

ALLYLDICYCLOPENTADIENYLTITANIUM(III) AND (DI)METHYLALLYL HOMOLOGUES

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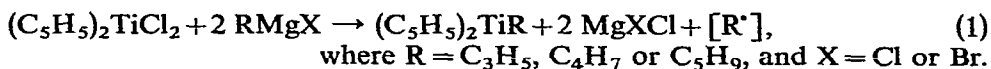
INTRODUCTION

Little is known, as yet, about organotitanium(III) compounds (for reviews see *e.g.* ref. 1). Trimethyltitanium, $(\text{CH}_3)_3\text{Ti}$, is only stable in solutions that are kept at low temperatures², but tricyclopentadienylyltitanium, $(\text{C}_5\text{H}_5)_3\text{Ti}$, has been isolated³. Dicyclopentadienylyltitanium monochloride, $(\text{C}_5\text{H}_5)_2\text{TiCl}$, is dimeric in the solid state⁴ and in benzene solution^{5,6}; probably the two metal atoms in the molecule are linked by two chloride bridges, as in the complexes $(\text{C}_5\text{H}_5)_2\text{TiCl}\cdot\text{ClAl}(\text{C}_2\text{H}_5)_2$ ⁷ and $\{(\text{C}_5\text{H}_5)_2\text{TiCl}\}_2\text{ZnCl}_2$ ⁸. X-ray analyses of these two complexes^{7,8} show that the cyclopentadienyl ligands are π -bonded to the titanium atoms. For the monomeric complex $(\text{C}_5\text{H}_5)_2\text{TiBH}_4$ a structure has been proposed in which Ti and B are linked by two hydrogen bridges⁹.

Allyl complexes of titanium(III)—or of an other oxidation state of titanium—are not known. In this paper the synthesis and some properties of allyldicyclopentadienylyltitanium(III)* and its methylallyl and dimethylallyl homologues will be described. The stable, but extremely air-sensitive compounds $(\text{C}_5\text{H}_5)_2\text{TiR}$ ($\text{R} = \text{C}_3\text{H}_5$, C_4H_7 or C_5H_9) are monomeric in benzene solution; they have one unpaired electron per molecule. Evidence will be presented showing that the (methyl)allyl ligands are π -bonded to the metal, as are the cyclopentadienyl ligands. It may be mentioned that the allyltitanium complexes bear some resemblance to species $\text{X}_n(\text{R})\text{Ti} \leftarrow \begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$ which have been proposed as intermediates in Ziegler-Natta catalytic systems (see *e.g.* ref. 11).

PREPARATION

The [(methyl)allyl]dicyclopentadienylyltitanium(III) complexes $(\text{C}_5\text{H}_5)_2\text{TiR}$, with $\text{R} =$ allyl, 1-methylallyl, 2-methylallyl, 1,3-dimethylallyl and 1,1-dimethylallyl, were prepared by reaction of 1 mole of dicyclopentadienylyltitanium dichloride with slightly more than 2 moles of the (methyl)allyl Grignard reagent in tetrahydrofuran or ether solution:



* For a preliminary communication see ref. 10.

The [(methyl)allyl]-DCT* complexes were isolated by evaporation (in vacuum) of the reaction mixture to dryness and extraction of the residue with pentane at room temperature; they were purified by recrystallization from pentane at -80° . The compositions of the products were established by chemical analyses and molecular-weight determinations in benzene (Table 1). The yields of pure product

TABLE 1

ANALYTICAL DATA OF [(METHYL)ALLYL]-DCT COMPLEXES $(C_5H_5)_2TiR$

R		Weight % C	Weight % H	Weight % Ti	RH gas (ml/g)	Mol.wt.
allyl	found	71.19	7.05	21.67	101	219
		71.16	7.07	21.68	101	218
	calcd.	71.24	6.89	21.86	102	219.2
1-methylallyl	found	72.18	7.48	20.58	95	234
		72.18	7.66	20.55	95	239
2-methylallyl	found	72.09	7.41	20.47	94	234
		72.29	7.45	20.48	94	235
	calcd.	72.10	7.35	20.54	96	233.2
1,3-dimethylallyl	found	72.85	7.82	19.25		245
		72.85	7.85	19.34		249
1,1-dimethylallyl	found	72.74	7.63	19.37		245
		72.88	7.61	19.62		
	calcd.	72.87	7.75	19.38		247.2

were of the order of 65 to 80%, except for the rather instable (1,1-dimethylallyl)-DCT complex.

The course of reaction (1) was followed by absorption spectroscopy in the visible range (Fig. 1). To a dilute solution of 1 mole of $(C_5H_5)_2TiCl_2$ in tetrahydro-

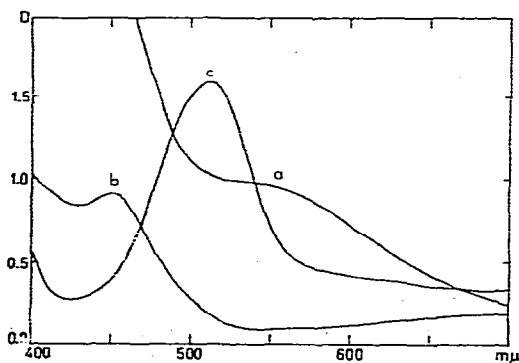
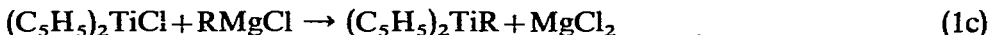
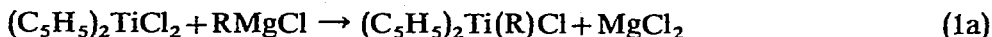


Fig. 1. Absorption spectra of: (a) $(C_5H_5)_2TiCl_2$ (20 mM) and C_3H_5MgCl (22 mM) in tetrahydrofuran; (b) solution (a) after refluxing for 2 h; (c) solution (b) with another 22 mM of C_3H_5MgCl .

* DCT = dicyclopentadienyltitanium(III).

furan (Fig. 2a) slightly more than 1 mole of C_3H_5MgCl was added at room temperature; the reaction mixture became dark red (yellow in thin layers) (Fig. 1a). When the resulting mixture was boiled, the colour of the solution changed to brown and finally to green and the spectrum indicates the presence of DCT monochloride (Fig. 1b, cf. Fig. 3a). Addition of a second mole of C_3H_5MgCl at room temperature led to the formation of the final complex allyl-DCT (Fig. 1c).

These observations are compatible with the following reaction scheme:



For $R = C_3H_5$, step (1a) proceeds at room temperature, while step (1b) requires a higher temperature [step (1b) is accelerated by light]. For $R = 1,3$ -dimethylallyl or 1,1-dimethylallyl, a green solution containing DCT-monochloride was obtained immediately if slightly more than 1 mole of Grignard reagent was added to a solution of 1 mole of $(C_5H_5)_2TiCl_2$ at room temperature; for $R = 1$ -methylallyl or 2-methylallyl the brown to green colour appeared after 15 to 30 minutes. (If the Grignard reagent is a bromide, mainly DCT monobromide is formed.) In these cases, both steps (1a) and (1b) appear to proceed at room temperature. Step (1c) proceeds at room temperature in all cases.

Due to the decrease in thermal stability of $(C_5H_5)_2Ti(R)Cl$ in the sequence $R = \text{allyl} > \text{methylallyl} > \text{dimethylallyl}$, the [(di)methylallyl]-DCT complexes may be prepared in ethereal solution, while the synthesis of allyl-DCT requires heating and, therefore, a solvent with a higher boiling point (tetrahydrofuran). In practice, the synthesis was often carried out by adding slightly more than 2 moles of Grignard reagent to 1 mole of $(C_5H_5)_2TiCl_2$, before the reaction mixture was heated. In this case, the reactions for $R = \text{(di)methylallyl}$ proceed as described, but the reaction for $R = \text{allyl}$ may take a different course (Fig. 2). The absorption spectrum of the reaction mixture of 2.2 moles of C_3H_5MgCl and 1 mole of $(C_5H_5)_2TiCl_2$ in tetrahydrofuran before heating is shown in curve 2b; it is not certain whether this spectrum is to be

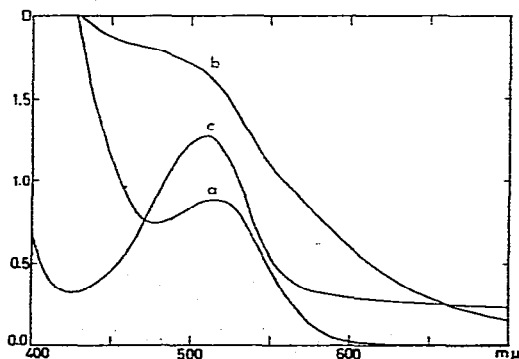


Fig. 2. Absorption spectra of: (a) $(C_5H_5)_2TiCl_2$ (20 mM) in tetrahydrofuran; (b) solution (a) with 44 mM of C_3H_5MgCl ; (c) solution (b) after refluxing for 1 h.

regarded as a superposition of the spectra of $(C_5H_5)_2TiClC_3H_5$ (Fig. 1a) and some allyl-DCT (Fig. 1c), or whether another compound, *e.g.* $(C_5H_5)_2Ti(C_3H_5)_2$, is present in the solution. After heating, allyl-DCT is again obtained (Fig. 2c).

In reaction (1) the allylic Grignard reagent acts both as a reducing agent (steps 1a + 1b) and as an alkylating agent (step 1c). It was tried, therefore, to replace half of the allyl Grignard by other reducing agents, in particular by zinc powder¹⁰ or Grignard reagents of branched alkyls¹². By refluxing of a mixture of 1 mole of $(C_5H_5)_2TiCl_2$ in tetrahydrofuran with 0.5 mole of zinc powder, DCT monochloride is formed¹³:



The zinc powder disappears and a homogeneous green solution is obtained (Fig. 3a). As the isolation of DCT monochloride proved to be cumbersome, the resulting

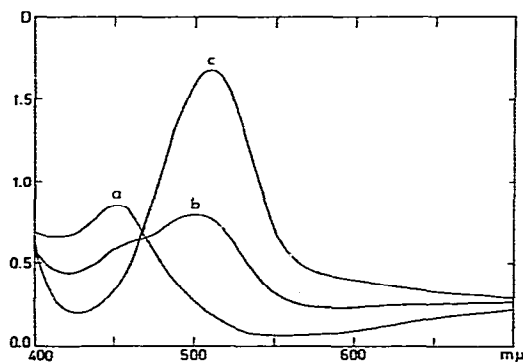
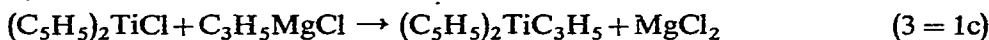
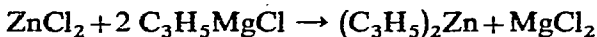


Fig. 3. Absorption spectra of: (a) $(C_5H_5)_2TiCl_2$ (20 mM) and Zn (10 mM) in tetrahydrofuran after refluxing for 1 h; (b) solution (a) with 22 mM of C_3H_5MgCl ; (c) solution (b) with another 22 mM of C_3H_5MgCl .

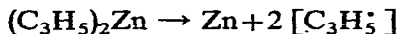
solution was used for further reactions. Allylmagnesium chloride (1.1 moles in tetrahydrofuran) was added, in order to carry out the reaction:



It was found, however, that only part of the Grignard reagent was used for this reaction (Fig. 3b), the other part reacting with zinc chloride to form allylzinc compounds, *e.g.* by:



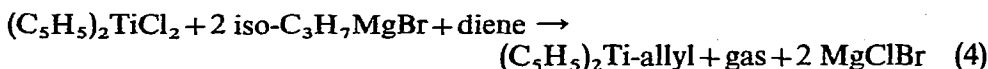
A grey powder, which was identified as metallic zinc, was slowly deposited on the walls of the reaction vessel, due to the decomposition of diallylzinc¹⁴:



For a complete conversion of 1 mole of the titanium compound to allyl-DCT at least 2 moles of the Grignard reagent were needed (Fig. 3c). This synthesis, therefore, does not offer advantages over that according to reaction (1).

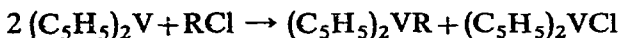
The reaction with Grignard reagents of branched alkyls, such as isopropylmagnesium bromide or *tert*-butylmagnesium chloride, led to an alternative synthesis of certain allyl-DCT complexes, in which the allyl Grignard reagent could be sub-

stituted by a diene. This synthesis can be represented by:

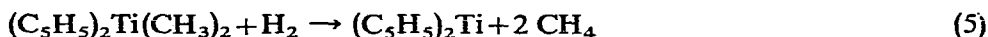


Details are given elsewhere^{12,15}. Although (1,2-dimethylallyl)-DCT was only prepared by the latter method, using isoprene as the diene¹², some of its properties are included in this paper, to allow a comparison with the properties of the other [(di)methylallyl]-DCT compounds.

It was also attempted to prepare allyl-DCT by reaction of allyl chloride with dicyclopentadienylnitrogen(II), on analogy of the reaction:



where R = alkyl, benzyl¹⁶ or allyl¹⁰. Dicyclopentadienylnitrogen was prepared by the method of Clauss and Bestian¹⁷ (Fig. 4a):



However, $(C_5H_5)_2Ti$ prepared by this method did not react in the expected way with allyl chloride. A purple product was obtained, characterized by a sharp absorption peak at 530 $m\mu$ (in hexane solution); the same product was obtained by reaction of Clauss and Bestian's $(C_5H_5)_2Ti$ with benzyl chloride or hydrogen chloride (see also under *Chemical Properties*).

CHEMICAL PROPERTIES

The [(methyl)allyl]-DCT complexes are stable compounds which can be stored under nitrogen. In samples kept in the dark at 0° no visible change had taken

TABLE 2

PHYSICAL PROPERTIES OF [(METHYL)ALLYL]-DCT COMPLEXES $(C_5H_5)_2TiR$

R	M.p. (°C)	Colour in solution	λ_{max}^a ($m\mu$)	ϵ ($mol^{-1} \cdot l \cdot cm^{-1}$)	Magnetic moment (B.M.)
allyl	111–112 (dec.)	violet	512	364	1.65; 1.65
1-methylallyl	96.5–97 (dec.)	blue-violet	539	364	1.67
2-methylallyl	dec. from 114	purple	497 595 ± 5	283 62	1.72; 1.70
1,3-dimethylallyl	91–91.5 (dec.)	blue	578	445	1.69; 1.71
1,1-dimethylallyl	dec. from 51	yellow to brown-red			1.47; 1.48
1,2-dimethylallyl ¹²	70.5–71 (dec.)	violet	522		

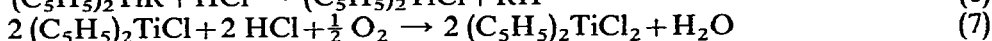
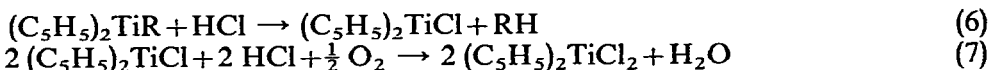
^a Absorption maxima between 400–1000 $m\mu$ in cyclohexane.

place after one year, while samples kept at room temperature had very slightly darkened. Exposition to direct sunlight for some hours (the maximum possible in the Netherlands) also led to a slight darkening of the compounds. At higher temperatures, the complexes decompose, either when melting or before melting (Table 2). Attempts

to sublime the complexes in vacuum (0.1 mm Hg) led to decomposition. In air, the complexes are oxidized immediately.

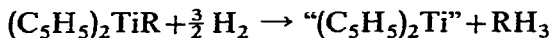
The complexes $(C_5H_5)_2TiR$ are soluble in many organic solvents; the colours of the solutions are given in Table 2. The solubilities in pentane increase in the sequence: $R = 1,1\text{-dimethylallyl} < 2\text{-methylallyl} \approx \text{allyl} < 1\text{-methylallyl} \leq 1,3\text{-dimethylallyl}$. The solubilities in ether, tetrahydrofuran and benzene are larger than that in pentane. The solutions are fairly stable, except for those of (1,1-dimethylallyl)-DCT; by boiling of its ethereal solution this compound is decomposed to give a green air-sensitive product, possibly a hydride (the spectrum is different from those shown in Fig. 4). In air, solutions of the complexes $(C_5H_5)_2TiR$ are oxidized immediately; in some cases a number of intermediate colours (blue, orange) are observed, before the final yellow oxidation product is formed.

The solid complexes $(C_5H_5)_2TiR$ react with 4 *N* hydrochloric acid with quantitative formation of RH (Table 1). By infrared analysis the gas formed was identified as propene for $R = \text{allyl}$, as 2-methylpropene for $R = 2\text{-methylallyl}$, and as 1-butene (with possibly traces of 2-butene) for $R = 1\text{-methylallyl}$. Benzene solutions of the complexes react with one equivalent of an ethereal solution of hydrogen chloride with formation of DCT monochloride (identified by absorption spectroscopy); with an excess of hydrogen chloride and air dicyclopentadienyltitanium dichloride is formed:



Dicyclopentadienyltitanium dichloride is also formed by reaction of allyl-DCT with an excess of organic chlorides, such as carbon tetrachloride, dichloromethane, or allyl chloride. (Carbon disulfide also decomposes allyl-DCT.) The complexes $(C_5H_5)_2TiR$ react with alcohols, such as methanol or octanol, under formation of RH; with water, too, a gradual gas evolution takes place in a smooth reaction.

Cyclohexane solutions of the [(methyl)allyl]-DCT complexes react with molecular hydrogen at room temperature and atmospheric pressure. In a smooth reaction 1.5 moles of hydrogen are gradually taken up per mole of the complex; no incubation time is observed. [This is in contrast to the reaction of dimethyldicyclopentadienyltitanium (IV) with molecular hydrogen which is rather fast after a certain incubation time¹⁷.] The reaction of the allyl-DCT complexes with hydrogen is complete only after some hours, except for (1,3-dimethylallyl)-DCT where it is much slower. The reaction products, green to greyish blue solutions, sometimes with a greyish precipitate, are very sensitive to oxygen. These observations may suggest that the following reaction has taken place:



However, the absorption spectra of the resulting solutions (Fig. 4) show that the products indicated by " $(C_5H_5)_2Ti$ " are not the same in all cases; at least two different products are to be distinguished:

- (i) For $R = 1,1\text{-dimethylallyl}$ the spectrum of the product (Fig. 4b) is very similar to that of the green product obtained by reaction (5) in hexane solution (Fig. 4a). Reaction of this product (in ether) with hydrogen chloride gives a purple mixture (absorption peak at 530 $m\mu$) which on exposure to the air gives an almost insoluble

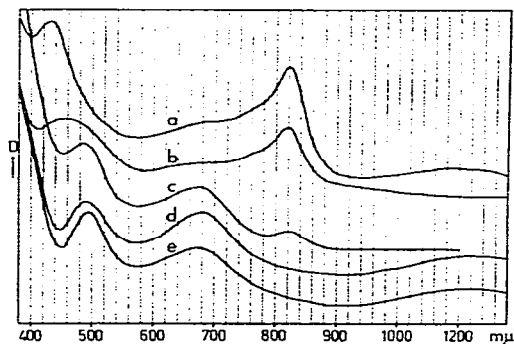


Fig. 4. Absorption spectra of reaction products of: (a) $(C_5H_5)_2Ti(CH_3)_2$ with hydrogen in hexane; (b) (1,1-dimethylallyl)-DCT with hydrogen in cyclohexane; (c) allyl-DCT with hydrogen in cyclohexane; (d) (2-methylallyl)-DCT with hydrogen in cyclohexane; (e) (1-methylallyl)-DCT with hydrogen in cyclohexane. The vertical scales of the various spectra are shifted.

dark green product [and a little of $(C_5H_5)_2TiCl_2$]. The dark green, probably polymeric product is diamagnetic. It contains cyclopentadienyl ligands π -bonded to titanium, chlorine and probably oxygen, but its composition appears to be somewhat variable.

- (ii) The spectra of the products of the reactions of (1-methylallyl)-DCT and (2-methylallyl)-DCT with hydrogen are shown in Figs. 4d, e. These products react with hydrogen chloride under gas evolution to form a green compound (probably DCT monochloride) which on exposure to air gives $(C_5H_5)_2TiCl_2$.

The product of the reaction of allyl-DCT with hydrogen (Fig. 4c) appears to be mainly (ii) with some (i) admixed; with hydrogen chloride it reacts in the same way as (ii).

The investigation of the reaction of $(C_5H_5)_2TiR$ with hydrogen in cyclohexane and other solvents is continued.

In DCT complexes, titanium usually has two ligands in addition to the two cyclopentadienyl groups; e.g. DCT monochloride dimerizes^{5,6} or it forms complexes with other metal halides^{7,8,18}. The allyl-DCT complexes, however, are monomeric; it was found that benzene solutions of the complexes do not react with donors such as triphenylphosphine, triphenylphosphine oxide or pyridine. Evidently, the allylic groups act as "bidentate" ligands. Solutions of the pure complexes in cyclohexane (20°) are no active catalysts for the polymerization of ethene.

PHYSICAL PROPERTIES AND STRUCTURE

The allyl-DCT complexes are paramagnetic; their magnetic moments (Table 2) correspond to one unpaired electron per unit of $(C_5H_5)_2TiR$ (calculated for spin-only: 1.73 B.M.). Due to the paramagnetism, NMR experiments were not successful; no proton resonance signals were observed, even if the applied magnetic field was varied by 100 Gauss (= 7000 ppm). The ESR spectrum shows a signal at $g \approx 2$.

The ultraviolet spectra of solutions of the complexes $(C_5H_5)_2TiR$ show strong absorption below 400 $m\mu$. In the spectral range from 400 to 1000 $m\mu$ one fairly sharp band is observed (except for $R = 1,1$ -dimethylallyl) with λ_{max} (Table 2) decreasing

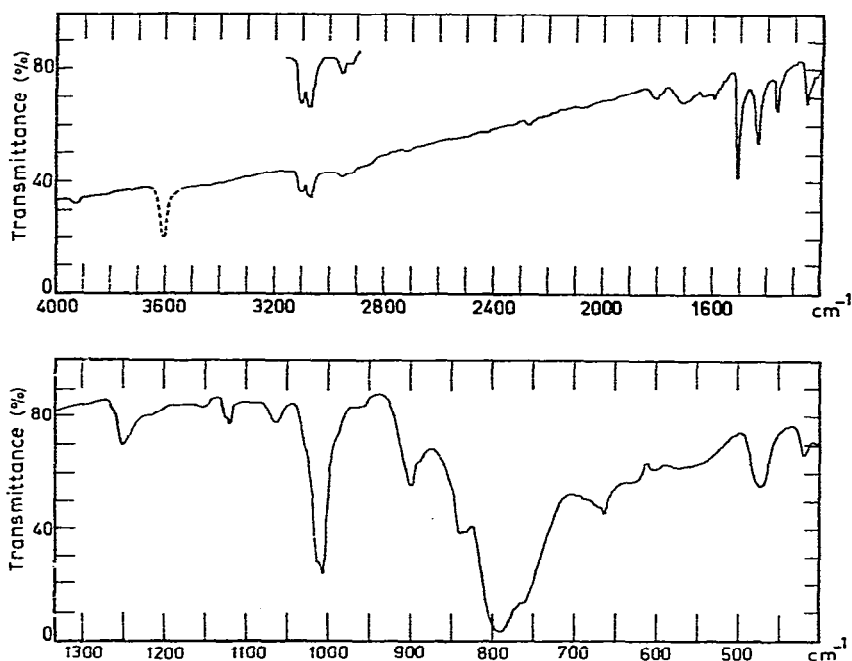


Fig. 5. Infrared transmission spectrum of allyl-DCT in a KBr disc.

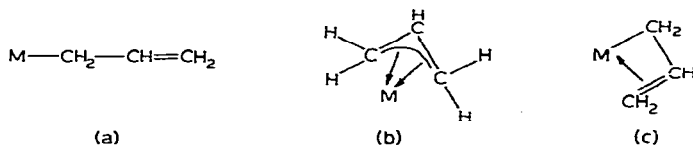
in the sequence: $R = 1,3\text{-dimethylallyl} > 1\text{-methylallyl} > \text{allyl} > 2\text{-methylallyl}$ (which shows a second, much weaker band). It appears that a methyl substituent increases λ_{max} if it is in position 1 or 3 (at least for the isomers isolated; see below), while it decreases λ_{max} if it is in position 2; for $R = 1,2\text{-dimethylallyl}$ λ_{max} is about the same as for $R = \text{allyl}$. It is remarkable that above sequence is the same as that of the solubilities of the complexes in pentane, while the melting points of the complexes (Table 2) show the inverse trend.

The infrared spectrum of allyl-DCT is shown in Fig. 5. (The absorption bands near 3600 and 1700 cm^{-1} are probably due to traces of oxidation products.) The bands at 3100 (w), 2920 (vw), 1435 (m), 1117 (w-m), 1006 (s), 840 (m-s) and 790 cm^{-1} (vs) are assigned as the normal vibrations of the cyclopentadienyl ligands¹⁹; in the (di)methylallyl homologues these bands are found at almost the same wave numbers and with the same intensities. These assignments are in agreement with the π -bonding (or perhaps "central σ -bonding"¹⁹) of the cyclopentadienyl groups to the metal, already to be expected from the method of preparation of the complexes and from their chemical properties.

In monomeric allyl complexes of transition metals²⁰ the metal may be bonded to the allyl group by:

- (a) a σ -bond to carbon atom 1 (" σ -bonded allyl");
- (b) coordinative bonding with the delocalized π -orbitals involving all three carbon atoms of the allyl group (" π -bonded allyl");
- (c) "asymmetric π -bonding", as found in $\text{C}_4\text{H}_7\text{PdClP}(\text{C}_6\text{H}_5)_3$ ^{21,31}; this has been regarded as an intermediate case and has been represented²¹ as shown below,

but the asymmetry may be merely due to a *trans*-effect (cf. ref. 31).



Complexes with a σ -bonded allyl group show a strong infrared absorption band (C=C stretch) in the range $1650\text{--}1600\text{ cm}^{-1}$, while in complexes with π -bonded allyl this band is shifted to lower frequencies^{22,23}. The allyl-DCT complexes show no pronounced absorption band between 1700 and 1550 cm^{-1} (a broad, very weak band near 1590 cm^{-1} is probably an overtone of the very strong band at 790 cm^{-1}), but a band of moderate to strong intensity at about 1500 cm^{-1} . This band is assigned as the asymmetric C=C stretch and its frequency is taken as evidence for π -bonding of the allyl ligands to the metal in the complexes $(\text{C}_5\text{H}_5)_2\text{TiR}$. The wave number of this band is strongly influenced by substitution: for R = allyl it is found at 1509 cm^{-1} , for R = 2-methylallyl at 1480 cm^{-1} , for R = 1-methylallyl at 1533 cm^{-1} , and for R = 1,3-dimethylallyl at 1546 cm^{-1} . These frequencies are fairly high for π -bonded allylic ligands. For allylsodium²⁴ the corresponding band lies at 1535 cm^{-1} ; for the $\pi\text{-C}_3\text{H}_5$ complexes of Ti at 1509 cm^{-1} , of Mn²² at 1505 cm^{-1} , of Fe²⁵ near 1470 cm^{-1} , of Co near 1470 cm^{-1} and of Ni near 1460 cm^{-1} . The decrease of the asymmetric C=C stretching frequency with increasing number of $3d$ electrons reflects the increase in "back-bonding" (and hence in covalency). In the corresponding complexes of $4d$ and $5d$ transition metals the C=C stretch is found at slightly lower frequencies: here, back-bonding is favoured by a stronger overlap. (The same trends are observed for the C-C stretching frequencies of π -cyclopentadienyl ligands in the range $1440\text{--}1400\text{ cm}^{-1}$).

The symmetric C=C stretching frequency of the allylic groups in the complexes $(\text{C}_5\text{H}_5)_2\text{TiR}$ is assigned to a band observed at $1010\text{--}1030\text{ cm}^{-1}$, nearly coinciding with a strong band of the cyclopentadienyl ligands; the allylic CCC deformation frequency of the complexes to a moderate to strong band at 474 cm^{-1} . Nearly all other observed bands can be assigned as CH stretching or deformation bands of the π -bonded allylic ligands, similar to the assignment by Fritz²⁶, but in view of the uncertainties in some of the assignments a discussion is postponed.

In π -bonded allyl complexes (model *b*) the substituents at carbon atoms 1 and 3 can occupy either the *syn*- or the *anti*-position in respect to the hydrogen atom at carbon atom 2. Therefore, two isomers are possible of (1-methylallyl)-DCT [and (1,2-dimethylallyl)-DCT] and three isomers of (1,3-dimethylallyl)-DCT. (Moreover, the 1-methylallyl, the 1,1-dimethylallyl, the 1,2-dimethylallyl, and one of the isomers of the 1,3-dimethylallyl complex occur in enantiomeric forms.) According to Lanpher²⁴ the frequency of the asymmetric C=C stretch of allylic anions increases in the sequence: 2-methylallyl < cyclohexenyl < *anti*-1-methylallyl < allyl < *syn*-1-methylallyl. In the complexes $(\text{C}_5\text{H}_5)_2\text{TiR}$ only one asymmetric C=C stretch is observed, the frequency of which increases in the sequence R = 2-methylallyl < allyl < 1-methylallyl < 1,3-dimethylallyl. This probably indicates that the 1-methylallyl and 1,3-dimethylallyl complexes have the *syn*- and *syn,syn*-configuration respectively. Models of the complexes also suggest that the *anti*-position of the substituents is less favourable. In (1,1-dimethylallyl)-DCT the unfavourable position (probably *anti*-) of

one of the methyl groups cannot be avoided, which explains the decreased stability. An X-ray diffraction study of (1-methylallyl)-DCT is being undertaken in order to establish the configuration of the complex.

EXPERIMENTAL

Starting materials

Dicyclopentadienyltitanium dichloride was prepared by the method of Wilkinson and Birmingham²⁷. 4-Chloro-2-pentene was prepared from 1,3-pentadiene as described by Pudovik and Sharipova²⁸; after three distillations over a Widmer column a product of b.p. 99–100° (lit.²⁸ 96–97°) was obtained. Commercial allyl chloride and 2-methylallyl chloride were distilled before use, while crotyl bromide (Fluka) and 1-chloro-3-methyl-2-butene (Eastman Organic Chemicals) were used without purification. The Grignard reagents were prepared using a threefold excess of magnesium; the solvents were tetrahydrofuran for the chlorides and diethyl ether for the bromides. The concentrations of the Grignard solutions (about 1.5 M for the chlorides and 1.0 M for the bromides) were determined by acidimetric titration. The solutions were stored in a container with a fused-on burette.

All experiments were carried out in an atmosphere of nitrogen which was purified by means of a BTS catalyst and dried by anhydrous magnesium perchlorate. Solvents were dried and distilled in the usual ways; before use, they were freed from oxygen by repeated degassing (by pumping under magnetic stirring) and saturating with nitrogen.

Preparation of allyl-DCT

A fresh solution of allylmagnesium chloride (44 mmoles) in tetrahydrofuran is dropwise added to a well-stirred mixture of powdered dicyclopentadienyltitanium dichloride (5 g, 20 mmoles) and tetrahydrofuran (125 to 150 ml), contained in the first bulb of a Schlenk-type three-bulb vessel²⁹. Some heat is evolved and the originally red solution turns purple. After the addition of Grignard solution is complete, the reaction mixture is stirred for 20 min at room temperature, then boiled under reflux for 45 min; the colour changes to violet (like permanganate). The solvent is removed in vacuum and the residue evaporated to complete dryness by sucking at an oil pump with a cold trap for 45 min. Pentane (350 ml) is added, cooled to –80° and the vessel is evacuated and sealed. (By way of precaution the access of daylight is reduced during the isolation.) The mixture is stirred for 3 h at room temperature, then kept overnight to allow the solid (mainly MgCl₂) to settle down. The supernatant solution is decanted into the second bulb and cooled slowly (duration 7 h) to –80°; dark violet crystals of allyl-DCT separate. The mother liquor is brought back to the first bulb and two more extractions are carried out. Finally, the solvent is distilled onto the cooled crystals, the crystals are dissolved by stirring at room temperature, the solution is decanted into the third bulb and cooled to –80°; pure allyl-DCT separates as clusters of violet needles. The solvent is brought back to the second bulb and another recrystallization is carried out. The vessel is opened under nitrogen, the crystals are brought into ampules which are sealed.

Operating as described, five syntheses gave yields of 2.8 to 2.9 g (64 to 66%) of pure allyl-DCT.

Preparation of (2-methylallyl)-DCT

2-Methylallylmagnesium chloride (42 mmoles) in tetrahydrofuran is dropwise added to 20 mmoles of $(C_5H_5)_2TiCl_2$ in 125–150 ml of ether. After half of the Grignard solution is added, the reaction mixture is stirred for 15 min; the mixture becomes brown-green. The remainder of the Grignard solution is added and the mixture refluxed for 5 to 10 min. The isolation and recrystallization of the product are carried out as described for allyl-DCT; yield 3.5 to 3.7 g (75 to 80%) of black-violet needles of pure (2-methylallyl)-DCT.

Preparation of (1-methylallyl)-DCT

The synthesis is carried out as described for (2-methylallyl)-DCT; butenylmagnesium bromide in ether is used as the Grignard solution. In this case, the reaction mixture is refluxed for 15 to 20 min; two extractions of the reaction mixture and only one recrystallization are sufficient for obtaining 3.7 g (80%) of violet platelets of pure (1-methylallyl)-DCT.

Preparation of (1,3-dimethylallyl)-DCT

The synthesis proceeds exactly as for (2-methylallyl)-DCT (the Grignard reagent is 1,3-dimethylallylmagnesium chloride in tetrahydrofuran), the isolation and recrystallization as in the case of (1-methylallyl)-DCT. Yield 3.0 to 3.2 g (60 to 65%) of dark-blue needles of pure (1,3-dimethylallyl)-DCT.

An alternative synthesis of (1,3-dimethylallyl)-DCT, namely by reaction of 1 mole of $(C_5H_5)_2TiCl_2$ with 2 moles of isopropylmagnesium bromide and an excess of pentadiene, has been reported elsewhere¹⁵. It has recently been found that 2 moles of pentadiene are sufficient for preparing (1,3-dimethylallyl)-DCT in 70% yield. Taking isoprene instead of pentadiene we prepared (1,2-dimethylallyl)-DCT in good yield¹².

Preparation of (1,1-dimethylallyl)-DCT

A solution of 1,1-dimethylallylmagnesium chloride (16.8 mmoles) in tetrahydrofuran is dropwise added to a stirred mixture of powdered $(C_5H_5)_2TiCl_2$ (2 g, 8 mmoles) and ether (70 ml), contained in a double Schlenk vessel equipped with a P3 filter. After half of the Grignard solution is added, the reaction mixture is refluxed for 30 min, then cooled at -20° and the remainder of the Grignard solution is dropwise added. When the addition of the reagent is complete, the reaction mixture is stirred for 30 min at -20° and for 1 h at 0° . While the product is kept at 0° , the solvent is removed in vacuum and the product evaporated to complete dryness by sucking at an oil pump with a cold trap (-180°) for 1 h. Cold pentane (350 ml) is added; the mixture is stirred at 0° for 4 h and at $10-15^\circ$ for another 30 min, then filtered. The reddish-brown filtrate is cooled to -80° ; black crystals of (1,1-dimethylallyl)-DCT separate. Yield 0.5 g (25%).

DCT monochloride

DCT monochloride was prepared by the methods of Natta *et al.*⁵ and Reid *et al.*³⁰ and by refluxing a mixture of $(C_5H_5)_2TiCl_2$ (1 g, 4 mmoles) and zinc powder¹³ (2 mmoles) in tetrahydrofuran (200 ml) for one hour. (In the latter reaction a large excess of zinc should be avoided, since it decomposes DCT monochloride.) In all

cases a green product was obtained, solutions of which (in tetrahydrofuran or benzene) had a rather sharp absorption maximum at $455 \pm 2 \text{ m}\mu$ (Fig. 3a) and a much weaker broad maximum about $700 \text{ m}\mu$. The same absorption spectrum was given by the products of reactions (6) and (1a + b); for reaction (1a + b) slightly more than the stoichiometric proportion of Grignard reagent is needed, otherwise the maximum at $455 \text{ m}\mu$ is obscured by the intense absorption of a brown intermediate product [probably containing both Ti(IV) and Ti(III)] below about $500 \text{ m}\mu$.

"Dicyclopentadienyltitanium(II)"

The product was prepared as described by Clauss and Bestian¹⁷, by contacting a stirred hexane solution of dimethyldicyclopentadienyltitanium(IV) with purified hydrogen. After a green precipitate was formed, the mixture was contacted with hydrogen for one more hour and then evaporated to complete dryness. The green powder (Fig. 4a) was stored in sealed ampules.

Mixtures of 1 mole of above product with cyclohexane were brought into contact with 0.5 or 1 mole of benzyl chloride; a purple mixture was obtained. This was treated with (gaseous) hydrogen chloride and the product studied by gas chromatography; no toluene was found, only bibenzyl.

Reaction of [(methyl)allyl]-DCT with hydrogen

Cyclohexane (50 ml, spectroscopically pure) was brought into contact with a gas burette filled with purified hydrogen. After equilibrium was reached, the complex $(\text{C}_5\text{H}_5)_2\text{TiR}$ (100–300 mg) was brought into the stirred liquid. A smooth reaction set in immediately. After 3 to 8 h no further hydrogen was taken up [except for (1,3-dimethylallyl)-DCT, which reacts much slower]. The uptake of hydrogen per mole of $(\text{C}_5\text{H}_5)_2\text{TiR}$, calculated from the change in volume (corrected for cyclohexane gas) is: for R = allyl 1.3 and 1.4 moles of H_2 ; for R = 1-methylallyl 1.48 and 1.51 moles of H_2 ; for R = 2-methylallyl 1.48 and 1.46 moles of H_2 .

Analyses

Elementary analyses of C, H and Ti (Table 1) were carried out at the Micro-analytical Department under supervision by Mr. W. M. Hazenberg; Ti was weighed as TiO_2 .

Molecular weights were determined from the freezing-point depression in benzene; the results (accuracy 3%) are included in Table 1.

For the determination of the R content of $(\text{C}_5\text{H}_5)_2\text{TiR}$, 200 to 300 mg of the compound were treated with 4 N hydrochloric acid (oxygen-free). The volume of the gas formed was measured in a gas burette (and corrected for the vapour pressure of the hydrochloric acid solution); the results (for 0° and 760 mm Hg pressure; accuracy 1%) are given in Table 1. Finally, the gas was dried by KOH, and identified by infrared spectroscopy.

The (uncorrected) melting points given in Table 2 were observed in sealed glass capillaries.

Spectra

Spectra in the visible range (and near ultraviolet) were recorded with a Zeiss spectrophotometer, type PMQ II; some data are given in Table 2. For the study of

spectra of reaction mixtures (Figs. 1, 2, 3) a Unicam spectrophotometer SP 800 was used; the solutions contained about 20 mmoles of the Ti compounds per litre, the thickness of the cell was 2 mm.

Infrared spectra in the range $4000\text{--}400\text{ cm}^{-1}$ were measured by Mr. F. W. Siegert by means of an EPI-G Hitachi Grating Infrared Spectrophotometer. The samples were embedded in KBr discs. KBr was freed from oxygen by evaporating an aqueous solution to complete dryness; this was twice repeated. Dry benzene was added and the mixture was again evaporated to dryness. The complex was added to part of the KBr and the mixture homogenized by magnetic stirring; another part of the KBr was used as a blank. The pellets were pressed in a nitrogen atmosphere. The infrared spectrum of (1,1-dimethylallyl)-DCT was not measured, since this compound was found to be decomposed by infrared radiation.

Magnetic measurements

Magnetic susceptibilities at room temperature were determined by the Faraday method; the measurements were performed by Drs. C. F. van Bruggen. The derived magnetic moments (corrected for induced diamagnetism) are given in Table 2; their accuracy is about 3%.

ESR spectra were recorded with a Varian V 4500 instrument (100 Kc modulation); for the NMR experiments a high-resolution instrument (Varian A60) and a wide-line instrument (Varian V 4210/V-FR 2503) were employed.

X-Ray diffraction

Single crystals of some of the complexes were studied by Mr. C. J. de Vries. (1,3-Dimethylallyl)-DCT (monoclinic; $a = 50.0\text{ \AA}$; $b = 25.7\text{ \AA}$; $c = 7.45\text{ \AA}$; $\beta = 90^\circ$) and (2-methylallyl)-DCT (orthorhombic; $a = 25.6\text{ \AA}$; $b = 44.7\text{ \AA}$; $c = 12.14\text{ \AA}$; space group *Pbca*) have very large unit cells. (1-Methylallyl)-DCT is monoclinic with four molecules per unit cell; a structure determination of this compound is in progress.

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SUMMARY

Allyldicyclopentadienylyltitanium(III) complexes $(C_5H_5)_2TiR$ with $R =$ allyl, 1-methylallyl, 2-methylallyl, 1,3-dimethylallyl, 1,1-dimethylallyl, have been prepared by reaction of 1 mole of dicyclopentadienylyltitanium dichloride with 2 moles of the (methyl)allyl Grignard reagent in ether or tetrahydrofuran solution. The stable, but extremely air-sensitive complexes are monomeric in benzene solution; they have one unpaired electron per molecule. The infrared spectra indicate that the (methyl)-allyl ligands are π -bonded to the metal, as are the cyclopentadienyl ligands. The methyl substituents at carbon atoms 1 and 3 probably prefer the *syn*-position. The

1,1-dimethylallyl complex in which both a *syn*- and an *anti*-methyl group are present, is much less stable than the other complexes. Some chemical properties of the complexes, in particular the reactions with hydrogen chloride [which gives $(C_3H_5)_2TiCl + RH$] and with molecular hydrogen (at room temperature and atmospheric pressure) have also been studied.

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