

## REACTIONS OF AN ALKENYLTITANOCENE

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### Summary

The alkenyltitanium compound  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  undergoes a reductive coupling reaction with acetone to give an alkoxy complex. With  $\text{CO}_2$ , 2,6-xylisocyanide, phenylisocyanate,  $\text{CS}_2$ , diphenylacetylene and CO, insertions occur.

### Introduction

In previous papers we described the reactions of alkyl and allyl compounds  $\text{Cp}_2\text{TiR}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) with unsaturated substrates [1–6]. The Ti–R bond in these complexes is very reactive and a variety of reaction types are observed. With  $\text{Cp}_2\text{Ti}$ -alkyl compounds reductive coupling is observed with ketones [1], but insertion with isocyanides, isocyanates, and carbon dioxide [1,2], disproportionation with carbon disulfide [2], and metallation with pyridines and quinolines [3,4]. Reactions of allyl derivatives  $\text{Cp}_2\text{Ti}(\eta^3\text{-allyl})$  with unsaturated substrates result in allyl migration and insertion and elimination reactions [5,6].

In this report we describe the preparation and reactions of the coordinatively unsaturated alkenyl complex  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$ . This compound can be regarded as an alkyl derivative  $\text{Cp}_2\text{TiR}$  in which R is functionalized by an  $\alpha$ -olefinic function. This results in a higher thermal stability of this complex compared to the alkyl analogues and sometimes in a different reactivity.

### Results and discussion

#### *Synthesis and properties of $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$ (1)*

The green crystalline title compound 1 was prepared from  $\text{Cp}_2\text{TiCl}$  and 1 eq. of *trans*-2-butenyl-2-lithium in 55% yield. The monomeric compound decomposes at 60°C and is thermally much more stable than sterically comparable alkyl analogues such as  $\text{Cp}_2\text{Ti}(\text{s-C}_4\text{H}_9)$ , which decompose below –30°C [1]. This high thermal stability of the alkenyl complex may be the result of Ti–R

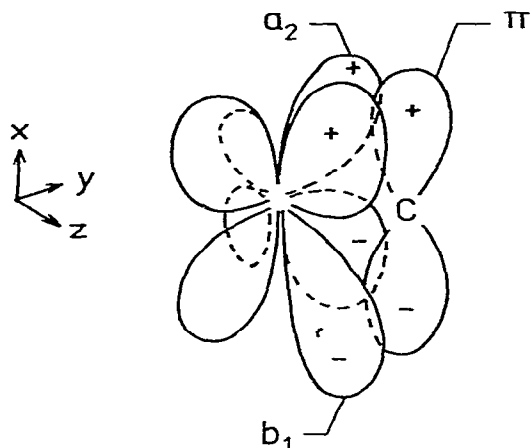


Fig. 1. Interaction of the  $b_1$  and  $a_2$  orbitals of Ti with the  $\pi$ -system of R (represented by  $p_x$  on C(1) of R) [8].

$\pi$ -interaction in this compound, owing to overlap of the empty  $b_1$  and  $a_2$  orbitals of Ti [7] with the filled  $\pi$ -orbital of the  $\alpha$ -unsaturated carbon atom in R, as suggested previously by Zeinstra et al. [8] (Fig. 1). As expected for a trivalent Ti compound, the EPR spectrum consists of a singlet ( $g = 1.962$ ). The UV-vis spectrum shows absorptions at 425 nm (sh) and 568 nm ( $\epsilon = 115$ ), thus resembling the spectra of related compounds  $\text{Cp}_2\text{TiR}$  [2,9,10]. The IR spectrum shows the characteristic absorptions for the  $\eta^5\text{-C}_5\text{H}_5$  group (3090, 1012, 790  $\text{cm}^{-1}$ ) and  $\nu(\text{C}=\text{C})$  of the alkenyl group at 1595  $\text{cm}^{-1}$  (Fig. 2).

Like other coordinatively unsaturated compounds  $\text{Cp}_2\text{TiR}$  this complex shows reversible adduct formation with dinitrogen to  $[\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)]_2\text{N}_2$  (below  $-60^\circ\text{C}$ ;  $\Delta H^0 = -9$  kcal/mol; this value is comparable to that of the *o*-tolyl analogue [11]). The UV-vis spectrum of this intensely blue coloured complex shows a charge transfer band at 605 nm ( $\epsilon > 10^4$ ) which is characteristic of this type of binuclear dinitrogen complex [9,11].

#### Reactions of $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$

Apart from adduct formation with dinitrogen, reactions of  $\text{Cp}_2\text{Ti}(\text{trans-}$

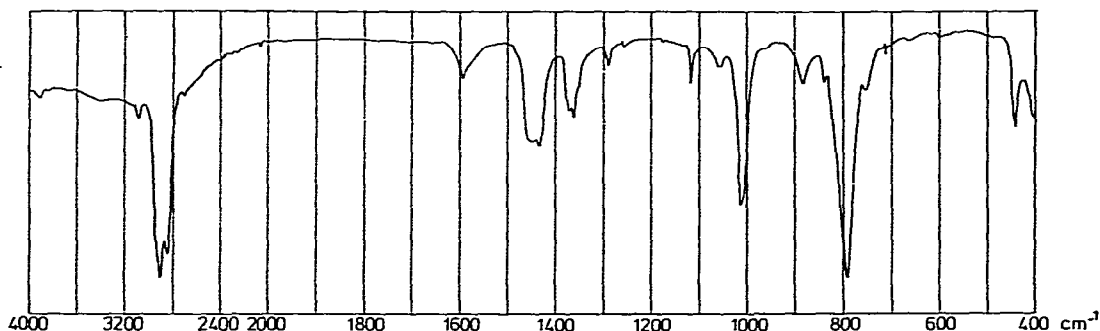
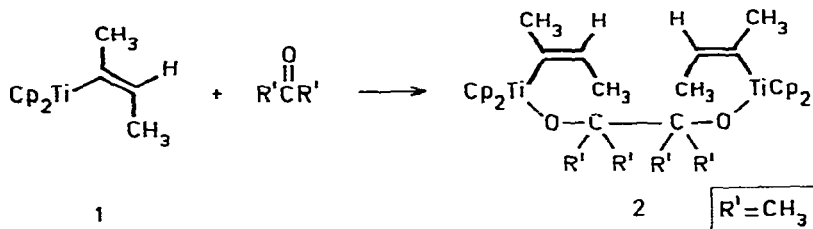


Fig. 2. IR spectrum of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (KBr, Nujol).

$C(CH_3)=CHCH_3$  (1) with ligands L show only two reaction types, viz. reductive coupling and insertion reaction.

Reductive coupling is observed in reaction of 1 with acetone, giving the diamagnetic alkoxy complex  $[Cp_2Ti(trans-C(CH_3)=CHCH_3)OC(CH_3)_2]_2$  (2, Scheme 1; 60%). This reaction is analogous to that observed with  $Cp_2Ti$ -alkyl



SCHEME 1

[1]. The  $^1H$  NMR spectrum clearly indicates the presence of the *trans*-2-buten-2-yl group (Fig. 3). It shows  $\delta(=CH(CH_3))$  as a broad doublet at 1.60 ppm ( $^3J$  7 Hz),  $\delta(-C(CH_3)=)$  at 2.16 ppm and the vinyl hydrogen as a quartet of quartets at  $\delta$  6.13 ppm ( $^3J$  7 Hz,  $^4J$  1.5 Hz) (the Cp ligands and the alkoxy methyl groups give singlets at  $\delta$  5.90 and 1.22 ppm, respectively). This indicates retention of configuration in reaction of 1 with acetone (and also in the formation of 1 from  $Cp_2TiCl$  and *trans*-2-butenyl-2-lithium).

The second reaction type observed in reactions with 1 is insertion. This occurs with  $CO_2$ ,  $CO$ , 2,6-xylylNC,  $C_6H_5NCO$ ,  $CS_2$  and  $C_6H_5CCC_6H_5$  (Scheme 2; the  $CO$  insertion is discussed separately below).

The reactions with  $CO_2$ , 2,6-xylylNC and  $C_6H_5NCO$  with formation of the carboxylato,  $\eta^2$ -iminoacyl and amido derivatives 3–5 respectively, proceed

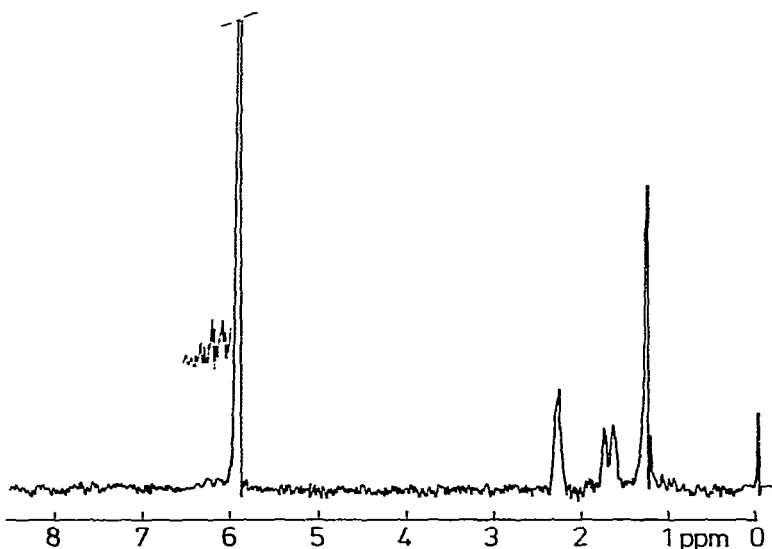
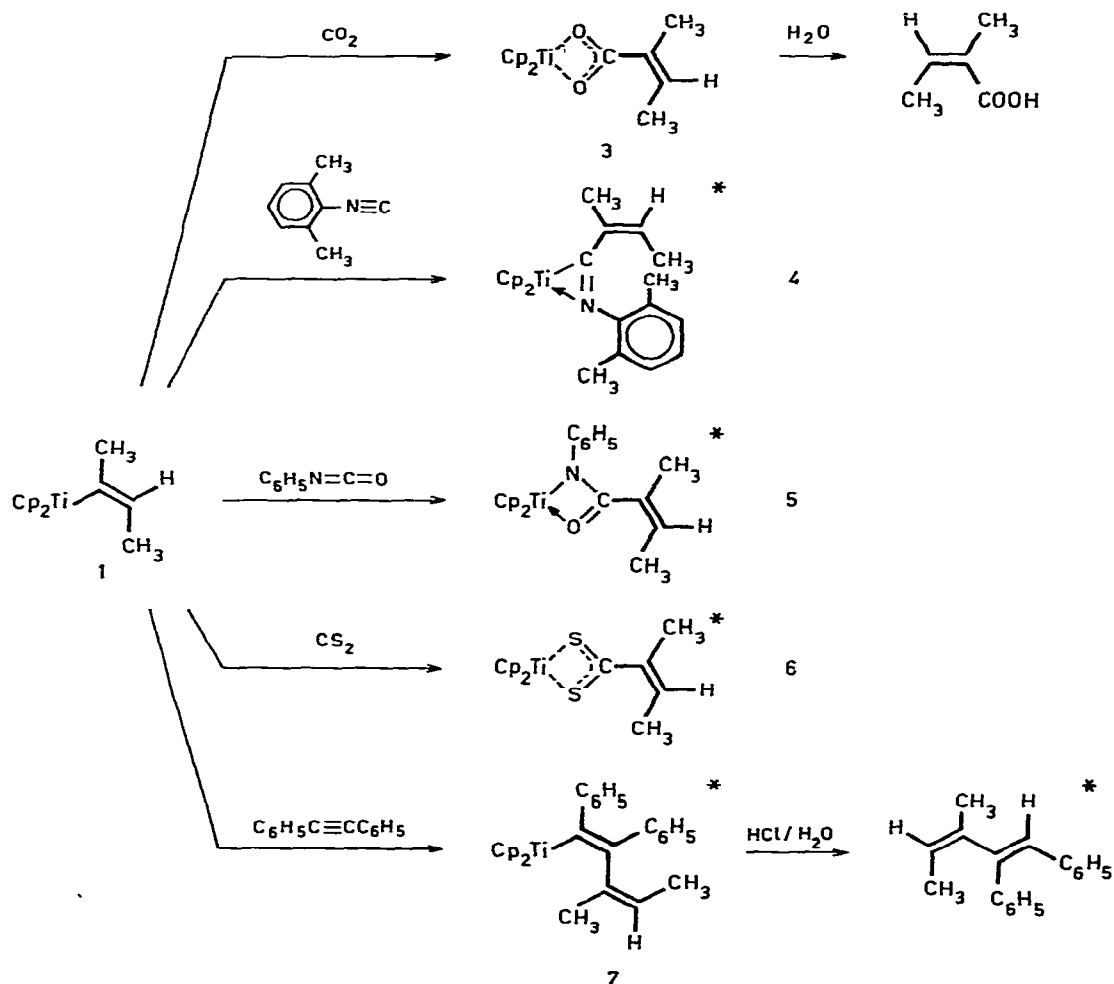


Fig. 3.  $^1H$  NMR spectrum of  $[Cp_2Ti(trans-C(CH_3)=CHCH_3)OC(CH_3)_2]_2$  (2) ( $C_6D_6$ , 30°C, TMS; solvent peaks are omitted).

analogously to the reactions observed with  $\text{Cp}_2\text{Ti-alkyl}$  [1,2]. Carbon disulfide and diphenylacetylene react differently; these insert into the Ti-C bond with formation of the dithiocarboxylato derivative  $\text{Cp}_2\text{TiSSC}(trans\text{-C}(\text{CH}_3)=\text{CHCH}_3)$  (6) and the alkenyl derivative  $\text{Cp}_2\text{TiC}(\text{C}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)=\text{CHCH}_3$  (7), respectively; whereas in similar reactions with  $\text{Cp}_2\text{Ti-alkyl}$  the group R is eliminated [2].



SCHEME 2

The insertion products 3–7, isolated in moderate yields, are paramagnetic, monomeric, and thermally stable crystalline compounds. The configuration of the alkenyl group in the complexes has been investigated in some detail only for the carboxylato derivative  $\text{Cp}_2\text{TiOOC}(trans\text{-C}(\text{CH}_3)=\text{CHCH}_3)$  (3). Hydrolysis of this compound gives angelic acid ( $\text{CH}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{COOH}$ , with *trans* methyl groups) as the only carboxylic acid (85%; Scheme 2). This again indicates retention of configuration for the alkenyl group in the carbonation of 1 and in the subsequent hydrolysis. By analogy we assume that the 2-buten-2-yl group also has the *trans* configuration in the other insertion products (4–7).

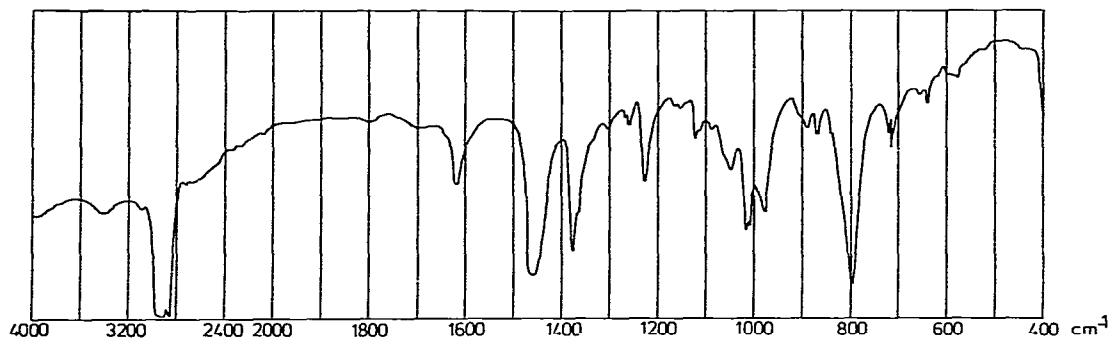


Fig. 4. IR spectrum of  $\text{Cp}_2\text{-TiSSC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (**6**) (KBr, Nujol).

The properties of the complexes **3–5** strongly resemble those of the alkyl analogues described previously [1,2]. In the IR spectra, for instance, apart from the olefinic absorptions  $\nu(\text{C}=\text{C})$ , which are found in the range  $1630\text{--}1665\text{ cm}^{-1}$ , the absorptions for the inserted ligands are entirely comparable. However, some properties of the complexes  $\text{Cp}_2\text{TiSSC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (**6**) and  $\text{Cp}_2\text{TiC}(\text{C}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)=\text{CHCH}_3$  (**7**) deserve further comment. The IR spectrum of the green-brown dithiocarboxylato complex **6** shows a band at  $1050\text{ cm}^{-1}$ , tentatively ascribed to  $\nu(\text{CS})$ ;  $\nu(\text{C}=\text{C})$  is found at  $1617\text{ cm}^{-1}$  (Fig. 4). The IR spectrum of the light brown alkenyl complex **7** is shown in Fig. 5. The bands around  $1600\text{ cm}^{-1}$  are assigned to aryl and/or olefinic absorptions. The stereochemistry of this complex was not investigated in detail. Hydrolysis of the compound gave 1,2-dimethyl-3,4-diphenyl-1,3-butadiene (80%) but the stereochemistry of this product was not determined. Thus an exact structure assignment of **7** cannot be made, but we prefer the formulation shown in Scheme 2.

Carbon monoxide is highly reactive towards the  $\text{Cp}_2\text{TiR}$  compounds. As with isocyanides, which are isoelectronic with CO, adducts  $\text{Cp}_2\text{TiR} \cdot \text{CO}$  are isolated for derivatives in the case of electronegative R groups ( $\text{R} = \text{C}_6\text{F}_5$ ) [12], whereas for other R groups insertion occurs. Only one  $\eta^2$ -acyl insertion product,  $\text{Cp}_2\text{Ti}(\eta^2\text{-COR})$ , has been isolated so far, viz. the compound with  $\text{R} = o\text{-CH}_3\text{C}_6\text{H}_4$  [12]. For the other  $\text{Cp}_2\text{TiR}$  compounds ( $\text{R} = \text{alkyl, aryl}$ ) reactions proceed

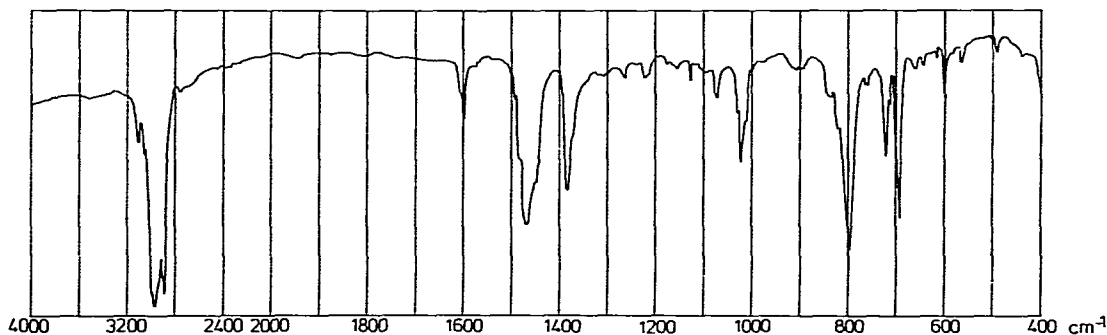
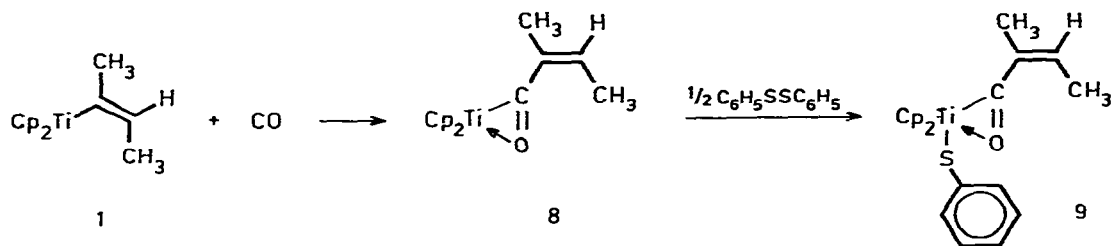


Fig. 5. IR spectrum of  $\text{Cp}_2\text{TiC}(\text{C}_6\text{H}_5)=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)=\text{CHCH}_3$  (**7**) (KBr, Nujol).



SCHEME 3

beyond the  $\eta^2$ -acyl stage, with formation of products difficult to identify. The carbonylation of  $\text{Cp}_2\text{Ti}(\eta^3\text{-allyl})$  gives less unequivocal information, since in that case the CO is reduced to triallylmethanol.

Carbonylation of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (1) affords the  $\eta^2$ -acyl insertion product  $\text{Cp}_2\text{Ti}(\eta^2\text{-CO-trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (8, Scheme 3; 40%). Traces of  $\text{Cp}_2\text{Ti}(\text{CO})_2$  are also formed, the amount increasing on prolonged reaction. The IR spectrum of the brown crystalline complex 8 shows  $\nu(\text{CO})$  at  $1482 \text{ cm}^{-1}$ , indicating  $\eta^2$ -coordination of the acyl ligand [12];  $\nu(\text{C}=\text{C})$  is found at  $1642 \text{ cm}^{-1}$  (Fig. 6). Oxidation of this trivalent Ti compound with  $\text{C}_6\text{H}_5\text{SSC}_6\text{H}_5$  yields the tetravalent complex  $\text{Cp}_2\text{Ti}(\text{SC}_6\text{H}_5)(\eta^2\text{-CO-trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (9, Scheme 3). The  $^1\text{H}$  NMR spectrum of this product confirms the presence of the *trans* alkenyl group, again indicating retention of configuration. The IR spectrum shows  $\nu(\text{CO})$  shifted to  $1563 \text{ cm}^{-1}$  (a similar trend is observed for the analogue obtained from  $\text{Cp}_2\text{Ti}(o\text{-CH}_3\text{C}_6\text{H}_4)$  [12]);  $\nu(\text{C}=\text{C})$  is found at  $1642 \text{ cm}^{-1}$ .

## Experimental

All experiments were carried out under argon unless otherwise stated. Solvents were distilled from benzophenoneketylsodium under nitrogen. *trans*-2-Butenyl-2-lithium was prepared according to ref. 13. 2,6-Xylylisocyanide was prepared according to ref. 14.  $\text{CO}_2$  and CO were purchased from Gardner Cryogenics or J.T. Baker Chemicals. Acetone, phenylisocyanate, carbon disulfide and diphenylacetylene were used as purchased.

IR spectra were recorded on a JASCO-IRA-2 spectrophotometer using Nujol

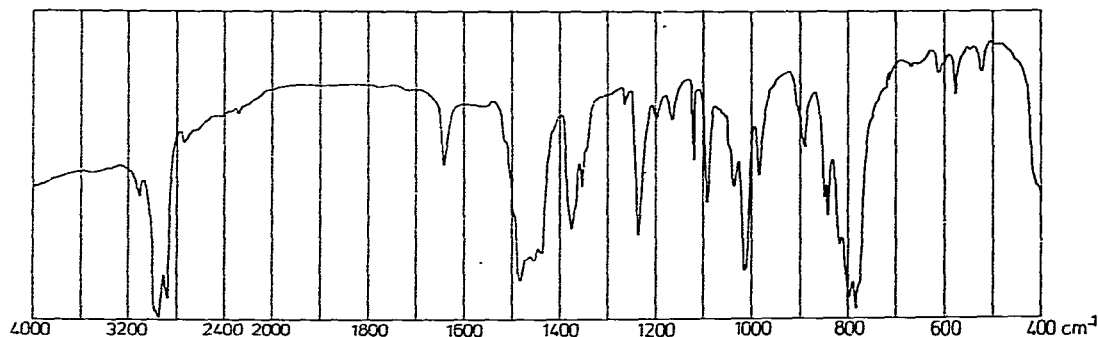


Fig. 6. IR spectrum of  $\text{Cp}_2\text{Ti}(\eta^2\text{-CO-trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (8) (KBr, Nujol).

mullets between KBr discs. UV-vis spectra were recorded with a Perkin-Elmer EPS-3T spectrophotometer. EPR spectra were recorded on a Varian E-4 EPR spectrometer with DPPH as external reference.  $^1\text{H}$  NMR spectra were recorded on a 60 MHz Hitachi-Perkin-Elmer R-24B spectrometer with TMS as internal standard. Chemical shifts are denoted in ppm downfield to TMS at  $\delta = 0$ . Mass spectra were recorded by Mr. A. Kiewiet on an AEI MS-902 instrument using an ionizing voltage of 70 eV. Molecular weights were determined by cryoscopy in benzene. Melting points and decomposition temperatures of solids were determined using a low temperature DTA apparatus with a heating rate of  $2\text{--}3^\circ\text{C}/\text{min}$ .

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

#### *Preparation of $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$ (1)*

To a suspension of 4.00 mmol of  $\text{Cp}_2\text{TiCl}_2$  in 30 ml of ether a solution of 4.00 mmol of  $i\text{-C}_3\text{H}_7\text{MgCl}$  in ether was added dropwise at  $0^\circ\text{C}$  during 15 minutes. After one hour the resulting green suspension of  $\text{Cp}_2\text{TiCl}$  was cooled to  $-78^\circ\text{C}$  and 4.00 mmol of *trans*-2-butenyl-2-lithium in ether were added during 15 minutes. After being allowed to warm slowly to  $0^\circ\text{C}$  (1 hour) the green reaction mixture was evaporated to dryness and extracted with 30 ml of *n*-pentane at  $0^\circ\text{C}$ . Cooling of the *n*-pentane extract to  $-78^\circ\text{C}$  gave green crystals of the title compound, which were isolated at  $0^\circ\text{C}$  (2.20 mmol; 55%). The product is very air-sensitive and dissolves readily in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C 70.34; H, 6.95; Ti, 20.03.  $\text{C}_{14}\text{H}_{17}\text{Ti}$  calcd.: C, 72.11; H, 7.35; Ti, 20.54%. Mol. weight (cryoscopically in benzene): found 228 (calcd. 233). Melting point (DTA)  $22^\circ\text{C}$ . Dec. temp. (DTA)  $60^\circ\text{C}$ . EPR (*n*-pentane,  $30^\circ\text{C}$ ): singlet at  $g = 1.962$  (line width 58 G). UV-vis (*n*-pentane,  $0^\circ\text{C}$ ).  $\lambda_{\text{max}}$  425 nm (sh), 568 nm ( $\epsilon = 115$ ). IR (KBr, Nujol):  $\nu(\text{C}=\text{C})$   $1595\text{ cm}^{-1}$ .

#### *Preparation of $[\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)\text{OC}(\text{CH}_3)_2]_2$ (2)*

To a solution of 2.00 mmol of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  in 40 ml of *n*-pentane at  $-78^\circ\text{C}$ , were added 2.00 mmol of acetone. On warming to room temperature (1 hour) a yellow precipitate of **2** formed. After stirring for one hour at room temperature the crude product was separated, and extracted with 100 ml of ether. Cooling the ether extract to  $-78^\circ\text{C}$  gave yellow crystals of the title compound **2** (1.20 mmol; 60%). The product is somewhat air-sensitive, insoluble in aliphatic hydrocarbons, moderately soluble in ethers and readily soluble in aromatic solvents. Elemental analysis. Found: C, 69.42; H, 7.90; Ti, 16.68.  $\text{C}_{34}\text{H}_{46}\text{O}_2\text{Ti}_2$  calcd.: C, 70.10; H, 7.96; Ti, 16.45%. MS ( $80^\circ\text{C}$ ):  $M^+$  ( $m/e$ ) 582. Dec. temp. (DTA)  $121^\circ\text{C}$ . IR (KBr, nujol):  $\nu(\text{C}=\text{C})$   $1600\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^\circ\text{C}$ ):  $\delta(-\text{C}(\text{CH}_3)_2-)$  1.22 ppm (s),  $\delta(=\text{CH}(\text{CH}_3))$  1.60 ppm (brd,  $^3J$  7 Hz),  $\delta(-\text{C}(\text{CH}_3)=)$  2.16 ppm (m),  $\delta(\text{Cp})$  5.90 ppm (s),  $\delta(=\text{CH}(\text{CH}_3))$  6.13 ppm (qxq;  $^3J$  7 Hz,  $^4J$  1.5 Hz).

#### *Preparation of $\text{Cp}_2\text{TiOOC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$ (3)*

$\text{CO}_2$  was introduced into a solution of 2.00 mmol of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  in 40 ml of *n*-pentane at room temperature. The reaction started almost immediately and was complete after 1 hour. The blueish-green solution

was filtered and cooled to  $-78^{\circ}\text{C}$ , to give green-blue crystals of **3** (1.30 mmol; 65%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 64.94; H, 6.50; Ti, 17.16.  $\text{C}_{15}\text{H}_{17}\text{O}_2\text{Ti}$  calcd.: C, 65.00; H, 6.18; Ti, 17.28%. Melting point (DTA)  $98^{\circ}\text{C}$ . Dec. temp. (DTA)  $>200^{\circ}\text{C}$ . EPR (n-pentane,  $30^{\circ}\text{C}$ ): singlet at  $g = 1.979$  (line width 4 G). IR (KBr, Nujol):  $\nu(\text{OCO, sym})$   $1443\text{ cm}^{-1}$ ,  $\nu(\text{OCO, asym})$   $1503\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1661\text{ cm}^{-1}$ .

*Hydrolysis of  $\text{Cp}_2\text{TiOOC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (**3**)*

To a solution of 1.00 mmol of **3** in 30 ml of ether at room temperature was added 1 ml of  $\text{H}_2\text{O}$ . The solution was then exposed to air, which induced a colour change from blue to yellow. After 1 hour the ether solution was filtered, dried over  $\text{CaCl}_2$  and evaporated, to give angelic acid,  $\text{CH}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{COOH}$  (0.85 mmol; 85%) [13].  $^1\text{H NMR}$  ( $\text{CCl}_4$ ,  $30^{\circ}\text{C}$ ):  $\delta(-\text{C}(\text{CH}_3)=)$  1.91 ppm (brs),  $\delta(=\text{CH}(\text{CH}_3))$  2.02 ppm (brd,  $^3J$  7 Hz),  $\delta(=\text{CH}(\text{CH}_3))$  6.13 ppm (brq),  $\delta(\text{COOH})$  10.8 ppm (brs). MS ( $100^{\circ}\text{C}$ ):  $M^+$  ( $m/e$ ) 100. IR (KBr, Nujol):  $\nu(\text{C}=\text{O})$   $1695\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1650\text{ cm}^{-1}$ .

*Preparation of  $\text{Cp}_2\text{TiC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)=\text{N-2,6-(CH}_3)_2\text{C}_6\text{H}_3$  (**4**)*

To a solution of 2.00 mmol of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  in 40 ml of n-pentane at room temperature was added 2.00 mmol of 2,6-xylylisocyanide. After stirring for 1 hour the resulting purple-blue solution was filtered and cooled to  $-78^{\circ}\text{C}$ , to give purple-blue crystals of **4** (0.80 mmol; 40%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 75.96; H, 7.29; Ti, 13.02.  $\text{C}_{23}\text{H}_{26}\text{NTi}$  calcd.: C, 75.82; H, 7.19; Ti, 13.15%. Mol. weight (cryoscopically in benzene): found 399 (calcd. 364). Melting point (DTA)  $122^{\circ}\text{C}$ . Dec. temp. (DTA)  $163^{\circ}\text{C}$ . EPR (n-pentane,  $30^{\circ}\text{C}$ ): singlet at  $g = 1.989$  (line width 4 G). IR (KBr, Nujol):  $\nu(\text{CN})$   $1562\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1634\text{ cm}^{-1}$ .

*Preparation of  $\text{Cp}_2\text{TiN}(\text{C}_6\text{H}_5)\text{C}(\text{O})(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (**5**)*

To a solution of 2.00 mmol of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  in 40 ml of n-pentane was added at room temperature 2.00 mmol of phenylisocyanate. After stirring for 1 hour the blue solution was filtered and cooled to  $-78^{\circ}\text{C}$  to give blue crystals of **5** (0.90 mmol; 45%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 71.35; H, 6.48; Ti, 13.97.  $\text{C}_{21}\text{H}_{22}\text{NOTi}$  calcd.: C, 71.59; H, 6.29; Ti, 13.60%. Mol. weight (cryoscopically in benzene): found 361 (calcd. 352). Melting point (DTA)  $101^{\circ}\text{C}$ . Dec. temp. (DTA)  $>200^{\circ}\text{C}$ . EPR (ether,  $30^{\circ}\text{C}$ ): singlet at  $g = 1.981$  (line width 4 G). IR (KBr, Nujol):  $\nu(\text{CO})$   $1520\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$   $1665\text{ cm}^{-1}$ .

*Preparation of  $\text{Cp}_2\text{TiSSC}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  (**6**)*

To a solution of 2.00 mmol of  $\text{Cp}_2\text{Ti}(\text{trans-C}(\text{CH}_3)=\text{CHCH}_3)$  in 40 ml of n-pentane at  $-78^{\circ}\text{C}$  were added 2.00 mmol of  $\text{CS}_2$ . After warming to room temperature (2 hours) the brown solution was filtered and cooled to  $-78^{\circ}\text{C}$ , to give green-brown crystals of **6** (0.60 mmol; 30%). The product is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers.



Elemental analysis. Found: C, 58.50; H, 5.69; Ti, 15.36.  $C_{15}H_{17}S_2Ti$  calcd.: C, 58.24; H, 5.54; Ti, 15.49%. Mol. weight (cryoscopically in benzene): found 298 (calcd. 309). Dec. temp. (DTA)  $166^\circ C$ . IR (KBr, Nujol):  $\nu(CS)$   $1050\text{ cm}^{-1}$ ,  $\nu(C=C)$   $1617\text{ cm}^{-1}$ .

*Preparation of  $Cp_2TiC(C_6H_5)=C(C_6H_5)C(CH_3)=CHCH_3$  (7)*

To a solution of 2.00 mmol of  $Cp_2Ti(trans-C(CH_3)=CHCH_3)$  in 40 ml of n-pentane were added at room temperature 2.00 mmol of diphenylacetylene. After stirring for 24 hours at room temperature the resulting brown solution was filtered and cooled to  $-78^\circ C$  to give light brown crystals of 7 (1.10 mmol; 55%). The compound is very air-sensitive and soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 81.42; H, 6.75; Ti, 11.64.  $C_{28}H_{27}Ti$  calcd.: C, 81.74; H, 6.62; Ti, 11.64%. Mol. weight (cryoscopically in benzene) found 441 (calcd. 411). Dec. temp. (DTA)  $142^\circ C$ . EPR (n-pentane,  $30^\circ C$ ): singlet at  $g = 1.980$  (line width 3 G). IR (KBr, Nujol):  $\nu(C=C)$   $1600\text{ cm}^{-1}$ .

*Hydrolysis of  $Cp_2TiC(C_6H_5)=C(C_6H_5)C(CH_3)=CHCH_3$  (7)*

An excess of HCl in  $H_2O$  was added at room temperature to a solution of 1.00 mmol of 7 in 30 ml of ether. 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 yield  $CH(CH_3)=C(CH_3)C(C_6H_5)=CHC_6H_5$  (0.80 mmol; 80%).  $^1H$  NMR ( $CCl_4$ ,  $30^\circ C$ ):  $\delta(=CH(CH_3))$  1.68 ppm (d,  $^3J$  7 Hz),  $\delta(CH_3)$  1.90 ppm (s),  $\delta(=CH(CH_3))$  5.23 ppm (q),  $\delta(=CHC_6H_5)$  6.48 ppm (s),  $\delta(C_6H_5)$  6.50–7.55 ppm (m). MS ( $100^\circ C$ ):  $M^+$  ( $m/e$ ) 234. IR (KBr, Nujol):  $\nu(C=C)$   $1610\text{ cm}^{-1}$ .

*Preparation of  $Cp_2Ti(\eta^2-CO-trans-C(CH_3)=CHCH_3)$  (8)*

CO was admitted to a solution of 2.00 mmol of  $Cp_2Ti(trans-C(CH_3)=CHCH_3)$  in 40 ml of n-pentane at  $0^\circ C$ . Reaction started almost immediately and was complete after 15 minutes. The resulting brown solution was filtered and cooled to  $-78^\circ C$  to give brown crystals of 8 (0.80 mmol; 40%). The compound is very air-sensitive and readily soluble in aliphatic and aromatic hydrocarbons and ethers. Elemental analysis. Found: C, 68.61; H, 6.70; Ti, 18.27.  $C_{15}H_{17}OTi$  calcd.: C, 68.98; H, 6.56; Ti, 18.34%. Mol. weight (cryoscopically in benzene): found 277 (calcd. 261). Dec. temp. (DTA)  $132^\circ C$ . EPR (n-pentane,  $30^\circ C$ ): singlet at  $g = 1.989$  (line width 3 G). IR (KBr, Nujol):  $\nu(CO)$   $1482\text{ cm}^{-1}$ ,  $\nu(C=C)$   $1642\text{ cm}^{-1}$ .

*Preparation of  $Cp_2Ti(SC_6H_5)(\eta^2-CO-trans-C(CH_3)=CHCH_3)$  (9)*

To a solution of 1.00 mmol of  $Cp_2Ti(\eta^2-CO-trans-C(CH_3)=CHCH_3)$  (8) in 30 ml of n-pentane at  $-78^\circ C$  was added 0.50 mmol of  $C_6H_5SSC_6H_5$ . On warming to room temperature (1 hour) a yellow precipitate of 9 formed. After several washings with n-pentane, 0.50 mmol (50%) of 9 was isolated. It is moderately air-sensitive, insoluble in aliphatic hydrocarbons but soluble in ether, THF and toluene.  $^1H$  NMR ( $CDCl_3$ ,  $30^\circ C$ ):  $\delta(-C(CH_3)=)$  1.97 ppm (brs),  $\delta(=CH(CH_3))$  2.12 ppm (brd,  $^3J$  7 Hz),  $\delta(Cp)$  5.46 ppm (s),  $\delta(C_6H_5)$  6.84–7.72 ppm (m),  $\delta(=CH(CH_3))$  could not be assigned. IR (KBr, Nujol):  $\nu(CO)$   $1563\text{ cm}^{-1}$ ,  $\nu(C=C)$   $1642\text{ cm}^{-1}$ .

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