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The Thermal Decomposition of Dibutylbis(η^5-cyclopentadienyl)titanium, other Dialkyl Metallocenes, and Di(η^5-pentamethylcyclopentadienyl)titanium

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The thermal decomposition of some dialkylbis(η^5-cyclopentadienyl)metals in pentane and toluene solutions at 60°–80 °C have been studied. The metals were Ti, Zr, Hf, Nb, Ta, Mo, and W. The alkyls were n-propyl, n-butyl, n-amyl, neopentyl, and neohexyl. Dineopentylbis(η^5-pentamethylcyclopentadienyl)titanium was also studied. In addition to the expected alkanes and alkenes, some methane, ethylene, and other hydrocarbons were obtained. The formation of these minor products is rationalized on the basis of δ- and γ-hydrogen elimination and metal carbene formation. A metallacycle pathway probably follows the hydrogen abstraction. Reproducible quantities of the products were obtained.

Introduction

In connection with our interest in the generation of reactive metallocene species [1] such as Cp_2Ti, we have undertaken a study of the thermal decomposition of dialkyl metallocenes.

Razuvaev *et al.* [2] have proposed homolytic cleavage of the Ti–C σ-bond as the main pathway in the thermal decomposition of Cp_2TiR_2 (R = alkyl or aryl) in solution. Dvorak *et al.* [3] studied the $Cp_2Ti(C_6H_5)_2$ thermolysis and suggested that benzene was formed by abstracting a proton from the second phenyl group and a phenylene titanium complex resulted. Boekel *et al.* [4] studied the diaryl and dibenzyl analogs and found that the product hydrocarbons formed by intramolecular hydrogen abstraction from another coordinated R group or from the cyclopentadienyl ligand. Whitesides and coworkers [5] studied the thermal decomposition of di-n-butyltitanocene at 250 °C in a gas chromatograph and found quantitative yields of a 1:1 mixture of butane and 1-butene. Beta-hydrogen elimination can account for those results.

Grubbs and Miyashita [6] have studied the decomposition of nickel and titanium metallacyclohexane and reported a carbenoid intermediate and methane production. The metal–carbene complexes were found to dimerize [7] and thus produce ethylene.

In this work small amounts of methane and ethylene and other hydrocarbons were found when dialkylbis(cyclopentadienyl) metals (alkyl = n-butyl, n-propyl, n-amyl, neopentyl and neohexyl and metal = Ti, Zr, Hf, Nb, Ta, Mo, and W) were decomposed in pentane or toluene at 60°–80 °C.

Experimental

All reactions and manipulations were performed under welding-grade argon purified before use by a BASF deoxygenation catalyst and molecular sieves (Linde 4A). All solvents were A.C.S. Reagent grade and were distilled from sodium-benzophenone under argon. Neopentyl chloride and neohexanol (t-amylcarbinol) were obtained from ICN Pharmaceuticals, Inc. Toluene-d_8 (>99%) was purchased from Aldrich Chemical Co.

Analytical GLC was performed by use of a Varian series 1400 FID chromatograph with a 20 ft × 1/8 in Durapak colum or a 13 ft Paraffin wax/5% $AgNO_3$ on Al_2O_3 column. Product yields were determined by response relative to an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6 spectrometer and Finnigan 4000 GC mass spectrometer. ^{13}C NMR spectra were measured on a Varian CFT-20 spectrometer with TMS as internal standard.

Preparation of Alkyllithium Reagents

Except for the solution of n-butyllithium in hexane which is commercially available (Aldrich Chemical Co.), the solutions of n-alkyllithium reagents in n-pentane or diethyl ether were prepared from the corresponding chlorides or bromides by the previously reported procedures [2].

Neopentyllithium in n-pentane was prepared from neopentyl chloride. A mixture of 30 g neopentyl chloride and a two-fold excess of finely chopped

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lithium wire in 500 mL n-pentane was stirred and refluxed under argon for ten days. The excess Li metal and LiCl were removed by filtration and the neopentyllithium was isolated from the filtrate by cooling and reducing the volume *in vacuo* and yielded 90% white, crystalline $LiCH_2CMe_3$. The white solid was then dissolved in freshly distilled n-pentane, diethyl ether or toluene and stored at $-10°$.

Neohexyllithium ($LiCH_2CMe_2Et$) was prepared from neohexyl bromide which was obtained from the reaction of neohexyl alcohol and $P(n\text{-}C_4H_9)_3Br_2$. A sample of 16 g (0.16 mol) dry neohexyl alcohol (t-amylcarbinol) was mixed with 43 mL (0.17 mol) of freshly distilled tri-n-butylphosphine in 85 mL of dry dimethylformamide, DMF, in an argon atmosphere. About 8 ml of bromine was added slowly while the reaction flask was cooled in an ice bath. After being stirred for 6 h, all volatile material was then removed by vacuum distillation into a receiver cooled in a dry ice bath. Cold water was added and neohexyl bromide was separated. Neohexyl bromide (yield 90%) was then dried and distilled at 55°/40 torr. A 12 g neohexylbromide sample and a two-fold excess of Li wire were placed in 150 mL n-pentane under argon and stirred and refluxed for 12 days. The mixture was filtered and the neohexyllithium (>80%) was isolated from the filtrate. It was dissolved in n-pentane, diethyl ether or toluene and stored at $-10°$.

Preparation of Di-η-Butylbis(cyclopentadienyl)-titanium

A sample of 2 g (8 mmol) Cp_2TiCl_2 was suspended and stirred in 25 mL diethyl ether at -78 ℃. An ethereal solution of n-butyllithium (16 mmol) was added slowly by a syringe. The reaction mixture was stirred at -78 ℃ for 36 h. During this period, the mixture turned dark red. About 100 μL of methanol was then injected to destroy any unreacted n-butyllithium. The solvent was removed at -78 ℃ to give an orange-red residue. The residue was chromatographed on an alumina column which had been thoroughly dried and flushed with argon. This column was provided with a cooling jacket, and maintained at -78 ℃. The column was eluted with n-pentane and an orange band was collected as it eluted. The orange pentane solution was then concentrated at -78 ℃ *in vacuo* and the product was stored below -78 ℃.

Di-n-butylbis(cyclopentadienyl)titanium was characterized by its chemical reactions. Treatment of orange pentane solution with anhydrous HCl gas yielded n-butane and Cp_2TiCl_2 in a molar ratio of 1.98:1. Similar treatment with DCl gas or concentrated D_2SO_4 gave 1-deuterobutane with isotopic yield >99%. When the orange solution was treated with bromine, the dark red Cp_2TiBr_2 and 1-bromobutane were formed. GLC analysis of 1-bromobutane and weighing Cp_2TiBr_2, showed that the molar ratio of Cp_2TiBr_2 to 1-bromobutane was 1:1.88.

Thermal Decomposition of Di-n-Alkylbis(cyclopentadienyl)titanium

A pentane or toluene solution of Cp_2TiBu_2 was stirred at $-60°$ to $-78°$ for 5 h, then warmed up to 60°. The gases produced were injected into the GC for analysis. Cyclopropane was the internal standard. Subsequent analyses gave the same results, indicating complete decomposition. After complete decomposition, the products produced were collected by distillation into a liquid nitrogen trap. On being warmed to room temperature, the product gases were analyzed by GLC in the vapor phase as well as the liquid phase and their composition was determined.

The thermal decomposition of the other di-n-alkylbis(cyclopentadienyl)titanium compounds were carried out as follows: A sample of Cp_2TiCl_2 was suspended in n-pentane or diethyl ether at -78 ℃. Two equivalents of alkyllithium in n-pentane or diethyl ether were added slowly. After the reaction mixture was stirred at -78 ℃ for 36 h, small amount of methanol was injected into the flask to destroy the excess alkyllithium reagent. The solvent was removed *in vacuo* at -78 ℃ and toluene was added. After being stirred at -78 ℃ for 5 h, the toluene solution was warmed to 60 ℃. The products were analyzed by GLC as above. The composition of products was unaffected by chromatographing the solution through alumina.

Preparation and Decomposition of Di-Neohexyl and Di-Neopentylbis(cyclopentadienyl)titanium

A sample of 1 g (4 mmol) Cp_2TiCl_2 was treated with neohexyl- or neopentyllithium (8 mmol) in 30 mL diethyl ether or n-pentane at -78 ℃ for 2 days. About 100 m of methanol was injected to destroy any unreacted lithium reagent. Removal of the solvent at -78 ℃ left an orange sludge. The product was chromatographed by a procedure analogous to that used for di-n-butylbis(cyclopentadienyl)titanium with n-pentane as the eluting solvent. A clear orange pentane solution was obtained and concentrated.

Treatment of the orange pentane solution with anhydrous HCl gave neohexane or neopentane and Cp_2TiCl_2 with the molar ratio of 1.93:1. Similar treatment with bromine yielded neohexyl bromide and Cp_2TiBr_2. The molar ratio of neohexyl bromide to Cp_2TiBr_2 was 1.90:1. The characterization of di-neopentylbis(cyclopentadienyl)titanium was the same as that used for the neohexyl compound.

The procedures for the thermal decompositions at 80 ℃ are similar to those used for the di-n-butyl compound. When a toluene solution of the neohexyl compound (1 mmol) and 20 ml of ethylene was stirred at -78 ℃ for 5 h, decomposition at 80 ℃ gave 2.5% butenes and butane.

Preparation and Decomposition of di-neopentylpermethyltitanocene

Dichloropermathylthanocene was prepared by the method of Bercaw [8]. In a separate flask, 50 mg neopentyllithium was dissolved in 25 mL ether. The latter solution was added, by use of a syringe, to the former under argon at –78 °C. The mixture was stirred vigorously and warmed to room temperature slowly, and then stirred for an additional 20 min at room temperature. The mixture was cooled again to –30 °C and 20 mL methanol was introduced to destroy excess neopentyllithium. The solvent and excess methanol was removed under reduced pressure at –30 °C. The resulting residue was extracted with 50 ml freshly distilled n-pentane and the solution was filtered through a fritted Schlenk tube with a cooling jacket at –78 °C. A clear orange-yellow solution was obtained. An attempt to crystallize dineopentylpermethyltitanocene was not successful, but the decomposition of this solution by HCl at –78 °C produced dichloropermethyltitanocene and neopentane in a ratio of 1/2. The percentage recovery of dichloropermethyltitanocene was greater than 95%.

The pentane solution of dineopentylpermethyltitanocene was transferred by a syringe into a glass pressure bottle under argon. Pentane was removed under reduced pressure. The orange residue was dissolved in 20 mL freshly distilled toluene at –78 °C. The pressure bottle was warmed to room temperature slowly before it was put into an oil bath at 80 °C. The toluene solution of dineopentylpermethyltitanocene was stirred vigorously under argon at 80 °C for 24 h. Gas products were analyzed by use of the FID GC with a column of Durapak (20″ × 1/8″) at 60 °C. Methane (5.1%), ethylene (4.2%), isobutylene (15%) and neopentane (75%) were found together with trace amounts of C_3 and C_4 hydrocarbons.

When toluene-d_8 was used as a solvent, a large amount of CH_2D_2 was detected as methane by GC-MS.

Preparation of Perdeuterotitanocene Dichloride

Sodium cyclopentadienide-d_5 (18 g) was dissolved in 120 mL tetrahydrofuran, THF, under argon. The solution was added to 10 mL (17 g), titanium tetrachloride by use of a syringe at –30 °C. The mixture was stirred vigorously and refluxed overnight. The solvent was removed under reduced pressure. The residue was transferred into a thimble in a Soxhlet extractor. HCl-saturated chloroform was used as the extracting solvent. On cooling the chloroform solution, $(C_5D_5)_2TiCl_2$ separated and was collected by filtration. The yield was approximately 50%. The mass spectrum of the red crystals showed major peaks at m/z = 258 (M^+), 223, 188, 153, 118, 83, 70.

Preparation and Decomposition of Di-neopentylperdeuterotitanocene

Perdeuterotitanocene dichloride (0.52 g) was suspended in 50 mL diethylether under argon. An ether solution of neopentyllithium (100 mL; 0.34 g) was introduced into the mixture at –78 °C. The solution was warmed slowly to 0 °C and stirred at this temperature for two additional hours. The solvent was removed *in vacuo*. The residue was extracted by freshly distilled n-pentane (50 mL). The mixture was filtered under argon at –78 °C.

The above freshly-prepared solution was transferred into a glass pressure bottle under argon at –78 °C. The solvent was removed at low temperature *in vacuo*. Freshly-distilled toluene (40 mL) was introduced by using a syringe at –78 °C. The solution was first warmed to room temperature slowly and then heated to 80 °C for 24 h. The mass spectroscopic analysis of the gaseous products did not indicate the presence of CH_2D_2.

Metal–Carbene Trapping Experiments

A toluene solution of $Cp_2TiBu^t_2$ (1.5 mmol) and 1 mL of freshly distilled cyclohexene were stirred at –78 °C for 3 h, then warmed to 60 °C. After being stirred at 60 °C for 36 h, the product was collected by distillation into a liquid nitrogen trap. On being warmed to room temperature, the product was analyzed by GLC on a 32 ft × 1/8 in 10% Carbowax 20 M/chromosorb W column and a 13 ft × 1/8 in Paraffin was 15% $AgNO_3$ on Al_2O_3 column, compared with authentic sample, and the yield of norcarane was 1.51%.

In the cases of the neopentyl and neohexylbis(cyclopentadienyl)titanium compounds, solutions were irradiated with a medium pressure mercury arc lamp at –78 °C, but no ethylene or isobutylene was produced.

Preparation of Metallocene Chlorides

Vanadocene monochloride and the metallocene dichlorides [10–12] of Nb, Ta, Mo and W were prepared as previously reported.

The new compound trichlorobis(cyclopentadienyl) tantalum (Cp_2TaCl_3) was prepared and characterized as follows: A sample of 5.4 g (15 mmol) tantalum pentachloride ($TaCl_5$) was treated with 15 mmol of $Mg(C_5H_5)_2$ in 100 mL of toluene. After being stirred at room temperature for 24 h, the toluene was removed *in vacuo* and a yellow residue remained. A yellow crystalline compound, Cp_2TaCl_3, was obtained by sublimation of the yellow residue at 260°/0.01 torr. Characterization was made by IR spectroscopy that showed a band pattern characteristic of biscyclopentadienyl complexes and by mass spectrometry. The characteristic IR peaks were 1440 (s), 1340 (m), 1125 (vw), 1015 (m) and 855 (s) cm^{-1}. The principal ions in mass spectra were Cp_2TaCl_3

TABLE I. Minor Products from Thermal Decomposition of n-Alkyl Transition Metals in Toluene at 60 °C.

Compounds	Decomposition Products Other Than α-Hydrogen Elimination Products (%)		
	CH_4	C_2H_4	Other Hydrocarbons
Cp_2TiPr_2	1.9	1.1	C_6 (5.2%)
Cp_2TiBu_2	0.2	0.6	C_3 (0.1%), C_8 (not examined)
Cp_2TiAm_2	0.8	0.6	C_3 (0.9%), C_4 (0.3%), C_{10} (not examined)
Cp_2ZrBu_2	trace	trace	
Cp_2HfBu_2	trace	trace	
Cp_2NbBu_2	trace	trace	
Cp_2TaBu_2	0.6	0.2	

(M^+, m/e 417–421), Cp_2TaCl_2 (m/e 382–386) and $CpTaCl_2$ (m/e 317–321).

Preparation and Thermal Decomposition of Neohexyl Metallocene Derivatives

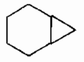
A sample of the appropriate metallocene chloride was treated with the required amount of neohexyllithium reagent in diethyl ether or n-pentane at –78 °C for two days. Methanol (100 μL) was injected to destroy any unreacted lithium reagent. The solvent was removed at –78 °C and toluene was then added to dissolve the residue. After being stirred at –78° for 5 h, the toluene solution was warmed to 80 °C. The product gases were injected into the GC for analysis. Replicate experiments gave identical results, indicating complete decomposition. Results are given in Table III. The decomposition of Cp_2ZrR_2, Cp_2HfR_2 and Cp_2NbR_2 (R = neohexyl) only gave trace amounts (<0.01%) of ethylene and isobutylene.

Results and Discussion

In this study the thermal decomposition of dialkyl metallocenes, Cp_2MR_2, has been examined, where R = n-propyl, n-butyl, n-amyl, neopentyl and neohexyl and M = Ti, Zr, Hf, Nb, Ta, Mo and W. In the initial studies, toluene solutions of the n-alkyl derivatives of Ti, Zr, Hf, Nb, and Ta metallocenes were stirred at –78 °C, heated to 60 °C and the organic products were separated and identified by gas chromatography. The principal products were the n-alkanes and alkenes as previously reported [5]. However small amounts of methane and ethylene and, in some cases, other hydrocarbons were also found (Table I).

Thermolysis of a toluene solution of dineopentylpermethyltitanocene (1) at 80 °C produces methane (5.1%), ethylene (4.2%), isobutylene (15%) and neopentane (75%). There are also trace amount of C_3 and C_4 hydrocarbons found, but no direct reductive elimination product, 2,2,5,5-tetramethylhexane, was detected.

TABLE II. Metal–Carbenes Trapped by Cyclohexene.

Compounds	Product, Norcarane  (yield)
Cp_2TiPr_2	2.93%
Cp_2TiBu_2	1.51%
Cp_2TiAm_2	1.10%

Because the production of methane and ethylene may have resulted from metal–carbene formation, experiments were carried out with the thermal decomposition of the n-alkyls of titanocene in the presence of cyclohexene. Norcarane was observed in the products (Table II) and thus supports the idea of carbene formation. If δ-hydrogen elimination had occurred to form a titanacyclopentane, for example, the ethylene may have formed from the decomposition of the metallacycle as reported by Grubbs and Miyashita [6]. A ^{13}C NMR signal at 359.07 ppm was observed in the di-neopentylbis(cyclopentadienyl)-titanium at –50 °C. It is probably due to the resonance characteristic of a carbene α-carbon atom bound to the titanium [8].

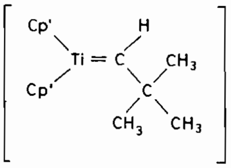
To determine whether δ- or γ-hydrogen elimination can occur, the experiments with the neopentyl- and neohexyl- groups were performed, since no β-hydrogens are present. Toluene solutions of dineopentylbis(cyclopentadienyl)titanium and also the dineohexyl compound were first stirred at –78 °C and then warmed to 80 °C and the products were analyzed and separated by gas chromatography. In the case of the neopentyl compound, the major product was neopentane, but small amounts of methane and ethylene (~1%) were found and some isobutylene (~1.2%) was also detected. More extensive studies were made with the dineohexyl-derivatives of bis(cyclopentadienyl)titanium, vanadium, tantalum, molybdenum and tungsten. In each case methane, ethylene, and isobutylene were formed and some C_3 and C_4 hydrocarbons as well (Table III).

TABLE III. Decomposition Products of Neohexyl Metal Complexes Formed by Other than α-Hydrogen Elimination. Toluene Solution at 80 °C.

Neohexyl (mmol)	Complexes (R = Neohexyl)	Products of Thermal Decomposition Other Than α-Hydrogen Elimination (%)				
		CH_4	C_2H_4	C_3	C_4	$H_2C{=}C(CH_3)_2$
Cp_2TiR_2	(0.82)	3.09	1.24	0.12	1.11	1.27
Cp_2TiR_2 [a]	(0.87)	0.97	2.65	0.34	1.66	2.31
Cp_2VR	(0.45)	2.59	1.20	0.30	0.87	1.36
Cp_2TaClR_2	(0.31)	1.39	1.29	0.10	2.34	1.87
Cp_2MoR_2	(0.31)	3.28	2.05	0.10	2.69	2.23
Cp_2WR_2	(0.31)	3.03	2.14	0.20	2.36	2.02

[a] Decomposition was at 80° after stirring in toluene at –60° to –78° for a week.

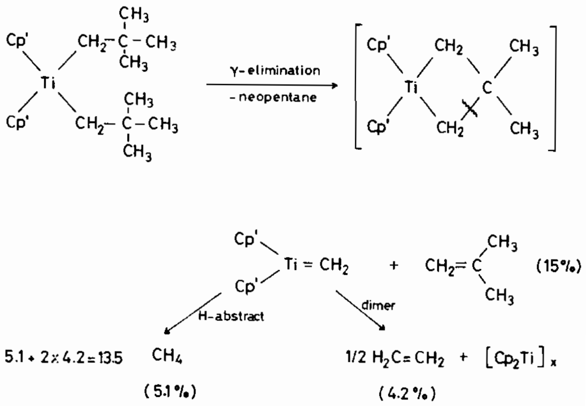
In the case of the dineopentyl(permethylcyclopentadienyl)titanium α- and γ-hydrogen elimination are the only two possible pathways besides homolytic cleavage of the Ti–carbon bond. Alpha-hydrogen elimination will lead to a Ti–carbene intermediate.



But in an attempt to trap the carbene by cyclohexene in the thermolysis of dineopentyltitanocene, norcarane was the only product. The absence of substituted norcarane suggested that a higher carbene was not present and the presence of norcarane suggested the presence of the simple unsubstituted carbene. γ-hydrogen elimination seems to be a plausible mechanism to form methylene complex via a metallocycle. Subsequent cleavage of one of the carbon–carbon bonds in the metallocycle produces isobutylene, one of the major products, and a $Ti{=}CH_2$. A ^{13}C NMR study of the thermally-decomposed solution of dineopentyltitanocene showed a singlet at 356 ppm from TMS at –50 °C, which is characteristic evidence for a Ti–carbene.

Ethylene is expected to be formed by dimerization of 2 mol of a metal–carbene. Methane is produced by H-abstraction from either the cyclopentadienyl rings or the solvent. The perdeuterated sample, $(C_5D_5)_2Ti[CH_2C(CH_3)]_2$, led to no deuterium in the methane. However, when the dineopentylpermethyltitanocene was thermally decomposed in toluene-d_8, a large amount of CD_2H_2 was found in the methane, clearly indicating that the metal–carbene abstracts hydrogen from the solvent.

According to this mechanism, the number of mol of isobutylene formed should be equal to that of metal carbene which subsequently produces methane and ethylene. So, the sum of the percentage of methane and ethylene should be equal to that of isobutylene, that is, 5.1 + 4.2 X 2 = 13.5. The small difference, 1.5%, could represent the amount of metal carbene which is oligomerized to produce the trace amounts of C_3 and C_4.



Analysis of the solution did not indicate any of the product of direct reductive elimination and agrees with the orbital symmetry approach of Akermark, *et al.* [12], who showed that reductive elimination was symmetry forbidden thermally for d^0 transition metal dialkyls.

In the cases of the neopentyl and neohexyl compounds, it is proposed that δ- or γ-hydrogen elimination leads to a metallacycle and ultimately ethylene and isobutylene. The major products, neopentane or neohexane, must be the result of α-hydrogen elimination with the needed protons coming from the solvent.

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