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A Kinetic and Mechanistic Study of the Thermolysis of Bis(pentamethylcyclopentadienyl)dimethyltitanium(IV)[†,‡]

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The thermal decomposition of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_3)_2$ in toluene solution follows clean first-order kinetics and produces a single titanium product $(\eta^5\text{-}C_5Me_5)(C_5Me_4CH_2)Ti(CH_3)$, concurrent with the evolution of 1 equiv of methane. Labeling studies using $(\eta^5\text{-}C_5Me_5)_2Ti(CD_3)_2$ and $(\eta^5\text{-}C_5Me_5\text{-}d_{15})_2Ti(CH_3)_2$ show the decomposition to be intramolecular and the methane to be produced by coupling of a methyl group with a hydrogen from the other $TiCH_3$ group. Activation parameters, $\Delta H^* = 27.6(3)$ kcal·mol^{-1} and $\Delta S^* = -2.9$ (7) eu, for the decomposition of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_3)_2$ were measured. The decomposition of $(\eta^5\text{-}C_5Me_5)_2Ti(CH_3)_2$ proceeds 2.9 times faster than $(\eta^5\text{-}C_5Me_5)_2Ti(CD_3)_2$, at 98 °C, whereas no significant kinetic deuterium isotope effect is noted for $(\eta^5\text{-}C_5Me_5\text{-}d_{15})_2Ti(CH_3)_2$. The alternative decomposition pathways of α abstraction and α elimination, both leading to the titanium–methylidene intermediate $[(\eta^5\text{-}C_5Me_5)_2Ti{=}CH_2]$, are discussed.

Introduction

The organometallic chemistry of titanium(IV) provides many examples of isolable, yet thermally and photolytically unstable compounds containing Ti–C σ bonds.[4,5] Moderately stable compounds of the types TiR_4 (R = $CH_2C_6H_5$, C_6H_5, $CH_2C(CH_3)_3$, CH_2SiR_3), $TiRX_3$, $TiRX_3{\cdot}L$, and $TiRX_3{\cdot}L_2$ (R = alkyl, alkenyl, alkynyl, aryl; X = halide, alkoxide, amide; L = oxygen, sulfur, nitrogen, or phosphorus base) have been isolated. Evolution of RH usually accompanies decomposition, although in no case has the mechanism been fully investigated. Alkyl and aryl derivatives of dicyclopentadienyltitanium(IV) are generally more stable species, and their decomposition pathways have been more extensively studied.[6] Dvorak and coworkers have shown that the thermal decomposition of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ probably proceeds via an *o*-phenylene intermediate $[(\eta^5\text{-}C_5H_5)_2Ti(C_6H_4)]$ generated from orthohydrogen abstraction by the other phenyl group.[7]

The related compound, $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ (1), decomposes even at room temperature, rapidly in light and more slowly in the dark.[8,9] The mechanism(s) of the decomposition of 1 have proven difficult to establish, however. Van Leeuwen et al. have shown by chemically induced dynamic nuclear polarization (CIDNP) studies of photochemically initiated reactions of $(\eta^5\text{-}C_5H_4Me)_2Ti(CH_3)_2$ that homolysis of the Ti–CH_3 bond does occur.[10] Similar studies of the pathway for the thermal decomposition of 1 are not as conclusive. The favored mechanisms involve loss of the methane via α-H abstraction by the other methyl group or via α-H elimination and subsequent reductive elimination of CH_4.[11-13] The thermal decomposition of 1 is complicated by the apparent two-stage nature of the reaction in solution: α-H abstraction yielding CH_4 and a dark solution, followed by solid-catalyzed α-H abstraction coupled with ring-hydrogen abstraction. Furthermore, there is evidence for yet another minor pathway which results in ethane production in both solution- and solid-state decompositions.[11b] Due to these complicating features, a kinetic study of the decomposition of 1 has not been feasible. In view of the increasing interest in the nature of these proposed α-H abstraction and α-H elimination processes, for example as regards their possible participation in Ziegler–Natta polymerization of olefins[14] and in the synthesis of "Tebbe's reagent" $(\eta^5\text{-}C_5H_5)_2TiCH_2{\cdot}ClAl(CH_3)_2$ from $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $Al(CH_3)_3$,[15] a system more amenable to kinetic studies is clearly desirable. The bis(pentamethylcyclopentadienyl) analogue of 1, $Cp^*{}_2Ti(CH_3)_2$ (2) ($Cp^* \equiv \eta^5\text{-}C_5(CH_3)_5$) has been reported to be much more stable.[16] Upon heating to 110 °C in toluene solution 2 decomposes to form quantitatively

Table I. Summary of Rate Constants for the Decomposition Reaction of $Cp^*{}_2Ti(CH_3)_2$ (2) and Its Deuterated Analogues

temp, °C	$Cp^*{}_2Ti(CH_3)_2$ (2)	$Cp^*{}_2Ti(CD_3)_2$ (4)	$(Cp^*\text{-}d_{15})_2$-$Ti(CH_3)_2$ (5)
98.3	0.378 (18)[a]	0.128 (6)	0.382 (18)
115.5	2.05 (10)	0.683 (32)	1.93 (9)
127.2	6.07 (29)	2.17 (12)	5.78 (27)

$k_H/k_D{}^6 = 2.92$ (10); $k_H/k_D{}^{30} = 1.03$ (4)

[a] Units of 10^{-4} s^{-1} for all values of k_{obsd}. The entry in parentheses the error limit estimated to be one standard deviation based on repetition of the experiments. The standard deviation calculated from an analysis of residuals for any single experiment was always smaller.

[†] Dedicated to Rowland Pettit, respected scientist and friend.

[‡] Contribution No. 6691.

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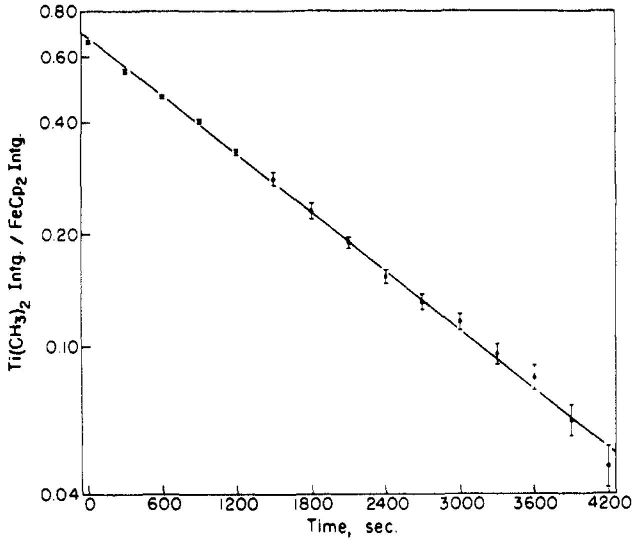


Figure 1. Representative plot of data from a kinetic run: the thermolysis of $Cp^*_2Ti(CH_3)_2$ (2) at 127.2 °C.

a turquoise compound of known composition (η^5-C_5Me_5)($C_5Me_4CH_2$)$TiCH_3$ (3), concurrent with the evolution of 1 equiv of methane (eq 1).

$$\underset{2}{Cp^*_2Ti(CH_3)_2} \xrightarrow{\Delta} \underset{3}{Cp^*(C_5Me_4CH_2)Ti(CH_3)} + CH_4 \quad (1)$$

Preliminary experiments indicated that cleanly first-order kinetic results could be expected from this thermal decomposition. A kinetic and mechanistic study of the thermal decomposition of 2 involving rate measurements taken over a range of temperatures and isotopic ^2H substitutions are reported herein.

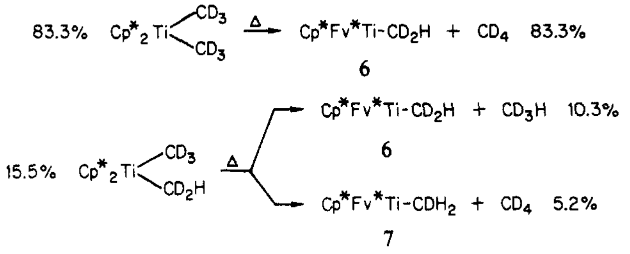
Results

The thermal decompositions of $Cp^*_2Ti(CH_3)_2$ (2) and its deuterated analogs $Cp^*_2Ti(CD_3)_2$ (4) and (Cp^*-d_{15})$_2Ti(CH_3)_2$ (5) in toluene solution were followed by ^1H and ^2H NMR at 98.3, 115.5, and 127.2 °C. The reaction kinetics, as measured by loss of starting dimethyl compound relative to an internal ferrocene reference with time, consistently proved to be cleanly first order for greater than 3 half-lives. A representative plot is presented in Figure 1. The observed rate constants are summarized in Table I. Attempts to determine the rate by measuring the increase in integrated intensity of the product Ti–CY_3 (Y = H or D) resonance, even when not complicated by the presence of more than one isotopic substitution pattern (vide infra), gave non-first-order plots. Rather, the plots are indicative of a subsequent, slower first-order reaction[17] in which the turquoise product 3 apparently decomposes slowly at the elevated temperatures used (eq 2), although no new signals were observed in the NMR.

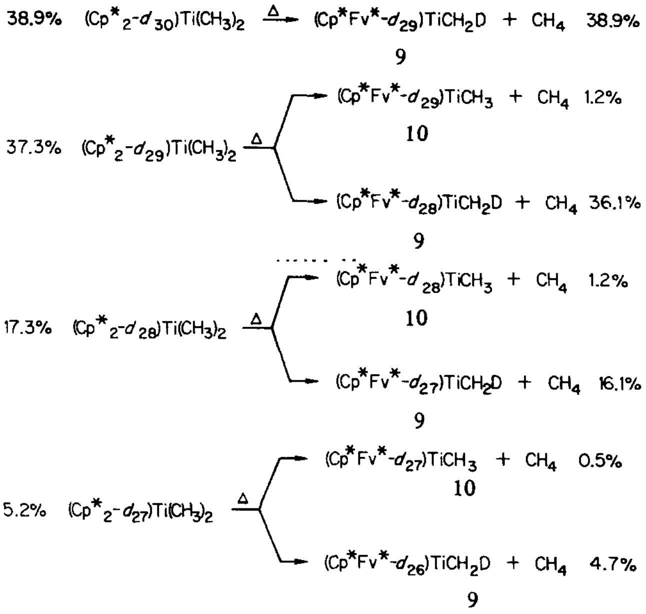
$$Cp^*_2Ti(CH_3)_2 \xrightarrow[-CH_4]{\Delta} Cp^*(C_5Me_4CH_2)TiCH_3 \xrightarrow{\Delta} ? \quad (2)$$

Verification of the intramolecular nature of the decomposition of 2 is provided by crossover experiments. A toluene solution of $Cp^*(C_5Me_4CH_2)TiCH_3$ (3) and $Cp^*_2Ti(CD_3)_2$ (4) (1:1) was heated in a sealed NMR tube at 110 °C for 2 h, the time scale of most of the kinetics experiments. No evidence for Ti–CH_3 exchange was found. In fact, the ^2H NMR spectrum (observed at 76.8 MHz) for this experiment was essentially identical with that found for the thermolysis of 4 alone (vide infra). A 1:1 toluene solution of $Cp^*_2Ti(CH_3)_2$ (2) and $Cp^*_2Ti(CD_3)_2$ (4) was also heated at 110 °C, but for 24 h, at which time most of 4 had decomposed. Again this sample showed no significant evidence of isotope or methyl group exchange during the course of the decomposition.

Scheme I. Statistical Product Distribution for Pyrolysis of 4 (97.0% Deuteration of Ti-CH_3 Groups; ($Cp^* \equiv \eta^5$-$C_5(CH_3)_5$; $Fv^* \equiv C_5(CH_3)_4CH_2$)



Scheme II. Statistical Product Distribution for Pyrolysis of 5 (96.9% Deuteration of η^5-$C_5(CH_3)_5$ Groups; $Cp^* \equiv \eta^5$-$C_5(CH_3)_5$; $Fv^* \equiv C_5(CH_3)_4CH_2$)



The isotopic labeling of the thermolysis products from the decomposition of $Cp^*_2Ti(CD_3)_2$ (4) and (Cp^*-d_{15})$_2Ti(CH_3)_2$ (5) were examined by ^1H (90- and 500.1-MHz) and ^2H (76.8-MHz) NMR, in which the upfield shifts caused by increasing deuterium substitution in CY_4 and Ti–CY_3 are clearly, although not base line, resolved. $Cp^*(C_5Me_4CH_2)Ti(CD_2H)$ (6) and CD_4 are the major products from the decomposition of 4. $Cp^*(C_5Me_4CH_2)Ti(CDH_2)$ (7) and CD_3H are also observed. The product ratios were quantified by peak area determinations. As can be seen from Scheme I and Table II, the observed values agree very well with those expected for an α-abstraction or α-elimination mechanism in which the leaving methyl group couples with a hydrogen from the other Ti–CH_3 group only. Note that a small amount (2%) of $Cp^*(C_5Me_4CH_2)Ti(CD_3)$ (8) is also observed. This product is most consistent with abstraction of a ring hydrogen by a CD_3 moiety to yield CD_3H and 8. Thus, a ring abstraction mechanism appears accessible in this system but represents only a very minor decomposition pathway. This will be considered further in the Discussion.

The ^1H and ^2H NMR spectra of the products of the thermolysis of (Cp^*-d_{15})$_2Ti(CH_3)_2$ (5) show only CH_4 and

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Table II. Observed Labeling Patterns and Theoretical Expectations for the Thermolysis of $Cp^*{}_2Ti(CD_3)_2$ (4) and $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ (5)

compd (isotopic purity)	obsd					expected[a]				
	CD_4	CD_3H	$TiCD_2H$	$TiCDH_2$	$TiCD_3$	CD_4	CD_3H	$TiCD_2H$	$TiCDH_2$	$TiCD_3$
4 (97%)	91 (3)	9 (3)	95 (3)	4 (3)	2 (1)	88	10	94	5	0
	CH_4		$TiCH_2D$	$TiCH_3$		CH_4		$TiCH_2D$	$TiCH_3$	
5 (96.9%)	100 (1)		96 (1)	4 (1)		100		96	3	

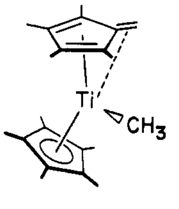
[a] Expected values are probability calculations based on the known isotopic purity of the starting compounds and calculated based on Schemes I and II. The observed isotope effect for compound 4 if included in the calculation does not produce significantly different values for the expected product ratio and is not used.

the Ti-containing products, $(Cp^*Fv^*\text{-}d_n)Ti(CH_2D)$ (**9**) ($Fv^* \equiv C_5(CY_3)_4CY_2$) and $(Cp^*Fv^*\text{-}d_n)Ti(CH_3)$ (**10**), in the expected ratio (Scheme II and Table II). To the limits of detection inherent in NMR spectroscopy, an α-abstraction or α-elimination mechanism appears to be the only one operative; there is no evidence for a ring-abstraction mechanism for **5**.

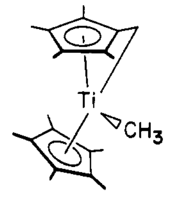
Returning to the kinetic data in Table I, there is a definite deuterium isotope effect on the thermolysis of $Cp^*{}_2Ti(CD_3)_2$ (**4**) ($k_H/k_D{}^6 = 2.92$ (10)), indicating that a methyl C–H bond is being broken in the transition state of the rate-determining step. In contrast, there is no significant isotope effect observed on the thermolysis of $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ (**5**) ($k_H/k_D{}^{30} = 1.03$ (4)). Thus, while the isotopic labeling indicates a ring methyl carbon–hydrogen bond is broken in the formation of the titanium product, this must occur after the rate-determining step.

An Arrhenius plot produced from the data of the thermolysis of $Cp^*{}_2Ti(CH_3)_2$ (**2**) correlates very well with the expected straight line ($r^2 = 1.000$) and yields values at 98.3 °C of 27.62 (28) kcal·mol^{-1} and −2.85 (71) eu for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively.

The structure of the turquoise product **3** is also of interest. Mass spectral and proton NMR data had suggested structures A and B, which may be thought of as related by resonance or, in MO theory, by assuming overlap of Ti atomic orbitals with those of the methyl-substituted fulvene ligand.[16] An attempt to determine an X-ray structure was unsuccessful; the crystal was disordered.[18] However, infrared and ^{13}C and ^1H NMR data seem to support A as the preferred structure. An olefinic C–H stretch at 3040 cm^{-1} is observed in the IR spectrum of **3**.[16] The ^1H spectrum at 500.1 MHz shows two doublets with coupling constant $^2J_{HH} = 4$ Hz assigned to the diasteriotopic hydrogens of the CH_2 group. This coupling constant is more consistent with the geminal sp^2 hydrogens of structure A, normally 0–3 Hz, than with the geminal sp^3 hydrogens of structure B, normally 12–15 Hz. The gated carbon spectrum at 126.8 MHz is the most telling, however. The carbon of the CH_2 group resonates at δ 73.9 with a $^1J_{CH} = 150$ Hz, values most consistent with sp^2 hybridization at carbon. The NMR data for **3** are similar to those observed for the terminal carbon atoms of the butadiene ligand in $(\eta^4\text{-butadiene})Ti(COT)$,[19,20] and $(\eta^4\text{-butadiene})ZrCp_2$.[21] Note, also, that the σ-bound CH_3 carbon is



A



B

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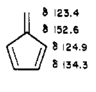
(18) A communication of the structure of a related species has appeared in the literature. Bis(μ-oxo)(η^1,η^5-1,2,3,4-tetramethyl-5-methylene-1,3-cyclopentadiene)bis[(methylcyclopentadienyl)titanium] is proposed to have a truly methylenic bridge to the second titanium. However, the authors present insufficient NMR and no ir data for the compound that would allow us to compare our results. Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703–704.

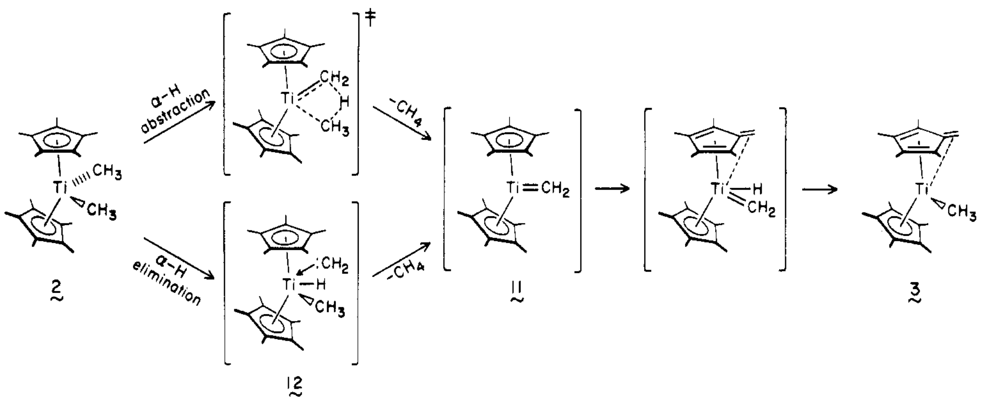
(19) Jolly, P. W.; Mynot, R. *Adv. Organomet. Chem.* **1981**, *19*, 257–304.

(20) Fulvene has the following chemical shifts in $CDCl_3$:



Hollenstein, R.; Philipsborn, W. V.; Vogeli, R.; Neuenschwander, M. *Helv. Chim. Acta* **1973**, *56*, 847–860.

Scheme III. Alternate Mechanisms for the Thermal Decomposition of $Cp^*_2Ti(CH_3)_2$



present as a further check. It resonates further upfield (δ 41.4) with a one-bond coupling of 119 Hz, consistent with other observations of sp^3-carbon atoms σ bound to a metal.[22,23]

Discussion

The labeling and crossover experiments detailed above clearly show the thermal decomposition of $Cp^*_2Ti(CH_3)_2$ (**2**) occurs primarily via a pathway in which one of the titanium–methyl groups obtains a hydrogen from its neighboring $Ti-CH_3$ group to form methane and the reactive $[Cp^*_2Ti{=}CH_2]$ species, which rearranges to **3** via hydrogen migration from a ring methyl group to the methylidene ligand (Scheme III). Evidence for direct abstraction of a hydrogen from a ring-methyl group by the departing $Ti-CH_3$ group is seen only in the thermolysis of $Cp^*_2Ti(CD_3)_2$ (**4**), where this process is a very minor pathway that produces only 2% of the final product. Since a moderate, positive kinetic isotope effect slowing the rate of the principal process by a factor of three is operative in the thermolysis of **4**, it is expected that the direct ring hydrogen abstraction mechanism can become competitive with the α-hydrogen abstraction/elimination mechanism only when the rate of the latter process is significantly slowed. Indeed, no ring-hydrogen abstraction is observed for **5**, which decomposed at the same rate as **2**.

It must be pointed out that our data do not allow us to choose between a formal α-abstraction mechanism and a formal α-elimination mechanism mediated by the titanium methylidene hydride species (**12**; Scheme III). The latter possibility would require generation of an unusual d^0 methylidene species, for which the $Ti{=}CH_2$ π-bonding might resemble the $Zr{=}C{=}O$ π-bonding described for a related complex, $Cp^*_2ZrH_2(CO)$.[24] Note that both mechanisms postulate the intermediacy of a titanium-methylidene species **11**, consistent with previous suggestions in the literature.[11-13,15c] Any mechanism not mediated by this species can be excluded by the results of our labeling studies. Although a titanium-methylidene species analogous to **11** has never been directly observed, "Tebbe's Reagent", $Cp_2TiCH_2AlClMe_2$ is one example in which such a titanium-methylidene complex has apparently been sufficiently stabilized by coordination for isolation as an adduct.[15a,b] Grubbs and co-workers have further postulated that formation of titanacycles from Tebbe's Reagent and olefin results from the olefin trapping the reactive $[Cp_2TiCH_2]$ fragment which has been freed from $AlMe_2Cl$.[15d,e]

Attempts to trap our proposed methylidene intermediate **11** with $AlMe_2Cl$ were unsuccessful. Adding $AlMe_2Cl$ to a toluene solution of $Cp^*(C_5Me_4CH_2)Ti(CH_3)$ (**3**) in an attempt to revert it to **11** led only to decomposition of **3**. When $AlMe_2Cl$ is added to a toluene solution of $Cp^*_2Ti(CH_3)_2$ (**2**), a loose complex is formed as proposed by Tebbe et al. for the reaction of $Cp_2Ti(CH_3)_2$ (**1**) with $AlMe_3$,[15a] so that the usual thermolysis pathways are apparently prevented from operating. A reaction did occur, and methane was produced during the thermolysis; however, NMR spectra of the resultant mixtures were not readily interpretable.

Returning to the mechanism of formation of the methylidene intermediate **11**, it is striking to note the similarity of the activation energy of this process (E_a = 28 $kcal \cdot mol^{-1}$) to those found by other researchers investigating the thermolysis of Cp_2TiR_2. Waters and co-workers[6] found activation energies of 20–29 $kcal \cdot mol^{-1}$ for the thermal decomposition of various $Cp_2Ti(R)Cl$ species. Boekel and co-workers[25] found similar values for the thermolysis of $Cp_2Ti(aryl)_2$. Waters and co-workers[6] emphasize that these values are consistent with a published Ti–C σ-bond strength of 31 $kcal \cdot mol^{-1}$[26a] and propose a bound-radical mechanism. However, they neglect an earlier report of the dissociation energy of the $Ti-CH_3$ bond as 60 $kcal \cdot mol^{-1}$.[26b] This value seems more reasonable and would discount near complete homolysis of the Ti–C bond in the transition state for these systems.

The observed activation energy thus indicates that no Ti–C or C–H bond is completely broken in the transition state of the rate-determining step. The rate-determining step, according to Scheme III, must either be methane formation (for the α-abstraction mechanism) or a 1,2-H shift to the titanium center (for the α-elimination mechanism). The observed isotopic effects yield little additional information which could allow for a differentiation between these two plausible alternatives. The lack of a significant k_H/k_D[30] indicate that ring methyl C–H moieties are not an integral feature of the transition state. A similar conclusion was also reached by Boekel and co-workers in their thermolysis of $Cp_2Ti(aryl)_2$.[25] The value of k_H/k_D[6] = 2.9 is not particularly helpful, either. The observed value

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results from a compound that is isotopically labeled in all titanium-methyl positions, so secondary effects are included. Further, the transition state is undoubtedly bent, which precludes extracting much information from the value, even if it represented only a primary kinetic isotope effect.[27,28] It is interesting to note, however, that the value of $k_H/k_D{}^6$, to the limits of our experimental error, does not vary with temperature, suggesting that the isotope effect is not due to zero-point energy differences but rather is found in the pre-exponential, or entropy, term. This feature may, in turn, indicate a loosely bound hydrogen in the transition state of the rate-determining step,[28,29] more in accord with the α-abstraction mechanism.

Experimental Section

General Considerations. All manipulations were performed using glovebox or high vacuum line techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$ and then from "titanocene".[16] NMR solvents were purified by vacuum transfer from activated molecular sieves (4A, Linde) and then from "titanocene". Hydrogen, deuterium, and nitrogen gases were passed over MnO on vermiculite and activated molecular sieves.[30]

^1H, ^2H, and ^{13}C NMR spectra were obtained by using JEOL FX90Q and Bruker WM500 spectrometers. Kinetic data were obtained by using the JEOL STACK*WAIT program and a thermostated probe. An example of a typical experiment is given below. Infrared spectra were recorded on a Beckman 4240 spectrophotometer.

Procedures. (1) $Cp^*{}_2Ti(CH_3)_2$ (2) and $Cp^*(C_5Me_4CH_2)Ti(CH_3)$ (3). Compounds **2** and **3** were prepared as previously reported.[16] They were refrigerated under N_2 until use. ^1H (500.1-MHz) and ^{13}C (125.8-MHz) spectra were obtained for **3**: ^1H data (C_6D_6, ppm relative to Me_4Si at δ 0.00) 1.77 (s, 15, Cp*), 2.03, 1.67, 1.43, 1.26 (all s, all 3, $C_5\mathit{Me}_4CH_2$), 1.14, 1.92 (d,d, 1,1, $^2J_{HH}$ = 4 Hz, $C_5Me_4C\mathit{H}_2$), −1.10 (s, 3, $TiC\mathit{H}_3$); ^{13}C data (C_6D_6, ppm relative to C_6D_6 at δ 128.0) 118.3 (s, C_5Me_5), 12.1 (q, $^1J_{CH}$ = 125 Hz, $C_5\mathit{Me}_5$), 119.6, 123.9, 125.0, 126.0, 130.1 (all s, $\mathit{C}_5Me_4CH_2$), 10.6, 11.1, 11.2, 14.7 (all q, $^1J_{CH}$ = 126 Hz, $C_5\mathit{Me}_4CH_2$), 73.9 (t, $^1J_{CH}$ = 150 Hz, $C_5Me_4\mathit{C}H_2$), 41.4 (q, $^1J_{CH}$ = 119 Hz, $Ti\mathit{C}H_3$).

(2) $Cp^*{}_2Ti(CD_3)_2$ (4). Compound **4** was prepared in the same manner as $Cp^*{}_2Ti(CH_3)_2$, above, except that $LiCD_3$ (97% isotopically pure, Stohler) was added to $Cp^*{}_2TiCl_2$ in place of $LiCH_3$.[16] The orange crystals were refrigerated under N_2 until use.

(3) $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ (5). Compound **5** was prepared from the titanium–ethylene species $Cp^*{}_2Ti(C_2H_4)$[31] as follows. D_2O was heated throughout a large glass bomb and a portion of the vacuum line in order to replace H^+ by D^+ at glass sites. $Cp^*{}_2Ti(C_2H_4)$ (1.20 g, 3.5 mmol) and toluene (20 mL) were placed in the bomb, which was then evacuated. Deuterium gas (~1.5 atm, 97% isotopically pure) was admitted to the bomb and the orange-red solution was allowed to stir at room temperature for ~10 h. The bomb was evacuated, refilled with D_2, and allowed to stir five more times. After the last evacuation, DCl was admitted and the purple-red solution stirred at room temperature for 24 h. The toluene was pumped away and purple-red solid $(Cp^*\text{-}d_{15})_2TiCl_2$ was washed out of the bomb with $CHCl_3$. The solution was evaporated to dryness and the brown solid was purified by Soxhlet extraction as described previously for $Cp^*{}_2TiCl_2$.[16] The yield of $(Cp^*\text{-}d_{15})_2TiCl_2$ was 1.35 g (91%; total isotopic purity = 96.9%). The infrared spectrum (KBr pellet) of $Cp^*\text{-}d_{15})_2TiCl_2$, when contrasted with that of $Cp_2{}^*TiCl_2$, showed the expected shift to lower frequencies of the C–H(D) stretch: IR data (KBr, cm^{-1}) 2238 (m), 2192 (m), 2060 (m), 1487 (m), 1473 (m), 1099 (s), 1069 (m), 1039 (s), 829 (m), 752 (w), 680 (w), 396 (s), 358 (s), 331 (s).

$(Cp^*\text{-}d_{15})_2TiCl_2$ (1.01 g, 2.4 mmol) was then reacted with $LiCH_3$ as described previously for $Cp^*{}_2Ti(CH_3)_2$.[16] Yield of $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ (**5**) was 0.61 g (66.8%) of orange-yellow needles. The compound was refrigerated under N_2 until use.

(4) Kinetic Measurements of Thermal Decomposition. The rates of decomposition were followed by monitoring the decrease in integrated intensity of the $TiCH_3$ or $TiCD_3$ peak of the starting dimethyltitanocene relative to an internal, nonreacting standard of $FeCp_2$ (recrystallized from benzene) or C_6D_6, respectively. FT NMR spectra were recorded automatically at preset time intervals by using the JEOL FX90Q STACK*WAIT routine. Standard ^1H and ^2H NMR accumulation parameters were used, and ^2H NMR spectra were ^1H decoupled.[32] Reaction temperatures were maintained by the JEOL probe temperature controller and were observed to be constant to within 0.4 °C by measuring the peak separation of ethylene glycol both before and after the decomposition experiments.

A typical ^1H NMR experiment involved 40 mg of $Cp^*{}_2Ti(CH_3)_2$ or $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ and 15 mg of $FeCp_2$ dissolved in 0.3 mL of toluene-d_8. A typical ^2H NMR experiment involved a similar amount of $Cp^*{}_2Ti(CD_3)_2$ and ~1 equiv of C_6D_6 dissolved in 0.3 mL of toluene-d_0. In both cases, 2–3 atm of N_2 was sealed into the NMR tube to prevent the toluene from refluxing at the elevated temperatures used in this study.

As the decomposition progressed, the Ti–C(H or D)$_3$ resonance of the starting material lost intensity, and plots of the decay of the ratio of the methyl integration/reference compound integration as a function of time showed first-order behavior for more than 3 half-lives. In experiments that were followed further, no deviation from first-order behavior was found even beyond 5 half-lives. As expected, the rate of decomposition was independent of the concentration of the dimethyl species over a fivefold range.

The values given in Table I are derived from the slopes of the semilog plots. The error represents one standard deviation estimated by repeating the experiments. An analysis of residuals for a single determination always gave a smaller estimate of the error.

Arrhenius plots of ln k vs. $1/T$ were constructed. For the thermal decomposition of $Cp^*{}_2Ti(CH_3)_2$ (**2**), a least-squares fit of the data to the Arrhenius equation in $k_{obsd} = \ln A - E_a/RT$ gave values of $\ln A = 28.24$ and $E_a/R = -1.427 \times 10^4$ or $A = 1.833 \times 10^{12}\ s^{-1}$ and $E_a = 28.36$ kcal·mol^{-1}. ΔH^* and ΔS^* were calculated from the usual equations ($\Delta H^* = E_a - RT$ and $\Delta S^* = R \ln (hA/kT)$) and are presented in the body of this paper. The error for these last two values represents one standard deviation estimated from changes in the values of $-E_a/R$ and ln A when the k_{obsd} are varied within their error limit. Analysis of residuals for the line gave much smaller estimates.

(5) Crossover Experiments. NMR tubes containing approximately equal amounts of $Cp^*{}_2Ti(CH_3)_2$ (**2**) and $Cp^*{}_2Ti(CD_3)_2$ (**4**) or $Cp^*(C_5Me_4CH_2)Ti(CH_3)$ (**3**) and $Cp^*{}_2Ti(CD_3)_2$ (**4**) in toluene solution were sealed under vacuum and heated to check for any evidence of methyl exchange or any other result which might indicate intermolecular reaction. Results were negative, as discussed in the body of the paper.

(6) Analysis of Isotopic Labeling in Thermolysis Products from $Cp^*{}_2Ti(CD_3)_2$ (4) and $(Cp^*\text{-}d_{15})_2Ti(CH_3)_2$ (5). Proton-decoupled ^2H (76.8-MHz) and ^1H (90-MHz) NMR spectra of thermolyzed samples of **4** and **5**, respectively, were taken and the region of interest—from δ ~0.2 for the methanes to δ ~−1.1 for the titanium methyl peaks—was expanded so that couplings and peak overlap could be clearly seen. Each spectrum was copied and peak areas determined by a cut-and-weigh procedure. Values given in Table II are the average from several determinations and the errors given are one standard deviation ($n - 1$ weighting).

(7) Attempted Trapping of Titanium–Carbene Species (11). In the first of two experiments conducted a roughly stoichiometric amount of $AlMe_2Cl$ was added to a yellow-orange

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[27] It is interesting to note that our measured $k_H/k_D{}^6 = 3.0$ from the thermolysis of **2** and **4** is equivalent to that found for the formation of Tebbe Reagent (**12**) through competition studies involving Cp_2TiCl_2 and equal amounts of $Al(CH_3)_3$ and $Al(CD_3)_3$. Ott, K.; Grubbs, R. H., personal communication.

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toluene-d_8 solution of $Cp^*{}_2Ti(CH_3)_2$ (**2**) (32 mg, 87 μmol) and $FeCp_2$ (140 μmol). The color changed immediately to an opaque red-orange. The tube was sealed under N_2. Red-orange crystals were noted after 1 h at room temperature. The ^1H NMR spectrum showed only resonances that could be assigned to the Cp*, Cp, and methyl hydrogens. The latter appeared at δ 0.22, midway between the methyl resonances of $Cp^*{}_2Ti(CH_3)_2$ (**2**) (δ 0.69) and $AlMe_2Cl$ (δ 0.38). Subsequent thermolysis of this tube in the JEOL FX90Q at 127.2 °C resulted in uninterpretable ^1H NMR spectra. Methane (δ 0.18) was produced, but other resonances were not clearly resolved.

The second experiment involved adding an excess of $AlMe_2Cl$ to a turquoise toluene-d_8 solution of $Cp^*(C_5Me_4CH_2)Ti(CH_3)$ (**3**) and $FeCp_2$ ($\sim$1:1). The color changed immediately to a green-brown solution which contained dark solid material. The tube was sealed under N_2. No ^1H NMR spectrum could be observed for this reaction mixture, however, suggesting the presence of paramagnetic products.

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Registry No. **2**, 11136-41-7; **3**, 36007-20-2; **4**, 83314-25-4; **5**, 83314-26-5; $AlMe_2Cl$, 1184-58-3; $LiCD_3$, 15772-82-4; $Cp^*{}_2TiCl_2$, 11136-36-0; $Cp^*{}_2Ti(C_2H_4)$, 83314-27-6; $(Cp^*\text{-}d_{15})_2TiCl_2$, 83314-28-7; D_2, 7782-39-0.

Mechanism of the Reaction of $[Fe_6C(CO)_{16}]^{2-}$ with Tropylium Bromide To Give $[Fe_4(CO)_{12}CCO_2CH_3]^-$ and the Molecular Structure of $(Et_4N)_2[Fe_5C(CO)_{12}Br_2]$, a Proposed Intermediate in This Reaction[†]

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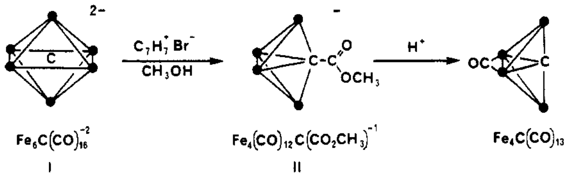
The reaction of $[Fe_6C(CO)_{16}]^{2-}$ with tropylium bromide in methanol, which yields $[Fe_4(CO)_{12}CCO_2CH_3]^-$, has been shown to comprise the sequential formation of $[Fe_5C(CO)_{15}]$, $[Fe_5C(CO)_{12}Br_2]^{2-}$, $[Fe_4C(CO)_{12}]^{2-}$, $[Fe_4C(CO)_{13}]$, and $[Fe_4C(CO)_{12}CCO_2CH_3]^-$. The structure of the hitherto unreported $(Et_4N)_2[Fe_5C(CO)_{12}Br_2]$ has been determined by X-ray diffraction. The cluster crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.361$ (2) Å, $b = 14.958$ (3) Å, $c = 23.472$ (6) Å, $\beta = 95.08$ (2)°, $V = 3973$ Å^3, and $Z = 4$. The geometry of the dianion may be regarded as based on the square-pyramidal $[Fe_5C(CO)_{15}]$ with two bromide ions replacing three carbonyls from one of the basal $Fe(CO)_3$ groups. Each of the proposed intermediates in the conversion of $[Fe_6C(CO)_{16}]^{2-}$ to $[Fe_4C(CO)_{12}CCO_2CH_3]^-$ has been isolated and their interconversion demonstrated.

Introduction

We recently reported[1] the synthesis of a novel iron carbidocarbonyl cluster $Fe_4C(CO)_{13}$ by a sequence of reactions involving the oxidative fragmentation of the hexanuclear octahedral cluster $[Fe_6C(CO)_{16}]^{2-}$ in methanol, followed by protonation (eq 1). $[Fe_4C(CO)_{13}]$ is of considerable interest as it is the neutral parent molecule of the Fe_4C series, a class of carbidocarbonyl clusters so far unique in that its members contain a carbon atom exposed to a degree sufficient to undergo chemical reactions.[2,3] All higher nuclearity carbidocarbonyl clusters have carbon atoms partially or totally shielded from potential chemical reactivity by encapsulating metal atoms. As a class of compounds, first discovered two decades ago, carbidocarbonyl clusters remained until recently principally of structural interest.[4]



(1)

Our observation of the formation of an organic functionality incorporating the exposed carbon atom—the CCO_2CH_3 group in II—has demonstrated the potential for CO-based chemistry at the CO-derived carbon atom in molecular clusters.[2] This focus of interest has a counterpart in heterogeneously catalyzed CO chemistry, where the intermediacy of surface-bound carbon atoms has recently

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[†] This paper is dedicated to the memory of the late Professor Rowland Pettit whose advice and encouragement as a consultant and friend were invaluable.

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