

## NEW DI- $\eta^5$ -CYCLOPENTADIENYLDIALKYNYL DERIVATIVES OF TITANIUM(IV)

R. JIMENEZ, M.C. BARRAL, V. MORENO \* and A. SANTOS

*Departamento de Química Inorgánica e Instituto de Química Inorgánica "Elhúyar" del C.S.I.C., Facultad de Ciencias Químicas, Universidad Complutense, Madrid-3 (Spain)*

(Received March 12th, 1979)

### Summary

A series of new stable dialkynyltitanium(IV) derivatives of the type  $(\eta^5\text{-R}'\text{C}_5\text{H}_4)_2\text{Ti}(\text{C}\equiv\text{CR})_2$  (R = phenyl, cyclohexyl, n-hexyl, 2,2-diphenylethyl and 2-cyano-2,2-diphenylethyl; R' = hydrogen, methyl) has been prepared by treatment of  $(\eta^5\text{-R}'\text{C}_5\text{H}_4)_2\text{TiCl}_2$  with  $\text{NaC}\equiv\text{CR}$  in ether. The compounds were characterized by elemental microanalysis and by infrared, electronic and  $^1\text{H}$  NMR spectroscopy.

### Introduction

Titanium compounds of the type  $\text{Cp}_2\text{TiR}_2$  (Cp = cyclopentadienyl) are well-known for R = alkyl or aryl [1–3] but few compounds with R = alkynyl have been described. Köpf and Schmidt [4] and Teuben and De Liefde Meijer [5] have described the synthesis and isolation of the relatively stable  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ , while Bruce et al. [6] reported the synthesis of the unstable and explosive  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}\equiv\text{CCF}_3)_2$ .

We describe below the synthesis and properties of some new stable complexes of the type  $\text{L}_2\text{TiR}_2$ , where L = cyclopentadienyl (Cp), methylcyclopentadienyl (MeCp); R = phenylethynyl (PE), cyclohexylethynyl (CHE), n-octynyl (HE), 4,4-diphenylbutynyl (DPB), 4-cyano-4,4-diphenylbutynyl (DPPN).

### Results and discussion

Table 1 lists the new compounds obtained and some of their properties. All the compounds are diamagnetic, stable to air and moisture, insoluble in water,

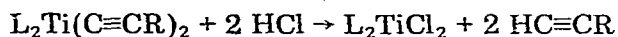
\* Address: Facultad de Ciencias. Carretera de Valldemossa, Palma de Mallorca (Spain).

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR DICYCLOPENTADIENYLDI(ALKYNYL) TITANIUM(IV) COMPLEXES

Compound	Colour	M.p. (°C) (dec.)	Analyses (found. (calcd.)) (%)		
			C	H	N
Cp <sub>2</sub> Ti(CHE) <sub>2</sub>	yellow	220	79.16 (79.58)	8.24 (8.16)	
Cp <sub>2</sub> Ti(HE) <sub>2</sub>	yellow	210	78.35 (78.78)	9.20 (9.09)	
Cp <sub>2</sub> Ti(DPPN) <sub>2</sub>	brown	100	82.20 (82.75)	5.64 (5.32)	4.30 (4.38)
Cp <sub>2</sub> Ti(DPB) <sub>2</sub>	dark-orange	110	85.42 (85.71)	5.97 (6.12)	
(MeCp) <sub>2</sub> Ti(PE) <sub>2</sub>	light-orange	230	82.53 (82.32)	5.34 (5.88)	
(MeCp) <sub>2</sub> Ti(CHE) <sub>2</sub>	yellow-orange	225	80.31 (80.00)	8.72 (8.57)	
(MeCp) <sub>2</sub> Ti(HE) <sub>2</sub>	orange	212	79.46 (79.24)	9.21 (9.43)	
(MeCp) <sub>2</sub> Ti(DPPN) <sub>2</sub>	ochre-orange	120	82.40 (82.88)	5.43 (5.71)	4.02 (4.20)
(MeCp) <sub>2</sub> Ti(DPB) <sub>2</sub>	red-orange	114	85.25 (85.72)	6.19 (6.49)	

and soluble in the more common organic solvents. They react with hydrogen chloride in anhydrous ether according to the equation:



The yield of L<sub>2</sub>TiCl<sub>2</sub> is almost quantitative, whereas the yield of HC≡CR depends on the reaction temperature. This may be due to partial polymerization of the acetylenic compound.

#### Infrared spectra

The IR spectra of these compounds show absorption bands at 3100 cm<sup>-1</sup> ν(C—H str.), 1450 cm<sup>-1</sup> ν(C—C str.), 1010 cm<sup>-1</sup> δ(C—H bend in plane) and 810 cm<sup>-1</sup> δ(C—H bend out of plane), which are characteristic of η<sup>5</sup>-bonded cyclopentadienyl groups. However, the characteristic absorption frequencies of the σ-bonded cyclopentadienyl groups are absent. On the other hand all these compounds exhibit the frequencies expected for σ-bonded alkyne groups.

The methylcyclopentadienyl derivatives also show the absorption bands characteristic of the methyl groups and a series of new ligand bands which are made active by the change of symmetry operated in the coordination to the metal.

The stretching frequency of the acetylenic group, ν(C≡C), in these compounds is always shifted towards the lower frequencies with respect to the corresponding starting acetylenic compounds. This is commonly observed with σ-acetylenic compounds of the transition metals, and can be due either to a d(π) → p(π\*) back-bonding of the metal to the ligand or to the increase of polarity of the acetylenic bond upon coordination to the metal. In our case the

TABLE 2

$\nu(\text{C}=\text{C})$  AND  $\nu(\text{C}\equiv\text{N})$  STRETCHING FREQUENCIES OF THE DICYCLOPENTADIENYLDIALKYNYL TITANIUM COMPOUNDS

Compound	$\nu(\text{C}=\text{C})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}\equiv\text{N})$ ( $\text{cm}^{-1}$ )
$\text{Cp}_2\text{Ti}(\text{PE})_2$	2065m (2122)	
$\text{Cp}_2\text{Ti}(\text{CHE})_2$	2070w (2113)	
$\text{Cp}_2\text{Ti}(\text{HE})_2$	2080m (2117)	
$\text{Cp}_2\text{Ti}(\text{DPPN})_2$	2085m (2120)	2200m (2240)
$\text{Cp}_2\text{Ti}(\text{DPB})_2$	2080w (2109)	
$(\text{MeCp})_2\text{Ti}(\text{PE})_2$	2045s (2122)	
$(\text{MeCp})_2\text{Ti}(\text{CHE})_2$	2050m (2113)	
$(\text{MeCp})_2\text{Ti}(\text{HE})_2$	2045w (2117)	
$(\text{MeCp})_2\text{Ti}(\text{DPPN})_2$	2100w (2120)	2200w (2240)
$(\text{MeCp})_2\text{Ti}(\text{DPB})_2$	2083m (2109)	

second factor undoubtedly is the more important.

Table 2 shows the  $\nu(\text{C}=\text{C})$  stretching frequencies of these new compounds together with the  $\nu(\text{C}\equiv\text{N})$  stretching frequencies of the DPPN derivatives. In the DPPN compounds the  $\nu(\text{C}\equiv\text{N})$  stretching frequency shifts from  $2240\text{ cm}^{-1}$  in the acetylenic starting compound to  $2200\text{ cm}^{-1}$  in the metal compounds, probably because of interaction of the nitrile groups with the metal.

### $^1\text{H}$ NMR spectra

Table 3 lists the proton chemical shifts of the new acetylenic compounds obtained.

In the compounds  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}\equiv\text{CR})_2$  shifts of the  $\delta$  values of the signals corresponding to the cyclopentadienyl protons are always below those of the halogenated starting derivatives; replacement of Cl ligands by alkynyl groups causes an increase in the electron shielding of the cyclopentadienyl ring protons. On the other hand the signals of the cyclopentadienyl ring protons of the methylcyclopentadiene derivatives appear at higher fields than that of the cyclopentadiene derivatives; this is because the methyl group modifies the distribution of the electronic density at the ring atoms, giving an electronic charge to the ring.

In the phenylacetylene, cyclohexylacetylene, and octyne derivatives of di- $\eta^5$ -cyclopentadienyltitanium, only a singlet is observed for the cyclopentadienyl rings, which implies that the protons of both rings are equivalent. In the case of the 4,4-diphenylbutyne derivative a multiplet is observed, and two multiplets are found for the 2,2-diphenyl-4-pentynenitrile derivative. These differences may be due to the greater size of these ligands, which must hinder free

TABLE 3  
 CHEMICAL SHIFTS ( $\delta$ ) FOR TITANIUM DERIVATIVES <sup>a</sup> OF THE TYPE  $L_2TiR_2$ 

Compound	$C_5H_5$ or $C_5H_4$	$C_6H_5$	$CH_3$	$CH_2$	CH	$CH_3(Cp)$
$Cp_2TiCl_2$ <sup>b</sup>	6.64s					
$Cp_2Ti(PE)_2$ <sup>c</sup>	6.40s	7.31s				
$Cp_2Ti(CHE)_2$	6.37s			1.70m		
$Cp_2Ti(HE)_2$	6.35s		1.03m	1.41m		
$Cp_2Ti(DPPN)_2$	6.19					
	6.29	7.21m		3.17d		
$CpTi(DPB)_2$	6.41m	7.36m		3.00d	4.20t	
$(MeCp)_2TiCl_2$	6.22t					
	6.43t					2.39s
$(MeCp)_2Ti(PE)_2$	6.13t	7.34s				2.40s
	6.40t					
$(MeCp)_2Ti(CHE)_2$	5.82m			1.80m		2.24s
	6.28m					
$(MeCp)_2Ti(HE)_2$	5.82m		1.00m	1.60m		2.35s
	6.28m					
$(MeCp)_2Ti(DPPN)_2$	5.25m	7.34		3.20d		2.24s
	5.75m					
$(MeCp)_2Ti(DPB)_2$	5.15m	7.35m		3.15d	4.15t	2.24s
	5.75m					

<sup>a</sup> s, singlet; d, doublet; t, triplet; m, multiplet. <sup>b</sup> See ref. 1. <sup>c</sup> See ref. 4.

rotation and cause non-equivalence of the rings. In the case of the DPPN derivative the effect is strengthened by the presence of the nitrile group, which, as revealed by its IR spectrum, interacts with the metal atom.

The presence of the methyl group in the methylcyclopentadiene derivatives destroys the equivalence of the rings protons, and multiplets are always observed.

 TABLE 4  
 ELECTRONIC SPECTRAL DATA FOR THE  $L_2TiR_2$  DERIVATIVES. (WAVELENGTHS AND EXTINCTION COEFFICIENTS AT THE ABSORPTION MAXIMA.)

Compound	$\lambda_{max}$ (nm)	$\log \epsilon$	$\lambda_{max}$ (nm)	$\log \epsilon$	$\lambda_{max}$ (nm)	$\log \epsilon$	$\lambda_{max}$ (nm)	$\log \epsilon$
$Cp_2TiCl_2$	526	2.35	392	3.40	320	3.81	256	4.24
$Cp_2Ti(PE)_2$			418	3.63	305	4.13	250	4.27
$Cp_2Ti(CHE)_2$			4.00	3.39	305	3.89	250	4.34
$Cp_2Ti(HE)_2$			405	3.37	305	3.87	250	4.15
$Cp_2Ti(DPPN)_2$			385	3.86	292	4.06	250	4.21
$Cp_2Ti(DPB)_2$			375	3.76	300	4.06	250	4.18
$(MeCp)_2TiCl_2$	530	3.45	394	3.30	320	3.83	260	4.24
$(MeCp)_2Ti(PE)_2$			420	3.75	264	4.15	250	4.68
$(MeCp)_2Ti(CHE)_2$			415	3.50	310	3.92	252	4.27
$(MeCp)_2Ti(HE)_2$			418	3.89	310	4.00	255	4.24
$(MeCp)_2Ti(DPPN)_2$			410	3.88	300	4.06	255	4.50
$(MeCp)_2Ti(DPB)_2$			396	3.65	324	4.00	262	4.42

### Electronic spectra

Table 4 gives the wavelengths of the absorptions of the electronic spectra of the compounds. The most noticeable difference between the electronic spectra of the alkyne derivatives and those of the  $L_2TiCl_2$  compounds is the absence of the absorption band at 520–530 nm. The absorption corresponding to the maximum centered at 250–260 nm has been assigned to an internal charge transfer in the cyclopentadienyl ligand, in agreement with the assignment proposed by Samuel [7], since its position is the same in the acetylenic derivatives as in the starting compounds. The two other absorptions are attributed to ligand  $\rightarrow$  metal charge transfer transitions, but it is difficult to assign these absorptions separately to transitions from a specific ligand.

### Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by standard methods. Before use, they were freed from oxygen by repeated degassing and saturating with nitrogen.

Dicyclopentadienyltitanium dichloride was purchased from Fluka and recrystallized from chloroform. Phenylacetylene (Merck), cyclohexylacetylene (Merck) and octyne (Fluka) were obtained from commercial sources and distilled before use.

Bis(methylcyclopentadienyl)titanium dichloride was prepared by reaction of stoichiometric quantities of sodium methylcyclopentadienide with titanium tetrachloride [8]. Sodium methylcyclopentadienide was prepared by reaction of methylcyclopentadiene monomer (Fluka) with finely dispersed sodium metal.

4,4-Diphenylbutyne (HDPB) was prepared from sodium amide (Fluka) (7.8 g, 0.2 mol), diphenylmethane (Fluka) (33.6 g, 0.2 mol) and propargyl bromide (Fluka) (23.8 g, 0.2 mol) in liquid ammonia/ether. The mixture was stirred for 2 h. This product was extracted with ether and recrystallized from methanol. Colourless crystals were obtained (35.5 g, 80% yield), m.p. 62°C. IR spectrum (characteristic frequencies):  $\nu(\equiv C-H)$  3278 and 3258  $cm^{-1}$ ;  $\nu(C\equiv C)$  2109  $cm^{-1}$ .  $^1H$  NMR spectrum:  $\delta$  1.96 triplet (H-C $\equiv$ ) ( $J$  2.6 Hz);  $\delta$  3.95 quartet (CH<sub>2</sub>) ( $J_1$  2.6 Hz,  $J_2$  7.3 Hz);  $\delta$  4.31 triplet (CH) ( $J$  7.3 Hz);  $\delta$  7.38 singlet (C<sub>6</sub>H<sub>5</sub>). Anal. Found: C, 92.74; H, 6.45. C<sub>16</sub>H<sub>14</sub> calcd.: C, 93.20; H, 6.80%.

2,2-Diphenyl-4-pentynenitrile (HDPPN) was prepared as described by Salmon-Legagneur and Brunet [9] with some modifications [10].

The sodium salts of the acetylenic compounds were prepared as described by Teuben et al. [5].

Titanium was determined gravimetrically as TiO<sub>2</sub>. C, H and N analyses were carried out with a Microanalytical Hewlett-Packard 185 apparatus. Infrared spectra in the region 4000–200  $cm^{-1}$  were scanned on a Perkin-Elmer 325 spectrometer and samples examined as KBr discs or Nujol mulls using CsI cells.  $^1H$  NMR spectra were measured at 60 MHz with a Perkin-Elmer R12 spectrometer in deuteriochloroform (using TMS as internal standard). Electronic spectra were recorded with a Beckman Acta III spectrophotometer; chloroform was used as solvent. Magnetic susceptibilities were determined by the Gouy method.

*Bisalkynyl derivatives. General method of preparation*

$\text{L}_2\text{TiCl}_2$  was added to a suspension of the sodium salt of the acetylenic compounds in anhydrous ether under an inert atmosphere and in 1/2 molar ratio. After being stirred for 4 h at room temperature the mixture was filtered and the filtrate was concentrated to about 1/3 of its initial volume. Pentane or hexane was added, and after 12 h at  $0^\circ\text{C}$  a precipitate appeared. The product was filtered through a G4 fritted disc, washed with pentane or hexane and dried in vacuum.

I. Sodium phenylethynylide (0.49 g, 4 mmol) and di(cyclopentadienyl)titanium dichloride (0.50 g, 2 mmol) yielded di(cyclopentadienyl)bis(phenylethynyl)titanium (0.49 g, 65%) as a yellow-orange microcrystalline solid. The IR,  $^1\text{H}$  NMR and electronic spectra were identical with those described by Köpf and Schmidt [4].

II. Sodium cyclohexylethynylide (0.52 g, 4 mmol) and dicyclopentadienyltitanium dichloride (0.50 g, 2 mmol) yielded dicyclopentadienyldicyclohexylethynyltitanium (0.46 g, 58%) as a yellow microcrystalline solid, m.p.  $220^\circ\text{C}$  (dec.). (Found: C, 79.16; H, 8.24; Ti, 12.32.  $\text{C}_{26}\text{H}_{32}\text{Ti}$  calcd.: C, 79.58; H, 8.16; Ti, 12.24%).

III. Sodium octynylide (0.53 g, 4 mmol) and dicyclopentadienyltitanium dichloride (0.50 g, 2 mmol) yielded dicyclopentadienyldioctynyltitanium (0.54 g, 56%) as a yellow microcrystalline solid, m.p.  $210^\circ\text{C}$  (dec.). (Found: C, 78.35; H, 9.20; Ti, 12.32.  $\text{C}_{26}\text{H}_{36}\text{Ti}$  calcd.: C, 78.78; H, 9.09; Ti, 12.12%).

IV. Sodium 4-cyano-4,4-diphenylbutynylide (0.51 g, 2 mmol) and dicyclopentadienyltitanium dichloride (0.25 g, 1 mmol) yielded dicyclopentadienylbis(4-cyano-4,4-diphenylbutynyl)titanium (0.32 g, 51%) as a brown microcrystalline solid, m.p.  $100^\circ\text{C}$  (dec.). (Found: C, 82.20; H, 5.64; N, 4.30; Ti, 7.23.  $\text{C}_{44}\text{H}_{34}\text{N}_2\text{Ti}$  calcd.: C, 82.75; H, 5.32; N, 4.38; Ti, 7.52%).

V. Sodium 4,4-diphenylbutynylide (0.41 g, 2 mmol) and dicyclopentadienyltitanium dichloride (0.25 g, 1 mmol) yielded dicyclopentadienylbis(4,4-diphenylbutynyl)titanium (0.31 g, 52%) as a dark-orange microcrystalline solid, m.p.  $110^\circ\text{C}$  (dec.). (Found: C, 85.42; H, 5.97; Ti, 8.41.  $\text{C}_{42}\text{H}_{36}\text{Ti}$  calcd.: C, 85.71; H, 6.12; Ti, 8.16%).

VI. Sodium phenylethynylide (0.49 g, 4 mmol) and bis(methylcyclopentadienyl)titanium dichloride (0.55 g, 2 mmol) yielded bis(methylcyclopentadienyl)bis(phenylethynyl)titanium (0.51 g, 63%) as a light orange microcrystalline solid, m.p.  $230^\circ\text{C}$  (dec.). (Found: C, 82.53; H, 5.34; Ti, 11.95.  $\text{C}_{28}\text{H}_{24}\text{Ti}$  calcd.: C, 82.32; H, 5.88; Ti, 11.76%).

VII. Sodium cyclohexylethynylide (0.52 g, 4 mmol) and bis(methylcyclopentadienyl)titanium dichloride (0.55 g, 2 mmol) yielded bis(methylcyclopentadienyl)bis(cyclohexylethynyl)titanium (0.46 g, 55%) as a yellow-orange microcrystalline solid, m.p.  $225^\circ\text{C}$  (dec.). (Found: C, 80.31; H, 8.72; Ti, 11.21.  $\text{C}_{28}\text{H}_{36}\text{Ti}$  calcd.: C, 80.00; H, 8.57; Ti, 11.43%).

VIII. Sodium octynylide (0.53 g, 4 mmol) and bis(methylcyclopentadienyl)titanium dichloride (0.55 g, 2 mmol) yielded bis(methylcyclopentadienyl)dioctynyltitanium (0.45 g, 54%) as an orange microcrystalline compound, m.p.  $212^\circ\text{C}$  (dec.). (Found: C, 79.46; H, 9.21; Ti, 11.56.  $\text{C}_{28}\text{H}_{40}\text{Ti}$  calcd.: C, 79.24; H, 9.43; Ti, 11.32%).

IX. Sodium 4-cyano-4,4-diphenylbutynylide (0.50 g, 2 mmol) and bis(meth-

ylcyclopentadienyl)titanium dichloride (0.28 g, 1 mmol) yielded bis(methylcyclopentadienyl)bis(4-cyano-4,4-diphenylbutynyl)titanium (0.33 g, 49%) as an ochre-orange microcrystalline solid, m.p. 120° C (dec.). (Found: C, 82.40; H, 5.43; N, 4.02; Ti, 7.43.  $C_{46}H_{38}N_2Ti$  calcd.: C, 82.88; H, 5.71; N, 4.20; Ti, 7.21%).

X. Sodium 4,4-diphenylbutynylide (0.41 g, 2 mmol) and bis(methylcyclopentadienyl)titanium dichloride (0.28 g, 1 mmol) yielded bis(methylcyclopentadienyl)bis(4,4-diphenylbutynyl)titanium (0.31 g, 50%) as a red-orange microcrystalline solid, m.p. 114° C. (Found: C, 85.25; H, 6.19; Ti, 8.03.  $C_{44}H_{40}Ti$  calcd.: C, 85.72; H, 6.49; Ti, 7.79%).

### Acknowledgement

Financial support from the Fondo Nacional para el Desarrollo de la Investigación Científica is gratefully acknowledged (Project No. 2118).

### References

- 1 P.C. Wailes, R.S.P. Coutts and H. Weigold, *Organometallic Chemistry of Titanium, Zirconium and Hafnium*, Academic Press, New York, 1974.
- 2 M.D. Rausch and H.B. Gordon, *J. Organometal. Chem.*, **74** (1974) 85.
- 3 H.J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, **4** (1970) 651.
- 4 H. Köpf and H. Schmidt, *J. Organometal. Chem.*, **10** (1967) 83.
- 5 J.H. Teuben and H.J. de Liefde Meijer, *J. Organometal. Chem.*, **17** (1969) 87.
- 6 M.I. Bruce, D.A. Harbourne, F. Waugh and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 356.
- 7 E. Samuel, *Bull. Soc. Chim. France*, (1966) 3548.
- 8 L.T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **9** (1959) 86.
- 9 F. Salmon-Legagneur and P. Brunet, *C.R. Acad. Sci. Paris*, **256** (1963) 4233.
- 10 M.C. Barral, R. Jiménez, E. Royer, V. Moreno and A. Santos, *Inorg. Chim. Acta*, **31** (1978) 165.