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Structure and Reactivity of Bis(pentamethylcyclopentadienyl)(ethylene)titanium(II), a Simple Olefin Adduct of Titanium

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Abstract: The synthesis and an X-ray diffraction study of bis(pentamethylcyclopentadienyl)(ethylene)titanium [$(\eta$-$C_5Me_5)_2Ti(\eta$-$C_2H_4)$] are reported. This complex represents the first example of an isolable ethylene adduct of titanium. Titanium–olefin complexes have been widely invoked as key intermediates in Ziegler–Natta olefin polymerization schemes. Whereas treatment of $(\eta$-$C_5Me_5)_2Ti(\eta$-$C_2H_4)$ with ethylene leads to only traces of polymer after months, $(\eta$-$C_5Me_5)_2Ti(\eta$-$C_2H_4)$ participates in a range of stoichiometric and catalytic reactions. These include the catalytic conversion of ethylene specifically to butadiene and ethane and the catalytic isomerization of alkenes.

Organotitanium chemistry has been a very active area of research since the first reports that mixtures of $TiCl_3$ and trialkylaluminum are active catalysts for the polymerization of ethylene and the formation of highly ordered polymers of the α-olefins.[2,3] In view of the scientific and commercial importance of olefin polymerization, significant effort has been directed toward the elucidation of the mechanism(s) of Ziegler–Natta-type catalysis. Although a number of substantially different mechanisms have been formulated,[4] the reaction is generally believed to occur via coordination of an olefin to an alkyltitanium complex, which then undergoes olefin insertion (or alkyl migration) to generate a new alkyltitanium species.[3,5] A key feature common to virtually all schemes is the proposed intermediacy of a titanium–olefin π complex. In this connection, it is significant that a simple olefin adduct of titanium has heretofore not been isolated and fully characterized.

Evidence for olefin complexes of zirconium has been presented. Addition of ethylene to $Zr(CH_2SiMe_3)_4$ produces low concentrations of an olefin adduct of unknown structure.[6] Dimeric complexes in which an olefin bridges two formal Zr(III) moieties have been more fully characterized: $[(\eta$-$C_5H_5)_2ZrCl]_2(\mu$-$CHPhCHPh)$[7] and $[ZrCl_3(PEt_3)_2]_2(\mu$-$CH_2CHMe)$;[8] the results of an X-ray diffraction study of one such complex, $[(\eta$-$C_5H_5)_2ZrCl]_2(\mu$-$CH_2CH_2)$, has been reported.[9] The ethylene complex $(\eta$-$C_5Me_5)_2Zr(\eta$-$C_2H_4)$ is strongly implicated as an important but unobserved intermediate in the ethylene-promoted reductive elimination of isobutane from $(\eta$-$C_5Me_5)_2ZrH(CH_2CHMe_2)$,[10] while existence of the corresponding propene and butene intermediates is suggested by the reactivity and fluxional behavior observed for the zirconium allyl hydride complexes $(\eta$-$C_5Me_5)_2ZrH(\eta$-$CH_2CHCHR)$ where R = H, Me.[11]

Our investigations on the interactions of olefins with bis(pentamethylcyclopentadienyl)titanium(II) have led to the preparation of the olefin complex $(\eta$-$C_5Me_5)_2Ti(\eta$-$C_2H_4)$. We report herein the results of an X-ray structure determination of this compound and some of the features of its reactivity.

Experimental Section

General Considerations. All manipulations were performed by using glove-box or high-vacuum techniques. Argon, nitrogen, and hydrogen were purified by passage over MnO on vermiculite and activated Linde 4A molecular sieves. Solvents were purified by vacuum transfer, first from $LiAlH_4$ and then "titanocene".[12] Benzene-d_6 and toluene-d_8 (Aldrich, Stohler) were dried over molecular sieves and vacuum transferred from "titanocene". Ethylene, propene, *cis*-2-butene, 1-butene, *trans*-2-butene, 1-hexene, and HCl (anhydrous) were freeze–pump–thaw degassed at least twice at −196 °C. Carbon monoxide (Matheson) was used directly from the cylinder. Ethylene-$^{13}C_2$ (90% ^{13}C, Merck, Sharp & Dohme, Ltd.) and ethylene-d_4 (98% D, Stohler) were freeze–pump–thaw degassed at −196 °C and distilled at −78 °C. Methyl iodide (MC&B) was vacuum transferred from CaH_2.

Propene-d_6 (>99% D) was prepared by reduction of $(CD_3)_2CO$ (Stohler, 99.5% D) to $(CD_3)_2CDOD$ by using $NaBD_4$ (Stohler, 99% D)/NaOD in D_2O (Stohler, 99.8% D) followed by dehydration over D_2O-washed Al_2O_3 at 300 °C.[13] Methyl isocyanide was prepared by literature procedures,[14] freeze–pump–thaw degassed, and vacuum transferred from molecular sieves. $[(\eta$-$C_5Me_5)_2Ti]_2(\mu$-$N_2)$ and $(\eta$-$C_5Me_5)_2Ti(CH_3)_2$ were prepared by previously reported methods.[15] $(\eta$-$C_5Me_5)_2TiCl_2$ was prepared by the procedure given in ref 15a with the following modifications: LiC_5Me_5 was used in place of NaC_5Me_5 and the resulting mixture of $TiCl_3/LiC_5Me_5$ in THF was heated at reflux for 3 days.

^1H, ^2H, and ^{13}C NMR spectra were recorded on Varian T-60 and EM-390, JEOL FX90Q, and Bruker WM-500 spectrometers. Spectra were taken in benzene or toluene solutions, and data are referenced to Me_4Si at δ 0. Infrared spectra were obtained on Beckman IR-12 and 4240 spectrophotometers. Spectra of solids were recorded as Nujol mulls in KBr plates; spectra of gases were measured with a 10-cm path length cell (NaCl windows) fitted with a stopcock and ball joint for attachment to a vacuum line. Mass spectrometric data were obtained on a Du Pont 21-492 mass spectrometer and a Kratos MS-25 GC-MS. Hydrocarbon gases were analyzed on a Varian 940 gas chromatograph equipped with a thermal conductivity detector with a 12-ft 13% DBT (dibutyl tetrachlorophthalate) on Chromosorb W column. Molecular weights were

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determined cryoscopically or by osmometry. Elemental analyses were performed by Alfred Bernhardt Analytical Labs, West Germany.

Procedures. $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$ (2). Sodium amalgam (300 g, 0.9% w/w) was added via syringe to an argon-blanketed toluene slurry (150 mL) of $(\eta\text{-C}_5\text{Me}_5)_2\text{TiCl}_2$ (3.40 g, 8.73 mmol). The argon atmosphere was replaced with ethylene and maintained at ca. 700 torr while the mixture was stirred for 72 h. The resulting yellow-brown solution was filtered, and the toluene and excess C_2H_4 were removed in vacuo to yield the crude product. Recrystallization from petroleum ether afforded 2.5 g (80%) of bright green **2**: IR 3657 (m), 3042 (s), 2981 (s),* 2963 (m),* 2935 (m),* 2904 (vs),* 2858 (s),* 2721 (m), 1490 (m), 1435 (m),* 1377 (vs),*, 1163 (w), 1127 (w), 1077 (vs), 1060 (w), 1023 (s), 875 (m), 802 (w), 749 (m), 668 (m), 627 (w), 612 (w), 581 (2), 538 (m), 500 (w), 465 (w), 413 (s) cm^{-1} (*measured in Halocarbonoil); ^{1}H NMR δ $\text{C}_5(\text{CH}_3)_5$, 1.68 (s); C_2H_4, 2.02 (s); ^{13}C NMR (mult, $^1J_{^{13}\text{C-H}}$ in Hz) δ $C_5(\text{CH}_3)_5$, 119.8 (s); $\text{C}_5(C\text{H}_3)_5$, 11.9 (q, 125); C_2H_4, 105.1 (t, 143.6). Anal. Calcd for $C_{22}H_{34}Ti$: C, 76.28; H, 9.89; mol wt (osmometry in C_6H_6), 346. Found: C, 76.14; H, 9.84; mol wt, 334.

$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-}^{13}\text{CH}_2{}^{13}\text{CH}_2)$ (2-$^{13}C_2$). Ethylene-$^{13}C_2$ (0.267 mmol) was condensed at −196 °C onto a frozen solution of $[(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$ (90 mg, 0.13 mmol) in 5 mL of toluene. The mixture was warmed to 25 °C and stirred for 20 min. The deep blue solution was frozen at −196 °C and the N_2 removed in vacuo. The mixture was warmed to 25 °C and stirred for an additional 10 min. Solvent was removed in vacuo from the light green solution to yield 90 mg of **2**-$^{13}C_2$ (96%): IR 3682 (vw), 3664 (vw), 3033 (s), 2725 (m), 1493 (m), 1165 (w), 1061 (s), 1047 (vs), 1024 (s), 867 (m), 805 (m), 666 (m), 641 (m), 615 (w), 591 (w), 570 (m), 551 (w), 490 (m), 415 (s), 375 (w) cm^{-1}.

$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{D}_4)$ (2-d_4). Ethylene-d_4 (0.3 mmol) and 5 mL of toluene were condensed at −196 °C onto $[(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$ (50 mg, 0.075 mmol). The mixture was warmed to 0 °C and stirred for 20 min at that temperature. Toluene, N_2, and excess C_2D_4 were removed in vacuo. The green crystalline **2**-d_4 was stored at −30 °C to minimize H-D scrambling: IR 3675 (vw), 3620 (vw), 2722 (m), 2280 (m), 2190 (m), 2159 (m), 2078 (w), 2000 (w), 1979 (vw), 1965 (m), 1946 (w), 1731 (m), 1536 (vw), 1489 (m), 1185 (m), 1161 (w), 1146 (w), 1097 (m), 1023 (s), 932 (m), 902 (w), 637 (w), 625 (vw), 615 (w), 591 (w), 564 (w), 549 (vw), 515 (s), 458 (m), 395 (m), 367 (w) cm^{-1}.

2 + CO. Excess CO (0.5 mmol) was partially condensed at −196 °C into an NMR tube containing a frozen solution of **2** (29 mg, 0.08 mmol) in 0.4 mL of toluene-d_8. The tube was sealed and the reaction monitored between −78 and −20 °C by ^{1}H and ^{13}C NMR. The rate of formation of $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(CO)}_2$ (**4**) and C_2H_4 appears to be limited by the solubility of **2** in cold toluene, but the reaction was complete after 3 h at −30 °C.

2 + CH_3NC. Methyl isocyanide (0.11 mmol) was condensed at −196 °C into an NMR tube containing a frozen solution of **2** (37 mg, 0.11 mmol) in 0.4 mL of toluene-d_8. The tube was sealed and the reaction monitored between −78 and −10 °C. After 1 h at −50 °C, the solution contained 0.5 equiv of unreacted **2**, 0.5 equiv of C_2H_4, and 0.5 equiv of $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(CNCH}_3)_2$ (**5**) (^{1}H and ^{13}C NMR). Above 0 °C, **5** was found to be unstable in solution or as a solid, decomposing to a number of unidentified products with liberation of some free CH_3NC: ^{1}H NMR δ $\text{C}_5(\text{CH}_3)_5$, 1.80 (s); CNCH_3, 2.90 (s); ^{13}C NMR δ $C_5(\text{CH}_3)_5$, 106.2 (s); $\text{C}_5(C\text{H}_3)_5$, 12.1 (q, 125); $\text{CN}C\text{H}_3$, 38.3 (q, 140).

2 + H_2. Hydrogenation of **2** was carried out by a procedure similar to that given for **2** + CO. The formation of $(\eta\text{-C}_5\text{Me}_5)_2\text{TiH}_2$ (**7**) and C_2H_6 was complete after 2 h at −50 °C.

2 + HCl. Hydrogen chloride (0.208 mmol) was condensed at −196 °C into an NMR tube containing a frozen solution of **2** (34 mg, 0.10 mmol) in 0.3 mL of toluene-d_8. The tube was sealed, and immediately upon warming to −78 °C, a reaction occurred, yielding ethane and a purple-red solid identified as $(\eta\text{-C}_5\text{Me}_5)_2\text{TiCl}_2$ (^{1}H NMR).

2 + CH_3I. Methyl iodide (0.58 mmol) was condensed at −78 °C onto a frozen solution of **2** (38 mg, 0.11 mmol) in benzene-d_6 (0.3 mL). The mixture was warmed to 80 °C for 90 min to yield $(\eta\text{-C}_5\text{Me}_5)_2\text{TiI(CH}_3)$ (**8**) and $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(CH}_3)_2$ (**6**) in a ratio of ca. 90:5 and ethylene (0.92 mol/mol **2**, ^{1}H NMR). Other attempts to prepare **8** resulted in materials that were 85–95% pure after recrystallization: ^{1}H NMR (**8**) δ $\text{C}_5(\text{CH}_3)_5$, 1.86 (s); CH_3, −0.41 (s).

$(\eta\text{-C}_5\text{Me}_5)_2\text{TiCl}$ (9). Toluene-d_8 (0.8 mL) and ethylene (0.3 mmol) were condensed at −196 °C into an NMR tube containing 55 mg of **1** (0.14 mmol) and 50 mg of **2** (0.14 mmol). The tube was sealed and the sample heated at 85 °C for 1 h. The NMR tube was broken, and the resulting slurry was dried in vacuo to yield a deep blue solid (80 mg), identified by IR as the previously described[16] $(\eta\text{-C}_5\text{Me}_5)_2\text{TiCl}$. Paramagnetic **9** is also formed during the preparation of **2** by partial reduction of **1**. A toluene solution of **9** (0.06 mmol in 7 mL) was treated with ethylene (0.130 mmol) at 25 °C for 30 min, then cooled to −78 °C, and stirred an additional 60 min. The residual gases were passed through two −78 °C traps, and 0.133 mmol of gas was collected via a Toepler pump.

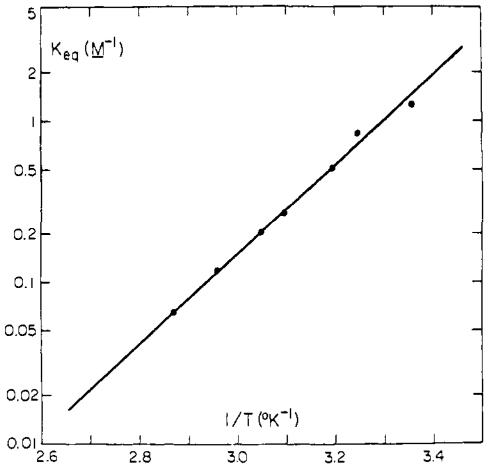

Figure 1. Temperature dependence of **2** + C_2H_4 ⇌ **10**.

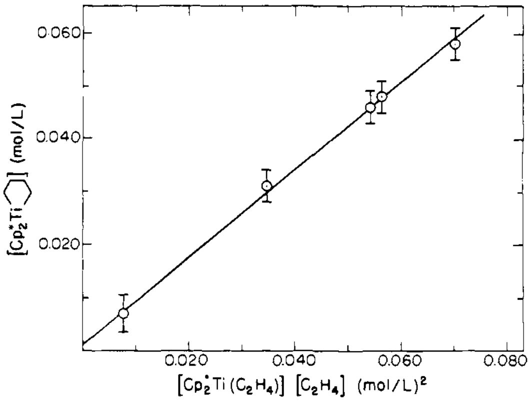

Figure 2. Equilibrium measurement of **2** + C_2H_4 ⇌ **10** at 34 °C.

2 + C_2H_4 ⇌ $(\eta\text{-C}_5\text{Me}_5)_2\overline{\text{TiCH}_2(\text{CH}_2)_2\text{CH}_2}$ (10). Toluene-d_8 (0.5 mL) and ethylene (0.710 mmol) were condensed at −196 °C into a NMR tube containing **2** (22.2 mg, 0.0641 mmol) and ferrocene (67.4 mg, 0.364 mmol). The NMR tube was sealed and [**2**], [**10**], and $[C_2H_4]$ were measured by ^{1}H NMR as a function of temperature from 25 to 75 °C (Figure 1). Since the equilibrium (Figure 2) favors **2** + C_2H_4 over **10** at available $[C_2H_4]$, **10** could not be isolated. The metallacyclopentane **10** was characterized by its chemical reactivity as well as by ^{1}H and ^{13}C NMR spectroscopy: ^{1}H NMR δ $\text{C}_5(\text{CH}_3)_5$, 1.80 (s); $\text{C}H_2(\text{CH}_2)_2\text{C}H_2$, 0.60 (m); $\text{CH}_2(\text{C}H_2)_2\text{CH}_2$, 1.72 (m); ^{13}C NMR δ $C_5(\text{CH}_3)_5$, 120.7 (s); $\text{C}_5(C\text{H}_3)_5$, 12.3 (q, 125); $C\text{H}_2(\text{CH}_2)_2C\text{H}_2$, 62.4 (t, 123); $\text{CH}_2(C\text{H}_2)_2\text{CH}_2$, 32.8 (t, 122); $^1J(^{13}\text{C}_\alpha\text{-}^{13}\text{C}_\beta) = 29$ Hz.

2 + 10 + HCl. Toluene (50 mL) and ethylene (13.2 mmol) were condensed at −196 °C onto **2** (50.5 mg, 0.146 mmol) contained in a thick-walled glass vessel fitted with a Teflon needle valve. The mixture was allowed to warm to 25 °C and was stirred overnight. The resulting orange-brown solution was cooled to −78 °C, and excess ethylene was removed in vacuo. Anhydrous HCl (0.784 mmol) was condensed at −196 °C onto a frozen solution of **2** and **10**. The reaction occurred immediately upon warming the mixture to −78 °C. Residual gases were condensed at −196 °C onto a frozen solution of NaOH (120 mg) in 1 mL of H_2O, and the mixture was warmed to 25 °C. The remaining gas was identified as a 60:40 mixture of ethane and butane (^{1}H NMR).

Isomerization of 1-Butene by 2. An NMR tube was charged with 0.5 mL of a benzene-d_6 stock solution containing **2** (61.6 ± 0.2 mg/mL, 0.178 M) and ferrocene (54.6 ± 0.7 mg/mL, 0.293 M) and cooled to −196 °C. 1-Butene (0.92 mmol) was condensed onto the frozen solution, and the tube was sealed. The sample was heated in an oil bath at 61 °C, and the reaction was monitored as a function of time by ^{1}H NMR. Additional samples, which contained varying amounts of 1-butene and added C_2H_4, were prepared to monitor the isomerization at 61, 72, 81, and 106 °C (Figure 3).

Isomerization of Propene and Propene-d_6 by 2. An NMR tube containing **2** (50 mg, 0.14 mmol), C_3H_6 (0.263 mmol), C_3D_6 (0.138 mmol), and C_6H_6 (0.40 mL) was sealed at −196 °C and heated to 81 °C. The

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[16] deBoer, E. J. M. Ph.D. Dissertation, University of Groningen, 1979.

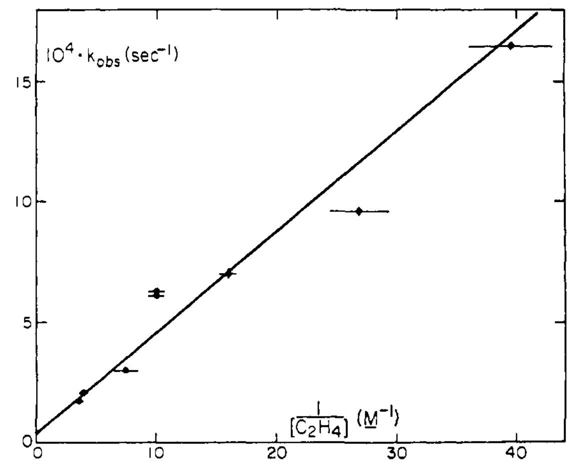

Figure 3. Ethylene concentration dependence of 1-butene isomerization reaction at 106 °C.

Table I. Crystal Data

$C_{22}H_{34}Ti$	tetragonal space group $P\bar{4}2_1m$
a, 10.8621 (4) Å	ρ_{exptl}, 1.15 ± 0.05 g cm^{-3}
c, 8.5008 (5) Å	ρ_{calcd}, 1.147 g cm^{-3}
V, 1002.97 (8) Å^3	λ (Mo Kα), 0.71069 Å
Z, 2	μ, 4.42 cm^{-1}

reactants were monitored for H–D exchange by ^{2}H NMR (13.7 MHz). Samples for monitoring the reaction at other temperatures as well as blanks were similarly prepared. In a separate experiment, the possibility of H–D exchange between **2** and C_3D_6 was checked by ^{2}H NMR and IR spectroscopy. Exchange was observed to be much slower than H–D exchange between C_3H_6 and C_3D_6 catalyzed by **2**.

Conversion of Ethylene to 1,3-Butadiene and Ethane Catalyzed by 2. Benzene-d_6 (0.5 mL), ethylene (0.543 mmol), and ethylene-$^{13}C_2$ (0.067 mmol) were condensed at −196 °C into an NMR tube containing **2** (60 mg, 0.17 mmol). After the tube was sealed, the sample was warmed to 25 °C and monitored by ^{1}H and ^{13}C NMR. Over a 10-month period, the intensities of the C_2H_4 and $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$ (**10**) resonances diminished as the resonances identified as 1,3-butadiene and ethane appeared and slowly increased. The total concentration of titanium species, [**2** + **10**], remained constant throughout. The tube was opened under vacuum, the volatile contents passed through two −78 °C cold traps, and 0.357 mmol gas (0.156 mmol of C_4H_6 and 0.201 mmol of C_2H_6 by ^{1}H NMR, MS) collected via a Toepler pump. The remaining solid in the tube was washed with petroleum ether and filtered to afford ca. 1 mg of polyethylene (IR).

A sample containing 1-butene (0.062 mmol), **2** (30 mg, 0.087 mmol), C_2H_4 (0.715 mmol), and toluene-d_8 (0.52 mL) was prepared and allowed to react at 25 °C. After 5 months, ethane and butadiene (ca. 0.07 mmol each) were observed, but no measurable changes (<3%) in [1-butene] or [**2** + **10**] were seen by ^{1}H NMR.

Toluene (5.0 mL) and ethylene (17 mmol) were condensed onto 240 mg of **2** (0.693 mmol) contained in a thick-walled glass vessel equipped with a Teflon needle valve. The mixture was warmed to 55 ± 3 °C and stirred at that temperature for 1620 h. The solution was cooled to 0 °C, and the residual gases were collected and identified as C_2H_6, C_4H_6, C_4H_8, and unreacted C_2H_4 (IR, GC–MS). The toluene from the residual solution was removed in vacuo; 230 mg of **2** was isolated along with 5 mg of polyethylene.

X-ray Structure Determination. Well-formed crystals of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ were obtained from a saturated toluene solution and sealed in glass capillaries under argon to prevent decomposition. A series of Weissenberg and precession photographs (Cu K_α and Mo K_α radiation) indicated that the crystals possess $4/mmm$ Laue symmetry with the systematic absences $h00$, odd. The choice of space groups was thus restricted to the two tetragonal space groups, $P42_12$ and $P\bar{4}2_1m$. Unit cell dimensions were determined by least-squares fit of $(\sin^2\theta)/\lambda^2$ to 15 reflections with 2θ values between 10 and 40°. Crystal data are given in Table I.

A 0.32 × 0.37 × 0.48 mm crystal was mounted with its c axis slightly skew to the ϕ axis of a modified Syntex P2$_1$ automatic X-ray diffractometer. Intensities were measured for all ($+h$, $+k$, $\pm l$) reflections between 3 and 70° in 2θ by using θ–2θ scans and a variable scan rate between 1.0 and 6.0° min^{-1} with graphite-monochromated Mo K_α radiation. The scan width varied linearly from 1.8° at $2\theta = 3°$ to 2.3° at $2\theta = 70°$ with 24-s background counts measured before and after each scan. A variance $\sigma^2(I)$ was calculated for each reflection on the basis of counting statistics and a term $(0.02S)^2$, where S is the scan count. The intensities of 4 check reflections measured every 100 reflections indicated that no crystal decomposition occurred during the data collection.

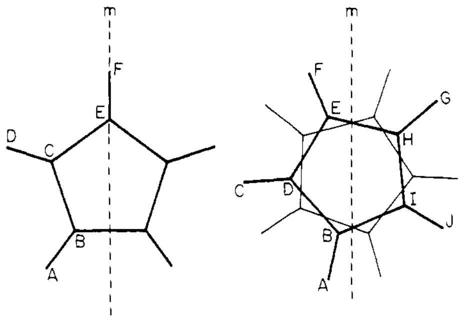

Figure 4. (a) Eclipsed ring model and (b) partially staggered ring model. Labels refer to crystallographically independent atoms.

The intensities and variances of the 5347 reflections were corrected for Lorentz and polarization effects but not for absorption (μ = 4.42 cm^{-1}). The intensities from equivalent reflections, ($+h$, $+k$, $\pm l$) and ($+k$, $+h$, $\pm l$), were averaged and 60 data for which $I < 0$ were assigned weights and F^2 equal to zero, leaving 1279 reflections in the working data set.

Solution and Refinement. The data were placed on an absolute scale by means of a Wilson plot, with scattering factors for Ti calculated by the method of Cromer and Waber and those for C and H by the method of Cromer and Mann.[17] Density measurements (CCl_4/C_7H_8)[18] indicated there are two molecules per unit cell (Table I). Without additional systematic absences, a Z value of 2 requires (i) mm or $\bar{4}$ molecular symmetry for space group $P\bar{4}2_1m$ or (ii) 4 or 222 symmetry for $P42_12$. A three-dimensional Patterson map was generated from which the titanium atoms were located at (0, 0.5, 0.22) and (0.5, 0, −0.22), thus ruling out $\bar{4}$ and 222 as possible symmetry elements. The space group $P\bar{4}2_1m$ was selected since $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ in its eclipsed-ring conformation possesses the necessary mm symmetry while $P42_12$ can only be accommodated by means of a 4-fold disorder. This choice is justified by the successful solution of the structure.

Placement of the Ti gave an R index $(\sum||F_o| - |F_c||/\sum|F_o|)$ of 0.34, with the data exhibiting the higher symmetry of space group $P4mm$. A carbon atom occupying a general position was located in the Fourier map, phasing the data in the space group $P\bar{4}2_1m$. Alternating structure factors calculations and difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. Several cycles of full-matrix least-squares refinement with anisotropic temperature parameters led to a structure with eclipsed C_5Me_5 rings (Figure 4a) and an R = 0.097. At this point in the refinement, a difference Fourier map clearly revealed the coordinates of the ethylene hydrogen; however, several anomalies suggested that the C_5Me_5 rings are actually staggered and that the crystallographic mm symmetry is satisfied by a statistical disordering of the rings. Refinement of a model having no C_5Me_5 carbons positioned on the mirror planes (Figure 4b) rapidly led to the correct structure.

Adopting the staggered-ring model, one finds that isotropic refinement of the titanium, the ethylene carbon, and the 10 carbon atoms of the C_5Me_5 ring, positioned from the Fourier map and assigned-site populations = 0.5, gives an R = 0.12. The ethylene hydrogen was located from the difference Fourier map, and positions for the 15 methyl hydrogens were calculated (C–H = 0.95 Å). Following isotropic refinement of all non-hydrogen atoms, the methyl hydrogens were positioned with the aid of difference Fourier maps, and a secondary extinction coefficient was introduced. All non-hydrogen parameters were anisotropically refined (three cycles) along with the positional and isotropic thermal parameters of the ethylene hydrogen to give an R value of 0.051. Full-matrix least-squares refinement rapidly converged after repositioning the methyl hydrogens from difference Fourier maps (the methyl hydrogen parameters were not refined). It should be noted that the C_5Me_5 rings are disordered due to a slight rotation about the Ti-ring centroid vector. The titanium atom and ethylene ligand are not disordered and are essentially unaffected by use of the staggered-ring model in lieu of eclipsed-ring geometry: C–C, 1.438 vs. 1.443 Å; Ti–C, 2.160 vs. 2.173 Å.

Final parameters are listed in Table II and give an R index of 0.050 and goodness-of-fit index, $[\sum w(F_o^2 - s^2F_c^2)^2/(N - P)]^{1/2}$, of 2.06, where

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(17) (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321. (b) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(18) Flotation method using large crystals.

Table **II**. Final Refined Atom Parameters (Coordinates × 10^4, U_{ij} × 10^3)$^{a-c}$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	0	5000	2206.4 (6)	37.3 (1)	37.3	31.9 (2)	2.1 (6)	0	0
C1	468 (2)	5468	4603 (3)	74 (1)	74	38 (1)	12 (2)	−10 (1)	−10
C2	1325 (6)	4188 (7)	197 (8)	50 (5)	102 (10)	29 (2)	31 (6)	−4 (2)	−9 (3)
C3	454 (7)	3290 (7)	610 (8)	55 (3)	74 (6)	61 (5)	9 (3)	−1 (4)	−28 (4)
C4	674 (14)	2880 (12)	2149 (10)	81 (5)	40 (3)	102 (9)	10 (3)	45 (8)	5 (6)
C5	1712 (11)	3565 (11)	2706 (6)	46 (5)	60 (7)	49 (2)	17 (6)	−6 (3)	2 (3)
C6	2048 (9)	4364 (11)	1526 (9)	27 (2)	56 (3)	51 (4)	2 (2)	0 (3)	−8 (4)
C7	1627 (6)	4619 (8)	−1406 (6)	103 (4)	239 (10)	53 (3)	98 (6)	40 (3)	40 (4)
C8	−421 (6)	2653 (9)	−549 (13)	89 (5)	190 (9)	246 (12)	37 (5)	−45 (5)	−175 (9)
C9	18 (14)	1805 (6)	2944 (12)	212 (13)	43 (3)	268 (11)	−4 (6)	154 (14)	13 (6)
C10	2350 (7)	3283 (8)	4214 (6)	116 (7)	179 (11)	64 (3)	93 (8)	−8 (3)	17 (4)
C11	3113 (6)	5231 (10)	1721 (9)	47 (3)	97 (5)	152 (6)	−17 (3)	9 (4)	−30 (6)
H1a	1287 (16)	5182 (21)	4942 (21)	5.66 (49)^d					

^{a} The final scale factor is 0.7659 (19). ^{b} The final value of the secondary extinction is 1.77 (22) × 10^{-6}.[44] ^{c} The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})]$. ^{d} The form of the isotropic temperature factor is $\exp[-B(\sin^2\theta)/\lambda^2]$.

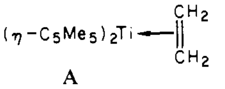
s is the scale factor, $N = 1279$ data, and $P = 106$ parameters. In the final cycle of refinement, no parameter shifted by more than 0.7σ. Except for a peak of 0.7e/Å^3 located at the Ti position, no residual electron density greater than 0.4e/Å^3 remained in the final difference Fourier map.

Results and Discussion

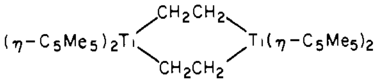
Synthesis and Characterization of (η-C_5Me_5)$_2$Ti(η-C_2H_4). Sodium amalgam reduction of (η-C_5Me_5)$_2$TiCl$_2$ (**1**) in toluene under ca. 700 torr of ethylene (eq 1) affords lime green (η-C_5Me_5)$_2$Ti(η-C_2H_4) (**2**) in high yield (>80%). Alternately, the treatment of [(η-C_5Me_5)$_2$Ti]$_2$(μ-N_2) (**3**) with ethylene rapidly and quantitatively produces **2** and N_2. Use of C_2D_4 in the latter procedure yields (η-C_5Me_5)$_2$Ti(η-C_2D_4) (**2**-d_4) (eq 2), although this isotopomer was found (IR and NMR) to undergo H-D exchange between the C_2D_4 and the CH_3 groups of the C_5Me_5 ligands ($t_{1/2} \simeq$ 24 h at 25 °C). Spectroscopic and molecular weight data strongly suggest a monomeric titanium(II) π-olefin structure (A) for **2** rather than a dimeric structure with bridging ethylenes (B). The monomeric structure of **2** has been confirmed by single-crystal X-ray diffraction techniques.

$$(\eta\text{-}C_5Me_5)_2TiCl_2 + 2Na + C_2H_4 \xrightarrow[3\text{ days}]{25\ ^\circ C} (\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 2NaCl \quad (1)$$

$$[(\eta\text{-}C_5Me_5)_2Ti]_2N_2 + 2C_2D_4 \xrightarrow[20\text{ min}]{0\ ^\circ C} 2(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2D_4) + N_2 \quad (2)$$



A



B

Structure of (η-C_5Me_5)$_2$Ti(η-C_2H_4). The molecular structure of **2** is shown in Figure 5, a stereoscopic view in Figure 6, and a stereoscopic view of the unit cell in Figure 7. The molecule consists of a dihapto ethylene ligand coordinated in the equatorial plane of a "bent sandwich" decamethyltitanocene fragment.

The skeletal geometry about the titanium can be viewed as trigonal, similar to the structures of (η-C_5H_5)$_2$MX compounds.[19,20] Alternately, it can be considered analogous to the numerous pseudotetrahedral (η-C_5H_5)$_2$MX$_2$ structures, with the two carbon atoms of the ethylene and the two C_5Me_5-ring centroids defining the vertices of a distorted tetrahedron. While the distortion from idealized trigonal or tetrahedral coordination, as measured by the ring centroid–Ti-ring centroid angle, is greater than that typically found for unsubstituted bis(cyclopentadienyl)titanium complexes, the value of 143.6 (4)° observed for **2** (R-Ti-R′, Table III) compares favorably with those found for other (η-C_5Me_5)$_2$Ti derivatives: 137.4 (1)° for (η-C_5Me_5)$_2$TiCl$_2$,[21] 139.2° for (η-C_5Me_5)$_2$Ti(CH$_3$)(OC)$_3$Mo(η-C_5H_5),[22] 145.7 (3)° for [(η-C_5Me_5)$_2$Ti]$_2$(μ-N_2),[20] and 147.9° for (η-C_5Me_5)$_2$Ti(CO)$_2$.[23] The large R-Ti-R angle in **2** is attributed, at least in part, to steric

Table **III**. Intramolecular Angles (Degrees)^a

C1-Ti-C1′	38.9 (1)	C7-C2-C3	126.9 (6)
C1-Ti-R	107.9 (3)	C7-C2-C6	125.5 (7)
C1-Ti-R′	106.4 (3)	C8-C3-C2	124.8 (7)
R-Ti-R′	143.6 (4)	C8-C3-C4	124.2 (8)
R-Ti-E	108.2 (3)	C9-C4-C3	125.2 (10)
		C9-C4-C5	128.3 (10)
Ti-C1-C1′	70.6 (1)	C10-C5-C4	123.0 (9)
Ti-C1-H1a	114.5 (10)	C10-C5-C6	129.4 (8)
C1′-C1-H1a	114.5 (12)	C11-C6-C2	127.7 (8)
H1a-C1-H1b	119.0 (16)	C11-C6-C5	121.3 (8)
C6-C2-C3	105.8 (7)	R-C2-C7	167.2 (8)
C2-C3-C4	109.8 (8)	R-C3-C8	170.7 (9)
C3-C4-C5	106.1 (9)	R-C4-C9	174.4 (12)
C4-C5-C6	107.2 (9)	R-C5-C10	172.3 (10)
C5-C6-C2	110.9 (8)	R-C6-C11	176.6 (10)

^{a} R = C_5Me_5 ring centroid; E = ethylene midpoint.

Table **IV**. Intramolecular Distances (Å)^a

Ti-C1	2.160 (4)	C2-C3	1.404 (10)
C1-C1′	1.438 (5)	C2-C6	1.389 (12)
C1-H1a	0.985 (20)	C3-C4	1.403 (14)
Ti-C2	2.402 (7)	C4-C5	1.432 (15)
Ti-C3	2.353 (8)	C5-C6	1.376 (14)
Ti-C4	2.417 (12)	C2-C7	1.478 (10)
Ti-C5	2.464 (10)	C3-C8	1.534 (12)
Ti-C6	2.400 (10)	C4-C9	1.525 (16)
Ti-R	2.092 (5)	C5-C10	1.489 (12)
Ti-E	2.037 (3)	C6-C11	1.501 (12)

^{a} R = C_5Me_5 ring centroid; E = ethylene midpoint.

Table V. Least-Squares Plane of Cyclopentadienyl Ring^a

atom	deviation (σ)^b	atom	deviation (σ)^b
C2	−0.018 (7)	C7	−0.215 (7)
C3	0.009 (8)	C8	−0.367 (7)
C4	0.002 (12)	C9	−0.225 (9)
C5	−0.014 (10)	C10	−0.138 (11)
C6	0.020 (10)	C11	0.017 (8)

^{a} $2.370 = -0.6227x + 0.7013y + 0.3470z$. Plane defined by C2 through C6. ^{b} Negative values denote displacement away from Ti.

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Table VI. Structural Data for Selected Ethylene and Heterocyclopropane Compounds

compound	C–C, Å	C–H, Å	α, deg	method	ref
C_2H_4	1.337 (2)	1.103 (2)	0	*a*	24
$(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2F_4)(\eta\text{-}C_2H_4)$	1.358 (9)	0.956 (40)	42.4	*b*	33a
$(\eta\text{-}C_5H_5)Rh(SO_2)(\eta\text{-}C_2H_4)$	1.366 (5)	0.95 (10)		*b*	33b
$KCl_3Pt(\eta\text{-}C_2H_4)\cdot H_2O$	1.375 (4)	1.087 (7)	32.5	*c*	25
$(PMe_2Ph)_2RuCl_2(CO)(\eta\text{-}C_2H_4)$	1.376 (10)	0.92 (18)	24 (11)	*b*	33c
$(\eta\text{-}C_5H_5)_2Nb(C_2H_5)(\eta\text{-}C_2H_4)$	1.406 (13)	0.98 (14)	52.5	*b*	26
$(\eta\text{-}C_5Me_5)Rh(PPh_3)(\eta\text{-}C_2H_4)$	1.408 (16)	0.90 (5)	38, 58	*b*	33d
$(PPh_3)_2Ni(\eta\text{-}C_2H_4)$	1.431 (15)			*b*	33e
$(PPh_3)_2Pt(\eta\text{-}C_2H_4)$	1.434 (13)			*b*	27
$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$	1.438 (5)	0.985 (20)	70 (4)	*b*	this work
$[(o\text{-}CH_3C_6H_4O)_3P]_2Ni(\eta\text{-}C_2H_4)$	1.46 (2)			*b*	33f
$(\eta\text{-}C_5Me_5)Ta(CHCMe_3)(PMe_3)(\eta\text{-}C_2H_4)$	1.477 (4)	1.090 (8)	68.5	*c*	28
$\overline{CH_2CH_2S}$	1.484 (3)	1.083 (2)	57.1	*d*	33g
$\overline{CH_2CH_2PH}$	1.502 (5)	1.093 (5)	61.0	*d*	33h

[a] Electron diffraction. [b] X-ray diffraction. [c] Neutron diffraction. [d] Microwave spectroscopy.

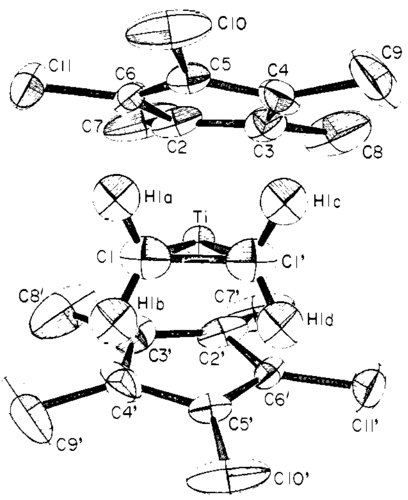

Figure 5. Structure of **2** showing labeling scheme. All thermal ellipsoids are shown at the 50% probability level, including H1a, H1b, H1c, and H1d.

crowding due to the bulky C_5Me_5 ligands.

The single crystallographically independent pentamethylcyclopentadienyl ring is planar and is bonded to the Ti with a small tilt (δ = 2.2 (3)°). The C_{ring}–C_{ring} and C_{ring}–C_{methyl} distances vary over a small range (1.376 (14) to 1.432 (15) and 1.478 (10) to 1.534 (12) Å, respectively) while the Ti–C_{ring} distances vary over a wider range (2.353 (8) to 2.464 (10) Å, Table IV). These variations are typical of the ranges found in other $(\eta\text{-}C_5Me_5)_2M$ species. Thus, the pentamethylcyclopentadienyl rings are considered to be coordinated in a normal, pentahapto manner to the titanium.

The displacements of the methyl groups out of the plane of the cyclopentadienyl ring are as much as 0.37 (1) Å (Table V); these displacements, the large R–Ti–R angle, and the partial staggering of the C_5Me_5 rings discussed previously (torsion angle τ = 26 (2)°) appear to greatly relieve the steric crowding between the C_5Me_5 ligands, as evidenced by the few short interring C···C distances (supplementary material): C7–C8', 3.32 (1) Å; C2–C2', 3.38 (1) Å; C2–C3', 3.37 (1) Å. In contrast, the large number of close nonbonding contacts may be cited as evidence of significant steric interaction between the ethylene and the C_5Me_5 ligands: C1–C4',

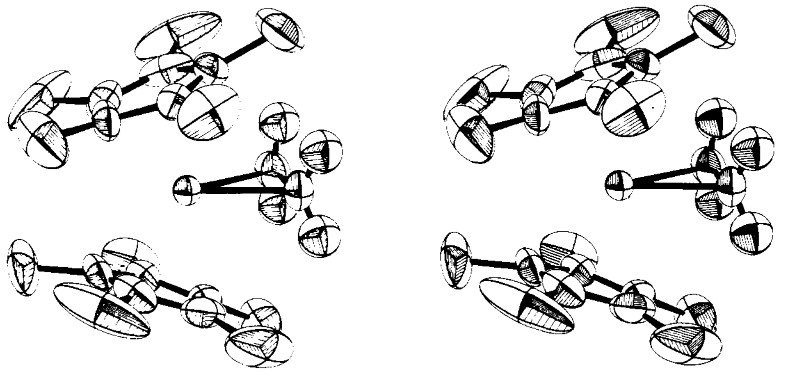

Figure 6. Stereoscopic view of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$.

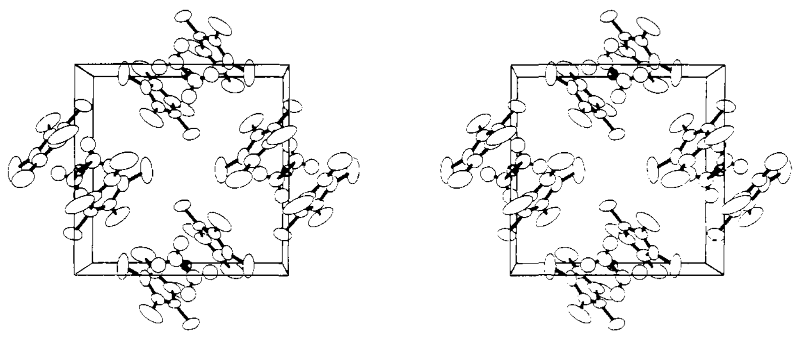

Figure 7. Stereoscopic view of the packing of the molecules in the unit cell.

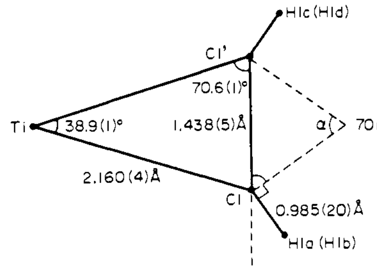

Figure 8.

3.02 (1) Å; C1–C5, 2.95 (1) Å; C1–C5′, 3.05 (1) Å; C1–C6, 3.35 (1) Å; C1–C9′, 3.32 (1) Å; C1–C10, 3.15 (1) Å; C1–C10′, 3.36 (1) Å. While all other interligand C···C contacts exceed 3.6 Å, there are also six short H···C contacts between the ethylene hydrogens and the carbons of the pentamethylcyclopentadienyl ligands. Therefore, it is not surprising that substituted alkenes such as propene or 1-butene do not form olefin complexes analogous to **2** by reaction with $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (**3**).

Details of the titanium–ethylene geometry warrant further discussion since **2** represents the first isolable monoolefin adduct of titanium. As illustrated in Figure 8, coordination of ethylene to the decamethyltitanocene fragment results in a substantial increase in the carbon–carbon bond length, from 1.337 (2) Å for free ethylene[24] to 1.438 (5) Å for **2** (C1–C1′, Table IV). This distance is significantly greater than that found for Zeise's salt (1.375 (4) Å)[25] and for many other olefin complexes (C–C, Table VI) but is in good agreement with the C–C bond distances found for ethylene adducts of low-valent, electron-rich metal centers (e.g., 1.406 (13) Å for $(\eta\text{-}C_5H_5)_2Nb(C_2H_5)(\eta\text{-}C_2H_4)$,[26] 1.434 (13) Å for $(PPh_3)_2Pt(\eta\text{-}C_2H_4)$,[27] 1.477 (4) Å for $(\eta\text{-}C_5Me_5)Ta(CHCMe_3)(\eta\text{-}C_2H_4)(PMe_3)$;[28] Table VI). Displacement of the hydrogen atoms from the planar ethylene geometry is also observed. Following the convention of Stalick and Ibers,[29] the extent of "bending" of the hydrogens away from the metal can be measured as the angle (α) between the normals of the C–H–H planes (Figure 8). The large α angle found for **2**, 70 (4)°, is comparable to those found for electron-rich metal ethylene compounds (Table VI).

The large α value and significant lengthening of the ethylene C–C bond observed for **2** and other electron-rich metal olefin compounds are considered indicative of substantial electron back-donation from the metal to the ethylene.[30] Back-donation in **2** can occur through overlap of the doubly occupied b_2 orbital of the metallocene with the ethylene π^* orbital and impart **2** with Ti(IV) metallacyclopropane character. On the basis of comparisons with other structural data, the structure of **2** would appear to be intermediate along the continuum between the Ti(II) ethylene and Ti(IV) metallacyclopropane limiting structures.[30]

Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$. The titanium ethylene complex undergoes facile reactions with a variety of substrates, as might be expected for a coordinatively unsaturated π-olefin species. Toluene solutions of **2** react with carbon monoxide above −78 °C to produce ethylene (1.0 mol/mol **2**), and the dicarbonyl compound, $(\eta\text{-}C_5Me_5)_2Ti(CO)_2$ (**4**) (eq 3).[15a] Similarly, treatment

$$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 2CO \rightarrow (\eta\text{-}C_5Me_5)_2Ti(CO)_2 + C_2H_4 \quad (3)$$

with methyl isocyanide (eq 4) results in quantitative displacement

$$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 2CNMe \rightarrow (\eta\text{-}C_5Me_5)_2Ti(CNMe)_2 + C_2H_4 \quad (4)$$

of C_2H_4. The resulting isocyanide compound, $(\eta\text{-}C_5Me_5)_2Ti(CNMe)_2$ (**5**), has been characterized only in solution by ^1H and ^{13}C NMR, since it is found to be unstable above 0 °C. The mild conditions under which these reactions occur are suggestive of an associative substitution pathway[31] as outlined in eq 5. Both CO

$$\begin{tikzcd}
(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) \arrow[r, "2L", "-C_2H_4"'] \arrow[d, shift right, "+L"'] & (\eta\text{-}C_5Me_5)_2TiL_2 \arrow[d, shift right, "-L"'] \\
{[(\eta\text{-}C_5Me_5)_2Ti(L)(\eta\text{-}C_2H_4)]} \arrow[u, shift right, "-L"'] \arrow[r, shift left, "-C_2H_4"] & {[(\eta\text{-}C_5Me_5)_2Ti(L)]} \arrow[l, shift left, "C_2H_4"] \arrow[u, shift right, "+L"']
\end{tikzcd} \quad (5)$$

and MeNC are sterically unhindered, π-acceptor ligands; thus, the addition of L (CO, MeNC) to the titanium ethylene complex would be expected to labilize the ethylene, leading ultimately to $(\eta\text{-}C_5Me_5)_2TiL_2$.

The ligand substitution chemistry of **2** may be contrasted with the behavior of the alkyl and aryl derivatives of Ti(III), Ti(IV), and Zr(IV). These coordinatively unsaturated compounds undergo rapid migratory insertion reactions with carbon monoxide and alkyl or aryl isocyanides to form acyl and iminoacyl complexes or products derived therefrom.[32] The reactivity of **2** with dihydrogen also differs qualitatively from the hydrogenolyses of dialkyl compounds of Ti(IV) and Zr(IV) such as $(\eta\text{-}C_5Me_5)_2TiMe_2$ (**6**). The latter species, formally a d^0 complex incapable of oxidative addition at the metal center, does not react with H_2 prior to its decomposition, even at elevated pressures.[15a] The hydrogenation of **2** to $(\eta\text{-}C_5Me_5)_2TiH_2$ (**7**), however, proceeds smoothly at −50 °C in aromatic solvents according to eq 6, similar to the rapid

$$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 2H_2 \rightarrow (\eta\text{-}C_5Me_5)_2TiH_2 + C_2H_6 \quad (6)$$

hydrogenations of $(\eta\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)TiCH_3$[15a] and $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}MeC{\equiv}CMe)$.[34] The striking differences in the reactivity of **2** with hydrogen (vis-à-vis **6**) are attributable to the facile formation of the formal 18-electron Ti(IV) intermediate $(\eta\text{-}C_5Me_5)_2TiH_2(\eta\text{-}C_2H_4)$.

A number of other reactions for $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ have been investigated briefly. Treatment of **2** at −78 °C with 2 equiv of anhydrous HCl results in the immediate liberation of ethane (1.0 mol/mol **2**) and generation of the dichloride **1** (eq 7). When

$$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 2HCl \rightarrow (\eta\text{-}C_5Me_5)_2TiCl_2 + C_2H_6 \quad (7)$$

1.0 mol HCl/mol **2** is employed, a small concentration of an ethyltitanium species is observed (NMR) in addition to C_2H_6, **1**, and unreacted **2**.[35] Excess methyl iodide slowly reacts with **2** at elevated temperatures (ca. 90 min at 80 °C) to release ethylene (0.92 mol/mol **2**) and form $(\eta\text{-}C_5Me_5)_2TiI(Me)$ (**8**) (ca.

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90%) with small amounts of other $(\eta\text{-}C_5Me_5)_2Ti$ derivatives (eq 8), predominantly **6** (by ^{1}H NMR).[36] A sluggish reaction also

$$(\eta\text{-}C_5Me_5)_2Ti(C_2H_4) + CH_3I \rightarrow C_2H_4 + (\eta\text{-}C_5Me_5)_2TiI(Me) + \mathbf{6} \quad (8)$$

occurs between the titanium ethylene complex and the dichloride **1**, as shown in eq 9. After 1 h of heating at 80 °C, benzene and

$$(\eta\text{-}C_5Me_5)_2Ti(C_2H_4) + (\eta\text{-}C_5Me_5)_2TiCl_2 \rightarrow 2(\eta\text{-}C_5Me_5)_2TiCl + C_2H_4 \quad (9)$$

toluene solutions of **1** and **2** (1:1) produce ethylene and the deep blue paramagnetic compound $(\eta\text{-}C_5Me_5)_2TiCl$ (**9**).[16] Between −78 and +80 °C, the formation of adducts such as $(\eta\text{-}C_5Me_5)_2TiCl(\eta\text{-}C_2H_4)$ and $[(\eta\text{-}C_5Me_5)_2TiCl]_2(\mu\text{-}C_2H_4)$ is not observed upon exposure of toluene solutions of **9** to added ethylene (≤1 atm).

Reactivity of $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ with Olefins. As shown in eq 10, ethylene reacts reversibly with **2** in aromatic solvents

$$(\eta\text{-}C_5Me_5)_2Ti(C_2H_4) + C_2H_4 \rightleftarrows (\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2} \quad (10)$$

to yield an equilibrium mixture containing $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$ (**10**), a compound previously noted by Whitesides as the product of the reaction between $(\eta\text{-}C_5Me_5)_2TiCl_2$ (**1**) and 1,4-dilithiobutane.[32d] The addition of higher olefins (C_2H_3R) to **2** does not result in the formation of metallacyclopentanes, presumably due to unfavorable steric interactions between the alkyl substituent and the bulky C_5Me_5 ligands (eq 11). The formation

$$(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + H_2C{=}CHR \not\rightarrow (\eta\text{-}C_5Me_5)_2\overline{TiCH_2CH_2CHRCH_2} \quad (11)$$

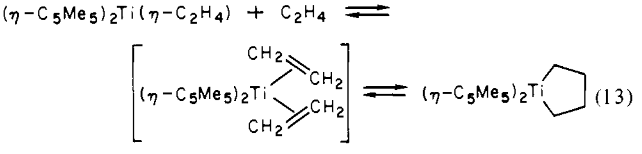
$$R = Me,\ Et,\ etc.$$

of **10** from **2** is an example of the reductive coupling of alkenes by an electron-rich metal center to give a metallacyclopentane, a reaction that has been observed with other low-valent titanium, zirconium, niobium, and tantalum complexes.[10,11,32,37]

Red-orange **10** is not sufficiently insoluble or stable to loss of C_2H_4 under vacuum to allow isolation and separation from **2**; however, it has been characterized in solution as a monomeric Ti(IV) metallacyclopentane complex by ^{1}H and ^{13}C NMR spectroscopy, chemical degradation (eq 12), and equilibria studies

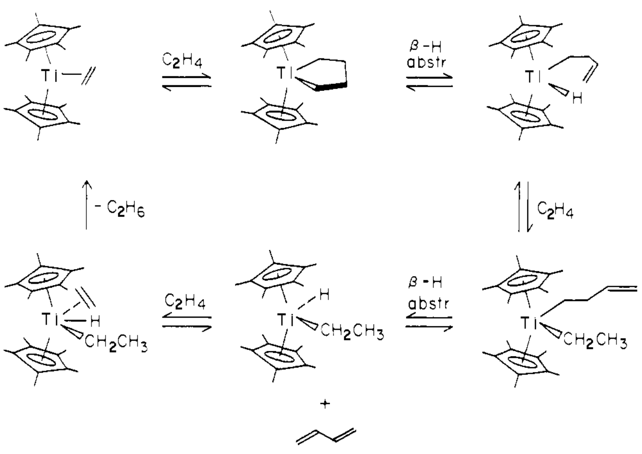
$$0.6(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4) + 0.4(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2} + 2HCl \rightarrow (\eta\text{-}C_5Me_5)_2TiCl_2 + 0.6C_2H_6 + 0.4C_4H_{10} \quad (12)$$

(Figures 1 and 2). The degradation products and the spectroscopic data are quite similar to those of the Zr(IV) compound $(\eta\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$[32e] and rule out the formulation of **10** as the Ti(II) bis(π-olefin) complex $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)_2$ (E). Such a species is suggested, however, as an intermediate in the reaction of **2** with ethylene (eq 13). Carbonylation (<5 atm)



of solutions containing **2**, **10**, and C_2H_4 results in the quantitative

Scheme I



formation of **4** (NMR); moreover, no organic products besides ethylene are detected (NMR, IR), consistent with the results previously reported for **10** + CO.[32d]

$$(\eta\text{-}C_5Me_5)_2Ti(C_2H_4) + (\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2} \xrightarrow{CO} (\eta\text{-}C_5Me_5)_2Ti(CO)_2 + C_2H_4 \quad (14)$$

Interestingly, benzene and toluene solutions containing **2** and **10** catalyze the conversion of ethylene specifically to 1,3-butadiene and ethane under very mild conditions (25 °C, ≤4 atm),[38] albeit turnover numbers are exceedingly small (eq 15). Doubly labeled

$$3C_2H_4 \xrightarrow[25\ ^\circ C]{[\mathbf{2} + \mathbf{10}]} CH_2{=}CHCH{=}CH_2 + C_2H_6 \quad (15)$$

butadiene and ethane are produced in addition to the unlabeled materials when a 9:1 mixture of natural and ^{13}C-enriched (90% $^{13}C_2$) ethylene is added to **2**, thus confirming that the butadiene and ethane are derived from ethylene. While traces of polyethylene are found (<2 mg, identified by IR), no butane or butenes are detected, and no decomposition of **2** is observed after 1 year at 25 °C (NMR). Only when the reaction is carried out at elevated temperatures (>55 °C) are small amounts of butene observed in addition to butadiene and ethane.

Investigation of the reaction shown above has been severely hampered by the exceedingly slow rate of conversion: at the ethylene pressures that are easily accessible (≤5 atm), the rate is ca. 1–2 turnovers/year at 25 °C on the basis of the total concentration of titanium species, [**2** + **10**]. The limited data that are available suggest that the observed rate of reaction is enhanced by increased ethylene concentrations. In another experiment, 1-butene is found to be stable under the reaction conditions; even after 6 months, the concentration of added 1-butene is unchanged[39] while the formation of butadiene and ethane is similarly unaffected.

These results argue against the specific formation of butadiene being due to the presence of an alkene disproportionation catalyst.[40] Moreover, they demonstrate the preferential involvement of C_2H_4 rather than 1-butene or 1,3-butadiene as the hydrogen-accepting substrate. Similar ethylene selectivity is observed for **2** (eq 11) and suggests the intermediacy of **10** in the reaction (eq 15). Recognizing that the product of β-hydrogen abstraction from **10** is an alkyl hydride complex of titanium, which, on the basis of the reactivity of related zirconium and tantalum systems,[41] may

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[36] The low reactivity of **2** with CH_3I vis-â-vis HCl and H_2 is not readily reconciled. It may be that oxidative addition of CH_3I is sterically disfavored, so that an iodine atom abstraction process is involved. The mixed nature of the products is also suggestive of a radical process rather than concerted oxidative addition (cf. H_2) or electrophilic attack at ethylene (cf. HCl).

[37] (a) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610 and references therein. (b) Gell, K. I.; Schwartz, J. *Ibid.* **1981**, *103*, 2687. (c) Datta, S.; Fischer, M. B.; Wreford, S. S. *J. Organomet. Chem.* **1980**, *188*, 353.

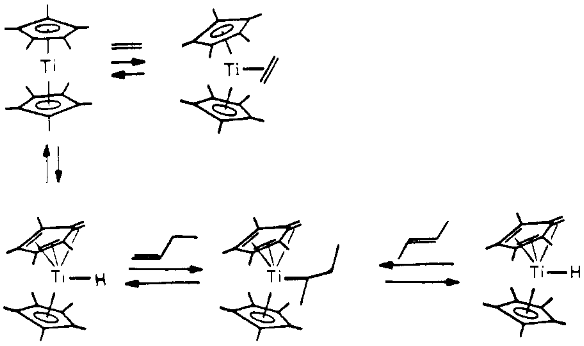
[38] (a) Two compounds have been reported as homogeneous catalysts for the combined dimerization/hydrogen-transfer reaction observed above. Both are dimeric complexes of titanium that, under ethylene, slowly yield butenes, traces of butane, and nonvolatile oligomers in addition to ethane and butadiene.[38b] (b) Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1977**, 560.

[39] At high [C_2H_4] and low temperatures, no isomerization is observed.

[40] Clerici, M. G.; DiGioacchino, S.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975**, *84*, 379.

[41] Bimolecular olefin addition prior to reductive elimination has been demonstrated for $(\eta\text{-}C_5Me_5)_2ZrH(CH_2CHMe_2) + C_2H_4$.[10] Intramolecular (unimolecular) olefin addition has been shown in the dimerization of 2-deuterio-1-pentene by the $(\eta\text{-}C_5Me_5)TaCl_2$ moiety.[37a]

Scheme II



undergo ethylene addition faster than reductive elimination, a possible mechanism for the formation of butadiene and ethane is outlined in Scheme I. The formation of a small amount of butadiene when the thermolysis of $(\eta\text{-}C_5Me_5)_2\overline{ZrCH_2(CH_2)_2CH_2}$ is performed in the presence of ethylene (but not when it is carried out under vacuum) may be similarly explained.[11b]

As mentioned earlier, the addition of propene, 1-butene, and 1-hexene to $[(\eta\text{-}C_5Me_5)_2Ti]_2(\mu\text{-}N_2)$ (**3**) does not result in the formation of the alkene analogues of the titanium ethylene adduct **2**, nor does displacement of ethylene, alkene oligomerization, or formation of metallacyclopentanes occur. Both **2** and **3**, however, catalyze the isomerization of 1-butene and 1-hexene to primarily *trans*-2-butene and *trans*-2-hexene, respectively.[42] The isomerization of 1-butene by **2** has been investigated and found to exhibit a first-order dependence on [**2**] and [1-butene], with an energy of activation (E_a) of 23.8 ± 1.4 kcal mol^{-1}. The rate of isomerization is inhibited by added ethylene. As shown in Figure 3, the isomerization of 1-butene at 106 °C varies linearly with $[C_2H_4]^{-1}$ for ethylene concentrations between 0.025 and 0.277 M and gives within experimental error an intercept of zero for $[C_2H_4]^{-1} \rightarrow 0$. Since the concentration of $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2(CH_2)_2CH_2}$ (**10**) is negligible under these conditions (Figure 2), the inverse $[C_2H_4]$ dependence for the reaction is most consistent with an ethylene-free, titanium species as the catalytically active component.

Transition-metal-catalyzed isomerization of alkenes has been discussed by Casey and Cyr.[43] The commonly observed pathway involves the reversible addition of an alkene to an often undetected metal hydride species to generate a metal alkyl intermediate, while an alternative mechanism—coordination of an alkene to a metal center, followed by activation of an allylic C–H bond to produce an allyl hydride intermediate—has been clearly established in only one instance. Since the addition of linear alkenes to $[(\eta\text{-}C_5Me_5)_2ZrN_2]_2(\mu\text{-}N_2)$ affords isolable allyl hydride derivatives of $(\eta\text{-}C_5Me_5)_2Zr$, the analogous $(\eta\text{-}C_5Me_5)_2TiH(\text{allyl})$ species were considered viable intermediates for the isomerization of 1-butene and 1-hexene by **2**. The two mechanisms may be distinguished by isomerization of a mixture of perdeuterio- and perprotioalkene; if the isomerization is hydride mediated, H–D scrambling among the alkene molecules will be observed, whereas no H–D scrambling should be detected if an allyl hydride mechanism obtains. Propene-d_0 and propene-d_6 (2:1), heated in a benzene solution of **2** at 71 °C, is found after 4 h to have undergone extensive H–D scrambling with their (degenerate) isomerization, as measured by ^2H NMR (eq 16). Furthermore, the appearance of resonances

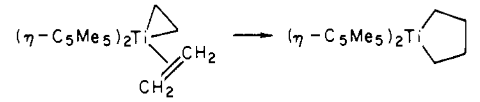
$$C_3H_6 + C_3D_6 \xrightarrow{[2]} C_3H_xD_{6-x} \quad 0 \leq x \leq 6 \qquad (16)$$

at δ 1.67 and 2.05 in the ^2H NMR spectrum establishes the presence of deuterated **2**. We conclude therefore that isomerization of alkenes by **2** must proceed via a metal hydride intermediate. A likely species consistent with the kinetic data is the tautomer of $(\eta\text{-}C_5Me_5)_2Ti$, $(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)TiH$ (**11**), a compound previously observed in equilibrium with $(\eta\text{-}C_5Me_5)_2Ti$. A likely mechanism for isomerization that involves **11** is outlined in Scheme II. This mechanism not only accommodates the observed H–D exchange accompanying the (degenerate) isomerization of C_3H_6 and C_3D_6 but also explains the incorporation of deuterium into ring methyl and ethylenic positions of **2**.

Conclusion

Structure and reactivity patterns characterize $(\eta\text{-}C_5Me_5)_2Ti(\eta\text{-}C_2H_4)$ as an electron-rich Ti(II) π-olefin complex. The presence of the bulky C_5Me_5 rings provide a limited stability range for **2**; its chemistry is dominated by loss of ethylene from the metal center, either as ethylene or ethane. Thus, **2** is a convenient source of the $(\eta\text{-}C_5Me_5)_2Ti$ fragment, the behavior of which is well documented.

Beyond establishing the titanium π-olefin adduct as a stable entity, the chemistry of **2** appears to bear little resemblance to olefin polymerization processes. Although the formation of the metallacyclopentane from ethylene complex might be considered a formal migratory insertion reaction involving the 18-electron, Ti^{IV}(metallocyclopropane)(π-olefin) compound, $(\eta\text{-}C_5Me_5)_2\overline{TiCH_2CH_2}(\eta\text{-}C_2H_4)$ (eq 17), the products formed by the addition of CO and $CNCH_3$ to **2** argue against such a description. The formation of the metallacyclopentane does demonstrate that **2** is capable of reactivity that retains the ethylene in the titanium product. Moreover, the butadiene–ethane (and butene) production, of minor importance in its own right, suggests that subsequent reactions that do not involve simple ethylene dissociation are possible. The interaction of **2** with other unsaturated organic substrates that utilize and more fully explore its reactivity will be reported in a forthcoming publication.



(17)

Acknowledgment. This work has been supported by the National Science Foundation (Grant CHE8024869). We also acknowledge use of the Southern California Regional NMR Facility and the support of NSF Grant 7916324A1. We thank Dr. Richard E. Marsh for his assistance with the X-ray experiments.

Registry No. 1, 11136-36-0; **2**, 83314-27-6; **2**-$^{13}C_2$, 84237-86-5; **2**-d_4, 84237-87-6; **3**, 52124-56-8; **4**, 11136-40-6; **5**, 84237-88-7; **6**, 11136-41-7; **7**, 12701-41-6; **8**, 84237-89-8; **9**, 73348-99-9; **10**, 61160-66-5; CO, 630-08-0; CH_3NC, 593-75-9; HCl, 7647-01-0; CH_3I, 74-88-4; ethylene, 74-85-1; ethylene-$^{13}C_2$, 51915-19-6; ethylene-d_4, 683-73-8; 1-butene, 106-98-9; propene, 115-07-1; propene-d_6, 1517-52-8; 1,3-butadiene, 106-99-0; ethane, 74-84-0; 1-hexene, 592-41-6; *trans*-2-butene, 624-64-6; *trans*-2-hexene, 4050-45-7.

Supplementary Material Available: Tables of intramolecular non-bonded distances and final methyl hydrogen parameters and structure factors (12 pages). Ordering information is given on any current masthead page.

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[42] Equilibrium concentrations of the *cis*-2-alkenes are achieved at a much slower rate. No 3-hexenes are detected.

[43] Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

[44] Equation 5 in: Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.