

## Reactivity of the dinuclear fulvalene cyclopentadienyl zirconium cationic species

### $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]^+$ with isocyanides and carbon monoxide: insertion reactions, spectroscopic characterization and synthetic aspects

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Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

#### Abstract

The dinuclear cationic zirconium compound  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **1** reacts in dichloromethane at  $-78^\circ\text{C}$  with three equivalents of RNC (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) via insertion into the Zr- $\mu$ -methylene bond to give the new zirconium cationic species  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{Cl})(\text{CN}^i\text{Bu})\{\mu\text{-}[\eta^2\text{-CN}^i\text{Bu-CH}_2\text{-}\eta^2\text{-CN}^i\text{Bu})\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **2** and  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{Cl})\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\{\mu\text{-}\eta^2\text{-}\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\text{-CH}_2\text{-}\eta^2\text{-}\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\}\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **3**, whereas reaction with CO affords the ketene compound  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-Cl})\{\mu\text{-OC(=CH}_2)\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **4**. The new complexes reported herein were characterized by elemental analysis and IR and NMR spectroscopy. © 2001 Published by Elsevier Science B.V.

**Keywords:** Zirconium; Dinuclear fulvalene compounds; Cations derivatives; Isocyanides insertion; Carbon monoxide insertion

#### 1. Introduction

The isolation of dinuclear Group 4 metal compounds based on the use of the bridging fulvalene ligand has received increasing interest over the recent years [1]. In addition to the use of the cationic  $d^0$  species  $[\text{MCp}_2\text{RL}]^+$  as homogeneous catalysts in alkene polymerization processes, much work has also been devoted to studying the reactivity of these mononuclear 14-electron cations with CO, RNC, olefins, acetylenes or allenes, leading to the discovery of novel organometallic compounds [2–4]. In contrast, cationic homo- and hetero-dinuclear Group 4 metal compounds have not received much attention [5], in spite of their significance in the polymerization processes [5b] and in many other

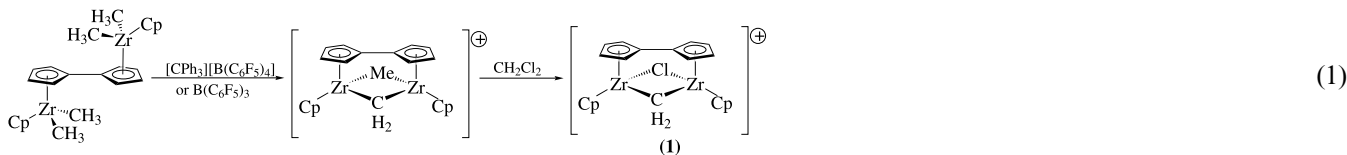
heterogeneous C–H activation and C–C bond formation catalytic reactions [6]. Novel dinuclear cationic zirconium complexes prepared from dialkynyl zirconocene derivatives have been reported as interesting reagents in stoichiometric and catalytic reactions [5e,7].

Different insertion reactions into the alkylidene-bridging group have been reported [8] for middle and late transition metal complexes. However, studies concerning the reactivity of the ‘Zr–CH<sub>2</sub>–Zr’ fragment are limited due to its inaccessibility. Some heterodimetallic Zr–Th and Zr–Al derivatives containing the  $\mu\text{-CH}_2$  unit are known [9]. We reported [10a] the immediate and quantitative formation of the red  $\mu\text{-CH}_2$  cationic species  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_3)(\mu\text{-CH}_2)(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]^+$  Eq. (1) from the reaction of the tetramethyl zirconium fulvalene complex  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{CH}_3)_2]_2\text{-}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]$  with  $[\text{CPh}_3]\text{[B(C}_6\text{F}_5)_4]$  or  $\text{B(C}_6\text{F}_5)_3$  in dichloromethane at  $-60^\circ\text{C}$ . The reactions

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of this cationic species with donor ligands and chloro-carbon solvents have been studied and the formation of the  $\mu$ -chloro  $\mu$ -methylene fulvalene cationic compound  $[\{Zr(\eta^5-C_5H_5)\}_2(\mu-CH_2)(\mu-Cl)(\mu-\eta^5-C_5H_4-\eta^5-C_5H_4)] [BMe(C_6F_5)_3]$  **1** [10b] was observed. The reactivity of dinuclear cationic zirconium species with unsaturated organic molecules has also been described [10c,d].



In this paper we report the results observed when isocyanides and carbon monoxide are inserted into the 'Zr-CH<sub>2</sub>-Zr' fragment of the cationic  $\mu$ -methylene zirconium compound **1**, and the structural characterization of the resulting products by elemental analysis and IR and NMR spectroscopic methods.

## 2. Results and discussion

### 2.1. Insertion of isocyanides

The reaction of the methylene-bridged cationic complex **1** with three equivalents of isocyanides RNC (R = 'Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in dichloromethane at -78 °C afforded the new zirconium cationic species  $[\{Zr(\eta^5-C_5H_5)\}_2(Cl)(CNR)\{\mu-[ \eta^2-C(NR)-CH_2-\eta^2-C(NR) ]\}(\mu-\eta^5-C_5H_4-\eta^5-C_5H_4)] [BMe(C_6F_5)_3]$  [R = 'Bu (**2**), 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**3**)] (Scheme 1) which were isolated (60–67% yield) as yellow crystalline solids and characterized by elemental analysis and IR and NMR spectroscopies.

When the same reactions were carried out using 1:1 and 1:2 molar ratios of these isocyanides, mixtures containing a low proportion of **2** or **3** together with unidentified products were obtained. Treatment of **1** with any molar ratio of isocyanide at room temperature allows only unaltered starting materials to be recovered, indicating that coordination of the isocyanide to the metal center before the insertion reaction is an entropically driven process with coordination consequently more favorable at low temperature. However, after the formation of compounds **2** and **3**, at low temperature,

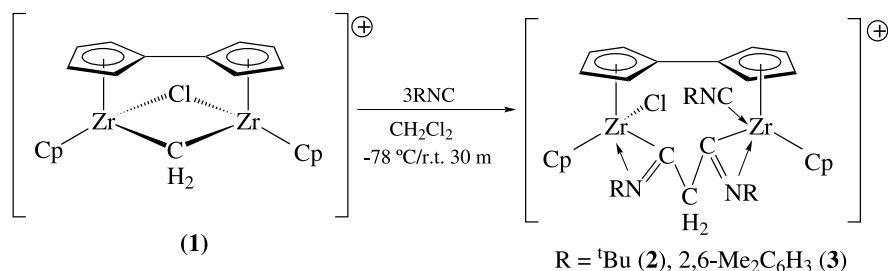
the isocyanide ligand remains coordinated when the substances are stored as solids at room temperature or in solution under an inert atmosphere.

Compounds **2** and **3** are oxygen and moisture sensitive and show remarkable thermal stability in the solid state. This allows them to be stored for weeks without

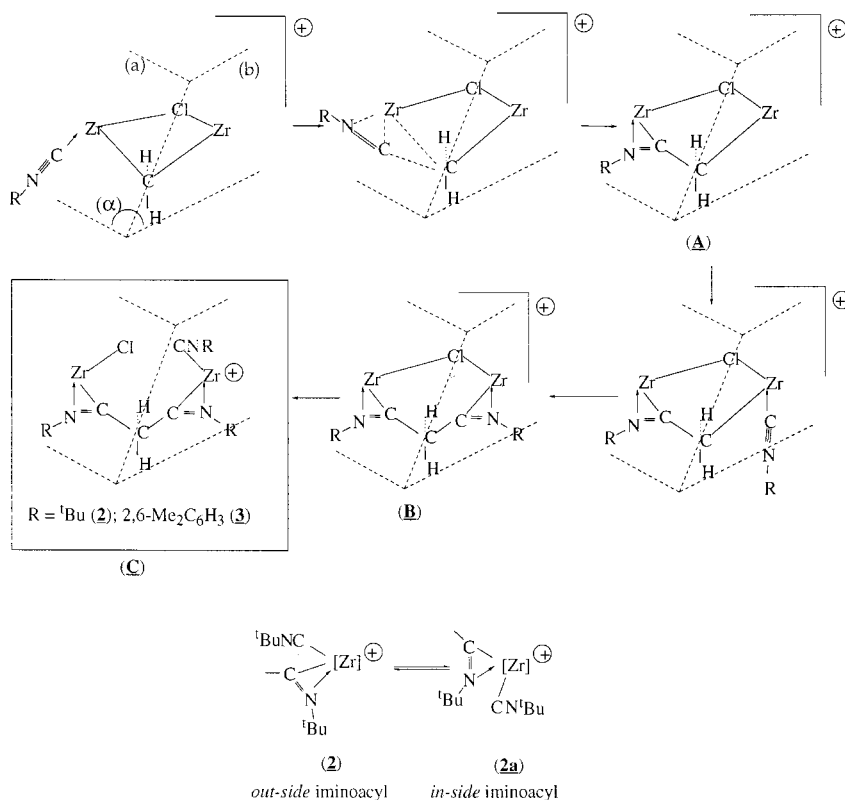
decomposition under an inert atmosphere, although they decompose in dichloromethane and chloroform solutions at room temperature and are insoluble in toluene and hydrocarbons.

The IR spectra of complexes **2** and **3** show  $\nu(C\equiv N)$  absorptions bands at 2199 and 2182 cm<sup>-1</sup>, respectively, which are shifted to significantly higher wavenumbers compared with the free isocyanides (2143 cm<sup>-1</sup> for 'BuN≡C and 2155 cm<sup>-1</sup> for 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N≡C). These data are consistent with isocyanides coordinated to a d<sup>0</sup> zirconium(IV) cationic compound. Characteristic IR absorptions between 1610 and 1588 cm<sup>-1</sup> due to  $\nu(C=N)$  vibrations were also observed [7,11].

The <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 195 K) spectra of **2** and **3** show two singlets, each integrating as 5H, due to non-equivalent cyclopentadienyl rings. The fulvalene protons appear as eight multiplets with a relative intensity of 1H, corresponding to two ABCD spin systems (see Section 4) and revealing that none of the protons are equivalent. The <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 233 K) spectra exhibit ten resonances for the fulvalene group and two resonances for the cyclopentadienyl ligands. This behavior demonstrates that they are dinuclear compounds containing two zirconium atoms with different ligand arrangements. The methylene protons appear as two doublets ( $\delta_{\text{average}} = 3.02$  for **2** and  $\delta_{\text{average}} = 3.57$  for **3**), as expected for an AB spin system, and the methylenic carbon atoms are identified in the <sup>13</sup>C{<sup>1</sup>H}-NMR spectra as a doublet of doublets (**2**) and as a pseudotriplet (**3**) in the region of  $\delta$  45–55 with <sup>1</sup>J<sub>CH</sub> coupling constants between 125–137 Hz. All the



Scheme 1.



Scheme 2. Planes (a) and (b) symbolize the bent metallocene wedges for the zirconium atoms and  $\alpha$  denotes the angle between both planes. The fulvalene ligand is omitted for clarity.

methylene protons and carbon resonances are significantly shifted upfield with respect to the corresponding signals in compound **1** [for example for compound **2**: <sup>1</sup>H-NMR:  $\Delta\delta_{\text{average}} = \delta_{\text{average}}(\mathbf{2}) - \delta_{\text{average}}(\mathbf{1}) = -4.48$  ppm; <sup>13</sup>C-NMR:  $\Delta\delta_{\text{average}} = \delta_{\text{average}}(\mathbf{2}) - \delta_{\text{average}}(\mathbf{1}) = -147.3$  ppm]. Two singlets and a broad signal shifted slightly to low field, all of them of the same relative intensity (9H), can be assigned to three different *tert*-butyl groups in **2**. Similar behavior was also observed in **3**, which shows four resonances of the same intensity (3H) due to the non-equivalent methyl protons on two different 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC ligands, indicating that there must be hindered rotation around N-aryl bonds, and one signal (6H) assigned to a third isocyanide ligand with equivalent methyl protons. The IR and NMR data for compounds **2** and **3** are consistent with the formulation drawn in Scheme 1.

Coordination of the isocyanide ligand to the empty orbital of the zirconium centers may locate the ligand *cis* to the methylene group or to the chloro bridges (Scheme 2). It is therefore reasonable to propose that the first two molecules of the isocyanide coordinate to each metal center *cis* to the methylene position and are immediately inserted into the 'Zr-CH<sub>2</sub>-Zr' bonds to give the bridging methylene-iminoacyl species (A) (see Scheme 2) followed by the methylene-di-iminoacyl species (B). The  $\eta^2$ -coordination of the nitrogen must be a

very weak interaction since the bridging methylene moiety avoids the *in-side* coordination which would provide a stronger bond [12]. This reaction is then followed by the cleavage of the  $\mu$ -chloro bridge with the coordination of the third isocyanide molecule to the resulting cationic zirconium center to give complexes **2** and **3** represented by (C). The IR  $\nu(\text{C}\equiv\text{N})$  absorption observed at higher wavelengths than for the free isocyanides demonstrates that the third isocyanide is coordinated to the metal rather than giving an assumed iminoketene by attack at the electrophilic iminoacyl carbon. The carbenoid character of the analogous acyl moiety is very well known and its reactivity has been studied extensively [13].

The cationic complexes **2** and **3** [(C) in Scheme 2] can therefore be considered as dinuclear molecules with two zirconium centers doubly bridged by the methylene-di-iminoacyl and fulvalene ligands. They could also be considered as one cationic zirconocene fragment coordinated to an iminoacyl ligand and stabilized by the coordination of an isocyanide adduct. Bochmann and Jordan have previously prepared some  $\eta^2$ -iminoacyl *tert*-butylisocyanide mononuclear cationic titanium and zirconium  $[\text{MCP}_2\{\eta^2\text{-N,C-C(Me)N}(\text{tBu})\}(\text{CN}^t\text{Bu})]^+$  complexes [11]. This structural disposition is the kinetic product of the reaction in which each iminoacyl nitro-

gen occupies the out-side position where  $\eta^2$ -coordination of the iminoacyl ligands, if it exists, would only involve a very weak interaction. *In-side* coordination of iminoacyl and related ligands is generally preferred [12], analogous to the preference of the *in-side*  $\eta^2$ -acyl conformer found in titanium and zirconium compounds as evidenced by the energy profiles studies [14]. However, X-ray crystallography shows that in the cationic compound  $[\text{ZrCp}_2(\eta^2\text{-N,C-picolyl})(\text{PMe}_3)]^+$  the nitrogen atom prefers to be coordinated *out-side* [15]. Some examples are also known in which the *in-side* and the *out-side* isomers are about equivalent in energy and the presence of a mixture of both isomers in solution was deduced from  $^1\text{H-NMR}$  spectroscopy [12,15,16]. With this *out-side* disposition the three isocyanide and di-iminoacyl *tert*-butyl ligands for complex **2** are not equivalent, giving three resonances for the corresponding protons in the  $^1\text{H-NMR}$  spectrum, while compound **3** gives one set of five resonances (integrating ratio of 3:3:3:3:6) for the methyl protons. There was a recent precedent for two non-equivalent methyl isocyanide groups in the neutral dinuclear complex  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{X}\}_2\{\mu\text{-CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}](\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]$  ( $\text{X} = \text{Cl}, \text{CH}_3$ ) [17] which has an asymmetric phenyl isocyanide bridge ligand. However, the dinuclear cationic complex  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CN}^t\text{Bu})(\text{CH}_3)\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}](\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)[\text{BMe}(\text{C}_6\text{F}_5)_3]$  [10d], which has a coordinated phenyl isocyanide ligand, shows equivalent methyl isocyanide groups in the NMR spectrum. The  $^{13}\text{C-NMR}$  ( $\text{CD}_2\text{Cl}_2$ ) spectra show two resonances for the iminoacyl carbon atoms in compound **3** at  $\delta$  235.1 and 238.3 whereas only one signal at  $\delta$  224.3 is observed for compound **2**. In both cases the resonances due to the carbon atom of the coordinated isocyanide were not observed [7b–d,11].

To make a definitive assignment, the spin–lattice relaxation times ( $T_1$  in s) for the methylene and *tert*-butyl protons were measured for compound **2** at 298 K and the values, which show characteristic  $T_1$  values, are summarized in Table 1 [18].

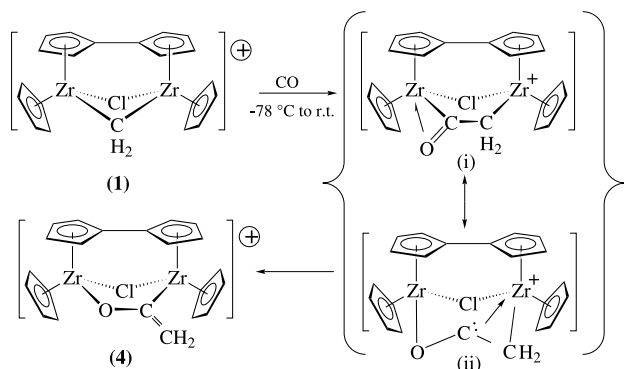
The resonance at  $\delta$  1.52, which shows a substantially higher  $T_1$  (2.660 s) value, has been assigned to the *tert*-butyl group of the coordinated isocyanide whereas

the resonances at  $\delta$  1.31 and 1.69, which have much closer  $T_1$  values (1.21 and 1.76 s, respectively), have been assigned to the *tert*-butyl groups of the two coordinated iminoacyl ligands. On the other hand, the  $T_1$  value for the resonance at  $\delta$  1.31 is lower than that for the resonance at  $\delta$  1.69, indicating a different coordination environment for the two corresponding *tert*-butyl groups. The signal at  $\delta$  1.31 can be assigned to the *tert*-butyl group bound to the iminoacyl substituent with stronger  $\eta^2$ -coordination to the cationic zirconium center, where the decreased  $T_1$  implies an increased interaction with the cyclopentadienyl protons. Consequently, the signal at  $\delta$  1.69 can be assigned to the *tert*-butyl group bound to the iminoacyl ligand with a weaker  $\eta^2$ -interaction than that bound to the neutral zirconium center. Analogous spectroscopic features have been observed for the few known  $[\text{MCp}_2\{\eta^2\text{-N,C-C}(\text{Me})\text{N}^t(\text{Bu})\}(\text{CN}^t\text{Bu})]^+$  complexes [11]. A similar behavior would be expected for complex **3**.

When the  $\text{CD}_2\text{Cl}_2$  solution of **2** was maintained at room temperature, a new compound **2a** was formed after 2 h. The  $^1\text{H-NMR}$  spectrum of **2a** exhibited resonances similar to **2** though shifted slightly (see Section 4). It showed two singlets for the cyclopentadienyl ring protons and eight multiplets for two ABCD spin systems corresponding to the fulvalene group (two and ten resonances, respectively, in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum). The  $^1\text{H-NMR}$  spectrum also contains two doublets ( $\delta_{\text{average}} = 3.05$ ,  $^2J_{\text{HH}} = 7.5$  Hz) for an AB spin system corresponding to the  $\text{CH}_2$  group with a methylenic carbon atom resonance centered at  $\delta$  55.7 in its  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum. Two singlets at  $\delta$  1.19 and 1.68 and a broad signal at  $\delta$  1.54 were also observed for the *tert*-butyl protons. After 24 h, the relative intensity of the resonances due to **2** and **2a** indicated a molar ratio of 1:1 and this spectral pattern remained unchanged for two weeks. When the same experiment was carried out by adding an excess of isocyanide to the  $\text{CD}_2\text{Cl}_2$  solution of **2** the transformation was more rapid and the same molar ratio resulted after 30 min. Compound **3** also showed a similar behavior. This behavior can be explained by considering that a more favorable structural disposition than that of **2** would be obtained if the isocyanide ligand is dissociated from the cationic zirconium center and then re-coordinated, moving the isocyanide ligand to the *cis* position in relation to the iminoacyl nitrogen atom, since it would leave this iminoacyl nitrogen atom in an *in-side*  $\eta^2$ -coordination (**2a**) (Scheme 2). The dissociation and re-coordination process occurs more rapidly with increased ligand concentration, which favors the isocyanide coordination. Similar interconversion of  $\eta^2\text{-N,C-picolyl}$  *in-side* and *out-side* coordinated cationic mononuclear zirconium isomers has been observed with an exchange of the coordinated and free THF to give a mixture of

Table 1  
NMR data for compounds **2** and **2a**: chemical shifts (ppm) and spin–lattice relaxation times [ $T_1$ ] (s) measured at 298 K for the methylene and *tert*-butyl protons

	Compound <b>2</b>	Compound <b>2a</b>
$-\text{CH}_2-$	3.80; [0.79] 2.25; [1.08]	4.85; [0.71] 1.26; [0.95]
$^t\text{Bu}$	1.31; [1.21]	1.19; [0.89]
$^t\text{Bu}$	1.69; [1.76]	1.68; [1.84]
$^t\text{Bu}_{\text{coordinated}}$	1.52; [2.660]	1.52; [2.660]



Scheme 3. Planes (a) and (b) symbolize the bent metallocene wedges for the zirconium atoms and  $\alpha$  denotes the angle between both planes. The fulvalene ligand is omitted for clarity.

both isomers in a 1:1 thermodynamic ratio which does not change after weeks at ambient temperature or after heating to 66 °C [15].

The  $T_1$  parameters for the *tert*-butyl and  $\text{CH}_2$  resonances of **2a** (see Table 1) are very close to those found for **2**. The most significant difference is the slightly lower  $T_1$  value found for the iminoacyl ligand coordinated to the zirconium on which the dissociation and re-coordination process takes place. All these data are in agreement with the structural dispositions proposed for **2** and **2a** as shown in Scheme 2.

## 2.2. Insertion of carbon monoxide

The migratory insertion of carbon monoxide or isocyanide ligands is one of the most simple and interesting organometallic reactions which usually gives structurally related acyl and iminoacyl complexes [19]. The results observed in the reaction with isocyanides motivated us to study a similar reaction of the 'Zr-CH<sub>2</sub>-Zr' unit with the isoelectronic carbon monoxide (CO) molecule. A Schlenk tube containing dichloromethane under an argon atmosphere was charged with **1**. After cooling to -78 °C the argon was replaced by CO. The initial red color of the solution changed to yellow and after appropriate work up an orange–yellow microcrystalline solid was isolated in ca. 76% yield which was characterized by elemental analysis, IR and RMN spectroscopies, as the  $\eta^2$ -ketene cationic complex [ $\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-Cl})\{\mu\text{-OC(=CH}_2)\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)\text{][BMe(C}_6\text{F}_5)_3]$  **4** (Scheme 3). Some ketene and related enolate complexes of the early transition metals with different coordination modes have been prepared by the insertion of CO into metal–alkyl bonds [20,21], but to the best of our knowledge compound **4** is the first example of a dinuclear zirconium cation containing the bridging  $\eta^2$ -coordinated ketene ligand.

Complex **4** does not insert any additional CO molecules, even under a carbon monoxide pressure of 1 atm at room temperature for weeks. Complex **4** is oxygen and moisture sensitive and its thermal stability allows it to be stored under an inert atmosphere for weeks as a solid. It is soluble in dichloromethane or chloroform, the solution remaining unchanged for days, but it is insoluble in toluene and hydrocarbons.

The IR spectrum of complex **4** shows a  $\nu(\text{CCO})$  stretching vibration at 1595  $\text{cm}^{-1}$ , shifted to lower wavenumbers with respect to those found for free ketenes (2100–2200  $\text{cm}^{-1}$ ) [20] and expected for ligands of this type coordinated to a metal center. The  $^1\text{H-NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 195 K) spectrum of compound **4** shows two singlets for the cyclopentadienyl protons and eight multiplets for the two fulvalene ABCD spin systems, integrating as 5H and 1H, respectively, consistent with non-equivalent ligand coordination at the zirconium atoms. Consequently, two and ten resonances were observed, respectively, in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CD}_2\text{Cl}_2$ , 233 K) spectrum. The  $^1\text{H-NMR}$  spectrum also shows two doublets ( $\delta_{\text{average}} = 4.80$ ,  $^2J_{\text{HH}} = 2.0$  Hz) corresponding to the non-equivalent protons bound to the  $\text{sp}^2$  ketene carbon. As expected the resonance due to this methylenic carbon is observed in the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum at higher field ( $\delta$  94.7,  $J_{\text{CH}} = 163.6$  Hz) [22] than that corresponding to the zirconium coordinated carbon ( $\delta$  190.6) which is in the range typical for the metal–acyl compounds [23]. All these spectroscopic data are consistent with the structure of compound **4** shown in Scheme 3.

Attempts to obtain crystals for **2–4** suitable for X-ray crystallography studies were unsuccessful making solid-state confirmation of the proposed structures impossible, preventing the crystallographic characterization.

Compound **1** reacts with only one molecule of CO by insertion in one of the Zr–C bond of the 'Zr<sub>2</sub>- $\mu$ -CH<sub>2</sub>' unit with subsequent rearrangement to give the final ketene disposition, in contrast to the double insertion process observed for the isocyanide molecules. Compared with isocyanides, CO has a lower  $\sigma$ -donor capacity providing very weak interactions with high valent cationic  $\text{d}^0$  metal centers. Its coordination is immediately followed by insertion, providing a  $\eta^2$ -acyl species with a high carbenoid character responsible for its rapid transformation into a more stable bridging  $\eta^2$ -ketene derivative (Scheme 3). This isomerization to the ketene complex is consistent with the oxycarbene-like character of the early transition metal–acyl derivatives with the subsequent migration of the carbene–carbon atom to the second zirconium center. Similar 1,1-hydrogen and silicon migrations have been considered for mononuclear zirconium and thorium complexes to explain rearrangements from acyl to enolate derivatives [21h–j]. To the best of our knowledge, precedents for

the related processes in dinuclear derivatives are yet to be known. The poor  $\sigma$ -donor character of CO ensures that the reaction does not go further and the ketene complex **4** is the final product of this reaction.

### 3. Conclusions

We can conclude that the fulvalene ligand is a very convenient system to link the two zirconium atoms and provides a valuable strategy to design new types of cationic dinuclear zirconium derivatives, and to study their chemical and structural behaviors. We have studied the reactivity of the methylene group bridging two zirconium centers in the dinuclear cationic compound  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **1**. The reaction with isocyanides and carbon monoxide affords dinuclear zirconium cationic species through insertion processes.

We have observed that it is possible to produce cationic methylene-di-iminoacyl species  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{Cl})(\text{CN}^i\text{R})\{\mu\text{-}[\eta^2\text{-C}(\text{NR})\text{-CH}_2\text{-}\eta^2\text{-C}(\text{NR})]\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **2** and **3** by the insertion of two molecules of RNC (R = *t*-Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) into the Zr–C bonds of the ‘Zr–CH<sub>2</sub>–Zr’ fragment whereas only one molecule of CO reacts to give the  $\eta^2$ -ketene complex  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-Cl})\{\mu\text{-OC}(\text{=CH}_2)\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  **4**.

### 4. Experimental

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glove box model HE-63 or VAC HE-543-6. Solvents were purified by distillation under argon from an appropriate drying agent (sodium–potassium alloy for hexane and P<sub>2</sub>O<sub>5</sub> for CH<sub>2</sub>Cl<sub>2</sub>). *tert*-Butyl isocyanide and 2,6-dimethylphenyl isocyanide (Aldrich) were commercially obtained and used without further purification.  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  [**10b**] was prepared by the procedure described in the literature. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer using KBr pellets. NMR spectra were recorded on a Varian Unity 500 Plus spectrometer and chemical shifts are referenced to SiMe<sub>4</sub> via residual protons (<sup>1</sup>H) or the carbon resonances (<sup>13</sup>C) of the solvent.

#### 4.1. Synthesis of $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{Cl})(\text{CN}^i\text{Bu})\{\mu\text{-}[\eta^2\text{-CN}^i(\text{Bu})\text{-CH}_2\text{-}\eta^2\text{-CN}^i(\text{Bu})]\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$ (**2**)

*tert*-Butyl isocyanide (0.12 ml, 1.02 mmol) was added

using a syringe to a solution of  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  (0.35 g, 0.34 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) at –78 °C. The color of the solution changed from red to yellow. The reaction mixture was stirred overnight and then warmed to room temperature (r.t.) and stirred for 30 min. The solvent was removed and **2** was obtained as a yellow microcrystalline solid. Re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane gave 0.29 g (59%) of **2** as an orange crystalline solid. IR (KBr, cm<sup>–1</sup>):  $\nu(\text{C}\equiv\text{N})$  2199,  $\nu(\text{C}=\text{N})$  1585, 1610; <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, 195 K):  $\delta$  = 5.66, 6.48 (s, C<sub>5</sub>H<sub>5</sub>, 2 × 5H), 5.26, 5.43, 5.67, 6.02, 6.30, 6.34, 6.46, 6.51 (two ABCD spin system, C<sub>10</sub>H<sub>8</sub>, 8 × 1H), 2.25, 3.80 (AB spin system, CH<sub>2</sub>, 2 × 1H, <sup>2</sup>J<sub>HH</sub> = 8.5 Hz), 1.31, 1.52, 1.69 (s, *t*-Bu 3 × 9H), 0.50 (br) *Me*B; <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz, 233 K):  $\delta$  = 106.8, 114.9 (C<sub>5</sub>H<sub>5</sub>), 102.1, 104.8, 104.9, 105.9, 109.9, 111.0, 114.8, 122.8, 124.2, 120.6 (C<sub>10</sub>H<sub>8</sub>), 53.6 (CH<sub>2</sub>, <sup>1</sup>J<sub>CH</sub> = 125.3 Hz and <sup>1</sup>J<sub>CH</sub> = 136.8 Hz), 224.3 (CN<sup>*i*</sup>Bu); 29–31, 60–61 (CN<sup>*i*</sup>Bu), ≈ 10 (br) *Me*BAR<sub>3</sub>. Anal. Found: C, 52.04; H, 4.02; N, 2.75. Calc. for C<sub>55</sub>H<sub>50</sub>BClF<sub>15</sub>N<sub>3</sub>Zr<sub>2</sub>: C, 52.15; H, 3.98; N, 3.32%.

**2a**: <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, 273 K):  $\delta$  = 5.77, 6.47 (s, C<sub>5</sub>H<sub>5</sub>, 2 × 5H), 5.21, 5.90, 6.14, 6.15, 6.27, 6.28, 6.39, 6.48 (two ABCD spin system, C<sub>10</sub>H<sub>8</sub>, 8 × 1H), 1.26, 4.85 (AB spin system, CH<sub>2</sub>, 2 × 1H, <sup>2</sup>J<sub>HH</sub> = 7.5 Hz), 1.19, 1.54, 1.68 (s, *t*-Bu 3 × 9H), 0.50 (br) *Me*B; <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz, 233 K):  $\delta$  = 106.0, 115.0 (C<sub>5</sub>H<sub>5</sub>), 98.5, 103.6, 106.0, 106.5, 109.7, 113.1, 113.4, 119.3, 122.0, 122.6, (C<sub>10</sub>H<sub>8</sub>), 55.7 (CH<sub>2</sub>), 212.0 (CN<sup>*i*</sup>Bu), 28–31, 60–61 (CN<sup>*i*</sup>Bu), ≈ 10 (br) *Me*BAR<sub>3</sub>.

#### 4.2. Synthesis of $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\text{Cl})\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{-H}_3)\}\{\mu\text{-}\eta^2\text{-}\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\text{-CH}_2\text{-}\eta^2\text{-}\{\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\}(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$ (**3**)

2,6-Dimethylphenyl isocyanide (0.12 g, 0.88 mmol) was added to a solution of  $[\{\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-}\eta^5\text{-C}_5\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)]\text{[BMe(C}_6\text{F}_5)_3]$  (0.30 g, 0.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) at –78 °C. The color of the solution changed from red to yellow. The reaction mixture was stirred overnight and then warmed to r.t. and stirred for 30 min. The solvent was removed and **3** was obtained as a yellow microcrystalline solid. Re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>–*n*-hexane gave 0.28 g (67%) **3** as an orange crystalline solid. IR (KBr, cm<sup>–1</sup>):  $\nu(\text{C}\equiv\text{N})$  2182,  $\nu(\text{C}=\text{N})$  1588, 1616; <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz, 195 K):  $\delta$  = 6.10, 6.17 (s, C<sub>5</sub>H<sub>5</sub>, 2 × 5H), 5.85, 5.97, 6.02, 6.12, 6.22, 6.29, 6.30, 6.38 (two ABCD spin system C<sub>10</sub>H<sub>8</sub>, 8 × 1H), 3.49, 3.65 (AB spin system, CH<sub>2</sub>, 2 × 1H, <sup>2</sup>J<sub>HH</sub> = 8.0 Hz), 7.06–7.38 (m, 9H), 1.81 (s, 3H), 1.86 (s, 3H), 2.17 (s, 3H), 2.32 (s, 3H), 2.18 (s, 6H) (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 0.50 (br) *Me*B; <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz, 233 K):  $\delta$  = 108.7, 111.1 (C<sub>5</sub>H<sub>5</sub>), 199.7, 104.8, 107.1, 108.5, 114.8, 116.9, 117.0, 118.1, 119.1, 119.7 (C<sub>10</sub>H<sub>8</sub>), 46.0 (CH<sub>2</sub>, <sup>1</sup>J<sub>CH</sub> = 125.1 Hz),

235.1, 238.3  $CN(2,6-Me_2C_6H_3)$ ,  $\approx 10$  (br)  $MeBAR_3$ . Anal. Found: C, 57.08; H, 3.69; N, 2.76. Calc. for  $C_{67}H_{50}BClF_{15}N_3Zr_2$ : C, 57.04; H, 3.57; N, 2.98%.

#### 4.3. Synthesis of $[\{Zr(\eta^5-C_5H_5)\}_2(\mu-Cl)\{\mu-OC(=CH_2)\}(\mu-\eta^5-C_5H_4-\eta^5-C_5H_4)] [BMe(C_6F_5)_3]$ (**4**)

A Schlenk containing  $CH_2Cl_2$  (15 ml) was charged with  $[\{Zr(\eta^5-C_5H_5)\}_2(\mu-CH_2)(\mu-Cl)(\mu-\eta^5-C_5H_4-\eta^5-C_5H_4)] [BMe(C_6F_5)_3]$  (0.35 g, 0.34 mmol). After the solution was cooled to  $-78^\circ C$  the argon atmosphere was replaced by CO. The reaction mixture was stirred for 2 h and then slowly warmed to r.t. The color of the solution changed from red to yellow. The solvent was removed and **4** was obtained as a yellow microcrystalline solid. Re-crystallization from  $CH_2Cl_2$ -*n*-hexane gave 0.27 g (76%) **4** as an orange crystalline solid. IR (KBr,  $cm^{-1}$ ):  $\nu(CCO)$  1595;  $^1H$ -NMR ( $CD_2Cl_2$ , 500 MHz, 195 K):  $\delta = 6.21, 6.22$  (s,  $C_5H_5$ ,  $2 \times 5H$ ), 5.61, 5.70, 6.06, 6.14, 6.29, 6.53, 6.72, 6.99 (two ABCD spin system,  $C_{10}H_8$ ,  $8 \times 1H$ ), 4.50, 5.10 (AB spin system,  $CH_2$ ,  $2 \times 1H$ ,  $^2J_{CH} = 2.0$  Hz), 0.48 (br)  $MeB$ ;  $^{13}C\{^1H\}$ -NMR ( $CD_2Cl_2$ , 125 MHz, 233 K):  $\delta = 111.0, 117.8$  ( $C_5H_5$ ), 101.9, 106.9, 111.7, 111.8, 113.2, 113.4, 114.7, 116.6, 117.7, 122.2 ( $C_{10}H_8$ ), 94.7 ( $CH_2$ ,  $^1J_{CH} = 163.6$  Hz), 190.6 (CO),  $\approx 10$  (br)  $MeBAR_3$ . Anal. Found: C, 47.48; H 2.41. Calc. for  $C_{42}H_{25}BClF_{15}OZr_2$ : C, 47.60; H, 2.36%.

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