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Reduction of (Diiminopyridine)iron: Evidence for a Noncationic Polymerization Pathway?

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Summary: A formally zerovalent Fe complex gave, upon activation, the same catalytic activity as the divalent precursor.

The very high activity displayed by late-metal complexes of the diiminopyridine ligands and of {2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$}(C$_5$H$_3$N) in particular as polymerization catalysts[1] has driven research not only toward understanding the mechanism behind this system but also toward exploring the chemistry of this ligand with other transition metals.[2,3] The information gathered to date has clearly demonstrated that the ligand is a nonspectator and that it can afford a variety of transformations by being directly involved in the reactivity of the metal center.[2,4] In addition, it may stabilize reduced species,[2,3,5] due to its ability to accommodate electrons (up to three) in the delocalized π system.[6] As a result, the appearance of complexes as low valent may be in fact deceiving.[5a,b] It is, however, remarkable that, despite the internal charge transfer occurring between the "low-valent" metal center and the ligand system, the high reactivity of the complex is preserved. This in turn creates perspectives for the possible usage of this ligand as an electron reservoir.[5b−d]

Mechanistic information about the interaction of the metal center with the activator has been obtained for several transition-metal complexes of this ligand system[2,3] but not for Fe, which displays the highest reactivity in this family of complexes. Furthermore, the actual oxidation state of iron in the catalytically active species has been the center of a debate. A trivalent Fe center was proposed by Gibson on the basis of Mössbauer and EPR studies.[7] The proposal was argued by Talsi et al., whose spectroscopic investigations suggested instead the involvement of a paramagnetic Fe(II) alkyl bridging the aluminum cocatalyst.[8] Computational studies have invariably assumed the presence of cationic divalent Fe in the active species, although there has been some discussion about the spin state of Fe(II).[9] Finally, recent intriguing findings by Chirik[10] have conclusively demonstrated that cationization of the Fe(II) alkyl derivative affords polymerization without need for further activation, thus adding the possibility to this complex picture that a cationic Fe(II) may be the catalytically active species.

In this paper we describe the reaction of the diiminopyridine−Fe complex[1] with MeLi, affording a reduced complex with the formal appearance of a *zerovalent* species which displays, upon activation with MAO, *catalytic activity identical with* that for the original *divalent* catalyst, also producing *a very similar polymer*.

MeLi, which is a far stronger alkylating agent and more reducing than MAO used to activate the catalyst, was chosen because no clearly defined species have been isolated so far from the direct reaction with the Al cocatalyst.

The reaction of the diiminopyridine−Fe complex with 2 equiv of MeLi has recently been reported to afford a monovalent [{2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$}(C$_5$H$_3$N)-FeMe] species.[10] We have observed that, during the same reaction, deep red crystals of the new species

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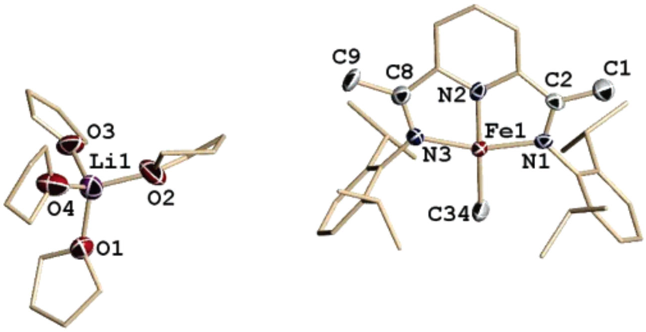
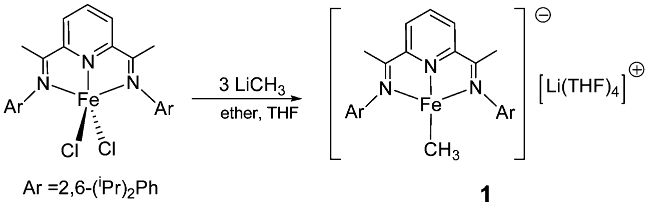


Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probability level. Relevant bond distances (Å) and angles (deg): Fe−N(1) = 1.917(6), Fe−N(2) = 1.849(6), Fe−N(3) = 1.915(5), Fe−C(34) = 2.015(8), C(1)−C(2) = 1.485(11), C(8)−C(9) = 1.515(10), N(1)−C(2) = 1.356(8), N(3)−C(8) = 1.377(9); N(1)−Fe−N(2) = 80.7(2), N(2)−Fe−N(3) = 80.4(3), N(3)−Fe−C(34) = 99.2(3), N(1)−Fe−C(34) = 99.6(3), N(1)−Fe−N(3) = 161.1(3), N(2)−Fe−C(34) = 178.9(4).

Scheme 1



$[\{2,6\text{-}[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(CH_3)]_2\}(C_5H_3N)FeMe][Li(THF)_4]\cdot 0.25THF$ (**1**) were occasionally formed in low yield. This formally zerovalent, new compound turned out to be the only isolable product of the reaction upon use of *3* equiv of MeLi and could be isolated in 64% yield in analytically pure form (Scheme 1).[11] The NMR spectrum (Figure S1, Supporting Information) was largely noninformative, as is typical of these paramagnetic systems.

The anionic moiety of the complex (Figure 1) is nearly isostructural with the *monovalent* neutral counterpart.[10] In contrast to the observations for other transition-metal systems,[4−6] the methyl groups attached to the imine functions *have not been deprotonated* by the strongly basic MeLi. Nonetheless, the metal has been reduced and the complex appears to contain the Fe metal in its *formal zerovalent* state. The reduction could be similar to that observed in the case of the more established Co analogue which, upon alkylation, afforded Co(I).[3] It is also quite possible that the reduction may be assisted by the ligand system, as in the case of the two-electron reduction observed with vanadium.[2a] In addition, an internal charge transfer may also occur in these species,[5a,b] which could result in **1** containing a monovalent Fe bonded to a radical anion or even a divalent Fe bound to a ligand dianion. In any case, the formation of **1** *has required two electrons*.

A d^8 square-planar Fe(0) complex such as **1** could reasonably be expected to be diamagnetic. However, the species is paramagnetic with a magnetic moment which steadily rises from an intercept of $\mu_{\text{eff}} = 1.30\ \mu_B$ at 0 K to reach the value of 6.45 μ_B at room temperature (Figure S2, Supporting Information). Although the magnetic behavior could not be properly simulated, it is possible that, similar to the case of the Nd congener,[5a] thermal population of ligand orbitals at the expense of the low-valent metal center occurs. Thus, an Fe(II) coupled to a diradical dianion is probably the most realistic description of this system.

DFT calculations (see the Supporting Information) were performed on the isolated anion, starting from the crystallographic atomic coordinates and assuming several spin states. A closed-shell true Fe(0) description could be ruled out. The singlet state is best described as containing intermediate-spin Fe(II), with each of the Fe unpaired electrons antiferromagnetically coupled to an electron in a ligand π^* orbital: i.e., it has a double-singlet-biradical structure. The triplet and quintet states, which are close in energy to the singlet, are similar but have the spins of one or two of the ligand π^* electrons inverted. Neither the calculated energies nor the comparison of calculated and experimental geometries allows assignment of the spin state of complex **1**. The electronic structure is very similar to that calculated for Co(I),[12] in the sense that it shows a biradical character with unpaired electrons in metal d orbitals antiferromagnetically coupled to ligand π^* orbitals. Different from the Co(I) complex, however, the Fe metal center uses both d_{xz} and d_{yz} for such biradical couplings, presumably because the d orbitals are high in energy due to the presence of the negative charge.

When a toluene solution of **1** was exposed to ethylene gas, there was no apparent color change nor polymer formation. However, addition of 500 equiv of MAO with exposure to 1 atm of ethylene led to the isolation of large amounts of polyethylene after 30 min of reaction. The activity of **1** was found to be 600 g of PE/(mmol h atm), which compares well, within experimental error, with the activity obtained for the divalent Fe starting complex under the same conditions (675 g of PE/(mmol h atm)). Even more striking is the fact that the polymers produced by **1** and the divalent precursor are *very similar* (Figure 2), clearly indicating that, in both polymerization reactions, the catalytically active species is the same.

The evidence reported here is hard to reconcile with a cationic Ziegler−Natta mechanism for ethene polymerization with **1** and, hence, also with the original Brookhart/Gibson $FeCl_2$ precursor. It should be also noticed that the polymer produced by the cationic Fe(II) derivative[10b] is completely different from that obtained in the present case. In addition, attempt to run a polymerization by activating **1** with BAr^F under the usual reaction conditions did not yield polymer in a

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[11] Experimental details: a solution of MeLi in ether (1.85 mL from a 1.6 M solution, 2.96 mmol) was added to a suspension of $\{2,6\text{-}[2,6\text{-}(i\text{-}Pr)_2PhN{=}C(CH_3)]_2(C_5H_3N)\}FeCl_2$ (0.600 g, 0.99 mmol) in ether at −35 °C. The color became dark brownish red. The ether was evaporated and THF was added, forming a dark red solution. This solution was concentrated and layered with ether, upon which time white solids precipitated and were discarded. The solution was again concentrated and layered with hexanes, forming dark red crystals overnight at room temperature (0.550 g, 0.64 mmol, 64% yield). Anal. Calcd (found) for $C_{51}H_{80}FeLiN_3O_{4.25}$: C, 70.73 (70.69); H, 9.31 (9.28); N, 4.85 (4.83). Crystal data for **1**: $C_{51}H_{80}FeLiN_3O_{4.25}$, $M_w = 1731.94$, monoclinic, $P2_1$, $a = 12.6741(19)$ Å, $b = 17.383(3)$ Å, $c = 24.089(4)$ Å, $\beta = 97.102(3)°$, $V = 5266.5(14)$ Å^3, $Z = 2$, $T = 211$ K, $F_{000} = 1880$, R1 = 0.0794, wR2 = 0.1804, GOF = 1.019. Magnetic measurements were carried out with a SQUID magnetometer by using samples weighed and sealed inside a drybox.

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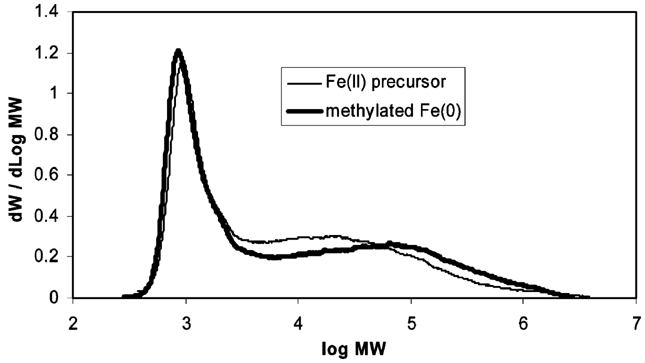

Figure 2. Comparative gel permeation chromatogram of the Fe(II) precursor and complex **1** (M_n = 1954, M_w = 76 377, M_z = 673 379, PD = 39.09 determined by high-temperature GPC in 1,2,4-trichlorobenzene).

significant amount. Furthermore, MAO is usually considered to be reducing rather than oxidizing,[7] and formation of a high-valent complex from the activation of **1** is not likely. Also, it should be observed that complex **1** still requires an excess of activator to perform polymerization. While in the case of the neutral [{2,6-[2,6-(i-Pr)$_2$PhN=C(CH$_3$)]$_2$}(C$_5$H$_3$N)FeMe] species[10] the role of the aluminum activator may well be that of forming a cationic species, this is certainly not the case for **1**. The removal of the coordinated MeLi unit by the Lewis acid may only provide a coordinatively unsaturated (ligand)Fe^0 *neutral* species which, in the light of Chirik results,[5c] most likely will give with olefin just labile coordination.

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Supporting Information Available: Complete crystallographic data (CIF) for complex **1** and text, tables, and figures giving additional characterization data as well as details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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