

SYNTHESIS AND PROPERTIES OF BIS(η^5 -CYCLOPENTADIENYL)-BIS(ALKYNYL)ZIRCONIUM(IV) COMPLEXES

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)

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Summary

The preparation of the air- and moisture-stable complexes (η^5 -R'C₅H₄)₂Zr-(C≡C-R)₂, (R = phenyl, cyclohexyl, n-hexyl, 2,2-diphenylethyl and 2-cyano-2,2-diphenylethyl; R' = hydrogen, methyl) is described. Their physical and chemical properties point to the presence of the (R'C₅H₄)₂Zr group and Zr-C≡σ-bonds. The compounds were characterized by elemental microanalysis and by infrared, ¹H NMR, and electronic spectroscopy.

Introduction

Very few bis(cyclopentadienyl)zirconium(IV) compounds of the type Cp₂ZrR₂ [1–3] (Cp = cyclopentadienyl; R = alkyl, aryl) have been described and their stabilities to air and moisture are low compared to those of the analogous bis(cyclopentadienyl)titanium(IV) derivatives [1]. Two zirconium(IV) compounds of general formula (η^5 -C₅H₄R)₂Zr(C≡C-C₆H₅)₂ (R = H, CH₃) have been reported [4], but their stabilities were not considered.

This work is a part of a series of investigations into alkynyl derivatives of Group IVA metals initiated previously with the study of various bis(η^5 -cyclopentadienyl)-bis(alkynyl)titanium(IV) complexes [5]. This paper describes the synthesis and properties of some new stable complexes of the type L₂ZrR₂, where L = cyclopentadienyl (Cp), methylcyclopentadienyl (MeCp); R = phenylethynyl (PE), cyclohexylethynyl (CHE), n-octynyl (HE), 4,4-diphenylbutynyl (DPB), 4-cyano-4,4-diphenylbutynyl (DPPN).

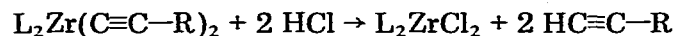
* Present address: Facultad de Ciencias. Carretera de Valldemossa, Palma de Mallorca (Spain)

Results and discussion

Table 1 lists analytical and physical data for the compounds obtained. The compounds are stable to air and moisture, diamagnetic, soluble in most of the usual organic solvents and insoluble in water.

In both series of cyclopentadienyl and methylcyclopentadienyl derivatives the solubility sequence observed is CHE \approx HE < PE < DPPN \approx DPB. The methylcyclopentadienyl derivatives are more soluble than the cyclopentadienyl derivatives, and the zirconium complexes more soluble than the titanium complexes previously described [5].

Hydrogen chloride breaks the metal-carbon σ -bonds with formation of the starting materials:



The yield of the acetylene depends on the reaction temperature, probably because of partial polymerization, whereas the yield of L_2ZrCl_2 is almost quantitative.

Infrared spectra

The IR spectra of all the complexes obtained show bands corresponding to the η^5 -cyclopentadienyl groups, the most characteristic being those at 3100 cm^{-1} (C-H str.), 1450 cm^{-1} (C-C str.), 1020 cm^{-1} (C-H bend, in plane) and 810 cm^{-1} (C-H bend, out of plane). The absence of bands corresponding to σ -bonded cyclopentadienyl group vibrations excludes the possibility of a σ -bond between the cyclopentadienyl group and the metal in these compounds [6].

The $\nu(C\equiv C)$ stretching frequency in these derivatives shifts towards the lower frequencies with respect to that of the starting acetylenic compounds. As is the case for the titanium(IV) derivatives [5], these shifts can be explained by an

TABLE 1
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE COMPOUNDS

Compound	Colour	M.p. ($^{\circ}\text{C}$) (dec.)	Analyses (%) Found (calcd.)			
			C	H	Zr	N
$\text{Cp}_2\text{Zr}(\text{CHE})_2$	yellow	230	71.29 (71.72)	7.45 (7.36)	20.37 (20.92)	
$\text{Cp}_2\text{Zr}(\text{HE})_2$	pale- yellow	225	71.45 (71.07)	7.96 (8.20)	21.20 (20.73)	
$\text{Cp}_2\text{Zr}(\text{DPPN})_2$	ochre	130	77.64 (77.53)	4.53 (4.22)	13.75 (13.36)	4.27 (4.11)
$\text{Cp}_2\text{Zr}(\text{DPB})_2$	ochre	135	79.94 (79.87)	5.20 (5.70)	14.84 (14.42)	
$(\text{MeCp})_2\text{Zr}(\text{CHE})_2$	white- yellow	234	72.12 (72.57)	8.10 (7.77)	19.24 (19.65)	
$(\text{MeCp})_2\text{Zr}(\text{HE})_2$	pale yellow	230	71.48 (71.95)	8.17 (8.56)	19.72 (19.49)	
$(\text{MeCp})_2\text{Zr}(\text{DPPN})_2$	ochre	136	77.52 (77.86)	5.78 (5.36)	13.06 (12.83)	3.21 (3.95)
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	white- yellow	132	79.85 (80.12)	5.84 (6.07)	13.64 (13.81)	

increase in the polarity of the C≡C bond in the ligand bonded to the metal with respect to that of the free acetylenic compound, as a consequence of the increase of the metal-carbon bond polarity. The possibility of the formation of an additional π -bond from the antibonding π^* orbitals of the acetylenic ligand and the d_{π} metal orbitals can be disregarded in view of the oxidation state of the metal.

In the case of DPPN derivatives the $\nu(\text{C}\equiv\text{N})$ stretching frequency shifts from 2240 cm^{-1} in the free acetylenic compound to 2180 cm^{-1} in the complexes, which indicates an interaction between the nitrile group and the metal. This shift is larger than those for the corresponding titanium(IV) derivatives [5], and can be attributed to the greater size of Zr^{IV} with respect to that of Ti^{IV} , which allows a closer approximation of the ligands.

Table 2 lists the $\nu(\text{C}\equiv\text{C})$ stretching frequencies of the compounds obtained, and the $\nu(\text{C}\equiv\text{N})$ stretching frequencies for the 2,2-diphenyl-4-pentyne nitrile derivatives.

¹H NMR spectra

The $\text{Cp}_2\text{Zr}(\text{C}\equiv\text{C}-\text{R})_2$ and $(\text{MeCp})_2\text{Zr}(\text{C}\equiv\text{C}-\text{R})_2$ derivatives show the resonances of the cyclopentadienyl ring protons at higher magnetic fields than those for the starting compounds Cp_2ZrCl_2 and $(\text{MeCp})_2\text{ZrCl}_2$; this is because the substitution of chlorine by the less electronegative alkynyl ligands leads to lower shielding of the ring protons.

It is noteworthy that in the bis(cyclopentadienyl)zirconium(IV) derivatives only a singlet is observed for all cyclopentadienyl ring protons, except for the

TABLE 2

$\nu(\text{C}\equiv\text{C})$ AND $\nu(\text{C}\equiv\text{N})$ STRETCHING FREQUENCIES OF THE BIS(CYCLOPENTADIENYL)-BIS-(ALKYNYL)ZIRCONIUM COMPOUNDS ^a

Compound	$\nu(\text{C}\equiv\text{C})$ (cm^{-1}) ^c	$\nu(\text{C}\equiv\text{N})$ (cm^{-1})
$\text{Cp}_2\text{Zr}(\text{PE})_2$ ^b	2073s (2122)	
$\text{Cp}_2\text{Zr}(\text{CHE})_2$	2060m (2113)	
$\text{Cp}_2\text{Zr}(\text{HE})_2$	2058m (2117)	
$\text{Cp}_2\text{Zr}(\text{DPPN})_2$	2069m (2120)	2180m (2240)
$\text{Cp}_2\text{Zr}(\text{DPB})_2$	2078w (2109)	
$(\text{MeCp})_2\text{Zr}(\text{PE})_2$ ^b	2078s (2122)	
$(\text{MeCp})_2\text{Zr}(\text{CHE})_2$	2058w (2113)	
$(\text{MeCp})_2\text{Zr}(\text{HE})_2$	2060w (2117)	
$(\text{MeCp})_2\text{Zr}(\text{DPPN})_2$	2080m (2120)	2180m(br) (2240)
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	2070w (2109)	

^a $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{N})$ values of starting acetylenic compounds are given in parentheses. ^b See ref. 4.

^c s = strong, m = medium, w = weak, br = broad.

DPPN derivative, where a multiplet is observed. As in the case of the analogous titanium (IV) compounds [5], the loss of equivalence of the cyclopentadienyl ring protons in the DPPN derivatives may be due to the ligand size and the interaction between the nitrile group and zirconium(IV). However for the zirconium(IV) derivative of DPB only a singlet is observed for these protons, whereas for the corresponding titanium(IV) compound [5] a multiplet is observed. This may be due to a free rotation of the cyclopentadienyl rings in the zirconium derivative because of its greater size.

In the methylcyclopentadiene derivatives one or two multiplets are observed for the ring protons. The presence of a methyl group in the cyclopentadienyl ring causes a loss of equivalence of the ring protons.

Table 3 summarizes the proton chemical shifts for the acetylenic compounds obtained.

Electronic spectra

The electronic spectra of Cp_2ZrCl_2 and $(\text{MeCp})_2\text{ZrCl}_2$ show three electronic transitions at 254, 290 and 340 nm. These transitions are observed at 250, 265 and 310 nm in the alkynyl derivatives. There are no appreciable differences in the wave-lengths of these transitions between the chloro and the alkynyl complexes. Since the transition observed at 245–255 nm remains almost unaltered on changing the ligand, it is assigned, as in the analogous titanium(IV) derivatives, to an internal transition of the cyclopentadienyl ligand. The other two absorptions are assigned to charge-transfer ligand \rightarrow metal transitions, but it is not easy to distinguish between the two organic ligands.

Table 4 lists the electronic spectral data for the compounds.

TABLE 3
CHEMICAL SHIFTS (δ , ppm) OF ZIRCONIUM DERIVATIVES OF THE TYPE L_2ZrR_2 ^a

Compound	C_5H_5 or C_5H_4	C_6H_5	CH_3	CH_2	CH	$\text{CH}_3(\text{Cp})$
Cp_2ZrCl_2 ^b	6.52s					
$\text{Cp}_2\text{Zr}(\text{PE})_2$ ^c	6.42s	7.27s				
$\text{Cp}_2\text{Zr}(\text{CHE})_2$	6.42s			1.65m		
$\text{Cp}_2\text{Zr}(\text{HE})_2$	6.32s		1.00m	1.35m		
$\text{Cp}_2\text{Zr}(\text{DPPN})_2$	6.30m	7.36m		3.00d		
$\text{Cp}_2\text{Zr}(\text{DPB})_2$	6.36s	7.32s		3.00d	4.30t	
$(\text{MeCp})_2\text{ZrCl}_2$ ^b	6.31m					
$(\text{MeCp})_2\text{Zr}(\text{PE})_2$ ^c	6.22m					2.35s
$(\text{MeCp})_2\text{Zr}(\text{CHE})_2$	6.12m	7.17s				2.33s
$(\text{MeCp})_2\text{Zr}(\text{HE})_2$	6.22m			1.80m		2.29s
$(\text{MeCp})_2\text{Zr}(\text{DPPN})_2$	5.99m					
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	6.25m		1.00m	1.62m		2.28s
$(\text{MeCp})_2\text{Zr}(\text{DPPN})_2$	5.91m					
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	6.25m	7.36m		3.10d		2.20s
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	5.75m					
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	6.20m	7.20m		3.10d	4.15t	2.19s
$(\text{MeCp})_2\text{Zr}(\text{DPB})_2$	5.70m					

^a s = singlet, d = doublet, t = triplet, m = multiplet. ^b see ref. 1. ^c see ref. 4.

TABLE 4
ELECTRONIC SPECTRAL DATA

Compound	λ_{\max} (nm) (log ϵ)
Cp_2ZrCl_2	332 (3.95), 292 (4.25), 254 (4.25)
$\text{Cp}_2\text{Zr(PE)}_2$	310 (3.58), 268 (3.94), 248 (4.15)
$\text{Cp}_2\text{Zr(CHE)}_2$	298 (3.07), 264 (3.72), 246 (4.01)
$\text{Cp}_2\text{Zr(HE)}_2$	300 (3.05), 264 (3.66), 248 (3.93)
$\text{Cp}_2\text{Zr(DPPN)}_2$	304 (3.69), 264 (4.02), 248 (4.16)
$\text{Cp}_2\text{Zr(DPB)}_2$	305 (3.28), 270 (3.87), 250 (4.01)
$(\text{MeCp})_2\text{ZrCl}_2$	340 (4.02), 301 (4.25), 254 (4.27)
$(\text{MeCp})_2\text{Zr(PE)}_2$	290 (3.76), 265 (3.94), 248 (4.09)
$(\text{MeCp})_2\text{Zr(CHE)}_2$	304 (3.28), 264 (3.72), 246 (3.99)
$(\text{MeCp})_2\text{Zr(HE)}_2$	304 (3.33), 264 (3.66), 248 (3.95)
$(\text{MeCp})_2\text{Zr(DPPN)}_2$	308 (3.81), 268 (4.07), 250 (4.18)
$(\text{MeCp})_2\text{Zr(DPB)}_2$	304 (3.35), 262 (3.94), 245 (4.04)

Experimental

Phenylacetylene (Merck), cyclohexylacetylene (Merck) and n-octyne (Fluka) were obtained from commercial sources and distilled before use.

Bis(cyclopentadienyl)zirconium dichloride and bis(methylcyclopentadienyl)zirconium dichloride were prepared as described by King [7] and Reynolds [8] respectively.

4,4-diphenylbutyne (HDPB) was synthesized by a published method [5].

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

The sodium salts of acetylenic compounds were prepared as previously described [11].

All experiments were performed under purified nitrogen. Organic solvents were purified by conventional methods. Before use, they were freed from oxygen by repeated degassing and saturating with nitrogen.

Elemental analyses for C, H, N were carried out with the Microanalytical Hewlett-Packard 185 apparatus. Zirconium was determined gravimetrically as ZrO_2 . Infrared spectra in the region $4000\text{--}200\text{ cm}^{-1}$ were scanned on a Perkin-Elmer 325 spectrometer and samples prepared 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 (with 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. The melting points were measured with a Buchi apparatus and are uncorrected; in all cases decomposition occurred on melting.

General method of preparation

The bis(alkynyl)zirconium derivatives were prepared in an inert atmosphere by reaction of a suspension of the corresponding sodium alkynylide in anhydrous ether and the appropriate L_2ZrCl_2 in a molar ratio of 2/1. After the addition of reagents, the mixture was stirred for 4 hours at room temperature,

filtered, and concentrated to about 1/3 of the initial volume. Pentane or hexane was added. After standing at 0°C for 24 hours a precipitate of $L_2Zr(C\equiv C-R)_2$ appeared. This was filtered off on a G-4 fritted disc, washed with pentane or hexane, and dried in vacuum.

Bis(cyclopentadienyl)bis(phenylethynyl)zirconium(IV). Sodium phenylethynylide (0.49 g, 4 mmol) and bis(cyclopentadienyl)zirconium dichloride (0.58 g, 2 mmol) yielded 0.43 g (60%) of the complex, as an ochre microcrystalline solid. This compound was previously obtained by Jenkins et al. [4] from $Cp_2Zr[N(CH_3)_2]_2$ and phenylacetylene. The IR and 1H NMR spectra of the compounds obtained by both methods are identical.

Bis(cyclopentadienyl)bis(cyclohexylethynyl)zirconium(IV). Sodium cyclohexylethynylide (0.52 g, 4 mmol) and bis(cyclopentadienyl)zirconium dichloride (0.58 g, 2 mmol) yielded 0.45 g (53%) of the complex, as a pale yellow microcrystalline solid, m.p. 230°C (dec.). (Found: C, 71.29; H, 7.45; Zr, 20.37. $C_{26}H_{32}Zr$ Calcd.: C, 71.72; H, 7.36; Zr, 20.92%).

Bis(cyclopentadienyl)bis(octynyl)zirconium(IV). Sodium octynylide (0.53 g, 4 mmol) and bis(cyclopentadienyl)zirconium dichloride (0.58 g, 2 mmol) yielded 0.44 g (51%) of the complex, as a pale yellow microcrystalline solid, m.p. 225°C (dec.). (Found: C, 71.45; H, 7.96; Zr, 21.20. $C_{26}H_{36}Zr$ Calcd.: C, 71.07; H, 8.20; Zr, 20.73%).

Bis(cyclopentadienyl)bis(4-cyano-4,4-diphenylbutynyl)zirconium(IV). Sodium 4-cyano-4,4-diphenylbutynylide (0.51 g, 2 mmol) and bis(cyclopentadienyl)zirconium dichloride (0.29 g, 1 mmol) yielded 0.31 g (48%) of the complex, as an ochre microcrystalline solid, m.p. 130°C (dec.). (Found: C, 77.64; H, 4.53; N, 4.27; Zr, 13.75. $C_{44}H_{34}N_2Zr$ Calcd.: C, 77.53; H, 4.22; N, 4.11; Zr, 13.36%).

Bis(cyclopentadienyl)bis(4,4-diphenylbutynyl)zirconium(IV). Sodium 4,4-diphenylbutynylide (0.41 g, 2 mmol) and bis(cyclopentadienyl)zirconium dichloride (0.29 g, 1 mmol) yielded 0.30 g (49%) of the complex, as an ochre microcrystalline solid, m.p. 135°C (dec.). (Found: C, 79.94; H, 5.20; Zr, 14.84. $C_{42}H_{36}Zr$ Calcd.: C, 79.87; H, 5.70; Zr, 14.42%).

Bis(methylcyclopentadienyl)bis(phenylethynyl)zirconium(IV). Sodium phenylethynylide (0.49 g, 4 mmol) and bis(methylcyclopentadienyl)zirconium dichloride (0.64 g, 2 mmol) yielded 0.52 g (58%) of the complex, as a light brown microcrystalline solid. This compound was obtained by Jenkins et al. [4] from bis(methylcyclopentadienyl)bis(dimethylamido)zirconium and phenylacetylene. The IR and 1H NMR spectra of the compounds obtained by both methods are identical.

Bis(methylcyclopentadienyl)bis(cyclohexylethynyl)zirconium(IV). Sodium cyclohexylethynylide (0.52 g, 4 mmol) and bis(methylcyclopentadienyl)zirconium dichloride (0.64 g, 2 mmol) yielded 0.45 g (50%) of the complex, as a white-yellow microcrystalline solid, m.p. 234°C (dec.). (Found: C, 72.12; H, 8.10; Zr, 19.24. $C_{28}H_{36}Zr$ Calcd.: C, 72.57; H, 7.77; Zr, 19.65%).

Bis(methylcyclopentadienyl)bis(octynyl)zirconium(IV). Sodium octynylide (0.53 g, 4 mmol) and bis(methylcyclopentadienyl)zirconium dichloride (0.64 g, 2 mmol) yielded 0.44 g (49%) of the complex, as a pale yellow microcrystalline solid, m.p. 230°C (dec.). (Found: C, 71.48; H, 8.17; Zr, 19.72. $C_{28}H_{40}Zr$ Calcd.: C, 71.95; H, 8.56; Zr, 19.49%).

Bis(methylcyclopentadienyl)bis(4-cyano-4,4-diphenylbutynyl)zirconium(IV). Sodium 4-cyano-4,4-diphenylbutynylide (0.51 g, 2 mmol) and bis(methylcyclopentadienyl)zirconium dichloride (0.32 g, 1 mmol) yielded 0.31 g (44%) of the complex, as an ochre microcrystalline solid, m.p. 136°C (dec.). (Found: C, 77.52; H, 5.78; N, 3.21; Zr, 13.06. C₄₆H₃₈N₂Zr Calcd.: C, 77.86; H, 5.36; N, 3.95; Zr, 12.83%).

Bis(methylcyclopentadienyl)bis(4,4-diphenylbutynyl)zirconium(IV). Sodium 4,4-diphenylbutynylide (0.41 g, 2 mmol) and bis(methylcyclopentadienyl)zirconium dichloride (0.32 g, 1 mmol) yielded 0.30 g (45%) of the complex as a white-yellow microcrystalline solid, m.p. 132°C (dec.). (Found: C, 79.85; H, 5.84; Zr, 13.64. C₄₄H₄₀Zr Calcd.: C, 80.12; H, 6.07; Zr, 13.81%).

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