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Synthesis and thermolysis of $\mathrm{Cp}^*(\mathrm{C_5Me_4CH_2})\mathrm{TiR}$ complexes

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Abstract

Substitution of the chloride in $\mathrm{Cp}^*\mathrm{FvTiCl}$ with MR ($\mathrm{Fv = C_5Me_4CH_2}$; R = Me, $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2CMe_3}$, $\mathrm{CH=CH_2}$, M = Li; R = $\mathrm{CH_2Ph}$, M = K; R = $\mathrm{C_3H_5}$, M = MgCl; R = Ph, M = Na · NaCl) gives $\mathrm{Cp}^*\mathrm{FvTiR}$. NMR spectroscopic evidence points towards a series of structurally related compounds with a bent-sandwich geometry. The substituent R is positioned in the wedge, midway below the exocyclic methylene group and a neighbouring methyl group of the fulvene. Thermolysis of $\mathrm{Cp}^*\mathrm{FvTiR}$ gives, dependent on the substituent R, reduction to $\mathrm{Cp}^*\mathrm{FvTi}$ (R = $\mathrm{CH_2Ph}$) or the double ring metallated $\mathrm{Cp}^*[\mathrm{C_5Me_3(CH_2)_2}]\mathrm{Ti}$ (R = $\mathrm{CH_2XMe_3}$, X = C, Si) or $\mathrm{Cp}^*\mathrm{FvTiCH{=}CHMe}$ (R = η^3-$\mathrm{C_3H_5}$).

Keywords: Titanium; Titanocene; Thermolysis; Alkyl; Fulvene; NMR

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1. Introduction

The thermolysis of bispermethylcyclopentadienyl metal hydrocarbyls of the early transition metals and lanthanides has led to several ring metallated, tetramethyl fulvene ($\mathrm{Fv = C_5Me_4CH_2}$) complexes, either as intermediates or as isolable complexes [1–8]. For the Group 4 metals, these involve $\mathrm{Cp}^*\mathrm{FvTi}$, $\mathrm{Cp}^*\mathrm{FvTiH}$, $\mathrm{Cp}^*\mathrm{FvTiMe}$, $\mathrm{Cp}^*\mathrm{FvZrPh}$ and $\mathrm{Cp}^*\mathrm{FvHfCH_2Ph}$ [1–4]. The fulvene structure is also found in the thermolysis products of $\mathrm{Cp}_2^*\mathrm{MH}$ (M = Y, Sm) [5], $\mathrm{Cp}^*\mathrm{M}(\mu\text{-H})(\mu\text{-}\eta^5{:}\eta^1\text{-C_5Me_4CH_2})\mathrm{MCp}_2^*$, forming a bridge between the two metal centres. The highly reactive fulvene ligand engages in a number of reactions. Ketones and nitriles couple to the exocyclic methylene group, leading to functionalized Cp ligands [9]. Butadiene was reported to react with $\mathrm{Cp}^*\mathrm{FvZr}^+$ cation to yield $\mathrm{Cp}^*\mathrm{Zr}(\eta^5{:}\eta^3\text{-}\mathrm{C_5Me_4CH_2CH_2CHCHCH_2})^+$ [6]. C–H activation is also frequently observed in Group 3 and 4 fulvene complexes, and we will focus on this here. The fulvene ligand may undergo further metallation to give double tucked-in allyldiene $\mathrm{C_5Me_3(CH_2)_2}$ structures, as in the thermolysis of $\mathrm{Cp}^*\mathrm{FvTi}$ to $\mathrm{Cp}^*[\mathrm{C_5Me_3(CH_2)_2}]\mathrm{Ti}$ [10–12], or yield a bridging ligand between two centres as in $\{\mathrm{Cp}^*\mathrm{Zr}[(\mu\text{-}\eta^5);\eta^1,\eta^1\text{-}\mathrm{C_5Me_3(CH_2)_2}]\}_2$ [11] and in dimeric $[\mathrm{Cp}^*\mathrm{Ce}(\mu\text{-}\eta^5;\eta^1;\eta^1\text{-}\mathrm{C_5Me_3(CH_2)_2})\mathrm{CeCp}_2^*]_2$ [13,14]. Such 1,2-double metallated Cp^* ligands are also obtained in the thermolysis of $\mathrm{Cp}^*\mathrm{Ta(V)}$ and $\mathrm{Cp}_2^*\mathrm{W(IV)}$ hydrides [15].

An interesting feature of the tetramethyl fulvene ligand is its ability to accept a hydrogen atom to form a (new) Cp^* derivative. If this occurs intramolecularly, an isomerization results. For example, isotope scrambling in $\mathrm{Cp}^*\mathrm{FvZrPh}$ between the Fv and the Ph ligands shows that the orthophenylene $\mathrm{Cp}_2^*\mathrm{Zr(C_6H_4)}$ is formed reversibly [3]. Heating $\mathrm{Cp}^*\mathrm{FvHfCH_2Ph}$ gives $\mathrm{Cp}_2^*\mathrm{Hf}(\text{-}o\text{-}\mathrm{C_6H_4CH_2})$ [4] and thermolysis of $\mathrm{Cp}^*\mathrm{FvMCH_2SiMe_3}$ (M = Zr [11], Th [16]) yields the metallasilacyclobutane $\mathrm{Cp}_2^*\mathrm{M}(\mu\text{-CH_2})_2\mathrm{SiMe_2}$. The intermolecular reaction between a C–H bond and a fulvene affords a Cp^* metal carbyl species: this can be considered a first step towards the functionalization of alkanes and aromates. The latter type of reactions are found for fulvene complexes of the strong Lewis-acidic Group 3 and lanthanide elements. In $\mathrm{Cp}_2^*\mathrm{MR}$ (M = Sc, Lu; R = Me; M = Y, Ce; R = H), transient $\mathrm{Cp}^*\mathrm{FvM}$ species react intermolecularly with C–H bonds of alkanes or aromates to give $\mathrm{Cp}_2^*\mathrm{MR}$ derivatives [7,8,14].

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The properties of the tetramethyl fulvene ligand with respect to C–H activations are thus dual in character: it may serve as a sink or as a source for hydrogen atoms.

In the trivalent titanium compound Cp*FvTi, multiple H/D exchange occurs between the fulvene and C_6D_6, demonstrating that the much weaker Lewis acid Ti can also activate C–H bonds (cf. Ref. [3]; the thermally very stable aryl derivative Cp_2^*TiPh, however, was never observed in these exchange processes). Recently, we found a high yield route to tetravalent Cp*FvTiCl, a versatile starting material for the synthesis of titanium fulvene derivatives Cp*FvTiR (R = alkyl, aryl). We studied the thermolysis of these compounds to establish thermal rearrangements involving C–H activations, with the objective of using these reactions for stoichiometric or catalytic transformations. Here we report on the outcome of this introductory study.

2. Results

2.1. *Synthesis and characterization of Cp*FvTiR complexes*

The starting material for compounds Cp*FvTiR is the monochloride derivative Cp*FvTiCl (**1**) [9]. Complex **1** is prepared in high yields from the paramagnetic Cp*FvTi by oxidation with $PbCl_2$ [17] (Eq. (1)). The chloride in **1** may be substituted for alkyl or aryl group by salt metathesis with alkali metal alkyl or Grignard reagents (Eq. (2)). Reaction of **1** and EtLi yields the ethene adduct of titanocene $Cp_2^*Ti(\eta^2\text{-}C_2H_4)$ [18], without observation of the likely intermediate Cp*FvTiEt (Eq. (3)).

$$\mathrm{Cp^*FvTi + 0.5PbCl_2 \rightarrow Cp^*FvTiCl + 0.5Pb} \qquad (1)$$

$$\mathrm{Cp^*FvTiCl + RM \rightarrow Cp^*FvTiR + MCl} \qquad (2)$$

$$R = Ph\ (\mathbf{3}),\ = Na \cdot NaCl;\ R = Me\ (\mathbf{2})\ [2],$$
$$\mathrm{CH_2SiMe_3}\ (\mathbf{5}),\ \mathrm{CH_2CMe_3}\ (\mathbf{6}),$$
$$\mathrm{CH = CH_2}\ (\mathbf{7}),\ \mathrm{M = Li;\ R = CH_2Ph}\ (\mathbf{4}),$$
$$\mathrm{M = K;\ R = C_3H_5}\ (\mathbf{8}),\ \mathrm{M = MgCl}$$

$$\mathrm{Cp^*FvTiCl + EtLi \rightarrow Cp_2^*Ti(\eta^2 - C_2H_4) + LiCl} \qquad (3)$$

The spectroscopic properties of **2–7** are consistent with the formulation as fulvene alkyl complexes. Detailed information on the structure of compounds **1–8** in solution was obtained by NMR techniques (Tables 1–3). The methyl substituents of the fulvene ligand in **1** give rise to four distinct singlets at 1.20, 1.44, 1.72 and 2.16 ppm. The diastereotopic protons of the exocyclic methylene group of the fulvene ligand are observed as two characteristic doublets at 1.48 and 2.63 ppm. The HMBC spectrum in combination with NOE data allows a complete assignment of these resonances [^{1}H-detected multiple bond correlation (HMBC); nuclear Overhauser effect (NOE); rotating frame Overhauser enhancement spectroscopy (ROESY)]. The chemical shift increases along the ring in one direction, with the resonance of the methyl groups at highest field next to the highest field resonance of the two methylene protons (and vice versa for the lowest field resonances, cf. Fig. 1). The resonances of the fulvene methyl and methylene groups of the other compounds (**2–7**) are listed in Table 3, along with those of other known Cp*FvTiR com-

Table 1
Proton NMR data of group R in Cp*FvTiR

Compound	Assignment	δ (ppm)	Int (H)	m	J(HH) (Hz)
Cp*FvTiPh (**3**)	Ph	5.97	2	pt	7.3
		7.0	3	m	
Cp*FvTiBz (**4**)	CH_2	−0.56	1	d	13.2
		2.43	1	d	13.2
	Ph	6.31	2	m	
		6.97	3	m	
Cp*FvTiCH$_2$CMe$_3$ (**5**)	CH_2	0.71	1	d	11
		−1.39	1	d	11
	CMe$_3$	1.03	9	s	
Cp*FvTiCH$_2$SiMe$_3$ (**6**)	CH_2	0.19	1	d	10.6
		−1.32	1	d	10.6
	SiMe$_3$	0.13	9	s	
Cp*FvTiC$_2$H$_3$ (**7**)	Ti–CH	5.17	1	dd	18.9, 14.8
	C=CH$_2$ c	5.67	1	dd	14.8, 4
	t	4.25	1	dd	18.9, 4
Cp*FvTi(C$_3$H$_5$) (**8**)	CH	3.95	1	p	12.4
	CH_2	2.27	4	d	12.4
Cp*FvTiCHCHMe (**9**, 41 °C)	Me	1.8	3	d	5.5
	CH	4.61	1	d	17.1
		4.33	1	dq	17.1, 5.5

Table 2
^{13}C NMR data of Cp*FvTiR compounds

Compound (temperature)	Assignment	δ (ppm)	mult	J(C–H) (Hz)
Cp*FvTiCl (1)	Cp*	12.43	q	126.6
		121.41	s	
	$\mathrm{C}_5\mathit{Me}_4$	10.60	q	126.6
		11.12	q	126.5
		11.56	q	126.6
		15.37	q	126.6
	$\mathit{C}_5\mathrm{Me}_4$	125.8	s	
		121.58	s	
		126.0	s	
		129	s	
		136	s	
	$=\mathrm{CH}_2$	79.04	t	153.1
Cp*FvTiPh (3)	Cp*	11.88	q	126.6
		120.01	s	
	$\mathrm{C}_5\mathit{Me}_4$	14.65	q	127.6
		10.83	q	126.6
		10.82	q	126.6
	$\mathit{C}_5\mathrm{Me}_4$	122.2	s	
		124.8	s	
		127.5	s	
		128.48	s	
		130.9	s	
	$=\mathrm{CH}_2$	78.6	t	149
	Ph	123.05	dt	158, 7
		125.61	dd	155, 7
		126.9	dd	153, 7
		128.57	dt	152, 8
		129.15	dt	150, 8
		200.95	s	
Cp*FvTiCH$_2$Ph (4)	Cp*	12.25	q	126
		126.6	s	
	$\mathrm{C}_5\mathit{Me}_4$	10.66	q	126.6
		11.16	q	126.6
		11.59	q	126.6
		13.71	q	126.5
	$\mathit{C}_5\mathrm{Me}_4$	119	s	
	$=\mathrm{CH}_2$	77.68	t	149.9
	Ti–CH$_2$	55.28	t	118.6
	Ph	149.86	s	
		122.41	dt	159, 7.5
		127.21	dm	162.1
		131.26	dm	153.2
Cp*FvTiCH$_2$CMe$_3$ (5)	Cp*	12.92	q	126.4
		119.41	s	
	$\mathrm{C}_5\mathit{Me}_4$	11.2	q	125.6
		11.7	q	125.5
		13.07	q	126.6
		16.27	q	126.6
	$\mathit{C}_5\mathrm{Me}_4$	119.8	s	
		125.4	s	
		127.3	s	
		127.5	s	
		130	s	
	$=\mathrm{CH}_2$	77.1	t	149.6
	TiCH$_2$	67.2	t	117.4
	$\mathrm{C}\mathit{Me}_3$	37.2	q	123
	$\mathit{C}\mathrm{Me}_3$	37.04	s	
Cp*FvTiCH$_2$SiMe$_3$ (6)	Cp*	12.58	q	126.6
		118.9	s	
	$\mathrm{C}_5\mathit{Me}_4$	10.84	q	125.6
		11.41	q	125.4
		12.35	q	124.1
		15.65	q	126.6
	$\mathit{C}_5\mathrm{Me}_4$	119.9	s	
		125.0	s	
		125.8	s	
		126.6	s	
		130.1	s	
	$=\mathrm{CH}_2$	76.11	t	150
	TiCH$_2$	45.76	t	107
	SiMe$_3$	6.14	q	117
Cp*FvTiC$_2$H$_3$ (7)	Cp*	12.17	q	126.1
		118.82	s	
	$\mathrm{C}_5\mathit{Me}_4$	10.58	q	125.5
		10.69	q	126.6
		10.87	q	127.3
		16.66	q	126.6
	$\mathit{C}_5\mathrm{Me}_4$	120.84	s	
		121.40	s	
		123.99	s	
		125.98	s	
	$=\mathrm{CH}_2$	76.20	t	150.2
	Ti–CH	208.0	d	117.2
	CH=CH$_2$	113.6	td	151.6, 4
Cp*FvTiC$_3$H$_5$ (8, 10°C)	Cp*	12.17	q	125.7
		111.98	s	
	$\mathrm{C}_5\mathit{Me}_4$	11.14	q	126
		11.35	q	126
		12.43	q	126
		13.02	q	126
	$\mathit{C}_5\mathrm{Me}_4$	112.76	s	
		113.61	s	
		115.57	s	
		116.05	s	
		125.39	s	
	$=\mathrm{CH}_2$	64.69	t	152.9
	CH	121.99	d	146.8
	CH$_2$	62.6	t	151.1
Cp*FvTiCH=CHMe (9)	Cp*	12.02	q	125.7
		118.8	s	
	$\mathrm{C}_5\mathit{Me}_4$	10.57	q	126.3
		10.66	q	126.3
		10.84	q	125.7
		15.9	q	126.9
	$\mathit{C}_5\mathrm{Me}_4$	120.63	s	
		121.7	s	
		125.63	s	
		130.6	s	
	$=\mathrm{CH}_2$	75.99	t	149.5
	TiCH	120.96	d	
	$\mathrm{C{=}}\mathit{C}\mathrm{H}$		d	
	$\mathrm{C{=}CH}\mathit{Me}$	24.82	q	123.9

pounds. The fulvene methyl groups show four singlets, which can be separated into four groups at mean (standard deviation) of 1.24 (0.026), 1.44 (0.026), 1.66 (0.17) and 2.01 (0.29) ppm. The latter two are very

Table 3
^1H NMR data of Cp^* and Fv ligands in Cp^*FvTiR in C_6D_6

	Cl	Me [a]	Ph	CH_2Ph	CH_2CMe_3	CH_2SiMe_3	Vinyl	Allyl	CH=CH(Me)	$C(Me)=CH_2$ [b]	$C(Me)=CH_2$ [b]
Cp^*	1.79	1.77	1.62	1.82	1.84	1.79	1.73	1.695	1.739	1.784	1.782
Me	1.20	1.26	1.27	1.20	1.24	1.26	1.22	1.212	1.25	1.268	1.226
	1.43	1.47	1.47	1.40	1.42	1.41	1.41	1.444	1.445	1.45	1.464
	1.71	1.67	1.62	1.28	1.95	1.83	1.59	1.722	1.622	1.675	1.683
	2.15	2.03	1.29	2.15	2.40	2.19	1.96	1.809	1.899	1.998	2.032
CH_2	1.47	1.14	1.48	1.18	1.22	1.24	1.28	2.173	1.322	1.348	1.406
	2.62	1.92	1.93	1.99	1.90	2.01	1.31	2.793	1.805	1.908	1.90

[a] Ref. [3].
[b] Ref. [19].

receptive to changes of the group R, the low field resonance showing the largest fluctuations. The resonances centred around 1.24 and 1.44 ppm on the contrary are found practically unchanged throughout the whole series of compounds. The same trend is found for the diastereotopic protons of the exocyclic methylene group, where one resonance is found at 1.31 (standard deviation 0.11), the other at 1.93 ppm (0.3 ppm). This indicates that the methylene (in particular the proton with the low field resonance) and one methyl group are in the very close vicinity of the substituent R. For the solution structure of these compounds we therefore propose that the methylene is pointing away from the plane through the ring centroids and Ti, with R binding between the methylene and one methyl group, as visualized in Fig. 1. This is corroborated by the NOE between Cp^* and the fulvene methyl groups at 1.2 (strongest) and 1.4 ppm (weaker), the only signals due to cross-relaxation between the Cp^* and the Fv ligand in the ROESY spectrum of **1**. It indicates that one side of the fulvene ligand is tilted towards the Cp^* (Fig. 1(b)).

A coordinated fulvene can be considered as either a neutral or a dianionic ligand, and along this line of argument the fulvene complexes are Ti(II), respectively Ti(IV), compounds [20]. One distinguishing property is the hybridization of the fulvene methylene group (cf. Ref. [21]). The chemical shift and the C–H coupling constant of the ^{13}C NMR resonances in compounds **1**–**7** are characteristic of an olefinic sp^2 centre. The resonance is found between 75 and 79 ppm with $J(C-H) \geq 150$ Hz. In the allyl derivative **8**, this resonance is shifted to somewhat higher field (at 64 ppm, $^1J(C-H) = 153$ Hz), but this is due to the η^3-allyl group. This bonding also has a marked influence on the colour of the compounds: **1**–**7** are green but **8** is orange. The green colour results from a weak absorption band around $\lambda = 650$ nm ($\varepsilon_{mol} \approx 100$ l mol^{-1} cm^{-1}), probably originating from a d–d transition. This also demonstrates that these complexes contain at least partly reduced Ti(IV), and indicates a neutral olefinic coordination for the fulvene ligands.

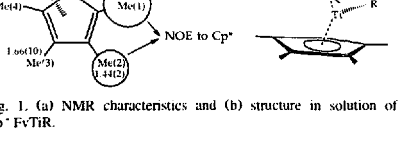

Fig. 1. (a) NMR characteristics and (b) structure in solution of Cp^*FvTiR.

2.2. *Thermolysis of Cp^*FvTiR*

With the synthesis of **2**–**8**, a series of structurally comparable fulvenes has become available, which were subjected to thermolysis. The decomposition pathways of Cp^*FvTiR show a remarkable dependence on the group R. In a number of cases Ti–C bond homolysis was observed, in other cases decomposition follows a concerted pathway, the fulvene ligand accepting or donating a hydrogen. $Cp^*FvTiPh$ (**3**) is thermally very robust and no decomposition was found after four days at 150 °C in toluene-d_8.

2.2.1. *Radical decomposition*

Heating the benzyl derivative $Cp^*FvTiCH_2Ph$ (**4**) to 110 °C results in the formation of trivalent titanium compound Cp^*FvTi along with 1,2-diphenylethane (Eq. (4)). This contrasts with the orthometallation observed in the thermolysis of Cp^*FvMCH_2Ph to yield $Cp_2^*MCH_2$-*o*-C_4H_6 (M = Zr [11], Hf [4]). Reduction to trivalent Ti is often a favourable option in titanium chemistry, definitely with the inherently weak metal–benzyl bond [the observed correlation between *D*(M–C) and the corresponding *D*(H–C) implies that the M–CH_2Ph bond is weaker than, for example, the M–CH_3 bond, as the C–H bond in toluene is weaker than the C–H bond in methane [22]], whereas in the heavier Group 4 congeners concerted pathways are preferred (see for example Ref. [23]). Titanium is apparently too small to let the benzyl ligand reach the transition state for a C–H activation, and bond homolysis becomes energetically the lowest pathway.

$$Cp^*FvTiCH_2Ph \rightarrow Cp^*FvTi + 0.5(PhCH_2)_2 \qquad (4)$$

Table 4
Rates constants for the decomposition of $Cp^*FvTiCH_2CMe_3$ (5)

Temperature (K)	k (10^{-5} s^{-1})
300	1.6
306	4.2
313	9.1
320	28
325	36

2.2.2. *Concerted decomposition*

Decomposition to a tetravalent titanium compound is observed for **5–8**. Thermolysis of $Cp^*FvTiCH_2CMe_3$ gives the double metallated product $Cp^*[C_5Me_3(CH_2)_2]Ti$ (Eq. (5)). The reaction follows first order kinetics for at least three half-lives, with $\Delta H^{\ddagger} = 110(1)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -30(5)$ J (mol^{-1} K^{-1}) between 300 and 325 K (Table 4). These values are characteristic of intramolecular C–H activations in early transition metal compounds, proceeding through a σ-bond metathesis [2–4,8,17] (thermolysis studies of hydrocarbyls [24])

$$Cp^*FvTiCH_2R' \rightarrow Cp^*[C_5Me_3(CH_2)_2]Ti + CH_3R' \quad (5)$$

$R' = H$ [11,12], CMe_3, $SiMe_3$

The trimethylsilylmethyl derivative **5** is much more stable, it only transforms noticeably into $Cp^*[C_5Me_3(CH_2)_2]Ti$ and Me_4Si at temperatures over 370 K. In contrast, its decomposition does not follow first order kinetics. An initial slow decomposition is followed by a faster process (Fig. 2). No efforts were made to elucidate this process in detail, which can be quite complicated in these systems, as was found in the thermolysis of Cp_2^*TiR [25]. The methyl derivative **2** also thermolyses to give $Cp^*[C_5Me_3(CH_2)_2]Ti$. For this reaction to proceed, even temperatures well over 400 K are needed [11,12].

The allyl derivative **8** isomerizes to $Cp^*FvTiCH{=}CHMe$ (**9**) [26]. In this process, reversible hydrogen migration to Fv and from the intermediate formed Cp^* ligand takes place through four observable intermediates, $Cp_2^*Ti(CH_2{=}C{=}CH_2)$, two isomers of $Cp^*FvTiCMe{=}CH_2$ and $Cp_2^*Ti(HC{\equiv}CMe)$. The details of this reaction are the subject of another paper [19].

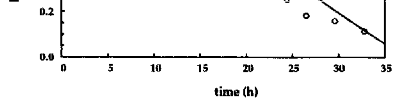

Fig. 2. Decomposition of $Cp^*FvTiCH_2SiMe_3$ at 381 K in benzene-d_6 as monitored by ^1H NMR, showing the relative intensity of the trimethylsilyl signal, and an extrapolated linear fit to the first six data points.

3. Concluding remarks

A series of derivatives of the type Cp^*FvTiR was prepared. The structure in solution could be described on the basis of its NMR properties. It shows that the fulvene is bound as polyolefin, rather than as a cyclopentadienyl–alkyl; the geometry is such that the reactive exocyclic methylene, the H-accepting entity, is in the very close vicinity of group R. C–H bond breaking in group R though is only observed for R = Et, allyl, which both have β-hydrogen atoms, and for the *ortho* hydrogens of the phenyl group in **3**, as was demonstrated by the slow H/D exchange between a deuterium labelled Ph-d_5 group and the fulvene and Cp^* methyl hydrogens [4] (this was also observed in $Cp^*CpTi[Ph\text{-}d_5]$ [27]). The derivatives with β-hydrogens in a flexible chain can be orientated towards the exocyclic methylene of the fulvene ligand, and the activation of the CH bond in group R can occur without much activation energy.

Evidence for the activation of α or γ C–H bonds was not found. In the thermolysis of the subclass of derivatives without β-hydrogens, $Cp^*FvTiCH_2R'$ (R′ = H, CMe_3, $SiMe_3$), a hydrogen is abstracted from a methyl group of the fulvene ligand to yield $Cp^*[C_5Me_3(CH_2)_2]Ti$. For R′ = CMe_3 this is a facile process, in contrast to derivatives with R′ = H or $SiMe_3$, where considerably higher temperatures are necessary for conversion. This could be the consequence of a kind of pre-orientation of a fulvene methyl group towards the neopentyl ligand in **5**, whereas this is not the case in the methyl, trimethylsilylmethyl or benzyl derivatives. Another reason may lie in electronic differences which cause the neopentyl as the most electron-rich derivative to decompose the fastest. Its HOMO has the greatest spatial extension, allowing the facile proton abstraction of a fulvene methyl group. The thermolysis of compound **6** indicates that an additional reaction path becomes accessible at higher temperatures. The same seems to hold for the benzyl derivative **7**, where the additional pathway is a Ti–C bond homolysis.

4. Experimental

4.1. *General considerations*

All operations were performed in an inert atmosphere with rigorous exclusion of oxygen and moisture using

Schlenk, vacuum-line or glove-box techniques. Solvents were thoroughly dried (ether, THF and pentane over Na/K alloy, toluene over Na) and distilled prior to use. C_6D_6 and THF-d_8 were vacuum transferred from Na/K alloy. IR spectra were recorded on a Mattson Galaxy spectrometer as Nujol mulls between KBr disks. NMR spectra were recorded on Bruker WH-90, WM 250, AC 250 or DRX 600 Avance, Jeol FX-90Q or JNM GX400 or Varian VXR-300 spectrometers. Chemical shifts are reported in parts per million and referenced to residual protons in deuterated solvents (C_6D_6 $\delta = 7.15$ ppm; THF-d_8 $\delta = 3.58$ ppm) for ^{1}H NMR and to characteristic multiplets for ^{13}C NMR (C_6D_6 $\delta = 127.98$ ppm; THF-d_8 $\delta = 67.4$ ppm). Elemental analyses were carried out at the Microanalytical Department of the University of Groningen.

4.2. *Cp* FvTiCl (1)*

Cp* FvTi (0.632 g, 1.99 mmol) [25] was dissolved in 20 ml of THF. $PbCl_2$ (0.551 g, 1.98 mmol) was added and the mixture was stirred for 0.5 h during which time the colour changed to green. The THF was removed in vacuum and the mixture was extracted with pentane. In several crops, 0.648 g of **1** (1.84 mmol, 92%) was isolated as dark green crystals. IR (cm^{-1}): 3060 (w), 2720 (w), 1070 (w), 1020 (s), 950 (w), 930 (m), 835 (m), 770 (w), 710 (w), 680 (w), 490 (m), 410 (w), 365 (m). Anal. Found: C, 67.34; H, 8.18; Ti, 13.35; Cl, 10.12. $C_{20}H_{29}ClTi$ Calc.: C, 68.09; H, 8.29; Ti, 13.58; Cl, 10.05%.

4.3. *Cp* FvTiPh (3)*

Cp* FvTiCl (0.264 g, 0.748 mmol) and PhNa · NaCl (0.270 g, 1.7 mmol) were stirred for 4 h in 10 ml of pentane. The solution was filtered and concentrated. After crystallization at −80 °C, 134 mg of **3** (0.34 mmol, 45%) in the form of green crystals was isolated. IR (cm^{-1}): 3050 (m), 2720 (w), 1560 (m), 1410 (m), 1365 (w), 1235 (w), 1160 (w), 1147 (w), 1080 (w), 1050 (w), 1025 (s), 995 (w), 860 (m), 830 (m), 800 (w), 730 (vs), 710 (vs), 620 (w), 590 (w), 515 (m), 420 (w). Anal. Found: C, 78.82; H, 8.64; Ti, 12.12. $C_{26}H_{34}Ti$ Calc.: C, 79.19; H, 8.69; Ti, 12.14%.

4.4. *Cp* FvTiCH$_2$Ph (4)*

Cp* FvTiCl (0.272 g, 0.770 mmol) and KCH_2Ph (0.163 g, 1.25 mmol) were stirred in 10 ml of toluene for 18 h. The solvent was evaporated and the residue was extracted with 10 ml of pentane. Crystallization at −80 °C yielded 0.079 g of **4** (0.397 mmol, 52%). IR (cm^{-1}): 3060 (w), 3040 (w), 2720 (w), 1590 (m), 1095 (m), 1070 (w), 1020 (m), 900 (w), 845 (w), 800 (w), 740 (s), 700 (s), 500 (w), 480 (w). Anal. Found: C, 78.37; H, 8.80; Ti, 11.89. $C_{27}H_{36}Ti$ Calc.: C, 79.39; H, 8.88; Ti, 11.73%.

4.5. *Cp* FvTiCH$_2$CMe$_3$ (5)*

Cp* FvTiCl (572 mg, 1.62 mmol) was dissolved in 5 ml of pentane and at 0 °C 6.5 ml of 0.25 M $LiCH_2CMe_3$ (1.62 mmol) was added. After stirring overnight at room temperature, the solution was filtered and concentrated. Crystallization at −80 °C yielded 370 mg of **5** (0.953 mmol, 59%) as green crystals. IR (cm^{-1}): 3040 (w), 1650 (w), 1355 (m), 1250 (m), 1200 (m), 1080 (w), 1060 (w), 1020 (s), 850 (m), 840 (m), 600 (m), 470 (w). Anal. Found: C, 76.83; H, 10.24; Ti, 12.43. $C_{25}H_{40}Ti$ Calc.: C, 77.29; H, 10.38; Ti, 12.33%.

4.6. *Cp* FvTiCH$_2$SiMe$_3$ (6)*

Cp* FvTiCl (699 mg, 1.98 mmol) and $LiCH_2SiMe_3$ (183 mg, 1.94 mmol) were suspended in 10 ml of pentane at 0 °C. After stirring overnight the solution was filtered and concentrated. Crystallization at −80 °C afforded 585 mg of **6** (1.44 mmol, 73%). IR (cm^{-1}): 3060 (w), 2720 (w), 1350 (m), 1280 (w), 1250 (m), 1240 (s), 1070 (w), 1020 (s), 920 (w), 890 (vs), 850 (bs), 740 (s), 720 (s), 660 (s), 600 (w), 580 (w), 550 (m), 470 (w). Anal. Found: C, 71.40; H, 9.97; Ti, 11.77. $C_{24}H_{40}TiSi$ Calc.: C, 71.37; H, 9.97; Ti, 11.84%.

4.7. *Cp* FvTi(C$_2$H$_3$) (7)*

Cp* FvTiCl (0.486 g, 1.376 mmol) was dissolved in 10 ml of ether. At room temperature, 7.25 ml of a 0.19 M LiC_2H_3 solution in ether was added to this mixture. The colour became bluish-green. After stirring for 24 h the solvents were removed in vacuo, and the resulting sticky mass was extracted with pentane. After concentrating the solution to approximately 1 ml, the vessel was held at −80 °C for three days, during which time a greenish-blue precipitate formed: 108 mg of **7** (0.32 mmol, 23%). IR (cm^{-1}): 3080 (vw), 3030 (w), 27020 (w), 1780 (w), 1540 (w), 1210 (m), 1170 (w), 1070 (w), 1025 (s), 930 (w), 900 (s), 850 (m), 830 (m), 800 (w), 740 (m), 600 (w), 580 (w), 530 (m), 400 (w).

4.8. *Cp* FvTi(η^3-C$_3$H$_5$) (8)*

Cp* FvTiCl (0.978 g, 2.77 mmol) was dissolved in 10 ml of THF and at −60 °C 3.0 ml of 0.94 M C_3H_5MgCl in THF (2.8 mmol) was added. The reaction mixture was warmed slowly to 0 °C. The colour changed to orange. The reaction mixture was evaporated to dryness and extracted with pentane. Cooling the pentane extracts to −80 °C yielded 309 mg of **8** as orange crystals (0.86 mmol, 31%). During synthesis and work-up, the temperature did not exceed 0 °C. IR (cm^{-1}):

3080 (w), 1530 (m), 1270 (w), 1165 (w), 1070 (w), 1020 (s), 830 (m), 805 (m), 775 (w), 605 (w), 590 (w). Anal. Found: C, 76.36; H, 9.52; Ti, 13.72. $C_{23}H_{34}Ti$ Calc.: C, 77.08; H, 9.56; Ti, 13.36%.

4.9. Kinetic study of decomposition

The rate of decomposition of compound **5** was followed by monitoring the decay of the ^tBu signal in the ^1H NMR spectrum. Under experimental conditions, 0.02 M solutions in C_6D_6 in sealed tubes were heated in a Bruker WH-90 spectrometer. For **6**, sealed tubes containing the compound in C_6D_6 solution were heated in a thermostated oven. Periodically ^1H NMR spectra were recorded after cooling to room temperature. Temperatures were constant within 0.2 °C. Other decompositions were monitored in a similar way.

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References

[1] J.E. Bercaw, *J. Am. Chem. Soc.*, *96* (1974) 5087; J.E. Bercaw, R.H. Marvich, L.G. Bell and H.-H. Brintzinger, *J. Am. Chem. Soc.*, *94* (1972) 1219.

[2] C. McDade, J.C. Green and J.E. Bercaw, *Organometallics*, *1* (1981) 1629.

[3] L.E. Schock, C.P. Brock and T.J. Marks, *Organometallics*, *6* (1987) 232.

[4] A.R. Bulls, W.P. Schaefer, M. Serfas and J.E. Bercaw, *Organometallics*, *6* (1987) 1219.

[5] K.H. Den Haan and J.H. Teuben, *J. Chem. Soc., Chem. Commun.*, (1986) 682; W.J. Evans, T.A. Ulibarri and J.W. Ziller, *Organometallics*, *10* (1991) 134.

[6] A.D. Horton, *Organometallics*, *11* (1992) 3271.

[7] M.E. Thompson and J.E. Bercaw, *Pure Appl. Chem.*, *56* (1984) 1; P.L. Watson, *J. Am. Chem. Soc.*, *105* (1983) 6491; D. O'Hare, J. Manriquez and J.S. Miller, *J. Chem. Soc., Chem. Commun.*, (1988) 491.

[8] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc.*, *109* (1987) 203.

[9] R. Fandos, A. Meetsma and J.H. Teuben, *Organometallics*, *10* (1991) 2665; R. Fandos, J.H. Teuben, S. Helgersson and S. Jagner, *Organometallics*, *10* (1991) 1637.

[10] J.W. Pattiasina, C.E. Hissink, J.L. De Boer, A. Meetsma and J.H. Teuben, *J. Am. Chem. Soc.*, *107* (1985) 7758.

[11] J.W. Pattiasina, *Thesis*, University of Groningen, 1988.

[12] K. Mach, V. Varga, V. Hanus and P. Sedmera, *J. Organomet. Chem.*, *415* (1991) 87.

[13] M. Booy, A. Meetsma and J.H. Teuben, *Organometallics*, *10* (1991) 3246.

[14] M Booy, *Thesis*, University of Groningen, 1989.

[15] F.G.N. Cloke, J.C. Green, M.L.H. Green and C.P. Morley, *J. Chem. Soc., Chem. Commun.*, (1985) 945; G. Parkin, E. Bunel, B.J. Burger, M.S. Trimmer, A. Van Asselt and J.E. Bercaw, *J. Mol. Catal.*, *41* (1987) 21; V.C. Gibson, T.P. Kee, S.T. Carter, R.D. Sanner and W. Clegg, *J. Organomet. Chem.*, *418* (1991) 197.

[16] J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.J. Schultz and J.M. Williams, *J. Am. Chem. Soc.*, *108* (1986) 40.

[17] G.A. Luinstra and J.H. Teuben, *J. Chem. Soc., Chem. Commun.*, (1987) 849.

[18] S.A. Cohen, P.R. Auburn and J.E. Bercaw, *J. Am. Chem. Soc.*, *105* (1983) 1136.

[19] P.H.P. Brinkmann, G.A. Luinstra and A. Saenz, in preparation.

[20] J.A. Bandy, V.S.B. Mtetwa, K. Prout, J.C. Green, C.E. Davies, M.L.H. Grenn, N.J. Hazel, A. Izquierdo and J.J. Martin-Polo, *J. Chem. Soc., Dalton Trans.*, (1985) 2037.

[21] R. Beckhaus, J. Oster and T. Wagner, *Chem. Ber.*, *127* (1994) 1003.

[22] J.A. Labinger and J.E. Bercaw, *Organometallics*, *7* (1988) 926.

[23] R.F. Jordan, *Adv. Organomet. Chem.*, *32* (1992) 325.

[24] S.L. Latesky, A.K. McMullen, I.P. Rothwell and J.C. Huffmann, *J. Am. Chem. Soc.*, *107* (1985) 5981; L. Chamberlain, J. Keddington, I.P. Rothwell and J.C. Huffmann, *Organometallics*, *1* (1982) 1098; J.W. Bruno, M.R. Duttera, C.M. Fendrick, G.M. Smith and T.J. Marks, *Inorg. Chim. Acta*, *94* (1984) 271 and references cited therein.

[25] G.A. Luinstra and J.H. Teuben, *J. Am. Chem. Soc.*, *114* (1992) 3361.

[26] P.H.P. Brinkmann, M.-H. Prosenc and G.A. Luinstra, *Organometallics*, *14* (1995) 5481.

[27] A.C. Dros, G.A. Luinstra, J.J. Eshuis, A. Meetsma and J.H. Teuben, in preparation.