Journal of Organometallic Chemistry, 349 (1988) C7–C10
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Formation and reactivity of the ethylene complex $Cp_2TiC_2H_4$. The crystal structure of $(Cp_2TiEt)_2O$

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(Received April 20th, 1988)

Abstract

The reaction of $Cp_2Ti(PMe_3)_2$ (**1**) and ethylene affords the 16-electron species $Cp_2TiC_2H_4$ (**2**). In a reaction of **2** and ethylene under pressure, 1-butene and *trans*-2-butene are formed catalytically. With water, **2** reacts to give the dinuclear μ-oxo complex $(Cp_2TiEt)_2O$ (**3**) the structure of which has been determined by X-ray diffraction.

Monoolefin complexes of low valent titanium have attracted considerable attention because they are regarded as model compounds [1–4] for the Ziegler–Natta polymerization of olefins. Up to now only one titanium ethylene complex, $(C_5Me_5)_2TiC_2H_4$, has been fully characterized, and some of its reactions studied [3].

The discovery of $Cp_2Ti(PMe_3)_2$ [5] (**1**) as a highly reactive source for titanocene [5,6] offers a new approach to novel titanocene derivatives. We now report that the reaction of **1** with an excess of ethylene in pentane at room temperature affords the new ethylene complex $Cp_2TiC_2H_4$ (**2**) as the only organometallic product.

$$\underset{(\mathbf{1})}{Cp_2Ti(PMe_3)_2} + C_2H_4 \rightarrow \underset{(\mathbf{2})}{Cp_2TiC_2H_4} + 2\ PMe_3$$

Although **2** could not be obtained as an analytically pure solid [7*], it was readily characterized by means of its ^1H NMR, ^{13}C NMR and mass spectra [8*]. The

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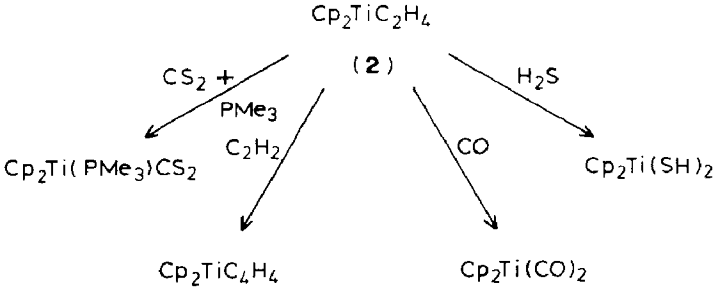
* Reference number with asterisk indicates a note in the list of references.

0022-328X/88/$03.50

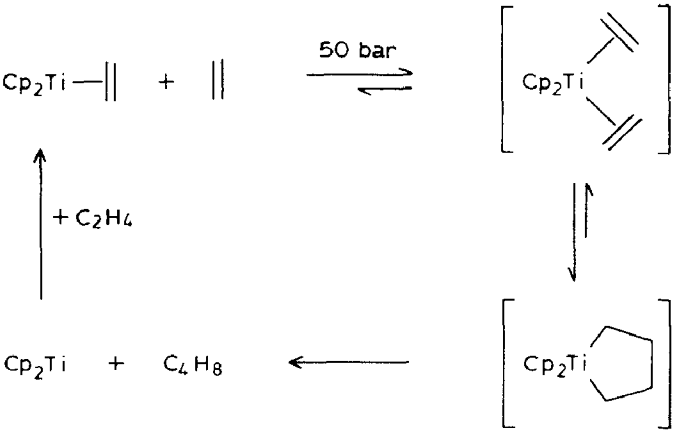
chemical reactions of **2** argue in favour of the formulation proposed. The product does not contain PMe_3, as shown by the absence of a signal in the ^{31}P NMR spectrum [9*].

A pentane solution of **2** reacts with CS_2/PMe_3, C_2H_2, CO, and H_2S to give the known products $Cp_2Ti(PMe_3)CS_2$ [10], $Cp_2TiC_4H_4$ [6], $Cp_2Ti(CO)_2$ [5,6], and $Cp_2Ti(SH)_2$ [11] (see Scheme 1).



Scheme 1

A reaction of **1** [12*] or **2** and an excess of ethylene under pressure at room temperature produces 1-butene and *trans*-2-butene (1/1) in a catalytic manner (Scheme 2).



Scheme 2

The reaction stops as soon as the pressure drops to 15 bar. Under the pressure conditions, a bis-ethylene complex can be formed and this can be converted into a titanacyclopentane species. The latter can release butene upon fragmentation, and the resulting Cp_2Ti fragment can regenerate the starting material **2** by uptake of ethylene, thus completing the catalytic cycle. The equilibrium between bis-ethylene-metal complexes and metallacyclopentane species had been noted in earlier studies [1,13].

Another noteworthy reaction of **2** is the formation of the μ-oxo complex $(Cp_2TiEt)_2O$ (**3**) upon hydrolysis of **2** [14*].

$$\underset{(2)}{2\,Cp_2TiC_2H_4} + H_2O \rightarrow \underset{(3)}{Cp_2EtTi\text{-}O\text{-}TiEtCp_2}$$

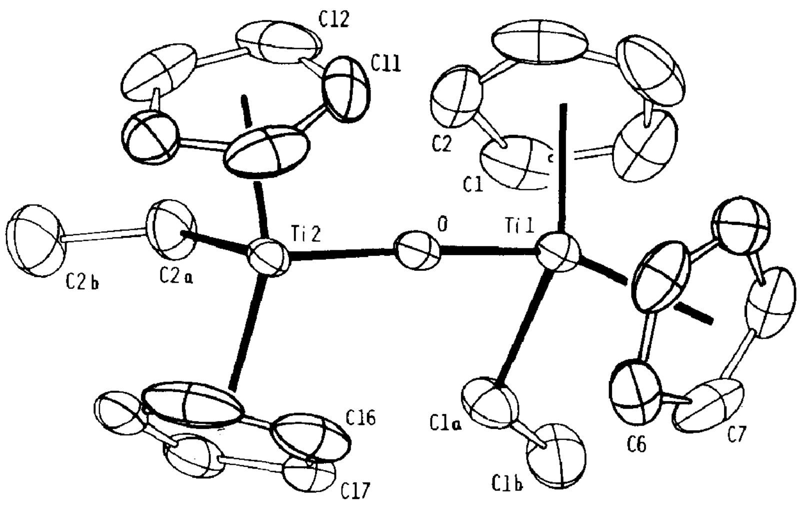


Fig. 1. ORTEP plot of the structure of 3 showing 50% probability ellipsoids. Selected bond distances (Å): Ti(1)–O, 1.840(3); Ti(2)–O, 1.838(3); Ti(1)–C(1a), 2.225(5); C(1a)–C(1b), 1.516(7); C(2a)–C(2b), 1.497(8); Ti(1)–Z(1), 2.12; Ti(2)–Z(11), 2.10. Selected bond angles (deg): Ti(1)–O–Ti(2), 173.7(2); O–Ti(1)–C(1a), 91.2(2); O–Ti(2)–C(2a), 91.2(2); Ti(1)–C(1a)–C(1b), 124.7(3); Ti(2)–C(2a)–C(2b), 125.9(4); Z(1)–Ti(1)–Z(6), 127.3; Z(11)–Ti(2)–Z(16), 129.3 (Z = center of Cp ring).

Although each titanium atom in **3** formally contains 16 electrons, **3** is fairly stable in the solid state (dec. 160 °C) and in solution towards β-hydrogen elimination. This result can be explained in terms of additional π-bonding of the oxo ligand to the two titanium atoms [15,16]. The identity of **3** was indicated by the spectroscopic data [17*] and confirmed by an X-ray crystallographic structure determination (Fig. 1) [18*].

The most striking structural feature of the pseudotetrahedral **3** is the nearly linear Ti–O–Ti bond angle (173.3(2)°). A similar arrangement is also known for the chloro derivative $(Cp_2TiCl)_2O$ (173.8°) [19], $(Cp_2Ti)_2O$ [16], and related titanium(III) and titanium(IV) oxo complexes [16]. The Ti–O bond lengths (1.840(3) and 1.838(3) Å) fall in the usual range for dinuclear titanium oxo complexes [16].

Reactions of **1** with other olefins are being studied, along with the catalytic properties of the resulting intermediates.

Acknowledgements. The authors are grateful to the National Science Foundation (M.D.R.), to the NATO (M.D.R. and H.G.A.), and to the Deutsche Forschungsgemeinschaft (H.G.A.) for support of this research.

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7 Compound **2** can be prepared from the reaction of **1** with excess C_2H_4 in pentane solution at room temperature. The liberated PMe_3 is removed in vacuo. The orange red product is very air sensitive as a solid and loses C_2H_4. An acceptable elemental analysis could not be obtained.

8 Spectroscopic data for **2**: ^{1}H NMR (C_6D_{12}, 90 MHz) δ 4.72 (s, 10 H, Cp), 0.62 (s, 4 H, C_2H_4); $^{13}C\{^1H\}$ NMR (C_6D_{12}, 22.5 MHz) δ 99.3 (s, Cp), 122.8 (s, C_2H_4). MS: $m/e = 178$ $(M - C_2H_4)^+$.

9 It is noteworthy that **1** and acetylene form $Cp_2Ti(C_2H_2)PMe_3$ [6].

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12 Compound **1** (150 mg, 0.45 mmol) is dissolved in 30 ml of pentane. The solution is transferred into a 100 ml autoclave and pressured with 50 bar of ethylene. Within 15 min the ethylene pressure drops to 15 bar and remains constant. The reaction cycle can be repeated 4 times. Gas chromatographic analysis of the reaction indicates that 1-butene and *trans*-2-butene are the only products (1/1).

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14 An equivalent amount of H_2O is added to **2** in pentane solution. After 2 h stirring the solvent is removed under vacuum. The yellow residue is dissolved in 50 ml of toluene, the solution is filtered, and set aside at $-18\,^{\circ}$C to deposit crystals. Yield: 68%. Dec. 160 °C. MS: m/e 401 $(M - \text{Et})^+$, 372 $(M - 2\,\text{Et})^+$, 178 $(Cp_2Ti)^+$. Anal. Found: C, 66.81; H, 7.03. $C_{24}H_{30}OTi_2$ calcd.: C, 66.98; H, 7.04%.

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17 Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.85 (s, 20 H, Cp), 1.47 (q, 4 H, CH_2), 1.31 (t, 6 H, CH_3, ^3J(H,H) 7.3 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 112.0 (s, Cp), 48.0 (s, CH_2), 19.6 (s, CH_3).

18 Crystallographic data for **3**: $C_{24}H_{30}OTi_2$, monoclinic, $P2_1/c$, a 17.011(4), b 7.997(2), c 15.921(4) Å, β 103.52(5)°, $Z = 4$, D(measd) 1.35 g cm^{-3}, D(calcd) 1.357 g cm^{-3}, μ(Mo-K_α) 7.1 cm^{-1}. A total of 3708 unique reflections were collected at 20 °C on a Philips PW1100 difrractometer (Mo-K_α, λ 0.71069 Å, max 2θ 50°). The structure was solved by the Patterson method and completed by ΔF syntheses. The refinement was arrived at on the basis of 3400 data ($I > \sigma(I)$); $R = 0.064$, $R_w(F) = 0.064$. Tables of atomic coordinates and bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

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