **Ic** was alkylated in situ with $[Al(C_2H_5)_3]$ (Zr:Al = 1:2) then activated with **Va**. [d] Isotactic polypropylene with 92.9 % isotacticity (NMR). [e] Solvent: *n*-hexane. [f] **Ie** was alkylated in situ with triisobutylaluminum (Zr:Al = 1:360) and then activated with **Vb**.

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15.4 ($SiCH_2$), 20.0 ($SiCH_2CH_2$), 34.2 (Cl_2BCH_2); $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = 63.1$.

Va: *n*BuLi (6.35 mL, 10.1 mmol; 1.6 M in hexane) was added dropwise over 20 min to a solution of C_6F_5Br (2.5 g, 10.1 mmol) in hexane (60 mL) at -70 °C. The resulting suspension was stirred for 2 h at -70 °C. Then a solution of **IIIa** (445 mg, 0.85 mmol) in hexane (5 mL) was added dropwise over 5 min, and the reaction mixture was warmed to room temperature over 3 h and stirred over night. A solution of $[C_6H_5N(CH_3)_2H]^+Cl^-$ (536 mg, 3.4 mmol) in CH_2Cl_2 (20 mL) was then added and the mixture stirred over night. After removal of the volatiles in vacuum the residue was extracted with CH_2Cl_2 (40 mL), filtered through kieselguhr, and the colorless filtrate evaporated to dryness under vacuum. After washing with hexane (2x20 mL) the product was obtained as a colorless wax. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -13.4$; $^{19}F\{^1H\}$ NMR $\delta = -133.0$ (m, 2 F, *o*-F), -165.4 (m, 1 F, *p*-F), -168.4 (m, 2 F, *m*-F).

IIIb: As described for **IIIa** a mixture of $HSiEt_3$ (23.3 g, 0.2 mol) and **IIb** (12.4 g, 166 mmol) was slowly added dropwise to BCl_3 (23.5 g, 0.2 mol) at -65 °C. After the addition was complete the mixture was warmed to room temperature and stirred over night. Following work up as for **IIIa** the product was isolated as a colorless oil that partially crystallized on the walls of the flask. ^1H NMR (CD_2Cl_2): $\delta = 0.4$ (m, 4 H, Si-C^aH_2-C^bH_2-Si), 0.5 (m, 6 H, Si-C^cH_2), 1.6 (m, 12 H, C^dH_2-C^eH_2-BCl_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 3.3 (Si-C^aH_2), 4.8 (Si-C^bH_2), 15.1 (Si-C^cH_2), 20.1 (Si-C^dH_2), 34.4 (br. s, Cl_2B-C^eH_2); $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = 63.1$.

Vb: *n*BuLi (6.35 mL, 10.1 mmol; 1.6 M in hexane) was added dropwise within 20 min to a solution of C_6F_5Br (2.5 g, 10.1 mmol) in hexane (60 mL) at -70 °C. The resulting suspension was stirred at -70 °C for 2 h. Then a solution of **IIIb** (487 mg, 0.28 mmol) in hexane (5 mL) was added dropwise over 5 min, the reaction mixture was then slowly warmed to room temperature over 3 h and stirred over night. Following the addition of $[C_6H_5N(CH_3)_2H]^+Cl^-$ (536 mg, 3.4 mmol) in CH_2Cl_2 (20 mL), the solution was stirred over night, and the volatiles were removed in vacuum. After the addition of CH_2Cl_2 (40 mL), the solution was filtered through kieselguhr and the colorless filtrate evaporated to dryness under vacuum. After washing with hexane (2x20 mL) the product was obtained as a colorless wax. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): $\delta = -13.2$; $^{19}F\{^1H\}$ NMR: $\delta = -132.7$ (m, 2 F, *o*-F), -165.4 (m, 1 F, *p*-F), -168.2 (m, 2 F, *m*-F).

IIIc: As described for **IIIa** a mixture of $HSiEt_3$ (16 mL, 11.6 g; 100.2 mmol) and **IIc** (6.1 g, 2.5 mmol) was added dropwise to BCl_3 (8.5 mL, 11.5 g; 97.7 mmol) at -70 °C so that the temperature never rose above -60 °C. After the addition (ca. 1.5 h) the reaction mixture was stirred at -70 °C for a further 30 min then warmed to room temperature and stirred for a further 15 h. To remove a small amount of pyrophoric, highly volatile components the mixture was purged with argon (bubbler with dilute NaOH) for 2 h. Finally the remaining volatiles were removed under vacuum while the reaction mixture was slowly warmed to 40 °C. The product was obtained as a colorless wax. $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = 62.2$.

Vc: *n*BuLi (12.7 mL, 1.6 M in hexane; 20.2 mmol) was added dropwise to a stirred solution of C_6F_5Br (5.0 g, 20.2 mmol) in hexane (120 mL) at -70 °C. The reaction mixture was stirred for a further 2 h at this temperature. **IIIc** (1.0 g, 0.2 mmol) in toluene (10 mL) was added dropwise, the reaction mixture was warmed to room temperature over 3 h, and was then stirred for a further 60 h. After the addition of *N,N*-dimethylundecylammonium-chloride (1.6 g, 6.7 mmol) in CH_2Cl_2 (40 mL) and stirring for 20 h at room temperature the volatiles were removed under vacuum, and the residue was extracted with CH_2Cl_2 (40 mL) and filtered through kieselguhr. The filtrate was evaporated to dryness under vacuum giving the product as a pale yellow wax. $^{11}B\{^1H\}$ NMR ($CDCl_3$): $\delta = -13.9$; $^{19}F\{^1H\}$ NMR: $\delta =$ -127.5 (m, 2 F, *o*-F), -160.6 (m, 1 F, *p*-F), -163.0 (m, 2 F, *m*-F).

Polymerizations: The solvent (toluene or hexane), triisobutylaluminum, and the metallocene catalyst (standard solution in toluene) were placed in either a 1.4 L steel autoclave (Table 2, entries 4 and 7) or a 250 mL glass reactor (Table 2, entries 1–3, 5, 6). For the copolymerization reaction the comonomer was also placed in the reactor (entry 6: 1-hexene 5 mL; entry 7: propene 50 g). The reactor was equilibrated at the reaction temperature and ethene (propene for entry 5) introduced to the required pressure. The polymerization was started by the addition of a standard solution from **Va**, **Vb**, or **Vc** in toluene or CH_2Cl_2. Ethene (propene for entry 5) was continously introduced and a constant pressure was maintained. The polymerization was terminated with methanol, the precipitated polymer collected by filtration, washed with methanol, and dried in a vacuum oven.

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[21] Aliphatic hydrocarbons are usually used as the polymerization medium for industrial Ziegler–Natta polymerization in solution or slurry. Compared to toluene aliphatic hydrocarbons offer advantages in the isolation of the polymer (separation, purification, drying).

[22] The polymerization tests described in refs. [3a–x] were carried out with cationic metallocenes are usually terminated after a few minutes. To determine the activity the yield of polymer is extrapolated to a polymerization time of 1 h. Conclusions concerning the actual life time of the active catalytic species are not possible.

[23] For bulk and gas-phase polymerization homogeneous metallocene catalysts are usually used immobilized on a support (e.g., silica gel). To date there are only a few examples of supported, MAO-free metallocene catalysts with noncoordinating anions (supported metallocene catalysts; see for example, *Metalorganic Catalysts for Synthesis and Polymerisation* (Ed.: W. Kaminsky), Springer, New York, **1999**, pp. 307–431). In the polyborates of the type **Va–c** the noncoordinating anions are fixed to a "dendrimer surface". Dendrimers have various advantages over standard supports: defined molecular size, monodispersed particle-size distribution, an easily accessible surface, and a controllable number of catalytic centers.

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The First Barium–Carborate Complex: Synthesis and Structural Investigation**

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Of all the metallaboranes the Group 1 compounds are some of the most often encountered, in that they are common starting materials in the syntheses of higher order heteroborane clusters. Although, there is no evidence as to the role of the Group 1 metal in their reactions with other metal reagents, it has generally been assumed that they do not play an active role.[1] The Group 1 metallacarboranes are also the most common precursors in the syntheses of the p-, d-, and f-block metallacarboranes. There seems to be a more direct metal involvement with the smaller, C_2B_4 cages.[1c,d] For example, the structure of the dilithium compound shows that one [(tmeda)Li] unit (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) occupies the apical position above the C_2B_3 face of the carborane, with the other solvated Li atom being *exo*-polyhedrally bound through two B–H bridges.[2] While assignment to a *closo*-carborane is consistent with both the structure and the cage electron pair count of eight, it is not apparent that the $[(\text{tmeda})\text{Li}]^+$ ion is in any way isolobal with a B–H group; the apical position might simply be that favored by electrostatic interactions. The compound could alternatively be described as a half-sandwich lithium complex in which the *nido*-carborane dianion is η^5-bonded to the capping Li atom. The structures of several Group 1 compounds in the C_2B_4- and C_4B_8-carborane systems have been reported.[1c,d, 3] Structural information available on the Group 2 metal complexed boranes is not plentiful, and, with several notable exceptions, seems to be limited to the two smallest members of that group, beryllium and magnesium.[4–7] In contrast to the boranes, there have been a number of reports on the Group 2 metallacarboranes,[3] one reason being that a carbon plus a Group 2 element combination is isoelectronic with two boron atoms. This isoelectronic relationship led Popp and Hawthorne to explore the syntheses and properties of the beryllacarboranes in MC_2B_9 cage systems.[8, 9] While the structures of the beryllacarboranes could not be determined, the heavier Group 2 metals form structurally known metallacarboranes with the *nido*-$[7,9\text{-}C_2B_{10}H_{12}]^{2-}$ ligand.[10, 11] The 1,1,1,1-$(CH_3CN)_4$-*closo*-1,2,4-$CaC_2B_{10}H_{12}$ was the first structurally characterized Group 2 metallacarborane. The Ca ion, which is coordinated by four CH_3CN molecules, resides above the C_2B_4 face of the carborane. A similar reaction with SrI_2 produced the novel polymeric strontium carborane, [1,1,1-$(CH_3CN)_3$-*closo*-1,2,4-$SrC_2B_{10}H_{12}]_n$, whose structure shows a cage geometry similar to that of the calcium carborane, except that one of the solvating CH_3CN molecules is replaced by a set of Sr-H-X bridge bonds to a neighboring carborane, where X can be a boron atom on the lower belt of the carborane and a carbon atom on its C_2B_4 upper ring.[11] However, the magnesacarboranes were limited to the 2,3-C_2B_4 and 2,4-C_2B_4 cage systems. The reactions of their mono- and dianions with various magnesium reagents have been studied by Hosmane and co-workers and showed that contrasting results can be obtained from slight changes in the carborane and magnesium reagents.[12, 13] Nonetheless, there have been no reports on similar carborane complexation with the heaviest Group 2 metal, barium. Here we report the first barium half-sandwich complex of any carborane and/or borane cage systems of which we are aware. The reaction of tetrakis(tetrahydrofuran)barium bis[tris(trimethylsilylmethyl)zincate][14] (**1**) with 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane in THF yields nearly quantitatively barium bis(carborate) **2** (Scheme 1). Only one of the trimethylsilylmethyl groups of

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