this stage. We have found that the reaction occurs also in the dark. In THF solutions, 1 reacts with MeCHO at room temperature, producing **5** and H_2. Variable-temperature $^{31}P\{^1H\}$ NMR studies show the existence of a diamagnetic intermediate species in the range −60 to −40 °C exhibiting an AM_3 spin system (at −60 °C, $\delta(P_{apical})$ 146.5, $\delta(P_{equatorial})$ 55.4, $J(PP) = 29.8$ Hz). At higher temperature, this species rapidly decomposes to the paramagnetic σ-acyl **5**. The NMR pattern is typical for trigonal-bipyramidal Co(I) complexes of the formula $[(PP_3)CoL]$,[2] and therefore, one may reasonably suggest the formation of a kinetic product containing intact MeCHO coordinated via the C=O group in either η^2(C,O) or η^1(O) bonding modes.[9] Unfortunately, the poor stability of the complex has not allowed us to isolate it.

The only reversible reaction is the one with ethylene, affording the yellow orange π-ethylene complex $[(PP_3)Co(C_2H_4)]BPh_4$ (**6**),[10] which converts to the precursor **1** under a stream of N_2 at 90 °C.

In light of the fact that the loss of the N_2 ligand from **1** is induced by neither heat nor vacuum, we propose that this chemistry readily occurs in the solid state because the phosphine arms of PP_3 have sufficient motional freedom in the lattice at 90 °C to permit access to small organic molecules. Such a motion may involve either unfastening of a phosphine arm of PP_3[11] or a simple opening of a P–Co–P angle in the equatorial plane of the trigonal bipyramid. Interestingly, below 90 °C no appreciable reaction occurs between **1** and organic molecules, suggesting the existence of a thermal barrier to the creation of a coordination site at the metal.

The small organic molecules could penetrate the crystals of **1**, dissolving in the extensive hydrophobic region comprised of ten phenyl substituents and six methylenic groups per molecule.[1] As a matter of fact, the substitution of BF_4^-, PF_6^-, or $SO_3CF_3^-$ for BPh_4^- in **1** significantly lowers the yields of the solid–vapor reactions involving CH_2O and C_2H_2, whereas no reaction occurs with MeCHO and C_2H_4. The larger size of the tetraphenylborate counteranion, causing larger channels in the crystal lattice, could play a role in determining the selectivity of the reactions.

Acknowledgment. Thanks are due to the EEC for the contract SC1.0227.C and to "Progetti Finalizzati Chimica Fine II", CNR, Rome, Italy. We are indebted to Dr. J. Gelsomini (University of Florence) for the DSC measurements and to Mr. Dante Masi (ISSECC, CNR) for the X-ray analysis.

Supplementary Material Available: Text describing experimental details, syntheses, and characterization of $[(PP_3)Co(C{=}CH_2)]BPh_4$, $[(PP_3)Co(H)(C{\equiv}CH)]BPh_4$, $[(PP_3)Co(C_2H_4)]BPh_4$, and $[(PP_3)Co(COMe)]BPh_4$ and X-ray crystallographic data for $1{\cdot}0.5THF$, including a labeled PLUTO drawing, experimental details (Table I), selected distances and angles (Table II), and atomic coordinates and thermal parameters (Table III) (8 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(9) Mendez, N. Q.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473.

(10) **6**: $^{31}P\{^1H\}$ NMR (121.42 MHz, acetone-d_6), AM_3 spin system temperature-invariant spectrum from −80 to +30 °C, at −70 °C $\delta(P_A)$ 162.63, $\delta(P_M)$ 70.78, $J(P_AP_M) = 47.21$ Hz; ^1H NMR (299.946 MHz, acetone-d_6, 20 °C) $\delta(C_2H_4)$ 2.99 ppm, br quartet, $J(HP_{terminal}) = 4.9$ Hz. Anal. Calcd for $C_{68}H_{66}BCoP_4$: C, 75.85; H, 6.18; Co, 5.46. Found: C, 75.13; H, 6.20; Co, 5.54.

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Formation of Ion Pairs in the Ziegler Ethylene Polymerization Catalyst System $Cp_2Ti(Cl)CH_2SiMe_3–AlCl_3$[1]

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Summary: Monitoring the interaction of ((trimethylsilyl)methyl)titanocene chloride with aluminum chloride in polar halocarbons by ^1H, ^{13}C, and ^{27}Al NMR spectroscopy has yielded direct spectral evidence for the generation of equilibrating solvent-separated and contact ion pairs, $Cp_2Ti(CH_2SiMe_3)^+$ and $AlCl_4^-$. Such ion pairs are effective catalysts for the polymerization of ethylene, and as required by this action, Me_3Si fragments from the titanocene component are incorporated into the linear, high-density polyethylene formed. X-ray diffraction data on ((trimethylsilyl)methyl)titanocene chloride (space group $P2_1/n$; $R = 0.042$; $R_w = 0.050$; $\rho(max) = 0.43$ e/Å^3) reveal an unusually short Ti–CH_2 bond (2.162 Å) and an anti conformational arrangement of the Me_3SiCH_2 group with the Ti–Cl bond.

In recent studies of soluble Ziegler catalysts[2] for the polymerization of ethylene,[3] we had obtained indirect evidence that such titanium–aluminum cocatalytic combinations generate ionic organotitanium intermediates that are the actual active polymerization sites.[4-6] Subsequently, excellent investigations of other groups, such as those of Jordan, Marks, Bochmann, and Taube, have lent strong corroboration to this viewpoint and have shown its applicability to zirconium-catalyzed polymerizations as

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(1) Organometallic Compounds of Group III. 47. Part 46: Eisch, J. J.; Caldwell, K. R. *New Science in Transition Metal Catalyzed Reactions*; Advances in Chemistry 230; American Chemical Society: Washington, DC, in press.

(2) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979; p 670.

(3) Homogeneous titanium catalysts for the polymerization of ethylene are customarily termed Ziegler catalysts (Long, W. P. *J. Am. Chem. Soc.* **1959**, *81*, 5312), while heterogeneous titanium catalysts for polymerizing ethylene and 1-alkenes are called Ziegler–Natta catalysts.

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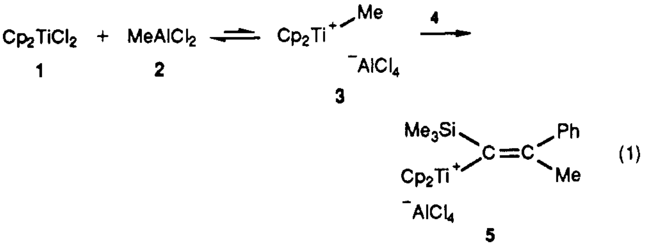
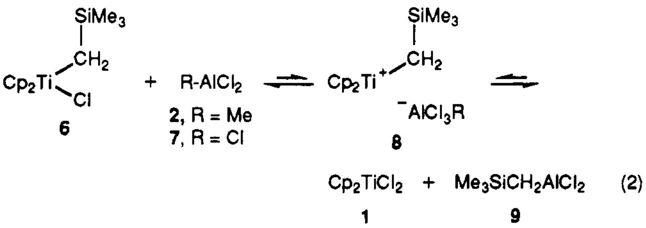
well.[7-10] What remains to be shown is what type of ions or ion pairs would be formed in a polymerization medium and whether fragments of the ion thought to be the active catalyst would be incorporated into the polymer.

Initially, we attempted to clarify the route of cationic polymerization by a study of the titanocene dichloride (**1**)-methylaluminum dichloride (**2**) catalyst system.[11] In this system, the supposed active catalytic intermediate formed, namely methyltitanocenium tetrachloroaluminate (**3**), was trapped as its ionic adduct **5** with trimethyl(phenylethynyl)silane (**4**) and its crystal structure determined (eq 1).[5] Attempts to observe the postulated catalytic ion pair by multinuclear magnetic resonance proved unsuccessful.[15] However, since the trimethylsilyl group in **5** appeared to have a pronounced stabilizing effect on this ion, we reasoned that the Me_3Si group might exert a similar stabilizing influence on the supposed ionic intermediates such as **3**. Were this to be the case, the precise ionic nature of such Ziegler polymerization catalysts could be ascertained by direct observation.



(1)

By employing the known ((trimethylsilyl)methyl)titanocene chloride (**6**)[12] with Lewis acids such as $AlCl_3$ (**7**) and $MeAlCl_2$ (**2**), we are pleased to report that we have obtained direct spectral evidence for the heterolysis of the Ti-Cl bond in **6** and the formation of ion pairs (eq 2).



(2)

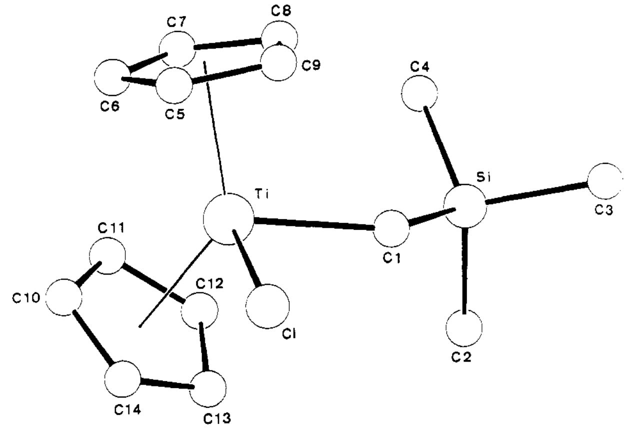
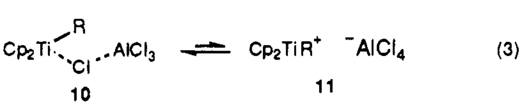


Figure 1. Molecular structure of ((trimethylsilyl)methyl)titanocene chloride (**6**), $Cp_2TiCH_2SiMe_3(Cl)$. Important bond distances (Å) and angles (deg) are as follows: Ti–Cl = 2.379 (1), Ti–C(1) = 2.162 (3), Ti–C(5) = 2.410 (3), Ti–C(6) = 2.372 (4), Ti–C(7) = 2.354 (3), Ti–C(8) = 2.382 (4), Ti–C(9) = 2.398 (3), Ti–C(10) = 2.382 (4), Ti–C(11) = 2.385 (3), Ti–C(12) = 2.369 (3), Ti–C(13) = 2.380 (4), Ti–C(14) = 2.402 (4), Ti–D(1) (ring centroid) = 2.072, Ti–D(2) = 2.082, Si–C(1) = 1.866 (3), Si–C(2) = 1.875 (3), Si–C(3) = 1.875 (4), Si–C(4) = 1.868 (4), C(5)–C(6) = 1.385 (5), C(5)–C(9) = 1.392 (5), C(6)–C(7) = 1.380 (6), C(7)–C(8) = 1.387 (5), C(8)–C(9) = 1.379 (5), C(10)–C(11) = 1.335 (5), C(10)–C(14) = 1.351 (6), C(11)–C(12) = 1.375 (6), C(12)–C(13) = 1.406 (7), C(13)–C(14) = 1.359 (9); D(1)(ring centroid)–Ti–D(2) = 131.4, D(2)–Ti–Cl = 107.4, C(1)–Ti–Cl = 92.0 (1), C(4)–Si–C(3) = 108.0 (2), C(4)–Si–C(2) = 108.7 (2), C(4)–Si–C(1) = 114.7 (2), C(3)–Si–C(2) = 106.3 (2), C(3)–Si–C(1) = 107.3 (1), C(2)–Si–C(1) = 111.4 (1), Si–C(1)–Ti = 136.9 (1), C(9)–C(5)–C(6) = 107.8 (3), C(7)–C(6)–C(5) = 108.3 (3), C(8)–C(7)–C(6) = 107.8 (3), C(9)–C(8)–C(7) = 108.4 (3), C(8)–C(9)–C(5) = 107.7 (3), C(14)–C(10)–C(11) = 109.1 (4), C(12)–C(11)–C(10) = 108.8 (4), C(13)–C(12)–C(11) = 106.4 (4), C(14)–C(13)–C(12) = 106.9 (4), C(13)–C(14)–C(10) = 108.8 (4).

Thus, when **6** and **7** are admixed in $CDCl_3$ at 25 °C, the ^1H NMR signals of **6** at 2.26 (CH_2) and 6.32 (Cp) ppm are shifted to 3.04 and 6.51 ppm, respectively. The ^{13}C NMR signals of **6** at 115.6 (Cp), 79.8 (CH_2), and 2.8 (CH_3) ppm are changed, upon addition of **7**, to signals at 117.2 and 2.8 ppm while the signal at 79.8 ppm disappears.[13] Most informative and decisive is the ^{27}Al NMR spectrum of **6** and **7**. In 1,2-dichloroethane at −23 °C, the most prominent peak observed immediately after admixing is at 103.3 ppm, which corresponds to the reported value for the $AlCl_4^-$ ion.[14] Equally revealing were temperature-dependence ^{27}Al NMR studies performed on both mixtures of **6** and **7** and mixtures of titanocene dichloride (**1**) and **7** in CH_2Cl_2 between +20 and −60 °C. At +20 °C the ^{27}Al signal for these systems occurs at 103.7 ppm as a broad singlet ($w_{1/2}$ = 310.6 Hz); at −60 °C the signal is at 103.0 ppm, significantly sharpened ($w_{1/2}$ = 49.9 Hz). The signal's temperature dependence can be readily explained and simulated through the equilibration of the solvent-separated $AlCl_4^-$ ion (**11**) at 103.3 ppm with a second tetracoordinated aluminate anion absorbing at 104 ppm, namely the contact ion pair $Cp_2TiR^{+}\cdots ClAlCl_3^-$ (**10**) (eq 3).



$$Cp_2Ti(R)\cdots Cl\cdots AlCl_3 \rightleftharpoons Cp_2TiR^{+}\ {}^{-}AlCl_4 \qquad (3)$$

Equilibrium constants for eq 3 range from 0.11 at +20 °C to 2.31 at −60 °c for the system of **1** and **7**. This shows that **11** is favored at lower temperatures. Similar studies demonstrate that, as expected, polar solvents and high dilution also shift the equilibrium to the right.[15]

From these data we conclude that solvent-separated ion pair **8** is formed from **6** and **7**. Upon long reaction times, **8** ultimately is converted (>90%) into titanocene dichloride

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(7) Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268.

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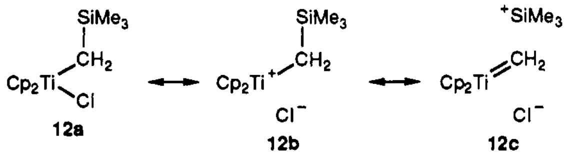
(13) A careful but unsuccessful search for the ^{13}C methylene signal in this system (25 000 scans) forces us to conclude that the transformation of **6a** into **9** (eq 2) has largely occurred over the time period (12 h) required for accumulating the ^{13}C spectral data.

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

(15) Details concerning such temperature-dependent ^{27}Al, ^1H, and ^{13}C NMR spectra and their quantitative spectra simulation will be published shortly: Eisch, J. J., Pombrik, S. I., Tsiao, C. Unpublished studies. That the temperature-dependent line widths of this ^{27}Al NMR signal is due largely to this exchange process, rather than merely to variable quadrupolar relaxation broadening, is substantiated by the ^1H and ^{13}C spectra of these same systems. Both spectra show temperature-dependent signals similar to those of the ^{27}Al spectra, and at −60 °C both spectra resolve into two separate peaks, whose area ratios yield K_{eq} values comparable to those obtained from the ^{27}Al NMR spectrum simulation according to eq 3.

(1) and ((trimethylsilyl)methyl)aluminum dichloride (**9**; ^{1}H NMR 6.64, -0.07, -0.61 ppm; ^{13}C NMR 120.7, 0.1 ppm).[16]

In order to learn whether the Me_3Si group in **6** might be exerting a σ-hyperconjugative stabilizing influence on the positively polarized titanium center in **6** itself, the X-ray crystal structure of **6** was determined. Two interesting features emerge from this analysis (Figure 1): (1) the trimethylsilyl group adopts a conformation exclusively anti to the Ti–Cl bond[17] and (2) the Ti–CH_2 bond distance at 2.166 (3) Å is significantly shorter than comparable bonds between titanium and sp^3-hybridized carbon, such as the Ti–CH_2 bond at 2.22 Å in $(Cp_2Ti{-}CH_2CH_3)_2O$.[18] Both the conformational preference and the shortening of the Ti–CH_2 bond in **6** are suggestive of the operation of σ-bond hyperconjugation depicted in resonance structures **12a–c**.



12a **12b** **12c**

The importance of polar contributors **12b** and **12c** is further reflected in the effect of polar or donor solvents on the methylene signal in the ^{1}H NMR spectrum of **6**. (1) Polar solvents shift the CH_2 signal downfield: 2.02 (CCl_4) → 2.16 (CH_2Cl_2) → 2.25 ppm ($CDCl_3$).[19] (2) Coordinating solvents (:D) shift the CH_2 signal upfield: 2.02 (CCl_4) → 1.96 (CD_3SOCD_3) → 1.83 ppm ($OP(NMe_2)_3$).[20]

Finally, combining **6** with **7** or with **2** in 1,2-dichloroethane yields a homogeneous catalyst effective for the polymerization of ethylene at 0 °C. The resulting polyethylene melts up to 139 °C and displays infrared absorption bands characteristic of those of high-density linear polyethylene.[21] Furthermore, a mass spectrum of the HDPE thus obtained displayed fragments containing trimethylsilyl end groups and between 22 and 25 ethylene units.[22] This demonstrates that ion pair **8** is the active site in these polymerizations and that of necessity the Me_3Si group therefore becomes incorporated into the final polymer.

Acknowledgment. We gratefully acknowledge the support of this research both by Grant CHE-8714911 from the National Science Foundation and by NSF Travel Grant INT 8813722, which permitted J.J.E. to perform research at the Max-Planck-Institut für Kohlenforschung. J.J.E. also wishes to thank the director of this institute, Professor Dr. Günther Wilke, for fostering this international research effort. Finally, Dr. Sofya I. Pombrik, visiting scientist at SUNY-Binghamton from the Institute of Organo-Element Compounds, Academy of Sciences, Moscow, USSR, has aided us greatly by obtaining multinuclear NMR spectral data on ion pairs in this system.

Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **6** (5 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(16) The ultimate formation of **1** and **9** from **6** and **7** accords well with the general observation that the following equilibrium lies much to the left:[5]

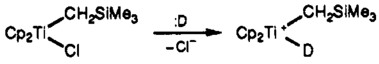
$$Cp_2TiCl_2 + RAlCl_2 \rightleftharpoons Cp_2TiRCl + AlCl_3$$

(17) Force field calculations (SYBYL 5.3, Tripos Associates, Inc., St. Louis, MO; force field, Tripos (Ver. 5.2) with extensions) on the related system $Cp_2Zr(CH_2SiMe_3)Cl$ lead to the suggestion that the syn conformer should be actually more stable than the anti conformer by 1.5 kcal/mol. Of course, such a calculation does not take into account any effect of electron delocalization such as σ-bond hyperconjugation (Angermund, K.; Krüger, C.; Nolte, M. Unpublished studies, MPI für Kohlenforschung, Mülheim an der Ruhr, FRG).

(18) Alt, H. G.; Schwind, K. H.; Rausch, M. D.; Thewalt, U. *J. Organomet. Chem.* 1988, *349*, C7. The Ti–CH_2 bond length in **6** rather resembles those between titanium and sp^2-hybridized carbon, as in **5** (2.13 Å) or in dicyclopentadienyltitanacyclopentadiene derivatives (2.15 Å).

(19) The solvent shifts with the halomethanes do not correlate strictly with dipole moment. Part of their effect may stem from hydrogen-bonding solvation: $Cp_2Ti(CH_2SiMe_3)Cl\cdots HCH_nCl_{3-n}$.

(20) The solvent shifts with such polar coordinating solvents (:D) could be reconciled with pentacoordination of titanium: on the flank side bearing the Ti–Cl bond (cf. crystal structure in Figure 1). However, given the stabilizing effect of the Me_3Si group on the titanocenium cation, displacement of the chloride ion and formation of the solvated titanocenium cation (**13**) is more likely:



6 **13**

(21) Infrared bands for the polyethylene were observed at (cm^{-1}) 2920, 2860, 1477, 1466, 1370, 1248, 728, and 717.

(22) The mass spectrum was measured at 70 eV on a deep-insertion sample.

Thermolysis of a Siladigermirane: Evidence for the Formation of a Germasilene

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Summary: Thermolysis of hexamesitylsiladigermirane in the presence of methanol gives two products: dimesityl(dimesitylmethoxysilyl)germane (**4**) and dimesitylmethoxygermane (**5**).

The synthesis of stable derivatives of both silenes[1] and disilenes[2] was first reported a decade ago. In the intervening years, a wealth of information has been obtained on the physical properties and the chemistry of these and similar species.[3] Not surprisingly, these compounds have proven to be invaluable as starting materials for the

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(1) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* 1981, 191. Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* 1982, *104*, 5667.

(2) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* 1981, *214*, 1343.

(3) For reviews on M=M systems see the following studies. Si=C: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* 1986, *25*, 1. Wiberg, N. *J. Organomet. Chem.* 1984, *273*, 141. Si=Si: West, R. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 1201. Si=M: Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015. Ge=M: Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* 1990, *90*, 283.

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