

# Exploring reactivity of a bis-sulfonium zirconocene-ate dimer: Synthesis of various zwitterionic phosphonium anionic zirconocene complexes

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Dedicated to Professor Doctor Gerhard Erker on the occasion of his 60th birthday  
in recognition of his important contributions in organometallic chemistry.

## Abstract

Formal [3+2] cycloaddition reactions between the bis-sulfonium zirconocene-ate dimer  $[\text{Cp}_2\text{ZrS}^{\ominus}\text{CHPhCH}=\text{C}(\text{PPh}_2)_2]^{\oplus}$  **1a** and methylpropionate, benzaldehyde and carbon disulfide afforded stable zwitterionic phosphonium zirconocene-ate complexes **2–4**, respectively, with two orthocondensed five-membered heterocycles. X-ray crystal structure of **4** has been determined. Elemental chalcogens (S, Se, Te) gave rise also to a new variety of five-coordinate zirconium(IV) complexes (**5–7**) by a formal [3+1] cycloaddition reaction. In these bicyclic zirconates, sulfur is included in a five-membered ring while the second chalcogen is in a four-membered one.  
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**Keywords:** Zwitterionic complexes; Zirconocene-ate; Anionic zirconocene; Phosphonium; Sulfonium; Chalcogens

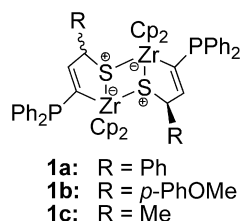
## 1. Introduction

Among the tremendous development of the chemistry of transition metal complexes, zirconocene complexes play a particular role. Since the discovery of the catalytic properties of zirconium metallocenes, the usefulness of such complexes for the development of modern synthetic methodology has been demonstrated [1,2]. In these applications, bis(cyclopentadienyl) complexes have been extensively studied and presented very often a synthetical interest. Beside the classical 16-electron zirconium complexes, cationic 14-electron *ansa* metallocenes are the most active catalytic species in the homogeneous polymerization processes of olefins while transient 14-electron zirconocene equivalents such as alkene, alkyne or aryne complexes and related one are the key intermediate species in various stoichiometric transformations. In parallel, pentavalent 18-

electron complexes are often postulated as key intermediates in a number of both stoichiometric and catalytic reactions. Only some of these zirconocene-ate complexes have been isolated and characterized by X-ray diffraction [3]. Furthermore few reactions are described starting from stable zwitterionic zirconocene complexes in marked contrast with the reactivity of unstable anionic ones. Recently we reported a novel class of reactive zirconates: the bis-sulfonium zirconocene-ate dimers **1** prepared from a toluene solution of diphenylphosphinoacetylene and a zirconocene thioaldehyde species generated *in situ* from dimethylzirconocene and  $\text{RCH}_2\text{SH}$ . These 18-electron zirconium complexes have been cleaved with borane to afford the corresponding monomeric  $\text{BH}_3$  protected phosphinozirconathiolanes, thus pointing out a weak association through bridging sulfur atom in dimers **1** [4,5]. Pursuing our exploration of the reactivity of these promising dimers, here we describe the easy access to a novel class of stable zwitterionic phosphonium thiozirconocene-ate complexes containing up to three different Zr–X (X = S, C, O or Se or Te)  $\sigma$ -bonds using both

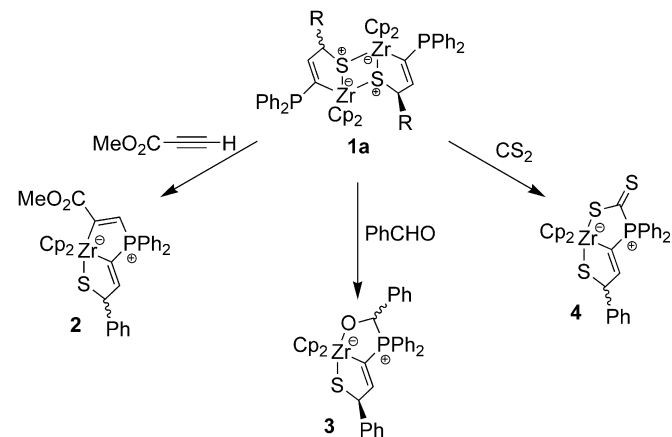
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nucleophilic properties of tertiary phosphines and the Lewis acid character of zirconium(IV) complexes.



## 2. Results and discussion

Formal [3+2] cycloaddition reactions [6] involving the bis-sulfonium zirconocene-ate dimer **1a** and methylpropiolate, benzaldehyde or carbon disulfide led to zwitterionic



Scheme 1. Synthesis of zwitterionic (phosphonium anionic zirconocene-ate) complexes **2–4** by [3+2] cycloaddition.

phosphonium anionic zirconocene complexes (**2–4**) containing at least one group 16 atom (S, O) directly bonded to the metal (Scheme 1).

Thus, addition of  $\text{HC}\equiv\text{CCO}_2\text{Me}$ ,  $\text{PhCHO}$  and  $\text{CS}_2$  (2 equiv.) to a suspension of  $[\text{Cp}_2\text{ZrSCHPhCH}=\text{C}(\text{PPh}_2)]_2$

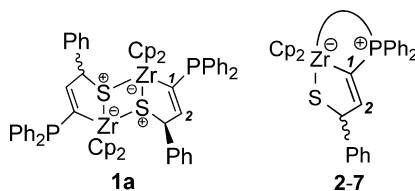
**1a** (mixture of diastereoisomers in a 1:1 ratio) in toluene at room temperature gave in 72–84% isolated yield the complexes **2–4**. From their elemental analysis, compounds **2–4** appeared to have a correct composition for a 1:0.5 adduct of the two starting reagents [alkyne, aldehyde or heterocumulene: **1a**]. The  $^{31}\text{P}$  NMR spectra showed the clean formation of a unique phosphorus product (singlet,  $32.6 < \delta < 38.4$  ppm) in the region expected for a zwitterionic (phosphonium anionic zirconium) derivative [7–9]. As found for the analogous organo-zirconocene-ate complexes reported by Majoral's group (prepared from the phosphinozirconaindene  $\text{Cp}_2\text{ZrC}(\text{PPh}_2)\text{CH}(o\text{-C}_6\text{H}_4)$  and various terminal alkynes), complex **2** was obtained as one regioisomer [7]. Surprisingly, only one racemate was detected for zirconate **3** suggesting a diastereoselective cycloaddition of benzaldehyde with the dimer **1a**. In addition to the two singlets corresponding to the unequivalent  $\eta^5$ -cyclopentadienyl ligands, the  $^1\text{H}$  NMR spectra revealed the presence of the ethylenic and the methylenic protons from the thiolane skeleton (Table 1). Typical  $^{13}\text{C}$  NMR data were detected for these pentavalent zirconocene-ate complexes (Table 1) [7–9]. The signal of the  $\text{sp}^2$ -carbon atom (C1) linked to zirconium and phosphorus was significantly shifted to high field with a low carbon–phosphorus coupling constant ( $\delta$  from 158.7 to 164.7 ppm with  $0 \leq {}^1J_{\text{PC}} < 8.3$  Hz, to be compared with  $\delta = 181.3$ , 180.8 ppm,  ${}^1J_{\text{PC}} = 92.2$  Hz for **1a** and  $\delta = 191.5$  ppm,  ${}^1J_{\text{PC}} = 49$  Hz for  $\text{Cp}_2\text{ZrC}(\text{PPh}_2)\text{CH}(o\text{-C}_6\text{H}_4)$  [10]). In marked contrast, the deshielded chemical shift at 172–

Table 1  
Selected NMR spectroscopic data<sup>a</sup> for the anionic five-coordinate zirconocene complexes **2–7**<sup>b</sup>

Compound	$\delta^{31}\text{P}$	$\delta^1\text{H}$ ( $J_{\text{HP}}$ ) <sup>a</sup>		$\delta^{13}\text{C}$ ( $J_{\text{CP}}$ ) <sup>a</sup>	
		Cp	=CH	C1	C2
<b>1a</b> <sup>c</sup>	−1.1, −1.4	5.56, 5.71, 5.94, 6.08	6.78, 6.85 (15.6)	180.8, 181.8 (92.2)	154.2, 155.1 (9.2)
<b>2</b>	35.6	5.88, 6.03	7.91 (18.8)	159.5 (8.3)	174.4 (3.5)
<b>3</b>	32.6	5.99, 6.15	7.32	164.7	172.2
<b>4</b>	38.4	5.83, 6.10	7.31 (11.8)	158.7	176.8 (2.8)
<b>5</b>	33.0	5.92 (1), 6.06 (1)	7.45	152.3	164.8
<b>6</b>	19.6 <sup>d</sup>	5.91, 6.07	7.56 (9.4)	152.4 (10.3)	165.3 (4.6)
<b>7</b>	−36.4 <sup>d</sup>	5.88, 6.13	7.92	154.0 (20.7)	165.9

<sup>a</sup> Chemical shifts in ppm and couplings (between parentheses) in Hz.

<sup>b</sup> The numbering system is as follows:



<sup>c</sup> Both diastereoisomers.

<sup>d</sup>  $J_{\text{PSc}} = 490$  Hz,  $J_{\text{PTc}} = 1171$  Hz.

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