Mono(cyclopentadienyl)titanium(II) Complexes with Hydride, Alkyl, and Tetrahydroborate Ligands: Synthesis, Crystal Structures, and Ethylene Dimerization and Trimerization Catalysis

Yujian You and Gregory S. Girolami*

School of Chemical Sciences, The University of Illinois at Urbana−Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Received December 18, 2007

The mono(cyclopentadienyl)titanium(II) complex $CpTiCl(dmpe)_2$ has been prepared by treating $(CpTiCl_2)_x$ with *n*-butyllithium in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe). Subsequent treatment of this titanium(II) species with methyllithium or *n*-butyllithium affords the alkyl and hydride analogues $CpTiMe(dmpe)_2$ and $CpTiH(dmpe)_2$, respectively. The X-ray crystal structures of $CpTiX(dmpe)_2$ (X = Cl, Me, H) have been determined, and all possess unusually long metal−ligand distances owing to steric crowding in the first coordination sphere of these formally eight-coordinate complexes. Analogous treatment of $[Cp^*Ti(BH_4)Cl]_2$ with *n*-butyllithium in the presence of a chelating phosphine affords the mono(pentamethylcyclopentadienyl)titanium(II) complexes $Cp^*Ti(BH_4)(\eta^2\text{-PP})$, where PP is dmpe or (*tert*-butyl)tris(dimethylphosphinomethyl)silane (trimpsi). All of these titanium(II) complexes are catalysts for the oligomerization of alkenes. For example, ethylene is dimerized to 1-butene; subsequent coupling reactions of 1-butene with ethylene gives the ethylene trimers 2-ethyl-1-butene and 3-methyl-1-pentene. The product distribution most strongly supports a coupling mechanism that proceeds via metallacyclopentane intermediates. As judged from the similarity of the product distributions, we propose that the catalytically active species in the Alphabutol process for the dimerization of ethylene to 1-butene are titanium(II) centers.

Introduction

Heterogeneous Ziegler−Natta catalysts have been known for more than 50 years and today account for more than 90% of the polyethylene and polypropylene produced worldwide.[1,2] A general recipe for these catalysts involves the alkylation of titanium(III) chloride with triethylaluminum; a wide range of modifications of this basic recipe populate the patent literature.[3] A significant development in recent years has been the invention and implementation of supported formulations of homogeneous alkene polymerization catalysts such as metallocenes, which afford unprecedented control over the polydispersity, the stereo- and regioselectivity, and the microstructure of the polymers.[4–7]

An industrial process that is closely related to Ziegler−Natta catalysis is the Alphabutol process for the dimerization of ethylene to 1-butene.[8–13] This homogeneous catalysis process, which produces half of the 1-butene used to make linear low-density polyethylene, currently is practiced in 20 plants operating worldwide and is used to produce 400 000 tons of 1-butene per year.[14] The catalysts for this process are prepared from titanium(IV) alkoxides and trialkylaluminum reagents, but it remains unclear why they convert ethylene to short-chain oligomers rather than polymers. One possibility, which is addressed in the current paper, is that the oxidation states of the catalytically active titanium centers in the Ziegler−Natta and Alphabutol processes are different.

There has been much discussion about the oxidation state responsible for the catalytic activity of heterogeneous Ziegler−Natta catalysts. Although catalysts based on titanocenes and related molecules are invariably derivatives of titanium(IV),[4–7] there is relatively little evidence that this oxidation state is responsible for the activity seen in the $TiCl_3$-based heterogeneous systems.[15–17] Instead, the evidence strongly suggests that the catalytically active species in these heterogeneous catalysts is a lower oxidation state, most likely titanium(III).[1,2,18–21]

A few studies suggest that titanium(II) species may be responsible for heterogeneous Ziegler−Natta catalysis.[22–26] Unfortunately,

---

* Corresponding author. E-mail: girolami@uiuc.edu.

(1) Kissin, Y. V. *Alkene Polymerization Reactions with Transition Metal Catalysts*; Elsevier: Amsterdam, 2008.

(2) Kissin, Y. V. *Isospecific Polymerization of Olefins with Heterogeneous Ziegler Natta Catalysts*; Springer-Verlag: New York, 1985.

(3) Pullukat, T. J.; Hoff, R. E. *Catal. Rev. Sci. Eng.* **1999**, *41*, 389–428.

(4) Chien, J. C. W. *Top. Catal.* **1999**, *7*, 23–36.

(5) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377–1390.

(6) Alt, H. *Coord. Chem. Rev.* **2006**, *1*, 250, and following articles in the same issue.

(7) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691–2720.

(8) Zhukov, V. I.; Val'kovich, G. V.; Skorik, B. N.; Petrov, Y. M.; Belov, G. P. *Russ. J. Appl. Chem.* **2007**, *80*, 1195–1200.

(9) Commereuc, D.; Chauvin, Y.; Gaillard, J.; Léonard, J.; Andrews, J. *Hydrocarb. Processes, Int. Ed.* **1984**, *6311*, 118–120.

(10) Al-Sa'doun, A. W. *Appl. Catal., A* **1993**, *105*, 1–40.

(11) Al-Sherehy, F. A. *Stud. Surf. Sci. Catal.* **1996**, *100*, 515–523.

(12) Commereuc, D.; Forestiere, A.; Gaillard, J. F.; Hugues, F. *DGMK Tagungsber.* **1997**, *9705*, 141–148; *Chem. Abstr.* **1998**, *129*, 16410.

(13) Bré, A.; Chauvin, Y.; Commereuc, D. *Nouv. J. Chim.* **1986**, *10*, 535–537.

(14) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3740–3747.

(15) Kashiwa, N.; Yoshitake, J. *Makromol. Chem.* **1984**, *185*, 1133–1138.

(16) Fregonese, D.; Glisenti, A.; Mortara, S.; Rizzi, G. A.; Tondello, E.; Bresadola, S. *J. Mol. Catal. A* **2002**, *178*, 115–123.

(17) Ntais, S.; Siokou, A. *J. Mol. Catal. A* **2006**, *245*, 87–92.

(18) Chien, J. C. W.; Weber, S.; Hu, Y. *J. Polym. Sci. Part A* **1989**, *27*, 1499–1514.

10.1021/om701263v CCC: $40.75

there is little support for or against this suggestion in studies of well-characterized titanium(II) species in solution. Titanium(II) complexes of stoichiometry (η^6-arene)$Ti(AlCl_4)_2$ and (η^5:η^1-$C_5Me_4SiMe_2NR$)Ti(η^4-diene) have been reported to polymerize alkenes after activation by cocatalysts such as $B(C_6F_5)_3$ or MAO,[25–27] but there is no evidence that the catalytically active species generated in situ are still Ti^{II} species. Few molecular titanium(II) alkyls have been reported, and there are fewer studies of the reactions of such complexes with alkenes. We were the first to describe the isolation of a titanium(II) alkyl, the methyl complex $TiMe_2(dmpe)_2$, where dmpe is the chelating diphosphine 1,2-bis(dimethylphosphino)ethane.[28,29] This complex is an active alkene dimerization catalyst; the catalysis takes place by means of metallacyclobutane intermediates, and the catalyst resting states are alkene complexes of stoichiometry $TiX_2(CH_2{=}CH_2)$(η^2-dmpe)(η^1-dmpe).[30,31] We have also prepared and structurally characterized a closely related titanium(II) complex of 1,4-diphenylbutadiene, $TiMe_2(dmpe)(1,4\text{-}C_4H_4Ph_2)$.[31]

As part of our exploration of the chemistry of titanium(II) complexes,[28,29,32,33] here we describe the synthesis of mono(cyclopentadienyl)titanium(II) alkyls, hydrides, and borohydrides of the form $CpTiRL_x$ and Cp^*TiRL_x. Titanium(II) complexes containing one cyclopentadienyl ring are rare, and essentially all the known examples are stabilized by strong π-acceptors such as carbon monoxide or conjugated dienes. For example, the Ti^{II} hydrides $(C_5R_5)TiH(CO)_2(dmpe)$ (R = H, Me) have been prepared by protonation of the anionic species $[(C_5R_5)Ti(CO)_2(dmpe)^-]$.[34,35] The chloride analogue $Cp^*TiCl(CO)_2(dmpe)$ can be synthesized by the reduction of Cp^*TiCl_3 with sodium naphthalenide in the presence of dmpe followed by treatment with CO, but the product is unstable in solution.[34,35] A related phosphinimide complex, $Cp^*Ti(N{=}PBu^t)(CO)_2$, has also been described.[36] Several diene complexes Cp^*TiX(diene), where X is an anionic group, are also known.[27,37–41]

The reactivities of these new $CpTiRL_x$ and Cp^*TiRL_x complexes toward alkenes have also been investigated. We show that ethylene and propene are catalytically oligomerized to a distribution of short-chain alkene products that is identical to that generated in the Alphabutol process. We have been able to identify some of the catalytic intermediates, all of which are titanium(II) species, thus lending support to the contention that this oxidation state catalyzes the oligomerization of alkenes by means of metallacyclopentane species and is almost certainly responsible for the chemistry seen in the Alphabutol process. Portions of this work have been reported previously.[42]

Results and Discussion

Synthesis of $CpTiX(dmpe)_2$ (X = Cl, Me, H). We investigated several different routes to mono(cyclopentadienyl)titanium(II) compounds. Others have shown that reduction of the titanium(IV) complex $CpTiCl_3$[43] with Mg at −30 °C in the presence of PMe_3 gives good yields of the Ti^{III} complex $CpTiCl_2(PMe_3)_2$.[44] Interestingly, previous attempts to reduce $CpTiCl_3$ with the stronger reductant sodium naphthalenide in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) resulted in the isolation of the Ti^{IV} species $CpTiCl_3(dmpe)$; lower oxidation state species are undoubtedly generated in this reaction, but were not isolated.[45] We find that reduction of $CpTiCl_3$ with 2 equiv of sodium amalgam in the presence of dmpe affords the titanocene complex $Cp_2Ti(dmpe)$ as the principal isolable product. This complex, which previously had been prepared by treatment of $TiCl_2(dmpe)_2$ with NaCp,[46] shows a characteristic peak at δ 69.2 in its $^{31}P\{^1H\}$ NMR spectrum. Attempts to reduce $CpTiCl_3$/dmpe mixtures with other conventional reductants such as sodium or magnesium have not afforded any isolable titanium(II) products. A different approach, treatment of $TiCl_2(dmpe)_2$ with 1 equiv of NaCp, also affords only the titanocene complex $Cp_2Ti(dmpe)$.

We subsequently turned to *n*-butyllithium as a potential reducing agent. The use of this reagent as a reductant in early transition metal chemistry is well precedented.[47,48] We find that treatment of $CpTiCl_3$with 1 equiv of $LiBu^n$ in the presence of dmpe generates the known[49] titanium(III) species $CpTiCl_2(dmpe)$. Treatment of $CpTiCl_3$ with 2 equiv of $LiBu^n$ in the presence of dmpe gives low yields of a mixture of the metallocene $Cp_2Ti(dmpe)$ and a second species tentatively formulated as $CpTiCl(dmpe)_2$ on the basis of its NMR spectra. Fortunately, we find that treatment of the titanium(III) compound[50] $[CpTiCl_2]_n$ with 1 equiv of $LiBu^n$ in

---

(19) Fregonese, D.; Mortara, S.; Bresadola, S. *J. Mol. Catal. A* **2001**, *172*, 89–95.

(20) Zakharov, V. A.; Makhtarulin, S. I.; Poluboyarov, V. A.; Anufrienko, V. F. *Makromol. Chem.* **1984**, *185*, 1781–1793.

(21) Al-Arifi, A. S. N. *J. Appl. Polym. Sci.* **2004**, *93*, 56–62.

(22) Werber, F. X.; Benning, C. J.; Wszolek, W. R.; Ashby, G. E. *J. Polym. Sci. Part A-1* **1968**, *6*, 743–754.

(23) Chien, J. C. W.; Nozaki, T. *J. Polym. Sci. A, Polym. Chem.* **1991**, *29*, 505–514, and references therein.

(24) Kim, S. H.; Somorjai, G. A. *Proc. Natl. Acad. Sci.* **2006**, *103*, 15289–15294, and references therein.

(25) Albizzati, E.; Giannini, U.; Balbontin, G.; Camurati, I.; Chadwick, J. C.; DallOcco, T.; Dubitsky, Y.; Calimberti, M.; Morini, G.; Maldotti, A. *J. Polym. Sci., Part A* **1997**, *35*, 2645–2652.

(26) Kaminsky, W.; Park, Y. W. *Macromol., Rapid Commun.* **1995**, *16*, 343–346.

(27) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132–3134.

(28) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339–1348.

(29) Jensen, J. A.; Wilson, S. R.; Schultz, A. J.; Girolami, G. S. *J. Am. Chem. Soc.* **1987**, *109*, 8094–8096.

(30) Spencer, M. D.; Morse, P. M.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 2057–2059.

(31) Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1997**, *16*, 3055–3067.

(32) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2107–2113.

(33) Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, *29*, 4167–4169.

(34) Frerichs, S. R.; Stein, B. K.; Ellis, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 5558–5560.

(35) Ellis, J. E.; Stein, B. K.; Frerichs, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 4066–4075.

(36) Graham, T. W.; Kickham, J.; Courtenay, S.; Wei, P. R.; Stephan, D. W. *Organometallics* **2004**, *23*, 3309–3318.

(37) Blenkers, J.; Hessen, B.; van Bolhuls, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459–469.

(38) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105–119.

(39) Abboud, K. A.; Nickias, P. N.; Chen, E. Y. X. *Acta Crystallogr. C* **2001**, *57*, 1408–1409.

(40) Dahlmann, M.; Schottek, J.; Fröhlich, R.; Kunz, D.; Nissinen, M.; Erker, G.; Fink, G.; Lkeinschmidt, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1881–1886.

(41) Tomaszewski, R.; Lam, K.-C.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174–4182.

(42) You, Y.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 4655–4657.

(43) KingR. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. *1*, p 78.

(44) Razavi, A.; Mallin, D. T.; Day, R. O.; Rausch, M. D.; Alt, H. G. *J. Organomet. Chem.* **1987**, *333*, C48−C52.

(45) Hughes, D. L.; Leigh, G. J.; Walker, D. G. *J. Organomet. Chem.* **1988**, *355*, 113–119.

(46) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2347–2350.

(47) Green, M. L. H.; Silverthorn, W. E. *J. Chem. Soc., Dalton Trans.* **1973**, 301–306.

(48) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1860–1869.

(49) Green, M. L. H.; Lucas, C. R. *J. Organomet. Chem.* **1974**, *73*, 259–264.

(50) Lucas, C. R.; Green, M. L. H. *Inorg. Synth.* **1976**, *16*, 237–240.

the presence of dmpe in diethyl ether at −78 °C gives a dark brown-red solution, from which black crystals of $CpTiCl(dmpe)_2$ (**1**) can be obtained in 51% yield after crystallization from pentane or diethyl ether:

$$1/n[CpTiCl_2]_n + LiBu^n + 2\ dmpe \rightarrow \underset{\mathbf{1}}{CpTiCl(dmpe)_2} + LiCl + \text{“}C_4H_9\text{”}$$

This complex is the titanium analogue of the known zirconium(II) and hafnium(II) species $CpZrCl(dmpe)_2$ and $CpHfCl(dmpe)_2$.[51–54]

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **1** at −80 °C are consistent with a pseudooctahedral structure in which the Cp ring (counted here as occupying one coordination site) is trans to the chloride ligand. Specifically, the PMe_2 groups are diastereotopic, one methyl environment being proximal to the Cp ring and the other distal. The ^1H NMR spectrum contains two backbone PCH_2 resonances for the same reason, whereas the $^{13}C\{^1H\}$ NMR spectrum shows, as expected, that there is only one PCH_2 resonance. The protons of the Cp group resonate at δ 4.25, a chemical shift that is considerably shielded relative to the δ 6.5 shift seen for $CpTiCl_3(dmpe)$.[45] The increased shielding of the Cp resonances in **1** is consistent with its low oxidation state. The $^{31}P\{^1H\}$ NMR chemical shift of **1** is δ 34.3.

The NMR resonances of **1** are relatively broad even at −80 °C. For example, the ^1H NMR resonance due to the Cp ring in **1** has a line width of 15.0 Hz; this value increases to 28.5 Hz at room temperature. The variable-temperature $^{31}P\{^1H\}$ NMR spectra of an approximately equimolar mixture of **1** and free dmpe suggest that the phosphine ligands in **1** are labile; the line widths of both resonances are ~15 Hz at −80 °C and about 200 and 350 Hz for **1** and dmpe, respectively, at room temperature. Exchange between **1** and free dmpe is the simplest explanation of the temperature-dependent behavior seen. The possibility that molecules of **1** are engaged in a singlet/triplet equilibrium, as has been seen for some other titanium(II) species,[55] can be ruled out because this mechanism should selectively broaden the resonance due to **1**.

The titanium(II) complex **1** is a good starting material for the preparation of other mono(cyclopentadienyl)titanium(II) complexes. Treatment of **1** with 1 equiv of methyllithium affords the new titanium(II) alkyl $CpTiMe(dmpe)_2$ (**2**) as black crystals in 56% yield. A similar reaction of **1** with 1 equiv of *n*-butyllithium affords the titanium(II) hydride $CpTiH(dmpe)_2$ (**3**) in 53% yield:

$$CpTiCl(dmpe)_2 + LiMe \rightarrow \underset{\mathbf{2}}{CpTiMe(dmpe)_2} + LiCl$$

$$CpTiCl(dmpe)_2 + LiBu^n \rightarrow \underset{\mathbf{3}}{CpTiH(dmpe)_2} + LiCl + C_4H_8$$

Presumably, the conversion of **1** to the hydride complex **3** involves a β-hydrogen elimination step.

Although pure samples of compounds **1**−**3** are stable at room temperature in the solid state, solutions of the methyl complex **2** are best kept below 0 °C. In addition, significant amounts of the byproduct $Cp_2Ti(dmpe)$ form if the reaction solutions are kept too long at −10 °C (for compound **2**) or at room temperature (for compounds **1** and **3**).

The NMR spectra of the methyl complex **2** are similar to those of **1** except for the additional features due to the Ti-Me group. The ^1H NMR spectrum of **2** at −80 °C shows a quintet at δ −1.18 for the Ti-Me group ($^3J_{PH}$ = 9.2 Hz). This chemical shift is comparable to that of δ −1.86 seen for the Zr analogue, $CpZrMe(dmpe)_2$,[54] but it is deshielded relative to the δ −5.72 chemical shift seen for the 14-electron titanium(II) methyl complex $TiMe_2(dmpe)_2$.[29] The $^{13}C\{^1H\}$ NMR spectrum of **2** shows a quintet for the Ti-Me group at δ 11.3 ($^2J_{PC}$ = 10.6 Hz), which is upfield of the shift seen for $TiMe_2(dmpe)_2$ (δ 18.9);[29] the methyl resonance of $CpZrMe(dmpe)_2$ in the $^{13}C\{^1H\}$ NMR spectrum has not been reported. The NMR resonances for compound **2** are broad like those of **3**, probably for similar reasons.

In contrast, the NMR resonances for the hydride **3** are sharp even at room temperature (Figure 1). Presumably, the smaller steric demands of the hydride ligand reduce the steric repulsions, and the strong σ-donor ability of the hydride ligand should increase the extent of metal-to-phosphine π back-bonding. For both of these reasons, dissociation of the phosphine ligands should be suppressed. The most interesting feature of the ^1H NMR spectrum of **3** is the hydride resonance, which appears as a quintet at δ −0.05 with $^2J_{PH}$ = 55.5 Hz. For comparison, the chemical shifts of the titanium(II) carbonyl hydrides $CpTi(CO)_2(dmpe)H$ and $Cp^*Ti(CO)_2(dmpe)H$ are δ −1.65 and −1.71, respectively.[34,35] The chemical shift of the hydride ligand in $CpZrH(dmpe)_2$[54] has not been reported.

The solid state structures of **1**−**3** have been determined crystallographically (Figure 2). As expected from the NMR data, the geometries of the complexes are best described as distorted pseudo-octahedra (considering the Cp group to occupy one coordination site). The Cp−Ti−X unit is nearly linear: the Cp−Ti−X angle is 177.2°, 177.2°, and 175.1° for **1**, **2**, and **3**, respectively. For steric reasons, the four phosphorus atoms in each complex are displaced toward the X group (X = Cl, Me, H) and away from the Cp ring.

The metal−ligand distances are unusually long (Table 1), and this phenomenon strongly suggests that these complexes are severely crowded. For example, the Ti−X bond distances are Ti−Cl = 2.612(1) Å in **1**, Ti−CH_3 = 2.385(2) Å in **2**, and Ti−H = 1.96(6) Å in **3**; these distances are all considerably longer than the corresponding Ti−X distances in $TiCl_2(dmpe)_2$ (2.446(4) Å),[28] $TiMe_2(dmpe)_2$ (2.219(2) Å),[29] and $CpTi(CO)_2(dmpe)H$ (1.75(7) Å).[34] In **1** the Ti−Cl distance is

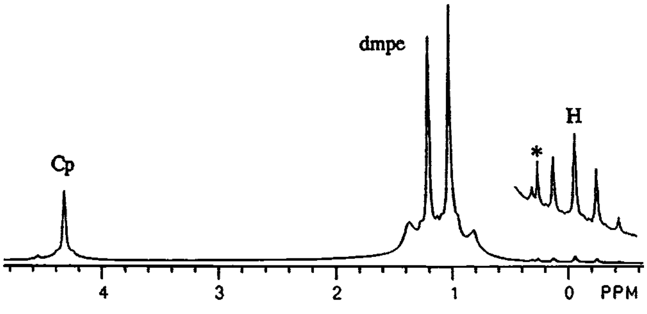


Figure 1. 300 MHz ^1H NMR spectrum of $CpTiH(dmpe)_2$, **3**, in C_6D_6 at 25 °C. The asterisk indicates peaks due to stopcock grease.

---

(51) Gambarotta, S.; Chiang, M. Y. *Chem. Commun.* **1987**, 698–699.

(52) Wielstra, Y.; Gambarotta, S.; Chiang, M. Y. *Organometallics* **1988**, *7*, 1866–1867.

(53) Wielstra, Y.; Gambarotta, S.; Roedelof, J. B.; Chiang, M. Y. *Organometallics* **1988**, *7*, 2177–2182.

(54) Wielstra, Y.; Gambarotta, S.; Spek, A. L. *Organometallics* **1990**, *9*, 572–577.

(55) The titanium(II) compound $TiCl_2(dmpe)_2$[21] exists as a mixture of singlet and triplet species in solution. In contrast, $Ti(BH_4)_2(dmpe)_2$[22,25] is a triplet molecule, whereas $TiMe_2(dmpe)_2$[22] is diamagnetic. In all of these molecules, the magnetism is dependent on the magnitude of the electron−electron repulsions and the splitting between the d_{xy} and the d_{xz}, d_{yz} orbitals.[26]

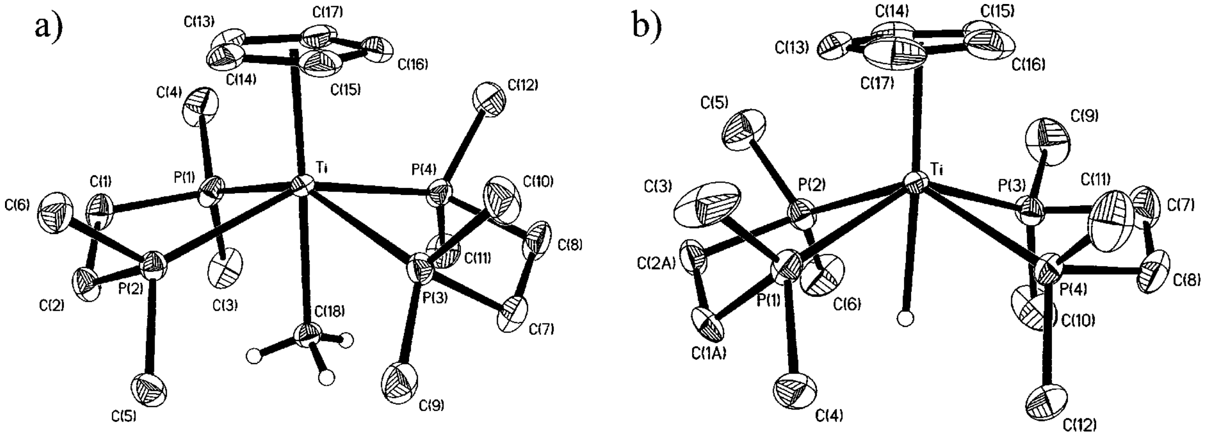


Figure 2. ORTEP plot of (a) $CpTiMe(dmpe)_2$, **2**; (b) $CpTiH(dmpe)_2$, **3**. The 35% probability ellipsoids are shown, except for the hydrogen atoms, which are depicted as arbitrarily sized spheres.

Table 1. Important Bond Distances (Å) and Angles (deg) for 1−3

distance/angle	$CpTiCl(dmpe)_2$	$CpTiMe(dmpe)_2$	$CpTiH(dmpe)_2$
Ti−C (13)	2.316 (3)	2.322 (3)	2.294 (5)
Ti−C (14)	2.271 (3)	2.319 (3)	2.338 (5)
Ti−C (15)	2.365 (3)	2.403 (3)	2.415 (5)
Ti−C (16)	2.470 (3)	2.482 (3)	2.411 (5)
Ti−C (17)	2.445 (3)	2.431 (3)	2.336 (5)
Ti−X	2.6119 (11)	2.385 (2)	1.96 (6)
Ti−P (1)	2.6071(12)	2.5627(9)	2.506(2)
Ti−P(2)	2.5951 (12)	2.5724 (9)	2.494 (2)
Ti−P (3)	2.5924 (13)	2.5629 (9)	2.514 (2)
Ti−P (4)	2.6135 (13)	2.5854 (9)	2.539 (2)
P (1)−Ti−P (2)	77.09 (4)	77.26 (3)	77.21 (5)
P (3)−Ti−P (4)	77.11 (4)	77.50 (3)	76.30 (5)
P (1)−Ti−P (4)	98.21 (4)	96.27 (3)	90.68 (5)
P (2)−Ti−P (3)	91.87 (4)	92.80 (3)	90.05 (6)
C (13)−Ti−X	149.17 (9)	150.51 (9)	144 (2)
C (14)−Ti−X	150.73 (9)	151.38 (10)	148 (2)
C (15)−Ti−X	150.76 (9)	150.45 (10)	155 (2)
C (16)−Ti−X	149.35 (8)	148.93 (10)	155 (2)
C (17)−Ti−X	148.59 (9)	148.91 (10)	148 (2)

remarkably similar to the Zr–Cl distance in $CpZrCl(dmpe)_2$ (2.629(2) Å),[51] despite the 0.1 Å difference in the ionic radii[56] of Ti and Zr. The Ti−H bond distance in **3** can also be compared to those in the Ti^{III} hydrides $Cp^*\{C_5Me_4CH_2(C_5H_3MeN)\}TiH$ (1.70(4) Å)[57] and $Cp_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)Ti_2(\mu\text{-}H)_2 \cdot 1.5C_6H_6$ (1.73(4) Å),[58] although these comparisons are made difficult by the large estimated standard deviations of these parameters.

The Ti−P bond distances are 2.602(1) Å in **1**, 2.571(1) Å in **2**, and 2.513(2) Å in **3**. Interestingly, these distances are similar to those seen for other Ti^{II} phosphine complexes: for example, the Ti−P distances in $TiCl_2(dmpe)_2$,[28] $TiMe_2(dmpe)_2$,[29] and $CpTiH(CO)_2(dmpe)$[34] are 2.586(5), 2.519(5), and 2.513(2) Å, respectively. One possibility is that the steric crowding in the $CpTiX(dmpe)_2$ molecules, which should lengthen the Ti−P bond distances relative to those in the $TiX_2(dmpe)_2$ analogues, are counterbalanced by the electron-donating character of the cyclopentadienyl ring, which should shorten the Ti−P bonds owing to π-back-bonding effects. In comparison, the Zr−P bond distance in $CpZrCl(dmpe)_2$ was determined to be 2.708(3) Å.[51]

Another interesting feature of the structures of **1**−**3** is that the Cp rings are slightly tilted so that the Ti−C distances are not all equal; this is not evidence of a change in hapticity (for example to η^3) because the planarity of the ring is preserved. The "tilt angles" (defined as the angle between the metal−centroid vector and the vector normal to the Cp plane) for **1**−**3** are 6.3°, 5.4°, and 4.0°, respectively. The tilt angle thus decreases as the size of the group trans to the Cp ring decreases. The tilting of Cp rings in other systems has been explained in terms of both electronic[59] and steric[45,60] effects; because compounds **1**−**3** are 18-electron molecules (and thus not susceptible to electronically driven tilting phenomena), the tilting seen here is certainly the result of steric repulsions. For instance, C(16) and C(17), which form the longest Ti−C distances, are located near two of the dmpe methyl groups. The nonbonded contacts C(16)−P(4) (3.16 Å), C(16)−C(11) (3.22 Å), C(17)−P(1) (3.15 Å), C(17)−C(3) (3.20 Å), H(16)−C(11) (2.52 Å), and H(17)−C(3) (2.63 Å) are shorter than the sum of the van der Waals radii[61] of the respective atoms (C−P = 3.60 Å; C−C = 3.70 Å; and C−H = 3.20 Å).

Synthesis of $Cp^*Ti(BH_4)(dmpe)$ and $Cp^*Ti(BH_4)(\eta^2$-trimpsi). We have also studied the synthesis of titanium(II) complexes bearing one pentamethylcyclopentadienyl ring. Treatment of Cp^*TiCl_3 with various reductants in the presence of tertiary phosphines such as PMe_3 or dmpe has not been successful: no lower valent titanium products could be isolated. We found, however, that reduction of the titanium(III) borohydride complex $[Cp^*TiCl(BH_4)]_2$ to titanium(II) products can be carried out in the same way as for the Cp compounds above. Thus, treatment of $[Cp^*TiCl(BH_4)]_2$ at −78 °C in Et_2O with $LiBu^n$ in the presence of tertiary phosphines yields complexes of the type $Cp^*Ti(BH_4)(\eta^2\text{-}PP)$, where PP is dmpe (**4**) or trimpsi (**5**); trimpsi = (*tert*-butyl)tris(dimethylphosphinomethyl)silane. These complexes are obtained as dark brown crystals in 65% and 55% yield, respectively, after crystallization from pentane.

$$1/2\ [Cp^*TiCl(BH_4)]_2 + LiBu^n + PP \rightarrow$$

$$Cp^*Ti(BH_4)(PP) + LiCl + \text{“}C_4H_9\text{”}$$

$$PP = \text{dmpe},\ \mathbf{4}$$

$$\text{trimpsi},\ \mathbf{5}$$

Only one other titanium(II) tetrahydroborate complex is known: $Ti(BH_4)_2(dmpe)_2$.[29,32] One titanium(0) tetrahydroborate complex,

---

(56) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(57) Pattiasina, J. W.; van Bolhuis, F.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 330–331.

(58) Troyanov, S. I.; Antropiusova, H.; Mach, K. *J. Organomet. Chem.* **1992**, *427*, 49–55.

(59) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(60) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 2033–2040.

(61) Pauling, L. *The Nature of the Chemical Bond,* 3rd ed.; Cornell University Press, 1960; p 260.

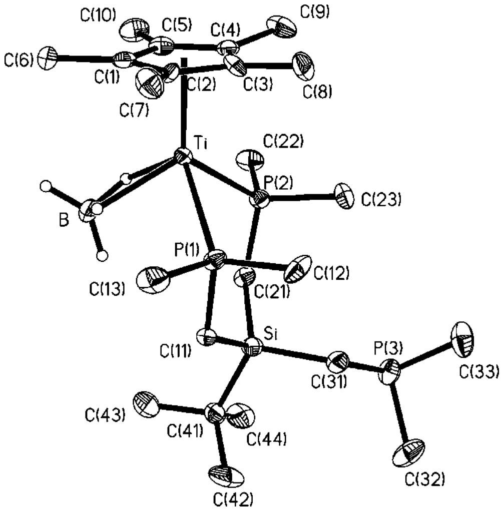


Figure 3. ORTEP plot of Cp*Ti(BH_4)(trimpsi), **5**. The 35% probability ellipsoids are shown, except for the hydrogen atoms, which are depicted as arbitrarily sized spheres.

[$Ti(BH_4)(CO)_4^-$], has been described;[62] all other titanium tetrahydroborates are trivalent: among the known compounds are $Cp_2Ti(BH_4)$,[63,64] [$CpTiCl(BH_4)]_2$,[65] [$Cp^*TiCl(BH_4)_2]_2$,[66] and a series of $Ti(BH_4)_3(L)_2$ complexes where L is an ether or phosphine.[67–69]

The IR spectra of **4** and **5** both contain two strong terminal B−H stretching bands between 2300 and 2400 cm^{-1} and bridging B−H stretching bands near 2240 and 2080 cm^{-1} that are characteristic of bidentate BH_4 groups.[70] It has been suggested previously that the frequency difference between the terminal and bridging B−H stretches of η^2-BH_4 groups varies systematically with the ionicity of the M−BH_4 interaction.[32] From the criteria specified previously, we can conclude that the Ti−(η^2-BH_4) interactions in **4** and **5** are among the intermediate type: neither covalent nor ionic bonding predominates.

^{1}H NMR studies of **4** and **5** clearly show that these molecules are paramagnetic. For example, the resonance due to the methyl groups of the Cp* ligand appears at δ 57; the methyl and methylene protons of the phosphine ligands have been shifted as well, although not to as great a degree.

The solid state structure of the trimpsi complex **5** has been determined crystallographically (Figure 3). An interesting feature of **5** is that the potentially tridentate ligands BH_4^- and trimpsi are both bidentate. The overall coordination environment about the titanium center may be described as a four-legged piano stool (or a three-legged piano stool if the small-bite η^2-BH_4 ligand is considered to occupy one coordination site).

The average Ti−P bond distance of 2.570(2) Å in **5** (Table 2) is similar to those of other Ti^{II} phosphine complexes (see above), but is significantly shorter than that in $Ti(BH_4)_2(dmpe)_2$ (2.626(1) Å).[22,25] Similarly, the Ti···B contact of 2.445(7) Å in **5** is shorter than that of 2.534(3) Å in $Ti(BH_4)_2(dmpe)_2$, but corresponds well with the value of 2.46 Å predicted for a normal Ti^{II}−(η^2-BH_4) interaction.[32] The crystallographic result supports the conclusion from the IR spectrum: **5** has a much more covalent Ti−BH_4 interaction than that seen in $Ti(BH_4)_2(dmpe)_2$, which has considerable ionic character.

Table 2. Important Bond Distances (Å) and Angles (deg) for 5

Distances			
Ti−P (1)	2.571 (2)	Ti−B	2.445 (7)
Ti−P (2)	2.568 (2)	Ti−H (1)	2.02 (4)
Ti−C (1)	2.342 (5)	Ti−H (2)	1.97 (5)
Ti−C (2)	2.340 (5)	B−H (1)	1.14 (5)
Ti−C (3)	2.366 (5)	B−H (2)	1.11 (5)
Ti−C (4)	2.408 (5)	B−H (3)	1.05 (6)
Ti−C (5)	2.379 (5)	B−H (4)	0.98 (6)
Angles			
H (1)−B−H (2)	106 (3)	H (1)−Ti−H (2)	54 (2)
H (3)−B−H (4)	121 (5)	P (1)−Ti−P (2)	86.48 (5)

We have briefly investigated the reactivity of the Cp*Ti^{II} compounds **4** and **5**. We have been unable to isolate organometallic products from the reaction solutions generated by treatment of **4** or **5** with organolithium reagents (LiR where R = Me, CH_2CMe_3, CH_2SiMe_3, or $CH(SiMe_3)_2$) or organopotassium reagents (KCH_2Ph). If the reactions are conducted at 0 °C, starting material can be recovered nearly quantitatively from the reaction mixtures; if the reactions are conducted at room temperature, decomposition ensues and no well-defined product is isolated.

Reactions of the New Titanium(II) Complexes with Ethylene. The chloro, methyl, and hydride compounds **1**−**3** react with ethylene to form mostly dimers and branched trimers; no linear trimers are seen.[71] Thus, addition of ethylene (15 equiv) to toluene-d_8 solutions of **1**−**3** at room temperature results in the formation of 1-butene, 3-methyl-1-pentene, and 2-ethyl-1-butene within 1 hour as monitored by NMR spectroscopy. The 1-butene is the first oligomer to be generated, whereas the trimers appear later in the oligomerization process; a typical product distribution after the ethylene is consumed is a 70:15:15 ratio of 1-butene, 3-methyl-1-pentene, and 2-ethyl-1-butene. Trace amounts of butane and 3-methylpentane are also generated; presumably, these alkanes arise via hydrolysis of important catalytic intermediates. The product distributions are very similar to those generated by the catalysts used in the Alphabutol process, which are prepared from titanium(IV) alkoxides and trialkylaluminum reagents.[8–14] Over a period of tens of hours, the 1-butene is slowly isomerized to a mixture of 1-butene and *cis*- and *trans*-2-butene in a 2:1:1 relative ratio.

The rate of catalysis decreases in the order hydride **3** > methyl **2** > chloride **1**. The hydride compound **3** converts 15 equiv of ethylene completely into the above oligomers in a few minutes at room temperature or in less than 1 h at 5 °C. The average turnover rate is about 1000 h^{-1} at room temperature and 1 atm, or about 25 000 g h^{-1} (mol catalyst)$^{-1}$. At the end of the oligomerization reaction, the ^{1}H NMR resonances due to **3** are still strong. Thus, unlike the analogous zirconium system,[54] insertion of ethylene into the metal−H bond is (surprisingly!) unfavorable.

The Cp* compound **4** also catalyzes the oligomerization of ethylene, but much more slowly than the Cp compounds. Only

---

(62) Fischer, P. J.; Young, V. G.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 195–197.

(63) Nöth, H.; Hartwimmer, R. *Chem. Ber.* **1960**, *93*, 2238–2245.

(64) Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 232–236.

(65) Semenenko, K. N.; Lobkovskii, E. B.; Shumakov, A. L. *J. Struct. Chem. (Engl. Transl.)* **1976**, *17*, 912–914.

(66) Kim, D. Y.; You, Y. J.; Girolami, G. S. *J. Organomet. Chem.*, in press.

(67) Franz, H.; Fusstetter, H.; Nöth, H. *Z. Anorg. Allg. Chem.* **1976**, *427*, 97–113.

(68) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644.

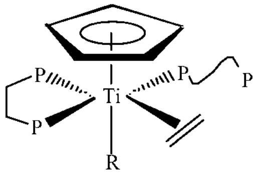
(69) Goedde, D. M.; Girolami, G. S. *Inorg. Chem.* **2006**, *45*, 1380–1388.

(70) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263–293.

(71) For a review of catalytic ethylene dimerization and oligomerization processes, see: Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 1–121.

traces of 1-butene are observed in the $^{13}C\{^1H\}$ NMR spectrum after a C_6D_6 solution of **4** and ethylene has been kept at room temperature for 4 h. Over a period of several days, the ethylene is oligomerized to a mixture of 1-butene, 3-methyl-1-pentene, and 2-ethyl-1-butene in a ratio of approximately 48:32:20. Because the catalytic rate is slow, decomposition of the catalytic intermediates is more prevalent. Thus, significant amounts of butane and 3-methylpentane are also produced: the butane to 1-butene ratio is 1:1.4, and the 3-methylpentane to 2-ethyl-1-butene ratio is 1:2.9.

Low-temperature NMR studies have allowed us to observe organotitanium intermediates in the catalytic cycle. When the hydride complex **3** in toluene is treated with excess $^{13}C_2H_4$ at −80 °C, the $^{31}P\{^1H\}$ NMR spectrum shows that the predominant Ti-containing species in solution is still the starting material **3**. Small resonances at δ 28.5 and −12.2 due to a second species are also present, however. These resonances are assigned to the two ends of a chelating dmpe ligand bound to Ti, the two ends of which are trans to a unidentate dmpe and to a coordinated ethylene ligand, respectively. In addition, there is a broad resonance near δ −48 that is due to a bound unidentate dmpe ligand and free dmpe undergoing rapid chemical exchange. The $^{13}C\{^1H\}$ NMR spectrum of this solution contains doublets at δ 54.7 and 60.4 with $^1J_{CC} = 32.4$ Hz due to a coordinated ethylene ligand. The $^1J_{CC}$ coupling constant is comparable to that of 39.2 Hz found for the ethylene group in $TiMe_2(C_2H_4)(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$.[30] There are no resonances assignable to a ^{13}C-labeled ethyl ligand; this result is consistent with the finding above that ethylene does not insert into the Ti−H bond. Taken together, the NMR data are consistent with the conclusion that the resting state of the catalyst is the hydride **3**, but that in the presence of excess ethylene this species is in equilibrium with the titanium(II) ethylene complex $CpTiH(C_2H_4)(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$, with the following structure (R = H):



The presence of two $^{13}C\{^1H\}$ NMR resonances for the ethylene ligand is consistent with the low symmetry of this structure. It is probable that the ethylene ligand lies in the same plane as the three coordinated phosphorus atoms; such a geometry maximizes the back-bonding from the filled titanium d_{xy} orbital to the ethylene π^* MO. The inequivalence of the two ends of the ethylene ligand means that rotation of the ethylene ligand about the Ti−ethylene axis must be slow on the NMR time scale. This observation also is consistent with the proposed structure: back-bonding to the d_{xy} orbital would be lost if the ethylene ligand were to rotate about the Ti−ethylene bond axis. A similar structure is adopted by $TiMe_2(C_2H_4)(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$.[30]

When the sample of $(dmpe)_2$ and excess $^{13}C_2H_4$ is warmed to −50 °C, new doublets ($^1J_{CC} \approx 35$ Hz) appear at δ 88.5, 64.0, 62.0, 58.0, and −21.5 due to other organotitanium complexes. The chemical shifts are consistent with the presence of titanacyclopentanes, titanium alkenes, and titanium 1-butenyl compounds (see below).

Similar results are obtained when solutions of the methyl complex **2** and excess ethylene are allowed to stand at −50 °C for 20 min, except that the resting state of the catalyst is a coordinated ethylene complex, and only small amounts of the starting material **2** are present. The $^{13}C\{^1H\}$ NMR spectrum of this sample taken at −80 °C contains new resonances for a coordinated ethylene ligand at δ 50.2 and 61.6. In the $^{31}P\{^1H\}$ NMR spectrum of the same sample, equal-intensity resonances are apparent at δ 34.5 and 7.9, due to a chelating dmpe ligand bound to Ti, and a broad resonance near δ −48 due to rapid chemical exchange between a bound unidentate dmpe ligand and free dmpe. In the ^1H NMR spectrum, there is a new resonance at δ −0.8 due to the Ti−Me group of this ethylene coordination complex. As for the Ti−H complex, there is no evidence of insertion of ethylene into the Ti−Me bond; no propene is evident among the organic products, for example. All of these features are attributable to the Ti^{II} alkyl/alkene complex $CpTiMe(C_2H_4)(\eta^2\text{-dmpe})(\eta^1\text{-dmpe})$.

Having established that the titanium(II) complexes react with ethylene to generate titanium(II) ethylene products without insertion into the Ti−H or Ti−Me bond, we turn to the question of the mechanism by which ethylene is oligomerized to the observed distribution of dimers and trimers. The related titanium(II) compound $TiMe_2(dmpe)_2$[28,29] and several other early transition compounds with d^2 electronic configurations[52,54,72–75] are known to oligomerize alkenes. Invariably, the catalytic mechanism involves coupling two ethylene ligands to form metallacyclopentane intermediates,[76–78] followed by β-hydrogen elimination to form a 3-butenyl/hydride intermediate that can reductively eliminate 1-butene. A similar mechanism is undoubtedly responsible for the dimerization of ethylene to 1-butene, which is subsequently isomerized to *cis*- and *trans*-2-butene under the catalytic conditions. Interestingly, in our titanium complexes, we do not see the quantitative conversion to a butadiene complex, as seen in the analogous reaction of $CpZr(dmpe)_2Me$ with ethylene.[54]

The ethylene trimers are secondary products formed by cross-coupling of ethylene and the initial dimerization product, 1-butene. The exclusive formation of the branched trimers 3-methyl-1-pentene and 2-ethyl-1-butene, with no formation of linear trimers, provides a key mechanistic insight. Coupling of ethylene and 1-butene can give two possible metallacyclic intermediates: intermediate **I**, in which the ethyl substituent is attached to β-carbon atom of the metallacyclopentane ring, and intermediate **II**, in which the ethyl substituent is in the α-position (see Scheme 1). Because no linear hexenes are seen among the products, the formation of intermediate **II** must be disfavored, most likely due to unfavorable steric repulsions between the α-ethyl substituent and the crowded titanium center. Scheme I also shows that the β-ethylmetallacyclopentane intermediate **I** can undergo a β-hydrogen elimination/reductive elimination sequence in two different ways; the observed 1:1 ratio of 3-methyl-1-pentene and 2-ethyl-1-butene shows that these two pathways are followed at nearly identical rates.

---

(72) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353–366.

(73) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315–1317.

(74) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610–5618.

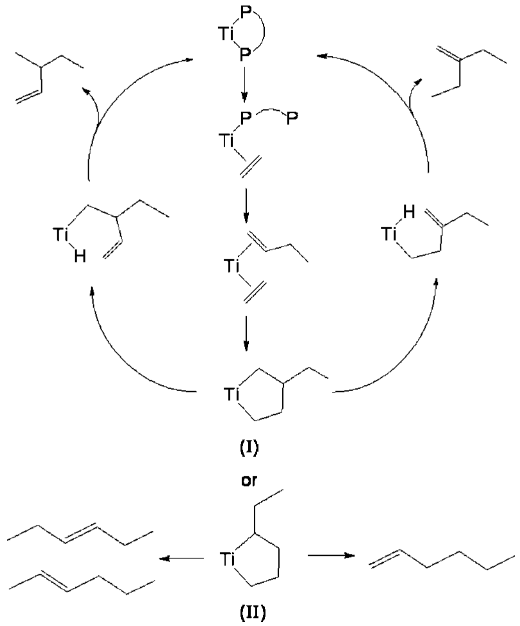
(75) There is some evidence that the oligomerization of alkenes by titanium complexes bearing ansa benzylcyclopentadienyl ligands occurs by means of titanium(II) intermediates. See: Hessen, B. *J. Mol. Catal.* **2004**, *213*, 129–135. de Bruin, T. J. M.; Magna, L.; Raybaud, P.; Toulhoat, H. *Organometallics* **2003**, *22*, 3404−3413. Tobisch, S.; Ziegler, T. *J. Am. Chem. Soc.* **2004**, *126*, 9059−9071.

(76) Zheng, F.; Sivaramakrishna, A.; Moss, J. R. *Coord. Chem. Rev.* **2007**, *251*, 2056–2071.

(77) Blom, B.; Clayton, H.; Kilkenny, M.; Moss, J. R. *Adv. Organomet. Chem.* **2006**, *54*, 149–205.

(78) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136–1143.

Scheme 1. Metallacyclopentane Mechanism for Coupling of Ethylene and 1-Butene



One alternative mechanism involves sequential ethylene insertion into a Ti−R or Ti−H bond followed by β-elimination; this mechanism is often responsible for the oligomerization of ethylene by late transition metal catalysts.[79] This mechanism can be ruled out because it predicts incorrectly that linear hexenes should be formed. Furthermore, the methyl complex **2** should react with ethylene to give 1 equiv of propene (or a higher odd-carbon alkene); no such odd-carbon products are detected.[80] The exclusive formation of branched hexenes also rules out a mechanism involving metallacycloheptane intermediates, which are responsible for ethylene trimerization by certain chromium and tantalum catalysts.[81–87] Thus, we conclude that these titanium(II) systems oligomerize ethylene via a Ti^{IV} metallacyclopentane intermediate, which subsequently undergoes β-H migration and reductive elimination to regenerate the Ti^{II} center and afford the observed oligomeric products.

One important and industrially relevant conclusion of our work stems from the close similarity of our distributions of ethylene oligomers to those seen in the Alphabutol process.[8–14] This similarity strongly suggests that the catalytically active species in this latter process are almost certainly titanium centers in the 2+ oxidation state, which oligomerize ethylene by means of titanacyclopentane intermediates.[13] In fact, we propose that the oligomerization of ethylene to dimers and trimers by titanium-based catalysts is diagnostic of the presence of the titanium(II) oxidation state. Finally, the oxidation state of the catalytically active titanium centers is very likely to be responsible for the different chemistry seen in the Alphabutol and heterogeneous Ziegler−Natta processes: the former is based on titanium(II), whereas the latter is based on a higher oxidation state, either titanium(III) or titanium(IV).

Experimental Section

All experiments were conducted under argon using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone immediately before use. The compounds (CpTiCl$_2$)$_n$,[50] [Cp*TiCl(BH$_4$)]$_2$,[65] 1,2-bis(dimethylphosphino)ethane (dmpe),[88] and (*tert*-butyl)tris(dimethylphospinomethyl)silane (trimpsi)[89] were prepared according to literature procedures. The reagents LiBu^n, LiMe, and LiBH$_4$ were purchased from Aldrich and used as received. Ethylene (Matheson) was purified by sequential passage through concentrated H$_2$SO$_4$, NaOH pellets, molecular sieves (Linde 4A), and BTS catalysts (BASF). ^{13}C$_2$H$_4$ (Isotec) was used without purification.

Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 1750 infrared Fourier transform spectrometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus in sealed capillaries under argon. NMR studies were carried out on General Electric QE300 and GN300NB spectrometers. Chemical shifts are reported in δ units (positive chemical shifts to higher frequency) relative to TMS. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the University of Illinois; some of the carbon analyses are slightly low, probably owing to incomplete combustion related to the formation of refractory titanium carbide.

(Cyclopentadienyl)chlorobis[1,2-bis(dimethylphosphino)ethane]titanium(II), CpTiCl(dmpe)$_2$, 1. A suspension of (CpTiCl$_2$)$_n$ (2.59 g, 14 mmol) in diethyl ether (90 mL) was cooled to −72 °C, and to the mixture were added dmpe (5 mL, 30 mmol) and *n*-butyllithium (8.8 mL of a 1.6 M solution in hexanes, 14 mmol). The mixture was allowed to warm to room temperature over 1.5 h. The solution turned brown and a gas was generated. After the mixture had been stirred for an additional 2 h, the solvent was removed under vacuum. The brown residue was washed quickly with pentane (2 × 15 mL); the wash solutions contain Cp$_2$Ti(dmpe). The residue was extracted with pentane (800 mL), and the extract was filtered, concentrated to 750 mL, and cooled to −20 °C. The black prismatic crystals were isolated by filtration and dried. One additional crop of crystals could be obtained by concentration and cooling of the mother liquors. Subsequent crops were contaminated by impurities such as Cp$_2$Ti(dmpe). Yield: 3.24 g (51%). Mp: 117 °C. Anal. Calcd: C, 45.5; H, 8.31; P, 27.6; Cl, 7.90; Ti, 10.7. Found: C, 45.1; H, 8.39; P, 27.2; Cl, 7.68; Ti, 10.8. ^{1}H NMR (C$_7$D$_8$, −80 °C): δ 4.25 (s, Ti-Cp), 1.67 (s, PCH$_2$), 1.38 (s, PMe$_2$), 0.65 (s, PCH$_2$ + PMe$_2$). ^{13}C{^{1}H} NMR (C$_7$D$_8$, −80 °C): δ 87.8 (s, Ti-Cp), 30.5 (br s, PCH$_2$), 18.6 (s, PMe$_2$), 17.0 (s, PMe$_2$). ^{31}P{^{1}H} NMR (C$_7$D$_8$, −80 °C): δ 34.3 (s). IR (cm^{-1}): 3084 w, 1426 m,

---

(79) Speiser, F.; Braunstein, P.; Saussine, W. *Acc. Chem. Res.* **2005**, *38*, 784–793.

(80) Wass, D. F. *Dalton Trans.* **2007**, 816–819.

(81) Andes, C.; Harkins, S. B.; Murtuza, S.; Oyler, K.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 7423–7424.

(82) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *J. Organomet. Chem.* **2004**, *689*, 3641–3668.

(83) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Haasbroek, D.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H. *J. Am. Chem. Soc.* **2005**, *127*, 10723–10730.

(84) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166–10167.

(85) Wass, D. F. *Dalton Trans.* **2007**, 816–819.

(86) Agapie, T.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2007**, *129*, 14281–14295.

(87) Another alternative mechanism, metathesis via alkylidene/hydride intermediates, can account for the products seen, but only if several factors hold true: the alkene must react with the alkylidene group to form a metallacyclobutane in which the alkene substituent resides on the β-carbon of the metallacycle, the hydride must add to the least substituted α-carbon of the metallacycle to form a new Ti-alkyl, and β-H elimination from the titanium alkyl must occur from the least substituted β-carbon. The first and last of these postulates would be understandable if the catalytic intermediates are sterically crowded, so that these steps occur in such a fashion to minimize steric repulsions between the ligands. The second of the postulates, however, generates the sterically most demanding titanium-alkyl intermediate, a feature that seems internally inconsistent with the other two. See: McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519–3520.

(88) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203–206.

(89) Gardner, T. G. Ph.D. Thesis, University of Illinois at Urbana−Champaign, 1989.

1295 m, 1271 m, 1117 w, 1075 w, 1007 m, 936 s, 924 s, 883 s, 864 w, 830 w, 796 m, 762 w, 733 w, 710 s, 686 m, 631 s.

(Cyclopentadienyl)methylbis[1,2-bis(dimethylphosphino)ethane]titanium(II), CpTiMe(dmpe)$_2$, 2. To a cold (−72 °C) suspension of CpTiCl(dmpe)$_2$ (1.28 g, 2.85 mmol) in diethyl ether (80 mL) was added methyllithium (2.6 mL of a 1.8 M solution in diethyl ether, 2.88 mmol). The resulting mixture was gradually warmed to −10 °C over 2 h and was maintained at that temperature for 5 h. The solvent was removed under vacuum, and the residue was extracted with pentane (140 mL) at 0 °C. The deep red extract was filtered, and the filtrate was concentrated to 70 mL and cooled to −20 °C. The black plates were collected by filtration and dried. Yield: 0.62 g (56%). Mp: 79−80 °C. Anal. Calcd: C, 50.5; H, 9.41; Ti, 11.2. Found: C, 49.7; H, 9.22; Ti, 11.4. ^{1}H NMR (C_7D_8, −80 °C): δ 4.37 (s, Ti-Cp), 1.44 (s, PCH_2), 1.21 (s, PMe_2), 0.87 (s, PMe_2), 0.70 (s, PCH_2), −1.18 (quintet, J_{PH} = 9.2 Hz, Ti-Me). $^{13}C\{^1H\}$ NMR (C_7D_8, −80 °C): δ 84.6 (s, Ti-Cp), 30.5 (br s, PCH_2), 18.9 (s, PMe_2), 18.5 (s, PMe_2), 11.3 (quintet, J_{PC} = 10.6 Hz, Ti-Me). $^{31}P\{^1H\}$ NMR (C_7D_8, −80 °C): δ 45.0 (s). IR (cm^{-1}): 1421 s, 1293 m, 1274 m, 1116 m, 1069 w, 1005 s, 931 vs, 904 s, 880 s, 858 w, 827 w, 781 s, 728 w, 702 s, 680 s, 620 s.

(Cyclopentadienyl)hydridobis[1,2-bis(dimethylphosphino)ethane]titanium(II), CpTiH(dmpe)$_2$, 3. To a cold (−72 °C) suspension of CpTiCl(dmpe)$_2$ (0.414 g, 0.92 mmol) in diethyl ether (60 mL) was added *n*-butyllithium (0.59 mL of a 1.6 M solution in hexanes, 0.94 mmol). The resulting mixture was warmed to 0 °C over 3 h and then was kept at room temperature for 1 h. The solvent was removed under vacuum, and the residue was extracted with pentane (50 mL). The brown-red extract was filtered, and the filtrate was concentrated to 10 mL and cooled to −20 °C. The resulting black crystals were isolated by filtration and dried. Yield: 0.20 g (53%). Mp: 137−139 °C. Anal. Calcd: C, 49.3; H, 9.25; P, 29.9; Ti, 11.6. Found: C, 48.2; H, 9.07; P, 30.5; Ti, 11.0. ^{1}H NMR (C_6D_6, 20 °C): δ 4.32 (s, Ti-Cp), 1.37 (s, PCH_2), 1.20 (s, PMe_2), 1.02 (s, PMe_2), 0.81 (s, PCH_2), −0.06 (quintet, J_{PH} = 55.5 Hz, Ti-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 85.4 (s, Ti-Cp), 33.2 (pseudo quintet, "J_{PC}" = 7.9 Hz, PCH_2), 26.1 (s, PMe_2), 20.0 (s, PMe_2). ^{31}P NMR (C_6D_6, 20 °C): δ 56.8 (br d, J_{PH} = 55.1 Hz). IR (cm^{-1}): 1420 s, 1330 m, 1286 m, 1269 s, 1109 m, 1065 w, 1000 m, 927 vs, 881 s, 823 w, 784 s, 705 s, 674 s, 624 s, 603 m, 453 m.

(Pentamethylcyclopentadienyl)(tetrahydroborato)[1,2-bis(dimethylphosphino)ethane]titanium(II), Cp*Ti(BH$_4$)(dmpe), 4. To a cold (−72 °C) suspension of [Cp*TiCl(BH$_4$)]$_2$ (0.137 g, 0.59 mmol) in diethyl ether (40 mL) were added *n*-butyllithium (0.37 mL of a 1.6 M solution in hexanes, 0.59 mmol) and 1,2-bis(dimethylphosphino)ethane (0.14 mL, 0.84 mmol). The mixture was allowed to warm to room temperature and then was stirred for 4 h. The solvent was removed under vacuum, and the residue was extracted with pentane (60 mL). The brown extract was filtered, and the filtrate was concentrated to 40 mL and cooled to −20 °C to afford dark brown crystals. Yield: 0.13 g (65%). Mp: 161−163 °C. Anal. Calcd: C, 55.2; H, 10.1; B, 3.11; Ti, 13.8. Found: C, 55.3; H, 10.2; B, 3.02; Ti, 12.7. ^{1}H NMR (C_6D_6, 20 °C): δ 65.7 (s, fwhm = 1700 Hz, Ti-Cp*), 22.3 (s, fwhm = 500 Hz, PCH_2 + PMe_2), −2.51 (s, fwhm = 240 Hz, PCH_2 + PMe_2). IR (cm^{-1}): 2358 s, 2329 s, 2233 m, 2081 s, 1415 s, 1327 m, 1298 w, 1280 m, 1124 s, 1086 w, 1024 w, 1007 w, 942 s, 927 s, 889 s, 860 w, 830 w, 788 w, 725 s, 697 s, 645 m.

(Pentamethylcyclopentadienyl)(tetrahydroborato)[η^2-(*tert*-butyl)tris(dimethylphosphino)silane]titanium(II), Cp*Ti(BH$_4$)(η^2-trimpsi), 5. To a cold (−72 °C) suspension of [Cp*TiCl(BH$_4$)]$_2$ (0.296 g, 1.27 mmol) in diethyl ether (50 mL) were added *n*-butyllithium (0.80 mL of a 1.6 M solution in hexanes, 1.28 mmol) and (*tert*-butyl)tris(dimethylphosphinomethyl)silane (0.50 mL, 1.34 mmol). The mixture was allowed to warm to room temperature and then was stirred for 4 h. The solvent was removed under vacuum, and the residue was extracted with pentane (100 mL). The brown extract was filtered, and the filtrate was concentrated to 60 mL and cooled to −20 °C to afford black crystals. Yield: 0.355 g (55%). Mp: 140−142 °C. Anal. Calcd: C, 54.3; H, 10.3; B, 2.13; P, 18.3; Ti, 9.42. Found: C, 53.4; H, 10.3; B, 2.10; P, 17.5; Ti, 9.42. ^{1}H NMR (C_6D_6, 20 °C): δ 57.8 (s, fwhm = 5800 Hz, Ti-Cp*), 34.6 (s, fwhm = 2700 Hz, Ti-PMe$_2$-*CH$_2$*), 15.7 (s, fwhm = 1100 Hz, Ti-PMe$_2$); 1.0 (m, Ti-PMe$_2$ + t-Bu + SiCH$_2$PMe$_2$), −5.3 (s, fwhm = 1700 Hz, Ti-PMe$_2$-*CH$_2$*). IR (cm^{-1}): 2388 s, 2352 s, 2245 w, 2082 s, 1364 s, 1314 m, 1290 m, 1280 m, 1130 vs, 1114 m, 1097 w, 1086 m, 1059 w, 1012 w, 936 vs, 903 vs, 867 s, 826 s, 784 vs, 766 s, 725 s, 706 m, 678 m, 640 m, 554 w.

Table 3. Crystal Data for 1−3 and 5

crystal data	**1**	**2**	**3**	**5**
M	448.7	428.28	414.25	508.36
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$Pbca$	$C2/c$	$P2_1/n$
a (Å)	9.996(3)	13.780(4)	11.419(5)	16.279(4)
b (Å)	13.711(4)	17.776(6)	14.684(6)	9.103(2)
c (Å)	17.241(6)	18.726(6)	26.877(9)	20.746(5)
β (deg)	98.46(3)	90	93.46(3)	100.13(2)
V (Å^3)	2337.3(13)	4587(3)	4498(3)	3026.4(12)
ρ_{calc} (g cm^{-3})	1.275	1.24	1.223	1.116
Z	4	8	8	4
μ (mm^{-1})	0.752	0.651	0.661	0.49
F(000)	952	1840	1776	1104
$\theta_{min.}$, $\theta_{max.}$ (deg)	1.91, 22.97	2.16, 24.97	1.52, 24.98	1.47, 24.97
total unique data	3244	4027	3918	5306
no. params	216	328	270	470
R_1 ($F_o^2 > 2\sigma(F_o^2)$)[a]	0.0339	0.0331	0.0493	0.0576
wR_2 (F^2, all data)[b]	0.0924	0.0893	0.1645	0.1483

[a] $R_1 = \sum|F_o| - |F_c| |/\sum|F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$. [b] $wR_2 = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all reflections.

Spectroscopic Studies of the Reactions of the Organotitanium Species with Ethylene. In a typical NMR study, a solution of the organotitanium reagent (0.08 mmol) in toluene-d_8 (0.8 mL) was transferred to a 5 mm NMR tube. The tube, which was fitted with a female joint and capped with a gas adapter, was connected to a gas manifold by means of a latex hose. Doubly labeled $^{13}C_2H_4$ (ca. 1.4 mmol; measured volumetrically) was condensed into the NMR tube, and the tube was flame-sealed and kept at −196 °C until it was inserted in the NMR probe. The course of the oligomerization process was followed as the samples warmed in the probe. The oligomerization products were determined by analysis of $^{13}C\{^1H\}$ NMR COSY spectra. At room temperature, the ^{13}C NMR chemical shifts of the products are as follows: 1-butene (δ 140.5, 113.5, 27.1, 13.3), *trans*-2-butene (δ 125.8, 18.9), *cis*-2-butene (δ 124.8, 18.9), 2-ethyl-1-butene (δ 152.8, 106.9, 29.3, 12.7), 3-methyl-1-pentene (δ 144.6, 112.8, 39.9, 29.5, 20.0, 11.9).

X-ray Crystallography.[90] X-ray quality crystals of **1**−**3** and **5** were obtained by crystallization from pentane at −20 °C. In each case, the single crystal was mounted to a thin glass fiber using Paratone-N oil. Data were collected at 198 K on an Enraf-Nonius CAD4 diffractometer. Crystallographic data are summarized in Table 3. The structures were solved by the Patterson method for **1** and by direct methods for **2**, **3**, and **5**. Vector map/E-map and unweighted difference Fourier calculations were applied to locate the correct positions for all the non-hydrogen atoms. All non-H atoms were refined with anisotropic thermal coefficients in the final cycle of full-matrix least-squares refinement on F^2. Independent isotopic displacement coefficients were refined for each hydrogen atom in **5**. The hydride atom in **3** was refined with an independent displacement parameter. All other H atoms in **1**−**3** were placed in idealized positions, with displacement parameters set equal to 1.2 times U_{eq} (methylene) or 1.5 times U_{eq} (methyl) of the adjacent non-H atom.

---

(90) For details of the crystallographic procedures and programs used, see: Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139–2144**.**

In **3**, the backbone carbons of one of the chelating dmpe ligands were disordered. The disordered dmpe ligands were restrained to equivalent geometry with an effective standard deviation of 0.03 Å. The site occupancy for the major conformer was 0.51(1).

Acknowledgment. We thank the American Chemical Society Petroleum Research Foundation for support of this research and Scott Wilson and Teresa Prussak-Wieckowska of the University of Illinois for assistance with the X-ray crystal structure determination.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**, **2**, **3**, and **5** are available free of charge via the Internet at http://pubs.acs.org.

OM701263V