

Protonolysis of Fe–C bonds of a diiminopyridineiron(II) dialkyl complex by acids of different strengths: Influence of monoanionic ligands on the spectroscopic properties of diiminopyridine–FeY₂ complexes



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ABSTRACT

The reaction of the dialkyliron complex [Fe(CH₂SiMe₃)₂(^{Mes}BIP)] (^{Mes}BIP = 2,6-bis((*N*-mesityl)acetimidoyl)pyridine) with protic acids (HY) of different strengths (Y = C₆F₅O, CF₃CO₂, Cl, CF₃SO₃) invariably leads to the cleavage of both Fe–C bonds, independent of the Fe/HY ratio used (either 1:2 or 1:1), affording the corresponding complexes [FeY₂(^{Mes}BIP)]. Relevant spectroscopic features of these compounds, such as paramagnetic ¹H NMR shifts and UV–Vis absorption bands, exhibit a marked dependence on the nature of Y.

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1. Introduction

Olefin polymerization or oligomerization catalysts based on iron complexes of 2,6-bisiminopyridine (BIP) ligands have attracted much interest due to their high activity and the abundance and low toxicity and of iron [1]. In addition, the modular design of BIP ligands facilitates the variation of the stereoelectronic environment of the active centre, enabling a precise control of the molecular weight of the polymers. It is usually assumed that, similarly to other polymerization systems, activation of [FeX₂(BIP)] complexes with alumoxanes or other organoaluminum-based co-catalysts give rise to catalytically active alkyliron species. Such a classic Ziegler–Natta mechanism gained strong support in 2005, when Chirik prepared cationic complexes of the type [Fe(R)(S)(^{iPr}BIP)]⁺ (^{iPr}BIP = BIP ligand with 2,6-diisopropylphenyl as aryl substituent in the imine; S = OEt₂, THF, or none) by protonation of dialkyl precursors with [HNPhMe₂]⁺ [BPh₄][−] [2], and demonstrated that such cationic iron alkyls behave as highly active single-component catalysts for ethylene polymerization. However, the precise nature of the active species on the real catalysts generated with the aid of alkylaluminum co-catalysts is still the subject of some controversy. The latter are known to play a very important role in the catalytic process, influencing both the activity and the molecular weight distribution of the polyolefinic products [3]. Indeed, spectroscopic investigations of the aluminium-activated iron catalysts by Bryliakov and Talsi have revealed that the interaction of [FeX₂

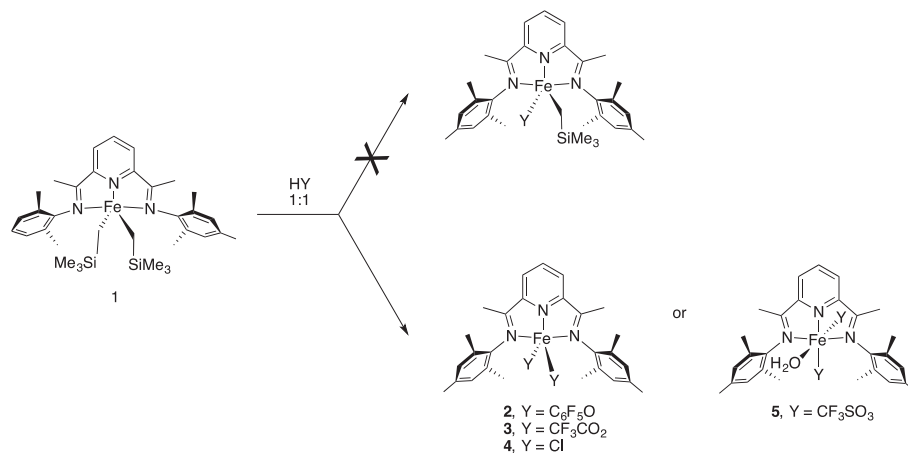
(BIP)] complexes with organoaluminum reagents gives rise to both neutral and cationic bimetallic Fe/Al species that very likely have an active participation in the polymerization process [4]. In addition, it has been recognised that the counteranion that balances the electric charge of active cationic species plays a role of crucial importance in the performance of most homogeneous Ziegler–Natta polymerization catalysts [5]. Thus, it seems very likely that iron complexes of the type [Fe(R)(Y)(BIP)] (where Y symbolizes an anionic ligand) should exhibit significant differences in their ability to act as polymerization catalysts, as the coordinating strength of Y or its ability to interact with the co-catalysts can be varied widely. Several years ago, we reported a general methodology that provides access to iron dialkyl complexes of the type [Fe(CH₂SiMe₃)₂(BIP)] [6], and we wondered whether these complexes could react selectively with protic acids HY of different strengths to afford the desired [Fe(CH₂SiMe₃)(Y)(BIP)] complexes. As we show in this contribution, it turned out that such mixed ligand compounds are not stable or cannot be produced through this route. Instead, the protonation reaction affords symmetrical [FeY₂(BIP)] derivatives. This allowed us to compare some of the key spectroscopic features of these compounds and analyse how these properties are influenced by the nature of the anionic Y ligand.

2. Results and discussion

We investigated the reactions of the readily available dialkyl complex [Fe(CH₂SiMe₃)₂(^{Mes}BIP)] (1) with four protic acids of different strengths: Pentafluorophenol (pK_a = 5.4), trifluoroacetic acid

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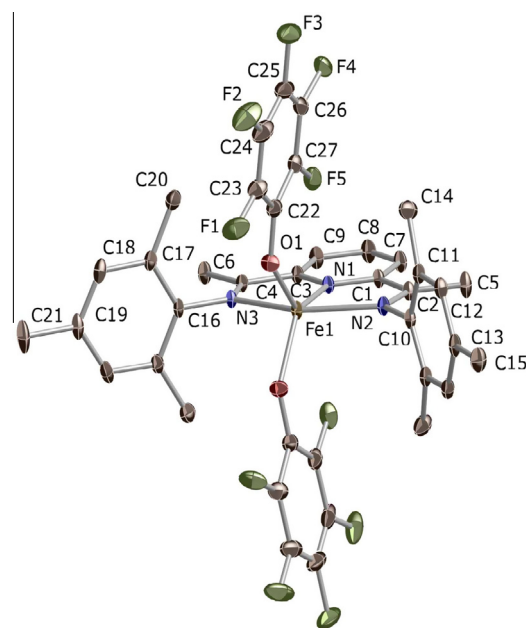
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Scheme 1.

($pK_a = 0.2$), hydrogen chloride ($pK_a = -7$) and triflic acid ($pK_a = -12$) [7].¹ Stoichiometric (1:1) amounts of the acids diluted in THF were slowly added to the solutions of the iron dialkyl in the same solvent at $-80\text{ }^\circ\text{C}$, and then allowed to slowly warm to room temperature. In spite of the care taken to control the reaction conditions, these reactions invariably led to products **2–5** resulting from the cleavage of both Fe–C bonds of **1** (Scheme 1). The products were precipitated by addition of hexane, leaving purple mother liquors containing unreacted **1**. As expected, higher yields of all four products were obtained when the acids and the iron alkyl were reacted in 2:1 ratio. These results suggest that the non-symmetrical alkyl complexes $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(\text{Y})(^{\text{Mes}}\text{BIP})]$ are unstable and rapidly disproportionate in solution affording a mixture of the corresponding symmetrical complexes. This conclusion is also supported by Chirik's observation that the reaction of the mixed complex $[\text{Fe}(\text{CH}_2\text{SiMe}_3)(\text{Cl})(\text{Py})_2]$ with *i*PrBIP does not afford the intended (chloro)trimethylsilylmethyl derivative $[\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{Cl})(^{\text{iPr}}\text{BIP})]$, but a mixture of the dialkyl and dichloro complexes [8].

Apart from the well-known chloro derivative **4** [3], none of the rest of the products, **2**, **3** and **5**, has been described previously. They are all paramagnetic with $\mu_{\text{eff}} = 5.0\text{--}5.6\ \mu_{\text{B}}$ at room temperature, consistent with a high-spin configuration with four unpaired electrons. Crystals of **2** and **5** suitable for X-ray analysis were obtained by recrystallization. Figs. 1 and 2 show ORTEP views of these two complexes, and Table 1 collects selected bond lengths and angles. Remarkably, very few iron bisiminopyridine complexes containing alkoxy or aryloxy ligands have been reported before [9], and to the best of our knowledge, no dialkoxy or diaryloxy derivatives are known so far. Similarly to the analogous halide complexes $[\text{FeX}_2(^{\text{Mes}}\text{BIP})]$ ($\text{X} = \text{Cl}, \text{Br}$), the iron centre of the aryloxy **2** exhibits a distorted trigonal bipyramidal geometry, with the imine nitrogen atoms occupying the axial positions. The τ parameter [10], that describes the distortion degree between perfect bipyramidal trigonal ($\tau = 1$) and square pyramidal ($\tau = 0$) geometries, takes the value 0.84 for this compound. A crystallographically imposed mirror plane bisects the molecule through the iron and the three nitrogen atoms and relates the pentafluoroaryloxy moieties. The latter are oriented in such a way that one of the *ortho* fluorine substituents (F5) approaches to the iron atom. This conformation could be favoured by an attractive electrostatic interaction, but the Fe–F5 distance (3.0149(12) Å) is too long to mean any significant

Fig. 1. ORTEP view of the X ray structure of compound **2**.

¹ pK_a values in water. Note that the acid strength of HY is inversely related to the basicity of Y[−] ligands, which correlates with their ability to donate electron density to the metal centre. Aqueous pK_a were selected because they are available for the four acids used in this work, but note that the acid strengths of HOTf, HCl, acetic acid and phenol holds in water, acetonitrile and dichloroethane, see Ref. [7a].

chemical bonding. As it is usually found in this type of compounds, the Fe–N bonds involving the imino groups are somewhat different, decreasing the overall molecular symmetry from C_{2v} (if both Fe–imine bonds were identical) to C_s . The structure of complex **5** contains, in addition to the triflate ligands, a molecule of water attached to the iron centre. The presence of an aqua ligand is also revealed by a strong absorption at 3345 cm^{-1} in the IR spectrum of this compound. Very likely, this water comes from adventitious traces of moisture in the solvents during the synthesis or the recrystallization of this complex, and its presence reveals the strong Lewis acidity of the corresponding bis-triflate precursor. Britovsek has reported related Fe(II) and Mn(II) bis-triflate complexes with BIP ligands. Interestingly, the Mn(II) derivative containing the ^{Me2}BIP ligand (*N*-aryl groups = 2,6-dimethylphenyl) was also isolated as the monohydrate $[\text{Mn}(\text{OTf})_2(\text{OH}_2)(^{\text{Me2}}\text{BIP})]$ [11]. Goldberg has recently reported a mixed iron(II) thiolate-triflate complex, $[\text{Fe}(\text{OTf})(\text{SPh})(^{\text{iPr}}\text{BIP})]$ [12]. The geometry of the iron centre in **5** is approximately octahedral, with the aqua ligand and one of the triflate ligands occupying “axial” positions, i.e., perpendicular to the main coordination plane defined by the three N atoms of the BIP ligand and the second triflate group. This

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