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Stereoselective Olefin Polymerization Catalysts Generated by the Transfer-Epimetalation of Olefins or Acetylenes with Dialkyltitanium(IV) Complexes: Three-Membered Metallocycles as Proposed Chiral Sites[1]

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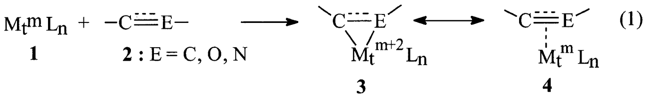
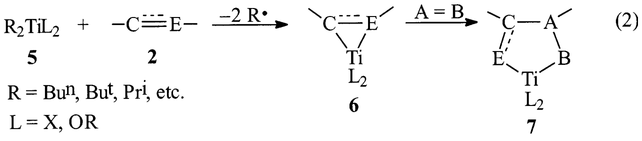
Summary: Efficient transfer-epimetalations of simple olefins and acetylenes by R_2TiL_2 reagents ($R = Bu^n$, Bu^t; $L = X$) are readily achieved in THF at −78 °C to generate titanacyclopropa(e)ne intermediates, readily capable of inserting various unsaturated addends (olefin, acetylene, nitrile). Analogous epimetalations conducted in hydrocarbons lead to the stereoselective polymerization of 1-alkenes and the cyclotrimerizations of acetylenes. The 2-substituted-1-halotitanacyclopropyl cation is proposed as the active site for stereoselective olefin polymerization.

The oxidative addition of subvalent transition metal reagents ($\mathrm{M_t}^m\mathrm{L}_n$, **1**) to various C═C, C≡C, C═O, or C═N linkages (as in **2**) with the formation of three-membered metallocycles (**3**) has been termed epimetalation (eq 1).[2] The bonding character of the metallocyclic adduct can range from a metallacycloprop(en)yl ring (**3**) having two σ-like C−$\mathrm{M_t}$ bonds and a higher oxidation number for the metal center, $\mathrm{M_t}^{m+2}$, to a π-complex (**4**) having little change in the $\mathrm{M_t}^m$ oxidation number. Assigning the relative importance of resonance structures **3** and **4** requires careful evaluation of the structural parameters of the individual adduct if isolated or of its observed chemical reactions.[2−4] Recently, we have discovered that such epimetalations can be achieved more rapidly, cleanly, and in higher yields by means of dialkyltitanium(IV) complexes (**5**) by a process of coordination-induced reductive elimination leading to titanium(II) carbenoid transfer (eq 2).[5] The adducts of such transfer-epimetalations (**6**) 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 **7**. In donor solvents such as THF such insertions are generally limited to single units of A = B.





We now wish to report that such transfer-epimetalations 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 **6** 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.[6] In hydrocarbon suspensions, on the other hand, R_2TiL_2 (especially L = X) causes the immediate polymerization of ethylene and of α-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 preponderantly isotactic polymerization in such hydrocarbon media.[6] Comparison of the ^{1}H and ^{13}C NMR spectra of the resulting polymers with authentic spectra of both the isotactic and atactic polyolefin has permitted the following estimates of the overall empirical isotacticity of the polymer produced by $Bu^t_2TiCl_2$ (**8**): propylene (88%), 1-hexene (100%), and styrene (77%).[6]

That the three-membered titanocycle (**11** or **12**) is formed in a donor solvent like THF at 25 °C from the *transfer*-epimetalating action of $Bu^t_2TiCl_2$ (**8**) or $Bu^n_2TiCl_2$ with ethylene (**9**) or with diphenylacetylene (**10**), respectively, is demonstrated by the chemical-trapping reactions depicted in Scheme 1. Titanacyclopropane **11** inserted benzonitrile to yield upon deuteriolysis β-deuteriopropiophenone (**14**), and titanacyclopropene **12** underwent deuteriolysis with acetic acid-*d* to produce

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[1] Part 26 of the series Organic Chemistry of Subvalent Transition Metal Complexes; Part 25: Eisch, J. J.; Gitua, J. N. *Organometallics* **2003**, *22*, 24.

[2] Eisch, J. J. *J. Organomet. Chem.* **2001**, *617−618*, 148.

[3] Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Krüger, C. *Eur. J. Inorg. Chem.* **2001**, 77.

[4] Eisch, J. J.; Gitua, J. N.; Otieno, P. O.; Shi, X. *J. Organomet. Chem.* **2001**, *624*, 229.

[5] (a) Eisch, J. J.; Gitua, J. N. *Organometallics* **2003**, *22*, 24. (b) The characterization of the complexes $Bu^t_2TiCl_2$ (**8**) and $Bu^n_2TiCl_2$ follows from their mode of formation from the interaction of 2 equiv of RLi with 1 equiv of $TiCl_4$ in THF at −78 °C. Warming up, removal of volatiles, and extraction of the residue with toluene led to the quantitative separation of the LiCl byproduct and the isolation of analytically pure $TiCl_2$•2THF in 95% yield. The high yield of titanium dichloride implies the presence of the precursors $Bu^n_2TiCl_2$ in ~95% yield. (Eisch, J. J.; Shi, X.; Lasota, J. *Z. Naturforsch.* **1995**, *50b*, 342).

[6] Experimental details concerning the transfer-epititanation of ethylene, propylene, and diphenylacetylene by $Bu^t_2TiCl_2$ in THF, the polymerization of ethylene and α-olefins by $Bu^t_2TiCl_2$ in hexane, and the determination of the isotacticity of the resulting polyolefins by NMR spectroscopy are given in the Supporting Information.

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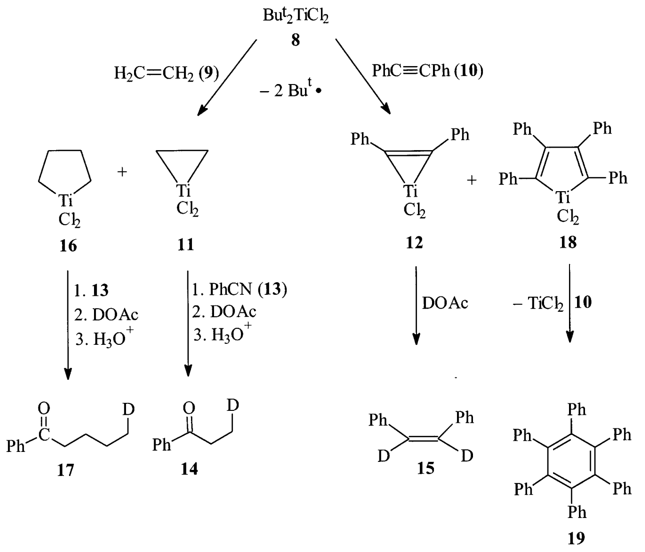
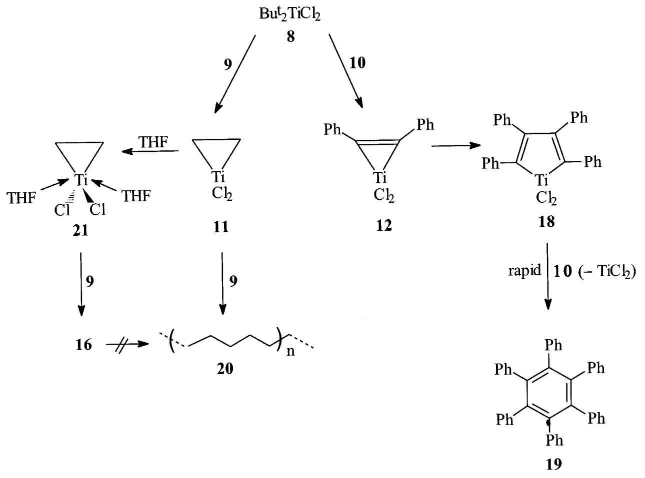
Scheme 1

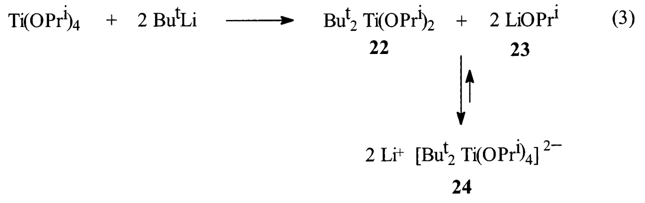


cis-stilbene-$d_{1,2}$ (**15**). That both the three-membered titanacycles (**11** and **12**) underwent some insertion of a second monomer unit to form **16** and **18**, respectively, was revealed by the chemical derivatization with benzonitrile leading as well to ε-deuteriovalerophenone (**16** → **17**) and the isolation of some hexaphenylbenzene from the deuteriolytic workup (**12** → **18** → **19**).[6] When, on the other hand, the interaction of $Bu^t_2TiCl_2$ (**8**) with ethylene (**9**) or with diphenylacetylene (**10**) is conducted starting at −78 °C in either hexane or toluene, the ethylene (**9**) is immediately and exothermically polymerized to linear polyethylene (**20**) and the diphenylacetylene (**10**) undergoes rapid cyclotrimerization to hexaphenylbenzene (**19**) (Scheme 2).[6,7] The absence of polymerization of ethylene (**9**) and the slow cyclotrimerization of diphenylacetylene (**10**) by $Bu^t_2TiCl_2$ in *tetrahydrofuran solution* may readily be attributed to the THF solvation of the three-membered titanocycle active site (e.g., **21**[8a] from **11**), which would reduce the electrophilicity of the titanium(IV) initiator and thus the ease of its attack upon the π-electron system of **9** or **10**.[8b,c] Similarly, the failure of $Bu^t_2Ti(OPr^i)_2$ (**22**) 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 **24**, which is formed from **22** and the hydrocarbon-soluble lithium salt **23**.[9] Such coordination would reduce the electrophilic character of the titanium(IV) center in **22**.

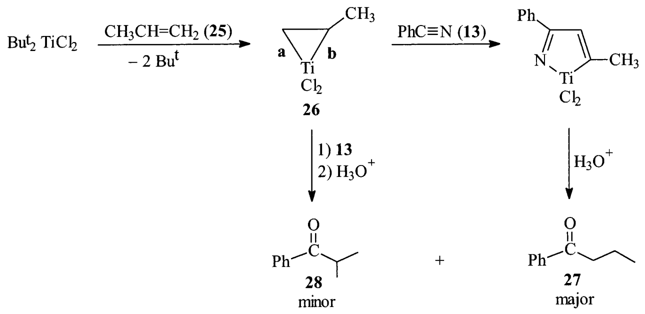
Scheme 2



Scheme 3



Scheme 4



In a parallel fashion, passing propylene gas (**25**) 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 **26** by transfer-epimetalation. The presence of **26** was established by trapping with benzonitrile (**13**) and observing the generation of principally butyrophenone (**27**) (Scheme 4). Thus benzonitrile inserted selectively into the sterically more accessible C−Ti bond, **a**, of **26**; only a minor amount of isobutyrophenone (**28**), the insertion product of **13** into bond **b**, was detectable.[10]

The selectivity exhibited in the benzonitrile insertion into titanacyclopropane **26** forms the basis for an

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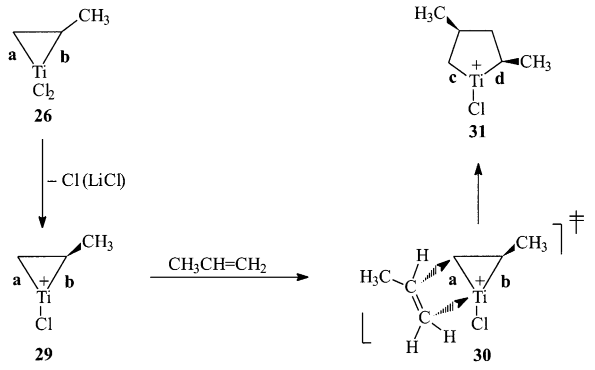
(7) Previous work has reported the polymerization of ethylene by passing the gas into mixtures of *n*-butyllithium and $TiCl_4$ combined in ratios of 0.75:1.0 to 6.0:1.0 in hydrocarbon media *under a nitrogen atmosphere* at room temperature: Friedlander, H. N.; Oita, K. *Ind. Eng. Chem.* **1957**, *49*, 1885. Frankel, M.; Rabani, J.; Zilkha, A. *J. Polym. Sci.* **1958**, *28*, 387. Again, 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: Zilkha, A.; Calderon, N.; Ottolenghi, A.; Frankel, M. *J. Polym. Sci.* **1959**, *40*, 149. 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 2 equiv of RLi and 1 equiv of $TiCl_4$, are kinetically stable to decomposition into $TiCl_2$ at −78 °C. 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 (5 g PE/g Ti·atm·h, refs 2, 4, and Eisch, J. J.; Pombrik, S. I.; Shi, X.; Wu, S. C. *Macromol. Symp.* **1995**, *89*, 221). 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 (Eisch, J. J.; Chan, T., unpublished studies). 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.

(8) (a) The representation of **21** as a bis-tetrahydrofuran solvate in THF solution is consistent with the known complexes: $TiCl_4 \cdot 2THF$; $(C_6H_5)_4Ti \cdot 2Et_2O$, and $MeTiCl_3 \cdot 2THF$ (Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium and Hafnium*; Academic Press: New York, 1974; Chapter 2. (b) Stoichiometric quantities of Lewis bases with respect to Ti and Al reagents in Ziegler−Natta catalysts have long been known to inhibit olefin polymerization (ref 11a, pp 112−115). (c) Eisch, J. J.; Boleslawski, M. P. *J. Organomet. Chem.* **1987**, *334*, C1.

(9) Eisch, J. J.; Gitua, J. N. *Eur. J. Inorg. Chem.* **2002**, 3091.

Scheme 5



appealing model explaining the isotactic polymerization of propylene and other α-olefins by these R_2TiCl_2 catalysts in hydrocarbon medium.[11] Up to the present, the most widely accepted model for the stereoselective polymerization of α-olefins in heterogeneous phase has been that proposed by Cossee and Arlman and modified by Allegra.[12] According to their scheme, an alkylated Ti center, Ti−R, located on the lateral face of the $TiCl_3$ crystal lattice, interacts with an α-olefin coordinated on an adjacent octahedral site. On steric grounds the addition of the Ti−C bond to the coordinated olefin is greatly favored in one conformation, and thereby the ensuing polymer chain growth occurs preferentially with an isotactic configuration.

The present metallocyclopropane model hypothesizes that a titanacyclopropane, such as **26**, is formed in solution or in heterogeneous phase by the transfer-epimetalation of the α-olefin by a dialkyltitanium(IV) dichloride, as depicted in Scheme 5. Because of the high rate of polymerization, even at −78 °C, **26** most likely is converted to the titanacyclopropyl cation **29** by coordinative abstraction of the chloride anion into the LiCl lattice.[13] For steric reasons, the next propylene unit would insert into bond **a** of **29**, approaching the ring from the side opposite (underneath) 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 (**30**) (Scheme 5). The resulting five-membered titanacyclic cation **31** 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 **31**.

In summary, we have demonstrated that dialkyltitanium(IV) dichlorides in donor solvents are able to effect the transfer-epimetalation of olefins or acetylenes with the formation of titanacyclopropane or titanacyclopropene intermediates. Such intermediates from simple olefins should no doubt be formed either in 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 five- or seven-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.[14] 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 **29** in Scheme 5, thus appears to be an excellent model for rationalizing the observed stereoselectivity in the formation of isotactic poly(α-olefins) from terminal alkenes.

Acknowledgment. Our research on reactions of group 4 metal alkyls over the past decade has 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 investigation has been funded by the Alexander von Humboldt Stiftung, Bonn, Germany, which has provided the principal investigator with a Senior Scientist Award. Technical advice and assistance have been generously given by Drs. Fredrick A. Owuor and Peter O. Otieno.

Note Added In Proof. In most recent studies we have extended the present proposal of titanacyclopropyl chiral cations as olefin polymerization sites to the conventional Ziegler catalyst system, $TiCl_4$ with Et_3Al. Thus admixing 1 equiv of $TiCl_4$ with 2 equiv of Et_3Al in hexane at −78 °C gave an initially *homogeneous* solution of the products, Et_2TiCl_2 and 2 equiv of Et_2AlCl. In the first orienting reaction the addition of diphenylacetylene to such solution, warming to 25 °C, and then adding D_2O led to almost a quantitative isolation of 1,2-dideuterio-*cis*-stilbene. This finding is consistent with the tranfer-epititanation of the acetylene by Et_2TiCl_2 (cf. Scheme 1, **8** + **10** → **12**). In the second reaction the addition of ethylene to such a solution led to the exothermic formation of linear, high-density polyethylene. This observation fits the outcome depicted in Scheme 2, **8** → **11** → **20**. In the final reaction the addition of propylene to such a solution caused the rapid precipitation of polypropylene that was up to 80% isotactic, a stereoselective polymerization readily accommodated by the model outlined in Scheme 5.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The observed ratio of **27** to **28** in the reaction of **26** with benzonotrile is 4.0:1.0.

(11) (a) The vade mecum in the field of Ziegler−Natta olefin polymerization up to 1979: Boor, J., Jr. *Ziegler−Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (b) More recent and authoritative surveys include: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(12) (a) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99. (b) Arlman, E. J. *J. Catal.* **1964**, *3*, 89. (c) Arlman, E. J. *J. Catal.* **1966**, *5*, 178. (d) Arlman, E. J. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1217. (e) Allegra, G. *Makromol. Chem.* **1971**, *145*, 235.

(13) The Lewis acidity of unsolvated ion-pairs of lithium chloride for chloride anions is evident in the experimental detection of diamond-shaped, bridged lithium chloride dimers in the vapor phase at over 800 °C by means of electron diffraction (∠Cl−Li−Cl = 108° ± 4°): Bauer, S. H.; Tadishi, I.; Porter, R. F. *J. Chem. Phys.* **1958**, *33*, 685.

(14) Pertinent to note, moreover, is that $Bu^n{}_2TiCl_2$ or $Bu^n{}_2Ti(OPr^i)_2$ can also effect the stoichiometric transfer-epimetalation in hexane or toluene solution (ref 5) of 1,2-substituted ethylenes, such as *cis*-stilbene and acenaphthylene, without ensuing polymerization. The substituents at the olefinic carbons appear to block further insertions into the C−Ti bonds of the titanacyclopropane intermediate. But such successful, stoichiometric transfer-epimetalations in hydrocarbons argue for the similar epimetalation of ethylene and α-olefins as the crucial first step in their polymerization.