Synthesis and Catalytic Activity of Mono(cyclopentadienyl)titanium(II) Complexes: X-ray Crystal Structures of CpTiX(Me2PCH2CH2PMe2)2 (X = Cl, Me, H) and Cp*Ti(η^2-BH4)[η^2-(Me2PCH2)3Si(t-Bu)]

Yujian You, Scott R. Wilson, and Gregory S. Girolami

The School of Chemical Sciences, The University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801

Received August 18, 1994

Summary: New mono(cyclopentadienyl)- and mono(pentamethylcyclopentadienyl)titanium(II) complexes have been prepared that are active for the oligomerization of ethylene to the dimer 1-butene and the trimers 2-ethyl-1-butene and 3-methyl-1-pentene. The mechanism of the catalysis is proposed to involve titanacyclopentane intermediates.

Low-valent organotitanium complexes continue to be of interest as potential catalysts for the polymerization of alkenes1 and as stoichiometric reagents in organic synthesis.2 Low-valent titanium complexes with one cyclopentadienyl ring are especially rare;3 we report here the synthesis and characterization of several new mono(cyclopentadienyl)titanium(II) complexes. The ability of these alkyl, hydride, and tetrahydroborate complexes to catalyze the oligomerization of ethylene will also be described.

Treatment of the titanium(II) compound (CpTicl2)5 with 1 equiv of n-butyllithium and 2 equiv of 1,2-bis(dimethyphosphino)ethane (dmpe) in diethyl ether at −78 °C, followed by warming to room temperature, gives a dark brown-red solution from which black crystals of mono(cyclopentadienyl)titanium(II) complex in good yield by using more conventional reducing agents such as sodium amalgam. Treatment of 1 with 1 equiv of methylithium in diethyl ether at −78 °C, followed by warming to −10 °C and crystallization from pentane, affords the titanium(II) alkyl CpTiMe(dmpe)2 (2) as black crystals in 56% yield.6 A similar reaction of 1 with 1 equiv of n-butyllithium affords the titanium(II) hydride CpTiH(dmpe)2 (3) in 53% yield.7

These new mono(cyclopentadienyl)titanium(II) complexes are diamagnetic: all three show sharp 1H and 13C NMR signals for the Cp ring. For each complex, there are two PMe2 resonances for the dmpe ligands; these are due to the methyl groups that are proximal and distal with respect to the Cp ring. The 1H NMR spectrum of 2 at −80 °C shows a quintet at δ −1.18 for the Ti-Me group (Jp-Me = 9.2 Hz). This chemical shift is comparable to that of δ −1.86 seen for the Zr analogue CpxMe(dmpe)8 but is deshielded relative to the δ

(5) Anal. Calcd for 1: C, 50.5; 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. 1H NMR (CD2Cl2, −80 °C): δ 2.45 (s, Ti-Cp), 1.87 (s, PCH2), 1.38 (s, PMe2), 0.95 (s, PCH + PMe2), 13C{1H} NMR (CD2Cl2, −80 °C): δ 87.5 (s, Ti-Cp), 30.6 (br s, PCH2), 18.6 (s, PMe2), 17.0 (s, PMe2). 31P{1H} NMR (CD2Cl2, −80 °C): δ 34.3 (s).
(6) Anal. Calcd for 2: C, 50.5; H, 9.41; Ti, 11.2. Found: C, 49.7; H, 9.22; Ti, 11.4. 1H NMR (CD2Cl2, −50 °C): δ 4.37 (s, Ti-Cp), 1.44 (s, PCH2), 1.21 (s, PMe2), 0.87 (s, PMe2), 0.70 (s, PCH2), −18 (quintet, Jp-Me = 9.2 Hz, Ti-Me). 13C{1H} NMR (CD2Cl2, −50 °C): δ 84.6 (s, Ti-Cp), 30.5 (s, br, PCH2), 18.9 (s, PMe2), 18.5 (s, PMe2), 11.3 (quintet, Jp-Me = 10.6 Hz, Ti-Me). 31P{1H} NMR (CD2Cl2, −50 °C): δ 45.0 (s). (7) Anal. Calcd for 3: C, 49.5; H, 9.26; Ti, 11.6. Found: C, 48.2; H, 9.07; P, 30.5; Ti, 11.0. 1H NMR (CD2Cl2, 20 °C): δ 4.52 (s, Ti-Cp), 1.37 (s, PCH2), 1.20 (s, PMe2), 1.02 (s, PMe2), 0.81 (s, PCH2), −0.06 (quintet, Jp-Me = 55.5 Hz, Ti-Me). 13C{1H} NMR (CD2Cl2, 20 °C): δ 85.4 (s, Ti-Cp), 33.2 (pseudoquartet, Jp-Me = 7.9 Hz, PCH2), 28.1 (s, PMe2), 20.0 (s, PMe2). 31P NMR (CD2Cl2, 20 °C): δ 56.8 (br d, Jp-Me = 55.1 Hz).

0276-7339/94/2313-4655$0.50 © 1994 American Chemical Society
-5.2 chemical shift seen for the 14-electron titanium(II)-methyl complex TiMe2(dmpe). The 1H NMR spectrum of 3 at 20 °C contains a binomial quintet for the titanium hydride ligand at δ -0.06, with JH = 55.5 Hz. For comparison, the chemical shifts of the titanium-(11) methyl complex TiMe2(dmpe)2 have been compared to those of 1,7(5), 1,7(4), and 1,7(3) Å seen in Cp2ZrCl(dmpe)2. The Ti-Me distance of 2.385(2) Å in 2 is also much longer than that of 2.219(2) Å in TiMe2(dmpe). The Ti-H bond distance of 1.96(6) Å in 3 can be compared to those of 1.75(7), 1.70(4), and 1.73 Å seen in Cp2TiCl(dmpe)2. The absence of unbranched hexenes among the C6 products rules out a mechanism involving partial insertion of ethylene into a Ti-H or Ti-R bond. Instead, the products formed can be readily explained by a mechanism involving reductive coupling of two alkenes to give a metallacyclopentane intermediate, which then subsequently β-eliminates and then reductively eliminates to afford the product alkenes. The C6 isomers formed indicate that reductive coupling of ethylene and 1-butene exclusively generates a metallacyclopentane with the ethyl substituent β to the metal. Low-temperature 13C{1H} NMR spectra of solutions of 2 and 3 suggest that peaks near δ 50.2 and 61.6 due to a bound ethylene ligand; we have formulated the product.

Addition of ethylene (15 equiv) to toluene solutions of 1–3 results in the formation of 1-butenes, 3-methyl-1-pentene, and 2-ethyl-1-butene in a molar ratio of about 76:15:15; the rate of catalysis is in the order 3 > 2 > 1. For 3, the ethylene is completely converted to these products in less than 1 h at 5 °C. Similar cataytic activity has been seen for the 14-electron titanium(II) complexes TiH(dmpe)2 (X = Cl, Me). The absence of unbranched hexenes among the C6 products rules out a mechanism involving partial insertion of ethylene into a Ti-H or Ti-R bond. Instead, the products formed can be readily explained by a mechanism involving reductive coupling of two alkenes to give a metallacyclopentane intermediate, which then subsequently β-eliminates and then reductively eliminates to afford the product alkenes. The C6 isomers formed indicate that reductive coupling of ethylene and 1-butene exclusively generates a metallacyclopentane with the ethyl substituent β to the metal. Low-temperature 13C{1H} NMR spectra of solutions of 2 and 3 suggest that peaks near δ 50.2 and 61.6 due to a bound ethylene ligand; we have formulated the product.

Addition of ethylene (15 equiv) to toluene solutions of 1–3 results in the formation of 1-butenes, 3-methyl-1-pentene, and 2-ethyl-1-butene in a molar ratio of about 76:15:15; the rate of catalysis is in the order 3 > 2 > 1. For 3, the ethylene is completely converted to these products in less than 1 h at 5 °C. Similar catalytic activity has been seen for the 14-electron titanium(II) complexes TiH(dmpe)2 (X = Cl, Me). The absence of unbranched hexenes among the C6 products rules out a mechanism involving partial insertion of ethylene into a Ti-H or Ti-R bond. Instead, the products formed can be readily explained by a mechanism involving reductive coupling of two alkenes to give a metallacyclopentane intermediate, which then subsequently β-eliminates and then reductively eliminates to afford the product alkenes. The C6 isomers formed indicate that reductive coupling of ethylene and 1-butene exclusively generates a metallacyclopentane with the ethyl substituent β to the metal. Low-temperature 13C{1H} NMR spectra of solutions of 2 and 3 suggest that peaks near δ 50.2 and 61.6 due to a bound ethylene ligand; we have formulated the product.
of this reaction as the Ti\textsuperscript{II} alkyl/alkene complex CpTiMe-(C\textsubscript{5}H\textsubscript{4})(dmpe)(\eta\textsuperscript{1}-dmpe).

We have also been able to prepare titanium(II) pentamethylcyclopentadienyl (Cp*) complexes. Treatment of Cp*TiCl\textsubscript{3} \textsuperscript{(20)} with excess LiBH\textsubscript{4} in diethyl ether at \(-78\) °C, followed by warming to \(-10\) °C and crystallization from toluene, affords in 48\% yield the green titanium(III) complex [Cp*TiCl(BH\textsubscript{4})\textsubscript{2}] \textsuperscript{(4)}, \textsuperscript{(21)} which is the Cp* analogue of the previously reported complex [Cp*TiCl(BH\textsubscript{4})\textsubscript{2}] \textsuperscript{(3)}. Treatment of \(4\) at \(-78\) °C in Et\textsubscript{2}O with 1 equiv of n-butyllithium in the presence of dmpe or tert-butyldi(dimethylphosphino)methylsilane (trimpsi) yields dark brown crystals of the titanium(II) complexes Cp*Ti(BH\textsubscript{4})(dmpe) \textsuperscript{(5)} \textsuperscript{(23)} and Cp*Ti(BH\textsubscript{4})(trimpsi) \textsuperscript{(6)} \textsuperscript{(24)} in 65\% and 55\% yield, respectively, after crystallization from pentane.

Unlike \(1-3\), the Cp* compounds \(5\) and \(6\) are paramagnetic. The infrared spectra of \(4-6\) in the 2000\textendash2600 cm\textsuperscript{-1} region indicate that the tetrahydroborate group is \(\nu_3\) in \(4\) but \(\nu_2\) in \(5\) and \(6\).\textsuperscript{(25)} The X-ray crystal structure of the trimpsi complex \(6\) confirms the presence of the bidentate BH\textsubscript{4}\textsuperscript{-} group (Figure 2).\textsuperscript{(26)} Somewhat surprisingly, the potentially tridentate trimpsi ligand is bound to the metal center in a bidentate fashion. These titanium(II) pentamethylcyclopentadienyl complexes also catalyze the oligomerization of ethylene to mixtures of 1-butene, 2-ethyl-1-butene, and 3-methyl-1-pentene at a rate similar to that of \(1\). Other reactions of these new organotitanium(II) complexes are currently under investigation.

Acknowledgment. We thank the Exxon Educational Foundation for support of this research and Teresa Prussak-Wieckowska of the University of Illinois for assistance with the X-ray crystal structure determination.

Supplementary Material Available: Tables of crystal data, atomic coordinates, thermal parameters, and all bond distances and angles for \(1-3\) and \(6\) (47 pages). Ordering information is given on any current masthead page.

OM940663N