Homoleptic and Heteroleptic Barium Benzyl Complexes: Synthesis and Reactivity as Initiators for Anionic Styrene Polymerizations

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Dibenzylbarium is prepared in yields of 80−90% by reaction of the tetramethyl ethylenediamine adduct of benzyllithium with the bis-THF adduct of barium bis(bis-trimethylsilylamide) or with barium bis(2,4,6-tri-*tert*-butyl phenolate). It is converted, by reaction with diphenylmethane in THF, to bis(diphenylmethyl)barium in 90% yield and, by reaction with 1,1-diphenylethene in THF, to bis(1,1,3-triphenylpropyl)barium in essentially quantitative yield. The latter is soluble also in hydrocarbon solvents, while dibenzylbarium and bis(diphenylmethyl)barium are soluble only in THF. Reaction of the bis-chelate complex $(C_5Me_4SiMe_2C_6H_5)_2Ba$, the phenyl residues of which are coordinated to the Ba center, with each of the bis(arylalkyl)barium species generates heteroleptic barium complexes with one chelate and one reactive arylalkyl ligand. Homoleptic and heteroleptic triphenylpropylbarium complexes both induce, in cyclohexane solution, living polymerization of styrene to atactic polystyrene.

Introduction

Alkyl and arylalkyl (e.g., benzyl) compounds of the heavier alkaline earth metals have been the subject of relatively few studies, compared, for example, to the highly developed chemistry of alkylmagnesium compounds.[1] While Ca, Sr, and Ba compounds with cyclopentadienyl[2−4] and other organyl anions stabilized by extensive charge delocalization[5] have been studied rather thoroughly, only a small number of simple alkyl derivatives of these metals have been synthesized and characterized so far.[6]

Metathesis reactions, for example, between Ba−dialkoxy and Mg−dialkyl compounds,[7] as well as reactions of Ca, Sr, or Ba metal—often in a highly dispersed state—with an organyl halide or an ether,[8] with a reactive hydrocarbon,[9] or with an alkyl compound of a more easily reducible metal,[10−12] have been studied in this regard. The metal dialkyl compounds produced by these reactions show interesting capabilities to induce anionic polymerization of styrene or butadiene derivatives,[13,14] but were mostly obtained as mixtures with side products and coproducts and were thus often only partly characterized.

Pure dibenzylbarium, which proved to be highly active as an initiator of styrene polymerization in THF solutions, has been obtained by reaction of a barium mirror with dibenzylmercury.[11,14] Despite its interesting reac-

(1) Review: Lindsell, W. E. In *Comprehensive Organometallic Chemistry II;* Abel, W., Stone, F. G. A., Wilkinson, G.; Housecoft, C. E., Eds.; Pergamon Press: Oxford, 1995.

(2) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem*. **1987**, *325*, 31.

(3) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* **1988**, *7*, 725.

(4) Hanusa, T. P. *Polyhedron*, **1990**, *9*, 1345. Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128. Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843. Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *J. Organomet. Chem*. **1992**, *429*, 143. Burkey, D. J.; Williams, R. A.; Hanusa, T. P. *Organometallics* **1993**, *12*, 1331. Tanner, P. S.; Hanusa, T. P. *Polyhedron* **1994**, *13*, 2417. Westerhausen, M.; Hartmann, M.; Schwarz, W. *J. Organomet. Chem*. **1995**, *501*, 359. Overby, J. S.; Hanusa, T. P. *Organometallics* **1996**, *15*, 2205.

(5) Harvey, M. J.; Hanusa, T. P.; Young, V. G., Jr. *Angew. Chem., Int. Ed*. **1999**, *38*, 217.

(6) Eaborn, C.; Hawkes, S. A.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Chem. Commun*. **1997**, 1961. Cloke, F. G. N.; Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun*. **1991**, 724.

(7) Baidakova, Z. M.; Kristalnyi, E. V.; Arest-Yakubovich, A. A. *J. Gen. Chem. USSR* **1977**, *47*, 962.

(8) Beckmann, E. *Chem. Ber.* **1905**, *38*, 904. Gilman, H.; Schulze, F. *Bull. Soc. Chim. France, Ser. 4* **1927**, *41*, 1333. Lapkin, I. I.; Rybakova, M. N.; Belonovich, I.; Novoselitskaya, L. M. *J. Gen. Chem. USSR* **1972**, *42*, 2670. Masthoff, R.; Schüler, H.; Krieg, G. *J. Organomet. Chem*. **1968**, *13*, 37. Tang, L. C.; Mathis, C.; Francois, B. *J. Organomet. Chem*. **1983**, *243*, 359.

(9) Coles, M. A.; Hart, F. A. *J. Organomet. Chem*. **1971**, *32*, 279. Favier, J.-C.; Fontanille, M.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1971**, 526.

(10) West, P.; Woodville, M. C. United States Patent 3,776,281, 1973.

(11) West, P.; Woodville, M. C. United States Patent 3,718,703, 1973.

(12) Zemlyanichenko, M. A.; Sheverdina, N. I.; Chernoplekova, V. A.; Kocheshkov, K. A. *J. Gen. Chem. USSR* **1972**, *42*, 832. Paleeva, I. E.; Sheverdina, N. I.; Kocheshkov, K. A. *J. Gen. Chem. USSR* **1974**, *44*, 1091.

(13) Allan, K. A.; Gowenlock, B. G.; Lindsell, W. E. *J. Polym. Sci., Polym. Chem. Ed*. **1974**, *12*, 1131. Nakhmanovich, B. I.; Basova, R. V.; Arest-Yakubovich, A. A. *Macromol. Sci., Chem*. **1975**, *A9*, 575. Basova, R. V.; Nakhmanovic, B. I.; Arest-Yakubovich, A. A. *Polym. Sci. USSR* **1976**, *18*, 2129. Lindsell, W. E.; Robertson, F. C.; Soutar, I. *Eur. Polym. J*. **1983**, *19*, 115.

(14) Nakhmanovic, B. I.; Arest-Yakubovich, A. A. *Dokl. Phys. Chem. (Engl.)* **1976**, *228*, 426. Arest-Yakubovich, A. A. *Russ. Chem. Rev. (Engl.)* **1981**, *50*, 601. De Groof, B.; Van Beylen, M.; Szwarc, M. *Macromolecules* **1975**, *8*, 396. De Groof, B.; Mortier, W.; Van Beylen, M.; Swarc, M. *Macromolecules* **1977**, *10*, 598.

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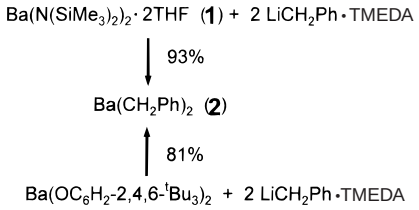
Scheme 1



tion chemistry, rather limited studies have been reported for this compound, probably due to its inconvenient synthesis.

We have thus set out to make these compounds more easily accessible. Here we report on convenient syntheses for dibenzylbarium, on its transformation to other homoleptic and heteroleptic barium complexes with benzylic ligands, and on the activities of these species in anionic styrene polymerization.

Results and Discussion

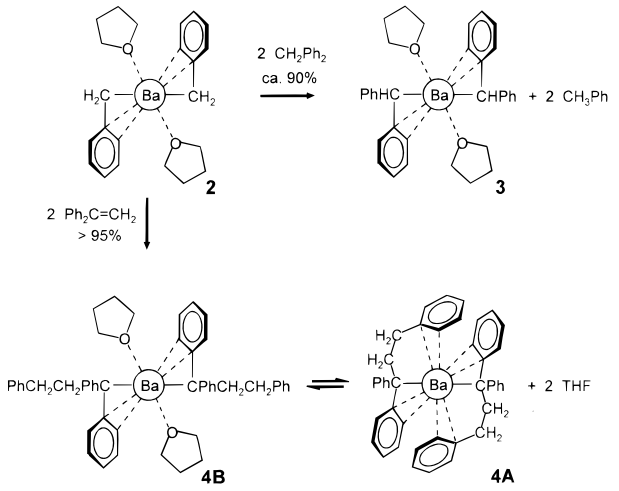
1. Synthesis of Dibenzylbarium. Since dibenzylbarium has been reported to be rather insoluble in toluene or diethyl ether,[11] we have tried to find metathesis reactions between soluble barium derivatives and easily accessible magnesium or lithium compounds, which would yield dibenzylbarium, $Ba(CH_2Ph)_2$, as the only insoluble product.

Initial attempts in this regard with the tetrahydrofuran (THF) adduct of barium bis(bis-trimethylsilylamide), $Ba(N(SiMe_3)_2)_2{\cdot}2THF$ (**1**),[15] and the dioxane adduct of dibenzylmagnesium, $Mg(CH_2Ph)_2{\cdot}O_2C_4H_8$,[16] in toluene/diethyl ether solution were partly successful: An orange precipitate was obtained, the ^1H NMR spectrum of which in d_8-THF indicated the presence of both benzyl and trimethylsilylamide groups and, hence, an incomplete metathesis reaction. When a THF solution of this mixed product was covered by a layer of hexane, slow diffusion-induced crystallization gave, in 40% overall yield, practically pure dibenzylbarium (**2**), void of any trimethylsilyl signals and with a residual magnesium content of only 0.5% (see Experimental Section).[17]

Improved results were obtained when **1** was reacted, in diethyl ether solution, with 2 equiv of the tetramethyl ethylenediamine (TMEDA) adduct of benzyllithium:[18] After stirring overnight, dibenzylbarium was isolated in 93% overall yield, in the form of an orange precipitate, free of any side products, as judged by its ^1H NMR spectrum (Scheme 1).

Similarly satisfactory results were obtained when a solution of barium bis(2,4,6-tri-*tert*-butyl phenolate)[19] in toluene/THF (10:1) was treated with 2 equiv of $LiCH_2Ph{\cdot}TMEDA$ at room temperature overnight (cf. Scheme 1). From this reaction, complex **2** precipitated in 81% yield. Remarkably, **2** was obtained free of any ether, THF, or TMEDA adducts from the reactions described above.[20] Apparently, the coordination requirements of the Ba^{2+} centers in **2** are met—better than by an ether oxygen atom—by coordination of the phenyl rings; intermolecular binding of each benzyl moiety to more than one Ba^{2+} center is probably the cause of the rather low solubility of **2** even in ether solvents.

Scheme 2



2. Other Homoleptic Barium Compounds with Benzylic Ligands. To get access to more soluble dialkyl barium compounds, we have tried to convert dibenzyl barium into more highly substituted dialkyl barium derivatives by reaction with appropriate hydrocarbons. Diphenylmethane, which is more acidic than toluene,[21] was found to react with **2** under formation of bis(diphenylmethyl)barium, $Ba(CHPh_2)_2$ (**3**). The reaction does not go to completion, however. Instead, reaction of **2** with 6 equiv of diphenylmethane in THF solution gave, after 48 h at room temperature, a 8:1 mixture of **3** and **2** (Scheme 2). The possibility to force this reaction further, for example, by removal of the toluene coproduct, was not pursued, since **3** was found to be similarly insoluble as **2** in nonpolar hydrocarbon solvents such as toluene.

Reaction of **2** with slightly more than 2 equiv of diphenylethene (DPE), on the other hand, gave a practically quantitative insertion of one DPE molecule into each Ba–benzyl bond, as expected from related reactions of DPE with other anionic species. After reacting for 16 h at room temperature in ethylbenzene/THF (7:1) solution and subsequent evaporation of the solvent, bis(1,1,3-triphenylpropyl)barium, $Ba(Ph_2CCH_2CH_2Ph)_2$ (**4A**), was obtained as a dark red, rubber-like solid (Scheme 2). An otherwise analogous reaction in toluene/THF solution gave, after evaporation of the solvent, the THF adduct $Ba(Ph_2CCH_2CH_2Ph)_2{\cdot}2THF$ (**4B**). Complexes **4A** and **4B** are both easily soluble in hydrocarbon solvents such as benzene or toluene. Both were characterized by their room-temperature ^1H NMR spectra in C_6D_6 (see Experimental Section).

(15) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121. Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96.

(16) Pocker, Y.; Exner, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 6764.

(17) None of the analogous reactions of **1** with diphenylmagnesium, with bis(2-phenylethyl)magnesium or with the dioxane adduct of bis(2-methylallyl)magnesium gave the corresponding barium diorganyl as an insoluble product.

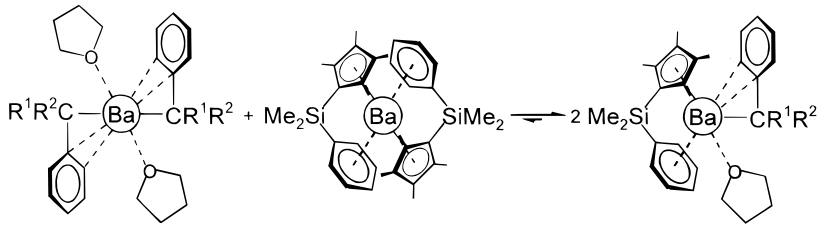
(18) Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988; p 38.

(19) Drake, S. R.; Otway, D. J.; Hursthouse, M. B.; Abdul Malik, K. M. *Polyhedron* **1992**, *11*, 1995.

(20) Analogous reactions of Ca or Sr bis(bis-trimethylsilylamide) with $LiCH_2Ph{\cdot}TMEDA$ did not yield the respective dibenzyl compounds as insoluble products.

(21) Streitwieser, A., Jr.; Ni, J. X. *Tetrahedron Lett.* **1985**, *26*, 6317. Streitwieser, A., Jr.; Hollyhead, W. B.; Sonnichsen, G.; Pudjaatmaka, A. H.; Chang, C. J.; Kruger, T. L. *J. Am. Chem. Soc.* **1971**, *93*, 5096.

Scheme 3



2 : R^1, R^2 = H
3 : R^1 = Ph, R^2 = H
4 : R^1 = Ph, R^2 = CH_2CH_2Ph

5

7 : R^1, R^2 = H
8 : R^1 = Ph, R^2 = H
9 : R^1 = Ph, R^2 = CH_2CH_2Ph

Interestingly, sharp signals for the methylene and phenyl protons were observed in d_8-toluene solutions of complex **4B**, together with those of two coordinated THF molecules, while the THF-free complex **4A** gave rise to rather broad signals in both the aliphatic and aromatic regions. This broadening is most likely caused by fast, reversible coordination of the Ph_2C and CH_2CH_2Ph phenyl rings to the Ba^{2+} center in complex **4A**. At lower temperatures, all ^1H NMR signals are extremely broadened; even at −80 °C, there is no indication of an approach to the slow exchange limit. At increased temperatures, on the other hand, significant line-sharpening results (see Supporting Information). Two sharp CH_2CH_2 resonances with a distinct coupling pattern indicate that interchange of free and coordinated CH_2CH_2Ph phenyl units becomes fast at 80−90 °C.

At this temperature, the typical high-field-shifted Ph_2C para proton resonance appears as a septet, with ca. 3.2 Hz separation and approximate 1:2:3:4:3:2:1 ratio. This can be explained by a triplet splitting with the usual $^3J_{Hp-Hm}$ coupling constant of 6−7 Hz, apparent also in **4A**, which is superimposed by a triplet splitting with a $^4J_{Hp-Ho}$ coupling constant of 3−3.5 Hz. This value is rather large but might be accounted for by the unusual electronic situation due to the $Ph_2C^-\cdots Ba^{2+}$ coordination in **4B**. At any rate, the equivalence of the ortho protons as well as of the meta protons indicates that rotation of both Ph_2C phenyl rings around their $C_{ipso}-C_\alpha$ bonds becomes fast at 80−90 °C.

As expected, addition of a small excess of THF to C_6D_6 solutions of **4A** caused all NMR signals to become as sharp as those observed in solutions of **4B**. Coordination of THF thus appears to accelerate the interchange between free and coordinated phenyl rings sufficiently to restore the rotational freedom of both the CH_2CH_2-Ph and CPh_2 groups.

3. Heteroleptic Barium Complexes with Benzylic Ligands. Dibenzylbarium (**2**) provides access also to heteroleptic barium complexes which contain, in addition to the reactive arylalkyl residue R, some relatively inert auxiliary ligand, e.g., to complexes of the type $(C_5Me_5)BaR$ or $(C_5Me_4SiMe_2Ph)BaR$, where the $SiMe_2$-linked phenyl ring might function as an additional ligand group. In this context, the Schlenk-type equilibria connecting homoleptic and heteroleptic complexes (Scheme 3) had to be characterized.

For this purpose, the novel tetramethyl cyclopentadienyl chelate complex $(C_5Me_4SiMe_2Ph)_2Ba$ (**5**) and, for comparison, the known permethyl bis-cyclopentadienyl complex $(C_5Me_5)_2Ba\cdot 2THF$ (**6**)[2,3] were prepared by reaction of the barium bis-amide **1** with 2 equiv of the appropriate cyclopentadienyl ligands in their protonated form (see Experimental Section).

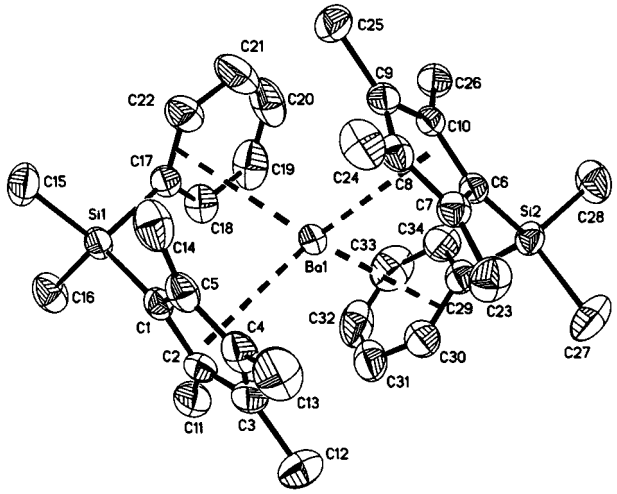


Figure 1. Crystal structure of the bis-chelate complex $(C_5Me_4SiMe_2C_6H_5)_2Ba$ (**5**), with broken lines connecting the Ba atom to the C_5-ring centroids and to the centroids of the two closest C atoms of each phenyl ring. H atoms omitted for clarity.

Complex **5** was obtained in the form of crystals suitable for a diffractometric structure determination (see Experimental Section). The resulting structural data document a coordination of the phenyl group of each ligand unit to the Ba^{2+} center (Figure 1, Table 1). With Ba−C distances ranging from 323 to 440 pm, the hapticity of the phenyl−Ba interaction cannot be unambiguously assigned. If bonding distances are arbitrarily limited to 345 pm, an η^2 coordination via the ipso- and one of the ortho-C atoms of the phenyl ring would be indicated. At any rate, the Ba^{2+} center appears rather closely shielded by its ligand environment. In accord with this, no THF ligand is found in complex **5**, even though it is prepared in the presence of THF, in distinction to the bis(permethylcyclopentadienyl)barium complex **6**, in which two molecules of THF are firmly coordinated to the Ba^{2+} center.[2−4]

In the ^1H and ^{13}C NMR spectra of **5** in C_6D_6 solution (see Experimental Section), each ligand unit appears C_s-symmetric, while the enantiomorphic solid-state structure shown in Figure 1 requires all ligand CH_3 groups to be diastereotopic. This indicates a fast interconversion between the enantiomers of **5** in solution, presumably by way of dissociation of one of the phenyl ligands.

Table 1. Bond Distances (in pm) and Angles (in deg) for Complex 5

Ba−C1	295.5(4)	Ba−C6	297.8(4)
Ba−C2	305.1(4)	Ba−C7	302.0(4)
Ba−C3	309.6(4)	Ba−C8	304.2(4)
Ba−C4	303.9(4)	Ba−C9	300.5(4)
Ba−C5	293.4(4)	Ba−C10	297.0(4)
Ba−CR1[a]	276.4(4)	Ba−CR2[a]	275.0(4)
Ba−C17	328.6(4)[b]	Ba−C29	345.5(4)[b]
Ba−C18	353.0(4)	Ba−C30	323.9(4)[b]
Ba−C19	389.5(5)	Ba−C31	366.1(5)
Ba−C20	402.8(5)	Ba−C32	422.2(6)
Ba−C21	381.2(6)	Ba−C33	439.2(6)
Ba−C22	344.0(5)[b]	Ba−C34	404.7(5)
Si1−C1	184.8(4)	Si2−C6	184.8(4)
Si1−C15	186.8(4)	Si2−C27	187.5(5)
Si1−C16	186.1(5)	Si2−C28	187.1(5)
Si1−C17	189.3(4)	Si2−C29	189.8(4)
CR1−Ba−CR2[a]	130.7		
C1−Si1−C17	105.2(2)	C6−Si2−C29	105.5(2)
C15−Si1−C16	106.3(2)	C27−Si2−C28	105.4(3)
Si1−C1−CP1[c]	5.9	Si2−C6−CP2[c]	5.1
Si1−C17−PH1[d]	5.2	Si2−C29−PH2[d]	5.8

[a] CR1 and CR2: centroids of lower- and higher-numbered C_5 rings, respectively. [b] Considered as bonding. [c] CP1 and CP2: mean planes of lower- and higher-numbered C_5 rings, respectively. [d] PH1 and PH2: mean planes of lower- and higher-numbered C_6 rings, respectively. All C(ipso)−Si bonds are bent to the inside of the adjacent C_5 or C_6 ring planes, i.e., toward the Ba atom.

Schlenk-type equilibria according to Scheme 3 were investigated for reactions of dibenzylbarium (**2**) and of bis(diphenylmethyl)barium (**3**) with complex **5** in d_8-THF solution and for reactions of the THF adduct of bis(1,1,3-triphenylpropyl)barium (**4B**) with complexes **5** and **6** in C_6D_6 solution.

d_8-THF solutions containing **2** and **5** in different ratios ranging from 6:1 to 1:2 gave ^{1}H NMR spectra at room temperature with only one set of signals each for the benzyl and for the chelate ligand. A broadening of the signals and slight changes in their chemical shift values relative to those of **2** and **5** (see Experimental Section) indicate that ligand interchange between **2** and **5** under formation of the heteroleptic complex $C_5Me_4SiMe_2$-PhBaCH_2Ph (**7**) is fast on the NMR time scale. For a quantitative evaluation of this equilibrium reaction, the NMR signals were too broad and the changes in chemical shifts too small. Interestingly, however, the benzyl signals were quite sharp again when the **5**:**2** ratio was increased to 2:1. This observation indicates that the heteroleptic complex **7** predominates in the presence of excess bis-chelate **5**; that is, that the equilibrium constant $K_{2,5} = [7]^2/([2][5])$ is distinctly greater than 1.

To study the exchange of the sterically more demanding diphenylmethyl group in complex **3** with the bis-chelate complex **5**, a different procedure was adopted. Due to its incomplete formation from complex **2** and diphenylmethane, solutions of complex **3** always contained minor amounts of unreacted complex **2**. Upon addition of the protonated chelate ligand $HC_5Me_4SiMe_2$-Ph to these solutions, complex **2** was completely converted to **5** and toluene, since its benzyl group is a stronger base than the diphenylmethyl group of complex **3**. Additional $HC_5Me_4SiMe_2Ph$ then reacted with **3** to give the heteroleptic complex $C_5Me_4SiMe_2$PhBaCHPh_2 (**8**). In the presence of an excess of Ba$(CHPh_2)_2$, only one set of chelate ligand signals was apparent; these were thus assignable to species **8**. In equilibrium mixtures of complexes **3**, **5**, and **8,** which resulted from the addition of excess chelate ligand, separate chelate ligand signals for bis-chelate **5** and heteroleptic complex **8** were observed. For the diphenylmethyl ligand only averaged signals were apparent, which moved to lower fields with increasing conversion of **3** to **8** (see Experimental Section).

Table 2. Relative Concentrations of Complexes 3, 5, and 8, Determined from ^{1}H NMR Signal Intensities (see Experimental Section), and Resulting Values of the Equilibrium Constant $K_{3,5}$ (left) and Corresponding Values for Complexes 4B, 5, and 9 and Equilibrium Constant $K_{4B,5}$ (right)

ratio[a]	[**3**]:[**5**]:[**8**]	$K_{3,5}$	ratio[a]	[**4B**]:[**5**]:[**9**]	$K_{4B,5}$
48:52	14:8:78	54	42:58	24:8:68	24
66:33	3.5:38:58	26	52:48	14:17:69	20
75:25	1.0:47:52	57	58:42	10:26:64	16
			77:23	2:53:45	20

[a] Ratio of (dimethylphenylsilyl)tetramethylcyclopentadienyl and diphenylmethyl or 1,1,3-triphenylpropyl ligands, respectively, present in the reaction mixture.

While exchange of the diphenylmethyl ligand in these equilibrium systems is too fast for the observation of separate signals, exchange of the chelate ligand is slow enough for the observation of well-resolved signals of the bis-chelate **5** and of the mixed complex **8**, which allowed separate integration and evaluation of their relative concentrations (Table 2). In this manner, the equilibrium constant for the reaction of **3** and **5** to **8** was determined as $K_{3,5} = [8]^2/([3][5]) = 45 \pm 15$, indicating a substantial preference for the heteroleptic product **8**.

Similar results were obtained when reactions between the bis-triphenylpropyl complex **4B** and complex **5** were studied in C_6D_6 solution: Also in this case, averaged signals were observed for the triphenylpropyl ligand, which thus appears to be rapidly exchanged in these reaction systems. Separate sets of chelate ligand signals were aparent, on the other hand, for the bis-chelate $(C_5Me_4SiMe_2Ph)_2$Ba (**5**) and the mixed species $C_5Me_4SiMe_2$-PhBa−C$Ph_2CH_2CH_2$Ph (**9**) (see Experimental Section). Satisfactory resolution of these signals allowed us to determine the equilibrium constant $K_{4B,5} = [9]^2/([4B][5]) = 20 \pm 4$ (Table 2). While this value is smaller by a factor of ca. 2 than that for the analogous reaction of the bis(diphenylmethyl) complex **3** with complex **5**, a strong preference for the heteroleptic species is still apparent.

In reaction systems containing complex **4B** together with the bis-THF adduct of permethylbarocene (**6**) finally, averaged broadened signals were observed for the triphenylpropyl as well as for the cyclopentadienyl ligands, thus indicating a rather rapid exchange of both ligands. While quantitative evaluations were not feasible here, a sharpening of the C_5Me_5 ligand signals in the presence of excess triphenylpropyl ligand indicates again that the heteroleptic complex C_5Me_5BaCPh_2CH_2-CH_2Ph (**10**) predominates under these conditions.

The results of these exchange experiments provide clear evidence for the predominance of heteroleptic complexes in those equilibria according to eq 1, for which separate signals of the mono- and bis-chelate species were observable. Even where only averaged signals were observed, a sharpening of the otherwise broadened chelate ligand signals in the presence of

excess arylalkyl ligand provides indirect evidence for the preferred formation of the heteroleptic species in these reaction systems. Apparently, the combination of cyclopentadienyl and of phenyl-substituted alkyl ligands in these species provides an optimal coordination environment for their Ba^{2+} centers.

In all cases, exchange of the arylalkyl ligands between homoleptic and heteroleptic species is found to be fast on the NMR time scale, as is that of the permethylcyclopentadienyl ligand. Exchange of the phenyl-linked tetramethylcyclopentadienyl chelate ligands, on the other hand, is found to be slow on the NMR time scale. Again, the combined coordination of an anionic cyclopentadienyl and a neutral aryl ligand, as it is apparent also in the structure of complex **5**, appears to be unique in providing kinetic stability to the otherwise rapidly exchanging Ba^{2+} complexes.

4. Polymerization of Styrene with Triphenylpropylbarium Complexes. The capability of benzylic barium ligands to induce anionic polymerization of styrene was tested with complex **4A**, $Ba(Ph_2CCH_2CH_2Ph)_2$, which is particularly soluble also in nonpolar hydrocarbons. Under strictly anhydrous conditions (see Experimental Section), 0.1 mol of styrene was added to a solution of 0.05 mmol of complex **4A** in 120 mL of cyclohexane at 40.0 °C. After ca. 2 h,[22] the reaction was quenched with methanol and polystyrene was isolated in essentially quantitative yield (see Experimental Section). A number-average molar mass of $M_n = 90\,000$, determined by GPC, is in reasonable agreement with the value of 104 000 expected from the 2000:1 ratio of monomer to bivalent initiator. This indicates that one polystyrene chain is derived from practically every one of the Ba^{2+}-bound triphenylpropyl residues. The polydispersity index $M_w/M_n = 1.20$, determined for this polymer by GPC, is significantly higher than that expected for a typical living polymerization.[23]

When polymerizations were conducted in three separate stages, by subsequent additions of 13, 26, and 52 mmol of styrene to 0.05 mmol of complex **4A** at 50 °C, polystyrene with M_n values of 12 600, 39 600, and 104 000 and with M_w/M_n values of 1.26, 1.29, and 1.44 was obtained in the first, second, and third stage, respectively. Comparison of the corresponding GPC curves with those obtained from a three-stage polymerization initiated with *sec*-butyllithium (Figure 2) indicates that the increased polydispersity index found with triphenylpropyl barium as initiator results mainly from some short-chain tailing, probably caused by a slow initiation step, rather than by increased chain termination.[24]

Polymerizations with the homoleptic complex **4A** were then conducted, at 40 °C and a monomer:initiator ratio of 2000:1, in the presence of the bis-chelate complex $(C_5Me_4SiMe_2Ph)_2Ba$ (**5**) in excess ratios of 1:2 and 1:4, such

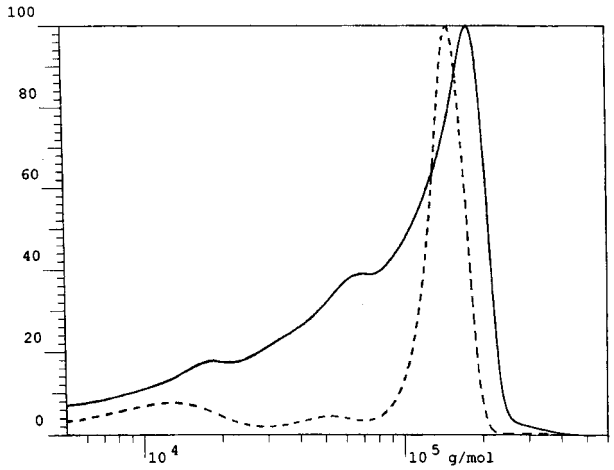


Figure 2. GPC curves for polystyrene obtained from a three-stage polymerization of 13, 26, and 52 mmol of styrene with 0.05 mmol of complex **4A** at 50 °C, with waiting times of 25 min between consecutive styrene additions (solid line), and from an analogous polymerization with 0.1 mmol of *sec*-butyllithium (broken line).

that the heteroleptic complex $C_5Me_4SiMe_2PhBaCPh_2CH_2CH_2Ph$ (**9**) is preponderantly formed in the Schlenk equilibrium (eq 1). From $K_{4B,5} = 20$ we can estimate that **9** dominates over **4A** in ratios of ca. 25:1 and 60:1, respectively. For the polymers obtained from these reaction runs after ca. 2 h,[25] values of $M_n = 122\,000$ and 102 000 and of $M_w/M_n = 1.3$ and 1.55, respectively, were determined by GPC. The rather reasonable agreement with the expected value of $M_n = 104\,000$ indicates that also in these reaction systems each triphenylpropyl group gives rise to one polymer chain, while the $C_5Me_4SiMe_2Ph$ chelate ligands remain unreactive. These polymers, as well as those made with **4A** alone, were found to consist of essentially atactic polystyrene by ^{13}C NMR spectroscopy.[26]

Conclusions

The results presented above show that the bis-triphenylpropyl complex **4A** as well as the mixed complex **9**, which contains also an inert chelate ligand, are capable of inducing anionic styrene polymerizations. The slightly broadened molecular weight distribution of polymers obtained with **4A** can be ascribed to a relatively slow initiation step: Due to the presence of four "barophilic" phenyl groups close to its metal center, **4A** is likely to react with styrene more slowly than a Ba−polystyryl species does. The additional increase of M_w/M_n in polymers made with complex **9** is probably due to further reductions of the rate of initiation by the sterically demanding chelate ligand.

In view of the fact that anionic polymerizations, for example, with lithium alkyl or arylalkyl derivatives give essentially atactic polymers, the lack of tacticity of polystyrene produced with complex **4A** is not surprising. It would have been conceivable, however, that the

(22) A temperature excursion of +0.9 °C occurred ca. 3 min after addition of styrene. This exotherm was comparable in extent and duration to that caused by an analogous reaction with 0.1 mmol of *sec*-butyllithium and would thus indicate roughly comparable reactivities of these lithium and barium alkyl initiators.

(23) With *sec*-butyllithium as initiator at a 1000:1 ratio, polystyrol with $M_w = 114\,000$ and $M_w/M_n = 1.06$ was obtained under otherwise identical conditions.

(24) GPC curves of polymers obtained by three-stage polymerization at 60 °C indicate that substantial (40−50%) chain termination occurs when ca. 60 min are allowed to elapse between consecutive styrene additions.

(25) Temperature excursions of +0.7 and +0.5 °C after ca. 3 min indicated a reactivity of the heteroleptic complex **9**, formed by addition of 2 and 4 equiv of **5**, respectively, which is not much lower than that of complex **4A** (cf. ref 22).

(26) Inoue, Y.; Nishioka, A.; Chujo, R. *Makromol. Chem.* **1972**, *156*, 207. Sato, H.; Tanaka, Y.; Hatada, K. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1667.

spatially extended chelate ligand in **9** might reduce free space at the Ba^{2+} center sufficiently to enforce an increased interaction of each entering styrene unit with the chiral polystyryl chain and hence its preferred enantiofacial orientation in the insertion-transition state, so as to give either predominantly isotactic or predominantly syndiotactic polystyrene.

Previously studied styrene polymerizations with barium alkyl initiators, which had been conducted in THF solutions,[14] had been reported to be propagated there predominantly by "free" (i.e., solvated) polystyryl anions, which are unlikely to exert any stereochemical control. In the nonpolar cyclohexane solvent used in our study, ionic intermediates of this kind are thermodynamically unfavorable. Here, tight Ba^{2+}−polystyryl ion pairs are likely to favor coordinative polymerization mechanisms, which can be expected to induce at least some degree of stereoselectivity.

That this possibility is not born out by our results is most probably connected with the rapid exchange of arylalkyl groups, i.e., also of growing polymer chains, found to occur between different Ba^{2+} centers. This exchange is undoubtedly accompanied by epimerization of the chiral carbanions bound to these metal centers. To conduct anionic, living styrene polymerizations with controlled stereochemistry, metal complexes will have to be found to which the growing arylalkyl chain is bound tightly enough to suppress its epimerization, while remaining still sufficiently reactive for efficient styrene insertions. It remains to be discovered how this demanding goal might be achieved.

Experimental Section

General Methods and Materials. Unless otherwise stated, all syntheses were conducted under strict exclusion of oxygen and humidity in Schlenk vessels on an argon-vacuum manifold or in a nitrogen-filled glovebox. Solvents were dried by distillation over the following drying agents: THF and diethyl ether over sodium−benzophenone; pentane over sodium−potassium alloy; hexane and cyclohexane over calcium hydride; toluene and ethyl benzene over sodium. The solvents were then degassed by evacuation at −78 °C for 2 h and stored under argon.

Cyclohexane for use as solvent for the anionic polymerizations was further purified by adding, to each liter of solvent, 2 mL of a 1.6 M solution of *n*-butyllithium in hexane and 0.5 mL of diphenylethene. The red solution was heated to reflux for 3 h. Cyclohexane was then distilled from these drying agents, stored in a stainless steel vessel under argon, and transferred to the polymerization autoclave by a stainless steel cannula as needed.

Styrene was distilled, immediately before being used for polymerization, under a reduced pressure of 12 mbar and stored over aluminum oxide pearls under an argon atmosphere. *n*-Butyllithium was used as a 1.6 M solution in hexane.

NMR spectra were recorded on JEOL FX90Q, Bruker AC250, and Bruker DRX600 spectrometers, using as internal standards residual ^{1}H NMR signals of the solvents (C_6D_6, 7.15 ppm; $CDCl_3$, 7.24 ppm; d_8-THF α-protons, 3.58 ppm) for ^{1}H NMR spectra and the signals of C_6D_6 (128.0 ppm) and of d_8-THF α-C atoms (67.4 ppm) for ^{13}C NMR spectra.

The following compounds were synthesized according to literature reports: Barium bis(bis(trimethylsilyl)amide)·2THF (**1**),[15] dibenzylmagnesium·dioxane,[16] benzyllithium·TMEDA,[18] barium bis(2,4,6-tri-*tert*-butylphenolate)·2THF.[19]

Dibenzylbarium (2). (a) To a solution of 4.35 g (14.8 mmol) of dibenzylmagnesium·dioxane in a mixture of 60 mL of toluene and 15 mL of diethyl ether was added dropwise a solution of 8.67 g (14.4 mmol) of barium bis[bis(trimethylsilyl)-amide]·2THF (**1**) in the same solvent mixture within 20 min. After stirring the reaction mixture for 14 h, the orange precipitate was collected by filtration and washed twice with 20 mL of diethyl ether. The solid residue was dissolved in 30 mL of THF and covered with a layer of 60 mL of pentane. After 24 h, an orange solid had formed. To complete the crystallization, the solvent layers were mixed. Dibenzylbarium (**2**) was thus obtained, by collecting the orange solid by filtration and washing with two 20 mL portions of diethyl ether, in 40% yield: ^{1}H NMR (δ in d_8-THF) 1.99 (4 H s, benzyl CH_2), 5.34 (2H t, *p*-phenyl), 5.75 (2H d, *o*-phenyl), 6.40 (4 H t, *m*-phenyl); ^{13}C NMR (δ in d_8-THF) 56.5 (benzyl CH_2), 103.6, 114,6, 131.4, 155.1 (phenyl-C).

Because of its great sensitivity to air and moisture, **2** was analyzed for its Ba and Mg contents as follows: 209 mg of **2** was hydrolyzed under argon in 10 mL of ion-free water. $BaSO_4$ was precipitated with sulfuric acid at 80 °C. After drying to constant weight at 600 °C, 141 mg of $BaSO_4$ were obtained, corresponding to a barium content of 40% (calcd 43%). Titration of the filtrate with a 0.1 M solution of $EDTA^{4-}$ at pH 10 with eriochrome black T as indicator gave a Mg content of 1.0 mg (0.5%).

(b) To a solution of 15.0 g (24.9 mmol) of **1** in 70 mL of diethyl ether was added, within 20 min, a solution of 10.7 g (49.8 mmol) of benzyllithium·TMEDA in 100 mL of diethyl ether at room temperature. After stirring for 14 h, the orange solid formed was collected by filtration, washed with three 20 mL portions of diethyl ether, and dried in vacuo. A total of 7.44 g of dibenzylbarium (93% yield) was thus obtained.

(c) To a solution of 12.2 g (16.7 mmol) of barium bis(2,4,6-tri-*tert*-butyl phenolate)·2THF in a mixture of 50 mL of toluene and 5 mL of THF was added a solution of 7.2 g (33.6 mmol) of benzyllithium·TMEDA in 30 mL of toluene in the course of 15 min. After stirring for 14 h, the orange solid formed was collected, washed with 20 mL of toluene and with 20 mL of diethyl ether, and dried in vacuo. In this manner, 4.35 g of dibenzyl barium (81% yield) was obtained. NMR spectral properties of the products obtained by procedures (b) and (c) were identical to those given for (a) above; in particular, signals assignable to $N(SiMe_3)_2$ or $OC_6H_3(t\text{-}Bu)_3$ groups were practically absent.

Bis(diphenylmethyl)barium (3A). A solution of 0.39 g (1.22 mmol) of **2** and 2.44 g (14.5 mmol) of diphenylmethane in 20 mL of THF was stirred for 2 days at room temperature. Removal of solvent in vacuo, extraction of the residue with two 25 mL portions of diethyl ether, and drying of the solid residue in vacuo gave 0.40 g of a red solid, which contained, as judged by its ^{1}H NMR spectrum, compounds **2** and **3A** in a ratio of ca. 1:8. ^{1}H NMR of **3A** (δ in C_6D_6): 4.18 (2 H s, CH), 5.99 (4 H t, *p*-phenyl), 6.53 (8 H d, *o*-phenyl), 6.76 (8 H t, *m*-phenyl). ^{13}C NMR (δ in d_8-THF): 81.4 (CH), 111.5, 118.1, 130.6, 145.7 (phenyl).

Bis(1,1,3-triphenylpropyl)barium (4A). To a suspension of 1.78 g (5.58 mmol) of **2** in a mixture of 70 mL of ethyl benzene and 10 mL of THF was added 2.50 mL (14.15 mmol) of diphenylethene (DPE) at room temperature. The dark red solution, which had formed after stirring overnight, was freed of small amounts of insoluble material by filtration and then completely evaporated in vacuo to give a highly viscous oil. This was washed with small volumes of diethyl ether or pentane and dried extensively in vacuo to give compound **4B** in practically quantitative yield as a glassy solid. Since the latter retained traces of diphenylethene and of solvent, it was not possible to determine an exact yield and an elementary analysis. ^{1}H NMR (δ in C_6D_6): 2.64 (4 H m, CH_2), 2.70 (4 H m, CH_2), 6.12 (4 H t, p-1-phenyl), 6.71 (16 H m, m,o-1-phenyl), 7.17 (10 H m, 3-phenyl). ^{13}C NMR (δ in C_6D_6): 35.2, 35.7 (CH_2), 92.9 (propyl), 111.9, 118.2, 125.9, 128.7, 128.9, 131.9, 142.7, 143.2 (phenyl). Signals of residual DPE (5.26 2 H s, 7.08−7.11

Table 3. ^{1}H NMR Shifts (δ in ppm) of the $Me_2Si(Ph)(C_5Me_4)$ and CH_2Ph Signals in Mixtures of Complexes 2 and 5 in d_8-THF Solution at Room Temperature

	$Me_2Si(Ph^b)(C_5Me_4)$ signals					CH_2Ph^b signals			
ratio[a]	$SiMe_2$	Cp-Me	Cp-Me	Ph^b	Ph^b	CH_2	p-Ph^b	o-Ph^b	m-Ph^b
0:100						1.98	5.35	5.75	6.41
14:86	0.47	1.96	2.02	7.15−7.18	7.37−7.41	2.00	5.37	5.73	6.41
42:58	0.47	1.96	2.02	7.16−7.19	7.38−7.41	2.06	5.36	5.67	6.39
66:33	0.46	1.92	1.99	7.15−7.18	7.27−7.30	2.13	5.31	5.62	6.34
100:0	0.46	1.92	1.98	7.15−7.19	7.27−7.31				

[a] Ratio of (dimethylphenylsilyl)tetramethylcyclopentadienyl and benzyl ligands present in the reaction mixture. [b] Ph = phenyl.

6 H m, 7.28−7.32 4 H m) and of diethyl benzene (1.07 3 H t, 2.43 2 H q, 7.03−7.19 5 H m) appeared with integrated intensities of ca. 2% in the ^{1}H NMR spectra of **4A**.

Bis(1,1,3-triphenylpropyl)barium·2THF (4B). An analogous reaction of 0.17 g (0.53 mmol) of **2** and 0.21 mL (1.14 mmol) of diphenylethene in a mixture of 20 mL of toluene and 1 mL of THF yielded, after workup as described above, the bis-THF adduct **4B** in practically quantitative yield. ^{1}H NMR (δ in C_6D_6): 1.27 (8 H m, THF), 2.67 (4 H m, CH_2), 2.79 (4 H m, CH_2), 3.22 (8 H m, THF), 6.13 (4 H t, p-1-phenyl), 6.78 (8 H t, m-1-phenyl), 6.84 (8 H d, o-1-phenyl), 7.20 (10 H m, 3-phenyl); ^{13}C NMR (δ in C_6D_6): (THF) 34.8, 36.1 (CH_2), 68.3 (THF), 90.0 (propyl), 111.4, 118.1, 125.9, 128.7, 128.9, 131.4, 143.3 143.9 (phenyl).

Bis(dimethylphenylsilyltetramethylcyclopentadienyl)-barium (5). Dimethylphenyl(tetramethylcyclopentadienyl)-silane was prepared by deprotonating 5.4 g (44 mmol) of tetramethylcyclopentadiene in 90 mL of THF by addition of 30 mL of a 1.6 M solution of *n*-butyllithium at −78 °C and warming slowly to room temperature and subsequent addition, again at −78 °C, of 8.3 g (49 mmol) of chlorodimethylphenyl-silane. After stirring for 24 h at room temperature, THF was evaporated in vacuo, the residue was taken up in 50 mL of pentane, insoluble materials were removed by filtration, and pentane was evaporated in vacuo. Distillation of the remaining yellow liquid in vacuo at 83−85 °C gave 7.5 g (29 mmol, 66% yield) of dimethylphenyl(tetramethylcyclopentadienyl)silane. ^{1}H NMR (δ in C_6D_6): 0.16 (6 H s, $SiMe_2$), 1.76 (12 H s, C_5Me_4), 2.99 (1 H s, C_5H) 7.15−7.20, 7.38−7.42 (5 H m, phenyl). ^{13}C NMR (δ in C_6D_6): −3.8 ($SiMe_2$), 11.3, 14.6 (C_5Me_4), 54.7 (C_4CH), 132.9, 135.9 (C_4CH), 127.8, 129.1, 134.0, 134.2 (phenyl). MS (EI,70 eV, 25 °C): *m/e* 256 (50, M^+), 135 (100, $M^+ - C_5Me_4H$), 120 (25, $M^+ - C_5Me_4H - CH_3$).

In 20 mL of toluene, 2.3 g (8.9 mmol) of dimethylphenyl-(tetramethylcyclopentadienyl)silane and 2.7 g (4.45 mmol) of barium bis(bis(trimethylsilyl)amide)·2THF (**1**) were stirred for 1 h at 60 °C. Evaporation of solvent in vacuo, washing of the solid residue with two 20 mL portions of pentane, and subsequent drying in vacuo gave 1.25 g (1.9 mmol, 43% yield) of complex **5** as a yellowish powder. When **5** was dissolved in toluene/THF and stored at −30 °C for several days, NMR spectrally pure **5** was obtained in the form of yellow crystals, which were suitable for a crystallographic structure determination (vide infra). ^{1}H NMR (δ in C_6D_6): 0.59 (12 H s, $SiMe_2$), 1.95 (12 H s, C_5Me_4), 2.00 (12 H s, C_5Me_4), 6.98−7.09 (10 H m, phenyl). ^{13}C NMR (δ in C_6D_6): 0.3 ($SiMe_2$), 11.4, 14.5 (C_5Me_4), 103.9, 120.2, 122.4 (C_5Me_4), 128.8, 130.1, 131.9, 141.9 (phenyl). Anal. Calcd for $BaC_{34}H_{46}Si_2$: C, 63.00; H, 7.15. Found: C, 62.48; H, 7.22.

Bis(pentamethylcyclopentadienyl)barium·2THF (6). In 20 mL of THF, 1.2 g (8.8 mmol) of pentamethylcyclopentadiene and 2.65 g (4.4 mmol) of barium bis(bis(trimethylsilyl)-amide)·2THF (**1**) were dissolved and stirred for 30 min at 55 °C. The solvent was then evaporated in vacuo at 60 °C and the solid residue washed with two 20 mL portions of pentane and dried in vacuo to give 1.3 g (2.4 mmol, 55% yield) of ^{1}H NMR spectrally pure, colorless complex **6**. The ^{1}H NMR spectrum of **6**—(δ in C_6D_6) 1.30 (8 H m, THF), 2.13 (30 H s, C_5Me_5), 3.29 (8 H m, THF)—corresponds to that reported in the literature.[3,4]

Table 4. ^{1}H NMR Shifts (δ in ppm) of the $CHPh_2$ Signals in Mixtures of Complexes 3 and 5 in d_8-THF Solution at Room Temperature

ratio[a]	CH	p-Ph^b	o-Ph^b	m-Ph^b
0:100	4.18	5.99	6.53	6.76
18:82	4.21	6.02	6.55	6.79
48:52	4.24	6.04	6.55	6.79
66:33	4.27	6.04	6.56	6.80
75:25	4.27	6.04	6.55	6.80

[a] Ratio of (dimethylphenylsilyl)tetramethylcyclopentadienyl and diphenylmethyl ligands present in the reaction mixture. [b] Ph = phenyl.

Reactions of Complex 5 with Barium Dialkyl Compounds 2, 3, and 4B. Quantities of 5−20 mg each of complex **5** and of dibenzyl barium (**2**) were dissolved in 0.5 mL of d_8-THF in NMR tubes. After ca. 2 h at room temperature, ratios of $Me_2Si(Ph)(C_5Me_4)$ and $CHPh_2$ ligands of 1:6, 1:1.4, 1.4:1, and 2:1 were determined in the resulting reaction mixtures by ^{1}H NMR integration. In all solutions, only average signals were detected for both ligands, with chemical shifts as listed in Table 3. While solutions containing an excess of complex **2** gave benzyl signals which were ca. 2−3 times as broad as those of **2** alone, rather sharp benzyl signals were obtained with solutions that contained an excess of **5**. Due to the small differences in chemical shifts and the incomplete resolution of most signals, a quantitative analysis in terms of concentrations of individual complex species was not attempted.

When a solution of ca. 10 mg of complex **3** in 0.5 mL of d_8-THF was allowed to react with increasing proportions of dimethylphenyl(tetramethylcyclopentadienyl)silane in an NMR tube for 2−3 h at room temperature, two separate ^{1}H NMR signal sets were observed for the methyl groups of the chelate ligand, those of the homoleptic complex **5** appearing at 0.46, 1.92, and 1.98 ppm and those of the heteroleptic complex **8** at 0.45, 1.89, and 1.97 ppm. The diphenylmethyl ligand gave only an averaged signal at slightly varying chemical shifts (Table 4). By addition of increasing proportions of complex **3** to the final reaction mixture it was shown that equilibrium concentrations of **3**, **5**, and **8** are reversibly reached from either side. Relative concentrations of these species in various reaction mixtures were determined from integrated intensities of signals at 1.92 ppm for **5** and at 1.89 ppm for **8**, that of **3** from the intensity of the *p*-phenyl signal at 6.02−6.04 ppm after subtraction of the part due to **8**, and lead to the values of $K_{3,5}$ listed in Table 2 in the Results and Discussion part.

Reaction between complexes **5** and **4B**, finally, was studied in a solution of ca. 10 mg of **5** in 0.5 mL of C_6D_6, to which increasing proportions of **4B** in C_6D_6 solution were added. While the triphenylpropyl ligand gave again only averaged signals (Table 5), separate ^{1}H NMR signal sets were observed for the methyl groups of the chelate ligand in **5**, at 0.59, 1.95, and 2.00 ppm, and in **9**, at 0.65, 2.00, and 2.15 ppm, i.e., at lower fields than in **5**. From the integrated intensities of the Me_2Si signals at 0.59 ppm for **5** and at 0.65 ppm for **9** and of the *p*-phenyl signal at 5.99−6.11 ppm for the sum of **4B** and **9**, the concentrations of **4B**, **5**, and **9** were determined to give the values of $K_{4B,5}$ likewise listed in Table 2.

Table 5. ^{1}H NMR Shifts (δ in ppm) of the Signals of the 1,1,3-Triphenylpropyl Group in Mixtures of Complexes 4B and 5 in C_6D_6 Solution at Room Temperature

ratio[a]	CH_2	CH_2	p-1-Ph[b]	o-1-Ph[b]	m-1-Ph[b]
0:100	2.67	2.79	6.13	6.78	6.84
23:77	2.69	2.75	6.11	6.78	6.80
42:58	2.69[c]	2.69[c]	6.07	6.76[c]	6.76[c]
77:23	2.69	2.57	6.00	6.73	6.61
92:8	2.70	2.49	5.99	6.73	6.58

[a] Ratio of (dimethylphenylsilyl)tetramethylcyclopentadienyl and 1,1,3-triphenylpropyl ligands present in the reaction mixture. [b] Ph = phenyl. [c] Unresolved signals.

Polymerization Reactions. Polymerizations were conducted with styrene in cyclohexane solution, under strict exclusion of moisture and air, in a thermostated stainless steel autoclave reactor.[27] A 110 mL portion of cyclohexane was transferred to the predried reactor, warmed to the temperature indicated, and then titrated with a solution of complex **4A** until a faint red color persisted. To this purified reaction medium, 1 mL of a solution containing 0.05 mmol of the initiator dissolved in ethyl benzene was then added. In a smaller reaction chamber, a mixture of 11.5 mL (0.1 mol) of styrene and 10 mL of cyclohexane was likewise titrated with initiator solution and then swiftly transferred to the autoclave, such that the ratio of monomer to bivalent initiator was 2000:1. After addition of monomer, slight temperature excursions inside the thermostated reactor were recorded.

After ca. 2 h, the reaction mixtures were quenched by reaction with methanol under an argon atmosphere. Solvents were evaporated, and the polymer was dried in vacuo at 120 °C for ca. 2 h. Molar mass distributions were determined by GPC and tacticities by ^{13}C NMR in $C_2D_2Cl_4$ solution at 377 K.[26] Results of these polymerization experiments are summarized in section 4; those of three-stage polymerizations with subsequent additions of 13, 26, and 52 mL of styrene are shown in Figure 2.

Crystal Structure Determination. Yellow, rhombohedral crystals of complex **5** with a size of ca. 0.2 × 0.3 × 0.3 mm, suitable for a diffractometric structure determination, were obtained by crystallization from toluene−THF at −30 °C. Space group, cell parameters, and X-ray diffraction intensities were determined, at 243(2) K, on a Siemens-P4 four-circle diffractometer (Mo Kα, λ 71.073 pm, graphite monochromator, ω-scan with $\Delta\omega$ 1.6°, $3.0 \le \dot{\omega} \le 30$ °/min, $2.20 \le \theta \le 27.01$°). The crystals of **5** were monoclinic, space group $P2_1/c$, with a 955.96(8) pm, b 1973.9(4) pm, c 1773.1(2) pm, β 104.555(8)°; V 3238.4(8) × 10^6 pm^3, $Z = 4$, d_{calcd} 1.330 g/cm^3, absorption coefficient 1.32 mm^{-1}. Of 6623 independent reflections, 5182 with $I > 2\,\sigma(I)$ were used with semiempirical absorption corrections. The structure was solved by direct methods (SHELXL-93). Refinement with a partially anisotropic model, using riding model techniques for H atoms, converged at $R_1 = 0.038$ and $R_2 = 0.0918$, goodness of fit 1.057, largest difference peak and hole 0.50 and −0.56 × 10^{-6} e/pm^3, respectively. Structural parameters for complex **5** are presented in Table 6; selected bond distances and angles, in Table 1. Further crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 138487. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

(27) The autoclave used for the polymerization studies was routinely freed from traces of moisture and air by heating in it a cyclohexane solution of *sec*-butyllithium and DPE to the same temperature and for the same time as for the polymerization reactions proper. For details of autoclave design see: Weeber, A. Dissertation, Universität Konstanz, 1999.

Table 6. Atomic Coordinates (×10^4) and Equivalent, Isotropic Thermal Parameters (pm^2 × 10^{-1}) for Complex 5

atom	x	y	z	U_{eq}
Ba(1)	3056(1)	3622(1)	2134(1)	29(1)
Si(1)	4232(1)	1922(1)	1396(1)	33(1)
Si(2)	1291(1)	4990(1)	3236(1)	35(1)
C(1)	3275(4)	2668(2)	884(2)	32(1)
C(2)	1732(4)	2775(2)	692(2)	38(1)
C(3)	1443(5)	3435(2)	400(2)	47(1)
C(4)	2760(5)	3746(2)	392(2)	45(1)
C(5)	3891(5)	3290(2)	694(2)	38(1)
C(6)	3056(4)	4918(2)	2993(2)	29(1)
C(7)	3460(4)	5136(2)	2308(2)	35(1)
C(8)	4874(4)	4906(2)	2351(2)	35(1)
C(9)	5362(2)	4545(2)	3052(2)	35(1)
C(10)	4269(4)	4551(2)	3454(2)	29(1)
C(11)	606(5)	2258(3)	751(3)	52(1)
C(12)	−42(6)	3740(3)	70(4)	73(2)
C(13)	2892(7)	4418(3)	8(3)	67(2)
C(14)	5479(6)	3441(3)	799(3)	55(1)
C(15)	6089(5)	1783(3)	1265(3)	52(1)
C(16)	3242(5)	1110(2)	1126(3)	51(1)
C(17)	4402(2)	2087(2)	2467(2)	35(1)
C(18)	3262(5)	1934(2)	2810(3)	46(1)
C(19)	3314(7)	2110(3)	3574(3)	65(2)
C(20)	4492(7)	2432(3)	4015(3)	67(2)
C(21)	5628(7)	2590(3)	3708(3)	69(2)
C(22)	5583(5)	2413(3)	2939(3)	49(1)
C(23)	2588(5)	5577(2)	1668(3)	52(1)
C(24)	5791(5)	5098(3)	1806(3)	51(1)
C(25)	6888(4)	4276(2)	3360(3)	48(1)
C(26)	4386(5)	4246(2)	4241(2)	41(1)
C(27)	−14(5)	5590(3)	2604(4)	62(2)
C(28)	1381(5)	5253(3)	4261(3)	57(1)
C(29)	458(4)	4112(2)	3071(3)	40(1)
C(30)	−189(4)	3880(3)	2318(3)	51(1)
C(31)	−665(5)	3223(3)	2173(4)	65(2)
C(32)	−528(6)	2771(3)	2778(5)	76(2)
C(33)	68(6)	2984(3)	3519(5)	78(2)
C(34)	569(5)	3640(2)	3674(4)	55(1)

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Supporting Information Available: For complex **5**, tables giving crystal data, data collection, solution and refinement details, atomic coordinates, anisotropic and isotropic displacement parameters, and bond distances and angles. For complex **4A**, ^{1}H NMR spectra in d_8-toluene solution at temperatures between +20 and +90 °C and for complex **4B** the ^{1}H NMR spectrum in C_6D_6 solution at 25 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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