The Synthesis and Reactivity of Group 4 Zwitterionic Complexes of the Type $M_t{}^+CH_2AlCl_3{}^-$: One-Component Stereoselective Polymerization and Oligomerization Catalysts for Olefins and Acetylenes[‡]

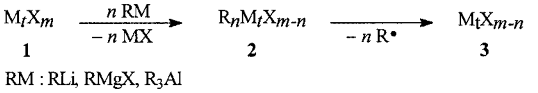
John J. Eisch*[a] and Peter O. Otieno[a]

Keywords: Titanium / Zwitterions / Polymerization catalysts / Stereoselectivity / Oligomerization

A reinvestigation of the interaction of $TiCl_4$ with 2 equiv. of Me_3Al in toluene between –78 °C and 25 °C over 24 h has now established that the ultimate black product obtained is an associated zwitterion of the type $[Ti^+–CH_2–AlCl_3{}^-]_n$, supported by multinuclear NMR spectroscopy and mass spectrometric and gasometric analyses of the gases evolved (CH_4, H_2) upon its protolysis. Chemical reactions of the zwitterion have corroborated specific aspects of its proposed structure: 1) its methylene character, by its transformation of benzophenone into 1,1-diphenylethylene; 2) its divalent titanium content, by the substantial reductive dimerization of benzophenone to tetraphenylethylene, and 3) its Lewis acidic Ti center, by its catalytic isomerization of *trans*-stilbene oxide to 1,1-diphenylacetaldehyde. Similar individual reactions of $ZrCl_4$ or $HfCl_4$ with Me_3Al have led to the analogous zwitterions $[Zr^+–CH_2–AlCl_3{}^-]_n$ and $[Hf^+–CH_2–AlCl_3{}^-]_n$, respectively. These zwitterions of Ti, Zr and Hf have been proven to be capable of the cyclotrimerization and/or polymerization of acetylenes with varying facility, as evidenced by their catalytic action on 1-hexyne, phenylacetylene, di-*n*-butylacetylene, and diphenylacetylene. Furthermore, all three zwitterions were able to polymerize ethylene, without any added cocatalyst, with an activity following the order Zr > Ti > Hf. The Ti and Zr zwitterions effected the stereoselective polymerization of propylene to yield 50% of isotactic polymer, and all three catalysts induced the polymerization of 1-hexene to yield 85% (Zr, Hf) or 100% (Ti) of isotactic polymer. These oligomerizations and stereoselective polymerizations of acetylenes and olefins can be rationalized through a model for the active site resembling a three-membered metallacyclopropa(e)nium ion intermediate formed from the attack of the Group 4 metal zwitterion on the unsaturated hydrocarbon.

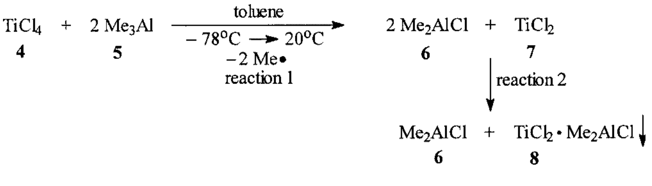
Introduction

In the course of investigating the reactions of transition metal salts **1** with alkyl main group metal compounds (RM) we have uncovered an efficient, general route to subvalent transition metal salts **3**, which proceeds by way of partially alkylated intermediates **2** and a subsequent α-elimination[2] (Scheme 1). This overall process, termed alkylative reduction,[2] has been proven to be successful for the preparation of $TiCl_2$,[2–5] $ZrCl_2$,[2,5] $HfCl_2$ [2,5] CrCl,[6] VCl,[2,7] and their alkoxide derivatives[8,9] in THF solution.



Scheme 1

The method was applied to the alkylation of $TiCl_4$ (**4**) with 2 equiv. of Me_3Al (**5**) to give $TiCl_2$ (**7**) (Scheme 2), and the reaction was conducted in toluene so as to avoid Lewis complexation of either the reactants or the products with any THF present.[3,4,10]



Scheme 2

After initiating the reaction between **4** and **5** at −78 °C (Scheme 2, reaction 1), bringing the mixture to 20 °C and collecting the black precipitate, we found by Ti and Cl analyses that this black solid was not $TiCl_2$ (**7**), but rather the analytical data agreed with a composition corresponding to $TiCl_2·Me_2AlCl$ (**8**). The fact that $TiCl_2$ (**7**) underwent complexation with Me_2AlCl (**6**) (reaction 2) was also re-

---

[‡] Organic Chemistry of Subvalent Transition Metal Complexes, 29. Part 28: Ref.[1]

[a] Department of Chemistry, The State University of New York at Binghamton,
P. O. Box 6000, Binghamton, New York 13902-6000, USA
Fax: (internat.) + 1-607-777-4865
E-mail: jjeisch@binghamton.edu

DOI: 10.1002/ejoc.200400190

flected in the finding that the toluene filtrate contained only half the expected amount of Me_2AlCl (**6**).

Since complex **8** displayed an unusually high activity in the polymerization of olefins, even in the absence of R_nAlCl_{3-n} or MAO as cocatalyst,[11] we have continued the study of its properties. As a result, we are now able to report on two most interesting properties of complex **8**: 1) it is a metastable complex that decomposes on storage with the loss of methane to yield a new black solid **9**, formulated as an associated zwitterion; and 2) complex **9** can catalyze the stereoselective polymerization of α-olefins and the cyclotrimerization of acetylenes. Furthermore, we have extended our studies on titanium prototype **9** to analogous complexes of zirconium and hafnium as well. These key discoveries now permit us to understand the high activity and stereoselectivity of such Group 4 zwitterionic catalysts in terms of their initial electrophilic epimetallation of the olefin or acetylene monomer.[12]

Results and Discussion

Reaction of Titanium(IV) Chloride (4) with Trimethylaluminum (5)

As previously reported, $TiCl_4$ (**4**) reacted with 2 equiv. of Me_3Al (**5**) in toluene for 90 min according to Scheme 2 with complete consumption of **5**, and the formation of black precipitate **8** and a toluene filtrate containing 1 equiv. of Me_2AlCl (**6**).[10a] In addition to Ti and Cl analyses, which are consistent with the composition of $TiCl_2{\cdot}Me_2AlCl$, the NMR spectrum of **8** displayed signals at $\delta = 1.37$ (^1H), 14.2 (^{13}C) and 101.5 (^{27}Al) ppm, which are in agreement with tetracoordinate aluminum in the Me_2AlCl moiety. However, when subsequent samples of the supposed black complex **8** were subjected to protolysis through gasometric analysis, the amount and composition of gas evolved was significantly different than that expected from **8** [Equation (1)]; instead of 2.5 mol-equiv. of a 4:1 mixture of methane and dihydrogen (the latter from $Ti^{2+} \rightarrow Ti^{3+}$) expected from **8**, 1.45 ± 0.05 equiv. of a 2:1 mixture of CH_4 and H_2 evolved from the black solid **9** [Equation (2)].

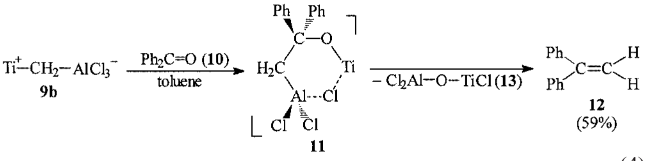
$$\underset{\mathbf{8}}{TiCl_2{\bullet}Me_2AlCl} + 3\,HOAc \longrightarrow TiCl_2(OAc) + AlCl(OAc)_2 + 2\,CH_4\uparrow + 0.5\,H_2\uparrow \qquad (1)$$

$$\underset{\mathbf{9a}}{Cl{-}Ti{-}CH_2{-}AlCl_2} + HOAc \longrightarrow TiCl(OAc)_2 + AlCl_2(OAc) + CH_4\uparrow + 0.5\,H_2\uparrow \qquad (2)$$

Furthermore, the signals in the ^1H and ^{13}C NMR spectra assigned to the Me_2AlCl group had essentially disappeared. New signals at $\delta = 4.12$ (^1H) and 68 (^{13}C) ppm appeared, but the signal in the ^{27}Al NMR spectrum indicative of tetracoordinate Al at $\delta = 101$ ppm was still present. Finally, in a PENDANT experiment, in the ^{13}C NMR spectrum the signal at $\delta = 68$ ppm underwent inversion, thereby establishing that the signal arises from a CH_2 group. These new findings compel us to conclude that complex **8** decomposes over time with the loss of methane to form **9a**, which, because of its ^{27}Al signal and limited solubility even in $CDCl_3$, is likely to exist as an associated zwitterion **9b** ($n \geq 2$) [Equation (3)].

$$\underset{\mathbf{8}}{n\,TiCl_2{\cdot}Me_2AlCl} \xrightarrow[-CH_4]{} \underset{\mathbf{9a}}{n\,Cl{-}Ti{-}CH_2{-}AlCl_2} \rightleftharpoons \underset{\mathbf{9b}}{[\overset{+}{Ti}{-}CH_2{-}AlCl_3^{-}]_n} \qquad (3)$$

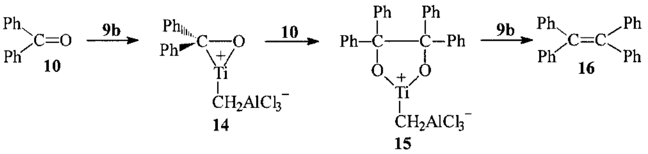
Further support for both the methylene−titanium linkage and the divalent titanium center in **9b** is provided by the reactions with benzophenone (**10**). The major product is 1,1-diphenylethylene (**12**), which can readily be viewed as resulting from the methylenation via **11**, just as the methylenetitanium(IV) compounds or Tebbe reagents achieve such a transformation with a carbonyl substrate [Equation (4)].



(4)

The necessity for an electrophilic Ti atom in **9b** is shown by the *lack* of formation of **12** when the reaction is attempted in ether. Solvation of **9b** by the Lewis base ether would obviously inhibit electrophilic attack of **9b** on the ketone. Further, a 1:1 mixture of **9b** and **10** produces only slightly more than a 50% yield, and this may be due to the Lewis basicity of by-product **13**, which would complex with **9b** thereby destroying its electrophilicity.

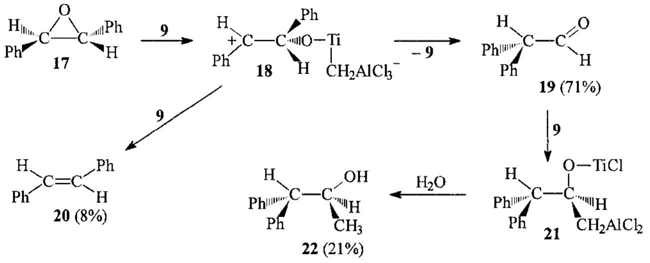
In a significant side reaction (19%), reagent **9b** causes the concurrent bimolecular reduction of some of the benzophenone (**10**) to form tetraphenylethylene (**16**), a reaction that is most characteristic of, and hence diagnostic for, divalent titanium.[2] The enormous potential for organic synthesis of this McMurry−Mukaiyama−Tyrlik process has been explored by a host of research groups.[13] It now seems likely that the C−C bond formation proceeds by way of epititanation to give **14**, with the insertion of **10** into such a strained C−Ti bond to yield **15** and ultimately **16**[2] [Equation (5)].



(5)

Finally, the strong Lewis acidity of **9b** was further demonstrated by its ability to isomerize *trans*-stilbene oxide (**17**) to 2,2-diphenylacetaldehyde (**19**) via zwitterion **18**. The same transformation of **17** into **19** is known to occur through BF_3/diethyl ether catalysis.[14] By conducting the reaction of a 1:1 mixture of **9** and **17** between −78 °C and

25 °C, deoxygenation of **17** by **9b** to form *trans*-stilbene (**20**) and the addition of **9b** to **19** to form **21** could be minimized (Scheme 3). The products of deoxygenation (**20**) and methylenation (**22**) could be further reduced by working with 10% of **9** as a catalyst. Under these conditions 94% of aldehyde **19**, 6% of olefin **20**, and none of methylenation product **22** resulted.



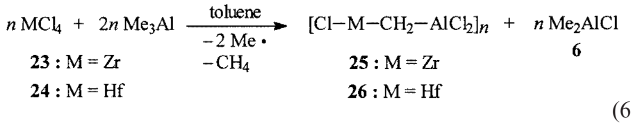
Scheme 3

The unequivocal determination of the solid-state molecular structure of an unknown organic compound generally emerges from a properly measured and analyzed data set from a single-crystal XRD procedure. But as has been astutely noted by the late Professor Leopold Ruzicka, “A crystal is a chemical graveyard”,[15] which implies that compounds isolated and analyzed in crystal form are necessarily only those with relative stability or inertness. If, as in the present case of **8** or **9b**, the solid is thermodynamically unstable or highly reactive as a catalyst, it is not unexpected that the XRD method may well be impractical, and an array of other measurements must be employed. Accordingly, as a precis of the evidence in support of the empirical formula of $AlCCl_3H_2Ti$ for **9a** or **9b**, we offer the following: 1) the yield of black solid **9** isolated was 94% of that expected from such a formula; 2) the yield of the Me_2AlCl by-product was essentially 100% of that expected according to reactions 1 and 2 of Scheme 2, and all starting Me_3Al had been consumed; 3) the type of gas and the amounts evolved in the protolysis of **9**, 1.45 mol-equiv. of a 2:1 molar ratio of CH_4 and H_2, was 97% of that expected from the protolysis according to Equation (2); 4) the ^1H and ^{13}C NMR spectra of **9** show signals for a CH_x group, which then in a ^{13}C PENDANT experiment was shown to undergo signal inversion and thus was unmistakably identified as a CH_2 group; 5) the sole ^{27}Al NMR signal in the spectrum of a solution of **9** was found at $\delta = 101$ ppm, a signal region that is typically associated with tetracoordinate aluminate anions (for example, that of $AlCl_4^-$ at $\delta = 103$ ppm); and 6) reagent **9** displayed its methylenating, titanium(II)-reducing and Lewis-acidic characteristics in discrete reactions with benzophenone [Equations (3) and (4)] and *trans*-stilbene oxide (Scheme 3), respectively.

With the empirical formula groupings of Ti^{II}, CH_2 and $AlCl_3^-$ indirectly but reliably established, we conclude that the only way that these elements can be arranged so as to give unique signals for the CH_2 and $AlCl_3$ groups is as the zwitterionic monomer associated as shown in **9b**. Any attempt to propose mixed associations of subunits of the type $ClTi-CH_2-TiCl$ and $Cl_2Al-CH_2-AlCl_2$ should lead to two or more CH_2 and tetracoordinate Al signals, contrary to that observed experimentally.

Reaction of Zirconium(IV) Chloride (23) or Hafnium(IV) Chloride (24) with Trimethylaluminum (5)

Based on our experience with $TiCl_4$ we were able to conduct the reactions of Me_3Al separately with $ZrCl_4$ (**23**) and with $HfCl_4$ (**24**), so as to obtain $[Cl-Zr-CH_2-AlCl_2]_n$ (**25**) as a purple solid in 94% yield and $[Cl-Hf-CH_2-AlCl_2]_n$ (**26**) as a green-brown solid in 93% yield, respectively [Equation (6)]. The zirconium analog **25** yielded 1.3 equiv. (87%) of a 2:1 mixture of CH_4/H_2, and the hafnium analog gave 1.2 equiv. (80%) of a 2:1 mixture of CH_4/H_2. Although in each case the toluene filtrate again contained about 50% of the expected by-product **6**, NMR spectroscopic data on **25** or **26** could not be recorded because of the insolubility of these complexes in $CDCl_3$ or other inert solvents.

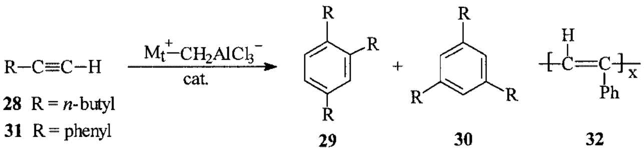


$$\underset{\substack{\mathbf{23}:\ M = Zr\\ \mathbf{24}:\ M = Hf}}{n\,MCl_4} + 2n\,Me_3Al \xrightarrow[-2\,Me\cdot\ -CH_4]{toluene} \underset{\substack{\mathbf{25}:\ M = Zr\\ \mathbf{26}:\ M = Hf}}{[Cl-M-CH_2-AlCl_2]_n} + \underset{\mathbf{6}}{n\,Me_2AlCl} \qquad (6)$$

Although the available physical data for **25** and **26** therefore do not compellingly support the suggested methylene structure or zwitterionic counterpart $M_t^+-CH_2-AlCl_3^-$ (**27**), the chemical reactions of **25** and **26** are exactly parallel to those of the titanium analog **9**. Thus, a 1:1 mixture of benzophenone (**10**) and the zirconium analog **25** yielded 55% of 1,1-diphenylethylene (**12**) and 25% of tetraphenylethylene (**16**). Analogously, albeit more slowly, the hafnium analog **26** gave 27% of **12** and 15% of **16** [cf. Equations (4) and (5)]. Further, in the isomerization of *trans*-stilbene oxide (**17**) to 2,2-diphenylacetaldehyde (**19**), catalytic amounts of **25** or **26** gave about 95% of **19** and 5% of olefin **20** (cf. Scheme 3). Therefore, based upon their similar chemical behavior to **9**, it can be concluded that **25** and **26** have structures analogous to **9a** or **9b**.

Reactions of the Zwitterionic Complexes $M_t^+-CH_2-AlCl_3^-$ (27 or 9, 25, 26, where M_t = Ti, Zr, Hf) with Acetylenes

The alkyl-substituted acetylene 1-hexyne (**28**) readily underwent cyclotrimerization with the use of Ti complex **9** or zirconium complex **25** as catalyst to form the isomeric 1,2,4- and 1,3,5-tributylbenzenes (**29**, **30**, respectively) at 25 °C. Similar ratios (45:55 for the 1,2,4/1,3,5 isomers) were obtained for the two catalysts. When Hf complex **26** was used as the catalyst in the cyclotrimerization of 1-hexyne under similar conditions, the reaction did not reach completion (42%) and the 1,2,4/1,3,5 isomer ratio was modestly reversed, 54:46 [Equation (7), R = *n*-butyl].

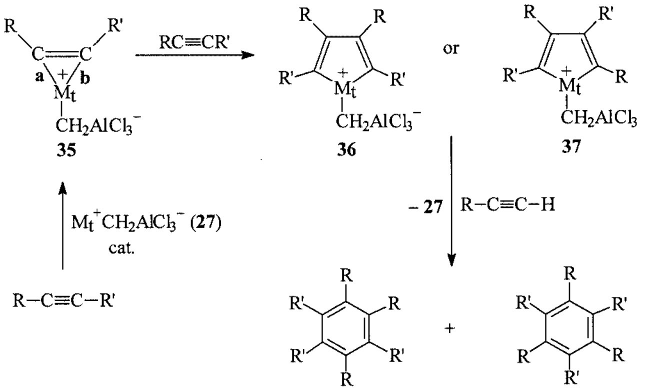


(7)

On the other hand, reaction of the aryl-substituted acetylene phenylacetylene (**31**) with these Group 4 zwitterions was interestingly different. The use of titanium analog **9** exclusively led to a 1,2,4/1,3,5 mixture of triphenylbenzenes through a cyclotrimerization reaction, while zirconium analog **25** gave a mixture of 64% of the isomeric cyclotrimers (45:55) and 36% of a poly(phenylacetylene) **32**, while hafnium analog **26** gave poly(phenylacetylene) (**32**) only.

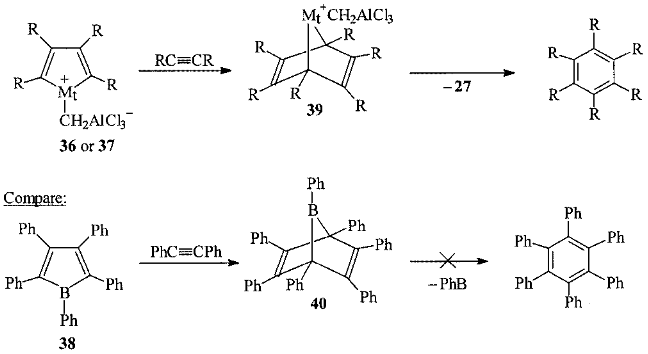
Finally, both diaryl- or dialkyl-substituted acetylenes, such as diphenylacetylene (**33**) or di-*n*-butylacetylene (**34**), underwent smooth cyclotrimerization in 60−90% yield in refluxing toluene with titanium complex **9** or zirconium complex **25** as catalyst.

In these previously studied reactions with acetylenes it has been shown that some divalent Group 4 reagents initiate the reaction by epimetallation of the C≡C bond, for example $TiCl_2$, $ZrCl_2$ or $HfCl_2$.[2] In the present case, such an epimetallation or oxidative addition reaction should be even more rapid because the zwitterions $M_t^+{-}CH_2{-}AlCl_3^-$ (**27**) can easily perform such additions as a charged electrophile (Scheme 4).



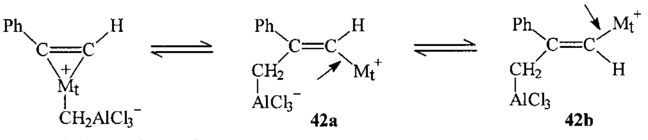
Scheme 4

Once intermediate **35** is formed, it can undergo a further rapid insertion of the RC≡CR′ unit either into bond **a** or bond **b** to form metallacyclic cations **36** and **37** With the empty np_z orbital on the metal center, these $4n$ π-electron systems would be highly destabilized by their Hückel antiaromatic character. Like their neutral boron counterpart **38** these metallacyclopentadienyl cations could alleviate the destabilization effects by undergoing a Diels−Alder reaction with a third RC≡CR′ (Scheme 5); however, thereafter the two systems differ with respect to the relative ease of aromatization of adducts **39** and **40**. For boron adduct **38**, aromatization would require the elimination of the high-energy phenylboron(I), whereas aromatization of **39** simply requires the regeneration of zwitterion $M_t^+{-}CH_2{-}AlCl_3^-$ (**27**) used as the cyclotrimerization catalyst.[16]



Scheme 5

The change from cyclotrimerization to polymerization in the reaction of phenylacetylene with $Zr^+{-}CH_2{-}AlCl_3^-$ or $Hf^+{-}CH_2{-}AlCl_3^-$ may be due to the relative stability of metallacyclopropenyl cation intermediate. With an empty np_z orbital on the metal center, the $4n + 2$ π-systems **41** would be more stable as a result of their Hückel aromatic character ($n = 0$).[17] However, as the $3p_z$ orbital of Ti is replaced by the higher-energy $4p_z$ orbital of Zr or $5p_z$ orbital of Hf, the effective overlap and hence the aromatic stabilization of the three-ring system may diminish, and ring-opening is favored [Equation (8)]. The site for acetylene insertion in the open-chain adducts **42a** or **42b** [arrows in Equation (8)] may then favor linear polymerization.[18]

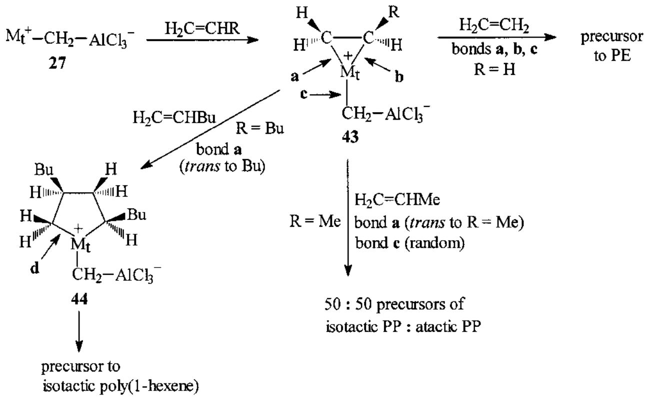


(8)

Reactions of the Zwitterionic Complexes $M_t^+{-}CH_2{-}AlCl_3^-$ (27 or 9, 25, 26, where M_t = Ti, Zr, Hf) with Olefins

Generally, in test polymerizations of olefins by these zwitterionic complexes, all three complexes were found to catalyze the polymerization process with the overall activity following the usual order, namely Zr > Ti > Hf. However, the degrees of stereoselectivity obtained with propylene and 1-hexene are worth noting: when the Ti and Zr zwitterions were used as the catalyst in the polymerization of propylene, 50% (within experimental error) of the polymer was isotactic; however, all three zwitterionic complexes essentially caused the stereoselective isotactic polymerization of 1-hexene (85%). The polymer resulting from the Ti catalyst was essentially 100% isotactic.

Our recent studies on the direct epititanation of olefins or acetylenes with titanium(II) reagents, as well as the transfer epititanation of these unsaturated substrates by dialkyltitanium(IV) compounds, have led to the suggestion that stereoselective polymerization of olefins by divalent Group 4 catalysts is initiated by epimetallation of the C=C bond.[1,12] From the results of the present study, the following mechanistic interpretation of the reactions of the divalent Group 4 zwitterions with olefins (Scheme 6) is proposed. In the first step $M_t^+-CH_2-AlCl_3^-$ (**27**) is involved in the electrophilic epimetallation of the olefin to generate intermediate **43**. For R = H, insertion of $H_2C=CH_2$ and ensuing nonstereoselective polymerization could occur randomly at $C-M_t$ bonds **a**, **b** or **c** of **43**. For R = CH_3, insertion into bond **a** of **43** would occur selectively over bond **b** because of the steric effect of the methyl group in **43** and also from the side *trans* to the methyl group, which would lead to isotactic polypropylene.[1,12] However, propylene could alternatively (with equal probability) insert in a head-to-tail nonstereoselective fashion into bond **c** to form atactic polypropylene. Finally, for R = Bu, it is postulated that steric hindrance probably retards the rate of insertion of the larger 1-hexene unit into bond **c** relative to the insertion of this olefin into bond **a** from the side *trans* to the butyl group. This view agrees with the finding that the shorter $Ti-CH_2$ bond undergoes essentially only isoselective polymerization, presumably at bond **a**, while the relatively longer $Zr-CH_2$ and $Hf-CH_2$ bonds permit 10−15% atactic polymerization, because of the greater accessibility of bond **c** to insertion of 1-hexyne units. Further insertions of 1-hexene units into **44** would also occur at bond **d**, *trans* to the butyl substituents.



Scheme 6

From the foregoing discussion, it should be clear that the high polymerization activity and unusual stereoselectivity of such zwitterionic catalysts can be qualitatively rationalized on a molecular basis by a process of electrophilic metallation, which leads to active sites that resemble a metallacyclopropyl cation **43**. In contrast to the Cossee−Arlman model, which is traditionally invoked to explain stereoselectivity in Ziegler−Natta olefin polymerization in a heterogeneous phase on the catalyst surface,[19a−19d] the present model is supported by chemical studies on actual titanacyclopropane intermediates, and it does not require a heterogeneous phase or solid surface.[1,12] The Cossee−Arlman model, on the other hand, is not supported by any experimental data but is based solely on theoretical calculations.[20]

Conclusions

The prolonged interaction of a Group 4 metal tetrachloride MCl_4 (M = Ti, Zr, Hf) with 2 equiv. of trimethylaluminum in toluene leads, through the reduction of the metal center, to the formation of associated, divalent metal zwitterions of the type $[M_t^+-CH_2-AlCl_3^-]_n$ (**27**) in high yield. Although only sparingly soluble in inert solvents, these zwitterions reflect their specific structural features by the kinds of chemical transformations they are capable of mediating. Their methylene character is revealed by their ready conversion of benzophenone into 1,1-diphenylethylene. Their divalent oxidation state is reflected in their reductive dimerization of benzophenone into tetraphenylethylene. Finally, their Lewis acidity is demonstrated by their ability to catalyze the isomerization of *trans*-stilbene oxide into 2,2-diphenylacetaldehyde and by the inhibition of this isomerization process when the zwitterion is mixed with diethyl ether.

Generally, these zwitterions have proved to be active oligomerization and polymerization catalysts for olefins and acetylenes, and the activity follows the order Zr > Ti > Hf in the polymerization of ethylene. Interesting degrees of selectivity of these processes were exhibited by these Group 4 zwitterions: 1) the cyclotrimerization or polymerization of phenylacetylene, Ti (only trimer formed) > Zr (trimer and polymer formed) > Hf (only polymer formed); 2) the degree of isotacticity in the polymerization of 1-hexene, Ti (100%) > Zr (85%); 3) the degree of isotacticity in the polymerization of propylene, Ti and Zr both 50%.

A comprehensive qualitative rationale of the foregoing oligomerization and polymerization findings can be formulated based upon a model involving electrophilic epimetallation of the unsaturated hydrocarbon by the Group 4 zwitterion. The three-membered metallacyclopropa(e)nium zwitterion intermediate could then couple the olefinic or acetylenic units by stereoselective insertion of the monomer into the C−M bond of the ring or by nonstereoselective insertion into the exocyclic CH_2-M bonds. The degree of isotacticity in the polymerization observed with propylene and with 1-hexene can be accommodated by a low (50%) or by a high (100%) preference for the insertion of propylene or 1-hexene into the C−M bond of the three-membered ring at the less hindered side and *trans* to the alkyl substituent(s) on the ring.

Experimental Section

Instrumentation, Analysis and Starting Reagents: All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal/benzophenone ketyl mixture prior to use.[21a] The IR spectra were recorded with a Perkin−Elmer instrument (model 457) and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^{1}H and ^{13}C) were recorded with a Bruker spectrometer (model EM-360) with tetramethylsilane (Me_4Si) used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me_4Si reference signal. The GC/MS measurements and analyses were performed with a Hewlett−Packard GC 5890/Hewlett−Packard 5970 mass-selective-detector instrument. The gas chromatographic analyses were carried out with a Hewlett−Packard instrument (model 5880) having a 30-m SE-30 capillary column. Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. $TiCl_4$, $ZrCl_4$, $HfCl_4$, and trimethylaluminum and dimethylaluminum chloride were obtained from commercial sources in at least 97% purity, and were stored or transferred for use under pure argon. Appropriate transfer techniques employing siphon, cannula or syringe have been described elsewhere.[21b]

Interaction of Titanium(IV) Chloride (4) with Trimethylaluminum (5): In our previous report on the interaction of 1 equiv. of $TiCl_4$ with 2 equiv. of Me_3Al in toluene at −78 °C with subsequent warming, the black precipitate isolated gave elemental analyses for titanium and chlorine that are consistent with the empirical formula $TiCl_2{\cdot}Me_2AlCl$ (**8**). Further work, including gasometric analyses of protolyzed samples of the black precipitate, revealed that this initial composition changed with time because of the evolution of a gas, which was shown to be about 1 equiv. of methane. This new observation, coupled with PENDANT NMR spectroscopic measurements and protolytic gasometric measurements, has led to the reformulation of the final black reaction product to an oligomeric zwitterion, $[Ti^+{-}CH_2{-}AlCl_3^-]_n$ (**9b**). The experimental details of the preparation and expanded characterization of the resulting black solid **9b** are given in the following section.

A solution of $TiCl_4$ in toluene (10.0 mmol, 10.0 mL of a 1.0 M solution) was mixed with *tert*-butylbenzene (10.0 mmol) to provide a standard peak at δ = 1.30 ppm in the ^{1}H NMR spectrum with which to estimate the amount of Me_2AlCl by-product (^{1}H NMR signal at δ = 1.40 ppm). This solution was cooled to −78 °C, after which a toluene solution of Me_3Al (20.0 mmol, 10.0 mL of a 2.0 M solution) was added dropwise with a gas-tight syringe, which led to the formation of a dark brown precipitate. In order to ensure complete decomposition, the reaction mixture was brought to 25 °C, and the resulting black suspension was stirred for a further 24 h. Filtration and washing with toluene gave a black filter cake and a colorless filtrate. The ^{1}H NMR spectrum of the filtrate revealed that about 1 equiv. of Me_2AlCl was present. The ^{27}Al NMR spectrum of the same concentrated filtrate showed a signal for Me_2AlCl at δ = 175 ppm but none for the starting Me_3Al (δ = 155 ppm). In an attempt to monitor the gas evolved during the reaction of $TiCl_4$ with Me_3Al, the reaction was carried out in a gasometric apparatus on a smaller scale (0.5 mmol of $TiCl_4$ in a total of 10 mL of toluene). After 24 h, about 2 mol (of the expected 3 mol) of methane evolved. Considering the high solubility of methane in toluene, this volume of gas is in approximate agreement with the amount expected for the formation of **9**. The black solid was subjected to reduced pressure for several hours which resulted in 1.95 g of product [94%, with the assumption of an empirical formula of CH_2AlCl_3Ti (**9**)]. A gasometric analysis of the solid (120 mg, 0.61 mmol) with glacial acetic acid (color change from black suspension to dark green solution) gave 20.4 mL at 0 °C and 760 Torr pressure or 1.45 ± 0.05 mol of a 2:1 mixture of methane/dihydrogen. The observed gas composition is in excellent agreement with that expected for the structural unit $Cl{-}Ti{-}CH_2{-}AlCl_2$ (**9**): 1.0 mol of CH_4 and 0.5 mol of H_2 for $Ti^{II} \rightarrow Ti^{III}$. Furthermore, the black solid was sufficiently soluble in $CDCl_3$ to provide NMR spectroscopic data, ^{1}H NMR: δ = 4.12 (br.) ppm. ^{13}C NMR ($CDCl_3$): δ = 68.2 (CH_2) ppm; in a PENDANT experiment, this ^{13}C signal at δ = 68.2 ppm underwent inversion, which confirms the presence of a CH_2 group; ^{27}Al NMR ($CDCl_3$): δ = 101 ppm.

The preceding reaction between $TiCl_4$ (15 mmol) and Me_3Al (30 mmol) in toluene was performed at −78 °C for 90 min, and the mixture was brought to 20 °C. The black precipitate was filtered off and washed with fresh toluene. Analysis of the dried black solid for titanium and for chlorine gave values of 22.5% Ti and 50.5% Cl. The expected values for $C_2H_6AlCl_3Ti$ are 22.7% Ti and 50.4% Cl. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) shows the signals for CH_3 at δ = 1.37 and 14.2 ppm, respectively, as expected for Me_2AlCl. Finally, the ^{27}Al NMR spectrum of **8** showed the signal for tetracoordinate Al at δ = +101.5 ppm.

Interaction of Zirconium(IV) Chloride (23) with Trimethylaluminum (5): In a manner analogous to the preceding reaction involving $TiCl_4$, $ZrCl_4$ (6.7 mmol) was allowed to react with Me_3Al (13.4 mmol). Filtration of the final reaction mixture gave a purple filter cake, 1.51 g [94%, with the assumption of an empirical formula of $CH_2AlZrCl_3$ (**25**)]. The ^{27}Al NMR spectrum of the filtrate showed only a signal for the Me_2AlCl by-product at δ = 178 ppm. Since the purple solid was insoluble in $CDCl_3$ and other inert solvents, no NMR spectroscopic data could be obtained. Gasometric protolysis of this purple sample, conducted in a manner similar to that with the titanium black solid, gave 1.3 mol of a 2:1 mixture of methane and dihydrogen (change from a purple sample to a brown reaction solution). The observed gas composition is consistent with the presence of 87% of the structural unit $Cl{-}Zr{-}CH_2{-}AlCl_2$ (**25**) in the purple solid.

Interaction of Hafnium(IV) Chloride (24) with Trimethylaluminum (5): In a similar reaction between $HfCl_4$ and Me_3Al on a 7.1 mmol scale for $HfCl_4$, a dark greenish brown filter cake resulted, 2.14 g [93% with the assumption of an empirical formula of $CH_2AlHfCl_3$ (**26**)]. Again, the ^{27}Al NMR spectrum of the filtrate shows the signal for Me_2AlCl at δ = 178 ppm only. Due to the insolubility of the greenish brown solid in inert solvents, no NMR spectroscopic data were attainable. Gasometric protolysis caused the greenish brown solid to form a dark brown solution, with the evolution of 1.2 mol of gas (a mixture of methane and dihydrogen). The observed gas composition is consistent with the presence of 80% of the structural unit $Cl{-}Hf{-}CH_2{-}AlCl_2$ (**26**) in the brown solid.

Methylenation of Benzophenone with Reagents of the Type $ClM_tCH_2AlCl_2$ (M_t = Ti, Zr, Hf for 9, 25, 26)

Titanium Reagent 9: Benzophenone (910 mg, 5.0 mmol) and toluene (150 mL) was added to a black suspension of **9** (5.0 mmol), and the mixture was heated at reflux for 8 h. Hydrolytic workup and flash column chromatographic separation of the soluble organic components on silica gel and with a hexane eluent gave 59% of 1,1-diphenylethylene (**12**), 19% of 1,1,2,2-tetraphenylethylene (**16**), and recovered ketone. Also it is worth noting that when this reaction was attempted in refluxing diethyl ether, no reaction was observed.

Zirconium Reagent 25: In a similar reaction, **25** reacted with benzophenone **10** (on the same scale) to yield 1,1-diphenylethylene (**12**) and 1,1,2,2-tetraphenylethylene (**16**) in 55% and 25% yields, respectively. With a 2:1 ratio of **25** and benzophenone, 70% of **12** and 18% of **16** were obtained.

Hafnium Reagent 26: A 1:1 ratio of **26** and benzophenone reacted in a similar manner to give only 27% of **12** and 15% of **16**.

Lewis Acid Isomerization of *trans*-Stilbene Oxide (17) by $ClM_tCH_2AlCl_2$ (M_t = Ti, Zr, Hf) (9, 25, 26)

Titanium Reagent 9: A mixture of **9** (5.0 mmol) and **17** (5.0 mmol) in toluene (160 mL) was prepared at −78 °C. Upon warming to 25 °C overnight, a dark brown solution formed. Usual hydrolytic workup and NMR spectroscopic analysis shows the formation of 71% of 2,2-diphenylacetaldehyde (**19**), 21% of 1,1-diphenyl-2-propanol (**22**), and 8% of *trans*-stilbene (**20**). These components were individually isolated by column chromatography, and their identity verified by NMR spectroscopic comparison with authentic samples. For **22**, an authentic sample was prepared from 2,2-diphenylacetaldehyde and MeMgI. When the above reaction was conducted on a catalytic scale [**9** (0.5 mmol) and epoxide **17** (5.0 mmol)], 94% of **19** and 6% of **20** were formed, and **22** was not detected.

Zirconium Reagent 25: On a scale similar to that with the titanium reagent **9**, a 1:1 mixture of **25** and epoxide **17** gave 62% of **19**, 28% of **20**, and 10% of **22**. When the reaction was conducted on a catalytic scale (1:10 of **25**/**17**), the product consisted of 96% of aldehyde **19** and 4% of **20**.

Hafnium Reagent 26: On a stoichiometric (1:1) or a catalytic scale (1:10) of **26**/epoxide **17**, this reaction produced 92−94% of **19** and 6−8% of **20**. Significantly, in both reactions **22** was not observed.

Cyclotrimerization of 1-Hexyne by $ClM_tCH_2AlCl_2$ (M_t = Ti, Zr, Hf) (9, 25, 26)

Titanium Catalyst 9: A black suspension of **9** (5.0 mmol) in toluene (60 mL) was stirred with phenylacetylene (30 mmol) at 25 °C for 24 h. Usual hydrolytic workup and solvent evaporation gave 98% of the triphenylbenzenes as a 45:55 mixture of 1,2,4/1,3,5 isomers (**29**/**30**), as shown by ^{1}H NMR spectroscopy.

Zirconium Catalyst 25: A similar reaction with **25** (8.0 mmol) and phenylacetylene (24 mmol) was subjected to the usual hydrolysis and flash column chromatographic separation on silica gel with a hexane/THF eluent. The products were a 45:55 mixture of 1,2,4-/1,3,5-triphenylbenzenes (**29**/**30**) (32%) and a dark red solid, poly(phenylacetylene) (**32**) (20%).

Hafnium Catalyst 26: A similar reaction with **26** (11 mmol) and phenylacetylene (33 mmol) yielded 95% of **32**; no cyclotrimers were detected upon ^{1}H NMR spectroscopic analysis. It should be mentioned that this catalyst also caused the cyclotrimerization of diphenylacetylene, but at a much lower rate (about 50% after 10 h in refluxing toluene).

Polymerization of Ethylene by $ClM_tCH_2AlCl_2$ (M_t = Ti, Zr, Hf): **9**, **25** or **26** (2.0 mmol) in cyclohexane (100 mL) was placed in a 250-mL Fisher−Porter polymerization bottle fitted with a screw-on metal cap with a gas-inlet. Ethylene gas [40 psi (2.7 atm)] was then fed into the stirred suspension for 1 h for Ti, only 3 min for Zr, and 30 min for Hf. During this time polyethylene precipitated and, especially for the Zr catalyst, an exothermic reaction was noted. Usual hydrolytic workup and drying of the insoluble polyethylene gave the following polymer amounts and activities (A, calculated as grams PE/gram M_t·h·bar): Ti, 7.1 g and A = 27; Zr, 2.6 g and A = 105; Hf, 7.4 g and A = 15. The retarding effect of toluene was shown by conducting the preceding procedure in that solvent; yield and activity: Ti, 4.4 g and A = 17; Zr, 3.1 g and A = 75. In all cases, the isolated polyethylene melted above 120 °C and below 140 °C, and its IR spectrum was identical to that of an authentic sample.

Polymerization of Propylene by $ClM_tCH_2AlCl_2$ (M_t = Ti, Zr, Hf): In the polymerization apparatus and experimental procedure employed for ethylene, the individual stereoselectivity of the Ti and Zr analogues of $ClM_tCH_2AlCl_2$ was explored. On a 5−8 mmol scale over a period of 60 min and with 40 psi (2.7 atm) of propylene, the following yields of polypropylene were observed: Ti, 1.96 g and Zr, 3.5 g. In each case the hydrolyzed ether slurry of polymer was filtered, and the insoluble polymer was rinsed with several portions of methanol, and the filtrate from the washing was combined with the original ether filtrate. With both the Ti and Zr catalyst, the insoluble polypropylene on the filter was *isotactic* and amounted to 50 ± 2% of the polypropylene formed. The other half of the polymer, which was isolated from the ether and methanol washings by removal of the solvent was *atactic*. The identification of these *isotactic*- and *atactic*-polypropylene fractions was achieved from the ^{13}C NMR spectra recorded in 1,2-[D$_4$]dichlorobenzene/*sym*-[D$_3$]trichlorobenzene (3:1, v/v) at 130 °C. Comparison with authentic spectra in the literature showed unique peaks, δ = 31.1 and 30.5 ppm for the *atactic*, and δ = 30.8 ppm for the *isotactic* polymer.[22]

Polymerization of 1-Hexene by the $ClM_tCH_2AlCl_2$ (Ti, Zr, Hf) Catalyst System: In a procedure employed for each catalyst but exemplified by the Ti analogue, a black suspension of $ClTiCH_2AlCl_2$ (**9**) (40.0 mmol) in cyclohexane (150 mL) was heated at reflux with 1-hexene (33.7 g, 400 mmol) for 10 h. Hydrolytic workup and separation, drying and solvent evaporation from the organic layer gave 18.4 g (55%) of poly(1-hexene) as a colorless viscous liquid. From the ^{1}H NMR ([D$_8$]toluene) and ^{13}C NMR spectra (1,2-[D$_4$]dichlorobenzene and *sym*-[D$_3$]trichlorobenzene at 130 °C), the sample was shown to be essentially *isotactic*.[23] A similar procedure applied to the zirconium analog **25** gave a 73% yield of poly(1-hexene), which was an 85:15 mixture of *isotactic* (MeOH-insoluble)/*atactic* (MeOH-soluble) polymers. Likewise, with the hafnium analog **26**, 1-hexene was polymerized in a 40% yield to give a 90:10 mixture of *isotactic*/*atactic* polymers.

Acknowledgments

This research has been conducted with the financial support from grants from Akzo Corporate Research America Inc. and the Boulder Scientific Company of Mead, Colorado. We are grateful to the Alexander von Humboldt Stiftung of Bonn, Germany, for a Senior Scientist Award to J. J. E. In addition, we are indebted to our colleagues, Dr. S. L. Pombrik and Dr. X. Shi, for significant preliminary experiments.

---

[1] J. J. Eisch, J. N. Gitua, P. O. Otieno, A. A. Adeosun, *Macromol. Symp.*, in press.

[2] J. J. Eisch, X. Shi, J. R. Alila, S. Thiele, *Chem. Ber./Recueil* **1997**, *130*, 1175−1187.

[3] J. J. Eisch, X. Shi, J. Lasota, *Z. Naturforsch., Teil B* **1995**, *50*, 342−350.

[4] J. J. Eisch, S. I. Pombrik, X. Shi, S. C. Wu, *Macromol. Symp.* **1995**, *89*, 221−229.

[5] J. J. Eisch; X. Shi, F. A. Owuor, *Organometallics* **1998**, *17*, 5219−5221.

[6] J. J. Eisch, J. R. Alila, *Organometallics* **1999**, *18*, 2930−2932.

[7] J. J. Eisch, P. O. Fregene, unpublished studies.

[8] J. J. Eisch, J. N. Gitua, *Organometallics* **2003**, *22*, 24−26.

[9] J. J. Eisch, A. A. Adeosun, J. N. Gitua, *Eur. J. Org. Chem.* **2003**, 4721−4727.

[10] [10a] J. J. Eisch, J. N. Gitua, P. O. Otieno, X. Shi, *J. Organomet. Chem.* **2001**, *624*, 229−238. [10b] The components involved in the reaction depicted in Scheme 2 are known to form the following complexes with THF: $TiCl_4 \cdot 2THF$, $Me_3Al \cdot THF$, $TiCl_2 \cdot 2\,THF$ and $Me_2AlCl \cdot THF$.

[11] In ref.[4] the polymerization activity of $TiCl_2 \cdot 2THF$, prepared by the alkylative reduction of $TiCl_4$ in THF with RLi or RMgX, was evaluated versus various Lewis acidic organoaluminum cocatalysts, such as MAO and Me_2AlCl.

[12] J. J. Eisch, J. N. Gitua, *Organometallics* **2003**, *22*, 4172−4174.

[13] [13a] T. Mukaiyama, T. Sato, J. Hanna, *Chem. Lett.* **1973**, 1041−1044. [13b] S. Tyrlik, I. Wolochowicz, *Bull. Soc. Chim. Fr.* **1973**, 2147−2148. [13c] J. E. McMurry, M. P. Fleming, *J. Am. Chem. Soc.* **1974**, *96*, 4708−4709. [13d] A. Fürstner, ed., *Active Metals*, Wiley-VCH, Weinheim, Germany, **1996**.

[14] J. N. Coxon, M. P. Hartshorn, W. Rae, *Tetrahedron* **1970**, *26*, 1091−1094.

[15] Quotation of Professor Leopold Ruzicka: “Ein Kristall ist ein chemischer Friedhof.”; cited by J. D. Dunitz in *Trans. Am. Crystallogr. Assoc.* **1984**, *20*, 1−14. We thank Professor Bruce M. Foxman of Brandeis University for locating the source of this arresting metaphor for us.

[16] J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc.* **1986**, *108*, 379−385.

[17] Cf. the analogous triphenylcyclopropenium cation: R. Breslow, H. W. Chang, *J. Am. Chem. Soc.* **1963**, *85*, 2033−2034.

[18] J. J. Eisch, B. Shafii, J. D. Odom, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 1847−1853.

[19] [19a] E. J. Arlman, P. Cossee, *J. Catal.* **1964**, *3*, 99−104. [19b] E. J. Arlman, *J. Catal.* **1964**, *3*, 89−98. [19c] E. J. Arlman, *J. Catal.* **1966**, *5*, 178−189. [19d] E. J. Arlman, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1217−1235.

[20] P. Pino, R. Mülhaupt, in *Transition Metal Catalyzed Polymerizations. Alkenes and Dienes*, part A (Ed.: R. P. Quirk), MMI Press, Harwood Academic Publishers, **1983**, pp. 14−15.

[21] [21a] J. J. Eisch, *Organometallic Syntheses*, Academic Press, New York, **1981**, vol. 2, pp. 3−28. [21b] J. J. Eisch, *Organometallic Syntheses*, Academic Press, New York, **1981**, vol. 2, pp. 28−37.

[22] Cf. reference spectra for *atactic*, *isotactic* and *syndiotactic* polypropylenes: R. Paukkeri, R. Vaananen, A. Lehtinen, *Polymer* **1993**, *34*, 2488−2494.

[23] Cf. reference spectra for *atactic* and *isotactic* poly(1-hexenes): J. C. W. Chien, B. N. Gong, *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1747−1754.

Received March 22, 2004