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Allyl derivatives of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Cl\}_3]$: X-ray crystal structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)(CH_2CH{=}CHMe)\}_3]$

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Abstract

Reactions of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Cl\}_3]$ (1) with Grignard reagents, RMgCl (R = allyl ($CH_2CH{=}CH_2$), crotyl ($CH_2CH{=}CHMe$)), in diverse ratios and conditions allow the characterization of the allyl oxotrimers $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3R_nCl_{3-n}]$ (n = 3, R = allyl, 2; n = 1, R = allyl, 4; n = 2, R = allyl, 5; n = 3, R = crotyl, 7). The complexes $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\pi\text{-}C_3H_5)_3]$ (2) and $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\pi\text{-}C_3H_5)_2Cl]$ (5) undergo thermal rearrangements, in a regio- and stereoselective way, to give the derivatives $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3\{\mu_2\text{-}CH_2CH(CH_2CH{=}CH_2)CH_2\}X]$ X = allyl (3) and X = Cl (6) respectively. These processes involve the migration of one allyl group to the β-carbon of the adjacent allyl ligand and the formation of a 2-allyl-1,3-propanediyl unit bridging two titanium atoms. The crystal structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\sigma\text{-}CH_2CH{=}CHMe)_3]$ (7) has been studied by X-ray crystallography and can be described as three $Ti(\eta^5\text{-}C_5Me_5)(\sigma\text{-crotyl})$ units linked through oxygen bridges forming a nearly planar Ti_3O_3 ring.

Keywords: Allyl; Oxide; Titanium

1. Introduction

Allyl transition-metal complexes constitute an important class of compounds in the field of organometallic chemistry. They are very useful as catalysts, catalyst precursors and stoichiometric reagents in organic synthesis [1]. To date, most of the chemistry of these complexes has been carried out for middle to late transition elements, and much less is known for the Group 3–5 metals. In the case of titanium, allyl compounds usually contain the metal center in low oxidation states [1], while the few reported examples in the maximum oxidation state are only mononuclear species: $Ti(NR'_2)_3(CH_2CR''CH_2)$ (R = Me, Et; R'' = H, Me), $Ti(NEt_2)_2(CH_2CMeCH_2)_2$ [2] and the cationic compound $\{[Ti(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}C_3H_5)]^+BF_4^-\}$ [3], recently prepared by oxidation of the titanium(III) allyl complex $Ti(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-}C_3H_5)$ with $[Fe(MeCp)_2]BF_4$.

Within our studies on the reactivity of the complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Cl\}_3]$ (1) [4,5], a model for either a metal or a metal oxide surface, we have attempted to incorporate one or more allyl ligands into the Ti_3O_3 core in order to compare the chemical behavior of these hydrocarbon groups with that of the trialkyl derivatives $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)R\}_3]$ (R = Me, Et, Pr, CH_2Ph) [4,6,7].

Here we report the preparation and characterization of new oxo-allyl trinuclear titanium(IV) derivatives, and also the conversion of some of these complexes into unexpected with the 2-allyl-1,3-propanediyl group bridging two titanium atoms. The synthesis and X-ray structure determination of the crotyl derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)(\sigma\text{-}CH_2\text{-}CH{=}CHMe)\}_3]$ (7) is also described.

2. Results and discussion

Treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Cl\}_3]$ (1) with either three equivalents or an excess of allylmagnesium chloride, in toluene at low temperature (0 °C, 1 h), leads to the isolation in good yield of the trisubstituted derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\eta^3\text{-}C_3H_5)_3]$ (2) (Scheme 1). The ^1H NMR spectrum of this compound (Table 1)

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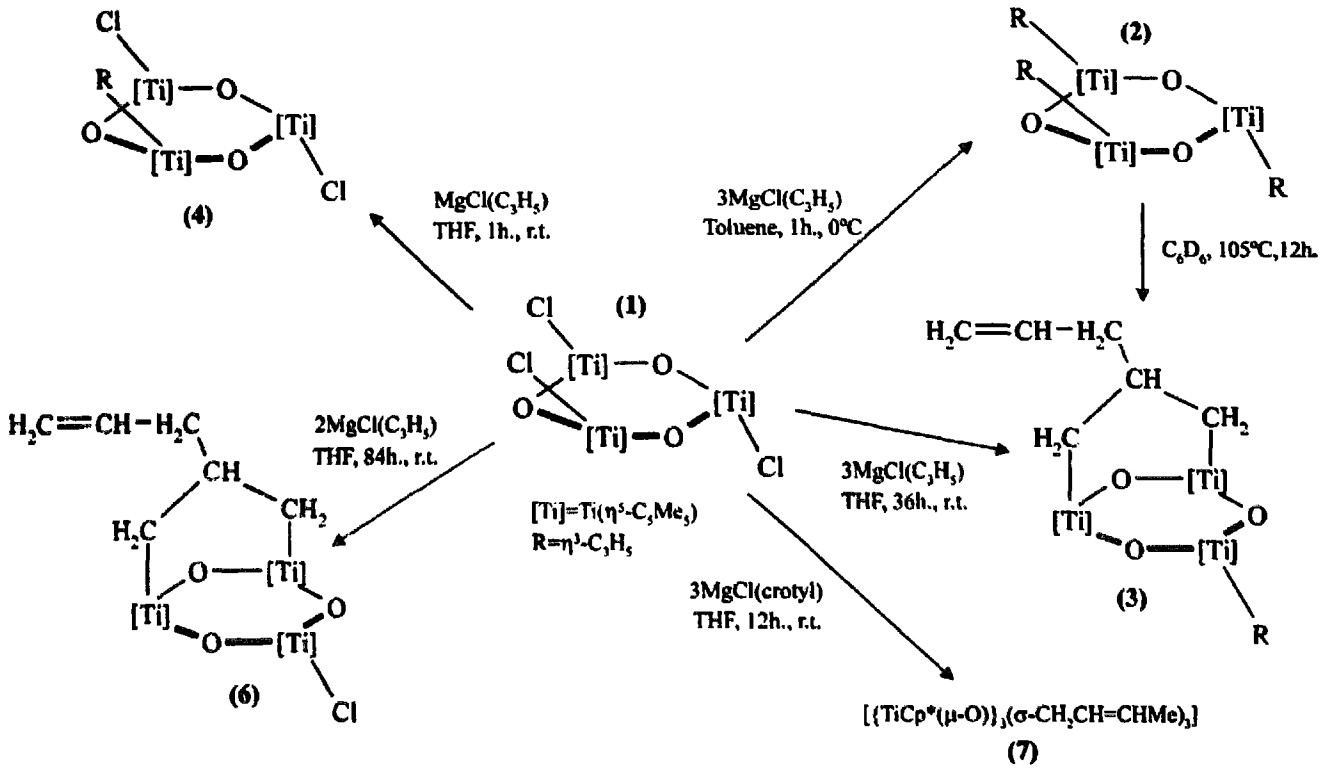


Scheme 1.

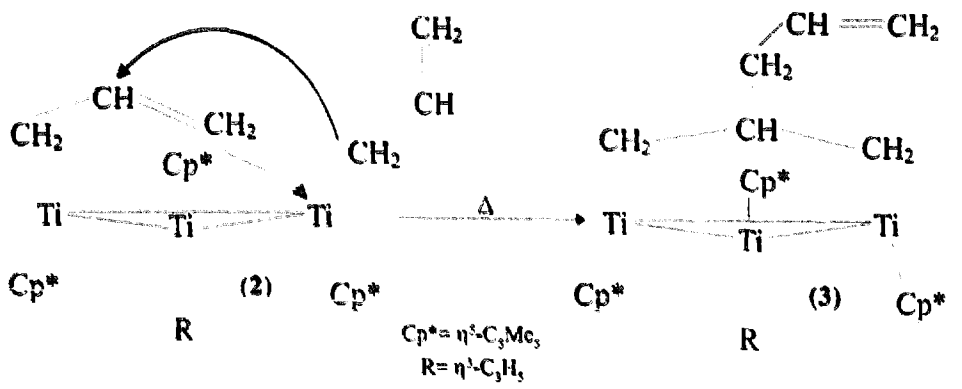
shows two signals in a 2:1 ratio corresponding to the η^5-C_5Me_5 ligands, denoting C_s symmetry. The allyl resonances, also in a 2:1 ratio, exhibit the well-known η^1-η^3 isomerization along with the free rotation around the carbon–carbon and metal–carbon single bonds, and are characterized by the equivalence of the CH_2 groups on the NMR timescale at room temperature.

The IR spectrum of **2** in KBr displays the characteristic absorptions of the η^5-C_5Me_5 group [8] and the typical strong band for the Ti–O–Ti unit in the region 750–800 cm^{-1} [4–7]. A moderate absorption found at 1604 cm^{-1} can be assigned to the carbon–carbon stretching vibration of the η^3-allyl ligands distorted towards an η^1-bound configuration, similar to those reported in the literature for the structurally characterized $Zr(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1,1,2\text{-}Me_3allyl)Br_2$ (1571 cm^{-1}) [9] and $ZrCp_2(\eta^3\text{-}1,2,3\text{-}Me_3allyl)Br$ (1571 cm^{-1}) [10].

Although the molecular ion peak is not observed, the EI-mass spectrum shows a fragmentation pattern with consecutive losses of allyl and ethylene groups. In particular, the peak with $m/e = 610$ $[M - 2(C_3H_5) - (C_2H_4)]^+$, can be associated with the formation of the μ_3-methylidyne complex $[(Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O))_3(\mu_3\text{-}CH)]$ [7].

However, if this reaction is carried out in THF at room temperature for 36 h, the product **3** (Scheme 1) is identified from the NMR and IR data. This complex contains one 2-allyl-1,3-propanediyl group bridging two titanium atoms and one η^3-allyl ligand which presents an analogous dynamic situation to that found for the complex **2**.

The ^1H and ^{13}C NMR spectra (Table 1) of this



Scheme 2.

Table 1
NMR data for complexes 2–7 in benzene-d_6 at 20°C

Compound	Assignation	^{1}H	^{13}C
2	η^5-C_5Me_5	1.96 (s, 15H), 1.97 (s, 30H)	11.6, 11.9 (q, ^1J = 126.5 Hz); 122.5, 122.8 (m)
	η^3-(CH_2CHCH_2)	3.59 (d, ^3J = 11.1 Hz, 8H); 3.48 (broad signal, 4H)	88.3 (t, ^1J = 138.4 Hz); 87.0 (broad signal)
	η^3-(CH_2CHCH_2)	6.28 (qu, 2H); 6.34 (qu, 1H), (^3J = 11.1 Hz)	144.7, 144.3 (d, ^1J = 145.7 Hz)
3	η^5-C_5Me_5	1.92 (s, 30H), 1.98 (s, 15H)	11.4, 11.6 (q, ^1J = 126.3 Hz); 122.1, 121.1 (m)
	η^3-(CH_2CHCH_2)	3.41 (d, 4H), 6.41 (qu, 1H), (^3J = 10.9 Hz)	86.2 (t, ^1J = 143.8 Hz), 145.1 (d, ^1J = 146.5 Hz)
	$-CH_2CH(CH_2CH{=}CH)CH_2-$	2.70 (m, $^3J_{H-H_{cis}}$ = +12.5 Hz)	53.2 (d, ^1J = 128.2 Hz)
	$-CH_2CH(CH_2CH{=}CH)CH_2-$	1.08 (d), 0.66 (dd), (^2J = −12.5 Hz)	81.4 (t, ^1J = 122.7 Hz)
	$-CH_2CH{=}CH_2$	2.05 (m, ^3J = 7.6 Hz, 2H)	53.2 (t, ^1J = 128.1 Hz)
	$-CH_2CH_A{=}CH_BH_C$)	5.96 (m, $^3J_{AB}$ = 9.05 Hz, $^3J_{AC}$ = 15.1 Hz, 1H)	138.8 (d, ^1J = 150.2 Hz)
	$-CH_2CH_A{=}CH_BH_C$)	5.07 (m, $^2J_{BC}$ = 2.4 Hz, ^4J < 1.5 Hz, 2H)	115.0 (t, ^1J = 154.8 Hz)
4	η^5-C_5Me_5	1.98, 2.05, 2.07 (s, 15H)	11.8, 12.1, 12.3 (q, ^1J = 126.7 Hz); 123.9, 127.4, 127.7 (m)
	η^3-(CH_2CHCH_2)	3.68 (d, 4H), 6.43 (qu, 1H), (^3J = 10.8 Hz)	91.3 (t, ^1J = 141.1 Hz), 144.3 (d, ^1J = 148.4 Hz)
5	η^5-C_5Me_5	2.02 (s, 30H), 2.01 (s, 15H)	11.9, 11.6 (q, ^1J = 126.6 Hz); 123.5, 122.8 (m)
	η^3-(CH_2CHCH_2)	3.60 (d, 8H), 6.32 (qu, 2H), (^3J = 11.1 Hz)	88.8 (t, ^1J = 140.6 Hz), 144.2 (d, ^1J = 146.5 Hz)
6	η^5-C_5Me_5	1.94 (s, 30H), 2.07 (s, 15H)	11.3, 12.4 (q, ^1J = 126.4 Hz); 122.0, 126.0 (m)
	$-CH_2CH(CH_2CH{=}CH_2)CH_2-$	2.78 (m, 1H), 1.16 (2H), 0.68 (2H)	53.1 (d, ^1J = 128.2 Hz), 82.6 (t, ^1J = 121.8 Hz)
	$-CH_2CH{=}CH_2$	2.03 (m, 2H), 5.98 (m, 1H), 5.09 (m, 2H)	52.9, 139.1, 114.9
7	η_1^5-C_5Me_5	1.98 (s, 15H), 1.99 (s, 30H)	11.5, 11.8 (q, ^1J = 125.6 Hz); 122.1, 122.4 (m)
	σ-$CH_2CH{=}CHMe$	1.87 (d, 6H), 1.80 (d, 3H), (^3J = 6.4 Hz)	18.3 (q, ^1J = 123.7 Hz)
	σ-$CH_2CH{=}CHMe$	2.33 (m, 6H)	66.8, 69.3 (t, ^1J = 122.6 Hz)
	σ-$CH_2CH{=}CHMe$	5.14 (m, ^3J = 14.9 Hz, 3H)	115.8, 116.7 (d, ^1J = 146.2 Hz)
	σ-$CH_2CH{=}CHMe$	5.91 (m, 3H)	138.0, 138.4 (d, ^1J = 143.7 Hz)

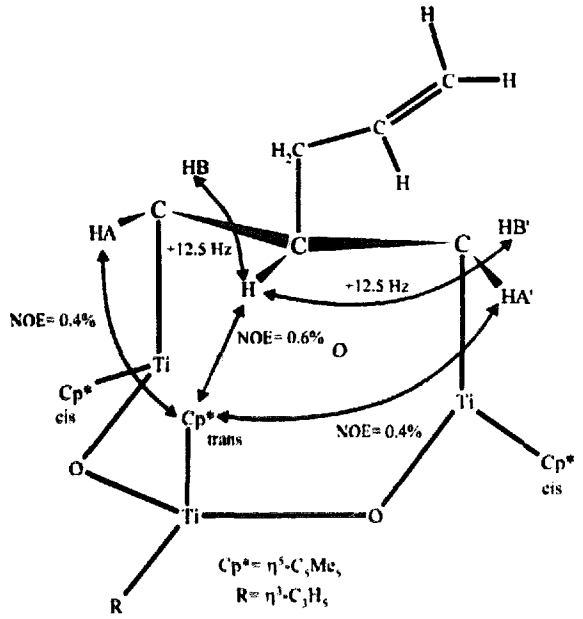


Fig. 1. Structural situation, NOE and coupling constants $H_{ax}-H_{ax}$ for the 2-allyl-1,3-propanediyl group in complex **3**.

unexpected complex demonstrates C_s symmetry, in agreement with the presence of two different types of η^5-C_5Me_5 ligand, in a 2:1 ratio, and the equivalence of the terminal carbon atoms of the Ti-CH_2-$CH(CH_2CH{=}CH_2)CH_2$-Ti fragment.

The proton resonances of the Ti-CH_2 groups are characterized by a $^3J_{H,H}$ = 12.5 Hz value within the range described in the literature for $H_{axial}-H_{axial}$ couplings in organic cyclohexanes [11]. This fact could mean that the central hydrogen of the 1,3-propanediyl ligand is situated in the axial position, while the σ-allyl substitute occupies the equatorial position with respect to the six-membered ring Ti-CH_2-CH_{axial}-CH_2-Ti-O (Fig. 1).

The structural situation is confirmed by the results of NOE homonuclear differential experiments. In particular, the irradiation over the signal of the inequivalent η^5-C_5Me_5 ligand results in an NOE at the bridging group: 0.6% for the central ($\delta = 2.70$ ppm) and 0.4% for the equatorial protons ($\delta = 1.08$ ppm).

The IR data are in agreement with the presence of the Ti_3O_3 core (773 vs), η^5-C_5Me_5 (2913 m, 1491 s, 1431 m, 1375 s, 1022 s) and π-allyl (1604 m) ligands; but, in contrast to **2**, an additional moderate absorption at 1631 cm^{-1}, corresponding to the stretching carbon–carbon double bond vibration of the bridging ligand -$CH_2CH(CH_2CH{=}CH_2)CH_2$- is observed.

Again, the molecular peak does not appear in the EM-mass spectrum of this complex, but the fragmentation pattern is comparable with that for the trisallyl **2** and suggests the possible thermal transformation of **2** into **3**. In fact, this transformation can be performed quantitatively by heating a benzene-d_6 solution of **2** at 105 °C for 12 h in an NMR tube, and it proceeds in a regio- and stereoselective way.

A reasonable explanation for this rearrangement would involve an intramolecular and intermetallic nucleophilic attack of one allyl ligand over the central carbon of the adjacent allyl group, as shown in Scheme 2.

The transformation observed for complex **2** appears to parallel that proposed by Maitlis and coworkers [12],

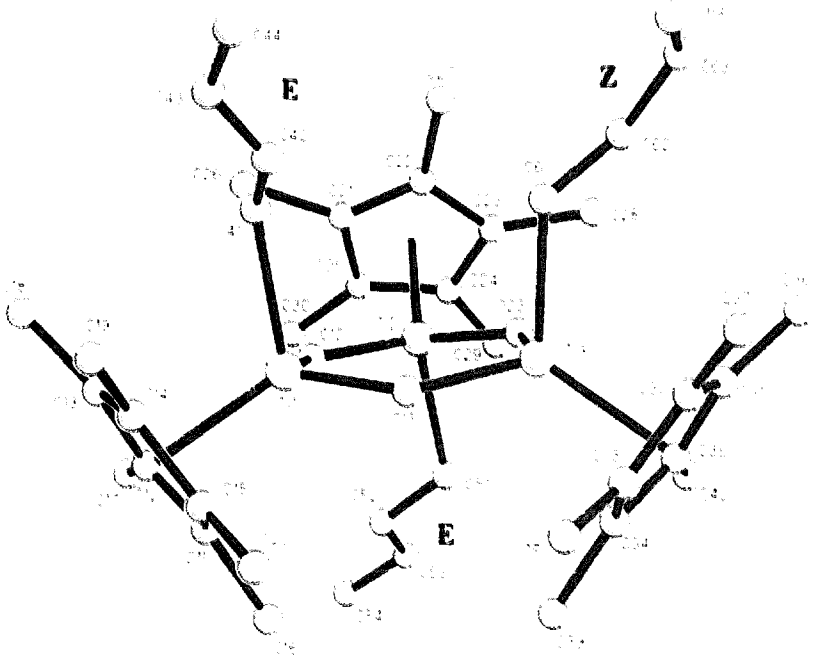


Fig. 2. Molecular structure of [{Ti(η^5-C_5Me_5)(μ-O)}$_3$(σ-$CH_2CH{=}CHMe$)$_3$] (**7**).

Table 2
Selected lengths (Å) and angles (deg) for compound 7 [a]

Ti(1)–O(12)	1.835(4)	C(42)–C(43)	1.21(1)
Ti(1)–O(13)	1.810(5)	C(43)–C(44)	1.50(2)
Ti(1)–C(41)	2.146(9)	Ti(3)–C(61)	2.13(1)
Ti(2)–O(12)	1.828(4)	C(51)–C(52)	1.42(1)
Ti(2)–O(23)	1.826(6)	C(52)–C(53)	1.37(1)
Ti(2)–C(51)	2.132(8)	C(61)–C(62)	1.41(2)
Ti(3)–O(13)	1.854(5)	C(63)–C(64)	1.51(2)
TI(3)–O(23)	1.824(5)	C(53)–C(54)	1.48(2)
C(41)–C(42)	1.51(1)	C(62)–C(63)	1.44(2)
Ti(1)–Cp*(1)	2.067	Ti(1)···Ti(2)	3.353
Ti(2)–Cp*(2)	2.065	Ti(1)···Ti(3)	3.364
Ti(3)–Cp*(3)	2.060	Ti(2)···Ti(3)	3.372
O(12)–Ti(1)–O(13)	105.5(2)	Ti(2)–O(23)–Ti(3)	134.6(3)
O(12)–Ti(2)–O(23)	106.1(2)	Cp*(1)–Ti(1)–O(12)	114.0
O(12)–Ti(1)–C(41)	96.9(3)	Cp*(1)–Ti(1)–O(13)	122.5
O(13)–Ti(3)–O(23)	104.2(2)	Cp*(1)–Ti(1)–O(41)	112.0
O(12)–Ti(2)–C(51)	100.6(3	Cp*(2)–Ti(2)–O(12)	116.9
O(13)–Ti(1)–C(41)	101.8(3)	Cp*(2)–Ti(2)–O(23)	117.0
O(13)–Ti(3)–C(61)	97.1(3)	Cp*(2)–Ti(2)–O(51)	116.0
O(23)–Ti(2)–C(51)	97.7(3)	Cp*(3)–Ti(3)–O(13)	121.1
O(23)–Ti(3)–C(61)	100.8(3)	Cp*(3)–Ti(3)–O(23)	116.1
Ti(1)–O(12)–Ti(2)	132.7(3)	Cp*(3)–Ti(3)–O(61)	114.2
Ti(1)–O(13)–Ti(3)	133.4(3)		

[a] Cp* is the centroid of the C_5Me_5 ring.

where the complex $[\{Rh(\eta^5\text{-}C_5Me_5)(\mu\text{-}CH_2)Cl\}_2]$ was treated with allylmagnesium chloride to give a product containing the β-substituted dimetallacyclopentane unit Rh–CH_2–CR(CH_2CR=CH_2)–CH_2–Rh (R = H, Me).

Similar reactions are also known for mononuclear species such as $[\{M(\eta^5\text{-}C_5Me_5)L(\eta^3\text{-allyl})\}^+X^-]$ (M = Rh, Ir; L = P^iPr_3, PMe_3, C_2H_4; X = BF_4, PF_6, OTf) [13], $[\{M(\eta^5\text{-}C_5H_5)_2(\eta^3\text{-allyl})\}^+]$ (M = Mo, W) [14], $[\{M(\eta^5\text{-}C_5Me_5)_2(\eta^3\text{-allyl})\}^+BF_4^-]$ (M = Ti, Zr) [3], $Zr(\eta^5\text{-}C_5Me_5)_2(allyl)_2$ [15] and $Ti(\eta^5\text{-}C_5Me_5)_2(allyl)$ [16].

Attempts to obtain the selective substitution of two of the three chloride ions in **1**, using toluene and/or THF, lead to mixtures of products where only the disubstituted derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\eta^3\text{-}C_3H_5)_2Cl]$ (**5**) and $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3\{\mu_2\text{-}(CH_2CH(CH_2CH=CH_2)CH_2)\}Cl$ (**6**) could be identified by NMR (Table 1). However, compound **6** can be isolated in acceptable yields (60%) by reaction of **1** with allylmagnesium chloride (1:2 ratio), in THF at room temperature (Scheme 1), even though it always appears slightly contaminated with complex **3** (ca. 7% by ^1H NMR).

In contrast, treatment of the starting product **1** with one equivalent, or a slight deficiency, of allylMgCl, in toluene and/or THF at room temperature, results in the formation of the monosubstituted derivative $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\eta^3\text{-}C_3H_5)Cl_2]$ (**4**) (Scheme 1). Unfortunately, this compound could not be isolated analytically pure due to the existence of small amounts of unchanged **1**. The NMR data of **4** (Table 1) are consistent with the substitution of one of the two chlorides in the cis position, at the less crowded side of **1**.

The reaction of **1** with crotylmagnesiumchloride (95%, predominantly *E*) has also been explored to study the effect of the allyl group methylation on how this ligand binds to the $Ti(\eta^5\text{-}C_5Me_5)O$ moieties. The addition of an excess of the Grignard reagent to the trichloride **1** results in the complete substitution of the chloride ions (Scheme 1) based on the analytical and structural data. The NMR spectra suggest the existence of geometric isomers with respect to the crotyl ligand double bond and clearly indicate that the isomer which contains

Table 3
Crystal and X-ray structural analysis data for **7**

Molecular formula	$Ti_3O_3C_{52}H_{66}$
Fw	762.7
Space group	$P\bar{1}$
Unit cell vol. (Å^3)	2157(1)
a (Å); α (deg)	11.678(4); 83.45(1)
b (Å); β (deg)	12.068(6); 85.40(1)
c (Å); γ (deg)	17.575(3); 61.30(1)
Z	2
Dcalc. (g cm^{-3})	1.74
F(000)	816
μ (cm^{-1})	5.68
Total no. of reflections measured	7836
No. of reflections measured with $I > 2\sigma(I)$	3152
R	0.073
Rw	0.066
GOF	1.662

the three σ-crotyl groups in an *E* configuration is present in ca. 90%. In the infrared spectrum of **7**, the absorption at 1634 cm^{-1} corresponding to ν(C=C) is also indicative of the crotyl ligands' σ-coordination. Probably, the methyl group bonded to the terminal carbon atom of the allyl groups provides sufficient steric bulk in the compound **7** to disfavour the π-coordination mode observed for the unsubstituted allyls in complexes **2–4**.

2.1. X-ray structure of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(CH_2CH{=}CHMe)_3]$ (7)

Red crystals of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(CH_2CH{=}CHMe)_3]$ (**7**) were grown from a pentane solution at −40 °C and the crystal used for the diffraction studies did not correspond to the expected *E,E,E* isomer but to the *E,Z,E* one. Fig. 2 shows the molecular structure of **7**, and selected bond lengths and angles

Table 4
Positional parameters and their estimated standard deviation for compound $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)(\sigma\text{-}CH_2CH{=}CHMe)_3\}]$ (7)

Atom	x	y	z	B (Å²)
Ti(1)	0.4222(1)	0.3342(1)	0.24688(8)	3.22(4)
Ti(2)	0.7060(1)	0.1180(1)	0.17292(8)	3.17(4)
Ti(3)	0.7009(1)	0.2327(1)	0.33983(8)	3.50(4)
O(12)	0.5293(4)	0.2200(4)	0.1790(3)	3.6(1)
O(13)	0.5222(4)	0.3053(4)	0.3280(3)	3.6(1)
O(23)	0.7720(4)	0.1470(4)	0.2546(3)	3.5(1)
C(11)	0.2833(7)	0.2497(7)	0.2859(5)	5.0(2)
C(12)	0.2607(7)	0.2855(7)	0.2095(5)	4.8(2)
C(13)	0.2006(7)	0.4227(7)	0.1996(5)	4.9(3)
C(14)	0.1911(7)	0.4618(7)	0.2728(5)	4.7(2)
C(15)	0.2407(7)	0.3548(7)	0.3267(5)	4.8(2)
C(16)	0.3406(8)	0.1127(8)	0.3235(7)	8.0(3)
C(17)	0.2825(9)	0.2010(9)	0.1459(6)	8.2(3)
C(18)	0.154(1)	0.502(1)	0.1249(6)	8.7(4)
C(19)	0.1187(9)	0.6028(8)	0.2909(7)	9.2(4)
C(20)	0.2369(9)	0.362(1)	0.4119(6)	8.3(4)
C(21)	0.6984(7)	0.2033(6)	0.0435(4)	3.9(2)
C(22)	0.7902(7)	0.2159(6)	0.0782(4)	4.1(2)
C(23)	0.8958(6)	0.0935(7)	0.0993(4)	4.5(2)
C(24)	0.8617(7)	0.0051(7)	0.0743(4)	4.3(2)
C(25)	0.7385(6)	0.0728(6)	0.0407(4)	3.6(2)
C(26)	0.5684(9)	0.3083(8)	0.0095(5)	6.3(3)
C(27)	0.7899(9)	0.3382(8)	0.0891(6)	7.8(3)
C(28)	1.0192(8)	0.067(1)	0.1380(6)	8.7(4)
C(29)	0.9532(9)	−0.1409(8)	0.0813(5)	7.9(3)
C(30)	0.6694(9)	0.0176(8)	0.0041(6)	6.6(3)
C(31)	0.8860(7)	0.1370(7)	0.4234(5)	4.7(2)
C(32)	0.7782(8)	0.2314(7)	0.4623(5)	5.4(3)
C(33)	0.6830(8)	0.1957(9)	0.4738(5)	6.1(3)
C(34)	0.7277(8)	0.0805(8)	0.4420(5)	6.4(3)
C(35)	0.8528(8)	0.0451(7)	0.4111(5)	5.4(3)
C(36)	1.0175(9)	0.127(1)	0.4019(6)	8.8(4)
C(37)	0.779(1)	0.342(1)	0.4982(6)	9.8(4)
C(38)	0.548(1)	0.268(1)	0.5171(6)	13.2(6)
C(39)	0.649(1)	0.008(1)	0.4427(8)	13.4(4)
C(40)	0.939(1)	−0.0785(9)	0.3724(7)	9.4(4)
C(41)	0.4244(7)	0.4982(7)	0.1866(5)	4.9(2)
C(42)	0.3992(9)	0.6101(8)	0.2289(6)	8.5(3)
C(43)	0.331(1)	0.7235(9)	0.2178(7)	9.8(4)
C(44)	0.312(1)	0.8322(9)	0.2607(7)	10.1(4)
C(51)	0.7198(8)	−0.0597(6)	0.2175(5)	5.2(2)
C(52)	0.6642(8)	−0.1235(7)	0.1830(5)	6.0(3)
C(53)	0.7300(9)	−0.2470(8)	0.1655(6)	7.1(3)
C(54)	0.674(1)	−0.3108(9)	0.1252(7)	11.1(4)
C(61)	0.7182(8)	0.4000(8)	0.3085(6)	6.5(3)
C(62)	0.837(1)	0.403(1)	0.2974(7)	9.9(4)
C(63)	0.871(1)	0.491(1)	0.3256(7)	10.4(4)
C(64)	0.791(1)	0.608(1)	0.3683(7)	11.1(5)

appear in Table 2, while Tables 3 and 4 summarize crystal and structural data respectively. No intermolecular interactions were found.

The structure of **7** is very similar to that reported several years ago for the trimer $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Me\}_3]$ [17], and can be described as three $Ti(\eta^5\text{-}C_5Me_5)(\sigma\text{-crotyl})$ units linked through oxygen bridges forming a nearly planar Ti_3O_3 ring. Two of the crotyl ligands and one $\eta^5\text{-}C_5Me_5$ fragment are situated above this plane, while the third crotyl ligand and the other two $\eta^5\text{-}C_5Me_5$ groups lie below it.

The averaged bond distances and angles Ti–O (1.83 Å), Ti-ring centroid (2.06 Å), Ti–O–Ti (133.6°) and O–Ti–O (105.2°) are comparable with those reported in the literature for the titanium organometallic oxides $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3X_3]$ (X = Me [17], Cl [18], Br [19]).

The $Ti\text{–}C_\alpha$(crotyl) distances, 2.13(1), 2.132(8) and 2. 146(9) Å, are in the range of those observed for $Ti\text{–}C(sp^3)$ bonds, not only for the trinuclear system $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Me\}_3]$, 2.09 Å (av.) [17], but also in the tetranuclear $[Ti_4(\eta^5\text{-}C_5Me_5)_4(\mu\text{-}O)_5Me_2]$ (2.11 Å, av.) [20], dinuclear $[\{Ti(\eta^5\text{-}C_5Me_5)Me(\eta^2\text{-}MeNNCPh_2)\}\{Ti(\eta^5\text{-}C_5Me_5)Me_2(\mu\text{-}O)\}]$ (2.11 Å, av.) [6] and mononuclear $[Ti(\eta^5\text{-}C_5Me_5)Me_3]$ (2.11 Å, av.) [21] systems.

Inside the crotyl groups, the $C_\alpha\text{–}C_\beta$ (1.47 Å) and $C_\beta\text{–}C_\gamma$ (1.34 Å) average distances are within the estimated range for double and single bonds respectively [22]. Furthermore, if we examine the torsion angles formed by the carbon atoms in each crotyl ligand, C(41)–C(42)–C(43)–C(44) (−177(1)°), C(51)–C(52)–C(53)–C(54) (−176(1)°) and C(61)–C(62)–C(63)–C(64) (−5(2)°), it is easy to deduce that the first two fragments show *E* configurations while the third one presents a *Z* configuration with respect to the double bond.

3. Experimental section

The synthesis and subsequent handling of compounds were conducted under anhydrous conditions in a dry oxygen-free argon atmosphere (Schlenk technique or MBraun glovebox). Solvents (reagent grade) were carefully dried over sodium–potassium alloy (pentane, hexane, toluene, diethyl ether, tetrahydrofuran) and distilled under argon immediately before use.

$[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)Cl\}_3]$ (**1**) was synthesized according to published methods [4,23]. Crotylmagnesium chloride was prepared by a standard Grignard procedure from crotyl chloride (95%, predominantly *E*, Aldrich), while allylmagnesium chloride (2 M in THF, Aldrich) was used as-received.

Elemental microanalyses were performed on a Heraeus CHN–O-Rapid microanalyzer. NMR spectra were recorded on a Varian Unity-300 and Varian Unity-500 Plus spectrometers, and ^1H and ^{13}C chemical shifts are reported in ppm (δ) relative to residual protons or carbons of the solvent or to TMS. IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer using KBr pellets. Electron impact (EI) mass spectra were performed at 70 eV on a Hewlett-Packard 5988 spectrometer. Thermal evolution of **2** to give **3** was carried out in a Roth autoclave Model III (300 ml), with a heater Model 30S (20–300 °C) and temperature regulator model DR 500.

3.1. Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\pi\text{-}C_3H_5)_3]$ (2)

Allylmagnesium chloride (1.24 ml, 2 M, 2.49 mmol), diluted in 15 ml of THF, was added dropwise to a stirred solution of **1** (0.50 g, 0.71 mmol) in 60 ml of toluene at 0 °C. Once the addition was concluded (1 h) the solvent was immediately removed in vacuo and the solid residue extracted with 60 ml of hexane. The solution was filtered, the solvent reduced to half volume and cooling to −40 °C afforded 0.40 g of **2** as an orange solid in 80% yield. IR (KBr, cm^{-1}): 2912 m, 1604 m, 1491 s, 1434 m, 1379 s, 1026 s, 770 vs. MS: *m/e* (assignment, rel. int.(%)): 679 ($(M-(C_3H_5))^+$, 4), 638 ($(M-2(C_3H_5))^+$, 20), 610 ($(M-2(C_3H_5)-(C_2H_4))^+$, 5), 597 ($(M-3(C_3H_5))^+$, 12). Anal. Found: C, 64.63; H, 8.29. $C_{39}H_{60}O_3Ti_3$. Calc.: C, 65.01; H, 8.39%.

3.2. Preparation of $[Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)]_3\{\mu_2\text{-}[CH_2CH(CH_2CH{=}CH_2)CH_2]\}(\pi\text{-}C_3H_5)$ (3)

This compound was prepared in a similar manner to **2** but the reaction mixture was allowed to warm to room temperature and stirred for 36 h in THF. 0.30 g of **3** as a yellow solid in 60% yield were obtained. IR (KBr, cm^{-1}): 2913 m, 1631 m, 1604 m, 1491 s, 1431 m, 1375 s, 1022 s, 773 vs. MS: *m/e* (assignment, rel. int.(%)): 679 ($(M-(C_3H_5))^+$, 10), 638 ($(M-2(C_3H_5))^+$, 17), 610 ($(M-2(C_3H_5)-(C_2H_4))^+$, 11), 597 ($(M-3(C_3H_5))^+$, 13). Anal. Found: C, 64.48; H, 8.48. $C_{39}H_{60}O_3Ti_3$. Calc.: C, 65.01; H, 8.39%.

3.3. Thermal rearrangement of complex 2 to give 3

An orange solution of **2** (30 mg) in C_6D_6 (0.60 ml) was sealed in an NMR tube and heated at 105 °C for 12 h. The product was identified as $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3\{\mu_2\text{-}[CH_2CH(CH_2CH{=}CH_2)CH_2]\}(\eta^3\text{-}C_3H_5)$ (**3**) by ^1H and ^{13}C NMR spectroscopy. Yield was quantitative (greater than 95%) by NMR, and the transformation regio- and stereoselective.

3.4. Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\pi\text{-}C_3H_5)Cl_2]$ (4)

Over a solution of **1** (0.50 g, 0.71 mmol) in 60 ml of THF at 0°C, a THF solution of (allyl)MgCl (0.36 ml, 2 M, 0.71 mmol) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was then removed in vacuo and the solid residue extracted with 50 ml of hexane. The resulting solution was filtered, concentrated to 20 ml and cooled to ca. −40°C. An orange crystalline solid of **4** (50% yield), contaminated with small amounts of unreacted **1** (ca. 20% by ^{1}H NMR), was obtained. Attempts to remove **1** by successive recrystallization in several solvents or mixtures of them were unsuccessful.

3.5. Preparation of $[Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)]_3\{\mu_2\text{-}[CH_2CH(CH_2CH{=}CH_2)CH_2]\}Cl$ (6)

A solution of (allyl)MgCl (0.74 ml, 2 M, 1.49 mmol) in 15 ml of THF was slowly added to 0.50 g (0.71 mmol) of **1** in 60 ml of THF at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 3 days. The solvent was then removed in vacuo and the solid residue extracted with 60 ml of hexane. The resulting solution was filtered, concentrated and cooled to ca. −40°C, affording a yellow crystalline solid of **6** (60% yield) slightly contaminated (ca. 7% by ^{1}H NMR) with **3**. Attempts to remove **3** were unsuccessful.

3.6. Preparation of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)\}_3(CH_2CH{=}CHMe)_3]$ (7)

(Crotyl)MgCl in diethyl ether (60 ml) was prepared by the standard method from crotyl chloride (0.27 ml, 2.84 mmol) and magnesium turnings (3.00 g). The obtained solution was filtered onto a solution of **1** (0.50 g, 0.71 mmol) in 60 ml of THF at 0°C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the solid residue extracted with 60 ml of pentane. The red solution was filtered, concentrated and cooled to −40°C to afford red crystals of **7** (0.35 g, 75%). IR (KBr, cm^{-1}): 2912 m, 1634 m, 1491 s, 1436 m, 1376 s, 1027 s, 759 vs. MS: *m/e* (assignment, rel. int.(%)): 652 ((M − $(C_4H_7)_2)^+$, 3), 597 ((M − $(C_4H_7)_3)^+$, 3), 110 ($(C_8H_{14})^+$, 24), 55 ($(C_4H_7)^+$, 100). Anal. Found: C, 66.12; H, 8.85. $C_{42}H_{66}O_3Ti_3$. Calc.: C, 66.15; H, 8.72%.

3.7. Crystallographic structural determination

Crystallographic and experimental details for the X-ray crystal structure determination are given in Table 3. Data collection were performed at 20°C using an Enraf–Nonius CAD4 diffractometer. The structure was solved by a combination of direct methods and Fourier synthesis, and refined by full-matrix least squares techniques. All the non-hydrogen atoms were refined anisotropically. H-atoms were included in calculated positions with thermal parameters equivalent to those of the atoms to which they are attached; all positional and thermal parameters were fixed in the last cycle of refinement. Final values of $R = 0.073$ and $Rw = 0.066$ (non-Poisson weighting scheme for all observed reflections) were obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from *International Tables for X-Ray Crystallography* [24]. Calculations were performed with the SDP package [25] and the programs MULTAN [26] and DIRDIF [27] on a Microvax II computer.

Tables of atom coordinates and thermal parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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