Journal of Organometallic Chemistry, 329 (1987) 61–67
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reactions of $Cp_2M(PMe_3)_2$ complexes (M = Ti, Zr) with acetylenes. Selective formation of *trans*-polyacetylene at low temperatures

Helmut G. Alt*, Heidi E. Engelhardt,
Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstrasse 30, D-8580 Bayreuth (F.R.G.)

Marvin D. Rausch* and Lawrence B. Kool
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003 (U.S.A.)

(Received January 6th, 1987)

Abstract

The reaction of $Cp_2Ti(PMe_3)_2$ with C_2H_2 gives the substitution product $Cp_2Ti(C_2H_2)(PMe_3)$, the titanacyclopentadiene $Cp_2Ti(C_4H_4)$, and *trans*-polyacetylene. A mechanism for the catalytic formation of polyacetylene is proposed. Substituted acetylenes $R^1C_2R^2$ ($R^1 \neq R^2$ = H, Me, Ph) react with $Cp_2Ti(PMe_3)_2$ in an analogous manner except that no polyalkynes are produced. The Zr derivative $Cp_2Zr(PMe_3)_2$ and C_2H_2 yield the labile $Cp_2Zr(C_2H_2)$ (PMe_3).

Introduction

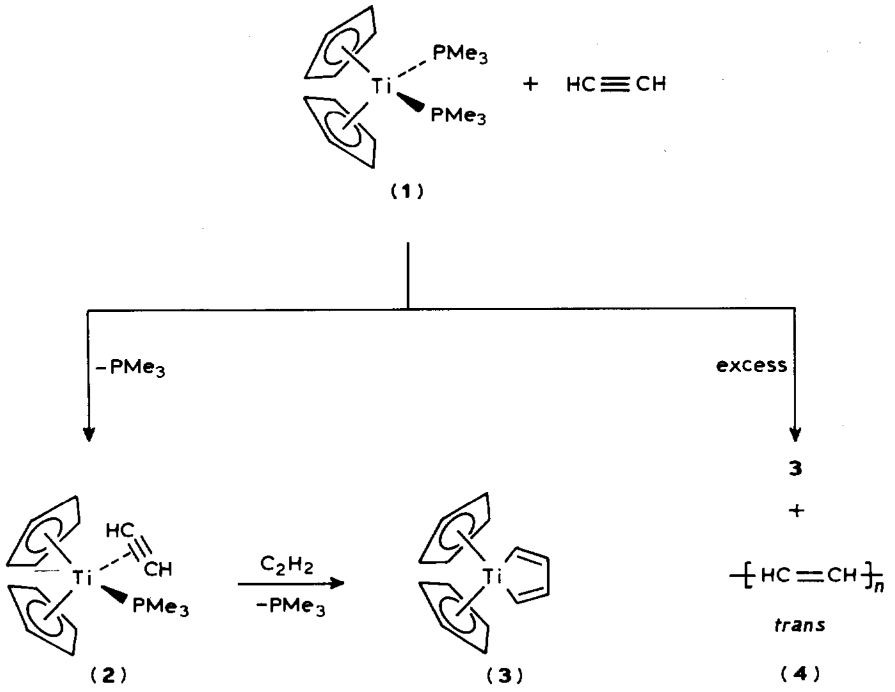
We recently demonstrated that $Cp_2Ti(PMe_3)_2$ (**1**) reacts readily with various acetylenes $R^1C_2R^2$ (R^1, R^2 = H, Me, Ph), yielding acetylene complexes of the type Cp_2Ti $(R^1C_2R^2)$ (PMe_3), titanacyclopentadienes $Cp_2Ti(C_4R^1_2R^2_2)$ and polyacetylene [1]. In this paper we present details of these reactions and of their extensions.

Results and discussion

Reaction of $Cp_2Ti(PMe_3)_2$ (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 $Cp_2Ti(C_2H_2)$-



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 $Cp_2Ti(C_4H_4)$ (**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 C=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, $^3J(P, H)$ 9.0 Hz and δ 6.99, $^3J(P, H)$ 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 $Cp_2Ti(C_2Ph_2)CO$ and $Cp_2Ta(C_2H_4)H$ (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 titanacyclopropene 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

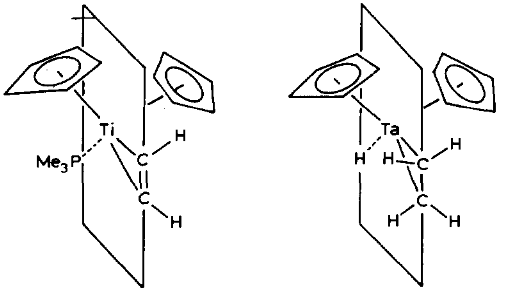


Fig. 1. Configurations of $Cp_2Ti(C_2H_2)PMe_3$ and $Cp_2Ta(C_2H_4)H$.

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, $CpCo(PMe_3)C_4H_4$ [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 $^2J(C, H)$ long-range couplings of C_α and C_β (C_α: $^1J(C, H)$ 145.3, $^2J(C, H)$ 10.3, $^3J(C, H)$ 8.5 Hz. C_β: $^1J(C, H)$ 150, $^2J(C, H)$ 12.0 and 15.4, $^3J(C, H)$ 3.4 Hz).

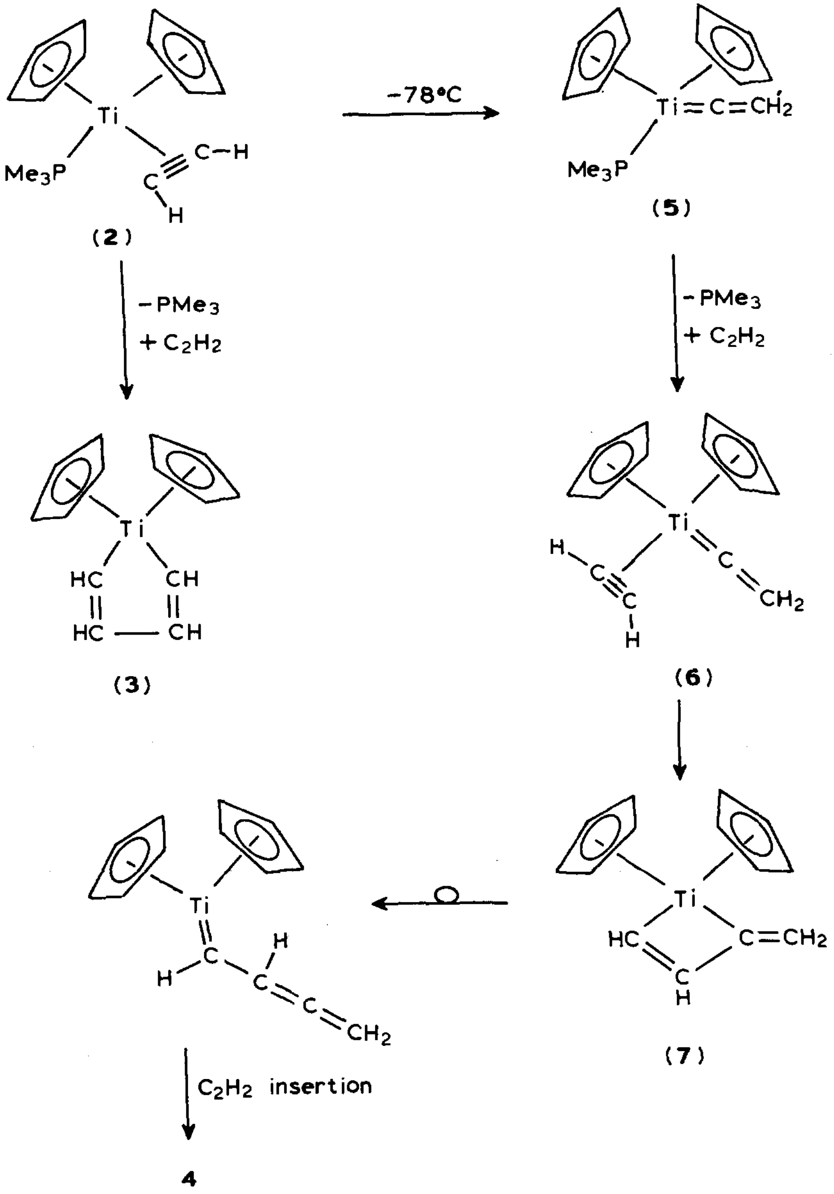
The mass spectrum of 3 shows the molecular ion ($m/e = 230$) as well as peaks derived from the fragmentation of this ion. The IR spectrum of 3 exhibits a band at 1442 cm^{-1} (KBr) that can be assigned to one of the two valence frequencies of the two C=C double bonds. The metallacyclic character of 3 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 C–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 $Cp_2(PMe_3)Ti{=}C{=}CH_2$ (**5**) (Scheme 2). Replacement of PMe_3 by C_2H_2 would give the corresponding acetylene-vinylidene intermediate $Cp_2(C_2H_2)Ti{=}C{=}CH_2$ (**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 $W(CO)_6$ 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**, $Cp_2Zr(PMe_3)_2$, also reacts with C_2H_2 in toluene-d_8 solution to form the white monosubstitution product $Cp_2Zr(C_2H_2)(PMe_3)$, 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 $Cp_2Ti(PMe_3)_2$ (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

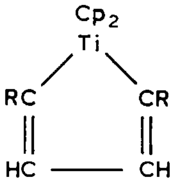
Table 1

IR, ^{1}H and ^{31}P NMR data for the acetylene complexes $Cp_2M(R^1C_2R^2)(PMe_3)$ (M = Ti, Zr)

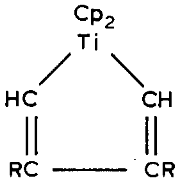
Compound	IR[a] ν(C=C) (cm^{-1})	^{1}H NMR[b]			^{31}P NMR[b]
		δ(Cp) [J(P, H)]	δ(alkyne) [J(P, H)], {J(H, H)}	$\delta(PMe_3)$ [J(P, H)]	
$Cp_2Ti(C_2H_2)(PMe_3)$	1618	5.25	H 8.82[9.0]; 6.99[5.4]	1.09(br)	28.1
$Cp_2Ti(PhC_2H)(PMe_3)$	1590	5.83	Ph 7.13(m); H[c]	0.93(d) [5.4]	26.8
$Cp_2Zr(C_2H_2)(PMe_3)$	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.

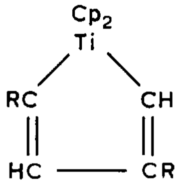
could initiate the polymerization of the alkyne. Treatment of **1** with one equivalent of the substituted alkyne $R^1C_2R^2$ (R^1, R^2 = H, Me, Ph) gives acetylene complexes $Cp_2Ti(PMe_3)$ $(R^1C_2R^2)$ analogous to **2**. Reaction of **1** with an excess of the alkyne results in the formation of titanacyclopentadienes analogous to **3** (R^1, R^2 = H, Me, Ph). Although two isomers could be expected for the mono-substituted acetylenic complexes, only one species was observed by ^{1}H NMR spectroscopy. Analogously, three isomeric titanacyclopentadienes (**8**–**10**) could result from reactions of **1** with monosubstituted alkynes:



(8)



(9)



(10)

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

The ^{1}H and ^{13}C NMR spectra of the titanacycle $Cp_2Ti(C_4H_2Me_2)$ indicate that an isomer of type **8** is the major product. This conclusion is based on the chemical

Table 2

^{1}H and ^{13}C NMR data for the titanacyclopentadienes $Cp_2Ti(C_4R^1_2R^2_2)$

Compound	^{1}H NMR[a]		^{13}C NMR[a]		
	δ(Cp)	$\delta(C_4R^1_2R^2_2)$	δ(Cp)	$\delta(C_4R^1_2R^2_2)$	
				C_α	C_β
$Cp_2Ti(C_4H_4)$	6.18	H_α 6.30(m); H_β 5.63(m)	113.0	198.5	124.8
$Cp_2Ti(C_4H_2Me_2)$	6.10	H 5.37; Me 1.60	112.0	201.5	115.2[b]
$Cp_2Ti(C_4Me_4)$	5.95	Me 1.28; 1.13	111.7	192.1	122.3[c]
$Cp_2Ti(C_4H_2Ph_2)$	6.24	Ph 7.23(m); H[d]	112.8	198.6 198.7	130.1 128.7

[a] In $CDCl_3$, r.t., δ in ppm. [b] δ(Me) 27.1 ppm. [c] δ(Me) 19.1; 14.0. [d] Not resolved due to overlap with phenyl.

shift of the two olefinic protons (compare ^{1}H NMR data for **3**), and on the fact that only one signal is observed in both the ^{1}H and ^{13}C NMR spectra. Additional confirmation is provided by the ^{1}H-coupled ^{13}C NMR spectrum, in which only the C_β carbon atoms exhibit ^1J(C,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. $C_{14}H_{14}Ti$ 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. (°C)	MS (m/e)
$Cp_2Ti(PhC_2H)(PMe_3)$	90	32	356
$Cp_2Ti(C_4H_4)$	54	45	230
$Cp_2Ti(C_4H_2Me_2)$	95	85	258
$Cp_2Ti(C_4Me_4)$	95	75	286
$Cp_2Ti(C_4Ph_4)$	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.

Acknowledgements

The authors are grateful to the National Science Foundation (M.D.R. and L.B.K.), to the NATO (H.G.A. and M.D.R.), to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (H.G.A.). A gift of trimethylphosphonium chloride from Knapsack/Hoechst AG is gratefully acknowledged.

References

1 H.G. Alt, H.E. Engelhardt, M.D. Rausch and L.B. Kool, J. Am. Chem. Soc., 107 (1985) 3717.
2 G. Fachinetti, C. Floriani, F. Marchetti and M. Mellini, J. Chem. Soc., Dalton Trans., (1978) 1398.
3 B. Demerseman and P.H. Dixneuf, J. Chem. Soc., Chem. Commun., (1981) 665.
4 B.H. Edwards, R.D. Rogers, D.J. Sikora, J.L. Atwood and M.D. Rausch, J. Am. Chem. Soc., 105 (1983) 416.
5 L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, U. Thewalt and B. Wolf, Angew. Chem., 97 (1985) 435; Angew. Chem. Int. Ed. Engl., 24 (1985) 394.
6 H. Yamazaki and Y. Wakatsuki, J. Organomet. Chem., 272 (1984) 251.
7 J.C.W. Chien, Polyacetylene: Chemistry, Physics and Material Science, Academic Press, New York, 1984.
8 T.J. Katz, T.H. Ho, N.Y. Shih, Y.C. Ying and V.I.W. Stuart, J. Am. Chem. Soc., 106 (1984) 2659.
9 T.J. Katz and S.J. Lee, J. Am. Chem. Soc., 102 (1980) 422.
10 H.H. Thoi, K.J. Ivin and J.J. Rooney, J. Chem. Soc., Faraday Trans., 78 (1982) 2227.
11 A. Mayr, K.C. Schaefer and E.Y. Huang, J. Am. Chem. Soc., 106 (1984) 1517.
12 H. Foley, L.M. Strubinger, T.S. Targos and G.L. Geoffroy, J. Am. Chem. Soc., 105 (1983) 3064.
13 S.J. Landon, P.S. Shulman and G.L. Geoffroy, J. Am. Chem. Soc., 107 (1985) 6739.
14 H. Alt and M.D. Rausch, J. Am. Chem. Soc., 96 (1974) 5936.
15 J.L. Atwood, W.E. Hunter, H. Alt and M.D. Rausch, J. Am. Chem. Soc., 98 (1976) 2454.
16 J. Mattia, D.J. Sikora. D.W. Macomber, M.D. Rausch, J.P. Hickey, G.D. Friesen and L.J. Todd, J. Organomet. Chem., 213 (1981) 441.
17 A. Famili, M.F. Farona and S. Thanedar, J. Chem. Soc., Chem. Commun., (1983) 435.