

**Preliminary communication**

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**Effects of Lewis acids and bases on the carbotitanation of unsaturated hydrocarbons and ketones with  $\eta^3$ -allyl(di- $\eta^5$ -cyclopentadienyl)titanium(III)**

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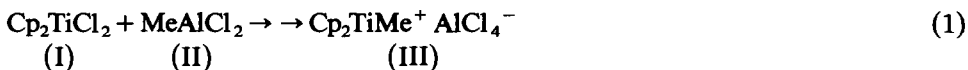
**Abstract**

The carbotitanating action of  $\eta^3$ -allyl(di- $\eta^5$ -cyclopentadienyl)titanium(III) toward ethylene and other unsaturated hydrocarbons, such as trimethyl(phenylethynyl)silane, and toward ketones has been shown to be promoted by Lewis acids strong enough to polarize the carbon-titanium bond, yet not so strong as to exchange the carbon group for halogen. Of the trio of acids,  $\text{Me}_3\text{Al}$ ,  $\text{Me}_2\text{AlCl}$  and  $\text{MeAlCl}_2$ , only  $\text{Me}_2\text{AlCl}$  is able to activate the carbon-titanium bond and thus to promote the polymerization of ethylene and the carbotitanation of the phenylethynylsilane. Evidence is adduced that the activated reagent in both reactions is the complex,  $\text{Cp}_2\text{Ti}(\text{allyl})\text{-Me}_2\text{AlCl}$ . By contrast, the carbotitanating activity of this complex is completely destroyed by addition of a Lewis base, such as THF. Towards ketones, the  $\text{Cp}_2\text{Ti}(\text{allyl})$  reagent can behave either as a carbotitanating agent or as a reducing agent. Which of these reactions is favored again depends upon the presence or absence of Lewis acids and bases. With Lewis acids or in non-donor solvents the  $\text{Cp}_2\text{Ti}(\text{allyl})$  reagent effects the addition of the allyl-titanium bond to the carbonyl group. On the other hand, in the presence of Lewis bases, such as THF,  $\text{Cp}_2\text{Ti}(\text{allyl})$  causes the bimolecular reduction or monomolecular reduction of the ketone to yield the glycol or secondary alcohol. The significance of these results to polymerization mechanisms and to organic synthetic applications is briefly discussed.

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The carbotitanation of unsaturated organic substrates has gained recognition not only as a versatile method in organic synthesis [1,2] but has been established as the initiating step in the polymerization of ethylene by soluble Ziegler catalysts [3] of the titanium(IV) type [4]. In the latter study we demonstrated that titanocene dichloride (I) is converted into the active catalyst, di- $\eta^5$ -cyclopentadienyl(methyl)-

titanium(IV) tetrachloroaluminate (III), by the alkylating and Lewis-acidic actions of the cocatalyst,  $\text{MeAlCl}_2$  (II) (eq. 1) [4]:

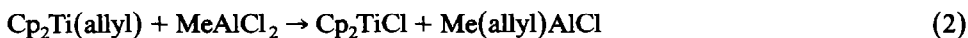


In the attempt to identify well-defined, soluble molecular systems of the titanium(III) type that would be capable of initiating polymerization\*, we have now examined the hydrocarbon-soluble complex,  $\eta^3$ -allyl(di- $\eta^5$ -cyclopentadienyl)titanium(III) (IV) [6] and have found that both Lewis acids and bases can exert a profound influence on its carbotitanating activity. Since these acid-base effects are most pertinent to the chemical applications of organotitanium reagents, we wish to outline here the nature of our findings.

A solution of reagent IV in hexane (20 mmol/l) does not, by itself, effect the polymerization of ethylene even under 3 atm of pressure and with temperatures up to 70°C. However, the addition of a sixfold molar excess of  $\text{Me}_2\text{AlCl}$  causes the violet color of IV to change to navy-blue and this resulting solution smoothly catalyzes the polymerization of ethylene. However, if in addition to the  $\text{Me}_2\text{AlCl}$  a sixfold molar excess of THF is added, the resulting solution exhibits no polymerization activity whatsoever.

The polyethylene thus formed from IV and  $\text{Me}_2\text{AlCl}$  (in the absence of THF) melts up to 137°C and hence is of the high-density type [3]. Its fragmentation pattern in the mass spectrometer (70 eV, deep insertion probe) exhibits a strong  $m/e$  peak at 41, which was much more intense than that exhibited by a sample of polyethylene produced by a  $\text{TiCl}_4/\text{Et}_2\text{AlCl}$  catalyst system. This observation gives strong support to the conclusion the allyl group of IV has been incorporated as an end-group in the polyethylene chain.

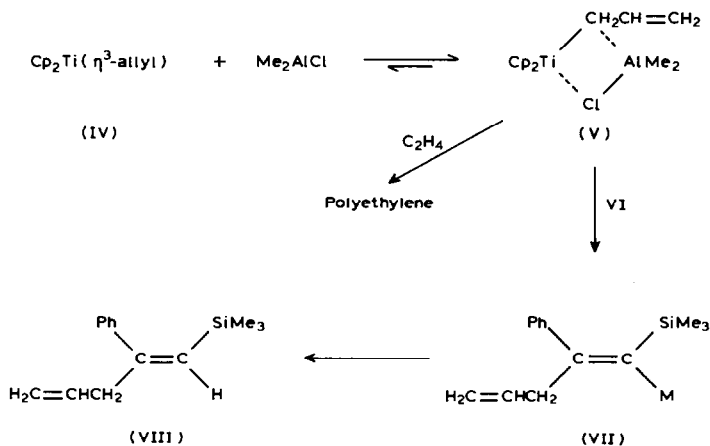
In contrast with the behavior of  $\text{Me}_2\text{AlCl}$ , it was found that admixing a sixfold excess of either  $\text{Me}_3\text{Al}$  or  $\text{MeAlCl}_2$  with IV did not produce an active polymerization catalyst. The solution of IV with  $\text{Me}_3\text{Al}$  underwent no change in its violet color, but that of IV with  $\text{MeAlCl}_2$  took on the characteristic green color of  $\text{Cp}_2\text{TiCl}$ . Evidence was obtained that  $\text{MeAlCl}_2$  caused the transfer of the allyl group from titanium to aluminum (eq. 2)\*\*:



The success of  $\text{Me}_2\text{AlCl}$  and the converse failures of  $\text{Me}_2\text{AlCl}$  with THF or of  $\text{Me}_3\text{Al}$  or  $\text{MeAlCl}_2$  to function as a polymerization cocatalyst with titanium reagent IV shows that the aluminum reagent must be a strong enough Lewis acid to activate IV for ethylene polymerization ( $\text{Me}_2\text{AlCl} > \text{Me}_3\text{Al}$  or  $\text{Me}_2\text{AlCl}/\text{THF}$ ) but not so strong as to induce exchange and thus to destroy the requisite carbon-titanium bond ( $\text{MeAlCl}_2$ ,  $\text{Me}_2\text{AlCl}$  \*\*). These findings suggest that the active catalyst

\* To the best of our knowledge, such hydrocarbon-soluble cyclopentadienyltitanium(III) catalysts have not received explicit attention by previous workers, although some work has been reported for such systems in halogenated solvents, where the titanium is known to be oxidized to titanium(IV) in situ [5].

\*\* Support for the exchange depicted in eq. 2 was gained by adding benzophenone to a mixture of IV and  $\text{MeAlCl}_2$ . Hydrolytic work-up permitted the isolation of  $\text{Ph}_2(\text{CH}_2=\text{CHCH}_2)\text{COH}$ , the expected allylation product from  $\text{Me(allyl)AlCl}$ . Such a product would not have arisen from  $\text{Cp}_2\text{Ti(allyl)}$ , which we have shown converts benzophenone into  $\text{Ph}_2(\text{allyl})\text{CCPh}_2(\text{allyl})$  [7].



Scheme 1.

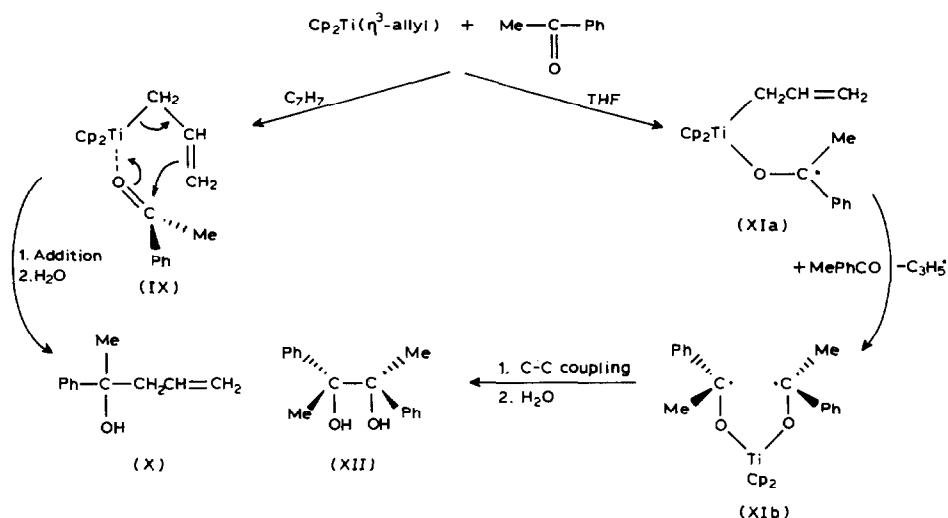
formed from IV and  $\text{Me}_2\text{AlCl}$  is a complex of the type depicted in V. In order to intercept such a possible intermediate, we chose as a bulky substitute for ethylene the unsaturated silane, trimethyl(phenylethynyl)silane (VI), so as to allow the initial carbotitanation to occur but to hinder repetitive reactions leading to polymers. Since VI was shown not to react with either IV or  $\text{Me}_2\text{AlCl}$  individually, any reaction of a 1/1 combination of them could be confidently attributed to a complex such as V. In fact, when IV and  $\text{Me}_2\text{AlCl}$  were allowed to react with silane VI in pentane solution at  $60^\circ\text{C}$ , the hydrolyzed reaction mixture permitted the isolation of *Z*-2-phenyl-1-trimethylsilyl-1,4-pentadiene (VIII) in good yield (Scheme 1) \*

With polar unsaturated substrates, such as ketones, the titanium reagent IV was found to act principally either as a carbotitanating agent or as a reducing agent, with the course of reaction strongly influenced by the absence or presence of a Lewis-basic or donor solvent. For example, a toluene solution of IV and methyl phenyl ketone in a 1/1 molar ratio reacted to yield chiefly (> 70%) the carbotitanation product, 2-phenyl-4-penten-2-ol (X). In THF solution, however, X was produced only in traces and the major product (> 75%) was that of bimolecular reduction, *d,l*-2,3-diphenyl-2,3-butanediol (XII) [8]. From these observations it appears that in non-donor solvents a carbotitanation proceeding by way of a six-membered coordinative complex IX is favored while in donor solvents like THF a single-electron-transfer pathway (XI) is of lower energy (Scheme 2) \*\*.

The reasons for favoring the involvement of a 2/1 complex of the ketone with the titanium are that more of XII is produced when a 2/1 ratio of the ketone/IV is employed and that the racemic stereochemistry of XII can be more readily understood if both ketonic units are coordinated with the same titanium as the new C-C bond is being formed (XIa  $\rightarrow$  XIb). Were two units of the type XIa involved, the *meso*-diastereomer of XII should have been formed. In both instances, the stereo-

\* The nature of the metal M in VII of Scheme 1 is not determinable from the present evidence. More likely, it is titanium (see ref. 4). But the stereochemistry of VIII, corresponding to a *syn*-carbometallation, was ascertained by the chemical shift of the vinyl proton (see ref. 2).

\*\* Compounds X and XII were identified by comparison with authentic samples.



Scheme 2.

chemistry should result from minimizing the repulsions of the methyl and phenyl groups [9].

The foregoing results open up the attractive prospect of fostering the carbotitanating action of organotitanium reagents by the use of adjuvant Lewis acids and by avoiding Lewis bases. Conversely, by the intentional use of donor solvents or Lewis bases the reducing action of titanium(III) reagents may be promoted. These insights into the role of Lewis acids and bases in organotitanium chemistry should prove valuable both in olefin polymerization and in organic synthesis.

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