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Dinuclear cationic zirconium complexes with the fulvalene ligand. Synthesis and reactivity [1]

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Abstract

The reaction of $B(C_6F_5)_3$ with the tetramethyl zirconium fulvalene derivative $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ **1a** in CH_2Cl_2 at $-60°C$ gives the cationic compound $[\{Zr(C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2a**. A similar reaction using the 1,3-di(*tert*-butyl) cyclopentadienyl derivative $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ **1b** affords a mixture of compounds, none of them being isolable as pure substances. However, monitoring the reaction of $B(C_6F_5)_3$ with **1b** by variable temperature NMR spectroscopy, between $-80°C$ and 25°C, permits the observation, at low temperature, of the intermediate dimethyl μ-methyl cationic species $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)\}_2(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+$ **8b** which decomposes with evolution of methane to give the μ-methylene, μ-methyl complex $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2b**. In dichloromethane or chloroform complexes **2a** and **2b** undergo slow conversion to the μ-chloro, μ-methylene derivatives $[\{ZrCp'\}_2(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ ($Cp' = C_5H_5$ **3a**, $1,3\text{-}^tBu_2\text{-}C_5H_3$ **3b**) by a halide abstraction process. Prolonged exposure of **3b** to chlorocarbons gives the dichloro μ-chloro compound $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)Cl\}_2(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **9b**. The addition of an excess of donor ligands to a solution of **2a** in dichloromethane-d_2 at $-60°C$ affords the cationic adducts $[\{Zr(C_5H_5)\}_2(CH_3)L(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ [L = PMe_3 (**4a**), PMe_2Ph (**5a**), PPh_3 (**6a**), THF (**7a**)] obtained as a mixture of *syn*- and *anti*- isomers. The compound **5a** can be isolated as an analytically pure sample when this reaction is carried out in CH_2Cl_2. © 1997 Elsevier Science S.A.

Keywords: Zirconium; Cyclopentadienyl derivatives; Cationic dinuclear derivatives

1. Introduction

Cationic d^0 species $[MCp_2R]^+$ (M = Ti, Zr, Hf), generated from the metallocene precursors MCp_2R_2, are now generally accepted as being the active species for the polymerization of olefins [1]. Much work has been devoted to the study of these mononuclear 14-electron cations. By contrast, Group 4 homo- and hetero-dinuclear cationic derivatives have attracted less attention [2] in spite of the importance of these systems in the alkene polymerization processes [15]. All of these known dinuclear cationic derivatives contain two metal centres linked by some bridging ligand. The deactivation of electrophilic d^0 catalysts by formation of dinuclear compounds has been proposed as important in alkene polymerization catalysis [3,6]. The fulvalene group is a particularly interesting ligand because it gives dinuclear compounds with short contacts between both metal atoms and even slight metal–metal interactions [4]. The nature of this ligand makes possible the *cis–trans* dispositions of the metal fragments with respect to the fulvalene plane, depending on electronic and steric factors [5]. We have recently described the reaction of the tetramethyl zirconium fulvalene complex $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1a** with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane, which at $-60°C$ leads to the immediate formation of the red μ-CH_2 cationic species $[\{Zr(C_5H_5)(CH_3)\}_2(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}$

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[1] Dedicated to Professor Rafael Usón on the occasion of his 70th birthday.

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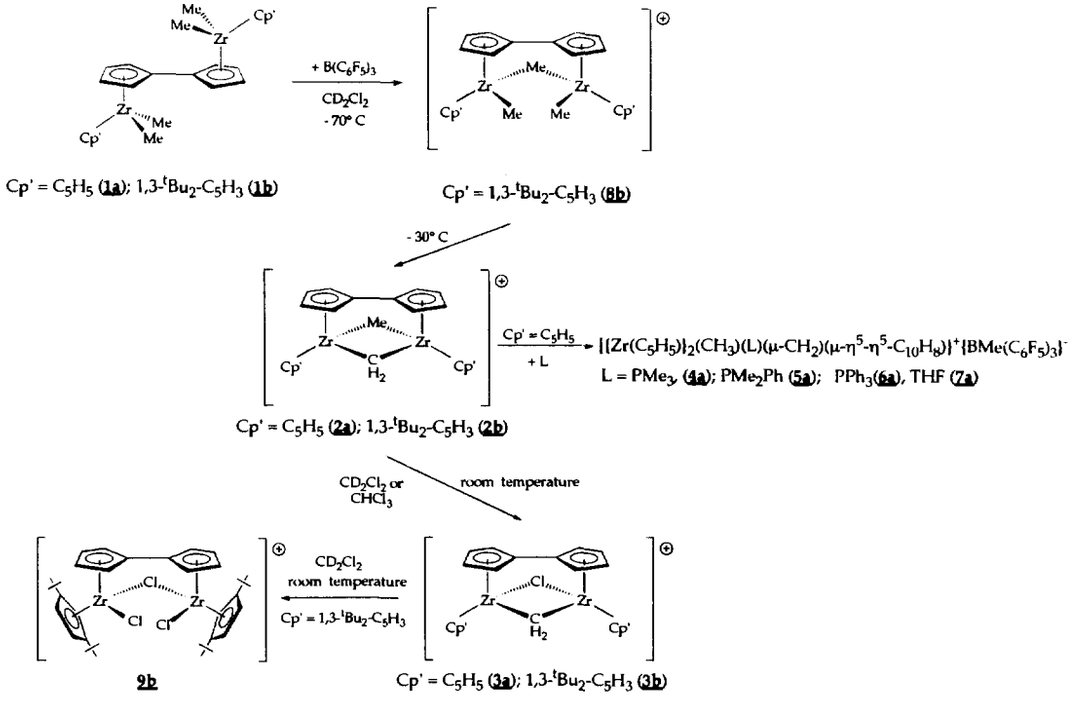


Scheme 1.

$C_{10}H_8)]^+$ **2a** in quantitative yield, which was spectroscopically characterized [6]. Here we report the analytical characterization of **2a** and its reactions with chlorocarbons solvents and with donor ligands for the preparation of new dinuclear cationic zirconium fulvalene complexes. The reaction of $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1b** with $B(C_6F_5)_3$ has been spectroscopically studied and allows us to observe the formation of the μ-methyl dimethyl species $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)]_2(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **8b** as an intermediate in the formation of the μ-methyl μ-methylene derivatives $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2b**. The compound **2b** evolves in chlorocarbons solvents with formation of μ-chloro fulvalene cationic species.

2. Results and discussion

The spectroscopic characterization of the compound $[\{Zr(C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2a** was previously described in the reaction of the tetramethyl zirconium fulvalene derivative $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1a** with $B(C_6F_5)_3$ in CH_2Cl_2 at $-78°C$ [6]. Complex **2a** has been now isolated as a red solid which, after repeatedly washing with cold ($-60°C$) hexane, gives an analytically pure sample in 74% yield (Scheme 1). The ^1H NMR spectrum of **2a** in CD_2Cl_2 indicates the presence of two molecules of CH_2Cl_2 which cannot be eliminated when the solid is maintained overnight under vacuum. The same product was obtained as a red oil, in toluene at room temperature, from which a final pure substance was more difficult to obtain.

At room temperature compound **2a** reacts slowly with CD_2Cl_2 to give the μ-chloro, μ-CH_2 derivative $[\{Zr(C_5H_5)\}_2(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **3a**. The μ-CH_2 ligand is identified, in the compounds **2a** and **3a**, by the AB spin system observed in the ^1H NMR spectrum and by the low field ^{13}C NMR signal (see Experimental Section). After 1 week in CD_2Cl_2, **3a** is formed in 62% yield. The formation of $CH_3\text{-}CD_2Cl$ ($\delta\,^1H = 1.64$, $^3J_{H-D} = 1.2$ Hz) is detected when the reaction is monitored by NMR spectroscopy. When **2a** is dissolved in $CHCl_3$ and stirred for 12 h at room temperature, **3a** is obtained as an analytically pure red solid in 49% yield.

Although the bulky 1,3-di(*tert*-butyl) cyclopentadienyl ring gives titanium and zirconium derivatives which have only low activities in olefin polymerization reactions, the ligand has proved useful for the identification by NMR of reaction intermediates of such processes [7]. The reaction of $B(C_6F_5)_3$ with $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1b** [8] [3] on a preparative scale between $-78°C$ and room temperature is

[3] ^1H NMR data for **1b**: (CD_2Cl_2, 25°C, 500 MHz): δ-0.40 (s, Zr-Me); 1.15 (s, ^tBu); 5.75 (t, ,3-$^tBu_2$-C_5H_3, $J_{H-H} = 2.75$ Hz); 6.39 (d, Hb, 1,3-$^tBu_2$-C_5H_3, $J_{H-H} = 2.75$ Hz); 5.84, 6.39 (AA'BB' spin system, $C_{10}H_8$).

more complex than the reaction of $B(C_6F_5)_3$ with **1a**, in the same conditions, and gives a mixture of compounds (**1b** (incomplete reaction), **2b, 3b, 9b**) which cannot be isolated as pure substances. However, monitoring the reaction of $B(C_6F_5)_3$ with **1b** by NMR spectroscopy allowed the identification of a new intermediate in the reaction sequence leading to the μ-methylene, μ-methyl type compounds **2** obtained from $[ZrCp'(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ ($Cp' = C_5H_5$; 1,3-$^tBu_2C_5H_3$).

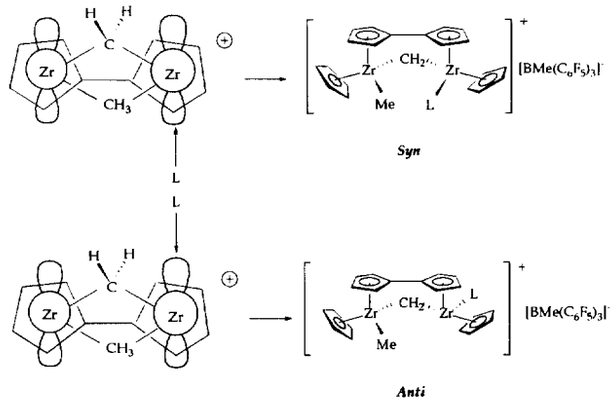
The reaction of **1b** with $B(C_6F_5)_3$ in CD_2Cl_2 was studied by variable temperature NMR spectroscopy, between -80°C and 25°C. The ^1H NMR spectrum, at -80°C, shows a Me–B resonance at δ 0.44, and broad signals at $\approx \delta$ -0.6 and δ 0.6, two singlets for the *tert*-butyl protons, and seven multiplets for the 1,3-$^tBu_2$-C_5H_3 and $C_{10}H_8$ ring protons. These data are indicative of the formation, at this temperature, of a cationic species. As the temperature rises a significant sharpening for the signals is observed. At -30°C the ^1H NMR spectrum shows singlets at δ -0.55 (3 H) and 0.57 (6 H) which were assigned to bridging and terminal methyl groups bonded to the zirconium atoms. The signals at δ 1.09 (18 H) and 1.17 (18 H) for the *tert*-butyl protons and the 7 multiplets at δ 5.82, 6.12, 6.35, 6.40, 6.80, 6.81 and 7.57 for the 1,3-$^tBu_2$-C_5H_3 and $C_{10}H_8$ ring protons are maintained. These data allow us to propose the formation, at low temperature, of the intermediate μ-methyl dimethyl cation $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)\}_2(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+$ **8b** as an intermediate in the synthesis of compound **2b**. Polarization transfer experiments at -20°C show the mutual exchange between the two types of methyl groups present in **8b**, indicative of a labile character in the Zr–Me_{bridge} bond. Above -10°C, C–H activation produces methane (identified by NMR spectroscopy: see experimental section), and the ^1H NMR spectrum shows the formation of the μ-methylene, μ-methyl cationic species $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2b**. The generation of **8b** can be explained by the same reaction as reported for the synthesis of dinuclear methyl complexes of the type $[\{M(C_5H_5)_2(CH_3)\}_2(\mu\text{-}CH_3)]^+$ [15]. The formation of a similar species is however not observed in the reaction of $B(C_6F_5)_3$ with the unsubstituted cyclopentadienyl complex $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1a**.

After 1 week in CD_2Cl_2 solution at room temperature, new resonances are observed in the ^1H NMR spectrum, indicative of the quantitative formation of the μ-chloro, μ-methylene derivative $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)\}_2(\mu\text{-}Cl)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **3b**. This is slowly converted (15 days in CD_2Cl_2 solution) into the dichloro μ-chloro compound $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)Cl\}_2(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **9b**. The formation of a yellow precipitate insoluble in all common solvents, identified as the tetrachloro fulvalene derivative $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)Cl_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$, is always also observed in the NMR tube. The compounds **2b**, **3b**, **8b** and **9b** have been spectroscopically characterized (see Experimental Section). Direct chloride abstraction processes from CH_2Cl_2 have been observed in other zirconium cationic systems to give chloride-bridged dinuclear cationic species [9].

The complexes **2** can be considered as containing one cationic 14-electron zirconium centre stabilised by adduct formation with a neutral dimethyl zirconocene unit. The bridging methylene complexes **2a** and **2b** must be formed via an α-hydrogen abstraction process through the intermediate species $[(ZrCp'CH_3)_2(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+$ ($Cp' = C_5H_5$; 1,3-$^tBu_2$-C_5H_3), identified by NMR spectroscopy in the case of $[\{Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)CH_3\}_2(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+$. Well defined products of α-H abstraction from zirconium alkyls are very rare [10,16] and in any case this process requires irradiation or warming to high temperature. Methylidene zirconium complexes involve the in situ detection of the thermally labile $Cp_2Zr=CH_2(PMePh)_2$ via reaction of $H_2C=PPh_3$ with a zirconocene phosphine complex [11] and the preparation of $[Zr(C_5Me_5)(C_2B_9H_{11})]_2(\mu\text{-}CH_2)$ [16] by thermolysis of $[Zr(C_5Me_5)(C_2B_9H_{11})(CH_3)]_x$ in toluene.

Recently the formation of dinuclear μ-methyl complexes of the type $[\{MCp'_2(CH_3)\}_2(\mu\text{-}CH_3)]^+$ (M = Zr, Hf; $Cp' = C_5H_5$; $Cp'_2 = Me_2Si(Ind)_2$, $C_2H_4(Ind)_2$) by treatment of $MCp'_2(CH_3)_2$ with $[CPh_3][B(C_6F_5)_4]$ at low temperature has been reported, to give thermally stable catalysts for the polymerization of ethylene and propene [15]. Catalytic activity is only possible if $[\{MCp'_2(CH_3)\}_2(\mu\text{-}CH_3)]^+$ dissociates into $MCp'_2(CH_3)_2$ and the active species $[MCp'_2(CH_3)]^+$. Our results establish that these μ-methyl intermediate species, modeled by **8b**, may evolve through irreversible α-hydrogen abstraction processes to give the μ-methyl, μ-methylene derivatives **2**. The complex **2a** generated in situ by reaction of **1a** with $[CPh_3][B(C_6F_5)_4]$ polymerises ethylene with very low activity (an order of activity magnitude lower than that of $[ZrCp_2Me]^+$ under comparable conditions) [6]. Although it has not yet been possible to identify μ-alkylidene complexes in olefin polymerization reactions with group 4 metal catalysts, the very facile formation of derivatives **2** suggests that α-H abstraction processes must be considered as possible side reactions in the deactivation step of such catalysts. However, complex **2a** is not completely catalytically inactive. This observation shows that, if bridging alkylidene complexes are involved in the catalyst deactivation step, they may contribute to the overall reduction in activity but may not represent the end-products of this deactivation process.

The addition of an excess of phosphine ligands to a solution of **2a** in dichloromethane-d_2 at -60°C affords



Scheme 2.

the cationic phosphine adducts $[\{Zr(C_5H_5)\}_2(CH_3)L(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ [L = PMe_3 (**4a**), PMe_2Ph (**5a**), PPh_3 (**6a**)] obtained as a mixture of two isomers. When these reactions are carried out in CH_2Cl_2, the compound **5a** can be isolated as an analytically pure bright yellow solid in high yield which darkens when stored without light protection.

The ^1H NMR spectra of **4a–6a** show two signals assignable to the terminal methyl ligands, four signals for C_5H_5 rings (two of these signals appear as doublets by the spin coupling with the phosphorus: $^1H\text{-}\{^{31}P\}$ experiments), sixteen multiplets for the fulvalene protons and two AB spin system for the $\mu\text{-}CH_2$ ligand, highfield shifted with respect to the AB spin system observed for **2a**. All these spectroscopic data indicate the presence of two isomers, *syn-* and *anti-* (Scheme 2) in a molar ratio Å 1:1.

The $^{31}P\text{-}\{^1H\}$ NMR spectra, at −20°C, of compounds **4a–6a** exhibit two lowfield signals [δ: −11.0 and −13.5 (**4a**); −0.44 and −2.60 (**5a**); 27.1 and 21.5 (**6a**)] indicative of the formation of metal–phosphorus bonds. Values of $\Delta\delta = [\delta_{compl.} - \delta_{ligand}]$, where $\delta_{compl.}$ and δ_{ligand} are the ^{31}P chemical shifts of the complex and the free ligand, respectively, decrease as the phosphine ligand volume increases [$\Delta\delta_{av} = 48$ (**4a**); 42 (**5a**) and 39 ppm (**6a**)]. The ^1H NMR spectra for **4a–5a** are temperature independent between −80 and +10°C.

As shown in Scheme 2, the bent '$ZrCp_2$' fragment possesses a LUMO with a_1 symmetry [12]. Given that the steric requirements of the CH_2 and CH_3 bridges are comparable, phosphine ligands may therefore approach the metal centre from the two possible directions, as shown in Scheme 2. Electronic influences or steric requirements of the incoming phosphine ligand appear to exert little selectivity, leading to the observed formation of *syn-* and *anti-* isomers with about equal probability.

In common with the reaction of **2a** with phosphine ligands, the addition of an excess of THF to a solution of **2a** in CD_2Cl_2 (molar ratio ≈ 3:1) at −80°C gives the *syn-* and *anti-* isomers (molar ratio ≈ 1:1) of $[\{Zr(C_5H_5)\}_2(CH_3)(THF)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ (**7a**). In contrast to the behaviour observed for the phosphine adducts, the ^1H NMR spectra (−80 to −10°C) of **7a** in CD_2Cl_2 are temperature dependent, showing the exchange between free and coordinated THF ($\Delta G^{\#248K} = 12.0$ kJ/mol), suggesting a lower stability than the phosphine species **4a–5a.** When the reactions of **2a** with donor ligands are carried out with a mixture of PMe_3 and THF or PMe_2Ph and THF, only the formation of **4a** and **5a** is observed, whereas a mixture of PPh_3 and THF gives both **6a** and **7a** simultaneously (ratio 1:1).

3. Experimental section

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (phosphorus pentoxide for dichloromethane and chloroform, sodium–potassium amalgam for hexane). PMe_3, PMe_2Ph and PPh_3 (Aldrich) were obtained commercially. $B(C_6F_5)_3$ [13], $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [14] and $[Zr(1,3\text{-}^tBu_2\text{-}C_5H_3)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ [8] were prepared as described in the literature. NMR spectra were recorded on Varian Unity 300 and Varian Unity 500-Plus spectrometers. ^1H and ^{13}C chemical shifts are reported in δ units relative to TMS standard, ^{31}P chemical shift was referenced to 85% H_3PO_4. C and H microanalyses were performed on a Perkin-Elmer 240B microanalyzer.

3.1. $[\{Zr(C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ 2a

$B(C_6F_5)_3$ (0.2 g, 0.4 mmol) was added to a suspension of $[Zr(C_5H_5)(CH_3)_2]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$ **1a** (0.2 g, 0.4 mmol) in 20 ml of dichloromethane, at −78°C, and the mixture was stirred for 30 min, and then warmed to room temperature to obtain a red solution. After filtration the solvent was evaporated to dryness to give a very air-sensitive burgundy-red oil, which was washed twice with cold and dried hexane to give a red solid. The product was dried under vacuum for 6 h and identified as $[\{Zr(C_5H_5)\}_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)]^+[BMe(C_6F_5)_3]^-$ **2a** (0.3 g, 0.30 mmol, 74% yield). Anal. Calc. for $C_{41}H_{26}Zr_2BF_{15}.2CH_2Cl_2$: C, 44.27; H, 2.57. Found: C, 44.45; H, 2.64. (The presence of two molecules of dichloromethane is maintained in repeated experiments). ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ −1.60 (s, 3H, $\mu\text{-}CH_3$); 0.49 (Me–B); 10.04, 4.39 (AB spin system; $J = 8.25$ Hz, $\mu\text{-}CH_2$); 6.15 (m, 4H, $C_{10}H_8$); 6.40 (m, 2H, $C_{10}H_8$); 6.42 (s, C_5H_5); 6.95

(m, 2H, $C_{10}H_8$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25°C, 125 MHz): δ 62.3 (μ-CH_3); 188.2 (μ-CH_2).

3.2. *[{Zr(C5H5)}2(μ-Cl)(μ-CH2)(μ-η5-η5-C10H8)]+[BMe(C6F5)3]− 3a*

0.20 g (0.20 mmol) of [{Zr(C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2a** were dissolved in chloroform and the solution was stirred at room temperature for 12 h. After filtration, the solvent was evaporated to dryness to give a red oil which was twice washed with cold and anhydrous hexane. The final solid obtained was dried under vacuum for 6 h and identified as [{Zr(C_5H_5)}$_2$(μ-Cl)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **3a** (0.09 g, 0.1 mmol, 49% yield). Anal. Calc. for $C_{40}H_{23}Zr_2BClF_{15}$: C, 47.24; H, 2.26. Found: C, 46.86; H, 2.73. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ 10.52, 4.38 (AB spin system; J = 8.5 Hz, μ-CH_2); 6.52 (s, C_5H_5); 6.88, 6.63, 6.30, 5.93 (m, $C_{10}H_8$); 0.5 (Me–B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25°C, 125 MHz): δ 200.9 (μ-CH_2); 114.9 (C_5H_5); 115.3, 111.8, 109.8, 109.7 ($C_{10}H_8$); 10.4 (Me–B).

3.3. *[{Zr(1,3-tBu2-C5H3)}2(μ-CH3)(μ-CH2)(μ-η5-η5-C10H8)]+[BMe(C6F5)3]− 2b*

Dichloromethane-d_2 (0.5 ml) was vacuum transferred at −80°C into an NMR tube containing the solids [Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)$_2$]$_2$(μ-η^5-η^5-$C_{10}H_8$) (0.02 g, 0.03 mmol) **1b** and B(C_6F_5)$_3$ (0.014 g, 0.03 mmol). The tube was warmed to 25°C affording a red solution. The ^1H NMR spectrum was obtained showing formation of [{Zr(1,3-^{t}Bu$_2$-C_5H_3)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2b**. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ 10.15, 4.29 (AB spin system; J = 8.0 Hz, μ-CH_2); -1.51 (s, 3H, Zr-CH_3-Zr); 0.48 (Me–B); 0.97 (s, 18H, 1,3-^{t}*Bu*$_2$-C_5H_3); 1.06 (s, 18H, 1,3-^{t}*Bu*$_2$-C_5H_3); 6.10, 6.27, 6.45, 6.80 (dt, $H_{1,3,2,4}$ ($C_{10}H_8$) $J_{1-2} = J_{1-3}$ = 3.5 Hz; $J_{1-4} = J_{2-3} = J_{3-4}$ = 1.9 Hz); 6.03 (t, Ha, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 2.5 Hz); 6.49 (dd, Hb, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 3.2 Hz); 7.60 (dd, Hb′, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 3.2 Hz). The presence of methane was observed at δ: 0.21 (sharp singlet).

3.4. *[{Zr(1,3-tBu2-C5H3)}2(μ-Cl)(μ-CH2)(μ-η5-η5-C10H8)]+[BMe(C6F5)3]− 3b*

Dichloromethane-d_2 (0.5 ml) was vacuum transferred at −80°C into an NMR tube containing the solids [Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)$_2$]$_2$(μ-η^5-η^5-$C_{10}H_8$) (0.02 g, 0.03 mmol) **1b** and B(C_6F_5)$_3$ (0.014 g, 0.03 mmol). The tube was warmed to 25°C and shaken for 7 days to afford a red solution. The ^1H and ^{13}C NMR spectra were obtained showing quantitative formation of [{Zr(1,3-^{t}Bu$_2$-C_5H_3)}$_2$(μ-Cl)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **3b**. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ 10.47, 4.21 (AB spin system; J = 7.0 Hz, μ-CH_2); 1.03 (s, 18H, 1,3-^{t}*Bu*$_2$-C_5H_3); 1.11 (s, 18H, 1,3-^{t}*Bu*$_2$-C_5H_3); 5.87, 6.41, 6.73, 6.74 (dt, $H_{1,3,2,4}$ ($C_{10}H_8$) $J_{1-2} = J_{1-3}$ = 3.4 Hz; $J_{1-4} = J_{2-3} = J_{3-4}$ = 2.3 Hz); 6.43 (t, Ha, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 2.7 Hz); 6.61 (dd, Hb, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 3.3 Hz); 7.25 (dd, Hb′, 1,3-^{t}Bu$_2$-C_5H_3, J_{H-H} = 3.3 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25°C, 125 MHz): δ 194.3 (μ-CH_2); 31.2, 31.5 [C-(CH_3)$_3$]; 33.0, 33.2 [*C*-(CH_3)$_3$]; 105.5, 109.0, 109.5, 110.8, 113.9, 114.9, 115.6, 116.0 (1,3-^{t}Bu$_2$-C_5H_3, +$C_{10}H_8$); 10 (Me–B).

3.5. *[{Zr(C5H5)}2(CH3)(PMe3)(μ-CH2)(μ-η5-η5-C10H8)]+[BMe(C6F5)3]− 4a*

A 2 M dichloromethane-d_2 solution of PMe_3 (0.5 ml, 0.1 mmol) was added at −78°C into an NMR tube containing the solid [{Zr(C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2a** (0.05 g, 0.05 mmol). The tube was warmed to room temperature affording a clear yellow solution. The ^1H and ^{31}P NMR spectra were obtained showing quantitative formation of [{Zr(C_5H_5)}$_2$(CH_3)(PMe_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **4a** as a *syn-* + *anti-* mixture. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ -0.54 (s, Zr-CH_3); −0.19 (s, Zr-CH_3); 0.5 (Me–B); 1.30 (d, J_{H-P} = 8.5 Hz, PMe_3); 1.31 (d, J_{H-P} = 8.3 Hz, PMe_3); 3.65 (dd, J_{H-H} = 1.9 Hz, J_{H-P} < 1.0 Hz, μ-CH_2); 5.90 (d, J_{H-P} = 1.8 Hz, C_5H_5); 6.12 (s, C_5H_5); 6.13 (d, J_{H-P} = 1.7 Hz, C_5H_5); 6.14 (s, C_5H_5); 5.3–6.6 (16 signals, m, $C_{10}H_8$); 8.45 (dd, J_{H-H} = 1.9 Hz, J_{H-P} = 1.4 Hz, μ-CH_2); 8.78 (dd, J_{H-H} = 1.9 Hz, J_{H-P} = 1.5 Hz, μ-CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25°C, 202 MHz): δ −11.0; −13.5.

3.6. *[{Zr(C5H5)}2(CH3)(PMe2Ph)(μ-CH2)(μ-η5-η5-C10H8)]+ [BMe(C6F5)3]− 5a*

10 ml (0.60 mmol) of PMe_2Ph were added to a cooled (−78°C) solution of [{Zr(C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2a** (0.30 g, 0.30 mmol) in 20 ml of dichloromethane. The solution turned clear yellow immediately. The reaction mixture was stirred for 5 min at this temperature and then warmed to room temperature. After filtration, the solvent was evaporated to dryness to give an orange oil which was twice washed with cold hexane. The final solid obtained was dried under vacuum for 6 h and identified as [{Zr(C_5H_5)}$_2$(CH_3)(PMe_2Ph)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **5a** (0.37 g, 0.25 mmol, 83% yield). Anal. Calc. for $C_{49}H_{37}Zr_2BF_{15}P$: C, 51.87; H, 3.26. Found: C, 51.57; H, 3.72. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz, *syn-* + *anti-* mixture): δ -0.50 (s, Zr-CH_3); −0.10 (s, Zr-CH_3); 0.5 (Me–B); 1.66 (d, J_{H-P} = 7.5 Hz, PMe_2Ph); 1.67 (d, J_{H-P} = 7.5 Hz, PMe_2Ph); 2.65 (dd, J_{H-H} < 1.0 Hz, J_{H-P} < 1.0 Hz,

μ-CH_2); 3.81 (dd, $J_{H-H} < 1.0$ Hz, $J_{H-P} < 1.0$ Hz, μ-CH_2); 5.98 (d, $J_{H-P} = 1.5$ Hz, C_5H_5); 6.19 (s, C_5H_5); 6.17 (d, $J_{H-P} = 1.7$ Hz, C_5H_5); 6.20 (s, C_5H_5); 5.3–6.6 (16 signals, m, $C_{10}H_8$); 7.4 (m, Ph); 8.62 (dd, $J_{H-H} < 1.0$ Hz, $J_{H-P} = 1.9$ Hz, μ-CH_2); 9.05 (dd, $J_{H-H} < 1.0$ Hz, $J_{H-P} = 1.9$ Hz, μ-CH_2). ^{31}P-{^1H} NMR (CD_2Cl_2, 25°C, 202 MHz, *syn-* + *anti-* mixture): δ −0.44; −2.60.

3.7. *[{Zr(C_5H_5)}$_2$(CH_3)(PPh_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ 6a*

Dichloromethane-d_2 (0.5 ml) was vacuum transferred at −78°C into an NMR tube containing the solids [{Zr(C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2a** (0.05 g, 0.05 mmol) and PPh_3 (0.026 g, 0.1 mmol). The tube was warmed to room temperature affording a clear yellow solution. The ^1H and ^{31}P NMR spectra were obtained showing quantitative formation of [{Zr(C_5H_5)}$_2$(CH_3)(PPh_3)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **6a** as a *syn-* + *anti-* mixture. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ -0.47 (s, Zr-CH_3); −0.11 (s, Zr-CH_3); 0.48 (Me–B); 2.92 (br, μ-CH_2); 4.0 (br, μ-CH_2); 6.10 (d, $J_{H-P} = 1.9$ Hz, C_5H_5); 6.12 (d, $J_{H-P} = 1.4$ Hz, C_5H_5); 6.21 (s, C_5H_5); 6.25 (s, C_5H_5); 5.3–6.6 (16 signals, m, $C_{10}H_8$); 7.4 (m, Ph); 8.91 (br, μ-CH_2); 9.21 (br, μ-CH_2). ^{31}P-{^1H} NMR (CD_2Cl_2, 25°C, 202 MHz): δ 21.5; 27.1.

3.8. *[{Zr(C_5H_5)}$_2$(CH_3)(THF)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ 7a*

Dichloromethane-d_2 (0.5 ml) was added at −78°C into an NMR tube containing the solid [{Zr(C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-η^5 − $C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **2a** (0.02 g, 0.02 mmol) and THF (3×10^{-3} g, 3.3×10^{-3} ml, 0.04 mmol). The tube was warmed to room temperature affording a clear yellow solution. The ^1H spectrum was obtained showing formation of [{Zr(C_5H_5)}$_2$(CH_3)(THF)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$-[BMe(C_6F_5)$_3$]$^-$ **7a** as a *syn-* + *anti-* mixture. ^1H NMR (CD_2Cl_2, −80°C, 500 MHz): δ -0.50 (s, Zr-CH_3); −0.56 (s, Zr-CH_3); 0.42 (Me–B); 2.06 (br, THF); 2.69 (br, μ-CH_2); 2.72 (br, μ-CH_2); 3.72 (br, THF); 6.15, 6.17, 6.28, 6.32 (br, C_5H_5); 5.2–7.0 (16 signals, m, $C_{10}H_8$); 7.51 (br, μ-CH_2); 7.62 (br, μ-CH_2).

3.9. *[{Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)}$_2$(μ-CH_3)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ 8b*

Dichloromethane-d_2 (0.5 ml) was vacuum transferred at −80°C into an NMR tube containing the solids [Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)$_2$]$_2$(μ-η^5-η^5-$C_{10}H_8$) (0.02 g, 0.03 mmol) **1b** and B(C_6F_5)$_3$ (0.014 g, 0.03 mmol). The tube was warmed to −30°C to afford a red–yellow solution. The ^1H NMR spectrum was obtained showing formation of [{Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)}$_2$(μ-CH_3)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **8b**. ^1H NMR (CD_2Cl_2, −30°C, 500 MHz: δ −0.55 (s, 3H, Zr-CH_3-Zr); 0.57 (s, 6H, Zr-CH_3); 1.09 (s, 18H, 1,3-^{t}Bu$_2$-C_5H_3); 1.17 (s, 18H, 1,3-^{t}Bu$_2$-C_5H_3)); 5.82, 6.12, 6.35, 6.40, 6.80, 6.81, 7.57 (7m, 1,3-^{t}Bu$_2$-C_5H_3 + $C_{10}H_8$).

3.10. *[{Zr(1,3-^{t}Bu$_2$-C_5H_3)Cl}$_2$(μ-Cl)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ 9b*

Dichloromethane-d_2 (0.5 ml) was vacuum transferred at −80°C into an NMR tube containing the solids [Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)$_2$]$_2$(μ-η^5-η^5-$C_{10}H_8$) (0.02 g, 0.03 mmol) **1b** and B(C_6F_5)$_3$ (0.014 g, 0.03 mmol). The tube was warmed to 25°C and shaken for 15 days to afford an orange solution. The ^1H NMR spectrum was obtained showing quantitative formation of [{Zr(1,3-^{t}Bu$_2$-C_5H_3)Cl}$_2$(μ-Cl)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ **9b**. ^1H NMR (CD_2Cl_2, 25°C, 500 MHz): δ 0.43 (Me-B); 1.21 (s, 18H, 1,3-^{t}Bu$_2$-C_5H_3); 1.23 (s, 18H, 1,3-^{t}Bu$_2$-C_5H_3); 5.70 (1H), 6.22 (1H), 6.53 (2H), 6.73 (1H), 6.78 (1H), 7.15 (1H) (1,3-^{t}Bu$_2$-C_5H_3 + $C_{10}H_8$).

4. Synopsis

The preparation of base-free dinuclear cationic zirconium complexes with the fulvalene ligand [{Zr(C_5H_5)}$_2$(μ-X)(μ-CH_2)(μ-η^5:η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ (X = Cl, CH_3) by reaction of B(C_6F_5)$_3$ with [Zr(C_5H_5)(CH_3)$_2$]$_2$(μ-η^5:η^5-$C_{10}H_8$) is described. By addition of donor ligands in dichloromethane solution, the cationic adducts [{Zr(C_5H_5)}$_2$(CH_3)L(μ-CH_2)(μ-η^5:η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ [L = PMe_3, PMe_2Ph, PPh_3, THF] are formed. In the reaction of B(C_6F_5)$_3$ with [Zr(1,3-^{t}Bu$_2$-C_5H_3)(CH_3)$_2$]$_2$(μ-η^5-η^5-$C_{10}H_8$) the formation of the cationic species [{Zr(1,3-^{t}Bu$_2$-C_5H_3)}$_2$(μ-X)(μ-CH_2)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ (X = CH_3, Cl) and [{Zr(1,3-^{t}Bu$_2$-C_5H_3)X}$_2$(μ-Y)(μ-η^5-η^5-$C_{10}H_8$)]$^+$[BMe(C_6F_5)$_3$]$^-$ (X = Cl, Y = Cl; X = CH_3, Y = CH_3) were identified by NMR spectroscopy.

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