

Formation of fulvene and dimethylenecyclopentenyl titanium complexes from bis(η^5 -tetramethylcyclopentadienyl)titanium(IV) precursors

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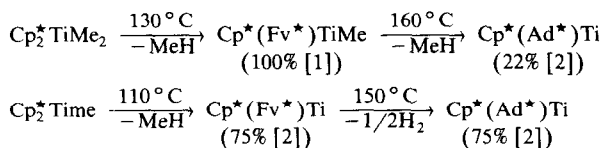
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Abstract

A mixture of isomeric $(\text{Me}_4\text{C}_5\text{H})(\text{Me}_3\text{C}_5(\text{CH}_2)\text{H})\text{TiMe}$ compounds was obtained by thermally induced methane elimination from $(\text{Me}_4\text{C}_5\text{H})_2\text{TiMe}_2$ at 130°C , analogous to the formation of $(\text{Me}_5\text{C}_5)(\text{Me}_4\text{C}_5(\text{CH}_2))\text{TiMe}$. The compound $(\text{Me}_5\text{C}_5)(\text{Me}_3\text{C}_5(\text{CH}_2)_2)\text{Ti}$ was newly prepared in 27% yield by boiling a $(\text{Me}_5\text{C}_5)_2\text{TiCl}_2\text{--LiAlH}_4$ mixture in toluene, followed by sublimation of the soluble product. By an analogous process, $(\text{Me}_4\text{C}_5\text{H})(\text{Me}_2\text{C}_5(\text{CH}_2)_2\text{H})\text{Ti}$ was obtained in 10% yield. Neither type of complex was formed by either method from titanocene derivatives with fewer methyl groups at cyclopentadienyl ligands.

Introduction

Synthetic routes to the 1,2,3,4-tetramethylfulvene (Fv^*) complexes $\text{Cp}^*(\text{Fv}^*)\text{--TiMe}$ ($\text{Cp}^* = \text{Me}_5\text{C}_5$, $\text{Fv}^* = \text{Me}_4\text{C}_5(\text{CH}_2)$) [1], $\text{Cp}^*(\text{Fv}^*)\text{Ti}$ [2] and the $\eta^3\text{:}\eta^4$ -1,2,3-trimethyl-4,5-dimethylenecyclopentenyl (allyldiene, Ad^*) complex $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ ($\text{Ad}^* = \text{Me}_3\text{C}_5(\text{CH}_2)_2$) [2] generally involve the elimination of methane or methane/hydrogen from permethyltitanocene methyl derivatives (Scheme 1). In addition, the first reported preparation of $\text{Cp}^*(\text{Fv}^*)\text{Ti}$ utilized the thermal dehydrogenation of permethyltitanocene Cp_2^*Ti [3]. The thermolytic demethanation and



Scheme 1

dehydrogenation reactions proceed selectively and, except for the preparation of $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ from $\text{Cp}^*(\text{Fv}^*)\text{TiMe}$, moderate to high yields were obtained. It has been clearly demonstrated by using selectively deuterated permethyltitanocene dimethyls that the leaving methyl group abstracts the hydrogen atom from the geminal Me group, thus affording a transient permethyltitanocene methylene species $\text{Cp}_2^*\text{Ti}=\text{CH}_2$ [4]. This species apparently participates in the formation of titanocene enolates $\text{Cp}_2^*\text{Ti}(\text{Me})-\text{O}-\text{C}(\text{R}')=\text{C}(\text{R}'')(\text{R}''')$ ($\text{R}', \text{R}'', \text{R}''' = \text{H}$ or alkyl) during the thermolysis of $\text{Cp}_2^*\text{TiMe}_2$ in the presence of ketones [5] or epoxides [6]. The analogous thermolysis of Cp_2TiMe_2 was less selective, yielding methane with an admixture of ethane; no titanium products were isolated and identified [7]. On the other hand, a titanocene species formed during the reduction of Cp_2TiCl_2 by LiAlH_4 in aromatic solvents under thermolytic conditions (110–160°C) yielded “dimeric titanocene”, $\mu-(\eta^5: \eta^5\text{-fulvalene})\text{-di-}\mu\text{-hydrido-bis}(\eta^5\text{-cyclopentadienyl-titanium})$ in almost quantitative yield [8]. A recent study of the interaction of titanocene monochlorides with LiAlH_4 under mild conditions showed that the products of ageing of titanocene tetrahydridoaluminate $\bar{\text{Cp}}_2\text{TiAlH}_4$ ($\bar{\text{Cp}} = \text{Me}_x\text{C}_5\text{H}_{5-x}$; $x = 0, 1, 3, 4, 5$) differed for the Cp^* complex and for the less methylated complexes: attempted sublimation *in vacuo* of a product of the ageing of $\text{Cp}_2^*\text{TiAlH}_4$ yielded pure $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ [9]. This suggested a simple preparation of $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ by the high-temperature reduction of $\text{Cp}_2^*\text{TiCl}_2$ with LiAlH_4 in aromatic solvents. As we are currently studying the preparation and properties of various titanocene derivatives in a series of compounds differing in the number of Me groups at the cyclopentadienyl ligands [9–11], we wished to establish how the number of Me groups affects the formation of fulvene ligands in the thermolysis of the $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds and the formation of dimethylenecyclopentenyl ligands in a novel preparative procedure based on a high-temperature reduction of the $\bar{\text{Cp}}_2\text{TiCl}_2$ compounds with LiAlH_4 .

Experimental

General

All manipulations were performed using a high-vacuum line operated with metal valves. Sealed glass devices equipped with magnetically breakable seals were used to handle the reaction components and products. NMR and ESR tubes and quartz optical cells were sealed after filling.

Chemicals

Methyl-substituted titanocene dichlorides $\bar{\text{Cp}}_2\text{TiCl}_2$ ($\bar{\text{Cp}} = \text{MeC}_5\text{H}_4$ (MeCp), 1,2,3- $\text{Me}_3\text{C}_5\text{H}_2$ (Me_3Cp), $\text{Me}_4\text{C}_5\text{H}$ (Me_4Cp), Me_5C_5 (Cp^*)) were prepared as previously reported [10]. Methylolithium (MeLi) was obtained from Fluka as a 1.6 M solution in diethyl ether. Finely crystalline LiAlH_4 (Metallgesellschaft, Frankfurt a.M.) was handled and weighed in dry air. Solvents (hexane, diethyl ether, toluene, benzene- d_6) were purified by boiling with LiAlH_4 followed by distillation *in vacuo*. They were stored in the vacuum line as solutions of dimeric titanocene.

Methods

^1H and ^{13}C NMR spectra were measured on a Varian VXR-400 instrument (400 and 100 MHz, respectively) in C_6D_6 at 25°C and were referred to the solvent signal

(δ_{H} 7.15 ppm, δ_{C} 128.0 ppm). Assignment of the spectra was based on the proton-coupled ^{13}C NMR, COSY, and HETCOR results.

Mass spectra were recorded on a JEOL JMS D-100 spectrometer at 75 eV. Samples in sealed capillaries were opened and inserted into the direct inlet under argon.

Electronic absorption spectra were measured on a Varian Cary 17 D spectrometer in the range 300–2000 nm in 0.1 and in 1.0 cm sealed quartz cells (Hellma).

ESR spectra were recorded on an ERS-220 spectrometer (Centre for Scientific Instruments, German Acad. Sci., Berlin, GDR) in the X-band.

Preparation of the $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds

The MeLi solution (1.6 M, 4 ml) was added under vacuum to a stirred suspension of $\bar{\text{Cp}}_2\text{TiCl}_2$ (3 mmol) in diethyl ether (20 ml) cooled by a dry ice/ethanol mixture. The reaction mixture was warmed to room temperature and, when all the $\bar{\text{Cp}}_2\text{TiCl}_2$ had disappeared, the ether was evaporated *in vacuo* and a yellow product was extracted with hexane. The Cp and MeCp compounds were crystallized from hexane solutions at low temperature as described elsewhere [7] and were stored as toluene solutions in the dark at 77 K. The Me_3Cp , Me_4Cp and Cp^* compounds were crystallized at ambient temperature and were stored as crystals or toluene solutions in a refrigerator. These compounds were characterized by their NMR and electronic absorption spectra.

(Me_3Cp) $_2\text{TiMe}_2$: ^1H NMR: δ -0.31 (s, Ti-CH₃, 6H); 1.94 (s, 12H); 2.18 (s, 6H); 5.10 (s, 4H). ^{13}C NMR: δ 10.86 (q, 2C); 13.47 (q, 4C); 45.97 (q, Ti-CH₃, 2C); 107.72 (d, 4C); 121.83 (s, 2C); 122.75 (s, 4C). UV-Vis (hexane): λ_{max} = 383 nm (sh).

(Me_4Cp) $_2\text{TiMe}_2$: UV-Vis (hexane): λ_{max} = 397 nm (sh). The ^1H and ^{13}C NMR spectra are listed in Table 1. The compound was also prepared by Courtot et al. [12] by the same procedure and its ^1H NMR spectrum agrees with that measured here.

$\text{Cp}^*_2\text{TiMe}_2$: ^1H NMR: δ -0.49 (s, Ti-CH₃, 6H); 1.95 (s, 30H). ^{13}C NMR: δ 11.34 (q, 10C); 48.70 (q, Ti-CH₃, 2C); 118.52 (s, 10C). UV-Vis (hexane): λ_{max} = 423 nm.

Thermolysis of the $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds

Toluene solutions of the $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds (3 mmol in 20 ml) in glass ampoules (200 ml) were heated in an oven at 130°C. The solutions of Cp_2TiMe_2

Table 1

^1H and ^{13}C NMR spectra of ($\text{Me}_4\text{C}_5\text{H}$) $_2\text{TiMe}_2$ ^a

Assignment	δ_{C}	n_{C}	mt	J	δ_{H}	n_{H}	mt
Ti-Me	47.76	2	Q	126.0	-0.582	6	s
C-1	108.33	2	D st	166.8, 3.9	4.487	2	s
C-2,5	117.95	4	dqq	4.1, 3.0, 1.1	-		
C-3,4	124.57	4	dqq	5.6, 3.0, 2.0	-		
Me-2,5	13.84	4	Qd	126.5, 1.6	1.511	12	s
Me-3,4	12.23	4	Q	126.0	2.027	12	s

^a The assignment is based on the following reasons: Singlet at δ_{H} 1.511 increases in intensity upon irradiation at 4.487 ppm and therefore represents Me-2,5. The irradiation of Me-2,5 in ^1H NMR spectrum removes the septet splitting of C-1 signal and simplifies the signals of C-2,5 and C-3,4 so that both their couplings to H-1 are discernible. Assuming that $^3J > ^2J$, the signal exhibiting larger coupling to H-1 was assigned to C-3,4.

Table 2

¹H and ¹³C NMR spectra of (Me₄Cp)(Me₃Fv)TiMe (major isomer)

Assignment ^a	δ _C ^a	n _C	mt	J	δ _H	n _H	mt
Ti-Me	39.88	1	Q	150.5	-1.085	3	s
C-1	107.86	1	D	166.1	4.403	1	s
C-2	115.92 ^b	1	S	—	—		
C-3	117.73 ^b	1	S	—	—		
C-4	119.17 ^b	1	S	—	—		
C-5	119.41 ^b	1	S	—	—		
Me-2	13.41 ^c	1	Q	126.0	1.729	3	s
Me-3	12.34 ^d	1	Q	126.1	1.894	3	s
Me-4	12.84 ^d	1	Q	126.5	2.129	3	s
Me-5	13.33 ^c	1	Q	126.0	1.919	3	s
C-1'	118.00	1	D	168.7	3.766	1	s
C-2'	123.61 ^c	1	S	—	—		
C-3'	127.13 ^c	1	S	—	—		
C-4'	128.63 ^c	1	S	—	—		
C-5'	128.88 ^c	1	S	—	—		
=CH ₂	74.41	1	T	150.5	1.058	1	d
					2.017	1	d
							J = 4.1
Me-N'	11.13 ^f	1	Q	126.2	1.714	3	s
Me-N'	13.44 ^f	1	Q	126.5	1.455	3	s
Me-N'	14.51 ^f	1	Q	125.8	1.439	3	s

^a Mutual position of =CH₂ and =CH- groups remains unknown; signals bearing the same superscript b-f can be interchanged; N = 2, 3, 4 or 5.

and (MeCp)₂TiMe₂ rapidly turned brown and, after 30 min, a black precipitate was formed. The solutions of the other compounds were heated for 4 h and gave a yellow-brown solution for (Me₃Cp)₂TiMe₂, a blue solution for (Me₄Cp)₂TiMe₂, and a turquoise solution for Cp⁺₂TiMe₂. The volatile products and toluene were pumped off and the products were extracted with hexane. After evaporation of hexane, only small amounts of intractable products were obtained from Cp₂TiMe₂ and (MeCp)₂TiMe₂, whereas an amorphous brown product was obtained almost quantitatively from (Me₃Cp)₂TiMe₂. However, the product did not sublime without decomposition, its UV-Vis spectrum displayed continuous absorption of decreasing intensity in longer wavelengths and its NMR spectra were uninterpretable.

The product from (Me₄Cp)₂TiMe₂ formed an oily blue liquid which was easily distilled *in vacuo* at 100 °C without decomposition. The MS molecular ion and a fragmentation pattern similar to that of Cp⁺(Fv⁺)TiMe identified the compound as (Me₄C₅H)(Me₃C₅)(CH₂)H)TiMe ((Me₄Cp)(Me₃Fv)TiMe). Its structure and the presence of four isomers were revealed by NMR spectroscopy; ¹H and ¹³C NMR spectra of the major isomer are listed in Table 2.

(Me₄Cp)(Me₃Fv)TiMe was obtained in a yield of 0.8 g (87%). MS spectrum (direct inlet, 50 °C, *m/z* (%)): 305 (*M*⁺, 28.5), 304 (*M*⁺, 100), 303 (17), 302 (28), 290 ([*M* - CH₃]⁺, 25), 289 ([*M* - CH₃]⁺, 77), 288 (24), 287 (48), 285 (28), 283 (14), 168 (8.5), 167 (18), 166 (16), 165 (14), 164 (16), 163 (13), 144.5 ([*M* - CH₃]²⁺, 5.5), 137 (largely [*M* - 2CH₃]²⁺, 16), 120 (8.5), 107 (9), 105 (22.5). Ions attributable to the presence of impurities were not detected. UV-Vis (hexane): λ_{max} = 575 nm (Fig. 1, B).

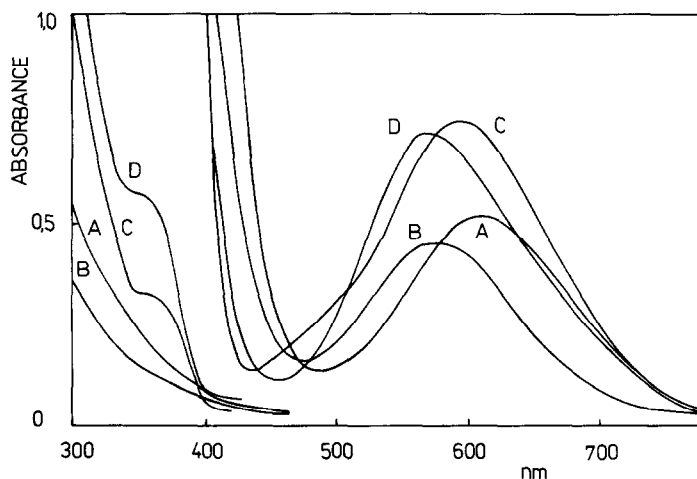


Fig. 1. Electronic absorption spectra of $\text{Cp}^*(\text{Fv}^*)\text{TiMe}$ (A), $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$ (B), $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ (C), and $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ (D) (in hexane, UV region $d = 0.1$ cm, Vis region $d = 1.0$ cm).

A turquoise crystalline compound obtained from $\text{Cp}_2^*\text{TiMe}_2$ was identified as $\text{Cp}^*(\text{Fv}^*)\text{TiMe}$ by comparison of its MS and NMR spectra with those reported in refs. 1 and 4, respectively. UV-Vis (hexane): $\lambda_{\text{max}} = 605$ nm (Fig. 1, A).

Preparation of dimethylenecyclopentenyl (allyldiene, Ad) compounds $\text{Cp}^(\text{Ad}^*)\text{Ti}$ and $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$*

The compounds were prepared by the high-temperature reaction of the appropriate Cp_2TiCl_2 compounds with LiAlH_4 followed by sublimation of the soluble reaction products. $\text{Cp}^*(\text{Ad}^*)\text{Ti}$. $\text{Cp}_2^*\text{TiCl}_2$ (1.55 g, 4 mmol) and LiAlH_4 (0.6 g, 16 mmol) were mixed in toluene under argon and the mixture was boiled with stirring for 8 h. After cooling to ambient temperature, the reaction vessel was pumped out to light negative pressure and sealed off the line. A dirty green solution was poured off from the black sediment into a side arm ampoule and was sealed off. Toluene was evaporated from this solution *in vacuo* and the residue was sublimed at $100^\circ\text{C}/10^{-3}$ Torr. The first, bright blue fraction, was separated by dissolving in hexane and was crystallized by cooling to give blue crystals. The yield of $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ was 0.34 g (27%). The ^1H and ^{13}C NMR spectra and the MS spectrum (direct inlet, 50°C) agreed satisfactorily with the published data [2]. UV-Vis (hexane): $\lambda_{\text{max}} = 360$ sh and 590 nm ($\epsilon(360) \gg \epsilon(590)$, see Fig. 1, C).

$(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$. $(\text{Me}_4\text{Cp})_2\text{TiCl}_2$ (1.44 g, 4 mmol) and LiAlH_4 (0.6 g, 16 mmol) were boiled in toluene for 6 h under argon. Subsequent treatment was the same as for $\text{Cp}^*(\text{Ad}^*)\text{Ti}$. The blue, most volatile sublimation fraction was dissolved in hexane. After evaporation of hexane, $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ was obtained as a waxy solid in a yield of 0.12 g (10%). The ^1H and ^{13}C NMR spectra revealed that the product is a mixture of two isomers, with the asymmetrical isomer predominating (Table 3). The MS spectrum showed the most abundant molecular ion to be m/z 288 (M^+) and was further characterized by three groups of ions in the order of decreasing intensity: $[M - n\text{H}_2]^+ > [M - (\text{C}_9\text{H}_{14} + n\text{H}_2)]^+ > [M - (\text{CH}_3 + n\text{H}_2)]^+$. The abundance of ions within the groups decreased with increasing value of n .

Table 3

^1H and ^{13}C NMR spectra of the major (asymmetrical) and the minor (symmetrical) isomers of $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$

Assignment ^a	δ_{C} ^a	n_{C}	mt	δ_{H}	n_{H}	mt	
<i>Major isomer</i>							
C-1	108.68	1 ⁱ	D	5.907	1	s	
C-2	119.97 ^b	1	S	–			
C-3	121.42 ^b	1	S	–			
C-4	121.44 ^b	1	S	–			
C-5	120.39 ^b	1	S	–			
Me-2	13.85 ^c	1	Q	1.718	3	s	
Me-3	12.32 ^d	1	Q	1.850	3	s	
Me-4	12.39 ^d	1	Q	1.877	3	s	
Me-5	13.96 ^c	1	Q	1.746	3	s	
C-1'	115.97	1	D	4.142	1	s	
C-2'	144.33 ^e	1	S	–			
C-3'	146.56 ^e	1	S	–			
C-4'	125.04 ^f	1	S	–			
C-5'	136.37 ^f	1	S	–			
$=\text{CH}_2\text{-}2'$	67.24 ^g	1	T	0.988	1	d	$J = 4.3 \text{ Hz}$
				1.094	1	d	
$=\text{CH}_2\text{-}3'$	69.91 ^g	1	T	0.692	1	d	$J = 3.7 \text{ Hz}$
				0.990	1	d	
Me-4'	10.37 ^h	1	Q	1.055	3	s	
Me-5'	12.23 ^h	1	Q	1.327	3	s	
<i>Minor isomer</i>							
C-1	108.94	1	D	6.146	1	s	
C-2,5	120.26	2	S	–			
C-3,4	125.52	2	S	–			
Me-2,5	14.34	2	Q	1.758	6	s	
Me-3,4	12.39	2	Q	1.780	6	s	
C-1'	124.84	1	D	5.258	1	s	
C-2',5'	125.56	2	S	–			
C-3',4'	146.02	2	S	–			
Me-2',5'	12.43	2	Q	1.105	6	s	
$=\text{CH}_2\text{-}3',4'$	67.04	2	T	ⁱ			

^a Signals bearing the same superscript (b–h) can be interchanged. ⁱ Assignment uncertain.

($n = 0\text{--}3$). UV-Vis (Hexane): $\lambda_{\text{max}} = 355 \text{ nm}$ and 570 nm ($\epsilon(355) \gg \epsilon(570)$), see Fig. 1, D).

Results and discussion

The thermolytic demethanation of the $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds in toluene at 130°C afforded fulvene derivatives of the $(\bar{\text{Cp}})(\bar{\text{Fv}})\text{TiMe}$ type for only the Cp^* and Me_4Cp compounds. Their yields were practically quantitative. The structures of $\text{Cp}^*(\text{Fv}^*)\text{TiMe}$ and $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$ are essentially the same, as follows from their ^1H and ^{13}C NMR spectra, which afford similar δ_{C} and $^1J(\text{CH})$ values for the CH_2 groups and very similar values for the other parameters (cf. ref. 4 and Table 2). The spectra of $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$, however, indicated the presence of four isomers (four singlets (^1H) and four quartets (^{13}C) in the Ti–Me region, three

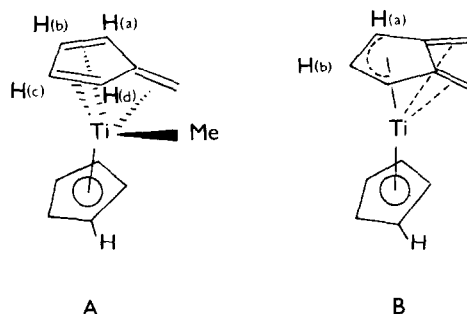


Fig. 2. Structures of the $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$ (A) and $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ (B) isomers: four isomers of A contain the hydrogen atom in the Me_3Fv ligand in positions denoted letters (a)–(d), respectively, the asymmetrical and the symmetrical isomers of B have the hydrogen atom position denoted by letters (a) and (b), respectively; the Me groups are omitted, the hydrogen atom position in the Me_4Cp ligands is not specified.

different exomethylenes (^{13}C , etc.); the data for the major component and their assignment are given in Table 2. The presence of four isomers implies that the Ti–Me bond is located away from the plane defined by the centroids of the Me_4Cp and Me_3Fv ligands and by the position of the Ti atom. Then the two pairs of isomers containing the $=\text{CH}-$ and $=\text{CH}_2$ groups of the Me_3Fv ligand in the vicinal and distant positions differ in the position of the $=\text{CH}-$ group of the Me_3Fv ligand with respect to the position of the Ti–Me bond (the same or opposite sides of the above mentioned plane) (see Fig. 2, A). The asymmetrical placement of the Ti–Me bond also induces a nonequivalency of the carbon atoms in the Me_4Cp ring (cf. NMR spectra of symmetrical $(\text{Me}_4\text{Cp})_2\text{TiMe}_2$ in Table 1) and probably accounts for the complete nonequivalence of the Me groups in the Fv^* ligand of $\text{Cp}^*(\text{Fv}^*)\text{TiMe}$ [4]. The NMR spectra of $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$ do not specify the mutual configuration of the $=\text{CH}-$ and $=\text{CH}_2$ groups in the major isomer; however, we assume that the distant position is more probable. It follows from the results of a single-crystal X-ray study of $(\text{Me}_4\text{Cp})_2\text{TiCl}_2$, indicating that the $=\text{CH}-$ groups were exclusively in the positions where the Me_4Cp rings were inclined towards each other [13]; hence, the hydrogen abstraction in the transient species $(\text{Me}_4\text{Cp})_2\text{Ti}=\text{CH}_2$ should involve predominantly the Me groups at distant positions to the $=\text{CH}-$ group.

The ESR study of the thermal treatment of $\text{Cp}_2^*\text{TiMe}_2$ and $(\text{Me}_4\text{Cp})_2\text{TiMe}_2$ in sealed ESR tubes revealed the formation of small amounts of paramagnetic byproducts ($g = 1.9781$, $\Delta H = 5.0$ G, $a_{\text{Ti}} = 9.0$ G for $\text{Cp}_2^*\text{TiMe}_2$ and $g = 1.9800$, $\Delta H = 3.8$ G for $(\text{Me}_4\text{Cp})_2\text{TiMe}_2$). Their structure is not known; that they differ from the $\bar{\text{Cp}}_2\text{TiMe}$ and $\bar{\text{Cp}}(\bar{\text{Fv}})\text{Ti}$ compounds [14] is shown by their smaller linewidth and higher g -values. Their concentrations were estimated to be less than 2% of the overall titanium content and were further lowered by the sublimation.

In contrast to the almost quantitative formation of $(\text{Me}_4\text{Cp})(\text{Me}_3\text{Fv})\text{TiMe}$, the less methyl-substituted $\bar{\text{Cp}}_2\text{TiMe}_2$ compounds gave no products of $(\bar{\text{Cp}})(\bar{\text{Fv}})\text{TiMe}$ type. Cp_2TiMe_2 and $(\text{MeCp})_2\text{TiMe}_2$ were decomposed mostly to insoluble black products and $(\text{Me}_3\text{Cp})_2\text{TiMe}_2$ afforded a brown, hexane-soluble, non-crystallizing material whose structure remains unknown. Its UV-Vis spectrum does not display

any distinct absorption band in the visible region and is thus incompatible with the spectra of the fulvene compounds (see Fig. 1). Since the elimination of methane from Cp_2TiMe_2 and Cp^*TiMe_2 was shown to proceed through hydrogen abstraction from the geminal Me group [4,7], the change in the structure of the products must be attributable to a change in the reactivity of $\text{Cp}_2\text{Ti}=\text{CH}_2$ intermediates induced by methyl substituents. Both the electron donation and the steric effects of Me groups increase the stability of the carbene intermediates and thus favour the intramolecular hydrogen transfer selectively yielding thermally stable fulvene complexes.

The η^3 : η^4 -allyldiene compounds $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ and $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ were prepared by a novel method which involves boiling a mixture of $\text{Cp}_2^*\text{TiCl}_2$ or $(\text{Me}_4\text{Cp})_2\text{TiCl}_2$ with LiAlH_4 in aromatic hydrocarbons. The compounds were obtained from dirty green products which were isolated from the reaction solutions after evaporation of toluene. Their sublimation afforded several products among which $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ and $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ were the most volatile. This preparative method for $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ is simple and the yield (27%) is slightly better than in the method using the thermal elimination of 2 molecules of methane from $\text{Cp}_2^*\text{TiMe}_2$ at 160°C (22%) [2]. The new compound $(\text{Me}_4\text{Cp})(\text{Me}_2\text{Ad})\text{Ti}$ was obtained only in a low yield (10%). It forms an oily product which consists of two isomers (Fig. 2, B) which were both identified on the basis of their ^1H and ^{13}C NMR spectra (Table 3). The minor component shows three different methyls, one exomethylene, two $=\text{CH}-$ groups and three quaternary carbon atoms; it corresponds to a symmetrical isomer. The major product has six different methyls, two exomethylenes, two $=\text{CH}-$ groups, and eight quaternary carbon atoms and corresponds to an unsymmetrical isomer. The asymmetry in the Me_2Ad ligand also induces asymmetry in the Me_4Cp ligand. The *exo*-methylene groups are assumed to be in *vicinal* positions by analogy with the structure of $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ which has been established by X-ray study of the structure of the product of reaction of $\text{Cp}^*(\text{Ad}^*)\text{Ti}$ with acetophenone [2].

In the series of Cp_2TiCl_2 compounds, the above treatment with LiAlH_4 afforded $\mu-(\eta^5:\eta^5\text{-fulvalene})\text{-di-}\mu\text{-hydrido-bis}(\eta^5\text{-cyclopentadienyltitanium})$ (dimeric titanocene) for Cp_2TiCl_2 [8] and an analogous methyl-substituted compound for $(\text{MeCp})_2\text{TiCl}_2$ [14], both in high yields. The structure of the dirty green products which were obtained from $(\text{Me}_3\text{Cp})_2\text{TiCl}_2$, $(\text{Me}_4\text{Cp})_2\text{TiCl}_2$ and $\text{Cp}_2^*\text{TiCl}_2$ is not yet known—the blue allyldiene derivatives were, however, obtained only from the Me_4Cp and Cp^* precursors (*vide supra*).

The valence state of titanium has been investigated in both the fulvene and allyldiene compounds [15]. The compounds are diamagnetic and exhibit one absorption band in the visible region. The band position is sensitive to the number of Me groups in the compounds: it is shifted to shorter wavelengths in the Me_4Cp compounds (Fig. 1). Shifts of similar magnitude are characteristic for transitions involving the cyclopentadienyl ligand orbitals, e.g., in the Cp_2TiMe_2 compounds (*vide supra*) and in CpTiCl_3 and $\text{CpTi}^{\text{III}}\text{Al}_2\text{Cl}_{8-x}\text{Et}_x$ ($x = 0-4$) complexes [10]. The molar extinction coefficients of these bands are higher than $300\text{ cm}^2\text{ mmol}^{-1}$ and this indicates that the titanium *d*-orbitals are strongly mixed with the π -orbitals of the Fv and Ad ligands. Correspondingly, no bands were found in the photoelectron spectra of these compounds in the region of the ionization energies of the titanium *d*-electrons. A full account of the photoelectron spectra of these compounds will be published in a forthcoming paper.

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