# Observation of the First Titanium Alkyl/Alkene Complex.
## The Key Intermediate in the Ziegler-Natta Mechanism for the Polymerization of Alkenes

Michael D. Spencer          Final Seminar          August 31, 1993

The observation by Ziegler [1] and Natta [2] that mixtures of titanium halides and alkyl aluminum compounds form highly reactive alkene polymerization catalysts is the basis of the current large scale manufacture of polyethylene and polypropylene (nearly 10 million tons per year) [3]. The most widely accepted mechanism for the Ziegler-Natta polymerization process was proposed by Cossee and Arlman in 1960 [4-8]. This mechanism proposes that coordination of an alkene to a titanium alkyl center precedes insertion of ethylene into the titanium carbon bond. However, no titanium alkyl/alkene complex has ever been prepared.

The complexes *trans*-TiX$_2$(dmpe)$_2$ (X = BH$_4$, Br, Cl, Me, and OPh) [9-11] all react with alkenes to give diamagnetic products. With ethylene, two complexes are formed: the mononuclear complex *trans*-TiX$_2$(C$_2$H$_4$)(dmpe)($\eta^1$-dmpe), and the dinuclear complex *trans*-[TiX$_2$(C$_2$H$_4$)(dmpe)]$_2$($\mu$-dmpe). These two species are in equilibrium in solution. The complex *trans*-[TiCl$_2$(C$_2$H$_4$)-(dmpe)]$_2$($\mu$-dmpe), **1**, can be isolated and an X-ray crystal structure confirms the trans geometry. The crystallographic results also show that the ethylene to resides in the plane described by the phosphine ligands.
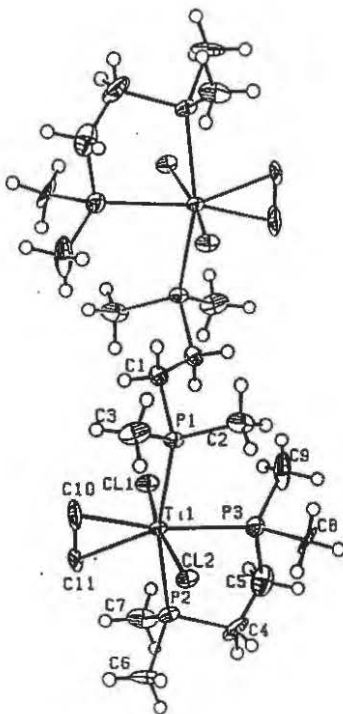


The ethylene complexes formed from *trans*-TiMe$_2$(dmpe)$_2$ are not as stable as those formed from *trans*-TiCl$_2$(dmpe)$_2$, but NMR spectroscopy supports the formation of complexes TiMe$_2$(C$_2$H$_4$)(dmpe)($\eta^1$-dmpe), **2**, and [TiMe$_2$(C$_2$H$_4$)(dmpe)]$_2$($\mu$-dmpe), **3**, which makes them the first titanium alkyl/alkene complexes observed. Heating solutions of **2** and **3** to -20 °C in the presence of excess ethylene results in the dimerization of ethylene to 1-butene with a turnover rate of 440 hr$^{-1}$. A few other early transition metal complexes react similarly but all of these are considerably less active [12-18]. In the reaction of TiMe$_2$-(dmpe)$_2$ with ethylene, Ziegler-Natta chemistry is not observed (i.e., there is no insertion of

ethylene into the Ti-CH$_3$ bonds) as evidenced by the lack of alkene products with an odd number of carbon atoms. The dimerization of ethylene is catalyzed by all of the TiX$_2$-(dmpe)$_2$ complexes, but at different rates (Me > BH$_4$ > Cl > OPh). Two mechanisms for the dimerization need to be considered [19]: (1) The oxidative coupling of two coordinated ethylenes followed by β-hydride abstraction and reductive elimination, or (2) the double insertion of ethylene into a titanium hydride followed by β-hydride elimination.
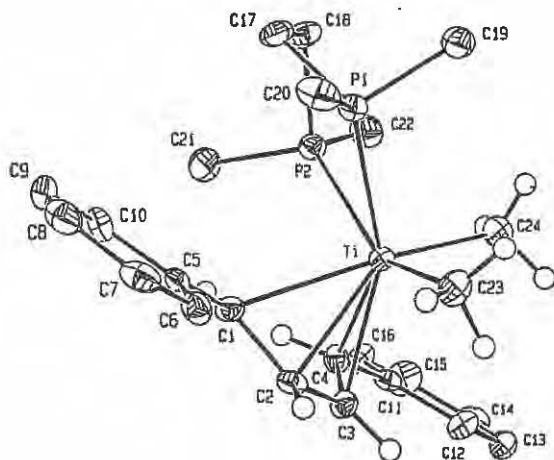


The oxidative coupling mechanism for the dimerization of ethylenes is supported by the following observations. Titanium bis(alkene) intermediates can be formed by the addition of butadiene or 1,4-diphenyl-1,3-butadiene to TiMe$_2$(dmpe)$_2$. The resulting species have the stoichiometry TiMe$_2$(η$^4$-C$_4$H$_4$R$_2$)(dmpe) (R = H, 4; R = Ph, 5) and the latter has been isolated and characterized crystallographically. At higher temperatures, the reaction of TiMe$_2$(dmpe)$_2$ with 1,3-butadiene proceeds further to form TiMe$_2$(C$_8$H$_{12}$)(dmpe), 6. The C$_8$H$_{12}$ ligand has the structure Ti-CH$_2$CHCHCH$_2$CH$_2$CHCHCH$_2$, and is formed by oxidative coupling of two butadienes and allylic rearrangement to expand the ring [20-22]. The reaction of TiMe$_2$(dmpe)$_2$ with styrene proceeds via the same reaction steps until the β-hydride abstraction occurs. Since the phenyl groups are alpha to titanium, an η$^3$-benzyl interaction changes the reductive elimination step to favor the loss of methane. A second β-hydride abstraction, loss of methane, and coordination of a third equivalent of styrene gives the observed product, the titanium(O) complex, Ti(η$^2$-styrene)(η$^4$-C$_4$H$_4$Ph$_2$)(dmpe), 7. These products support the intermediacy of several of the species in the proposed catalytic cycle; bis(alkene), 4 and 5; metallacycle, 6; and β-hydride abstraction, 7.

The inability of ethylene to insert into the Ti-CH$_3$ bond is partly due to the strong π-back bonding from the d$_{xy}$ orbital of titanium into the ethylene π* orbital, which fixes the ethylene ligand in the plane of the phosphine ligands. In addition, insertion of ethylene into the Ti-alkyl bond would eliminate the π-back bonding interaction completely, and such a reaction is probably uphill thermodynamically. In contrast, the π-back-bonding interaction promotes the coordination of a second alkene and the oxidative coupling of the two alkenes to a metallacyclopentane, which is the first step in the alkene dimerization pathway. The reactions of the Ti$_2$(dmpe)$_2$ complexes with other small molecules such as alkynes, CO, and silanes have also been carried out and some of these will be described.

References

1.   Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541.

2.   Natta, G.; Pasquon, l. *Adv. Catalysis* **1959**, *11*, 1.

3.  *Chem. Eng. News* **1993**, *71* (26), 44.

4.  Cossee, P. *Tetrahedron Lett.* **1960**, *17*, 12.

5.  Cossee, P. *J. Catalysis* **1964**, *3*, 80.

6.  Arlman, E. J. *J. Catalysis* **1964**, *3*, 89.

7.  Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

8.  Cossee, P. *Rec. Trav. Chim.* **1966**, *85*, 1151.

9.  Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans* **1985**, 1339.

10. Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem .Soc.* **1987**, *109*, 8094.

11. Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 4167.

12. Lefebvre, G.; Chauvin, Y. In "Aspects of Homogeneous Catalysis"; R. Ugo, Ed.; Carlo Manfredi: Editore-Milano, 1970; Vol. 1, p 107, and references therein.

13. Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R.; *J. Am. Chem. Soc.* **1978**, *100*, 5964.

14. Fellmann, J. D.; Rupprecht, G. A.; Schrock, R. R. *J. Am.. Chem. Soc.* **1979**, *101*, 5099.

15. Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752.

16. Shikata, K.; Miura, Y.; Nakaro, S.; Azuma, K. *Kyogo Kagaku Zasshi* **1965**, *68*, 2266; *Chem. Abstr.* **1966**, *64*, 15721.

17. Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353.

18. Tebbe, F. N. *U.S. Patent* 3 933 876 (1976); *Chem. Abstr.* **1976**, *84*, 165021.

19. Pillai, S. M.; Ravindranathan, M.; Sivaram, S. *Chem. Rev.* **1986**, *86*, 353.

20. Yasuda, H.; Okamoto, T.; Yamamota, H.; Nakamura, A. *Shokubai* **1986**, *28*, 97.

21. Kablitz, H.-J.; Wilke, G. *J. Organomet. Chem.* **1973**, *51*, 241.

22. Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844.