

Ethylene Polymerization Using Tetramethyl(2-methylthioethyl)cyclopentadienyl Complexes of Cobalt

Olafs Daugulis, Maurice Brookhart,* and Peter S. White

Department of Chemistry, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27599-3290

Received June 3, 2003

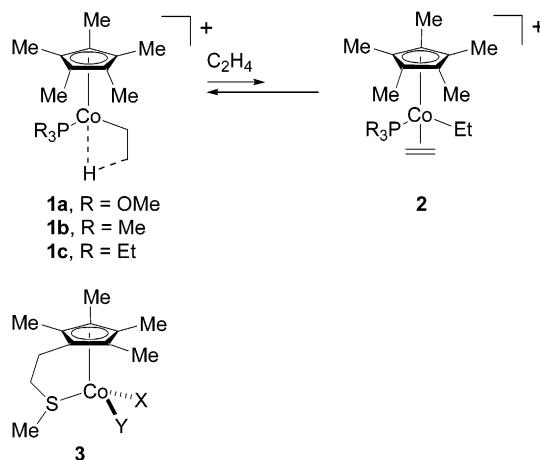
Tetramethyl(2-methylthioethyl)cyclopentadiene complexes of cobalt have been synthesized and tested in ethylene polymerization. In combination with MMAO-3A, tetramethyl(2-methylthioethyl)cyclopentadienylcobalt diiodide (**4**) was shown to polymerize ethylene to linear polyethylene with M_n 's in the range of 5000–68 000. The activity of the catalyst is improved compared to the previously described catalysts containing the $\text{Cp}^*\text{Co}^+(\text{PR}_3)$ unit. Cationic (tetramethyl(2-methylthioethyl)cyclopentadienyl)methylcobalt nitrile complexes **8** were also shown to be competent ethylene polymerization catalysts, producing polyethylene with similar properties as observed with **4**/MMAO-3A.

Introduction

During the past decade olefin polymerizations using late transition metal catalysts have attracted considerable attention.¹ Relative to early metal d^0 catalysts, different enchainment mechanisms are frequently observed for late metal systems leading to different polymer microstructures. In addition, reduced oxophilicity of these systems allows the copolymerization of ethylene and certain polar vinyl monomers.² In the mid 1980s we and others reported cobalt(III) complexes of the type **1**, which are well-defined ethylene polymerization catalysts.³ These complexes polymerize ethylene in a living fashion, producing polyethylenes with narrow polydispersities and moderate molecular weights. The catalyst resting state was shown to be a β -agostic complex, but alkyl ethylene complexes such as **2** were determined to be intermediates in the catalytic cycle.

Unfortunately, the activity of these complexes is relatively low, generally 1–2 turnovers/min at 1 atm ethylene.^{3c,f,g} Activity was shown to be dependent on the steric bulk of the complex; for example, the trieth-

ylphosphine derivative **1c** is not active as a polymerization catalyst, while trimethylphosphine and phosphite complexes **1a,b** do polymerize ethylene.^{3g} While the less bulky cyclopentadienyl derivatives are intrinsically more active than their pentamethylcyclopentadienyl analogues **1a,b**, they are substantially less stable and exhibit short lifetimes.^{3g}



We report here an investigation of Co(III) ethylene polymerization catalysts derived from the tetramethyl(2-methylthioethyl)cyclopentadienyl ligand (general structure **3**). The $-\text{SCH}_3$ pendant ligand is much less bulky than the PMe_3 or P(OMe)_3 ligands of **1a–c**. Furthermore, the π -donor properties of the sulfide ligand could conceivably lower the barrier to ethylene insertion through stabilization of the electron-deficient transition state for migratory insertion.

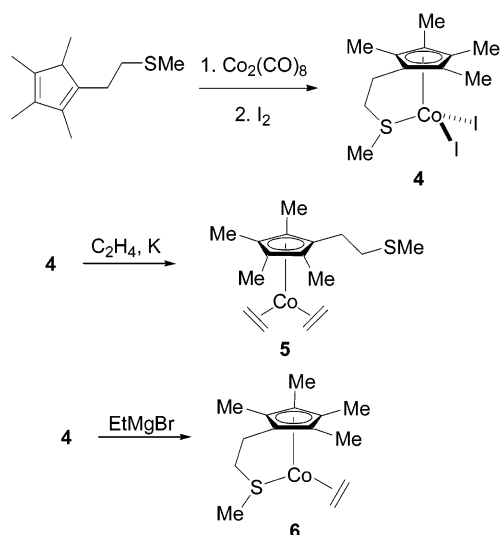
Results and Discussion

Synthesis of the Cobalt Complexes. Potential precursors to the catalytically active cationic cobalt(III) alkyl complexes include the cobalt(III) dihalides (activated with aluminum alkyls), the cobalt(I) ethylene

(1) For recent reviews see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. Pioneering studies: (d) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. (e) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (f) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.

(2) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Johnson, L. K.; McLaine, S. J.; Sweetman, K. J.; Wang, Y.; Bennett, A. M. A.; Wang, L.; McCord, E. F.; Ionkin, A.; Ittel, S. D.; Radzewich, C. E.; Schiffrino, R. S. WO 200344066, 2003. Review: (d) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(3) (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (b) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. (c) Brookhart, M.; Volpe, A. F., Jr.; DeSimone, J. M. *Polym. Prepr.* **1991**, *32*, 462. (d) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378. (e) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 326. (f) Enders, M.; Ludwig, G.; Pritzkow, H. *Organometallics* **2001**, *20*, 827. (g) Volpe, A. F., Jr. Thesis, University of North Carolina at Chapel Hill, 1991.

Scheme 1

complex (activated through protonation), and cobalt(III) dialkyl complexes activated through protonolysis. Syntheses of these precatalysts are described below.

Treatment of dicobalt octacarbonyl with tetramethyl-(2-methylthioethyl)cyclopentadiene^{4a,5} yields the intermediate dicarbonyl complex, which, without isolation, was oxidized with iodine to give tetramethyl(2-methylthioethyl)cyclopentadienylcobalt diiodide (**4**) in an excellent yield (Scheme 1). No ν_{CO} band is observed in the IR spectrum, indicating that the sulfide arm has displaced CO from the cobalt center. A halogen-bridged dimer structure with a decoordinated sulfide arm can be excluded on the basis of the observation of diastereotopic ring methyl groups by NMR spectroscopy (see Experimental Section). The bis-ethylene complex **5** was obtained by reduction of the diiodide with potassium in the presence of ethylene.⁶ Unfortunately, the ethylene complex is a very air-sensitive oil, and attempts to purify it were not successful. No conditions were found where the bis-ethylene complex could be converted to the monoethylene complex **6**. However clean samples of **6** could be obtained through treatment of **4** with ethylmagnesium bromide, initially anticipated to yield the cobalt diethyl complex. Recrystallization of the product from pentanes yielded a red-brown, air- and temperature-sensitive solid whose ^1H and ^{13}C NMR spectra showed that the cobalt ethylene complex **6** was formed. Presumably decomplexation of the sulfide arm from a diethyl complex, followed by β -hydride elimination, reductive elimination of ethane, and recoordination of sulfide, leads to the observed complex **6**.

The structure of the complex was verified by single-crystal X-ray diffraction analysis. The ORTEP diagram

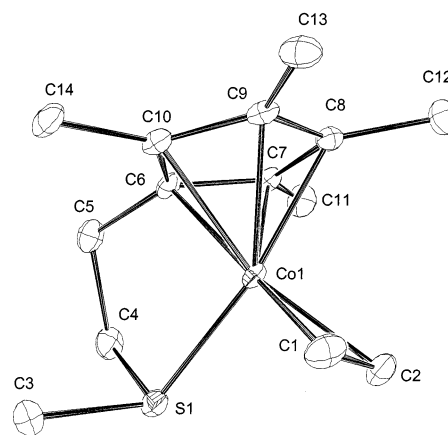
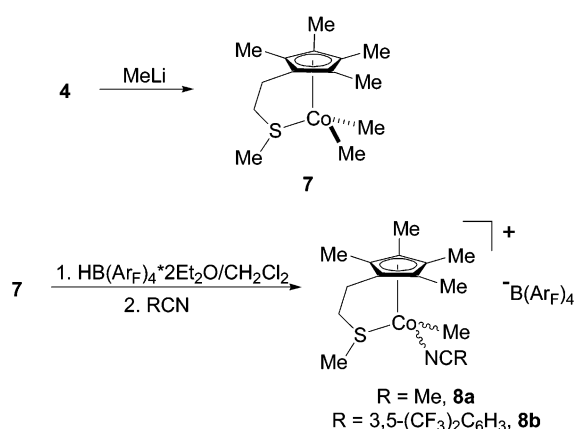


Figure 1. ORTEP view of **6**. Selected interatomic distances (Å) and angles (deg): Co(1)–S(1) = 2.1750(9), Co(1)–C(1) = 1.980(4), Co(1)–C(2) = 1.996(3), C(1)–C(2) = 1.400(6), Co(1)–S(1)–C(4) = 99.29(13), Co(1)–S(1)–C(3) = 111.49(16), C(3)–S(1)–C(4) = 99.65(21).

Scheme 2

of **6** is shown in Figure 1. The carbon–carbon bond length for the bound ethylene is somewhat elongated compared to free ethylene (1.400(6) vs 1.339 Å).⁷ The cobalt–sulfur bond length is 2.1750(9) Å, which is within the range of the reported values for Cp–Co complexes.⁸ As expected, the geometry around sulfur is approximately tetrahedral, with the nonbonding pair of electrons on S occupying the fourth site.

Due to the high sensitivity of the ethylene complex **6**, a more convenient entry into cationic cobalt(III) compounds was sought. The reaction of the diiodide with methyllithium afforded the corresponding dimethyl complex **7** as a red-violet, crystalline substance (Scheme 2).⁹ This compound is stable at RT in crystalline form; however, in chlorinated hydrocarbons slow decomposition is observed. Protonation of **7** using $\text{HB}(\text{Ar}_\text{F})_4 \cdot 2\text{Et}_2\text{O}$ ($\text{Ar}_\text{F} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) in CH_2Cl_2 followed by complexation with either acetonitrile or $3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\text{CN}$ afforded the cationic methyl nitrile complexes **8a,b** as violet-brown stable solids.

NMR Studies of the Complexes. Due to a significant barrier to inversion at the chiral sulfur atom, the

(4) (a) Krut'ko, D. P.; Borzov, M. V.; Petrosyan, V. S.; Kuz'mina, L. G.; Churakov, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1996**, 984 (in Russian). (b) Krut'ko, D. P.; Borzov, M. V.; Kuz'mina, L. G.; Churakov, A. V.; Lemenovskii, D. A.; Reutov, O. A. *Inorg. Chim. Acta* **1998**, 280, 257. A review about cyclopentadienylmetal complexes bearing pendant ligands: (c) Butenschön, H. *Chem. Rev.* **2000**, 100, 1527. For cyclopentadienylchromium complexes with pendant sulfide groups, see: (d) Döhning, A.; Göhre, J.; Jolly, P. W.; Kryger, B.; Rust, J.; Verhovnik, G. P. *J. Organometallics* **2000**, 19, 388.

(5) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, 28, 273.

(6) (a) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355. (b) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stämmler, H.-G. *Organometallics* **1993**, 12, 2980. (c) Holle, S.; Jolly, P. W. *J. Organomet. Chem.* **2000**, 605, 157. Reference 6c describes Cp–Co ethylene complexes with pendant amino groups.

(7) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L. E., Ed.; The Chemical Society: London, 1958.

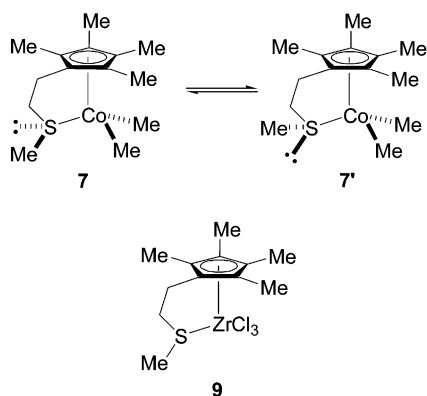
(8) (a) Sheldrick, W. S.; Hauck, E.; Korn, S. *J. Organomet. Chem.* **1994**, 467, 283. (b) Harada, T.; Takayama, C.; Kajitani, M.; Sugiyama, T.; Akiyama, T.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2645.

(9) (a) Preparation of $\text{CpCoMe}_2\text{PPh}_3$: Yamazaki, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, 38, 2212. (b) Protonation of $\text{CpCoMe}_2\text{PMe}_3$: Hofmann, W.; Werner, H. *Chem. Ber.* **1982**, 115, 119.

Table 1. Polymerization of Ethylene by 4/MMAO or PMAO-IP (entries 1–13) and 8a,b (entries 14–17) in Chlorobenzene^a

no.	pressure, psi	time, h	temp, °C	g PE	TOF, ^b h ⁻¹	<i>M</i> _n	Br/1000C ^c	MWD
1 ^d	14	2.83	26	5.0	630	11 800	9	2.4
2	400	3	5–6	3.4	4000	68 000	1	2.0
3	100	1	26–28	0.7	2500	23 500	3	2.2
4	400	1	28–31	3.5	12 500	28 000	3	2.1
5 ^e	400	1	28–31	3.7	13 200	23 800	2	2.4
6	400	1	28–31	3.9	13 900	28 000	2	2.2
7 ^e	400	1	28–31	3.8	13 600	29,000	2	2.0
8	400	3	26–31	6.7	8,000	30 900	1	2.1
9 ^f	400	0.25+0.75	28–31	3.6	12 900	21 100	2	3.0
10	800	0.5	28–32	2.8	20 000	22 900	2	2.1
11	800	1	28–32	4.2	15 000	31 100	2	1.9
12	400	0.5	59–62	2.2	15 700	7900	4	2.3
13	400	1.5	59–62	2.9	6900	5200	3	3.7
14 ^g	400	1	26–29	1.1	3900	24 700	10	1.9
15 ^h	400	1	26–29	0.3	1100	ND	ND	ND
16 ⁱ	400	1	26–31	2.6	6500	25 200	6	2.3
17 ^j	400	1	26–30	1.4	5000	31 600	4	2.0

^a 0.01 mmol precatalyst in 100 mL of chlorobenzene; entries 1–5, 8–13 MMAO-3A activator; entries 6–7 PMAO-IP activator, entries 2–4, 6, 8–13 Al/Co ratio 300. ^b TOF calculated assuming all Co is active. ^c Branching/1000C determined by ¹H NMR spectroscopy. ^d Al/Co ratio 220, 0.1 mmol precatalyst. ^e Al/Co ratio 1000. ^f Pressurize to 400 psi, polymerize for 15 min, then vent reactor, wait 3 h, then repressurize to 400 psi, polymerize for 45 min. ^g Catalyst **8a**, no activator. ^h Catalyst **8a**, no activator, 2 equiv of CH₃CN added. ⁱ Catalyst **8b** (0.014 mmol), no activator. ^j Catalyst **8b**, no activator.

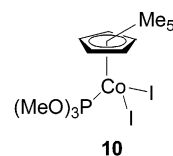


NMR spectra of complexes **4** and **7** exhibit signals for diastereotopic methyl groups on the cyclopentadienyl ring below room temperature. For complex **8a**, in which both the sulfur and cobalt centers are stereogenic, two diastereomers are observed at low temperature. The inversion process for **7** is shown above. To determine the energetics of inversion at sulfur, variable-temperature NMR studies of complexes **4**, **7**, and **8a** were carried out.¹⁰ For complex **4**, the barrier to inversion at sulfur was determined to be 15.8 ± 0.1 kcal/mol (tetrachloroethane-*d*₂) and for **7** 13.9 ± 0.1 kcal/mol (methylcyclohexane-*d*₄). For **8a** in THF-*d*₈, in which coalescence studies were carried out, a 1/0.64 ratio of diastereomers is observed. The barriers of inversion at sulfur were measured to be 15.3 ± 0.1 (minor to major diastereomer) and 15.6 ± 0.1 kcal/mol (major to minor diastereomer). For comparison, in complex **9** the barrier of inversion at sulfur is 10.5–11.2 kcal/mol depending on the solvent.^{4a}

Acetonitrile self-exchange in **8a** was studied in CD₂-Cl₂ solution at –2 °C by treatment of **8a** with a large

excess of CD₃CN. Since the first-order rate constant obtained by using 15 equiv of CD₃CN ($k_{\text{obs}} = (1.9 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, $\Delta G^\ddagger = 20.5 \pm 0.1$ kcal/mol) is nearly identical to the rate constant obtained using 47 equiv ($k_{\text{obs}} = (1.7 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, $\Delta G^\ddagger = 20.6 \pm 0.1$ kcal/mol), the exchange most likely proceeds by the rate-determining dissociation of acetonitrile ($k_{\text{obs}} = k_{\text{dissoc}}$) followed by trapping of the coordinatively unsaturated intermediate with free acetonitrile. However, rate-limiting dissociation of the sulfide ligand cannot be rigorously excluded.

Polymerization of Ethylene. Initially the polymerization of ethylene was studied using the combination of diiodide **4** with MMAO-3A in chlorobenzene (Table 1). Under 1 atm of ethylene at room temperature after 2.8 h polyethylene with $M_n = 11\,800$ (MWD = 2.4) was obtained with a turnover frequency (TOF) 630 TO/h. For comparison, catalyst **10**/MAO in toluene under 1 atm

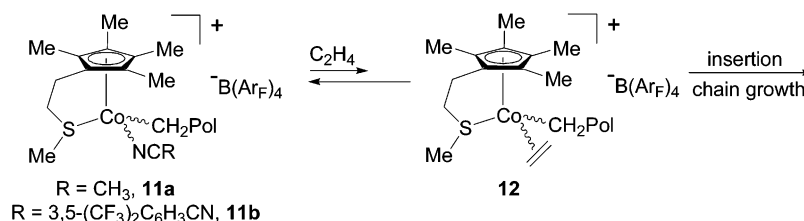


ethylene produces PE with $M_n = 9900$ (MWD = 4.5) and 42 TO/h (TOF corresponds to 3 h run).^{3g} At 5 °C, 400 psi ethylene pressure polyethylene with $M_n = 68\,000$ was obtained (entry 2, TOF = 4000 h⁻¹). As expected, at higher temperatures increased TOF (ca. 13 000 at RT) and decreased M_n (ca. 28,000) is observed (entry 4). The decrease in the calculated TOF in the 3 h run at 28–31 °C, 400 psi (entry 8) is probably due to the precipitation of the polymer. Polymerization for 15 min, followed by venting the reactor, waiting for 3 h, then repressurizing with ethylene, and polymerizing for an additional 45 min afforded almost the same amount of polyethylene as the 1 h uninterrupted run (compare entry 9 to entry 4).¹¹ These results suggest that catalyst

(10) Inversion of sulfides coordinated to transition metals has been widely studied. For a review, see: (a) Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, 32, 1. Recent examples: (b) Albéniz, A. C.; Espinet, P.; Lin, Y.-S. *Organometallics* **1996**, 15, 5010. (c) Dupont, J.; Gruber, A. S.; Fonseca, G. S.; Monteiro, A. L.; Ebeling, G. *Organometallics* **2001**, 20, 171. (d) Canovese, L.; Lucchini, V.; Santo, C.; Visentin, F.; Zambon, A. *J. Organomet. Chem.* **2002**, 642, 58. (e) Shan, X.; Espenson, J. H. *Organometallics* **2003**, 22, 1250.

(11) A referee has suggested that catalyst lifetime could be shortened under actual polymerization conditions. We cannot rule this out, but since the resting state is an agostic species, we believe this experiment accurately reflects catalyst stability under polymerization conditions.

Scheme 3



is stable for hours at room temperature. At 60 °C catalyst is unstable and reduced lifetimes and M_n 's (5000–8000) are observed (see entries 12 and 13).

The TOF is nearly linear with respect to ethylene pressure. A comparison of entries 3, 4, and 10 shows that as the pressure increases from 100 to 400 psi to 800 psi the corresponding increase in TOF is 2500/h to 12 800/h to 20 000/h. These results suggest that the major catalyst resting state under these conditions is a cobalt alkyl complex and not a cobalt alkyl ethylene complex, consistent with the observations in the case of the earlier P(OMe)_3 -based catalyst.³ As established in the case of the P(OMe)_3 complex **1a**, these kinetics are consistent with a preequilibrium between a cobalt agostic alkyl complex and a cobalt alkyl ethylene complex which favors the cobalt alkyl complex.

No significant difference was observed between using an Al/Co ratio of 300 and 1000 (entry 5 vs entry 4). PMAO-IP could also be used as activator with no difference between Al/Co ratios of 300 and 1000 (entries 6 and 7).

Monomodal molecular weight distributions of ca. 2 for polymer prepared from MMAO activation of diiodide indicate a single site catalyst. The use of large quantities of MMAO precludes NMR studies for identification of the catalyst resting state. On the basis of earlier studies, the likely resting state is a cationic cobalt alkyl complex, but since MMAO can serve as a reducing agent,¹² verification of this assumption is desired. While protonation of $\text{Cp}^*(\text{P(OMe)}_3)_3\text{Co}(\text{C}_2\text{H}_4)$ leads to an agostic ethyl complex^{3a} (a model for the catalyst resting state), similar attempts to generate a spectroscopically characterizable cationic agostic ethyl complex from low-temperature protonation of **6** have not been successful. However, as noted above, protonation of dimethyl complex **7** and trapping with CH_3CN yields the cationic methyl acetonitrile complex **8a**. This cationic methyl complex serves as an "activator-free" complex for ethylene polymerization (entry 14). At 400 psi ethylene, RT, polyethylene is produced with a very similar molecular weight, MWD, and branching level compared to PE produced under similar conditions with **4**/MMAO (entry 4). These results support a cationic Co(III) alkyl intermediate in the case of MMAO and PMAO activation. The lower TOF in the case of acetonitrile complex **8a** is proposed to be due to competitive binding of ethylene and CH_3CN at the Co(III) center, as shown in Scheme 3. Performing the polymerization under the conditions of entry 14, but with addition of 2 equiv of acetonitrile, further lowers the TOF to 1100 (entry 15), supporting the notion that the lower TOF is due to competitive

acetonitrile binding.¹³ The complex **8b**, containing the more weakly binding bis-3,5-trifluoromethylbenzonitrile, was also examined. As expected, this complex is more reactive than the acetonitrile complex **8a**, exhibiting a TOF of 5000–6500/h at 400 psi ethylene (entries 16, 17, Table 1). Using **8b**, chain growth could be observed by NMR spectroscopy at 0 °C in CD_2Cl_2 . Treatment of a 0.017 M solution of **8b** in CD_2Cl_2 with 9 equiv of ethylene results in consumption of C_2H_4 (ca. 3 equiv in 30 min) and growth of an alkyl chain. No vinylic resonances are evident. Only signals for coordinated nitrile are observed, indicating that the catalyst resting state is the cationic cobalt alkyl nitrile complex.

Branching densities in the polyethylene are quite low, 1–10 branches/1000 carbons, and are in the range of high-density polyethylene. T_m 's fall in the narrow range between 132 and 133 °C. Only vinylic end groups were detected in low molecular weight samples. The detection of vinylic end groups, the similarity of M_n values from MMAO activation of diiodide relative to the activator-free nitrile complexes **8**, and the insensitivity of molecular weight to Co/Al ratios all point to β -hydride elimination as the dominant chain transfer mechanism for both catalyst systems. No significant chain transfer to Al appears to occur in the MMAO-3A or PMAO-IP activated systems.

Summary

Polymerization of ethylene by cobalt complexes containing a tetramethyl(2-methylthioethyl)cyclopentadienyl unit has been investigated. In combination with MMAO-3A, tetramethyl(2-methylthioethyl)cyclopentadienylcobalt diiodide (**4**) was shown to polymerize ethylene, producing polyethylene with M_n up to 68 000. The activity of the catalyst is substantially improved compared to the previously described catalysts containing the $\text{Cp}^*\text{Co}^+(\text{PR}_3)$ unit. Cationic alkyl complexes [tetramethyl(2-methylthioethyl)cyclopentadienyl] $\text{Co}(\text{CH}_3)\text{L}^+$ ($\text{L} = \text{CH}_3\text{CN}$, **8a**; $(\text{CF}_3)_2\text{C}_6\text{H}_3\text{CN}$, **8b**) were synthesized as activator-free initiators. Although ethylene polymerization activity was reduced relative to **4**/MMAO due to competitive nitrile binding, the properties of the polyethylene produced were identical to those of polyethylene produced from MMAO activation. These results suggest that both systems involve a cationic Co(III) alkyl ethylene complex as the key intermediate and that

(12) (a) Kooistra, T. M.; Knijnenburg, Q.; Smits, J. M. M.; Horton, A. D.; Budzelaar, P. M. H.; Gal, A. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 4719. (b) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252.

(13) From exchange studies, the estimated rate of acetonitrile dissociation from **8a** at RT is ca. 0.04 s^{-1} . The measured TOF (ca. 1 s^{-1} at 400 psi ethylene) exceeds this value. This suggests that at high ethylene pressure the trapping of the agostic alkyl complex $[\text{Me}_4\text{CpCH}_2\text{CH}_2\text{SMe}]\text{Co}(\text{CH}_2\text{Pol})^+$ by ethylene and insertion is significantly faster than retrapping by acetonitrile to return to species **10a** (Scheme 3). Such a mechanism, in which a significant fraction of the catalyst rests as the acetonitrile complex, is fully consistent with suppression of the reactivity by added CH_3CN .

chain transfer occurs via β -hydride elimination and not through chain transfer to aluminum in the case of MMAO activation.

Experimental Section

General Considerations. All the operations related to catalysts were carried out under an argon atmosphere using standard Schlenk techniques. The ^1H and ^{13}C spectra were recorded using Bruker 300, 400, or 500 MHz spectrometers and referenced against residual solvent peaks (^1H , ^{13}C). Flash chromatography was performed using 60 Å silica gel (SAI). GPC was performed at DuPont Analytical in Wilmington, DE, using a Waters 150-C AL/GPC equipped with a Polymer Standards Service "polyolefin" high-speed GPC column. The mobile phase was 1,2,4-trichlorobenzene at 135 °C, flow rate of 5 mL/min, RI detector. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum transferred from P_2O_5 and degassed by repeated freeze–pump–thaw cycles. The following starting materials were used using literature procedures: $\text{HB}(\text{Ar}_\text{F})_4 \cdot 2\text{Et}_2\text{O}^{14}$ and tetramethyl(2-methylthioethyl)cyclopentadiene.^{4a} $\text{NaB}(\text{Ar}_\text{F})_4$ was purchased from Boulder Scientific; MMAO (modified methylaluminoxane) and PMAO-IP were from Akzo Nobel.

Analysis of polymer branching by ^1H NMR spectroscopy was carried out using a branched method.¹⁵ Since the end group signals (vinyl) were too small to be integrated correctly, the end group and allylic integrals were adjusted to match the molecular weight of polymer observed by GPC. In some polymers, trace amounts of residual MAO were observed upfield of the CH_3 group signals. The NMR was measured in bromobenzene- d_5 at 120 °C. Errors in coalescence and ΔG^\ddagger measurements were calculated assuming temperature variations of ± 1 K. Errors in rate constants were obtained assuming 5% error in measurements.

Spectral Data for the $\text{B}(\text{Ar}_\text{F})_4$ Counterion. The following ^1H and ^{13}C spectroscopic assignments of the $\text{B}(\text{Ar}_\text{F})_4$ counterion were invariant for different temperatures and are not reported in the spectroscopic data for each of the cationic complexes. $\text{B}[3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2]_4^-$ ($\text{B}(\text{Ar}_\text{F})_4$): ^1H NMR (CD_2Cl_2): δ 7.74 (br s, 8H), 7.57 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 162.2 (q, $J_{\text{C-B}} = 37.4$ Hz), 135.2, 129.3 (q, $J_{\text{C-F}} = 31.3$ Hz), 125.0 (q, $J_{\text{C-F}} = 272.5$ Hz), 117.9.

General Polymerization Procedure. Polymerizations were carried out in a mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple in the reaction mixture. The reactor was charged with chlorobenzene (100 mL) and heated for 1 h at 150 °C. After cooling to RT the solvent was poured out and the reactor heated under vacuum at 150 °C for 1 h. The reactor was filled with Ar, cooled to RT, pressurized to 200 psi ethylene, and vented three times. A solution of the catalyst in 100 mL of chlorobenzene was added to the reactor via cannula, the appropriate activator added via syringe, the reactor pressurized with ethylene to the required pressure, and the pressure maintained at this value during the polymerization. After that the reaction mixture was stirred for the appropriate time. The reactor was occasionally cooled with an external ice bath to keep the temperature in the desired range. After venting, the reaction mixture was poured into methanol and the polyethylene was washed with acidic methanol and then dried under vacuum at 80 °C. The solvent from precipitation was evapo-

rated and the distillate checked for oligomers by NMR. The following polymer T_m values were determined (entry number in Table 1: T_m , °C): 1, 132.2; 2, 132.5; 6, 133.0.

$[\text{Me}_4\text{CpCH}_2\text{CH}_2\text{SMe}]\text{CoI}_2$ (4). This compound was made using a precedent procedure.⁵ $\text{Co}_2(\text{CO})_8$ (3.28 g, 9.6 mmol, Strem) was mixed with 1,3-cyclohexadiene (1.3 mL, 13.6 mmol, Aldrich) and CH_2Cl_2 (10 mL). To the magnetically stirred brown-red solution was added dropwise a solution of $\text{Me}_4\text{-CpHCH}_2\text{CH}_2\text{SMe}$ (3.41 g, 17.4 mmol) in CH_2Cl_2 (10 mL) with venting into the atmosphere through a silicon oil bubbler (evolution of CO). The mixture was refluxed for 1.5 h. After evaporation under vacuum CH_2Cl_2 (10 mL) was added to the residue, followed by a dropwise addition of a solution of I_2 (4.85 g, 19.1 mmol, Fisher Scientific) in CH_2Cl_2 (80 mL) with venting into the atmosphere through a silicon oil bubbler (CO evolution). The solution was stirred for 1 h at RT, and the color changed from brown to dark green. After evaporation of about half of the solvent the residue was purified by flash chromatography on silica gel (17 \times 6.4 cm) in 1/1 CH_2Cl_2 /hexanes under air. The first 500 mL were blank. The eluent was changed to CH_2Cl_2 and the elution continued. The next 750 mL contained impurities followed by 1500 mL containing the desired product. Solvent was changed to 4/1 CH_2Cl_2 /EtOAc, and the next 1500 mL contained additional product. Fractions containing the product were evaporated to give a dark green solid (7.92 g, 89.6%). ^1H NMR (tetrachloroethane- d_2 , -10 °C): δ 4.11–3.97 (m, 1H); 3.91–3.77 (m, 1H); 2.43–2.22 (m, 2H); 2.28 (s, 3H); 2.11 (s, 3H); 2.08 (s, 3H); 2.00 (s, 3H); 1.97 (s, 3H). ^1H NMR (tetrachloroethane- d_2 , 105 °C): δ 4.00 (t, 2H; $J = 6.8$ Hz); 2.33 (t, 2H; $J = 6.8$ Hz); 2.32 (s, 3H); 2.17 (s, 6H); 2.15 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , 0 °C): δ 108.7; 97.4; 94.0; 90.3; 86.6; 54.3; 22.8; 21.9; 13.6; 13.0; 11.6; 10.0. Anal. Calcd for $\text{C}_{12}\text{H}_{19}\text{CoSiI}_2$: C 28.37, H 3.77. Found: C 28.71, H 3.79. Coalescence temperature of peaks at 2.11 and 2.00 ppm ($\Delta\delta = 33.2$ Hz) as well as 2.08 and 1.97 ppm ($\Delta\delta = 33.9$ Hz) was determined to be +41 °C (tetrachloroethane- d_2).

$[\text{Me}_4\text{CpCH}_2\text{CH}_2\text{SMe}]\text{Co}(\text{ethylene})_2$ (5). Complex 4 (0.508 g, 1.0 mmol) was mixed with K (0.086 g, 2.2 mmol). The mixture was cooled to 0 °C and the Schlenk flask flushed with ethylene followed by the addition of THF (10 mL). The mixture was stirred at 0 °C with continuous bubbling of ethylene until the color changed from green to brownish red (about 40 min) and then an additional 10 min. The solution was evaporated, and the residue was extracted with pentane and filtered through a pad of Celite. After evaporation a dark brown, very air-sensitive oil was obtained. Attempts to purify the complex were not successful due to noncrystallinity and instability. ^1H NMR (toluene- d_8 , 25 °C): δ 2.48–2.31 (m, 4H); 1.82 (s, 3H); 1.70–1.59 (m, 4H); 1.47 (s, 6H); 1.29 (s, 6H); 0.95–0.86 (m, 4H).

$[\text{Me}_4\text{CpCH}_2\text{CH}_2\text{SMe}]\text{Co}(\text{ethylene})$ (6). To a stirred suspension of 4 (0.508 g, 1.0 mmol) in diethyl ether (8 mL) was added EtMgBr (0.83 mL of a 3 M solution in diethyl ether, 2.5 mmol, Aldrich) at -78 °C. No reaction was observed. The cooling bath was removed and the solution concentrated under vacuum to half of the initial volume, followed by the addition of THF (5 mL). The solution was stirred at RT for 10 min. The color changed from green to black to red. The reaction mixture was filtered through a pad of Florisil cooled to -78 °C eluting with diethyl ether, the solvent was evaporated, and the residue was crystallized from a small amount of pentane at -30 °C. The product was isolated as red-brown crystals (0.13 g, 46.1%) that decompose at RT in the solid state and in solution. The structure was verified by X-ray crystallography. ^1H NMR (CD_2Cl_2 , -60 °C): δ 3.59–3.45 (m, 1H); 3.21–3.10 (m, 1H); 2.50–2.37 (m, 1H); 2.32 (s, 3H); 2.28 (s, 3H); 2.20–2.09 (m, 1H); 1.85 (s, 3H); 1.28–0.99 (m, 4H); 1.00 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ (CD_2Cl_2 , -30 °C): δ 106.6; 91.9; 88.9; 84.1; 80.8; 53.8; 31.3; 29.5; 22.1; 20.7; 11.9; 11.7; 9.0. Two Me peaks on the Cp overlap at 9.0 ppm.

(14) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(15) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935.

[Me₄CpCH₂CH₂SMe]CoMe₂ (7). To the solution of **4** (1.52 g, 3.0 mmol) in THF (30 mL) was added MeLi (4.2 mL of a 1.6 M solution in diethyl ether, 6.6 mmol, Aldrich) at -78°C . The color of the solution changed from dark green to red. The solution was stirred for 1 h at -78°C , the cooling bath was removed, and two-thirds of the solvent was evaporated under reduced pressure. The residue was filtered through a pad of Florisil at -78°C eluting with diethyl ether. The eluent was evaporated, the residue was dissolved in pentane (40 mL) and filtered through Celite into a Schlenk flask precooled to -78°C , and Celite was washed with additional pentane (10 mL). After 4 h the solvent was transferred away from the crystals by cannula, and the crystals were washed with a minimal amount of cold pentane and dried under vacuum. The product was obtained as red-violet crystals (0.41 g, 48.3%) and is stable at RT under inert atmosphere for at least days. ¹H NMR (methylcyclohexane-*d*₁₄, -10°C): δ 3.65–3.43 (m, 1H); 3.27–3.09 (m, 1H); 2.43–2.24 (m, 1H); 2.21–2.02 (m, 1H); 1.85 (s, 6H); 1.70 (s, 3H); 1.10 (s, 3H); 1.07 (s, 3H); -0.05 (s, 6H). ¹H NMR (methylcyclohexane-*d*₁₄, 60°C): δ 3.34 (t, 1H; $J = 6.8$ Hz); 2.18 (t, 1H; $J = 6.8$ Hz); 1.81 (s, 6H); 1.64 (s, 3H); 1.05 (s, 6H); -0.05 (s, 6H). ¹³C{¹H} (CD₂Cl₂, -10°C): δ 113.5; 89.5; 89.1; 86.4; 85.9; 55.0; 21.7; 16.5; 9.3; 9.0; 8.3; -6.0 ; -6.8 . Two Me peaks on the Cp overlap at 8.3 ppm. Anal. Calcd for C₁₄H₂₅CoS: C 59.14, H 8.86. Found: C 58.65, H 8.75. Coalescence temperature of multiplets centered at 3.5 and 3.2 ppm ($\Delta\delta = 107.4$ Hz) was determined to be 17°C , and that of multiplets at 2.3 and 2.1 ppm ($\Delta\delta = 65.7$ Hz) 11°C (methylcyclohexane-*d*₁₄).

[Me₄CpCH₂CH₂SMe]Co(Me)(NCCH₃)⁺B(Ar_F)₄[−] (8a). Solid HB(Ar_F)₄·2Et₂O (0.313 g, 0.31 mmol) was mixed with **7** (0.085 g, 0.30 mmol). After cooling to -78°C CH₂Cl₂ (2 mL) was added and the dark red-brown reaction mixture stirred for 15 min at that temperature followed by the addition of CH₃CN (78 μL , 1.5 mmol). The color changed to brown-red. After stirring for 15 min at -78°C the solution was warmed to RT, evaporated, coevaporated with hexanes, and dried under vacuum to give 0.35 g (99.4%) of product as a violet-brown solid. ¹H NMR (CD₂Cl₂, -10°C ; 1/1 mixture of diastereomers): δ 4.19–4.06 (m, 1H); 3.81–3.71 (m, 2H); 3.36–3.25 (m, 1H); 2.59–2.45 (m, 1H); 2.38–2.24 (m, 2H); 2.36 (s, 3H; complexed CH₃CN); 2.29 (s, 3H; complexed CH₃CN); 2.24–2.12 (m, 1H); 2.19 (s, 3H); 2.10 (s, 3H); 1.88 (s, 3H); 1.55 (s, 3H); 1.47 (s, 3H); 1.22 (s, 3H); 1.19 (s, 3H); 1.10 (s, 3H); 1.09 (s, 3H); 1.08 (s, 3H); 1.07 (s, 3H). Multiplets at 4.19, 3.36, 2.38 ppm are mutually coupled. Signals at 3.81, 2.59, 2.24 ppm are mutually coupled. ¹³C{¹H} (CD₂Cl₂, -40°C ; mixture of 2 diastereomers): δ 116.5; 115.6; 99.5; 99.2; 97.9; 96.3; 93.7; 93.1; 80.6; 77.2; 54.4; 52.3; 22.2; 21.2; 18.2; 15.8; 9.5; 9.4; 9.3; 9.2; 8.5; 8.4; 8.3; 7.8; 4.8; 4.7; 1.7; 0.3. Signals for two Cp ring carbons are missing. Anal. Calcd for C₄₇H₃₇CoBF₂₄SN: C 48.10; H 3.18; N 1.19. Found: C 47.78, H 3.04, N 1.26. Rates of inversion at sulfur in **8a** (THF-*d*₈ solution) were determined using line shape analysis of peaks at 2.52, 2.45 (set 1) and 2.20, 2.00 (set 2), which broaden and coalesce. The analysis was carried out at $+20$, $+25^{\circ}\text{C}$ (set 1) and $+30$, $+35$, $+40^{\circ}\text{C}$ (set 2).¹⁶ Using set 1 at $+20^{\circ}\text{C}$, $k_{\text{minor} \rightarrow \text{major}} = 29\text{ s}^{-1}$, $k_{\text{major} \rightarrow \text{minor}} = 19\text{ s}^{-1}$; at $+25^{\circ}\text{C}$, $k_{\text{minor} \rightarrow \text{major}} = 43\text{ s}^{-1}$, $k_{\text{major} \rightarrow \text{minor}} = 27\text{ s}^{-1}$. Using set 2 at $+30^{\circ}\text{C}$, $k_{\text{minor} \rightarrow \text{major}} = 66\text{ s}^{-1}$, $k_{\text{major} \rightarrow \text{minor}} = 42\text{ s}^{-1}$; at $+35^{\circ}\text{C}$, $k_{\text{minor} \rightarrow \text{major}} = 104\text{ s}^{-1}$, $k_{\text{major} \rightarrow \text{minor}} = 66\text{ s}^{-1}$; at $+40^{\circ}\text{C}$, $k_{\text{minor} \rightarrow \text{major}} = 172\text{ s}^{-1}$, $k_{\text{major} \rightarrow \text{minor}} = 110\text{ s}^{-1}$. Equilibrium ratio of the two diastereomers in THF-*d*₈ at 0°C is 1/0.637. ¹H spectra of **8a** in THF-*d*₈ are given in the Supporting Information.

[Me₄CpCH₂CH₂SMe]Co(Me)[3,5-(CF₃)₂C₆H₃CN]⁺B(Ar_F)₄[−] (8b). The reaction was carried out as in the case of

Table 2. Crystallographic Data Collection Parameters for **6**

formula	C ₁₄ H ₂₃ CoS
mol wt	282.33
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.17860(20)
<i>b</i> , Å	9.44180(20)
<i>c</i> , Å	15.8065(3)
β , deg	97.631(1)
<i>V</i> , Å ³	1357.70(5)
<i>Z</i>	4
dens calcd, Mg/m ³	1.381
<i>F</i> (000)	593.98
cryst dimens, mm	0.30 × 0.20 × 0.20
temp, °C	-100
radiation (λ , Å)	1.5418
2θ max, deg	140.0
μ , mm ^{−1}	11.09
total no. of rflns	8669
total no. of unique rflns	2413
no. of obsd data ($I > 2.5\sigma(I)$)	2069
no. of refined params	238
<i>R</i> _F , %	0.041
<i>R</i> _w , %	0.048
GOF	1.7705

8a, only after protonation 3,5-(CF₃)₂C₆H₃CN (56 μL , 0.33 mmol, Aldrich) was added instead of acetonitrile. After drying a violet-brown foam was obtained, 0.38 g (92.4%). ¹H NMR (CD₂Cl₂, -10°C ; 1.3/1 mixture of diastereomers): δ 8.26 (s, 1H); 8.23 (s, 1H); 8.1 (s, 2H; Ar_F-CN peaks overlap for both diastereomers); 4.26–4.11 (m, 1H); 3.88–3.74 (m, 2H); 3.44–3.29 (m, 1H); 2.69–2.48 (m, 1H); 2.47–2.35 (m, 2H); 2.34–2.16 (m, 1H); 2.24 (s, 3H); 2.17 (s, 3H); 2.10 (s, 3H); 1.95 (s, 3H); 1.60 (s, 3H); 1.53 (s, 3H); 1.30 (s, 3H); 1.29 (s, 3H); 1.21 (s, 3H); 1.20 (s, 6H; overlap of two Me groups); 1.17 (s, 3H). Multiplets at 4.26, 3.44, 2.47 ppm are mutually coupled. Signals at 3.88, 2.69, 2.34 ppm are mutually coupled. Anal. Calcd for C₅₄H₃₇CoBF₃₀SN: C 47.28, H 2.72, N 1.02. Found: C 47.02, H 2.60, N 1.04.

Acetonitrile Self-Exchange Kinetics for **8a.** To the solution of **8a** (10 mg, 0.0085 mmol) in CD₂Cl₂ (0.6 mL) cooled to -78°C was added CD₃CN (6.7 μL , 0.128 mmol). The NMR tube was placed in a probe cooled to -2°C and the loss of bound acetonitrile peaks at 2.36 and 2.29 ppm monitored versus time, giving $k_{\text{obs}} = 1.9 \times 10^{-4}\text{ s}^{-1}$, $\Delta G^{\ddagger} = 20.5 \pm 0.1$ kcal/mol. The second experiment was carried out as above, except using 21 μL (0.40 mmol) of CD₃CN. The following data were obtained: $k_{\text{obs}} = 1.7 \times 10^{-4}\text{ s}^{-1}$, $\Delta G^{\ddagger} = 20.6 \pm 0.1$ kcal/mol.

X-ray Crystal Structure (6**).** Diffraction data were collected on a Bruker SMART 1K diffractometer using the ω -scan mode. Refinement was carried out with the full-matrix least-squares method based on *F* (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection are given in Table 2.

Acknowledgment. We are grateful to DuPont and the National Science Foundation (CHE-0107810) for support of this research and to DuPont Analytical for GPC analyses.

Supporting Information Available: X-ray crystallography data for **6**, NMR data for **8a** in THF-*d*₈, and graphs for the determination of acetonitrile self-exchange rate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM030414B

(16) The DNMR simulations were performed with an updated version of WINDNMR (<http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm>). Reich, H. J. WinDNMR Dynamic NMR Spectra for Windows. *J. Chem. Ed. Software, Ser. D* **1996**, *3D*, No. 2.