Organometallics 1993, *12*, 3856-3863

Active Sites for Ethylene Polymerization with Titanium(IV) Catalysts in Homogeneous Media: Multinuclear NMR Study of Ion-Pair Equilibria and Their Relation to Catalyst Activity[1]

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Received February 10, 1993⊗

By means of a multinuclear NMR study of the complexes formed between $AlCl_3$ and either Cp_2TiCl_2 or $Cp_2Ti(CH_2SiMe_3)Cl$ in chloroalkane solution, isomeric forms of the resulting 1:1 complexes have been detected. The influence of temperature, concentration, ratio of the titanocene chloride to aluminum chloride, and the nature of the solvent upon the ^1H, ^{13}C, and ^{27}Al NMR spectra has been investigated. The spectral changes caused by the foregoing factors give compelling evidence for an equilibrium in such $Cp_2Ti(R)Cl{\cdot}AlCl_3$ complexes (R = Cl, CH_2SiMe_3) between comtact ion pairs (CIP), $Cp_2TiR{\cdots}Cl{\cdots}AlCl_3$, and solvent-separated ion pairs (SSIP), $Cp_2TiR^+\|AlCl_4^-$. More polar media and higher dilution have been shown to favor the solvent-separated ion pair isomer over the contact ion pair isomer. In π-basic solvents, such as arenes, evidence is offered that a 1:1:1 complex of $Cp_2Ti(R)Cl$, $AlCl_3$, and arene is formed reversibly. The isolation of such a complex with mesitylene and the failure to detect the formation of a complex with hexamethylbenzene indicate the operation of significant steric hindrance to complexation. These observations lead to the proposal that arenes form σ or η^1 complexes with the titanocenium cation and thus generate a third type of ion pair, the solvated cation–anion pair (SCAP) $Cp_2Ti(\eta^1\text{-arene})R^+AlCl_4^-$. Since these NMR studies of the soluble Ziegler polymerization catalyst system $Cp_2TiRCl\text{–}AlCl_3$ have permitted the determination of three types of ion pairs in solution, contact (CIP), solvent-separated (SSIP), and solvated cation–anion (SCAP), an attempt was made to correlate the polymerization activity toward ethylene of an analogous catalyst system, $Cp_2TiMeCl\text{–}Me_nAlCl_{3-n}$, with the dominant type of ion pair present under different experimental conditions. The following variations in the conditions of polymerization were made: polarity and donor character of the solvent, concentration of the catalyst, temperature, ratio of the titanium to the aluminum component, and the nature of the Lewis acid, Me_nAlCl_{3-n} (n = 0–3). From these studies it has been concluded that the solvent-separated ion pair is the most active catalyst and that the arene-solvated SCAP (when the polymerization is conducted in arene solution), $Cp_2Ti(arene)Me^+AlCl_4^-$, is the least active catalyst.

Introduction

The polymerization of olefins, diolefins, and acetylenes by the cocatalytic action of transition-metal salts and main-group organometallics clearly represents one of the most significant and influential discoveries of modern chemistry.[2] Although such Ziegler–Natta catalysts have been recognized for almost 40 years,[3] the molecular origin of this synergistic effect has come to light only recently. Particularly through studies of soluble ethylene polymerization catalysts, such as combinations of bis(η^5-cyclopentadienyl)titanium(IV) dichloride and alkylaluminum halides,[4] have the reactions occurring between the catalyst components been elucidated. From these studies the following insights emerge: (1) the titanium and aluminum components form 1:1 complexes with each other,[5-10] (2) cationic titanium centers are involved, as is evident from electric conductivity studies and solvent effects,[11,12] and (3) several equilibria are established, with the active site probably being a carbon–titanium bond.[13-15] Any doubt concerning the last point was removed in 1985, when we demonstrated that a combination of titanocene dichloride (1) and methylaluminum dichloride (2), which polymer-

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⊗ Abstract published in *Advance ACS Abstracts*, September 1, 1993.

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[11] (a) Dyachkovskii, F. S. In *Coordination Polymerization*; Chien, J. C. W., Ed.; Academic Press: New York, 1975; p 199. (b) Babkina, O. N.; Grigorian, E. A.; Dyachkovskii, F. S.; Shilov, A. E.; Shuvalova, N. M. *Zh. Fiz. Khim.* **1969**, *43*, 7.

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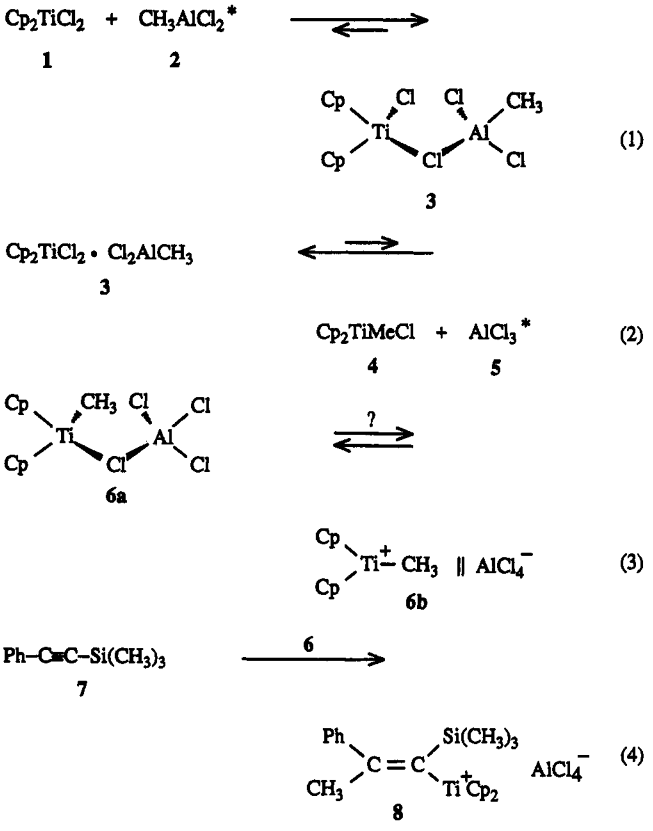
Scheme I

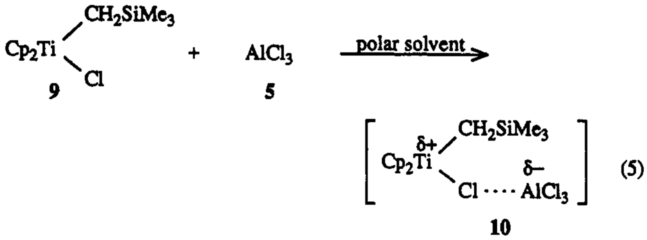


* Such aluminum chlorides generally exist as dimers in nondonor media.

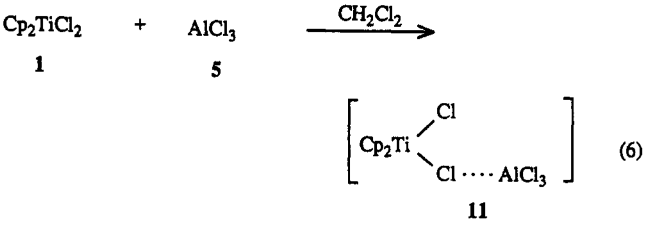
izes ethylene, reacts with the ethylene surrogate trimethyl(phenylethynyl)silane (**7**) to yield bis(η^5-cyclopentadienyl)((*E*)-2-methyl-2-phenyl-1-(trimethylsilyl)ethenyl)titanium(IV) tetrachloroaluminate (**8**).[16] With the detailed X-ray crystal structure of **8** in hand, we concluded that **9** had arisen from the regiospecific *syn*-carbotitanation of **7** by the active catalytic intermediate **6**, namely methyltitanocene tetrachloroaluminate. This active cationic polymerization catalyst was considered to have arisen by way of two preequilibria (eqs 1 and 2 in Scheme I), the first of which involves the formation of complex **3**, which we likewise were able to isolate and whose crystal structure we were able to determine. The existence of the second equilibrium leading to **6** is supported by our having trapped **4** and **5** in the form of adduct **8**. That this second equilibrium must lie much to the left follows from the failure, in this[16] and in previous studies,[5-10] to detect **4** or complex **6** by ultraviolet or multinuclear NMR spectroscopy (Scheme I). Vain attempts to isolate[17] or, until recently, even to detect such alkyltitanocenium(IV) cations by spectroscopy[18] are due both to unfavorable equilibria (*e.g* eq 3) and to the extremely dynamic behavior of titanocene(IV) halide–alkylaluminum halide systems. For example, on the NMR time scale, methyl exchange between methyltitanocene(IV) chloride (**4**) and aluminum chloride (**5**)[19] is relative fast even down to −90 °C and at equilibrium favors complex **3**.[18]

What remained unclear from such studies was whether the complex of **4** with **5** exists as a free, solvent-separated, unbridged ion pair (**6b**) or whether, as in **3**, a chloride-bridged or contact ion pair was formed preferentially (**6a**, step 3). This remaining uncertainty has great bearing on the ultimate question for Ziegler ethylene polymerization: Is the contact ion pair (**6a**) or the solvent-separated ion pair (**6b**) the more active site for ethylene polymerization?

In order to attempt to answer this question, we have undertaken a temperature-dependent multinuclear NMR study of the possible equilibrium depicted in step 3 of Scheme I. At lower temperatures we hoped to observe separate NMR signals attributable to different ion pairs similar to **6a** and **6b**. Since no detectable amount of **4** can be generated by starting with **1** and **2**, we have started instead with a titanocene derivative, $Cp_2Ti(Cl)R$, which already has the organic group attached to titanium. An especially advantageous R group is the (trimethylsilyl)methyl group, because recent observations indicate that such a group stabilizes a cationic titanium center and slows down alkyl group transfer from titanium to aluminum.[18] Accordingly, ((trimethylsilyl)methyl)titanocene chloride (**9**) and aluminum chloride (**5**) were allowed to interact in various polar solvents and the nature of adduct **10** was examined by low-temperature ^1H, ^{13}C, and ^{27}Al NMR spectroscopy (eq 5).



To verify the nature of such an interaction with a system where no net transfer of groups from titanium to aluminum could occur, the analogous complex **11** of titanocene dichloride (**1**) and aluminum chloride (**5**) was investigated by variable-temperature multinuclear NMR (eq 6).



In the following, it will be shown how the nature of the equilibrated complexation generalized by **10** and **11** changes as a function of temperature, concentration, ratio of reactants, and nature of the solvent. These changes,

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[12] Cationic zirconocene intermediates have been established either as active catalysts or as vital precursors to active centers for the polymerization of ethylene or propylene: (a) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. Our observation of ion-pairing phenomena with titanocene–aluminum chloride mixtures, as adumbrated in ref 18 and here reported in detail, suggests that such factors would conceivably be involved in zirconocene systems as well. We are collaborating with Professor H. H. Brintzinger of the University of Konstanz in exploring this possibility.

[13] Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1959**, *81*, 81.

[14] Dyachkovski, F. S. *Vysokomol. Soedin.* **1965**, *7*, 114.

[15] Fink, G.; Zoller, W. *Makromol. Chem.* **1981**, *182*, 3265.

[16] Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

[17] Cationic complexes of the type Cp_2Ti^+MeL and Ind_2Ti^+MeL (Ind = η^5-indenyl; L = NH_3, PMe_3, py, MeCN) have been isolated, but none of these complexes reacts with ethylene, butadiene, or acetylenes. (Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610).

[18] Eisch, J. J.; Caldwell, K. R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417.

[19] Eisch, J. J.; Caldwell, K. R. In *New Science in Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum, D. W., Eds.; Advances in Chemistry 230; American Chemical Society: Washington, DC, 1992; pp 575–590.

in turn, give an insight into the prevailing types of ion pairs under varying experimental conditions. Finally, the results of batch ethylene polymerization runs under varying conditions have been correlated with the predominating type of ion pair known to be initially present in such runs. This correlation has permitted us to conclude which type of ion pair is more reactive in ethylene polymerization in homogeneous media.

Experimental Section

Instrumentation. NMR analyses were performed on a Bruker AM-360 spectrometer. The ^1H, ^{13}C, and ^{27}Al NMR spectra were recorded at the frequencies 360.13 MHz (with a pulse repetition delay (RD) of 10 s and a line broadening factor (LB) of 0.2 Hz), 90.6 MHz (RD 2 s, LB 1 Hz) and 93.9 MHz (RD 1 s, LB 10 Hz), respectively. The ^1H and ^{13}C chemical shifts ($\delta(^1H)$ and $\delta(^{13}C)$) were determined relative to solvents and are reported with respect to tetramethylsilane. The $\delta(^{27}Al)$ signals are referred to an external standard of $AlCl_3{\cdot}6D_2O/D_2O$.

Preparation of Solutions of the $Cp_2Ti(R)Cl{\cdot}AlCl_3$ Complexes for the NMR Study. All reactions were carried out under argon while using standard inert-atmosphere techniques, and initially solvents were purified by standard procedures.[20] Because of the extreme sensitivity of titanium(IV) halide–alkylaluminum halide polymerization catalysts to traces of moisture (which would produce alkylaluminoxanes, themselves superior catalysts for olefin polymerizations[21]), solvents were purified and distilled from the final drying agent immediately before any spectral or polymerization run. For polymerizations a large excess of R_nAlX_{3-n} also was used (minimum of 6 equiv/equiv of the titanium compound) and this excess would serve to scavenge minute traces of any other protic sources.

Commercial titanocene dichloride was sublimed before use, and methyltitanocene(IV) chloride and ((trimethylsilyl)methyl)titanocene(IV) chloride were prepared and purified as described elsewhere.[19] Aluminum chloride was sublimed before use and added to the corresponding solution of bis(cyclopentadienyl)titanium derivative in a proper concentration under vigorous stirring at ambient temperature. Samples for NMR analysis were prepared and transferred into scrupulously dried vessels by using syringe techniques.[20] Because of the light sensitivity of titanocene(IV) derivatives, all such samples were shielded from light.[22,23]

Preparation of the $Cp_2TiCl_2{\cdot}MeAlCl_2{\cdot}C_6H_3Me_3$ Complex (12). A 2.5-mmol sample of $MeAlCl_2$ (as a 1.0 M solution in hexane) was gradually added to the dark orange solution of 2.5 mmol of Cp_2TiCl_2 in 35 mL of mesitylene. The reaction mixture turned dark cherry red, and a solid was precipitated, essentially quantitatively with respect to Cp_2TiCl_2. After 2 h the solid was filtered off, washed carefully with dry hexane, and dried *in vacuo* (25 °C at 1 mmHg) for 6 h. A sample of the terra-cotta-colored solid obtained was dissolved in $CDCl_3$. Integration of the ^1H NMR signals of the solution showed the presence of Cp_2TiCl_2 ($\delta(^1H)$ 6.59 ppm), mesitylene ($\delta(^1H)$ 6.70 and 2.11 ppm), and $MeAlCl_2$ ($\delta(^1H)$ 0.03 ppm) in an exact ratio of 1:1:1. Attempts are under way to obtain a single crystal of 12 for XRD analysis and purified solid samples for solid-state NMR and IR spectroscopy.

Catalyst Productivity Number Determination by Homogeneous Catalysis of Ethylene Polymerization in a Batch Mode. All polymerizations were conducted in a 250- or 500-mL resin-coated glass pressure bottle (Fischer–Porter) equipped with a metal head (polymer coated on the inside) bearing a pressure gauge, an inlet for gas and reagents by syringe, and a stopcock outlet for evacuation. Stirring was provided by a glass-coated magnetic stirring bar, and the temperature was controlled by a bath to within ±1 °C. The entire apparatus was dried in an oven at 110 °C, assembled while warm, and then repeatedly evacuated and refilled with purified argon.

Table I. Variations in the Productivity Number (PN) for the Homogeneous, Catalytic Polymerization of Ethylene by $Cp_2Ti(Me)Cl{\cdots}Me_nAlCl_{3-n}$ with Reaction Conditions[a]

run no.	solvent[b]	temp, °C[c]	concn, mmol L^{-1} [d]	ratio Ti:Al[e]	lewis acid	PN[f]
1	CH_2Cl_2	25	1.0	1:1	$MeAlCl_2$	140
2	CH_2Cl_2	25	1.0	1:2	$MeAlCl_2$	163
3	CH_2Cl_2	25	1.0	1:8	$MeAlCl_2$	140
4	CH_2Cl_2	25	0.26	1:8	$MeAlCl_2$	440
5	CH_2Cl_2	25	1.0	1:16	$MeAlCl_2$	94
6	CH_2Cl_2	25	1.0	1:8	Me_3Al	20[g]
7	CH_2Cl_2	25	1.0	1:8	Me_2AlCl	137
8	CH_2Cl_2	25	1.0	1:8	$AlCl_3$	112[h]
9	toluene	25	1.0	1:8	$MeAlCl_2$	49
10	toluene	25	0.26	1:8	$MeAlCl_2$	197
11	mesitylene	25	1.0	1:8	$MeAlCl_2$	11
12	toluene	70	1.0	1:8	$MeAlCl_2$	75
13	toluene	50	1.0	1:8	$MeAlCl_2$	69
14	toluene	25	1.0	1:8	$MeAlCl_2$	49
15	toluene	0	1.0	1:8	$MeAlCl_2$	10
16	toluene	−10	1.0	1:8	$MeAlCl_2$	<1

[a] The experimental conditions that were held constant during all of the polymerization runs were the following: an atmosphere of anhydrous, prepurified ethylene of 2.7 atm; 100-mL volume of solvent; 25-min duration of polymerization; a constant rate of magnetic stirring in a glass polymerization flask sealed with a pressure cap; exclusion of light. [b] The solvents were made anhydrous and distilled under Ar before use. [c] Temperature was controlled within ±1 °C. [d] Concentration is that of $Cp_2TiMeCl$, which was freshly synthesized and purified to >99% purity. [e] Ratio is the molar ratio of $CP_2TiMeCl$ to that of Me_nAlCl_{3-n}. [f] Productivity number (PN) is defined as grams of polyethylene per gram of $Cp_2TiMeCl$ per atm of monomer per hour and was found in six repeated runs to be reproducible to within ±5%. [g] The catalyst system turned blue after 5 min, signalling reduction of Ti(IV) to Ti(III). [h] Because of the higher solubility of $MeAlCl_2$ over $AlCl_3$ in CH_2Cl_2, this catalyst system was generated by admixing Cp_2TiCl_2 and $MeAlCl_2$.

The experimental conditions that were held constant during all of the polymerization runs were the following: an atmosphere of anhydrous, prepurified ethylene of 2.7 atm, 100- or 200-mL volume of solvent, 25-min duration of polymerization, constant rate of stirring, and exclusion of light. Through preliminary dissolving of the titanium and aluminum components in a given solvent and allowing the solution to stand, it was shown that only with Me_3Al was there any perceptible color change (orange-red to green and then to blue), signaling a reduction of Ti(IV) to Ti(III). Although the mixture of $Cp_2Ti(Me)Cl$ and Me_nAlCl_{3-n} in CH_2Cl_2, toluene, or mesitylene initially constitutes a homogeneous catalyst system, the precipitation of the polyethylene-coated catalyst particles, with time, turns the system into a heterogeneous catalyst. In order to learn how such heterogeneity would influence the catalyst productivity numbers and changes in experimental conditions, the productivity numbers were measured in the most *accelerating* solvent (CH_2Cl_2) for very *short time* periods (~100 s), while the catalyst system was still *homogeneous* because little or no polymer had yet *precipitated*. As might be expected, the productivity numbers (PN) were significantly higher: thus, the catalysis conditions employed for run 3 in Table I gave a PN of 140 after 25 min under heterogeneous conditions but a PN of 282 after 100 s under homogeneous conditions. Similar results were obtained with short-term polymerizations in toluene or mesitylene. But even 100-s polymerizations in homogeneous systems exhibit the same ordering of PN value: CH_2Cl_2 > toluene > mesitylene. Moreover, such short-term polymerizations in homogeneous media responded to concentration changes of the catalyst in a manner qualitatively similar to the 25-min polymerization runs in heterogeneous media. Thus, a 1:8 ratio of $Cp_2Ti(Me)Cl$ and $MeAlCl_2$ showed an increase in PN with decreasing concentration (PN, concentration in mmol L^{-1}): 174, 4; 228, 2; 282, 1). Therefore, we are confident that all the conclusions that we reach by comparing data for 25-min heterogeneous polymerization runs

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(20) Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2, pp 3–52.

(21) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99 and references cited therein.

(22) Davies, A. G. *Pure Appl. Chem.* **1982**, *54*, 23.

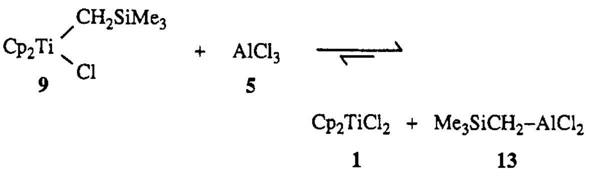
(23) Brindley, P. B.; Davies, A. G.; Hawari, J. A. A. *J. Organomet. Chem.* **1983**, *250*, 247.

are equally applicable to 100-s homogeneous runs. The prolongation of the run simply results in the range of measured PN values being depressed and compressed.

After the appropriate solvent and solutions of the reagents were introduced into the prepared reaction vessel by gastight syringe, the atmosphere of argon was displaced by the ethylene and the polymerization begun. The polymerization was terminated by shutting off the ethylene source and injecting 20 mL of 0.1 N aqueous HCl. The mixture was treated with 30 mL of water and filtered. The polyethylene was washed thoroughly with 0.1 N aqueous HCl and then with hexane. The polymer was dried and weighed. The catalyst productivity number, grams of polyethylene per gram of titanium compound per atmosphere of monomer per hour, was then calculated. On the basis of six or more identical runs with a given set of experimental conditions, values of PN were found to be reproducible to within ±5%.

Results

Interaction of ((Trimethylsilyl)methyl)titanocene Chloride (9) with Aluminum Chloride (5) and with Methylaluminum Chloride (2).[18,19] In $CDCl_3$ at 20 °C, as evidence by the ^1H and ^{13}C NMR spectra, a rapid exchange of the Me_3SiCH_2 group of **9** and the Cl group of **5** took place within 30 min after admixing to form greater than 90% of titanocene dichloride at equilibrium (eq 7).



$$Cp_2Ti(CH_2SiMe_3)Cl\ (\mathbf{9}) + AlCl_3\ (\mathbf{5}) \rightleftharpoons Cp_2TiCl_2\ (\mathbf{1}) + Me_3SiCH_2{-}AlCl_2\ (\mathbf{13}) \quad (7)$$

In the ^1H NMR spectrum the Cp signal of **1** emerged at 6.64 and the CH_2 and Me_3Si signals of **13** were displayed at −0.61 and −0.07 ppm, respectively. However, recording the ^1H spectrum immediately after admixing **9** and **5** uncovered a Cp singlet at 6.51 ppm (Cp of **9** at 6.32) and a CH_2 singlet at 3.04 ppm (CH_2 of **9** at 2.26); the intensity ratio of these new signals was 5:1. The downfield shift of these signals over their counterparts in **9** is consistent with complexation between **9** and **5** and the development of positive charge on titanium with resultant deshielding of the proximate Cp and CH_2 protons (*cf.* **10** in eq 5).

To slow down such group exchange, as exhibited in eq 7, with the goal of defining the nature of the positive titanium center in **10**, the interaction of **9** and **5** was conducted and monitored by multinuclear NMR at −23 °C, both in toluene and in 1,2-dichloroethane. In the ^1H spectra the Cp signal of the complex of **9** and **5**, after short reaction time, appeared at 5.77 and at 6.53 ppm, respectively (little shifted from 5.79 and 6.33 ppm); the CH_2 signal, however, now appeared at 4.08 and 3.00 ppm, considerably shifted from 2.12 ppm, its position for **9** alone in either solvent. After several hours in either solvent, the ^1H spectrum was that of a mixture of **1** and **13** (*cf.* eq 7). These transitory shifts, however, again are in accord with the presence of a positive titanium in the complex (*cf.* **10** in eq 5) but do not reveal how free the $Cp_2Ti{-}CH_2SiMe_3$ positive fragment is from the $Cl{-}AlCl_3$ negative fragment.

To this question, monitoring of the reaction mixture of **9** and **5** by ^{27}Al NMR spectroscopy was then able to provide an answer. After short reaction times in 1,2-dichloroethane at −23 °C, three peaks were evident (δ (%, peak width at half-height in Hz)): 103.3 (78, 268); 99.1 (6, 26); 98.1 ppm (6, 63).[24] The last peak arises from residual Al_2Cl_6 and that at 99.1 ppm most likely from a solvent–$AlCl_3$ complex.[25] The dominant peak at 103.3 ppm corresponds exactly to the value reported for the free $AlCl_4^-$ ion.[26] This observation permits the conclusion that $Cp_2Ti^+{-}CH_2SiMe_3$ and $AlCl_4^-$ in **10** exist, transitorily, in whole or in large part as free, solvent-separated ions in this polar, noncoordinating solvent at −23 °C. With time this peak broadens with a maximum shift to lower fields, indicating the formation of **13**, possibly complexed with **1**.[27]

To hinder the exchange of the Me_3SiCH_2 group in **9**, its interaction with the already alkylated $MeAlCl_2$ (**2**) was examined. Similar transient signals were observed in the ^1H NMR spectra in benzene and in chloroform at 25 °C: in the former solvent the Cp and CH_2 signals at 5.88 and 2.14 ppm were shifted to 5.98 and 2.92 ppm; in the latter, the corresponding signals at 6.32 and 2.26 ppm now occurred at 6.42 and 2.70 ppm. But again with time, exchange became noticeable (analogous to that in eq 7) through the formation of about 50% of titanocene dichloride (**1**) and $Me_3SiCH_2Al(Cl)Me$ (in C_6H_6: −0.11 (Me_3), −0.17 (Me), and −0.31 ppm (CH_2)).

Interaction of Titanocene Dichloride (1) and Aluminum Chloride (5).[28a] To obtain a better understanding of how titanocene dihalides and aluminum halides interact (*cf.* eqs 5 and 6) and yet avoid group-exchange equilibria (*e.g.*, eq 7), the systems $Cp_2TiCl_2{-}AlCl_3$ and $Cp_2TiBr_2{-}AlBr_3$ were examined by variable-temperature, multinuclear NMR spectroscopy and with variations in concentration and solvent polarity. Presented in Figure 1 are the ^1H NMR spectra of 1:1 mixtures of Cp_2TiCl_2 and $AlCl_3$ in methylene chloride at two concentrations and at five temperatures between +27 and −30 °C. In both cases, the singlet near 6.80–6.81 ppm at 27 °C resolves into two singlets at 6.90 and 6.77 ppm at −30 °C. The resolution into these two signals upon cooling and the coalescence into the one signal upon warming are fully reversible. It is furthermore noteworthy that, of the two, the high-field signal becomes dominant upon dilution (Figure 1a). Similar observations were made when the ^{13}C NMR spectra of 1:1 mixtures of Cp_2TiCl_2 and $AlCl_3$ in CH_2Cl_2 at two concentrations were examined (Figure 2). The singlet near 123 ppm at 25 °C resolved into two singlets, in a reversible fashion, near 123.3 and 122.6 ppm at −30 °C. Again the high-field singlet at −30 °C had significantly higher intensity in more dilute solution (Figure 2a). These results demonstrate the existence of two different types of

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(24) In preliminary studies on the temperature dependence of the ^{27}Al NMR signal for the systems Cp_2TiCl_2 and $AlCl_3$, as well as $Cp_2Ti(CH_2SiMe_3)Cl$ and $AlCl_3$ (both in a 1:1 ratio in CH_2Cl_2), the broad signal observed at 104 ppm at 20 °C was shifted toward 103 ppm and significantly narrowed as the temperature was lowered to −60 °C. The changes in the shape and position of the signal were interpreted by the line simulation program LINESIM to betoken the equilibrium between two different Al components (Eisch, J. J.; Pombrik, S.; Zheng, G. X. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 109; see also data cited in ref 18). However, more recent attempts to reproduce these observations with the newly tuned and programmed Bruker AM-360 spectrometer have been unsuccessful in showing line narrowing of the ^{27}Al signal with decreasing temperature. (The assistance of Mr. Claude Gey, visiting scientist from the Centre de Recherches sur les Macromolécules Végétales, CNRS, Grenoble, France, was invaluable in this reinvestigation). The reported equilibrium constants should accordingly be viewed with uncertainty until further study. There is little doubt, nevertheless, from low-temperature broadening of the ^{27}Al signal reported here that two Al components are in equilibrium at 20 °C.

(25) Brown, H. C.; Wallace, W. J. *J. Am. Chem. Soc.* **1953**, *75*, 6279 and references cited therein.

(26) Nöth, H.; Rürlander, R.; Wolfgardt, P. *Z. Naturforsch.* **1982**, *37B*, 29.

(27) The complex $Cp_2Ti(Cl)\cdots Cl\cdots AlMeCl_2$ displays its ^{27}Al peak in $CDCl_3$ solution at 118 ppm at 25 °C.[16]

(28) (a) The present ^1H and ^{13}C NMR spectra of the system $Cp_2TiCl_2{-}AlCl_3$, shown in Figures 1–4, show sharper resolution into singlets, especially at low temperature, than those previously reported.[24] (b) Eisch, J. J.; Mackenzie (née Zerche), K., unpublished studies, 1992.

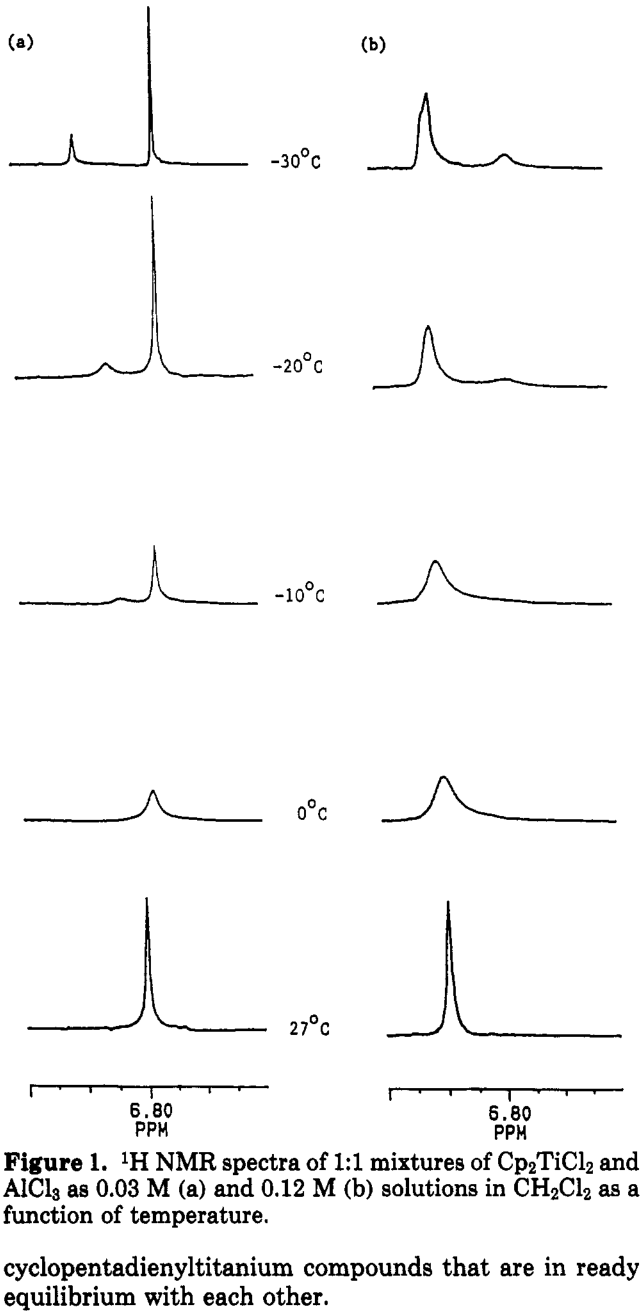


Figure 1. ^1H NMR spectra of 1:1 mixtures of Cp_2TiCl_2 and $AlCl_3$ as 0.03 M (a) and 0.12 M (b) solutions in CH_2Cl_2 as a function of temperature.

cyclopentadienyltitanium compounds that are in ready equilibrium with each other.

The variable-temperature ^{27}Al NMR spectrum of the Cp_2TiCl_2–$AlCl_3$ system at 0.1 M in CH_2Cl_2 displayed a broad, dominant peak at 104.5 ppm at 25 °C ($w_{1/2}$ = 356 Hz) with a minor shoulder peak at 99 ppm. Cooling the sample successively to −20, −40, and then −70 °C caused this peak to broaden and then to narrow selectively on its high-field side ($w_{1/2}$ = 563, 666, and 300 Hz, respectively). At the same time, a new, unresolved peak of comparable area began to emerge in the 98–100 ppm region ($w_{1/2}$ = 356 Hz). Limited solubility of the components and high viscosity at −70 °C prevented better peak resolution. Nevertheless, these ^{27}Al NMR results support the presence of at least two different aluminum-containing components, each of which is tetracoordinate.

The effect of solvent polarity on the ratio of the two cyclopentadienyltitanium components present in the Cp_2TiCl_2–$AlCl_3$ system was proved by recording the ^1H spectrum in CH_2Cl_2 containing 0, 20, or 33% of CCl_4 (v/v). As is evident from Figure 3, the singlet observed at 25 °C (column a) shifts from 6.75 to 6.82 ppm as the solvent contains more CCl_4 and thereby becomes less polar. In keeping with this, the ratio of the two peaks observed at

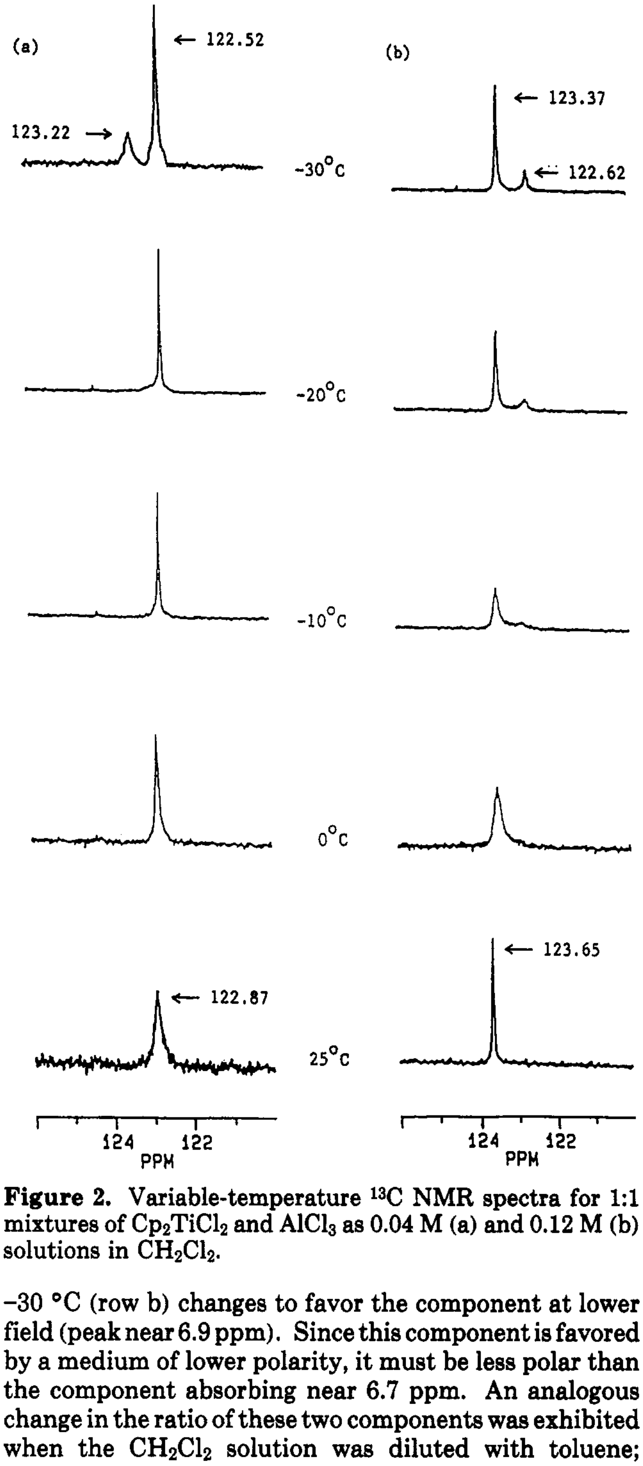


Figure 2. Variable-temperature ^{13}C NMR spectra for 1:1 mixtures of Cp_2TiCl_2 and $AlCl_3$ as 0.04 M (a) and 0.12 M (b) solutions in CH_2Cl_2.

−30 °C (row b) changes to favor the component at lower field (peak near 6.9 ppm). Since this component is favored by a medium of lower polarity, it must be less polar than the component absorbing near 6.7 ppm. An analogous change in the ratio of these two components was exhibited when the CH_2Cl_2 solution was diluted with toluene; integration of the two peaks at −30 °C permits the determination of equilibrium constants (Figure 4).

Similar observations were made with 1:1 mixtures of titanocene dibromide (**14**) and aluminum bromide (**15**) in 0.05 M solution in CH_2Br_2: at 25 °C a singlet appeared at 6.97 ppm, and at −30 °C this former signal split into two singlets at 7.01 and 6.85 ppm having an intensity ratio of 2.2:1.1.[28b]

Catalyst Productivity Numbers for the Homogeneous Catalysis of Ethylene Polymerization. Measuring and interpreting the kinetics of ethylene polymerization, even under initially homogeneous conditions, are difficult to perform in a reproducible and reliable manner.[29] In order to obtain some convenient, useful measure of the catalyst activity of the $Cp_2TiMeCl$–Me_nAlCl_{3-n} system, therefore, batch polymerizations were conducted under standardized experimental conditions

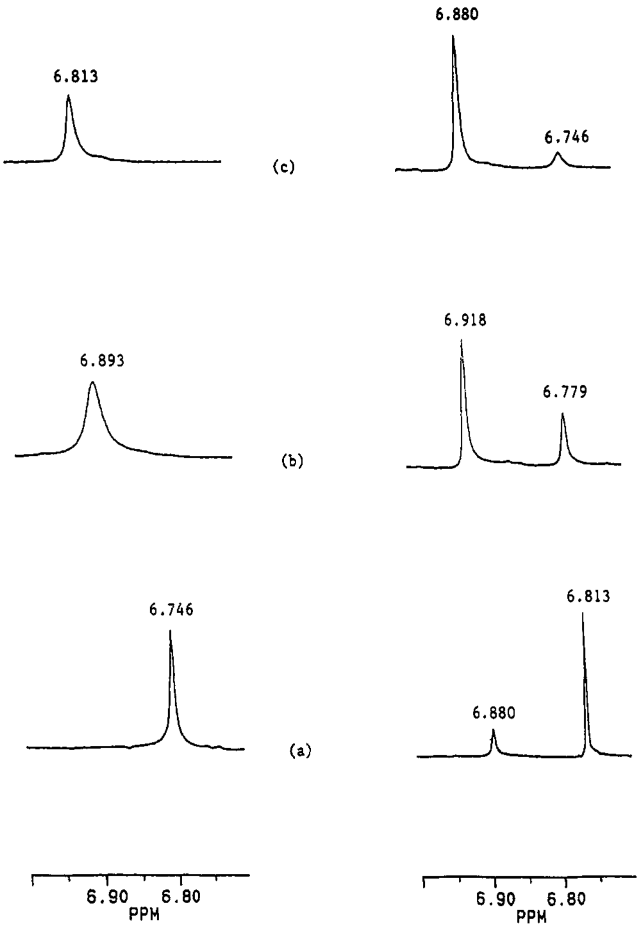


Figure 3. ^1H NMR spectra of 1:1 mixtures of Cp_2TiCl_2 and $AlCl_3$ as 0.03 M solutions in (a) CH_2Cl_2 (a), a 4:1 mixture of CH_2Cl_2 and CCl_4 (b), and a 2:1 mixture of CH_2Cl_2 and CCl_4 (c) at 25 °C (left column) and −30 °C (right column).

with individual variations in solvent, temperature, concentration, ratio of the Ti:Al components, and the nature of the Lewis acid aluminum cocatalyst. In order to produce an easily measurable amount of polyethylene, the polymerization runs were conducted for a standard 25-min period, during which time the initially homogeneous catalyst system turned heterogeneous. Such heterogeneity was shown not to be a controlling factor in altering the ranking of productivity numbers as the solvent polarity or catalyst concentration was changed by the following experiments (*cf.* Experimental Section). Polymerization runs of short duration (100 s), during which time the catalyst system remained homogeneous (little or no precipitation), gave essentially the same results: increasing the polarity of the solvent and decreasing the catalyst concentration increased the PN values.

On the basis of six runs under identical conditions, average productivity numbers were determined as grams of polyethylene per gram of methyltitanocene chloride (**16**) per atmosphere of ethylene per hour, which values were reproducible to within ±5% (Table I). The catalyst system in solution before polymerization was generally golden colored, consistent with the persistence of titanocene(IV). Only with Me_3Al as a cocatalyst (run 6) did a deep blue color develop after 5 min of admixing; this indicated alkylative reduction to titanocene(III).

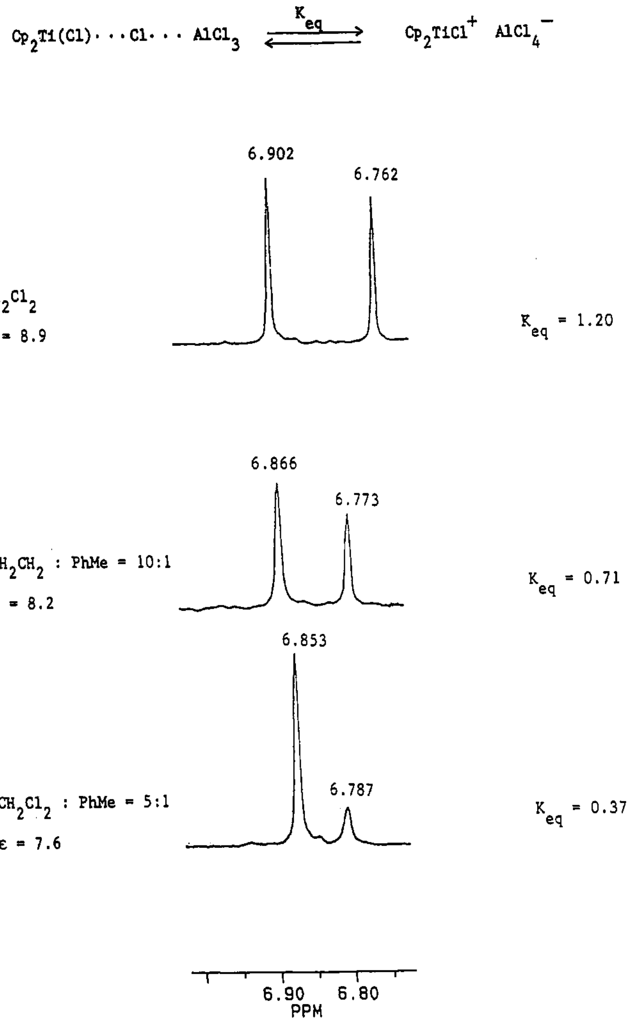
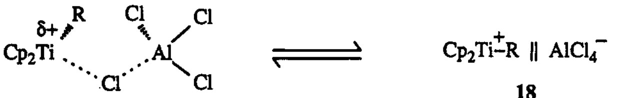


Figure 4. Equilibrium constants for the exchange reactions of contact ion pairs with solvent-separated ion pairs as a function of medium polarity (0.05 M).

Discussion

Interaction of Titanocene Chlorides and Aluminum Chlorides. From the foregoing variable-temperature, multinuclear NMR data, it is evident that the interaction of $AlCl_3$ (**5**) with $Cp_2Ti(Me)Cl$ (**16**),[19] with $Cp_2Ti(CH_2SiMe_3)Cl$ (**9**),[18] and even with Cp_2TiCl_2 (**1**) leads to the generation of some positive charge at titanium and the formation of the partly or wholly free $AlCl_4^-$ ion. Whether these effects find their explanation in either a contact-ion-pair structure (**17**) or a solvent-separated ion pair (**18**) (or both) remains to be decided (eq 8).



18

17a : R = Me
17b : R = CH_2SiMe_3
17c : R = Cl

(8)

As to the positive charge on titanium, several data support such a view: (1) the CH_3 group in **17a** and the CH_2 group in **17b** are shifted downfield in the ^1H spectrum by 1–2 ppm over their positions in **9** and **16**, analogous to the downfield shifts seen in protons adjacent to carbenium

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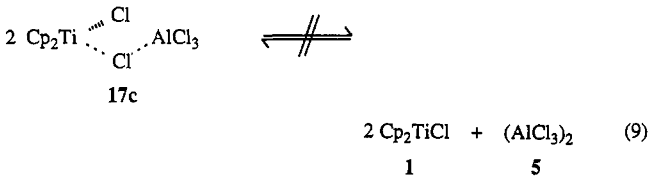
(29) Fischer, D. Untersuchungen zur Propenpolymerisation an Homogenen Zirconocen/Methylaluminoxan Ziegler-Natta Katalysatoren. Doctoral Dissertation, Albert-Ludwig University, Freiburg (Breisgau), Germany, 1992.

ion centers;[30] (2) the Cp protons in **17** also occur 0.2–0.3 ppm downfield from their positions in **1**, **9** and **16**; (3) in the known crystal structure of $Cp_2Ti(Cl)\cdots AlMeCl_2$ (**19**), the bridging chloro ligand has a Ti–Cl separation of 0.23 Å, greater than that of the unbridged Ti–Cl bond.[16] Either the presence of **17** or **18** in solution or a rapid equilibration between them at 25 °C would account for these observations.

That at least a significant proportion of such a 1:1 complex with $AlCl_3$ exists, below −20 °C, as **18** is indicated by the presence of a relatively sharp, dominant ^{27}Al peak at 103 ppm. This peak corresponds exactly to the value reported for the free $AlCl_4^-$ ion.[26] Upon warming, this signal broadens toward the low-field side and yields a maximum at 25 °C between 104 and 105 ppm. From the ^{27}Al spectra of similar complexes, this broadening is consistent with the equilibration depicted in eq 8. For example, **8**, whose crystal structure shows the presence of individual $Ph(Me)C{=}C(SiMe_3)Ti^+Cp_2$ and $AlCl_4^-$ ions, displays its ^{27}Al peak as a sharp singlet at 103.6 ppm (CH_2Cl_2). The bridged chloro species **3** has its sharp peak at 118.1 ppm.

Since the equilibrium of eq 8 was most likely operative in interconverting **17a**, **17b**, and **17c** into their solvent-separated counterparts **18**, we chose to study this equilibrium for the case where R = Cl (**17c** $\rightleftharpoons$ **18c**). In this situation, no competing reaction could occur whereby any alkyl group on titanium (**17a** and **17b**) could be transferred to aluminum (*cf.* eq 7). Cooling **17c** in either CH_2Cl_2 or toluene to below −20 °C gave two well-resolved signals for the Cp-ring protons or carbons (Figures 1 and 2). Neither signal occurred where the signals of any uncomplexed Cp_2TiCl_2 would have occurred if the low-temperature NMR spectra arose from the "freezing out" of the extensive dissociation of **17c** into its components (eq 9).


17c

$2\ Cp_2TiCl + (AlCl_3)_2$ (9)

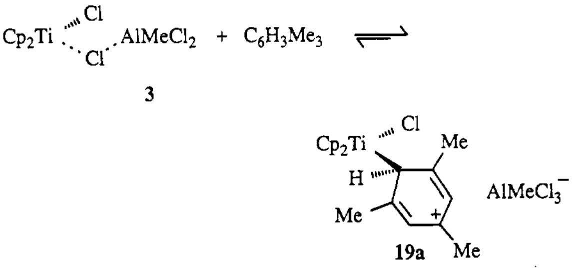
1 5

Further arguments against any significant dissociation of **17c** into **1** and **5** are the following: (1) admixing 1 equiv of both **1** and **5** in $CHCl_3$ gives essentially quantitative yields of **17c**; (2) treating 1 equiv of **1** with 2, 4, or 8 equiv of **5** leads to no significant change in the ratio of Cp signals observed in the ^1H spectrum at −30 °C. Were the equilibrium as in eq 9 involved, the ratio of Cp signals would change by the law of mass action.

The only reasonable interpretation, then, of the low-temperature NMR results is that the equilibration between **17c** (contact IP) and **18c** (solvent-separated IP) (eq 8) has been "frozen out". That such systems contain ions is evident from the pioneering work of Dyachkovskii and co-workers on electrical conductivity, electrodialysis, and polymerization of ethylene observed in halocarbons.[11,12] It remained to be learned whether such spectra at −30 °C responded to changes in concentration and in solvent polarity, as would be expected of CIP–SSIP equilibria. In accordance with Ostwald's dilution law, the two-particle, solvent-separated ion pairs (SSIP) should be favored at lower concentrations over one-particle, contact ion pairs (CIP), and that is what is observed (Figures 1 and 2). Furthermore, SSIP should be preferred over CIP as the medium becomes more polar, and again this is observed (Figures 3 and 4). From these observations, the high-field signal in the ^1H and ^{13}C NMR spectra at −30 °C can be assigned to the solvent-separated and the low-field signal to the contact ion pair.

The high-field SSIP signal can be rationalized in another way. From X-ray crystallographic measurements it is known that titanocenium cations, such as $Cp_2Ti^+(SiMe_3)C{=}C(Ph)Me$ and $Cp_2Ti^+(Cl)N{\equiv}CMe$, have a smaller Cp-ring–Ti separation (2.01–2.03 Å) than various neutral titanocene derivatives (2.06–2.08 Å).[31] The closer proximity of rings in the cationic derivatives should cause the induced magnetic fields, arising from ring currents, to shield the Cp protons more effectively.[32]

In the case of aromatic solvents there appears to be a third type of interaction involving **17c** and an aluminum chloride: when 1:1 combinations of **1** and $MeAlCl_2$ (**2**) were admixed in mesitylene, a 1:1:1 complex of **1** and **2** with mesitylene precipitated (**19**), which dissociated into its components in dilute $CDCl_3$ solution. Although the structure of **19** is as yet unknown, from the known structure of **3**, we suggest that **19** may involve σ-complexation (eq 10). We suggest an η^1-coordination of the arene in **19a**,


3

19a (10)

because the steric demands of η^2-coordination seem excessive for the restricted access to the Ti center and because such a complex was not formed with **3** and hexamethylbenzene. Were σ-complexation involved in **19a** and steric factors not decisive, this fully methylated arene should have been far superior in complexation.[33] From this observation, we conclude that sufficiently strong donor solvents can therefore also form solvated cation–anion pairs (SCAP).

Active Sites in Ethylene Polymerization in Homogeneous Media. With the ability of detecting and varying the types and proportions of ion pairs present in such catalyst systems, the question now can be asked: Which type of ion pair is the most active site for the polymerization of ethylene? In order to answer this question, we have measured the polymerization activity (productivity number PN in Table I) of the system $Cp_2TiMeCl$ and $MeAlCl_2$, while varying experimental conditions that would change the proportions of the three ion pairs **21** (CIP), **22** (SSIP), and **23** (SCAP). If a given experimental variation both increased the proportion of a given ion pair and increased the polymerization activity (PN), such an observation was taken as evidence that that type of ion pair is the most active polymerization site. When polymerization runs of short duration were also conducted under essentially homogeneous conditions (100 s), it was demonstrated that

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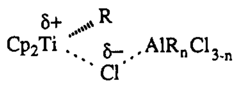
[30] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience: New York, 1972; p 267 and references cited therein.

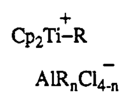
[31] Brownstein, S. K.; Gabe, E. J.; Han, N. F.; Lee, F. L.; LePage, Y.; Piotrowski, A. M.; Eisch, J. J. *J. Chem. Res., Synop.* **1992**, 214.

[32] Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; pp 180–183.

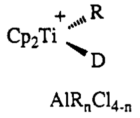
[33] Brown, H. C.; Brady, J. D. *J. Am. Chem. Soc.* **1952**, *74*, 3570.



21 (CIP)



22 (SSIP)



23 (SCAP)

the homogeneity or heterogeneity of the polymerization run did not change the ranking of the PN values obtained with different solvents and different catalyst concentrations.

Interpretation of the data in Table I permits the following conclusions: (1) a more polar, nondonor solvent (CH_2Cl_2 vs toluene) increases the PN (49 → 140, runs 3 and 9); (2) a more π-donor aromatic (mesitylene vs toluene) decreases the PN (49 → 11, runs 9 and 11); (3) lowering the concentration, both in CH_2Cl_2 and in toluene (1.0 → 0.26 mmol L^{-1}), markedly increases the PN (CH_2Cl_2, 140 → 440, runs 3 and 4; toluene, 49 → 197, runs 9 and 10); (4) increasing the temperature from −10 to +70 °C shows a threshold for polymerization (0 °C) and thereafter only a relatively modest increase in PN with increasing temperature (runs 12–16); (5) increasing the $MeAlCl_2$:$Cp_2TiMeCl$ ratio leads first to a significant increase (runs 1 and 2) and then a sharp decrease in PN (runs 3 and 5); (6) increasing the Lewis acidity of Me_nAlCl_{3-n} by employing successively Me_2AlCl, $MeAlCl_2$, and $AlCl_3$ has only a slight retarding effect on PN (140 → 137 → 112, runs 3, 7, and 8).

The observed changes in PN with variation in the experimental conditions for polymerization (*more* polar solvent, *lower* concentration, relative insensitivity to temperature increase above a threshold temperature, and relative insensitivity to the Lewis acid strength of Me_nAlCl_{3-n}) can best be reconciled with the conclusion that the solvent-separated ion pair $Cp_2Ti^+Me\|AlMe_nCl_{4-n}$ is the most active polymerization initiator in polar, nondonor solvents such as CH_2Cl_2.[34] If the contact ion pair $Cp_2(Me)Ti\cdots Cl\cdots Me_nCl_{3-n}$ were the active site, then the PN should have shown an increase at *higher* concentrations and in *less* polar solvents.

The relative insensitivity of PN to the Me_nAlCl_{3-n} species used as the Lewis acid with $Cp_2TiMeCl$ is consistent with the interpretation that even the weakest acid, Me_2AlCl, used in a 1:1 ratio (run 1), is sufficient to produce the SSIP (eq 11) in significant proportions. Used in a 1:2 ratio (run 2), $MeAlCl_2$ could shift the equilibrium of eq 11 to the right by the law of mass action. On the other hand, the deleterious effect on PN of a large ratio of Lewis acid to $Cp_2TiMeCl$ (1:1 → 16:1, PN of 140 → 94, runs 1 and 5) can be attributed to a transmethylation that destroys the crucial Ti–Me bond of $Cp_2TiMeCl$ (eq 12). In a similar vein, the negative effect of Me_3Al (run 6) is readily ascribed to the destruction of $Cp_2TiMeCl$ by reduction to Ti(III).

$$Cp_2TiMeCl + Me_2AlCl \rightleftharpoons Cp_2Ti^+Me\ AlMe_2Cl_2^- \qquad (11)$$

$$Cp_2TiMeCl + MeAlCl_2 \rightleftharpoons Cp_2TiCl_2 + Me_2AlCl \qquad (12)$$

From the lower PN displayed by $Cp_2TiMeCl$–$MeAlCl_2$ as one passes from CH_2Cl_2 (140, run 3) to toluene (49, run 9) to mesitylene (11, run 11), it is clear that the solvated cation–anion pair **24** is the dominant ion pair present as an η^1-complex in aromatics (eq 13) and that such a SCAP must be the least active polymerization site. The relative reactivity of these ion pairs in polymerization can therefore be ordered as SSIP ≫ CIP > SCAP. In reaching this conclusion, we are cognizant that we have not directly observed the operation of such ion pairs in these polymerization runs but that we deduce their presence as the only reasonable, unifying explanation for the response of such a polymerization catalyst system to changes in solvent, concentration, temperature, and the ratio and type of Lewis acid. Furthermore, we have demonstrated that the relative ranking of PN values is unchanged by the homogeneity or heterogeneity of the polymerization system.

(13)

Therefore, the conclusion that ion-pair equilibria and the proportion of solvent-separated ion pairs are responsible for the observed variations in the PN values is strongly supported by the empirical data obtained both in the 100-s and in the 25-min polymerization runs. Although one might hope for a less empirical, more quantitative correlation, no simple relationship, such as a direct or inverse proportionality, between the proportion of active ion pair and the observed PN values would be expected for such complex, partially heterogeneous systems. For this reason, we judge that short of complete, individual kinetic runs,[29] the present PN values provide reliable, albeit empirical, support for our analysis and interpretation of the role of ion pairs in polymerizations with this catalyst system.[35]

Over and beyond this important conclusion, there remains the further tantalizing question for Ziegler–Natta polymerization: what is the role of such ion pairs in the stereoregulation of α-olefin polymerization? Our current research is attempting to answer this question.

Acknowledgment. This research was supported by Grant CHE-8714911 from the National Science Foundation and by an unrestricted grant-in-aid from Witco GmbH, Bergkamen, the Federal Republic of Germany.

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[34] Despite its weakly donor character, CH_2Cl_2 is likely to be loosely coordinated to the cationic titanium center. The NMR spectral behavior of $Cp_2Ti^+MeBPh_4^-$ in CH_2Cl_2 has been interpreted in terms of the solvated cation $Cp_2Ti^+Me\cdot CH_2Cl_2$: Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780.

[35] With the aim of obtaining turnover numbers for ethylene polymerization more precise than the admittedly empirical productivity numbers we have here empoyed, a reviewer has made the helpful suggestion that we make a comparison of ethylene uptake rates at short times. Aside from the technical difficulties of such measurements (discussed at length in ref 29), we fear that such uptake numbers would be equally empirical and would suffer further from the drawback that part of the absorbed ethylene is converted into low-molecular-weight oils, rather than polyethylene. An apparent advantage in measuring PN values by our method is that such oligomeric oils are washed out of the resulting polymer by hexane before the yield of polyethylene is calculated. Thus, our PN method takes account only of that ethylene converted into hexane-insoluble polymer.