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Bis(imino)pyridine Iron(II) Alkyl Cations for Olefin Polymerization

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When activated with an excess of methylalumoxane (MAO), bis-(imino)pyridine iron and cobalt dichloride complexes are highly active for the polymerization and oligomerization of ethylene and α -olefins.¹ Despite intense interest from both academic¹ and industrial² laboratories, the mechanism of the activation process and the nature of the propagating species are not well understood. Recent studies with the cobalt catalysts are consistent with an MAOinduced reduction to Co(I) rather than formation of a discrete Co-(II) alkyl cation.³ Isolated bis(imino)pyridine cobalt(I) methyl and chloride complexes, when treated with MAO or a borate activator, are active for ethylene polymerization, suggesting that preformed cobalt alkyls are not a prerequisite for catalytic activity.³⁻⁵

For iron, the identity and oxidation state of the propagating species are more controversial. Initial experimental⁶ and computational⁷ results supported cationic iron(II) alkyls and hydrides upon activation with MAO. However, a combined Mössbauer and EPR spectroscopic study suggested that all of the iron is oxidized to the ferric form under catalytic conditions.⁸ Here we describe the synthesis and crystallographic characterization of bis(imino)pyridine iron(II) alkyl complexes and report their activity for ethylene polymerization. These results establish that ferrous alkyl cations are indeed catalytically competent.

We previously reported the divergent alkylation chemistry associated with the five-coordinate ferrous dichloride precursor, $(((2,6-CHMe_2)_2C_6H_3N=CMe)_2C_5H_3N)FeCl_2$ (('PrPDI)FeCl_2, **1-Cl_2**).⁹ Treatment with 2 equiv of small alkyllithiums such as MeLi yielded **1-Me**, the product of reductive alkylation, while larger reagents such as LiCH_2SiMe_3 furnished the ferrous dialkyl, **1-(CH_2SiMe_3)_2** (eq 1).



Treatment of **1-(CH₂SiMe₃)**₂ with [PhMe₂NH][BPh₄] in toluene resulted in protonation of one of the alkyl ligands to furnish a redbrown solid, tentatively identified as the base-free alkyl cation, [(PrPDI)Fe(CH₂SiMe₃)][BPh₄] (**2**). To obtain more crystalline products, the protonation reaction was repeated in the presence of neutral donors. In this manner, both the diethyl ether and THF adducts, [(PrPDI)Fe(CH₂SiMe₃)(L)][BPh₄] (L = Et₂O, **2-Et₂O**; THF, **2-THF**), were prepared and isolated in 54 and 74% isolated yields, respectively (eq 2). Solid-state magnetometry (Gouy method) produced magnetic moments of 4.8 and 4.6 μ B, consistent with high-spin, iron(II) complexes with four unpaired electrons.

Both **2-Et₂O** and **2-THF** have been characterized by X-ray diffraction, and the molecular structures of the compounds are presented in Figure 1 and are topologically similar. There are no obvious interactions between the iron cations and the $[BPh_4]$ anions. The geometry about iron is best described as distorted square



pyramidal, similar to $1-Cl_2^1$ and $1-(CH_2SiMe_3)_2$,⁹ with the donor ligand coordinated in the basal plane and the alkyl group occupying the apical site. For $2-Et_2O$, the iron atom lies 0.660(1) Å out of the ligand plane, and a similar value of 0.680(1) Å is found for 2-THF. The iron–carbon bond lengths of 2.087(5) and 2.034(3) Å for $2-Et_2O$ and 2-THF are comparable to the value of 2.062(3) Å for the apical alkyl group in $1-(CH_2SiMe_3)_2$.⁹

Attempts to induce alkyl abstraction in $1-(CH_2SiMe_3)_2$ with the neutral borane, $B(C_6F_5)_3$, resulted in silicon methide abstraction followed by rearrangement. The base-free cationic alkyl complex, $[(^{i}PrPDI)Fe(CH_2SiMe_2CH_2SiMe_3)][MeB(C_6F_5)_3]$ (3), was isolated as a red solid in 39% yield (eq 3). A similar abstraction–



rearrangement sequence has been observed with a titanium bis-(trimethylsilyl)methyl complex.¹⁰ In the present case, the preference for silicon methide over iron alkyl abstraction is most likely a result of the steric protection imparted by the bulky aryl groups that impede the approach of the Lewis acid to the metal center. Previously, we reported that activation of the corresponding fourcoordinate, α -diimine ferrous dialkyl with B(C₆F₅)₃ resulted in initial alkyl group abstraction, followed by aryl group transfer from boron to iron, affording a neutral Fe(II) aryl alkyl compound.¹¹ These results highlight the importance of terdentate ligands for catalysis and are consistent with the reduced polymerization activities observed with bidentate supporting ligands.¹²

Solid-state magnetometry on powdered samples of **3** yielded a magnetic moment of 4.6 μ B, consistent with the spin-only value for four unpaired electrons. Accordingly, the benzene- d_6 ¹H NMR spectrum of **3** exhibits the number of resonances for a $C_{2\nu}$ -symmetric compound that are paramagnetically shifted over a 250 ppm chemical shift range. The hydrogens attached to the carbon bound to iron were not located. Three singlets are observed for the [MeB(C₆F₅)₃] anion by ¹⁹F NMR spectroscopy; significantly, the para resonance is shifted upfield to -172.5 ppm.

The solid-state structure of **3**, determined by X-ray diffraction, is presented in Figure 1. The geometry about iron is best described as distorted square planar where the metal lies 0.316(1) Å out of



Figure 1. Molecular structures of 2-Et₂O, 2-THF, and 3 at 30% probability ellipsoids; anions and hydrogen atoms are omitted for clarity.

Table 1.	Ethvlene	Polymerization	Data ^a
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compound	time (min)	yield (g) ^b	productivity ^b (g∙mmol ⁻¹ ∙ h ⁻¹ ∙bar ⁻¹)	<i>M</i> n ^c (10 ³ g/ mol)	PDIc	melting temp (°C)
2-Et ₂ O 2-Et ₂ O 2-THF 3 1-Cl ₂ /MAO ^d	$5 \\ 30 \\ 30 \\ 5 \\ 5^{e}$	trace 0.43 trace 0.38 0.79	86 218 942	317 199 172	2.5 1.6 2.3	133 132 129

^{*a*} Polymerizations were carried out using 10 μ mol of catalyst in 10 mL of toluene at 23 °C with 1 bar of ethylene. ^b Mean values over two runs. ^c Determined by high-temperature GPC in 1,2,4-trichlorobenzene. ^d Fe:Al = 1:600. ^e Mass transfer problems after approximately 2 min.

the plane of the three nitrogens. This value is reduced compared to those found in 2-Et₂O and 2-THF, demonstrating a significant geometric distortion upon coordination of a ligand in the basal plane. The alkyl group is positionally disordered, and the metrical parameters are similar to those of the two other alkyl cations.

All three crystallographically characterized alkyl cations were evaluated for ethylene polymerization (Table 1). Ethylene polymerization with a mixture of 1-Cl₂ and MAO was also performed for comparison. While 2-THF is inactive, 2-Et₂O yields linear polyethylene albeit with low productivity, suggesting that dissociation of the donor ligand affords the catalytically active species. The base-free complex, 3, with the least coordinating anion, is the most active of the single-component compounds. Significantly, the polyethylene from the single-component polymerization is linear and contains olefinic end-groups, consistent with chain termination by β -hydrogen elimination. The molecular weights are slightly higher and the polydispersities narrower compared to those of the 1-Cl₂/MAO-produced polymer, due to elimination of chain transfer to aluminum typically encountered with MAO-activated catalysts.¹

In summary, we have reported the first examples of singlecomponent iron catalysts for olefin polymerization. While the nature of the active species for MAO-activated catalysts remains speculative, our results establish the competency of iron(II) alkyl cations as a propagating species. Importantly, these compounds will allow further investigation into both the kinetics and the mechanism of iron-catalyzed carbon-carbon bond-forming reactions.

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Supporting Information Available: Experimental procedures and crystallographic data for 2-Et₂O, 2-THF, and 3 (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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