

Reactions of $\text{Cp}_2\text{M}(\text{PMe}_3)_2$ complexes ($\text{M} = \text{Ti}, \text{Zr}$) with acetylenes. Selective formation of *trans*-polyacetylene at low temperatures

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Abstract

The reaction of $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ with C_2H_2 gives the substitution product $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_2)(\text{PMe}_3)$, the titanacyclopentadiene $\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$, and *trans*-polyacetylene. A mechanism for the catalytic formation of polyacetylene is proposed. Substituted acetylenes $\text{R}^1\text{C}_2\text{R}^2$ ($\text{R}^1 \neq \text{R}^2 = \text{H}, \text{Me}, \text{Ph}$) react with $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ in an analogous manner except that no polyalkynes are produced. The Zr derivative $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$ and C_2H_2 yield the labile $\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_2)(\text{PMe}_3)$.

Introduction

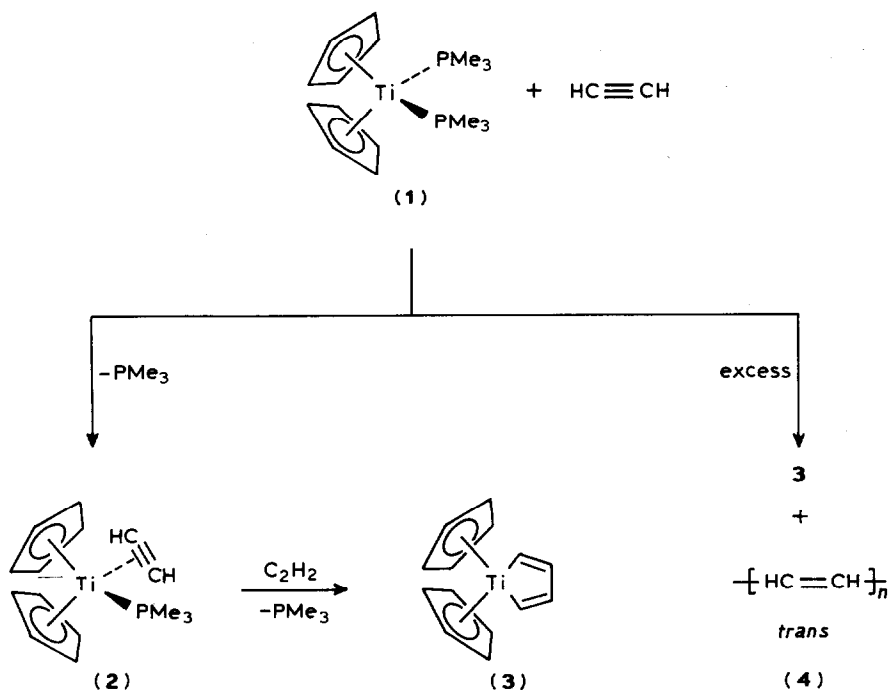
We recently demonstrated that $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ (**1**) reacts readily with various acetylenes $\text{R}^1\text{C}_2\text{R}^2$ ($\text{R}^1, \text{R}^2 = \text{H}, \text{Me}, \text{Ph}$), yielding acetylene complexes of the type $\text{Cp}_2\text{Ti}(\text{R}^1\text{C}_2\text{R}^2)(\text{PMe}_3)$, titanacyclopentadienes $\text{Cp}_2\text{Ti}(\text{C}_4\text{R}_2^1\text{R}_2^2)$ and polyacetylene [1]. In this paper we present details of these reactions and of their extensions.

Results and discussion

*Reaction of $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ (**1**) with C_2H_2*

Although a number of substituted acetylene complexes of titanocene exist [2–4], nothing is known about the corresponding C_2H_2 derivatives except for the information presented in our original communication [1].

The facile replacement of PMe_3 ligands in **1** under very mild conditions [5] allows the preparation of various acetylenic derivatives. The reaction of **1** and one equivalent C_2H_2 in cyclohexane solution at room temperature yields $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_2)$ -



Scheme 1. Products from **1** and C_2H_2 .

(PMe_3) (**2**). A similar reaction between **1** and an excess of C_2H_2 affords the titanacyclopentadiene $\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$ (**3**) in 55% yield and gives *trans*-polyacetylene (**4**) catalytically (Scheme 1).

Although **2** cannot be isolated as a pure solid, its IR, ^1H NMR and ^{31}P NMR spectroscopic data give clear evidence for its identity. The IR spectrum includes a band at 1618 cm^{-1} that is indicative of a $\text{C}=\text{C}$ double bond. The ^1H NMR spectrum exhibits two broad doublets for the C_2H_2 ligand, derived from coupling of two diastereotopic C_2H_2 protons with the ^{31}P nucleus of the PMe_3 ligand [δ 8.82, $^3J(\text{P}, \text{H})$ 9.0 Hz and δ 6.99, $^3J(\text{P}, \text{H})$ 5.4 Hz]. The Cp and the PMe_3 ligands give broad signals at δ 5.25 and 1.09 ppm, respectively. In the ^{31}P NMR spectrum there is a signal at δ 28.1 ppm. The line broadening of the signals in the ^1H NMR spectrum of **1** is probably due to the presence of small amounts of the paramagnetic **4**. These results imply that the CC axis of the C_2H_2 ligand lies in the symmetry plane of a pseudo-tetrahedral molecule, a configuration analogous to that of $\text{Cp}_2\text{Ti}(\text{C}_2\text{Ph}_2)\text{CO}$ and $\text{Cp}_2\text{Ta}(\text{C}_2\text{H}_4)\text{H}$ (Fig. 1) [1,2].

On the basis of these spectroscopic data and in view of the absence of a C_2H_2 ligand rotation around the alkyne metal bond axis, we formulate **2** as a titanacyclopentadiene derivative. This conclusion is supported by the reaction of **2** with gaseous hydrogen chloride to give ethylene and Cp_2TiCl_2 .

In contrast to **2**, the titanacyclopentadiene **3** can be obtained as analytically pure and has been fully characterized by IR, MS, ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of **3** (CDCl_3 , 20°C) shows a sharp singlet for the Cp ligands at 6.18 ppm and an AA'BB' pattern for the four protons of the metallacyclic ring in

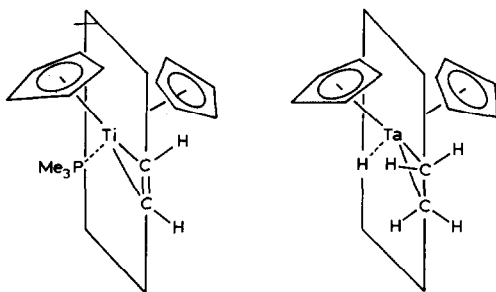


Fig. 1. Configurations of $\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_2)\text{PMe}_3$ and $\text{Cp}_2\text{Ta}(\text{C}_2\text{H}_4)\text{H}$.

the α - and β -positions (δ 6.30(m) and 5.63(m), respectively). These chemical shifts are consistent with those for the only other known C_4H_4 metallacycle, $\text{CpCo}(\text{PMe}_3)\text{C}_4\text{H}_4$ [6]. In the ^{13}C NMR spectrum of **3** (CDCl_3 , 20°C), the Cp rings give rise to a single resonance at δ 113.0 ppm. The carbon atoms of the C_4H_4 moiety directly bonded to the metal are more strongly deshielded (198.5 ppm) than the carbon atoms in the β -position (124.8 ppm). This assignment is also supported by the different $^2J(\text{C}, \text{H})$ long-range couplings of C_α and C_β (C_α : $^1J(\text{C}, \text{H})$ 145.3, $^2J(\text{C}, \text{H})$ 10.3, $^3J(\text{C}, \text{H})$ 8.5 Hz. C_β : $^1J(\text{C}, \text{H})$ 150, $^2J(\text{C}, \text{H})$ 12.0 and 15.4, $^3J(\text{C}, \text{H})$ 3.4 Hz).

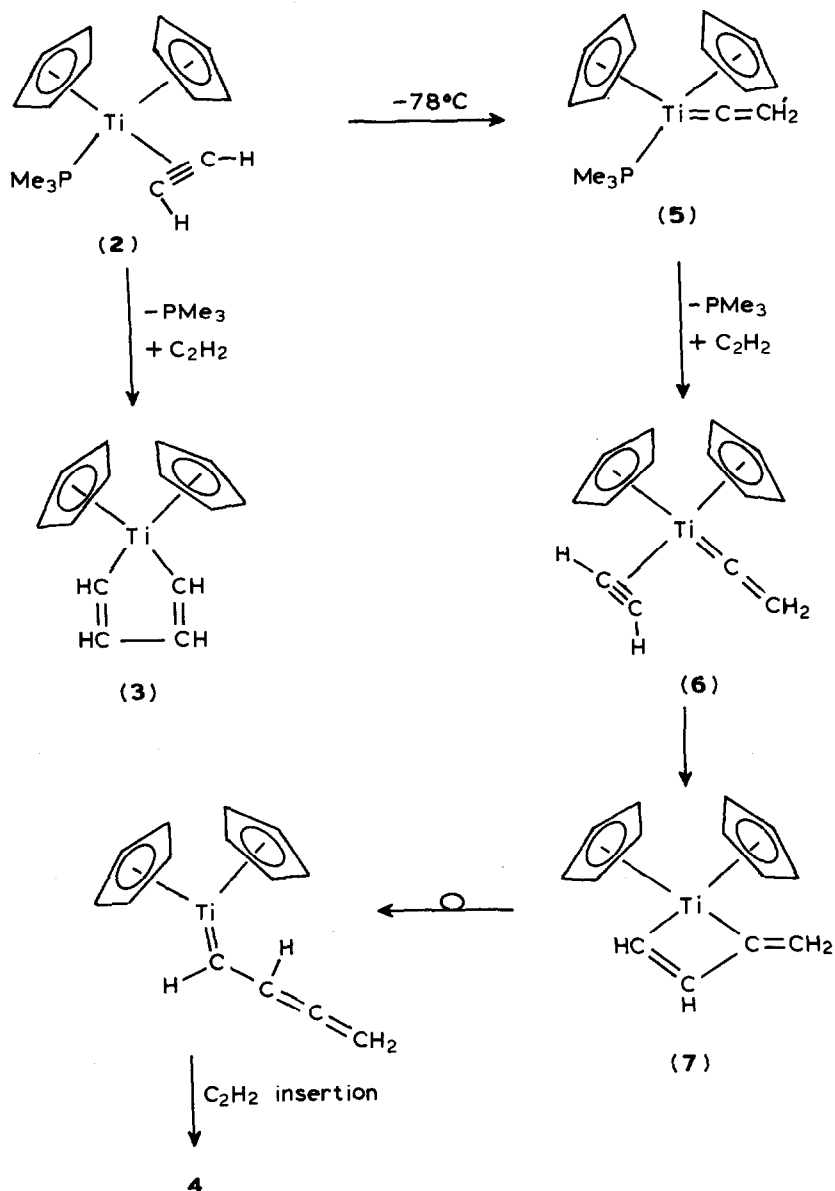
The mass spectrum of **3** shows the molecular ion ($m/e = 230$) as well as peaks derived from the fragmentation of this ion. The IR spectrum of **3** exhibits a band at 1442 cm^{-1} (KBr) that can be assigned to one of the two valence frequencies of the two $\text{C}=\text{C}$ double bonds. The metallacyclic character of **3** is further established by its reaction with HCl gas at -60°C to yield mainly 1,3-butadiene and Cp_2TiCl_2 , identified from their ^1H and ^{13}C NMR spectra.

The insoluble black residue resulting from the reaction of **1** and an excess of C_2H_2 can be formulated on the basis of elemental analysis and EPR and IR spectroscopy as exclusively *trans*-polyacetylene (**4**) [7]. Polymer **4** is formed gradually as the reaction solution is warmed from -78°C to room temperature. The product can be deposited as a homogeneous film.

The IR spectrum (in KBr) shows a very intense absorption at 1012 cm^{-1} assignable to a $\text{C}-\text{H}$ out-of-plane deformation frequency that is specific for the *trans*-isomer of **4**. The paramagnetism of **4** was confirmed by EPR spectroscopy [7].

Since metallacycle **3** is not an active catalyst for the formation of **4**, we suggest that the η^2 -acetylene complex **2** is converted into the vinylidene complex $\text{Cp}_2(\text{PMe}_3)\text{Ti}=\text{C}=\text{CH}_2$ (**5**) (Scheme 2). Replacement of PMe_3 by C_2H_2 would give the corresponding acetylene-vinylidene intermediate $\text{Cp}_2(\text{C}_2\text{H}_2)\text{Ti}=\text{C}=\text{CH}_2$ (**6**). The formation of polyacetylene from this intermediate could then occur via a metallacyclobutene complex **7**, followed by ring opening and subsequent acetylene insertion. Such a mechanism has been suggested by Katz and others for similar systems [8–11]. A photo-assisted polymerization of terminal alkynes by $\text{W}(\text{CO})_6$ has previously been reported by Geoffroy and his coworkers [12,13], suggesting that vinylidene complexes are precursors for the polyacetylene formation.

The Zr-analogue of **1**, $\text{Cp}_2\text{Zr}(\text{PMe}_3)_2$, also reacts with C_2H_2 in toluene- d_8 solution to form the white monosubstitution product $\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_2)(\text{PMe}_3)$, which was characterized by ^1H and ^{31}P NMR spectroscopy. Attempts to isolate this



Scheme 2. Suggested mechanism for the formation of 4.

compound have so far been unsuccessful because of its limited stability. An excess of C_2H_2 did not produce a zirconacyclopentadiene or polyacetylene.

Reaction of $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$ (1) with substituted acetylenes

In contrast to the reaction of 1 with C_2H_2 , reactions of substituted alkynes do not result in polyacetylene formation. Evidently the pathway to the corresponding titanacyclopentadienes is favored over that leading to a vinylidene complex that

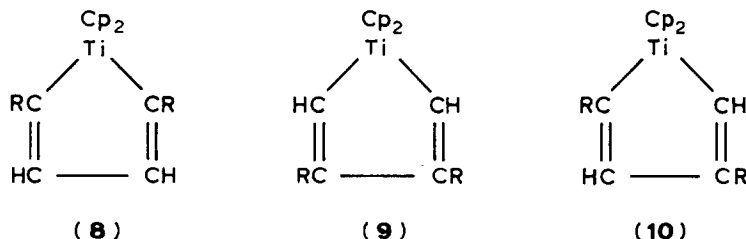
Table 1

IR, ^1H and ^{31}P NMR data for the acetylene complexes $\text{Cp}_2\text{M}(\text{R}^1\text{C}_2\text{R}^2)(\text{PMe}_3)$ ($\text{M} = \text{Ti}, \text{Zr}$)

Compound	IR ^a $\nu(\text{C}=\text{C})$ (cm^{-1})	^1H NMR ^b			^{31}P NMR ^b
		$\delta(\text{Cp})$ [$J(\text{P}, \text{H})$]	$\delta(\text{alkyne})$ [$J(\text{P}, \text{H})$], { $J(\text{H}, \text{H})$ }	$\delta(\text{PMe}_3)$ [$J(\text{P}, \text{H})$]	
$\text{Cp}_2\text{Ti}(\text{C}_2\text{H}_2)(\text{PMe}_3)$	1618	5.25	H 8.82[9.0]; 6.99[5.4]	1.09(br)	28.1
$\text{Cp}_2\text{Ti}(\text{PhC}_2\text{H})(\text{PMe}_3)$	1590	5.83	Ph 7.13(m); H ^c	0.93(d) [5.4]	26.8
$\text{Cp}_2\text{Zr}(\text{C}_2\text{H}_2)(\text{PMe}_3)$	1597	5.24[2.0]	H 7.97(d, d) [3.2] 9.86 (d, d) [7.1] {2.4}	0.98(d) [5.4]	2.0

^a In pentane solution. ^b In CDCl_3 , r.t., δ in ppm, J in Hz. ^c Not resolved due to overlap with phenyl.
d = doublet; d,d = double of doublets; m = multiplet; br = broad.

could initiate the polymerization of the alkyne. Treatment of **1** with one equivalent of the substituted alkyne $\text{R}^1\text{C}_2\text{R}^2$ ($\text{R}^1, \text{R}^2 = \text{H}, \text{Me}, \text{Ph}$) gives acetylene complexes $\text{Cp}_2\text{Ti}(\text{PMe}_3)(\text{R}^1\text{C}_2\text{R}^2)$ analogous to **2**. Reaction of **1** with an excess of the alkyne results in the formation of titanacyclopentadienes analogous to **3** ($\text{R}^1, \text{R}^2 = \text{H}, \text{Me}, \text{Ph}$). Although two isomers could be expected for the mono-substituted acetylenic complexes, only one species was observed by ^1H NMR spectroscopy. Analogously, three isomeric titanacyclopentadienes (**8–10**) could result from reactions of **1** with monosubstituted alkynes:



The ^1H , ^{13}C and ^{31}P NMR data for **2**, **3** and substituted acetylene complexes are given in Tables 1 and 2.

The ^1H and ^{13}C NMR spectra of the titanacycle $\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_2\text{Me}_2)$ indicate that an isomer of type **8** is the major product. This conclusion is based on the chemical

Table 2

 ^1H and ^{13}C NMR data for the titanacyclopentadienes $\text{Cp}_2\text{Ti}(\text{C}_4\text{R}_1^1\text{R}_2^2)$

Compound	^1H NMR ^a		^{13}C NMR ^a		
	$\delta(\text{Cp})$	$\delta(\text{C}_4\text{R}_1^1\text{R}_2^2)$	$\delta(\text{Cp})$	$\delta(\text{C}_4\text{R}_1^1\text{R}_2^2)$	
				C_α	C_β
$\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$	6.18	H_α 6.30(m); H_β 5.63(m)	113.0	198.5	124.8
$\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_2\text{Me}_2)$	6.10	H 5.37; Me 1.60	112.0	201.5	115.2 ^b
$\text{Cp}_2\text{Ti}(\text{C}_4\text{Me}_4)$	5.95	Me 1.28; 1.13	111.7	192.1	122.3 ^c
$\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_2\text{Ph}_2)$	6.24	Ph 7.23(m); H ^d	112.8	198.6	130.1
				198.7	128.7

^a In CDCl_3 , r.t., δ in ppm. ^b $\delta(\text{Me})$ 27.1 ppm. ^c $\delta(\text{Me})$ 19.1; 14.0. ^d Not resolved due to overlap with phenyl.

shift of the two olefinic protons (compare ^1H NMR data for **3**), and on the fact that only one signal is observed in both the ^1H and ^{13}C NMR spectra. Additional confirmation is provided by the ^1H -coupled ^{13}C NMR spectrum, in which only the C_β carbon atoms exhibit $^1J(\text{C},\text{H})$ coupling.

The titanacycle derived from the reaction of **1** with phenylacetylene can be assigned a structure of type **10** on the basis of similar arguments. In the ^{13}C NMR spectrum four different ring carbon atoms can be distinguished, a feature that is consistent only with the unsymmetrical isomer **10**.

Experimental

Reactions of **1** with C_2H_2 in cyclohexane

(a) *Preparation of 2 in solution.* A solution of 250 mg (0.76 mmol) of **1** in 100 ml of cyclohexane in a Schlenk tube is frozen and then evacuated. A stoichiometric amount (17 ml, 0.75 mmol) of C_2H_2 is added to, and the frozen solution is allowed to thaw a dark purple solution being formed immediately. The solvent is removed under high vacuum to leave a dark purple residue that changes gradually and is now only partly soluble in cyclohexane.

(b) *Preparation of 3.* A solution of 250 mg (0.76 mmol) of **1** in 50 ml of toluene in a Schlenk tube is cooled to -30°C and the Schlenk tube is then partly evacuated. A slight excess of C_2H_2 is allowed to flow into the Schlenk tube and the mixture is stirred for 20 min at room temperature then filtered through a frit. The solvent is removed from the filtrate in high vacuum and the yellow-green residue is dissolved in pentane. The solution is filtered and the solvent removed to leave the yellow, analytically pure **3**. Yield: 95 mg (55%), Dec. 45°C . MS: m/e 230 (M^+). Anal. Found: C, 71.31; H, 7.24. $\text{C}_{14}\text{H}_{14}\text{Ti}$ calc: C, 73.06; H, 6.13%.

(c) *Preparation of 4.* A solution of 250 mg (0.76 mmol) of **1** in 50 ml of toluene in a Schlenk pressure tube (volume of 300 ml) is frozen at -100°C . The tube is evacuated then filled with C_2H_2 . The solution is then allowed to warm to room temperature, to yield a dark suspension. Filtration through a frit yields **4** as a black insoluble material that absorbs oxygen. From the filtrate the titanacyclopentadiene **3** can be isolated (see (b)). Yield of **4**: 1.50 g. Anal. Found: C, 90.38; H, 7.59. C_xH_x : C, 92.26; H, 7.74%.

Reaction of **1** with substituted acetylenes

The reaction of **1** with substituted acetylenes proceeds as described in (a) and (b) above except that in no case are polyacetylenes formed. The reaction of **1** with

Table 3

Characteristic data of some acetylene and titanacyclopentadiene complexes

Complex	Yield (%)	Dec. ($^\circ\text{C}$)	MS (m/e)
$\text{Cp}_2\text{Ti}(\text{PhC}_2\text{H})(\text{PMe}_3)$	90	32	356
$\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)$	54	45	230
$\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_2\text{Me}_2)$	95	85	258
$\text{Cp}_2\text{Ti}(\text{C}_4\text{Me}_4)$	95	75	286
$\text{Cp}_2\text{Ti}(\text{C}_4\text{Ph}_4)$	93	202 (m.p.)	534

methylacetylene or dimethylacetylene yields only the corresponding titanacycles and no trimethylphosphine alkyne complexes. Characteristic data for the products are given in Table 3.

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