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SYNTHESIS OF ALLYLDICYCLOPENTADIENYLTITANIUM(III) COMPLEXES FROM DIENES

HENDRIK A. MARTIN* AND F. JELLINEK
Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Bloemsingel 10, Groningen (the Netherlands)

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SUMMARY

Reaction of isopropylmagnesium bromide (2 moles) with a mixture of dicyclopentadienyltitanium dichloride (1 mole) and suitable dienes in ether gives homologues of π-allyldicyclopentadienyltitanium(III). For 1,3-dienes the yields of allyldicyclopentadienyltitanium(III) complexes are of the order of 70–80%; they are lower for 1,4-dienes and 1,5-dienes, while no complexes are obtained from allenes. The complexes isolated are the most symmetrical ones of the possible isomers; the absorption spectrum in the visible range can be used as a guide for the identification of isomers. The substituents at carbon atoms 1 and 3 of the allyl group are in *syn*-position. This explains why no complexes could be obtained from olefins in which the diene system is part of a five- to eight-membered ring; however, the cyclododecadienyl complex, in which ring closure at the *syn*-positions is possible, was obtained when 1,5,9-cyclododecatriene was used as the olefin. The mechanism of the formation of allyldicyclopentadienyltitanium(III) complexes from dienes was studied. The first mole of iso-C_3H_7MgBr reduces Cp_2TiCl_2 to dicyclopentadienyltitanium(III) monobromide, which is converted to the unstable "active species" (Cp_2Ti-iso-C_3H_7 or Cp_2TiH) by the second mole of the Grignard reagent. The active species is trapped by the diene to give the final π-allylic complex.

INTRODUCTION

Allyldicyclopentadienyltitanium(III)[1,2] has been prepared by reaction of allylmagnesium chloride with dicyclopentadienyltitanium(IV) dichloride or dicyclopentadienyltitanium(III) monochloride according to:

$$Cp_2TiCl_2+2\ C_3H_5MgCl \rightarrow Cp_2TiC_3H_5+2\ MgCl_2+[C_3H_5^\bullet] \quad (1)$$

or:

$$Cp_2TiCl+C_3H_5MgCl \rightarrow Cp_2TiC_3H_5+MgCl_2 \quad (2)$$

Several (di)methylallyl homologues of allyl-DCT** were prepared by method (1)[2], while (1-phenylallyl)-DCT and (2-phenylallyl)-DCT were obtained by method (2)[3].

It has been shown by chemical and spectroscopic methods and by X-ray analysis that the allylic ligands are π-bonded to the metal (as are the cyclopentadienyl

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* Present address: Unilever Research Laboratory, Vlaardingen, The Netherlands.
** DCT = dicyclopentadienyltitanium(III).

rings) and that the methyl substituents at carbon atoms 1 and 3 of the allyl group occupy the *syn*-position[2,4].

An alternative method of preparation of substituted allyl-DCT complexes, namely by reaction of dicyclopentadienyltitanium dichloride with isopropylmagnesium bromide in the presence of a suitable diene, according to:

$$Cp_2TiCl_2 + C_nH_{2n-2} + 2\ \text{iso-}C_3H_7MgBr \rightarrow Cp_2TiC_nH_{2n-1} + 2\ MgClBr + \tfrac{3}{2}\,C_3H_6 + \tfrac{1}{2}\,C_3H_8 \qquad (3)$$

has been briefly reported[5]. In the present communication the scope of this synthesis and its mechanism are investigated. The absorption spectra of the allyl-DCT complexes in the visible range, which are a useful guide for the identification of isomers, are also discussed.

SCOPE OF THE METHOD

In our original experiments[5] five moles of 1,3-pentadiene were mixed with one mole of Cp_2TiCl_2 and ether, and two moles of isopropylmagnesium bromide (in ether) were added dropwise to the mixture. Gas evolution set in immediately; initially, the reaction mixture became very dark, but after half of the Grignard reagent was added the solution gradually turned blue. Crude (1,3-dimethylallyl)-DCT could be isolated from the reaction mixture in 73 % yield. After two recrystallizations the product was pure and identical with (1,3-dimethylallyl)-DCT prepared by reaction (1).

In subsequent experiments (some typical experiments are included in Table 1) it was found that 2 moles of 1,3-pentadiene per mole of Cp_2TiCl_2 were sufficient for obtaining (1,3-dimethylallyl)-DCT in good yield; if still less pentadiene was used a dark precipitate was formed in the reaction mixture (as in the absence of an olefin; see below), and the yield of the allylic complex decreased.

Other alkyl Grignard reagents were also used in place of isopropylmagnesium bromide. It will be seen from Table 1 that n-propylmagnesium bromide is about as effective as the isopropyl Grignard reagent, while tert-butylmagnesium bromide gives a lower yield of (1,3-dimethylallyl)-DCT. With methyllithium no allylic complex was obtained (nor was gas evolution observed), but $Cp_2Ti(CH_3)_2$ was formed[6]; no reduc-

TABLE 1

SYNTHESIS OF (1,3-DIMETHYLALLYL)-DCT FROM 1,3-PENTADIENE (mixture of *cis* and *trans*)
All quantities are calculated per mole of Cp_2TiCl_2.

1,3-Pentadiene (moles)	Grignard reagent (2 moles)	Atmosphere	Yield[a] (moles)
5	isopropyl-MgBr	N_2	0.73
2	isopropyl-MgBr	N_2	0.71
1	isopropyl-MgBr	N_2	0.33
2	n-propyl-MgBr	N_2	0.76
5	*tert*-butyl-MgCl	N_2	0.46
2	methyl-Li	Ar	0
2	methyl-Li	H_2	0

[a] Yield of crude (1,3-dimethylallyl)-DCT.

tion of T^{IV} had taken place. The experiment with methyllithium was also carried out in a hydrogen atmosphere. [(1,3-Dimethylallyl)-DCT reacts only extremely slowly with hydrogen in contrast to several other allyl-DCT complexes[2].] In this case the reaction was more complicated, but again no allyl-DCT compound was obtained.

Table 2 summarizes the results of reaction (3) starting from several dienes (or trienes); in all cases the molar ratio Cp_2TiCl_2/iso-C_3H_7MgBr was 1:2; the molar ratio Cp_2TiCl_2 : olefin was 1:2 to 3 (except for the gases butadiene and allene). The 1,3-pentadiene normally used as the olefin was a mixture of the *trans*- and *cis*-isomers; the same yield of (1,3-dimethylallyl)-DCT was obtained if it was replaced by the pure *trans*- or *cis*-forms. Replacement of 1,3-pentadiene by 1,4-pentadiene lowered the yield of (1,3-dimethylallyl)-DCT to 62%. If 2,3-pentadiene (1,3-dimethylallene) was used as the starting material, no allylic-DCT complex was obtained at all; the same was true if allene was taken as the olefin. Evidently, the addition of hydrogen at C2 of the allene group, necessary for the formation of the allylic group, does not take place.

TABLE 2

ALLYL-DCT COMPLEXES Cp_2TiR PREPARED FROM DIENES

All quantities are calculated per mole of Cp_2TiCl_2; in all cases 2 moles of isopropylmagnesium bromide were used.

Diene (2–3 moles[a])	Atmosphere	Yield[b] (moles)	R
1,3-Butadiene	N_2	0.30	1-methylallyl
1,3-Pentadiene (*cis* and *trans*)	N_2	0.71	1,3-dimethylallyl
1,3-Pentadiene (*trans*)	N_2	0.71	1,3-dimethylallyl
1,3-Pentadiene (*cis*)	N_2	0.69	1,3-dimethylallyl
2-Methyl-1,3-butadiene	N_2	0.79	1,2-dimethylallyl
3-Methyl-1,3-pentadiene	N_2	0.83	1,2,3-trimethylallyl
1,4-Pentadiene	N_2	0.62	1,3-dimethylallyl
1,5-Hexadiene	N_2 or Ar	0.27	1-methyl-3-ethylallyl
2,3-Pentadiene	N_2	0	
Allene	N_2	0	
1,3-Cyclopentadiene	N_2	0	
1,3-Cyclohexadiene	N_2	0	
1,3,5-Cycloheptatriene	N_2	0	
1,3-Cyclooctadiene	N_2	0	
1,5,9-Cyclododecatriene	Ar	<0.3?	cyclododecadienyl

[a] Except for the gases 1,3-butadiene and allene. [b] Yield of crude allylic complex.

The decrease in yield of allyl-DCT complex going from 1,3-pentadiene to 1,4-pentadiene is continued if 1,5-hexadiene is taken as the starting material. Obviously, this decrease in yield is related to the need for migration of the double bond.

Good yields of allyl-DCT complexes were obtained if 3-methyl-1,3-pentadiene or 2-methyl-1,3-butadiene (isoprene) were taken as the olefin. If 1,3-butadiene itself was used, the yield of allylic DCT complex was much lower and the product was very impure.

Preparation of allylic DCT complexes from cyclic olefins was also attempted. No complexes were obtained if the olefin was either cyclopentadiene, 1,3-cyclohexadiene, cycloheptatriene or 1,3-cyclooctadiene. However, a small yield of an allylic DCT complex was obtained if *trans,trans,trans*-1,5,9-cyclododecatriene was taken as the starting material. These results can be understood in terms of the structure of allyl-DCT complexes[4]. If the allylic group which is to become π-bonded to the metal is part of a small ring, the *anti*-positions at carbon atoms 1 and 3 have to be substituted. Since this is very unfavourable, no complex is formed. As shown by an X-ray analysis of a π-1,5-cyclododecadienylrhodium complex[7], the twelve-membered cyclododecadienyl ring is large enough for ring closure to occur between the *syn*-positions of the carbon atoms 1 and 3 of the allyl group; there need not be steric hindrance in the molecule of $Cp_2TiC_{12}H_{19}$. Since the allyl formation from *trans,trans,trans*-1,5,9-cyclododecatriene involves a large migration of the double bond, the yield of DCT complex is only small, as in the case of 1,5-hexadiene.

ISOMERISM AND ELECTRONIC SPECTRA

The allyl-DCT complex formed by reaction (3) with 1,3-butadiene as the diene must be (1-methylallyl)-DCT. The absorption spectrum in the visible range of the crude, impure reaction product has the absorption maximum at the same wavelength λ_{max} as pure (1-methylallyl)-DCT prepared by reaction (1). For reaction (3) with most of the other dienes, however, one might *a priori* expect the formation of two isomeric allyl-DCT complexes.

The possible products of reaction (3) with isoprene are (1,2-dimethylallyl)-DCT and (1,1-dimethylallyl)-DCT. X-ray analysis[4] showed the product to be the 1,2-dimethylallyl complex. This is not surprising since (1,1-dimethylallyl)-DCT is unstable because of steric hindrance[2,4] and would not survive the reaction conditions, nor isomerize to (1,2-dimethylallyl)-DCT[2]. The high yield of allyl-DCT complex indicates that virtually only (1,2-dimethylallyl)-DCT is formed. [This is in contrast to other transition metals, where (1,1-dimethylallyl)-complexes are preferably formed by reaction of isoprene with hydrides[8] or by protonation of π-isoprene complexes[9].] By analogy, the product of reaction (3) with 3-methyl-1,3-pentadiene is taken to be (1,2,3-trimethylallyl)-DCT and not (1-methyl-1-ethylallyl)-DCT which should be very unstable. This conclusion is supported by the absorption spectrum of the product (see below); the spectra of the crude and recrystallized products were identical.

Two stable products could be formed by reaction (3) with 1,3-pentadiene, namely (1,3-dimethylallyl)-DCT and (1-ethylallyl)-DCT. The absorption spectrum of the crude reaction product shows a maximum at 573 mμ (in cyclohexane); after recrystallization pure (1,3-dimethylallyl)-DCT, with λ_{max} 578 mμ, was obtained. Evidently, the crude product contains a contaminant. Originally[5], we assumed the contaminant to be (1-ethylallyl)-DCT which should have its absorption maximum near 540 mμ (see below). By modifications of the reaction conditions (addition of 1,3-pentadiene after the Grignard reagent was added) a product with λ_{max} 563 mμ was obtained (in low yield), which should contain a larger proportion of the contaminant. Treatment of the product with hydrochloric acid in ether, however, gave only *trans*-2-pentene [from (1,3-dimethylallyl)-DCT[4]], but no 1-pentene [which should be formed from (1-ethylallyl)-DCT and HCl[2]]. Evidently, 1-ethylallyl-DCT is not present in the crude reaction product and another contaminant must cause the shift of the absorption maximum.

If reaction (3) is carried out with 1,4-pentadiene as the olefin, the crude product has the same absorption maximum as pure (1,3-dimethylallyl)-DCT; evidently, no significant proportion of the contaminant or (1-ethylallyl)-DCT is formed. One case of formation of allylic complexes from 1,4-pentadiene, namely the reaction with $HCo(CO)_4$, has been reported previously[10]; here, the 1-ethylallyl complex is formed in addition to a small amount of 1,3-dimethylallyl complex. The latter isomer is virtually exclusively isolated by reaction of 1,3-pentadiene with hydrides[8] or by protonation of π-1,3-pentadiene complexes[9].

The product of reaction (3) with 1,5-hexadiene could be (1-methyl-3-ethylallyl)-DCT or (1-propylallyl)-DCT. By analogy with the reaction with 1,4-pentadiene, we assume the product to be the 1-methyl-3-ethylallyl complex. Moreover, the absorption maximum of the product in the visible range (λ_{max} 580 mμ) is virtually the same as that of the 1,3-dimethylallyl complex (λ_{max} 578 mμ) and that of the cyclododecadienyl complex (λ_{max} 580 mμ), both of which are 1,3-substituted.

In all cases studied, therefore, the allyl-DCT complex actually obtained is the most symmetrical one that could be formed, *i.e.* that one in which the environments of carbons 1 and 3 of the allylic group are as similar as possible. It may be remembered that the substituents at these atoms are in the *syn*-position[4].

As stated, the absorption maxima of solutions of allylic DCT complexes in the visible range can be used as a guide for the identification of isomers. The spectra do not depend on the solvent. Below 400 mμ the complexes show strong absorption. A fairly sharp absorption band is found in the range 490–580 mμ [except for (1,1-dimethylallyl)-DCT] (Table 3). In some of the spectra there are indications for a second, much weaker band at higher wavelengths. The wavelength λ_{max} of the band in the range 490–580 mμ is characteristic of the positions of the substituents in the allylic ligands. An alkyl substituent at carbon 2 lowers λ_{max} by 16 mμ, while an alkyl substituent at carbon 1 (in the *syn*-position) increases λ_{max} by 26 mμ; if both carbons 1 and

TABLE 3

ABSORPTION MAXIMA OF COMPLEXES Cp_2TiR IN THE RANGE 400–1000 mμ

R	Solvent[a]	Main maximum λ_{max} (mμ)	ε ($l \cdot mol^{-1} \cdot cm^{-1}$)	Other maxima λ_{max} (mμ)	Ref.
Allyl	a	512	364		2
1-Methylallyl	a	539	364		2
2-Methylallyl	a	497	283		2
1,1-Dimethylallyl	a			386?; 830±5	
1,2-Dimethylallyl	a	522			
1,3-Dimethylallyl	a	578	445		2
1,2,3-Trimethylallyl	a	563			
1-Methyl-3-ethylallyl	a	580			
Cyclododecadienyl	a	580			
1-Phenylallyl	b	573			
2-Phenylallyl	b	492			
Cl	c	458		695±10	
Br	c	469		698±4	
I	c	480		680±20	

[a] a = cyclohexane; b = tetrahydrofuran; c = benzene.

3 carry a *syn*-substituent λ_{max} increases by 67 mμ. This rule reproduces the observed values of λ_{max} (Table 3) within 1 mμ. The shifts in λ_{max} due to phenyl substituents in the allylic ligands are in the same direction as those caused by alkyl substituents, but somewhat larger (Table 3). A similar correlation of the positions of substituents with the (asymmetric) carbon–carbon stretching frequency of the allylic ligands in the infrared has been discussed elsewhere[4].

The fairly low values of the extinction coefficients, ε, of the absorption bands in the visible range[2] indicate that these bands are due to essentially *d–d* transitions of the metal. The shifts in λ_{max} caused by substituents are remarkably large. For comparison, the spectra of DCT monohalides in the visible range are also given in Table 3. It is seen that the rather sharp maximum about 455–480 mμ is shifted only by 11 mμ by the substitutions Cl→Br or Br→I. A much weaker maximum is found about 680–700 mμ, while the compounds show strong absorption below 350 mμ.

The spectrum of (1,1-dimethylallyl)-DCT is quite different from those of the other complexes; no sharp absorption band is found in the visible range (Table 3). In this complex the bond of the allylic ligand to titanium is considerably weakened by sterical hindrance, since one of the substituents occupies an *anti*-position[4].

ON THE MECHANISM OF THE REACTION

It had been suggested[5] that reaction (3) proceeds *via* a complex titanium hydride. Several experiments were carried out to test this hypothesis. In order to avoid a possible side reaction with nitrogen (*cf.* ref. 11), these experiments were carried out in an argon atmosphere. (Several of the syntheses listed in Tables 1 and 2 were also repeated in an argon atmosphere, but the results and yields did not differ from those of syntheses carried out under nitrogen.)

Isopropylmagnesium bromide (1 mole) in ether was added dropwise to dicyclopentadienyltitanium dichloride (1 mole) in ether at room temperature. Evolution of gas began immediately; infrared spectroscopy showed propene to be present in the gas. A green precipitate was formed and was identified by absorption spectroscopy as DCT monobromide. These observations are compatible with the following reaction course:

$$\mathrm{Cp_2TiCl_2 + iso\text{-}C_3H_7MgBr \rightarrow Cp_2TiBr + MgCl_2 + \tfrac{1}{2}\,C_3H_8 + \tfrac{1}{2}\,C_3H_6} \qquad (4)$$

(Analogous observations were made if tert-butylmagnesium chloride or n-propylmagnesium bromide were used instead of isopropylmagnesium bromide.)

If 1,3-pentadiene and one mole of isopropylmagnesium bromide are added to one mole of DCT monobromide, (1,3-dimethylallyl)-DCT is formed in virtually the same yield as obtained in reaction (3). It is very probable, therefore, that reaction (4) corresponds to the first steps of reaction (3).

1,3-Pentadiene alone does not react with DCT monobromide, but isopropylmagnesium bromide alone does react with DCT monobromide. A brown instable product is formed which decomposes immediately with gas evolution to form a dark precipitate. This reaction was studied in some detail.

Isopropylmagnesium bromide (2 moles) was added to Cp_2TiCl_2 (1 mole) in ether; evolution of gas took place. After the mixture was refluxed for 30 minutes the evolution of gas had stopped and a dark precipitate had formed. The supernatant solution gave an asymmetric ESR signal, while absorption spectroscopy indicated Cp_2TiBr still to be present in the solution. For brevity, we shall call the reaction product (dark precipitate+supernatant solution) the "2 : 1 mixture".

More of the Grignard reagent was added to the 2 : 1 mixture without heating. When the molar ratio of Grignard to Cp_2TiCl_2 was 3 : 1, the supernatant solution gave a symmetric ESR signal on which a weak triplet was superposed. The reaction product is called the "3 : 1 mixture".

When the molar ratio of Grignard to Cp_2TiCl_2 was 4 : 1, only the triplet ESR signal was observed in the almost colourless solution from which DCT monobromide had disappeared. The ESR signal was identical to that reported by Brintzinger[12]. The supernatant solution and the grey precipitate together form the "4 : 1 mixture".

To each of the 2 : 1, 3 : 1 and 4 : 1 mixtures defined above, an excess of 1,3-pentadiene was added. The 2 : 1 mixture very slowly became purple; after stirring for several days, a black powder was isolated (with λ_{max} 563 mμ in cyclohexane) which consisted of (1,3-dimethylallyl)-DCT and an unknown purple contaminant; the overall yield of (1,3-dimethylallyl)-DCT was of the order of 10 to 20%.

After the addition of 1,3-pentadiene, the 3 : 1 and 4 : 1 mixtures gradually became blue. The absorption spectra (with λ_{max} 578 mμ) indicated the presence of some (1,3-dimethylallyl)-DCT in the solutions; the purple contaminant was not found. In the ESR spectrum of the 4 : 1 mixture the original triplet signal was replaced by the signal of (1,3-dimethylallyl)-DCT. If 1,3-pentadiene and another mole of Grignard reagent were added to the 2 : 1 mixture (which still contains Cp_2TiBr), (1,3-dimethylallyl)-DCT could be isolated in about 45% yield. It may be remembered that 2 moles of Grignard per mole of Cp_2TiCl_2 suffice to give the allyl-DCT complex in 70% yield if an excess of the diene is present in the reaction mixture before the Grignard reagent is added.

These experiments show that the "active species" formed by reaction of Cp_2TiCl_2 with two moles of Grignard reagent (or by reaction of Cp_2TiBr with one mole of Grignard) is an unstable complex which is trapped by 1,3-pentadiene. We cannot, at present, decide whether the active species is $Cp_2TiC_3H_7$ formed by:

$$Cp_2TiBr + \text{iso-}C_3H_7MgBr \rightarrow Cp_2TiC_3H_7 + MgBr_2 \qquad (5)$$

or whether it is Cp_2TiH (as was originally surmised[5]) formed by decomposition of $Cp_2TiC_3H_7$:

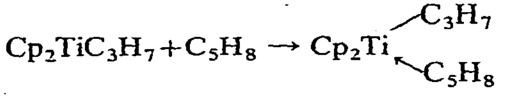
$$Cp_2TiC_3H_7 \rightarrow Cp_2TiH + C_3H_6 \qquad (6)$$

The reaction of Cp_2TiH with 1,3-pentadiene:

$$Cp_2TiH + C_5H_8 \rightarrow Cp_2TiC_5H_9 \qquad (7)$$

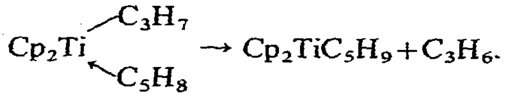
would be similar to that of other (stable) transition-metal hydrides with dienes.

On the other hand, it seems possible that the olefin is coordinated to $Cp_2TiC_3H_7$ to give a π-complex (which would be closely related to the intermediate assumed by several authors in the Ziegler–Natta reaction):



$$Cp_2TiC_3H_7 + C_5H_8 \rightarrow Cp_2Ti\begin{matrix} \nearrow C_3H_7 \\ \searrow C_5H_8 \end{matrix} \qquad (8)$$

This π-complex may be thought to decompose with hydrogen transfer directly from the isopropyl group to the diene:



$$Cp_2Ti\begin{matrix}C_3H_7\\C_5H_8\end{matrix} \rightarrow Cp_2TiC_5H_9 + C_3H_6. \qquad (9)$$

We tentatively suggest, therefore, that reaction (3) proceeds either by the following steps: (4), (5), (6), (7) or by: (4), (5), (8), (9).

If no olefin is present (or its concentration is too low), the "active species" is deactivated and more of the Grignard reagent is needed for a complete conversion of Cp_2TiBr. Therefore, the Grignard reagent should be involved in the deactivation reaction which must be fast compared to reaction (5). The product of this reaction still is able to react with 1,3-pentadiene to give (1,3-dimethylallyl)-DCT, but the reaction is much slower and the yield lower than in the case of reaction (3).

In view of these observations we suggest that the deactivation reaction is:

$$Cp_2TiH + iso\text{-}C_3H_7MgBr \rightarrow [Cp_2TiH_2]^- + C_3H_6 + \tfrac{1}{2}\,Mg^{2+} + \tfrac{1}{2}\,MgBr_2 \qquad (10)$$

The $[Cp_2TiH_2]^-$ ion would be coordinated to Mg^{2+} to form a complex which is only sparingly soluble in ether (but more soluble in THF).

The triplet ESR signal observed in the supernatant solutions of the 3 : 1 and 4 : 1 mixtures can be readily assigned to the $[Cp_2TiH_2]^-$ ion[13]. (Brintzinger's original interpretation[12] of the signal as due to $[Cp_2TiH]_2$ is incorrect[13].)

It may be remarked that the observations by Nechiporenko *et al.*[14] on the reaction of Cp_2TiCl_2 with ethylmagnesium chloride can be accounted for by reactions analogous to (4), (5), (6), (10).

EXPERIMENTAL

Experiments were carried out in an atmosphere of purified nitrogen or, in some cases, of purified argon. The (uncorrected) melting points were observed in sealed glass capillaries. Spectra were measured as described in ref. 2, except for the ESR spectra which were measured by Drs. D. A. Wiersma by means of a Varian E-3 EPR spectrometer.

Starting materials

Dicyclopentadienyltitanium dichloride and DCT monochloride were prepared as described in ref. 2. Solutions of DCT mono-bromide and -iodide were obtained by reaction of (1-methylallyl)-DCT[2] in benzene with hydrogen bromide in ether or hydrogen iodide in benzene. The monobromide was also prepared by reaction of Cp_2TiCl_2 with isopropylmagnesium bromide in molar ratio 1 : 1 [see below under (*n*)].

2,3-Pentadiene (1,3-dimethylallene) was prepared from 1,3-pentadiene by the method of Bouis[15]. 1,3-Pentadiene was converted to 2-chloro-3,4-dibromopentane[16]. Dehydrohalogenation by solid potassium hydroxide gave a liquid with b.p. 70–77°/36 mm. Dehalogenation was effected in ethanol by zinc powder. A mixture with a constant boiling point (44.6°, n_D^{20} 1.4208) was obtained which infrared spectroscopy and gas chromatography indicated to consist of the allene and ethanol. This mixture was treated with a large excess of anhydrous $CaCl_2$. After several distillations through a Vigreux column 1,3-dimethylallene was obtained in low yield with b.p. 47–49°, n_D^{20} 1.4257 (ref. 17: b.p. 48.3°, n_D^{20} 1.4284, n_D^{25} 1.4251). The infrared spectrum showed ethanol and 1,3- and 1,4-pentadiene to be absent; the characteristic intense C=C=C absorption was found at 1971 cm^{-1} (ref. 18: 1975 cm^{-1}), the characteristic C–H deformation band of symmetrically disubstituted allenes in the 870 cm^{-1} region[17] at 867 cm^{-1}.

3-Methyl-1,3-pentadiene was prepared from 3-methyl-2,4-pentanediol as described by Kyrides[19]. After two distillations over a Widmer column a product of b.p. 76° and n_D^{20} 1.4490 was obtained (ref. 20: b.p. 76–78°, n_D^{20} 1.4490); the infrared spectrum was in agreement with that reported in ref. 20. The other (liquid or gaseous) olefins were commercial products which were purified by distillation; the purity was checked by measurements of the refractivity and of the infrared spectrum (*cf.* ref. 3).

The Grignard reagents were prepared in diethylether; the concentration (between 1.0 and 2.0 *M*) was determined by acidimetric titration. Solvents were dried and distilled in the usual ways; before use, they were freed from oxygen.

Reaction with 1,3-pentadiene

(*a*) A solution of isopropylmagnesium bromide (40 mmoles) in ether was added dropwise to a stirred and cooled (at 0°) mixture of powdered dicyclopentadienyltitanium dichloride (5 g, 20 mmoles) and 1,3-pentadiene (2.72 g, 40 mmoles) in 80–100 ml of ether, contained in a double Schlenk vessel equipped with a P_3 filter. Gas evolution set in immediately; initially, the reaction mixture became very dark, but after half of the Grignard reagent was added, the solution gradually turned blue. After the addition of Grignard solution the mixture was stirred for three h at room temperature and refluxed for 30 min; the colour of the solution had intensified to dark blue and the gas evolution had stopped. The solvent was removed in vacuum and the product evaporated to complete dryness by sucking with an oil pump for 45 min. Pentane (300 ml) was added and the mixture stirred at room temperature for 45 min; the blue solution was filtered and slowly cooled to −80°. Crude (1,3-dimethylallyl)-DCT (3.5 g, 71%) separated as blue needles, m.p. 87–89° (dec.); λ_{max} 573 mμ (in cyclohexane). (Found: Ti, 19.62. $C_{15}H_{19}Ti$ calcd.: Ti, 19.38%.) The yield was the same, independent of whether *cis-* or *trans*-1,3-pentadiene or a mixture of the two forms was used as the starting material (*cf.* Table 2). The needles (which were stored at −18°) showed "weathering" after some days; this was caused by impurities, as it was not observed for the recrystallized product.

For purification the product was twice recrystallized from pentane (at −80°) in a Schlenk-type three-bulb vessel. The m.p. of 91–91.5° (dec.) and the absorption spectrum in cyclohexane (λ_{max} 578 mμ) are identical with those of (1,3-dimethylallyl)-DCT prepared by reaction (1)[2]. (Found: C, 73.23, 72.91; H, 7.90, 7.88; Ti, 19.41. $C_{15}H_{19}Ti$ calcd.: C, 72.87; H, 7.75; Ti, 19.38%.)

(*b*) The preparation of (1,3-dimethylallyl)-DCT was also carried out starting from other quantities of 1,3-pentadiene and with other Grignard reagents. The syntheses started from 20 mmoles of Cp_2TiCl_2 and were carried out in a completely analogous way as described above. The yields (of crude product) are given in Table 1.

(*c*) 1,3-Pentadiene (40 mmoles) was added to 20 mmoles of DCT monobromide and 100 ml of ether. The mixture was stirred for 15 h, but no visible change occurred.

After addition of 20 mmoles of isopropylmagnesium bromide (in ether) the solution became blue and (1,3-dimethylallyl)-DCT could be isolated in a yield of 69%. (This experiment was performed under argon.)

Reactions with other pentadienes

(*d*) Experiments were carried out as described under (*a*) with 5 and 6 ml (50 to 60 mmoles) of 1,4-pentadiene. After addition of the Grignard reagent the mixtures were stirred at room temperature for *ca.* 15 h before they were refluxed. Blue (1,3-dimethylallyl)-DCT with λ_{max} 578 mμ was obtained in a yield of 60 to 62% (the crystals showed no "weathering").

(*e*) Under identical conditions using 30 and 80 mmoles of 1,3-dimethylallene (2,3-pentadiene) as the olefin red-brown solutions were obtained from which no crystals could be isolated.

(*f*) Isopropyl Grignard reagent (56 mmoles) was added to 7 g (28 mmoles) of Cp_2TiCl_2 and 4.2 g (62 mmoles) of isoprene in 100 ml of ether. The synthesis proceeded exactly as described under (*a*). (1,2-Dimethylallyl)-DCT was isolated in a yield of 5.5 g (79%) with λ_{max} 522 mμ (cyclohexane); the small purple crystals had a m.p. of 69–73° (dec.).

For further purification the product was twice recrystallized from pentane (at −80°) in a Schlenk-type three-bulb vessel; in this way pure purple (1,2-dimethylallyl)-DCT was obtained with m.p. 70.5–71° (dec.); λ_{max} 522 mμ (cyclohexane). (Found: C, 73.12, 73.07; H, 7.76, 7.83; Ti, 19.07. $C_{15}H_{19}Ti$ calcd.: C, 72.87; H, 7.75; Ti, 19.38%.) In the infrared spectrum the carbon–carbon stretching frequency of the allylic ligand was found at 1499 cm^{-1}.

Reactions with hexadienes

(*g*) Experiments were carried out with 3.5 g (43 mmoles) of 1,5-hexadiene, as described under (*a*) and (*d*) both in an atmosphere of nitrogen and of argon. The extraction was performed with 90 to 100 ml of pentane. In both cases about 1.4 g (27%) of small blue crystals of (1-methyl-3-ethylallyl)-DCT were obtained with m.p. *ca.* 72° and λ_{max} 580 mμ. (Extraction with more pentane decreases the yield.) The carbon–carbon stretching frequency of the allylic ligand was observed at 1539 cm^{-1}.

(*h*) Working as under (*f*) with 28 mmoles of Cp_2TiCl_2, 4.6 g (58 mmoles) of 3-methyl-1,3-pentadiene and 56 mmoles of Grignard reagent in 130 ml of ether gave violet platelets of (1,2,3-trimethylallyl)-DCT in a yield of 6.1 g (83%). M.p. 73–75°; λ_{max} 563 mμ both for the crude and the recrystallized product; the carbon–carbon stretching frequency of the allylic ligand was observed as a weak band at 1499 cm^{-1}.

Reactions with 1,3-butadiene and allene

(*j*) Butadiene (10 ml) condensed in a cold trap was freed from oxygen and dissolved in 80 ml of ether (at 0°) which contained 4 g (16 mmoles) of Cp_2TiCl_2. The reaction was carried out in the same way as described under (*a*). Impure (1-methylallyl)-DCT (0.8 g = 21%) was obtained as a purple powder. A somewhat better yield (30%) was obtained, if the reaction mixture was not boiled, but worked up after standing at room temperature for 20 h. The product started to melt at about 45° and decomposed completely at 94°; λ_{max} 539 mμ. [Pure (1-methylallyl)-DCT crystallizes as violet platelets; m.p. 96.5–97° (dec.); λ_{max} 539 mμ in cyclohexane[2].]

(*k*) The reaction with allene was performed as under (*j*) except that the ether solution was kept saturated with allene during the (very slow) addition of Grignard reagent and for two h after the addition was complete. A red-brown pentane solution was obtained, which was not further investigated (allyl-DCT is violet[2]).

Reactions with cyclic olefins

(*l*) Reactions with 3 g (45 mmoles) of cyclopentadiene, 3 g (38 mmoles) of 1,3-cyclohexadiene, 5 g (54 mmoles) of cycloheptatriene or 4.5 g (41 mmoles) of 1,3-cyclooctadiene were carried out as described under (*d*). One to two h after the addition of the Grignard reagent a red or brown colour was observed, which disappeared after some hours. Dark-brown mixtures resulted, while in most cases decomposition products were deposited on the walls of the vessel. No precipitates could be observed after cooling the pentane extracts.

(*m*) A synthesis was carried out with 6.5 g (40 mmoles) of *trans,trans,trans*-1,5,9-cyclododecatriene as described under (*d*) (extraction with 100 ml of pentane). After cooling of the extract only a few green crystals (Cp_2TiBr?) and a trace of blue crystals were obtained. The supernatant (cold) blue pentane solution was decanted from the crystals and evaporated in vacuum at room temperature. A blue oil (4.5 g) was obtained with λ_{max} 580 mμ (in cyclohexane); it is likely, that the oil is strongly contaminated by non-volatile *trans,trans,trans*-1,5,9-cyclododecatriene.

Experiments concerning the mechanism

(*n*) 4 mmoles of isopropylmagnesium bromide in ether were added dropwise to 1 g (4 mmoles) of Cp_2TiCl_2 in 80 ml of ether at room temperature. Gas evolution set in immediately and the mixture turned green. The solvent was refluxed for 30 min. After cooling to room temperature the supernatant ether was decanted from the green precipitate which was completely freed from ether by evaporation in vacuum. Part of the precipitate was dissolved in benzene; the spectrum of the green solution (the residue was $MgCl_2$) was identical with that of DCT monobromide prepared from (1-methylallyl)-DCT and HBr (λ_{max} 468 mμ).

If slightly more than 1 equivalent of Grignard reagent (*i.e.* 1.1 equivalents) was added, a purple solution was obtained. The spectrum of the ether solution showed the DCT monobromide maximum at 468 mμ and a second maximum at 541 mμ.

(*o*) The following experiments were performed in an atmosphere of argon. 40 mmoles of isopropylmagnesium bromide (in ether) were added to 20 mmoles of Cp_2TiCl_2 in 100 ml of ether (at room temperature). After refluxing the mixture for 30 min gas evolution had stopped. A dark precipitate was formed together with a green to brown solution. With the "2:1 mixtures" obtained in this way the following experiments were performed:

(*i*) 10 ml of 1,3-pentadiene was added and the mixture stirred for about 65 h; the mixture gradually turned purple. It was evaporated to dryness, the residue extracted with 100 ml of pentane and the extract cooled to −80°; 2.1 g of a black powder was obtained with λ_{max} 563 mμ (in cyclohexane). (Extraction with 200 ml of pentane and complete evaporation of the pentane gave 2.6 g of the black powder.) Stirring of the black powder with an excess of isopropylmagnesium bromide and 1,3-pentadiene in ether for several days did not change the product.

The black powder was treated with hydrogen chloride in ether; the sample became green and later violet. Gas chromatography of the violet product indicated the presence of *trans*-2-pentene; 1-pentene was not found.

(*ii*) After saturating the 2:1 mixture with 1,3-butadiene and working in a similar way to that described above (the mixture gradually became red-purple), 1.2 g of a black powder was obtained with λ_{max} 535 mμ (in cyclohexane).

(*iii*) 20 mmoles of iso-C_3H_7MgBr and 10 ml of 1,3-pentadiene were added to the 2:1 mixture. A blue colour gradually developed, but there was no gas evolution. Working as described under (*i*) (extraction with 300 ml pentane) 2.4 g (47%) of impure blue needles (m.p. 76°) of (1,3-dimethylallyl)-DCT were obtained with λ_{max} 578 mμ (in cyclohexane).

(*iv*) The 2:1 mixture was evaporated to dryness after stirring for 65 h. Cyclohexane was added. The spectrum of the (green) supernatant liquid showed a maximum at 567 mμ due to Cp_2TiBr.

(*p*) For the ESR measurements, which were performed by Drs. D. A. Wiersma, the above experiments were repeated on a one-gram scale in a bulb with fused-on ESR tubes. Grignard solution was added to Cp_2TiCl_2 in ether (without heating); dark precipitates formed. ESR measurements were performed on the supernatant solutions one to two h after each addition; the molar ratios of Grignard to Cp_2TiCl_2 were 2:1; 2.1:1; 2.5:1; 3:1; 4:1. The first three gave an asymmetric signal with three lines, the 3:1 mixture a weak symmetric signal and the 4:1 mixture the same triplet signal as found by Brintzinger[12,13]. Heating of the 2:1 and 4:1 mixtures for 30 min at 35° gave only a somewhat better resolution of the ESR lines. Essentially the same observations as described were also made if THF was used as the solvent, but the supernatant solutions had to be diluted to obtain the same ESR signals as in ether; obviously, the precipitate is more soluble in THF than in ether. The absorption spectrum of the supernatant (ether) solution of the 4:1 mixture showed strong absorption below 450 mμ and a weak maximum at 528 mμ; DCT monobromide was not detected.

Addition of 2 ml of 1,3-pentadiene to the 4:1 mixture gave a blue solution; the triplet ESR signal disappeared and the signal of (1,3-dimethylallyl)-DCT was observed.

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