

REACTIONS OF TITANOCENE ALLYLS

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(Received August 21st, 1981)

Summary

$\text{Cp}_2\text{Ti}\eta^3$ -allyl and $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl react with carbon dioxide, phenylisocyanate, benzalaniline, acetone and acetonitrile to give insertion products which are formed via allyl migration. Normal insertion is observed with 2,6-xylylisocyanide. Carbonylation of $\text{Cp}_2\text{Ti}\eta^3$ -allyl affords $\text{Cp}_2\text{Ti}(\text{CO})_2$ and triallyl-methanol. With carbon disulfide and diphenylacetylene, allyl elimination reactions are observed.

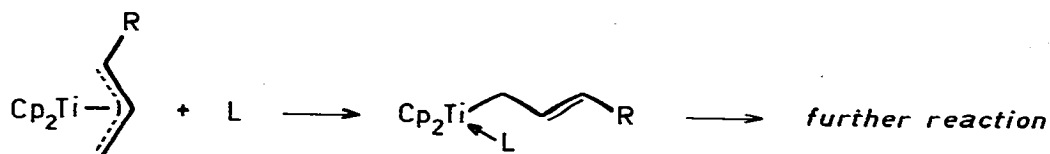
Introduction

In previous papers we described the various types of reaction of alkyl and alkenyl compounds Cp_2TiR ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with unsaturated substrates. Reductive coupling is observed with ketones [1,2], insertion with isocyanides [1–3], carbon monoxide [2], carbon dioxide [1,2], isocyanates [1,2], carbon disulfide [2] and acetylenes [2], disproportionation with carbon disulfide [3], and metallation with pyridines and quinolines [4,5].

In this report we describe reactions of the allyl derivatives $\text{Cp}_2\text{Ti}\eta^3$ -allyl (**1a**) and $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl (**1b**) with ligands L. Part of this study has been described briefly in a preliminary report [6].

Reaction of these η^3 -allyl complexes Cp_2TiR with sufficiently strong σ -donor ligands L will induce $\eta^3 \rightarrow \eta^1$ allyl rearrangement with formation of adducts $\text{Cp}_2\text{Ti}\eta^1$ -allyl · L (Scheme 1). For the 1-methylallyl derivative (**1b**) it is reasonable to assume the formation of an adduct in which the allyl group is bonded to Ti via the methylene carbon (Scheme 1) [7–9]. After adduct formation further reaction occurs. In the adduct stage, the situation is comparable to that in

SCHEME 1



1 a R=H

1 b R=CH₃

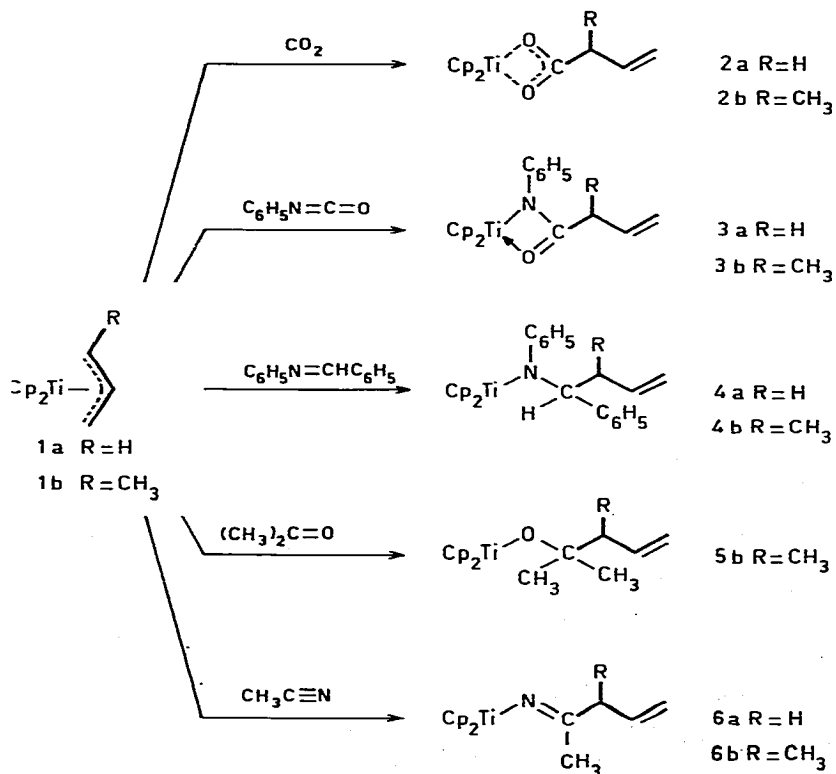
alkyl compounds except that the alkyl group is now functionalized with an olefinic function at the β -position. The question arose whether this would result in reactions different from the alkyl derivatives [1,3–5]. As will be shown below, this is indeed the case. The reactions observed are divided into allyl migration, insertion, and allyl elimination processes.

Results and discussion

Allyl migration reactions

Reactions of $\text{Cp}_2\text{Ti}\eta^3$ -allyl (1a) and $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl (1b) with carbon dioxide, phenylisocyanate, benzaniline, acetone and acetonitrile give high yields of the products 2–6 (Scheme 2). In all of the products obtained from

SCHEME 2



$\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl (**1b**) the allyl group is attached to the inserted ligand via its substituted end. Proof of this is provided by the IR spectra, which all show the characteristic absorptions for a terminal double bond; $\nu(\text{C}=\text{C})$ is found in the range $1620\text{--}1650\text{ cm}^{-1}$ together with a band in the range $900\text{--}920\text{ cm}^{-1}$, which is ascribed to a CH_2 out-of-plane deformation mode ($\delta_{\text{o.o.p.}}(\text{CH}_2)$) [9,10].

The reactions of **1a, b** with CO_2 and $\text{C}_6\text{H}_5\text{NCO}$ yield products similar to those described for other Cp_2TiR [1,2] compounds, i.e. carboxylato derivatives $\text{Cp}_2\text{TiOOCCH(R)CH}=\text{CH}_2$ (**2a, b**) and amido derivatives $\text{Cp}_2\text{TiN(C}_6\text{H}_5\text{)C(O)CH(R)CH}=\text{CH}_2$ (**3a, b**), respectively. The properties of these compounds are comparable to those earlier reported [1,2]. However, the reactions with $\text{L} = \text{C}_6\text{H}_5\text{-N=CHC}_6\text{H}_5$ to form the amido derivatives $\text{Cp}_2\text{TiN(C}_6\text{H}_5\text{)CH(C}_6\text{H}_5\text{)CH(R)-CH}=\text{CH}_2$ (**4a, b**) proceed entirely differently from that with $\text{Cp}_2\text{Ti-alkyl}$, for which a side-on coordinated benzalaniline complex of titanocene is formed [5]. The light brown crystalline complexes **4a, b** formed (70%) are thermally stable, paramagnetic and monomeric. The IR spectra of **4a** and **4b** (Fig. 1) show bands at 1290 cm^{-1} (**4a**) and 1289 cm^{-1} (**4b**), which are tentatively assigned to $\nu(\text{CN})$ (in benzalaniline $\nu(\text{CN})$ is found at 1627 cm^{-1} ; in secondary aromatic amines in the range $1260\text{--}1340\text{ cm}^{-1}$). The presence of a terminal double bond in both compounds is indicated by $\nu(\text{C}=\text{C})$ at 1640 cm^{-1} (**4a**) and 1649 cm^{-1} (**4b**) and $\delta_{\text{o.o.p.}}(\text{CH}_2)$ at 900 cm^{-1} (**4a**) and 902 cm^{-1} (**4b**). The reactions of **1a, b** with acetone and acetonitrile also proceed differently from those with other Cp_2TiR compounds, for which reductive coupling is observed [1]. Based on the products obtained after hydrolysis, as discussed later on, we tentatively ascribe an alkoxy type structure $\text{Cp}_2\text{TiOC(CH}_3\text{)}_2\text{CH(R)CH}=\text{CH}_2$ (**5**) to the yellow oily products formed with acetone, and an imino type structure $\text{Cp}_2\text{TiN=C(CH}_3\text{)-CH(R)CH}=\text{CH}_2$ (**6a, b**) to the purple products obtained with acetonitrile. The IR spectra of **6a, b** show bands at 1601 cm^{-1} (**6a**) and 1603 cm^{-1} (**6b**), assigned to $\nu(\text{CN})$, and bands indicative for a terminal double bond, i.e. $\nu(\text{C}=\text{C})$ at 1620 cm^{-1} (**6a**) and 1638 cm^{-1} (**6b**) and $\delta_{\text{o.o.p.}}(\text{CH}_2)$ at 914 cm^{-1} (**6a**) and 921 cm^{-1} (**6b**).

Support for the proposed structures of the compounds **2–6** given in Scheme 2 is also provided by the products obtained upon hydrolysis

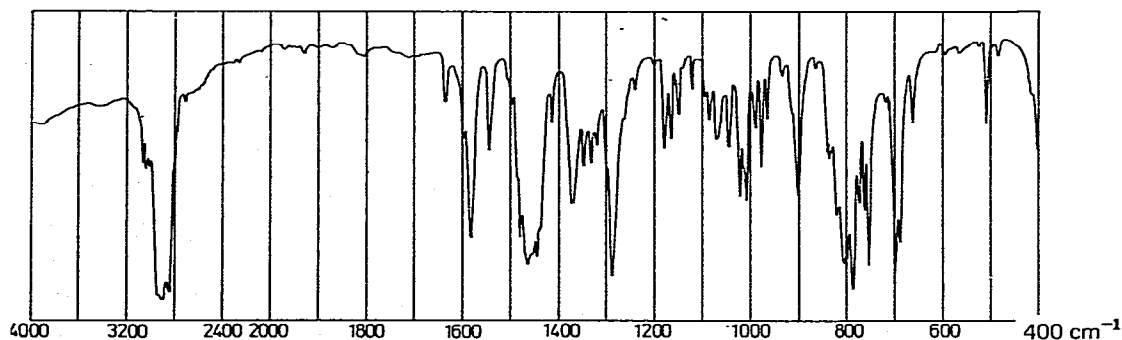
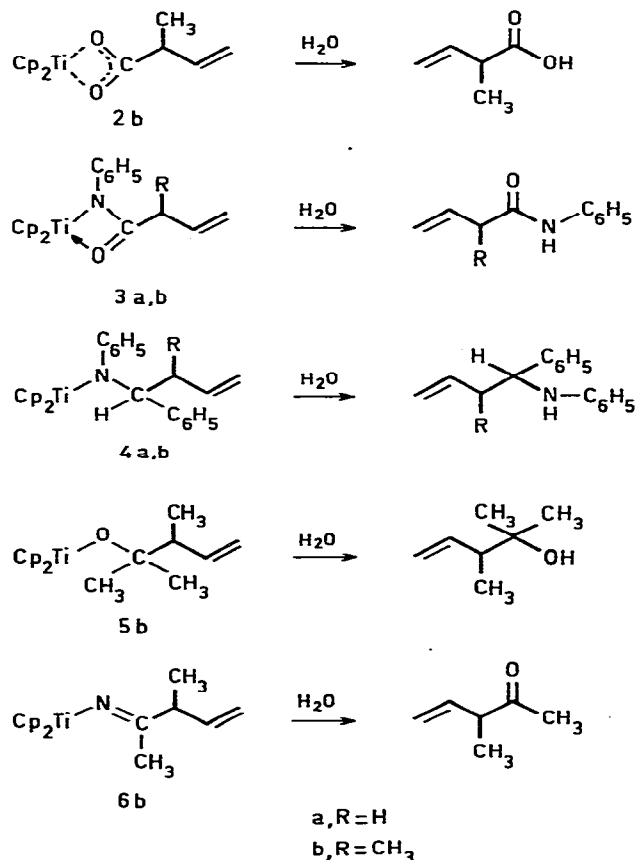


Fig. 1. IR spectrum of $\text{Cp}_2\text{TiN(C}_6\text{H}_5\text{)CH(C}_6\text{H}_5\text{)CH(CH}_3\text{)CH}=\text{CH}_2$ (**4b**) (KBr, Nujol).

(Scheme 3). The expected organic compounds are formed in high yields; car-

SCHEME 3



boxylic acids are obtained upon hydrolysis of 2, amides from 3, secondary amines from 4, alcohols from 5 and ketones from 6. These results unequivocally show that the 1-methylallyl group is again bonded to the inserted ligand via its substituted end.

The reactions of $\text{Cp}_2\text{Ti}\eta^3$ -allyl with CO_2 and ketones have recently been published independently by Sato et al. [11,12].

In connection with the mechanism of the reactions of $\text{Cp}_2\text{Ti}\eta^3$ -allyl (1a) and $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl (1b) with ligands L, as shown in Scheme 1, it should be noted that they all seem to proceed via insertion of L into the Ti-allyl bond. With 1b, regioselective product formation is observed, since the insertion takes place selectively at the substituted end of the allyl moiety. This might suggest that in the intermediate adduct the 1-methylallyl group is η^1 -bonded to Ti via its substituted end. This is unlikely, however, since η^3 -1-methylallyl complexes tend to form η^1 -complexes with L in which the allyl group is bonded via the methylene carbon [7,8]. Moreover, in the dicyclopentadienyl complexes studied here, adducts with the allyl group bonded via its substituted end would be sterically unfavourable. Also, if both adduct forms existed in an equilib-

rium mixture one would expect a mixture of two insertion products, which is not found. We therefore favour an intermediate adduct in which the 1-methylallyl group is bonded to Ti via the unsubstituted end. Evidently, rearrangement of the allyl group then occurs, with formation of the products described. The ligands used are all of the type $>C=O$, $>C=N$ - or $-C\equiv N$, and possess an electrophilic carbon atom, which, upon coordination of the ligands to Ti is in a β -position with respect to the metal. Possibly, the reaction proceeds via an electrocyclic process with complete allylic rearrangement. This process is envisaged for $L = CO_2$ in Fig. 2, and is based on the mode of reaction of allylic Grignards with organic carbonyl groups [13]. These reactions, which also proceed with main group-metal allyl complexes (although sometimes less regioselective) [13], should thus be regarded not as insertions but as allyl migrations. For such reactions it is obviously necessary that the ligands possess an electrophilic carbon atom β to Ti after coordination, thus enabling a 6-membered cyclic intermediate to be formed.

We also examined the reactions of 1a, b with ligands without β -electrophilic carbon atoms, as described below.

Insertion reactions

Reactions with 2,6-xylylisocyanide. Reaction of $Cp_2Ti\eta^3$ -allyl (1a) and $Cp_2Ti\eta^3$ -1-methylallyl (1b) with 2,6-xylylisocyanide results in insertion of the ligand into the Ti-allyl bond with formation of the η^2 -iminoacyl compounds $Cp_2TiC(CH_2CH=CHR)=N$ -2,6- $(CH_3)_2C_6H_3$ (7a, b; Scheme 4). Unlike the reactions described hitherto, with 1b insertion takes place at the unsubstituted end of the allylic fragment. The IR spectra of the paramagnetic, monomeric compounds 7a, b show $\nu(CN)$ at 1578 cm^{-1} (7a) and 1585 cm^{-1} (7b) (Fig. 3). The presence of a terminal double bond in 7a is indicated by $\nu(C=C)$ at 1649 cm^{-1} and $\delta_{o.o.p.}(CH_2)$ at 910 cm^{-1} . The band at 970 cm^{-1} in the spectrum of 7b is assigned to a CH out-of-plane deformation mode of an internal *trans* double bond [9,10] (Fig. 3).

To confirm the proposed structures of 7a, b, these compounds were oxidized with $C_6H_5SSC_6H_5$ to the tetravalent Ti compounds $Cp_2Ti(SC_6H_5)C(CH_2CH=CHR)=N$ -2,6- $(CH_3)_2C_6H_3$ (8a, b) (Scheme 4). The presence of a terminal double bond in 8a is indicated by $\nu(C=C)$ at 1649 cm^{-1} and $\delta_{o.o.p.}(CH_2)$ at 924 cm^{-1} ; the presence of an internal *trans* double bond in 8b is again indicated by $\delta_{o.o.p.}(CH)$ at 968 cm^{-1} . The presence of the $-CH_2CH=CHCH_3$ group in this complex is also shown by its 1H NMR spectrum (Fig. 4). It shows the methyl protons as a broad doublet at δ 1.67 ppm, the methylene protons give a multiplet signal at δ 3.31 ppm; the olefinic part of the spectrum is not well resolved since it partly coincides with the Cp resonance at δ 5.58 ppm.

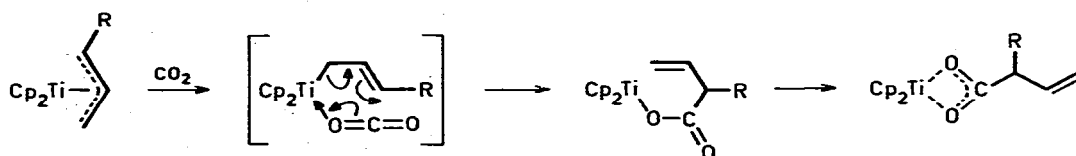
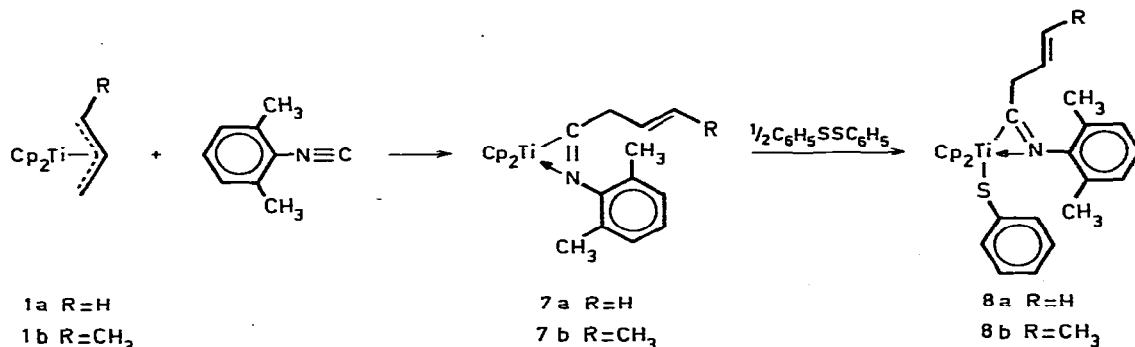


Fig. 2. Proposed mechanism for insertion of CO_2 into the $Ti-\eta^3$ -allyl bond: allyl migration.

The insertion of 2,6-xylylisocyanide into the unsubstituted end of the allyl

SCHEME 4



moiety of **1b** is obviously associated with the fact that the ligand does not possess a "β-electrophilic" carbon atom. This prevents an allyl migration via an electrocyclic mechanism; instead the CH₂CH=CHCH₃ group in the intermediate adduct behaves like an alkyl group and a normal insertion, analogous to that with Cp₂Ti-alkyl, takes place [1].

Carbonylation of Cp₂Tiη³-allyl. Reaction of Cp₂Tiη³-allyl (**1a**) with CO does not give an η²-acyl insertion product as with other compounds Cp₂TiR [2,14]. Instead, carbonylation of **1a** (pentane, 20°C, 1 hour) results in the formation of products reduced beyond the acyl insertion stage, i.e. Cp₂Ti(CO)₂ (45–65%) [15] and triallylmethanol (35–50%) (Scheme 5). The assumed first two steps in this reaction are well established for other compounds Cp₂TiR [2,14]. Possibly the carbinol is generated via diallylketone, which may be formed by alkylation of the acyl intermediate by **1a**. The product formation is very interesting, since it shows that reduction of CO to an alcohol has taken place in an aprotic medium. It provides the first example of insertion of CO into a Ti–C bond followed by reaction of the intermediate acyl ligand with other Ti–C bonds resulting in C–C bond formation. The reaction therefore is thought to proceed differently from the carbonylation of, for instance, Cp₂Ti(CH₂C₆H₅)₂, which yields Cp₂Ti(CO)₂ and (C₆H₅CH₂)₂CO. There ketone formation is

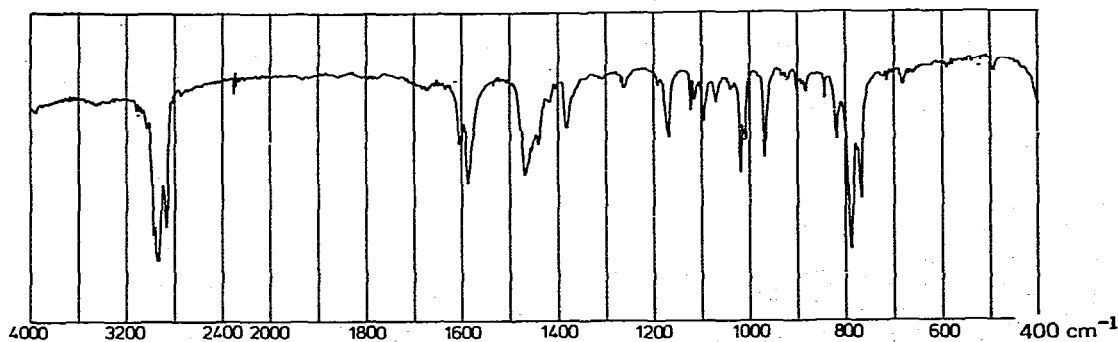
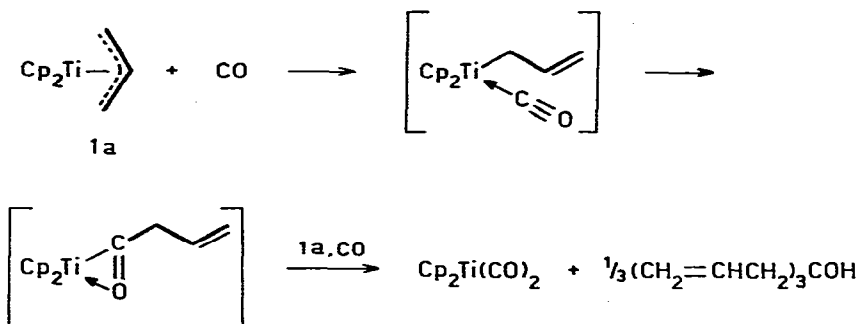


Fig. 3. IR spectrum of Cp₂TiC(CH₂CH=CHCH₃)=N-2,6-(CH₃)₂C₆H₃ (**7b**) (KBr, Nujol).

assumed to arise from coupling of an acyl and an alkyl group at the same Ti

SCHEME 5



atom [16]. The triallylmethanol formed is obviously easily separated from the Ti centre at which it is generated; its formation takes place without hydrolysis. The hydrogen needed may originate from the Cp rings, a process which is also involved in the thermal decomposition of Cp_2TiCH_3 [3]. Our system shows that it is possible to overcome the strongly oxophilic character of early transition metals, which is important in relation to studies on reduction of CO with such metals [17]. This reaction is of course, also of synthetic potential, since it involves reduction of CO with C—C bond formation.

Allyl elimination reactions

Reaction of $\text{Cp}_2\text{Ti}\eta^3\text{-allyl}$ (1a) with CS_2 and $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ results in cleavage

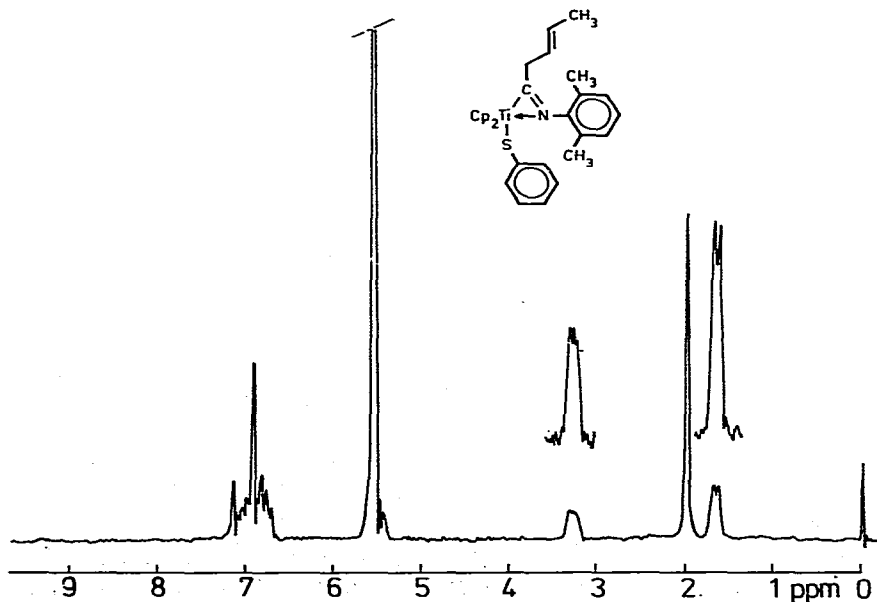
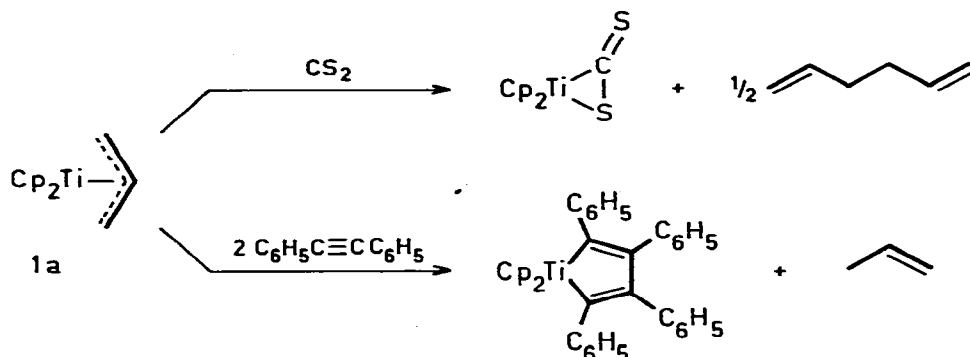


Fig. 4. ^1H NMR spectrum of $\text{Cp}_2\text{Ti}(\text{SC}_6\text{H}_5)\text{C}(\text{CH}_2\text{CH}=\text{CHCH}_3)=\text{N}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (88b) (CDCl_3 , TMS, 30°C).

of the Ti—allyl bond with formation of the products shown in Scheme 6. With

SCHEME 6



CS₂, the allyl elimination results in coupling of the allyl fragments to give 1,5-hexadiene (80%) and Cp₂Tiη²-CS₂ (85%) [18]. This very fast reaction proceeds in an entirely different way from that involving CO₂, where allyl migration is observed. Obviously the CS₂ carbon atom is not sufficiently electrophilic to allow an electrocyclic mechanism as shown in Fig. 2. Instead, as with isocyanides, the η¹-allyl group in the assumed intermediate adduct Cp₂Tiη¹-allyl · CS₂ behaves like an alkyl group. Alkyl derivatives Cp₂TiR react with CS₂ to form Cp₂Tiη²-CS₂ and Cp₂TiR₂ [3]. It is possible that also in the reaction with 1a, intermediate disproportionation to Cp₂Tiη²-CS₂ and Cp₂Ti(η¹-allyl)₂ takes place, after which CS₂ induces allyl coupling with Cp₂Ti(η¹-allyl)₂ to form 1,5-hexadiene and Cp₂Tiη²-CS₂.

Reaction of 1a with diphenylacetylene, which proceeds very slowly (6 days), results in allyl elimination with formation of propene and Cp₂TiC₄(C₆H₅)₄ (85%) [19] (Scheme 6). Possibly, as in the reaction with CS₂, the Ti—allyl bond is cleaved with formation of propene (with hydrogen abstraction from the solvent of reactants) and some form of titanocene, which reductively couples two acetylene units. It is noteworthy that, in contrast to the reaction with CS₂, no allyl coupling to 1,5-hexadiene is observed.

Experimental

All experiments were carried out under argon unless otherwise stated. Solvents were distilled from benzophenoneketylsodium under nitrogen. The compounds Cp₂Tiη³-allyl (1a) and Cp₂Tiη³-1-methylallyl (1b) were prepared according to ref. 20. 2,6-Xylylisocyanide was prepared according to ref. 21. CO₂ and CO were purchased from Gardner Cryogenics or J.T. Baker Chemicals. Phenylisocyanate, benzalaniline, acetone, acetonitrile, carbon disulfide and diphenylacetylene were purchased and used without purification.

IR spectra were recorded on a JASCO-IRA-2 spectrophotometer using Nujol mulls between KBr discs. EPR spectra were recorded on a Varian E-4 EPR spectrometer with DPPH as external reference. ¹H NMR spectra were taken with a 60 MHz Hitachi Perkin-Elmer R-24B spectrometer with TMS as internal stan-

dard. Chemical shifts are denoted in ppm downfield to TMS at $\delta = 0$. Electron impact mass spectra were recorded by Mr. A. Kiewiet on an AEI MS-902 instrument using an ionizing voltage of 70 eV. Combined gas chromatography-mass spectrometry was performed on a Finnigan 3300 system, interfaced to a Finnigan 6110 computer. The instrument was operated either in the electron impact mode, or in the negative ion chemical ionization mode, using a reactant gas mixture of N_2O and CH_4 , to generate the OH^- ion [22,23]. Samples were introduced via a 25 m \times 0.5 mm i.d. WCOT glass capillary column coated with CP Sil 5 (Chrompack, The Netherlands).

Molecular weights were determined by cryoscopy in benzene.

Melting points and decomposition temperatures of solids were determined using a low temperature DTA apparatus; heating rate 2–3°C/min.

Elemental analyses were performed in the Analytical Department of the Chemical Laboratories of this University.

Preparation of $Cp_2TiOOCCH(R)CH=CH_2$ (2a, b)

CO_2 was admitted to a solution of 2.00 mmol of $Cp_2Ti\eta^3$ -allyl in 40 ml of n-pentane at room temperature. The reaction started almost immediately and was complete after 2 hours. The resulting blue solution was filtered and cooled to $-78^\circ C$ to give blue crystals of 2a (1.50 mmol; 75%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 63.48; H, 5.85; Ti, 17.88. $C_{14}H_{15}O_2Ti$ calcd.: C, 62.01; H, 5.58; Ti, 17.66%. Mol. weight (cryoscopically in benzene): found 255 (calcd. 263). Melting point (DTA) $50^\circ C$. Dec. temp. (DTA) $172^\circ C$. EPR (n-pentane, $30^\circ C$): singlet at $g = 1.979$ (line width 5 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 915 cm^{-1} , $\nu(OCO, \text{sym})$ 1450 cm^{-1} , $\nu(OCO, \text{asym})$ 1532 cm^{-1} , $\nu(C=C)$ 1650 cm^{-1} . The compound 2b was prepared in the same way (85%). Elemental analysis. Found: C, 64.79; H, 6.16; Ti, 17.01. $C_{15}H_{17}O_2Ti$ calcd.: C, 65.00; H, 6.18; Ti, 17.28%. Melting point $12^\circ C$. EPR (n-pentane, $30^\circ C$): singlet at $g = 1.978$ (line width 5 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 918 cm^{-1} , $\nu(OCO, \text{sym})$ 1441 cm^{-1} , $\nu(OCO, \text{asym})$ 1528 cm^{-1} , $\nu(C=C)$ 1642 cm^{-1} .

Hydrolysis of $Cp_2TiOOCCH(CH_3)CH=CH_2$ (2b)

To a solution of 1.00 mmol of 2b in 30 ml of ether, 1 ml of H_2O was added at room temperature. The solution was then exposed to air, upon which the colour changed from blue to yellow. After 1 hour the ether solution was filtered, dried over $CaCl_2$ and evaporated to give $CH_2=CHCH(CH_3)COOH$ (0.68 mmol; 68%) [24]. 1H NMR (CCl_4 , $30^\circ C$): $\delta(CH_3)$ 1.29 ppm (d, 3J 7 Hz), $\delta(CHCH_3)$ 3.12 ppm (quintet), $\delta(CH=CH_2)$ 4.90–6.60 ppm (m), $\delta(COOH)$ 10.80 ppm (br, s). MS ($100^\circ C$): M^+ (m/e) 100. IR (KBr): $\delta_{o.o.p.}(CH_2)$ 921 cm^{-1} , $\nu(C=C)$ 1642 cm^{-1} , $\nu(C=O)$ 1712 cm^{-1} .

Preparation of $Cp_2TiN(C_6H_5)C(O)CH(R)CH=CH_2$ (3a, b)

To a solution of 2.00 mmol of $Cp_2Ti\eta^3$ -allyl in 40 ml of n-pentane, 2.00 mmol of phenylisocyanate were added at room temperature. After stirring for 1 hour the resulting blue solution was filtered and cooled to $-78^\circ C$, which gave blue crystals of 3a (1.20 mmol; 60%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental

analysis. Found: C, 70.94; H, 5.97; Ti, 14.15. $C_{20}H_{20}NOTi$ calcd.: C, 71.01; H, 5.96; Ti, 14.16%. Mol. weight (cryoscopically in benzene): found 317 (calcd. 338). Melting point (DTA) $55^{\circ}C$. Dec. temp. (DTA) $>200^{\circ}C$. EPR (ether, $30^{\circ}C$): singlet at $g = 1.981$ (line width 4 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 916 cm^{-1} , $\nu(CO)$ 1536 cm^{-1} , $\nu(C=C)$ 1646 cm^{-1} . Compound **3b** was prepared in the same way (65%). Elemental analysis. Found: C, 71.55; H, 6.45; Ti, 13.57. $C_{21}H_{22}NOTi$ calcd.: C, 71.59; H, 6.29; Ti, 13.60%. Mol. weight (cryoscopically in benzene): found 338 (calcd. 352). Melting point (DTA) $74^{\circ}C$. Dec. temp. (DTA) $>200^{\circ}C$. EPR (ether, $30^{\circ}C$): singlet at $g = 1.981$ (line width 3 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 917 cm^{-1} , $\nu(CO)$ 1540 cm^{-1} , $\nu(C=C)$ 1640 cm^{-1} .

Hydrolysis of $Cp_2TiN(C_6H_5)C(O)CH(R)CH=CH_2$ (3a, b)

To a solution of 1.00 mmol of **3a** in 30 ml of ether, 1 ml of H_2O was added at room temperature. The solution was then exposed to air, upon which a turbid white solution was formed. After 1 hour the ether solution was filtered, dried over $CaCl_2$ and evaporated to give $CH_2=CHCH_2C(O)NHC_6H_5$ (0.75 mmol; 75%) [25]. 1H NMR (CCl_4 , $30^{\circ}C$): $\delta(-CH_2-)$ 3.06 ppm (d, 3J 7 Hz), $\delta(CH=CH_2)$ 4.84–6.36 ppm (m), $\delta(C_6H_5)$ 6.74–7.70 ppm (m), $\delta(NH)$ 8.63 ppm (brs). MS ($100^{\circ}C$): M^+ (m/e) 161. IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 918 cm^{-1} , $\nu(C=C)$ 1640 cm^{-1} , $\nu(C=O)$ 1660 cm^{-1} , $\nu(NH)$ 3300 cm^{-1} . Compound **3b** was hydrolysed in the same way, to give $CH_2=CHCH(CH_3)C(O)NHC_6H_5$ (0.90 mmol; 90%) [26]. 1H NMR (CCl_4 , $30^{\circ}C$): $\delta(CH_3)$ 1.23 ppm (d, 3J 7 Hz), $\delta(CHCH_3)$ 3.02 ppm (quintet), $\delta(CH=CH_2)$ 4.84–6.30 ppm (m), $\delta(C_6H_5)$ 6.70–7.70 ppm (m), $\delta(NH)$ 8.71 ppm (brs). MS ($100^{\circ}C$): M^+ (m/e) 175. IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 921 cm^{-1} , $\nu(C=C)$ 1634 cm^{-1} , $\nu(C=O)$ 1660 cm^{-1} , $\nu(NH)$ 3260 cm^{-1} .

Preparation of $Cp_2TiN(C_6H_5)CH(C_6H_5)CH(R)CH=CH_2$ (4a, b)

To a solution of 2.00 mmol of $Cp_2Ti\eta^3$ -allyl in 100 ml of n-pentane, 2.00 mmol of benzalaniline were added at room temperature. After stirring for 12 hours the resulting brown solution was filtered and cooled to $-78^{\circ}C$, to give light brown crystals of **4a** (1.40 mmol; 70%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 77.52; H, 7.25; Ti, 11.91. $C_{26}H_{26}NTi$ calcd.: C, 77.99; H, 6.53; Ti, 11.96%. Melting point (DTA) $137^{\circ}C$. Dec. temp. (DTA) $146^{\circ}C$. EPR (ether, $30^{\circ}C$): singlet at $g = 1.981$ (line width 6 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 900 cm^{-1} , $\nu(CN)$ 1290 cm^{-1} , $\nu(C=C)$ 1640 cm^{-1} . The compound **4b** was prepared in the same way (70%). Elemental analysis. Found: C, 77.56; H, 6.99; Ti, 11.14. $C_{27}H_{28}NTi$ calcd.: C, 78.25; H, 6.81; Ti, 11.56%. Mol. weight (cryoscopically in benzene): found 384 (calcd. 414). Melting point (DTA) $141^{\circ}C$. Dec. temp. (DTA) $149^{\circ}C$. EPR (ether, $30^{\circ}C$): singlet at $g = 1.981$ (line width 4 G). IR (KBr, Nujol): $\delta_{o.o.p.}(CH_2)$ 902 cm^{-1} , $\nu(CN)$ 1289 cm^{-1} , $\nu(C=C)$ 1649 cm^{-1} .

Hydrolysis of $Cp_2TiN(C_6H_5)CH(C_6H_5)CH(R)CH=CH_2$ (4a, b)

To a solution of 1.00 mmol of **4a** in 30 ml of ether, 1 ml of H_2O was added at room temperature. The solution was then exposed to air, upon which a white turbid solution was formed. After 1 hour the ether solution was filtered, dried over $CaCl_2$ and evaporated to give $CH_2=CHCH_2CH(C_6H_5)NHC_6H_5$ (0.70 mmol;

70%). $^1\text{H NMR}$ (CCl_4 , 30°C): $\delta(-\text{CH}_2-)$ 2.42 ppm, (t, 3J 7 Hz), $\delta(\text{NH})$ 3.9 ppm (br, s), $\delta(\text{CHC}_6\text{H}_5)$ 4.24 ppm (t, 3J 7 Hz), $\delta(\text{CH}=\text{CH}_2)$ 4.79–6.07 ppm (m), $\delta(\text{C}_6\text{H}_5)$ 6.12–7.54 ppm (m). MS (100°C): M^+ (m/e) 223. IR (KBr): $\delta_{\text{o.o.p.}}$ (CH_2) 918 cm^{-1} , $\nu(\text{CN})$ 1312 cm^{-1} , $\nu(\text{C}=\text{C})$ 1638 cm^{-1} , $\nu(\text{NH})$ 3400 cm^{-1} .

Compound 4b was hydrolysed in the same way to give $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{NHC}_6\text{H}_5$ (70%) [27]. $^1\text{H NMR}$ (CCl_4 , 30°C): $\delta(\text{CH}_3)$ 1.01 ppm (d, 3J 7 Hz), $\delta(\text{CHCH}_3)$ 2.50 ppm (sextet, 3J 7 Hz), $\delta(\text{NH})$ 3.8 ppm (br, s), $\delta(\text{CHC}_6\text{H}_5)$ 4.00 ppm (d, 3J 7 Hz), $\delta(\text{CH}=\text{CH}_2)$ 4.82–6.08 ppm (m), $\delta(\text{C}_6\text{H}_5)$ 6.12–7.40 ppm (m). MS (80°C): M^+ (m/e) 237. IR (KBr): $\delta_{\text{o.o.p.}}$ (CH_2) 915 cm^{-1} , $\nu(\text{CN})$ 1313 cm^{-1} , $\nu(\text{C}=\text{C})$ 1639 cm^{-1} , $\nu(\text{NH})$ 3400 cm^{-1} .

Reaction of $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl with acetone and subsequent hydrolysis

To a solution of 2.00 mmol of $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl in 40 ml of ether, 2.00 mmol of acetone were added at room temperature. After stirring for two hours the resulting yellow-brown solution was evaporated to dryness to leave a yellow oil (5b). Hydrolysis of this in 30 ml of ether with an excess of HCl in H_2O at room temperature gave a red suspension (Cp_2TiCl_2). Filtration gave a light yellow ether solution which was dried over CaCl_2 and evaporated to leave $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{C}(\text{CH}_3)_2\text{OH}$ (1.30 mmol; 65%) [28]. $^1\text{H NMR}$ (CDCl_3 , 30°C): $\delta(\text{CHCH}_3)$ 0.90 ppm (d, 3J 7 Hz), $\delta(\text{C}(\text{CH}_3)_2)$ 1.03 ppm (s), $\delta(\text{OH})$ 1.86 ppm (s), $\delta(\text{CHCH}_3)$ 2.07 ppm (quintet), $\delta(\text{CH}=\text{CH}_2)$ 4.60–6.00 ppm (m). MS (100°C): M^+ (m/e) 114. IR (KBr): $\delta_{\text{o.o.p.}}$ (CH_2) 911 cm^{-1} , $\nu(\text{C}=\text{C})$ 1641 cm^{-1} , $\nu(\text{OH})$ 3420 cm^{-1} .

Reaction of $\text{Cp}_2\text{Ti}\eta^3$ -allyl and $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl with acetonitrile and subsequent hydrolysis

To a solution of 2.00 mmol of $\text{Cp}_2\text{Ti}\eta^3$ -1-methylallyl in 40 ml of n-pentane, 2.00 mmol of acetonitrile were added at room temperature. After stirring for 1 hour the light brown solution was evaporated to dryness to give a yellow oil which upon standing for about 2 hours solidified and turned purple. This purple product (6b) was suspended in 40 ml of n-pentane and 1 ml of H_2O was added at room temperature, the solution was exposed to air, and after about 24 hours a turbid white mixture formed. The solution was filtered, dried over CaCl_2 and evaporated to leave $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$ (1.20 mmol; 60%) [29]. $^1\text{H NMR}$ (CDCl_3 , 30°C): $\delta(\text{CH}_3)$ 2.00 ppm (s), $\delta(\text{CHCH}_3)$ 1.04 ppm (d, 3J 7 Hz), $\delta(\text{CHCH}_3)$ 3.05 ppm (quintet), $\delta(\text{CH}=\text{CH}_2)$ 4.79–6.01 ppm (m). MS (100°C): M^+ (m/e) 98. The compounds 6a, b are paramagnetic in solution. IR (6a, KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH_2) 914 cm^{-1} , $\nu(\text{CN})$ 1601 cm^{-1} , $\nu(\text{C}=\text{C})$ 1620 cm^{-1} . IR (6b, KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH_2) 921 cm^{-1} , $\nu(\text{CN})$ 1603 cm^{-1} , $\nu(\text{C}=\text{C})$ 1638 cm^{-1} .

Preparation of $\text{Cp}_2\text{TiC}(\text{CH}_2\text{CH}=\text{CHR})=\text{N}-2,6-(\text{CH}_3)_2\text{C}_6\text{H}_3$ (7a, b)

To a solution of 2.00 mmol of $\text{Cp}_2\text{Ti}\eta^3$ -allyl in 40 ml of n-pentane, 2.00 mmol of 2,6-xylylisocyanide were added at room temperature. After stirring for 1 hour the resulting red-purple solution was filtered and cooled to -78°C to give red-purple crystals of 7a (1.00 mmol; 50%). The product is very air-sensitive, and is readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 74.77; H, 6.96; Ti, 13.42. $\text{C}_{22}\text{H}_{24}\text{NTi}$ calcd.: C,

75.42; H, 6.91; Ti, 13.67%. Mol. weight (cryoscopically in benzene): found 346 (calcd. 350). Melting point (DTA) 122°C. Dec. temp. (DTA) 129°C. EPR (ether, 30°C): singlet at $g = 1.988$ (line width 3 G). IR (KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH₂) 910 cm⁻¹, $\nu(\text{CN})$ 1578 cm⁻¹, $\nu(\text{C}=\text{C})$ 1649 cm⁻¹. The compound 7b was prepared in the same way (80%). Elemental analysis. Found: C, 75.61; H, 7.33; Ti, 12.85. C₂₃H₂₆NTi calcd.: C, 75.82; H, 7.19; Ti, 13.15%. Mol. weight (cryoscopically in benzene): found 334 (calcd. 364). Melting point (DTA) 101°C. Dec. temp. (DTA) 110°C. EPR (ether, 30°C): singlet at $g = 1.988$ (line width 4 G). IR (KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH, *trans*) 970 cm⁻¹, $\nu(\text{CN})$ 1585 cm⁻¹.

Preparation of Cp₂Ti(SC₆H₅)C(CH₂CH=CHR)=N-2,6-(CH₃)₂C₆H₃ (8a, b)

To a solution of 1.00 mmol of Cp₂TiC(CH₂CH=CH₂)=N-2,6-(CH₃)₂C₆H₃ (7a) in 30 ml of n-pentane, 0.50 mmol of C₆H₅SSC₆H₅ was added at -78°C. On warming to room temperature (2 h) a yellow precipitate of 8a formed. After several washings with n-pentane 0.80 mmol (80%) of crude product was isolated. The compound can be purified by recrystallization from ether. It is moderately air-sensitive, insoluble in aliphatic hydrocarbons, but soluble in ether, THF and benzene. ¹H NMR (CDCl₃, 30°C): $\delta(\text{CH}_3)$ 2.09 ppm (s), $\delta(-\text{CH}_2-)$ 3.40 ppm (d, ³J 7 Hz), $\delta(\text{CH}=\text{CH}_2)$ 4.90–6.00 ppm (m), $\delta(\text{Cp})$ 5.64 ppm (s), $\delta(\text{aryl})$ 6.70–7.40 ppm (m). IR (KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH₂) 924 cm⁻¹, $\nu(\text{C}=\text{C})$ 1649 cm⁻¹, $\nu(\text{CN})$ 1682 cm⁻¹. The compound 8b was prepared in the same way (80%). Elemental analysis. Found: C, 72.94; H, 6.63; Ti, 9.90. C₂₉H₃₁NSTi calcd.: C, 73.55; H, 6.60; Ti, 10.12%. ¹H NMR (CDCl₃, 30°C) $\delta(\text{CHCH}_3)$ 1.67 ppm (br, d), $\delta(\text{arylCH}_3)$ 2.01 ppm (s), $\delta(\text{CH}_2)$ 3.31 ppm (m), $\delta(\text{Cp})$ 5.58 ppm (s), $\delta(\text{aryl})$ 6.70–7.30 ppm (m), the olefinic protons could not be assigned. IR (KBr, Nujol): $\delta_{\text{o.o.p.}}$ (CH, *trans*) 968 cm⁻¹, $\nu(\text{CN})$ 1680 cm⁻¹.

Carbonylation of Cp₂Ti η ³-allyl

CO was admitted to a solution of 4.00 mmol of Cp₂Ti η ³-allyl in 40 ml of n-pentane at room temperature. Reaction started immediately and was complete after 1 hour. The resulting brown solution was cooled to -78°C to give red-brown crystals of Cp₂Ti(CO)₂ (1.80 mmol; 45%; ¹H NMR; IR) [15]. Evaporation of the mother liquor gave a brown oil containing (CH₂=CHCH₂)₃COH. For purification of this carbinol, an ether solution of the oil was exposed to air, upon which a yellow precipitate formed. After 1 hour the ether solution was filtered, dried over CaCl₂ and evaporated, to give (CH₂=CHCH₂)₃COH (0.45 mmol; 35%) [30]. ¹H NMR (CCl₄, 30°C): $\delta(\text{OH})$ 1.48 ppm (s), $\delta(-\text{CH}_2-)$ 2.13 ppm (d, ³J 7 Hz), $\delta(\text{CH}=\text{CH}_2)$ 4.80–6.20 ppm (m). ¹³C NMR (acetone-*d*₆, 30°C): $\delta(-\text{CH}_2-)$ 44.2 ppm, $\delta(\text{CH}=\text{CH}_2)$ 117.8 ppm, $\delta(\text{CH}=\text{CH}_2)$ 134.8 ppm, $\delta(\text{COH})$ 72.9 ppm. IR (KBr): $\delta_{\text{o.o.p.}}$ (CH₂) 914 cm⁻¹, $\nu(\text{C}=\text{C})$ 1648 cm⁻¹, $\nu(\text{OH})$ 3480 cm⁻¹. The electron impact mass spectrum (120°C) showed no molecular ion (m/e 152), but only fragments such as $[M - \text{C}_3\text{H}_5]^+$ (m/e 111) and C₄H₅O⁺ (m/e 69). The molecular weight was determined by negative ion chemical ionization mass spectrometry, which showed the $[M - \text{H}]^-$ ion at m/e 151, formed by proton abstraction by the OH⁻ ion [22,23].

To determine exact yields, the experiment was also performed in a NMR tube. Cp₂Ti η ³-allyl was dissolved in C₆D₆ in a NMR tube and stored under CO.

After about 24 hours the originally purple, paramagnetic solution had become brown and diamagnetic. The ^1H NMR spectrum showed $\text{Cp}_2\text{Ti}(\text{CO})_2$ (65%) and $(\text{CH}_2=\text{CHCH}_2)_3\text{COH}$ (50%) to be present. Other signals could not be assigned.

Reaction of $\text{Cp}_2\text{Ti}\eta^3$ -allyl with carbon disulfide

To a solution of 2.00 mmol of $\text{Cp}_2\text{Ti}\eta^3$ -allyl in 30 ml of n-pentane, 2.00 mmol of carbon disulfide were added at room temperature. A yellow precipitate of $\text{Cp}_2\text{Ti}\eta^2$ - CS_2 formed immediately (1.70 mmol; 85%; IR) [18], and the colourless n-pentane solution contained 1,5-hexadiene (0.80 mmol; 80%; GC).

Reaction of $\text{Cp}_2\text{Ti}\eta^3$ -allyl with diphenylacetylene

To a solution of 2.00 mmol of $\text{Cp}_2\text{Ti}\eta^3$ -allyl in 30 ml of n-pentane, 4.00 mmol of diphenylacetylene were added at room temperature. After 6 days a green precipitate of $\text{Cp}_2\text{TiC}_4(\text{C}_6\text{H}_5)_4$ had formed (1.70 mmol; 85%; ^1H NMR; IR) [19], and the light brown n-pentane solution contained propene (GC).

Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

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