



## Intramolecular activation of a pendant nitrile group in Ti and Zr metallocene complexes

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### ABSTRACT

Several approaches to the intramolecular activation of a pendant nitrile group attached to the group 4 metallocene framework have been probed starting with the complexes  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN})\text{MCl}_2]$  ( $\text{M} = \text{Zr}$ , **1**;  $\text{M} = \text{Ti}$ , **2**). A reduction induced activation of the nitrile moiety was effected for the Zr derivative either by the treatment with Mg, or by the alkylation using *t*-BuMgCl followed by spontaneous reductive elimination. In both cases, the reactions finally yielded the zirconocene cyano complex with an intramolecularly tethered alkyl substituent,  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2)\text{Zr}(\text{CN-}\kappa\text{C})]$  (**4**), which resulted from the C–C bond cleavage in the pendant arm. Furthermore, a by-product was isolated which contained two zirconocene fragments bridged through a  $\text{MgCl}_2$  moiety featuring a rare  $\sigma, \pi$ -bridging mode of the pendant nitrile group,  $\{[(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-}\eta^5\text{-}\eta^2\text{:}\kappa\text{N-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN})(\mu\text{-Cl})\text{Zr}]_2\text{Mg}\}$  (**3**). The solid-state structure of **3** was elucidated and this compound together with the product **4** and the tentative intermediate  $\{[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-}\eta^2\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN})\text{Zr}]\}$  (**3'**) were also investigated by DFT calculations. In another approach, **1** and **2** were treated with  $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4] \cdot \text{Et}_2\text{O}$  to generate cationic complexes. Accidental hydrolysis of these species afforded complexes bearing an intramolecularly tethered amide group  $\{[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-}\kappa\text{O-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CONH}_2)\text{M}]\}$ , of which the Ti derivative (**6**) was isolated and structurally characterised. Finally, reaction of the zirconocene dimethyl complex  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN})\text{ZrMe}_2]$  (**8**) with  $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$  was studied.

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### Introduction

Metallocene complexes of group 4 elements have been developed in the course of past decades into a diverse class of compounds, having a number of applications, namely in organic synthesis and catalysis [1]. Early transition metals in these compounds are capable to activate bonds of various saturated and unsaturated substrates, which is the feature that has been explored extensively. Two types of species are essential in such processes: either complexes with a low-valent metal centre that are capable of oxidative additions [2], or highly electrophilic cationic species, which are typical particularly in the olefin polymerisation catalysis [3].

Considerable interest has been recently devoted to the preparation of variously functionalised group 4 metallocene complexes and even to chemical transformations of the attached functional groups [4,5]. However, the synthetic accessibility of functionalised complexes is often limited by the reactive nature of the metallocene moiety, which simply does not tolerate certain reagents and/or conditions. In some cases, on the other hand, intramolecular reactions of the attached group with the metal centre may be utilised to perform functional group transformations at the metallocene framework. Our group has previously studied activation reactions of pendant functional groups in group 4 metallocene complexes induced either by reduction, or by thermolysis of alkyl or aryl metallocene derivatives [6]. We have also recently reported the preparation of a series of group 4 bent metallocene complexes with pendant nitrile groups [7] and studied the possibility of transformations of such tethered functional moieties directly at transition metal complexes [8]. We have found that under certain conditions, alkylation of the pendant nitrile, accompanied by

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alkylation at the metal, leads to intramolecularly bound ketimide complexes [8a]. Herein, we present the results of our investigation into the intramolecular activation of a pendant nitrile group in Ti and Zr metallocene complexes by the reduction of metallocene dichloride or by the formation of cationic species generated by the chloride or methyl group abstraction.

## Results and discussion

### Reduction induced reactions of **1**

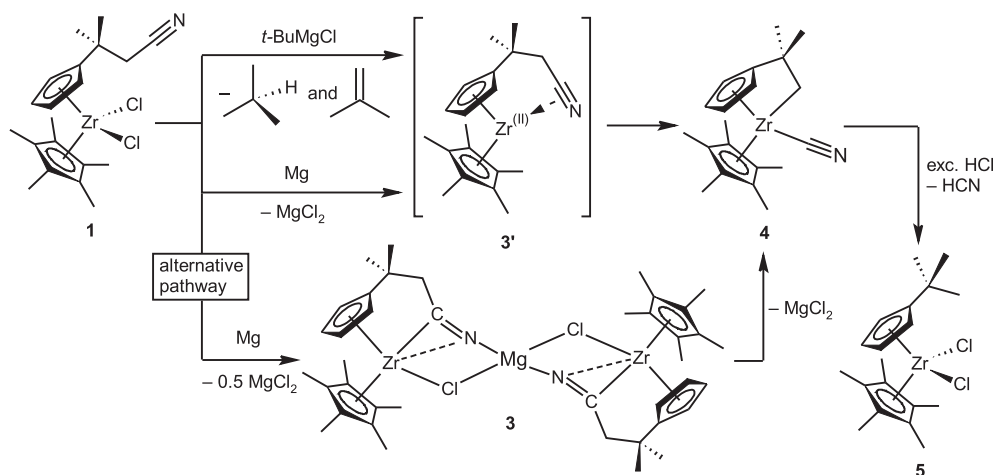
The metallocene dichlorides  $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN})\text{MCl}_2]$  ( $\text{M} = \text{Zr}$ , **1**;  $\text{M} = \text{Ti}$ , **2**) bearing one pendant nitrile arm and an auxiliary  $\eta^5\text{-C}_5\text{Me}_5$  ligand were chosen for the purpose of this study. These complexes were prepared by the metathesis route using the lithium cyclopentadienide ( $\text{C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN}$ )Li and the corresponding half-sandwich precursor  $(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_3$  as described previously [7,8a].

During attempts to effect alkylation of the pendant nitrile in complex **1** using various nucleophilic reagents, we found that the reaction of **1** with 2 molar equivalents of *t*-BuMgCl in THF leads, in contrast to the reactivity towards RLi and RMgBr ( $\text{R} = \text{Ph}$ , Me) [8a], to a markedly different outcome. Based on *in-situ* NMR spectroscopic investigations and further experimental evidences we propose the reaction sequence outlined in Scheme 1. Compound **1** is alkylated by 2 equivalents of the Grignard reagent and the formed dialkyl derivative undergoes a spontaneous reductive elimination. Such a behaviour of group 4 metallocene dialkyls capable of  $\beta$ -hydrogen elimination processes was previously described [9]. It should be noted that we did not observe the dialkyl intermediate by NMR spectroscopy. Instead, a mixture of the starting material and the tentative product of reductive elimination (**3'**) together with the expected hydrocarbon products (2-methylpropene and 2-methylpropane) had been observed since the early stages of the reaction (see Experimental part). Spectral data for the elusive Zr(II) intermediate species **3'**, especially the low field shifted signal for the nitrile carbon at  $\delta_{\text{C}}$  244.7 ppm and the set of non-equivalent signals for the coordinated ( $\eta^5\text{-}\eta^2\text{-C}_5\text{H}_4\text{CMe}_2\text{CH}_2\text{CN}$ ) ligand (cf. the pseudo- $\text{C}_s$  symmetrical starting compound **1**, which gives a simple spectral pattern) were indicative of an intramolecular side-on coordination of the nitrile group [10]. The species described above was however unstable and in the course of days reacted further to yield product **4**. Unfortunately, we were not able to isolate it from additional minor by-products of the reaction since it has been reluctant to crystallisation. Nevertheless, characteristic

spectral properties of **4** led us to the formulation of its structure as an intramolecularly tethered alkylzirconocene cyanide. Notably, the doublets in  $^1\text{H}$  NMR spectra for the Zr-bound methylene group at  $\delta_{\text{H}}$   $-1.21$  and  $-0.69$  ppm [11] and the carbon signal of the C-coordinated cyano group at  $\delta_{\text{C}}$  182.3 ppm, together with the band for the  $\text{C}\equiv\text{N}$  bond vibration at  $2118\text{ cm}^{-1}$  in the IR spectra (cf. the value for free nitrile in **1**:  $2237\text{ cm}^{-1}$ ) supported this hypothesis [12]. Further evidence was provided by the reaction of crude **4** with dry HCl, which afforded the *t*-butyl substituted zirconocene dichloride **5** [13] accompanied by small amounts of **1**.

It should be noted that similar oxidative cleavage of the C–CN bond likely led to the formation of a zirconocene cyano complex described by Rosenthal et al. as an unexpected oxidation product from the reaction of the alkyne complex  $[\text{Cp}^*\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{-SiMe}_3)]$  with 2 equivalents of  $\text{Ph}_2\text{CHCN}$  [12e]. On the other hand, nitriles generally reacted with low valent group 4 metallocenes giving rise to 1-metalla-2,5-diaza-cyclopenta-2,4-dienes as the coupling products [14], or, alternatively, to complexes bearing keteniminate ligands arising from the deprotonation of nitriles at the adjacent carbon atom (like in the case of  $\text{Ph}_2\text{CHCN}$ ) [15]. The pendant nitrile group in our case could not interact intramolecularly via its nitrogen atom with the metal in a  $\sigma$ -bonding fashion due to a steric strain, which likely resulted in the observed type of reactivity.

To further explore the reduction induced activation, we performed a reaction of **1** with a slight excess of magnesium in THF. Again, compound **4** was obtained as a major product, however, all attempts to isolate it failed. Attempting to separate the reaction products by crystallisation, the crystals of compound **3** were obtained instead, which were suitable for X-ray diffraction analysis (Fig. 1). NMR data for the crystalline material assigned to structure **3** revealed the presence of at least three major compounds in a molar ratio 1.5:1:1, having qualitatively the same sets of signals. The resonances for a non-symmetrical zirconocene moiety and signals for carbons of the  $\sigma,\pi$ -bridging nitrile moiety at  $\delta_{\text{C}} \sim 246$  ppm were again indicative of the pendant arm participating in the bonding of metallic fragments. A plausible explanation is the presence of diastereomeric species, one of which could be elucidated by single-crystal diffraction. An unambiguous assignment of spectral data was however not achieved. It is not clear, whether **3** is the sole intermediate in the formation of **4** or just a side-product formed by a partial reduction of the zirconocene. Nevertheless, the sample of **3** was not stable in solution and compound **4** was identified as its major decomposition product by NMR spectroscopy within several days.



Scheme 1. Reduction induced activation of the pendant substituent in complex **1**.

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