Macromol. Symp. **2004**, *213,* 187-198

Highly Active and Stereoselective Olefin Polymerization Catalysts Generated by the Transfer-Epimetallation of Olefins or Acetylenes with Dialkyltitanium(IV) Complexes: Three-Membered Metallocycles as Active Catalyst Sites[‡]

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Summary: Efficient transfer-epimetallations of simple olefins and acetylenes by R_2TiL_2 reagents ($R = Bu^n, Bu^t$; $L = X$) are readily achieved in THF at −78°C to generate titanacyclopropa(e)ne intermediates, readily capable of inserting various unsaturated addends (olefin, acetylene, nitrile). Analogous epimetallations conducted in hydrocarbons lead to the isotactic stereoselective polymerization of 1-alkenes and the cyclotrimerization of acetylenes. In place of the widely accepted Arlman-Cossee model for the active catalytic site, namely a Ti–C bond on the $TiCl_3$ crystal lattice, the 2-substituted-1-halotitanacyclopropyl cation formed in hydrocarbon media is proposed as the active site for stereoselective olefin polymerization.

Keywords: organotitanium catalytic sites; polyethylene; polyolefins; stereospecific polymers; Ziegler-Natta polymerization

Introduction

The essentially linear polymerization of ethylene achieved at low pressures by Karl Ziegler and coworkers in late 1953 and the stereoselective polymerization of *alpha*-olefins discovered by Giulio Natta and coworkers in early 1954 have transformed this period into an *annus mirabilis* of modern chemistry and industrial technology. These initial so-called Ziegler-Natta polymerization catalysts consisted of heterogeneous combinations of transition metal salts as the procatalyst with a main-group metal alkyl as the cocatalyst. In later modifications of titanium-based catalysts, titanium(III) chloride phases were produced on solid supports, such as $MgCl_2$, and the titanium(III) center then supposedly alkylated with R_nAlCl_{3-n} to produce the putative active chiral site for isotactic polymerization. More refined catalyst modifications thereafter

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[‡] Part 28 of the series, Organic Chemistry of Subvalent Transition Metal Complexes; Part 27: J.J. Eisch, A.A. Adeosun, J.N. Gitua, *Eur. J. Org. Chem.* **2003**, in press.

DOI: 10.1002/masy.200450918

employed a gamut of electron donors, which did in various degrees enhance the isotactic selectivity in *alpha*-olefin polymerization and whose action was explained in terms of selective coordination to and hence poisoning of the atactic sites by such donors.[1] Various theoretical models have been proposed for the nature of such chiral sites on the titanium(III) chloride crystal lattice. One of the most widely considered models is that proposed by Arlman and Cossee[2-5] and modified by subsequent workers, such as the variant put forward by Allegra.[6] A sobering, possibly prescient caveat about all such active-site models has been expressed by Pino and Mülhaupt in 1983: "The *weak point* of this approach (*i.e.*, theoretical calculations of models of the catalytic center) is the *choice of the model* on which calculations are made. As our knowledge of the structure of the catalytic center is *very scant*,... it only *seldom* happens that the calculations... *lead to a better understanding...*"[7] (italicized emphasis added).

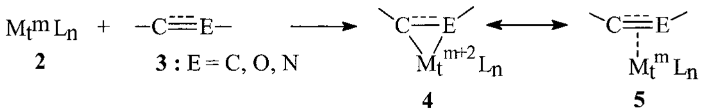
That the occurrence of either ethylene polymerization or stereoselective olefin polymerization does not require a heterogeneous catalyst became evident from studies of metallocenes as procatalysts, which at least initially form hydrocarbon-soluble systems with aluminum alkyl cocatalysts. Already in 1957, two different groups, those of Natta[8] and of Breslow,[9] showed that combinations of titanocene dichloride with an aluminum alkyl can polymerize ethylene in solution into the largely linear high-density form. In 1984 Ewen demonstrated for the first time that combinations of *rac*-ethylene-bis(indenyl)$TiCl_2$ with MAO polymerize propylene in homogeneous solution to an isotactic polypropylene with an unusual stereoblock structure[10] and the very next year Kaminsky and Brintzinger were able to produce highly isotactic polypropylene by employing *rac*-ethylene-bis(tetrahydroindenyl)$ZrCl_2$ with MAO.[11] The final barrier to achieving stereoselective polymerization in solution fell in 1988 when Ewen reported that combinations of isopropylidene(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ with MAO cause the highly syndiospecific polymerization of propylene.[12]

Thus chemists now recognize that local molecular chirality at an active site in fluid solution can suffice to induce stereoselectivity in olefin polymerization. This insight removes the necessity of postulating a chiral active site on the crystal lattice of titanium(III) chloride, as in the Arlman-Cossee model for the isotactic polymerization of *alpha*-olefins with heterogeneous Ziegler-Natta catalysts. Although the Arlman-Cossee model with its $TiCl_3$ crystal lattice may remain a *possible mode* for stereoselective olefin polymerization, its solid-state features are no longer a *structural necessity*.

For Ziegler-Natta olefin polymerization catalysts not involving soluble metallocene- or nonmetallocene-ligated transition metal complexes, it has been difficult until now to envision models of the catalytic center that were other than those based on the face or edge of a transition metal salt crystal lattice. Quite recently, in the course of studies of the reactions of dialkyltitanium(IV) salts with olefins,[13] we have made the serendipitous discovery that the first-formed products of such reactions in THF are titanacyclopropanes (**1**, such as **12** and **27** in Schemes 2 and 4) and that when such intermediates as **1** are generated in heterogeneous hydrocarbon media, isotactic polymerization of the *alpha*-olefins present ensues. These findings persuade us to propose **1** as a chiral molecular active catalytic site, in place of the Arlman-Cossee site on the $TiCl_3$ crystal lattice.

Results

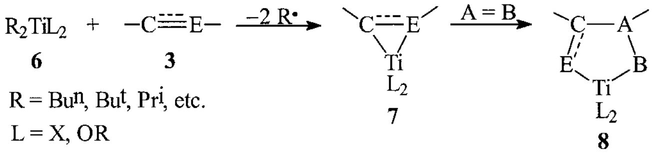
In studies extending over the last decade our group has been exploring the organic chemistry of early transition metal alkyls and subvalent metal salts.[14] From such research our particular attention has been drawn to the process of epimetallation, by which the oxidative addition of subvalent transition-metal reagents ($M_t^mL_n$, **2**) to various C=C, C≡C, C=O or C=N linkages (as in **3**) leads to the formation of three-membered metallocycles (**4**) (Eq. 1).[15] The bonding character



(1)

of the metallocyclic adduct can range from a metallacycloprop(en)yl ring (**4**), having two *sigma*-like C–M_t bonds and a higher oxidation number for the metal center, M_t^{m+2}, to a *pi*-complex (**5**) having little change in the M_t^m oxidation number. Assigning the relative importance of resonance structures **4** and **5** for an epimetallated product requires careful evaluation of the structural parameters of the individual adduct if isolated or of its observed chemical reactions.[15-17] Recently, we have discovered that such epimetallations can be achieved more rapidly, cleanly and in higher yields by means of dialkyltitanium(IV) complexes (**6**) by a process of coordination-induced reductive elimination leading to titanium(II) carbenoid transfer (Eq. 2).[13] The adducts of such transfer-epimetallations (**7**) reflect their titanacyclopropa(e)ne-ring character by undergoing the insertion of various addends A=B (CO_2, R–C≡C–H, R–C≡N,

$R_2C{=}O$) and thereby expanding to five-membered titanocycles **8**. In donor solvents like THF such insertions are generally limited to single units of A=B.

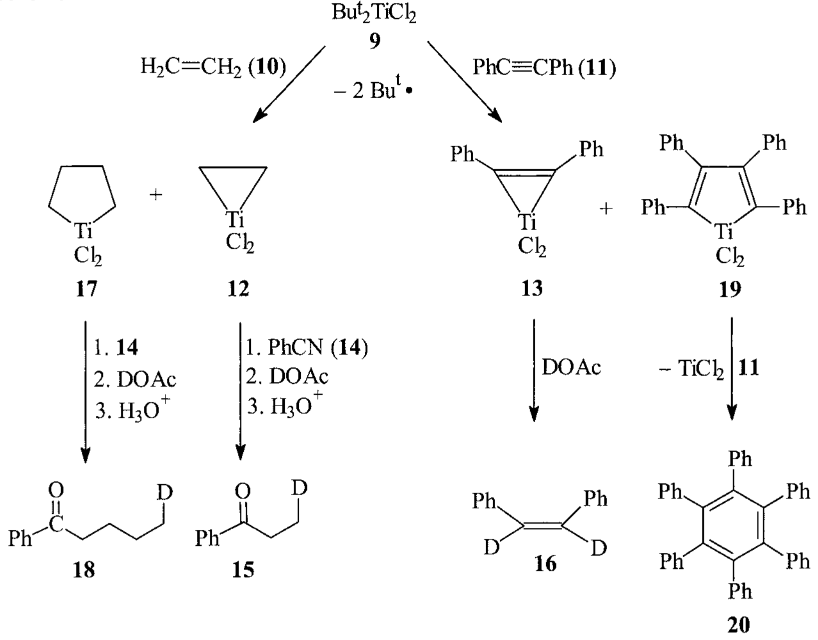


(2)

In an observation most pertinent to our quest for a defined chiral molecular catalytic site in Ziegler-Natta polymerizations, we now wish to report that such transfer-epimetallations by R_2TiL_2 reagents are readily achieved with simple olefins and acetylenes as well. More significantly, however, the resulting three-membered titanocycles show a dramatic difference in reactivity as a function of solvent. In donor solvents, for example as in THF, such adducts as **7** undergo a slow insertion of one or two olefin or acetylene units, as in Eq. 2, leading to the dimerization or trimerization of the monomer. In hydrocarbon medium, on the other hand, R_2TiL_2 (especially L = X) causes the immediate polymerization of ethylene and of *alpha*-olefins, as well as the cyclotrimerization of monosubstituted acetylenes, even at temperatures as low as −78°C. Moreover, the olefins, such as propylene, 1-hexene and styrene, were found to have undergone principally isotactic stereoselective polymerization in such hydrocarbons.

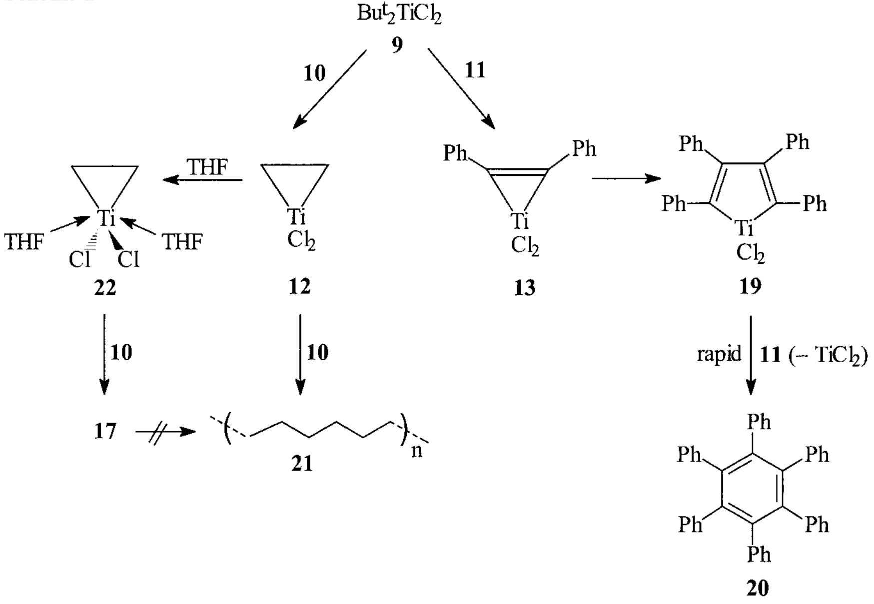
That the three-membered titanocycles (**12** or **13**) are formed in a donor solvent like THF at 25°C from the *transfer*-epimetallating action of $Bu^t_2TiCl_2$ (**9**) or $Bu^n_2TiCl_2$ with ethylene (**10**) or with diphenylacetylene (**11**), respectively, has been demonstrated by the chemical-trapping reactions depicted in Scheme 1. Titanacyclopropane **12** inserted benzonitrile to yield upon deuteriolysis β-deuteriopropiophenone (**15**), and titanacyclopropene **13** underwent deuteriolysis with acetic acid-d to produce *cis*-stilbene-$d_{1,2}$ (**16**). That both the three-membered titanocycles (**12** and **13**) underwent some insertion of a second monomer unit to form **17** and **19**, respectively, was revealed by the chemical derivatization with benzonitrile leading as well to ε-deuteriovalerophenone (**17** → **18**) and the isolation of some hexaphenylbenzene from the deuteriolytic workup (**13** → **19** → **20**). When, on the other hand, the interaction of $Bu^t_2TiCl_2$ (**9**)

Scheme 1

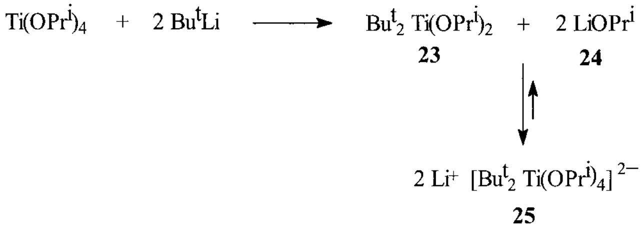


with ethylene (**10**) or with diphenylacetylene (**11**) is conducted starting at –78°C in either hexane or toluene, the ethylene (**10**) is immediately and exothermically polymerized to linear, high-density polyethylene (**21**) and the diphenylacetylene (**11**) undergoes rapid cyclotrimerization to hexaphenylbenzene (**20**) (Scheme 2). The absence of polymerization with ethylene (**10**) and the slow cyclotrimerization of diphenylacetylene (**11**) by $\mathrm{Bu^t_2TiCl_2}$ in *tetrahydrofuran solution* may readily be attributed to the THF-solvation of the three-membered titanocycle active site (*e.g.*, **22** from **12**), which would reduce the electrophilicity of the titanium(IV) initiator and thus the ease of its attack upon the *pi*-electron system of **10** or **11**.[18] Similarly, the failure of $\mathrm{Bu^t_2Ti(OPr^i)_2}$ (**23**) to initiate the polymerization of ethylene or the cyclotrimerization of diphenylacetylene at –78°C, even when generated in hexane or toluene (Scheme 3), most likely is due to the coordination complex **25**, which is formed from **23** and the hydrocarbon-soluble lithium salt **24**.[19] Such coordination would reduce the electrophilic character of the titanium(IV) center in **23**.

Scheme 2



Scheme 3



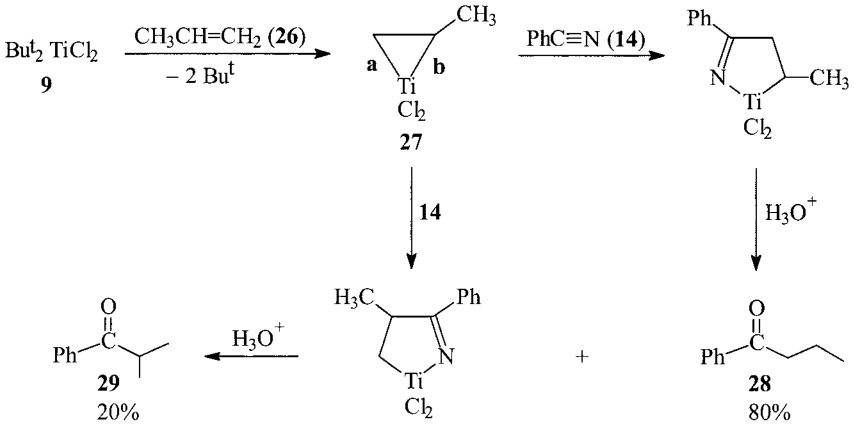
$$Ti(OPr^i)_4 + 2\ Bu^tLi \longrightarrow \underset{\mathbf{23}}{Bu^t_2\,Ti(OPr^i)_2} + \underset{\mathbf{24}}{2\ LiOPr^i}$$

$$\rightleftarrows$$

$$\underset{\mathbf{25}}{2\ Li^+\ [Bu^t_2\,Ti(OPr^i)_4]^{2-}}$$

In a parallel fashion, passing propylene gas (**26**) into a THF solution of $Bu^t_2TiCl_2$ or $Bu^n_2TiCl_2$ starting at –78°C and bringing the solution to 25°C causes the formation of **27** by transfer-epimetallation. The presence of **27** was established by trapping with benzonitrile (**14**) and observing the generation of principally butyrophenone (**28**) (80%) (Scheme 4). Thus benzonitrile inserted selectively into the sterically more accessible C–Ti bond, **a**, of **27**; only 20% of isobutyrophenone (**29**), the insertion product of **14** into bond **b**, was detectable.

Scheme 4



Discussion

The sterically controlled selectivity exhibited in the benzonitrile insertion into titanacyclopropane **27** forms the basis for an appealing model explaining the isotactic polymerization of propylene and other *alpha*-olefins by these R_2TiCl_2 catalysts in hydrocarbon medium.[1, 20] Up to the present, the most widely accepted model for the stereoselective polymerization of *alpha*-olefins in heterogeneous phase has been that of Arlman and Cossee cited above[2-5] or one of its modifications.[11] In the Arlman-Cossee view, an alkylated Ti center, Ti–R, located on the lateral face of the $TiCl_3$ crystal lattice, interacts with an *alpha*-olefin coordinated on an adjacent octahedral site (Figure 1). On steric grounds, the addition of the Ti–C bond to the coordinated olefin is greatly favored in the one conformation where the Ti–C bond and the C–C bond of the coordinated olefin are parallel to each other and as a result the ensuing polymer chain growth occurs preferentially with an isotactic configuration. In the Allegra counterproposal, the Ti–C bond and the C–C bond of the coordinated olefin are perpendicular to each other, thereby lessening steric repulsion (distances **a** and **b** in Figure 1).

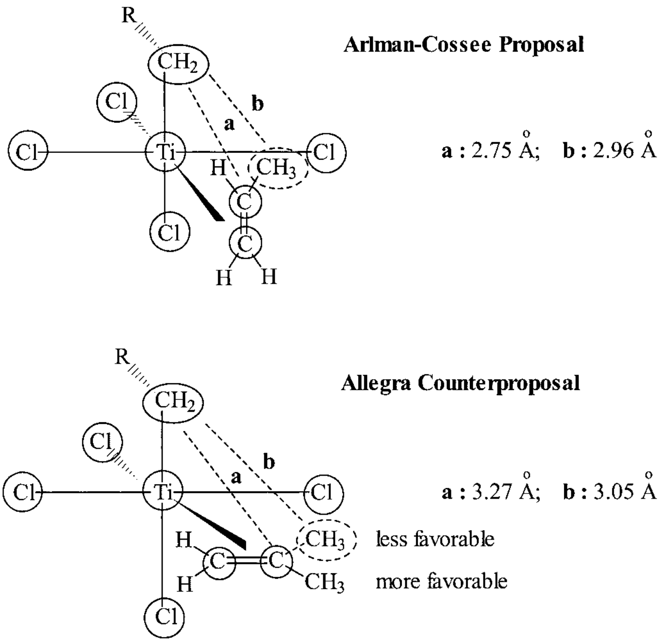
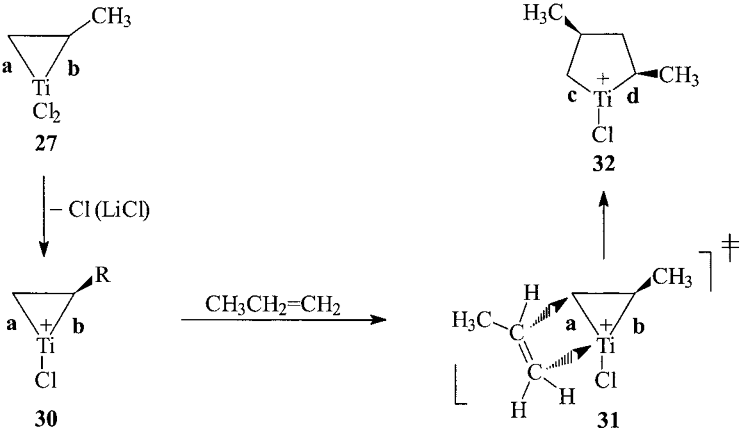


Figure 1. Arlman-Cossee proposal versus that of Allegra for the polymerization of *alpha*-olefins.

The present metallacyclopropane model hypothesizes that a titanacyclopropane, such as **27**, is formed in solution or in heterogeneous phase by the transfer-epimetallation of the *alpha*-olefin by a dialkyltitanium(IV) dichloride, as depicted in Schemes 4 and 5.[13b] Because of the high rate of polymerization, even at –78°C, **27** most likely is converted to the titanacyclopropyl cation **30** by coordinative abstraction of the chloride anion into the LiCl lattice.[21] For steric reasons, the next propylene unit would insert into bond **a** of **30**, approaching the ring from the side opposite (underneath) to that of the first projecting methyl group and with its own methyl group distal to the Ti–Cl cationic center and oriented exocyclic to the ring (**31**) (Scheme 5). The resulting five-membered titanocyclic cation **32** would have established a pattern for the head-to-tail, isotactic union of propylene units, which union could be propagated by further, similar insertions of propylene units at the sterically more accessible C–Ti bond, namely the underside of bond **c** in **32**.

Scheme 5



Although the present experimental results give ample support for the generation of titanacyclopropanes **12** and **27** and titanacyclopropene **13** through the transfer epititanation of ethylene, propylene or diphenylacetylene *in THF solution*, respectively, one might ask what convincing evidence can be marshaled in favor of such intermediates being formed as well in hydrocarbon solvents, *i.e.* under polymerization conditions. It is therefore pertinent to point out that $Bu^n_2TiCl_2$ or $Bu^n_2Ti(OPr^i)_2$ can also effect the stoichiometric transfer-epititanation in hexane or toluene solution of both diphenylacetylene and 1,2-disubstituted ethylenes, such as *cis*-stilbene and acenaphthylene, at low temperatures without ensuing polymerization.[13a] The 1,2-substituents at the olefinic carbons appear to block further monomer insertions into the C–Ti bonds of the titanacyclopropane intermediates. But such clean stoichiometric transfer-epititanations of these hindered olefins in hydrocarbons argue for similar epititanation of ethylene and α -olefins as the crucial first step in their polymerization.

A further objection to this present proposal of titanacyclopropane intermediates as the crucial first step in stereoselective α-olefin polymerization is to argue that some form of Ti(II) or Ti(III) may rather be involved in the present $Bu^t_2TiCl_2$ catalyst system. To counter any such suggestion, we offer these further observations as well as related commentary on previous work.

Previous research on the polymerization of ethylene has involved passing the gas into mixtures of *n*-butyllithium and $TiCl_4$ combined in ratios of 0.75:1.0 to 6.0:1.0 in hydrocarbon media under a nitrogen atmosphere at room temperature.[22, 23] Also by use of *n*-butyllithium and $TiCl_4$ propylene has been polymerized under similar conditions and the poly(propylene) found to be about 60% isotactic.[24]

With reference to our present work, however, we wish to point out that $Bu^n{}_2TiCl_2$ and $Bu^t{}_2TiCl_2$ intermediates, generated from two equivalents of RLi and one equivalent of $TiCl_4$, are kinetically stable at −78°C to decomposition into $TiCl_2$. But at 25°C such intermediates in THF decompose rapidly to $TiCl_2$, and their solutions in hydrocarbons decompose slowly as well. The hydrocarbon suspensions of the resulting $TiCl_2$ and LiCl at 25°C can polymerize either ethylene or propylene, albeit at a slower rate (5g PE/g Ti-atm-h).[25] Noteworthy also is that $TiCl_2$ is very reactive toward the "inert" nitrogen atmosphere via a redox reaction, such that ammonia is evolved upon hydrolysis.[26] Thus although previous workers may have generated $Bu^n{}_2TiCl_2$ in their experiments, it is not clear that this alkyl survived under their conditions or was the specific catalyst for the observed polymerizations. It equally follows that under our conditions (under argon and at −78°C) our observed polymerizations cannot be attributed to $TiCl_2$-catalysts or, *a fortiori*, Ti(III)-catalysis.

Conclusion

In summary, we have demonstrated that dialkyltitanium(IV) dichlorides in donor solvents are able to effect the transfer epimetallation of olefins or acetylenes with the formation of titanacyclopropane or titanacyclopropene intermediates. With 1,2-disubstituted olefins or acetylenes as substrates, the resulting epimetallated adducts are stable as formed, even in hydrocarbon media, and can be shown to be present by chemical trapping with D_2O (cf. **13** in Scheme 1). Such intermediates should no doubt also be formed either in THF or hydrocarbon solution, as we have shown, or in a heterogeneous phase, as we propose. These three-membered titanocycles in donor solvents are able to insert one or more unsaturated monomers with the generation of 5- or 7-membered titanocycles. These findings support the proposal that such titanocycles are also formed from R_2TiCl_2 and the olefins or acetylenes in hydrocarbon media (*cf. supra*). In such noncoordinating media, however, such titanocycles are able to promote rapid and stereoselective olefin polymerization and acetylene cyclotrimerization, most likely via insertion of monomers into titanacycloalk(en)yl cations. The postulated 2-substituted-1-titanacyclopropyl cation intermediate, such as **30** in Scheme 5, thus constitutes an excellent model for rationalizing the observed isotactic stereoselectivity in the formation of isotactic poly(*alpha*-olefins) from terminal alkenes.

Finally, the experimental evidence supporting the Arlman-Cossee model has been the XRD studies of the titanium(III) chloride salts that have been used in Ziegler-Natta catalysts. But to our knowledge, there has been no direct observation of the Ti–C bond postulated in their model (Figure 1). On the other hand, reliable chemical-trapping experiments have provided concrete evidence for the formation of titanacyclopropa(e)ne intermediates, which are formed from R_2TiCl_2 and olefins or acetylenes, both in donor solvents such as THF and in hydrocarbon dispersing media. Accordingly, the titanacyclopropyl-cation model for the active catalytic site may be judged at this point to have the better experimental corroboration.

Acknowledgments. Our investigations of Group 4 metal alkyls over the last decade have been supported at various times by Akzo Corporate Research America, The Boulder Scientific Company, the U.S. National Science Foundation and Solvay, S.A., Brussels, Belgium. The present research has been conducted under the auspices of the Alexander von Humboldt Stiftung, Bonn, Germany, which has provided the principal investigator with a Senior Scientist Award.

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