Communication

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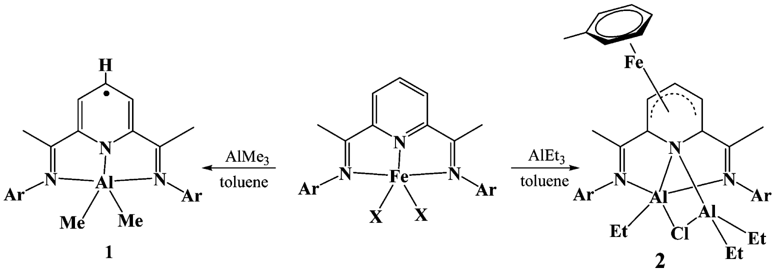
J. Am. Chem. Soc., **2005**, 127 (49), 17204-17206• DOI: 10.1021/ja056135s • Publication Date (Web): 12 November 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

Formation of a Paramagnetic Al Complex and Extrusion of Fe during the Reaction of (Diiminepyridine)Fe with AlR_3 (R = Me, Et)

Jennifer Scott,[†] Sandro Gambarotta,*[,†] Ilia Korobkov,[†] Quinten Knijnenburg,[‡] Bas de Bruin,[‡] and Peter H. M. Budzelaar[§]

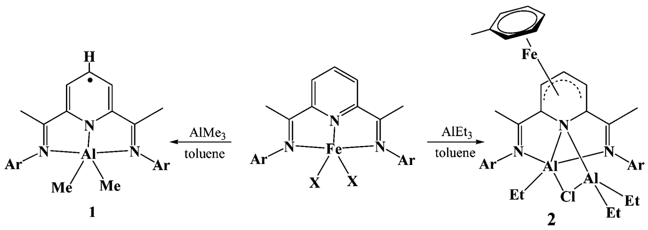
Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, Department of Molecular Materials, Radboud University, Nijmegen, The Netherlands, and Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Received September 15, 2005; E-mail: sgambaro@science.uottawa.ca

In the past decade, interest for the chemistry of imine-based ligand systems has been revitalized by the discovery that their complexes may act as supporting ligands for a variety of excellent catalysts with a range of applications.[1] The bis-imine pyridine ligand in particular has attracted considerable attention for its ability to provide unprecedented Ziegler−Natta catalysts based on late metals.[1c,d] Subsequent studies on these and other transition metal systems, aimed at elucidating the reaction mechanism and identifying the features which enable such a desirable catalytic behavior, have outlined a nonanticipated ability of this ligand to engage directly in the reactivity of the M−C bond, in turn resulting in an impressive variety of transformations.[2−10] Some of these transformations result in *reduction* of the metal center. On the other hand, the ability of the ligand π-system to accept a considerable amount of spin density[8] may actually cause *oxidation* of the metal center, thus providing species whose low-valent appearance is deceiving.[11−14] This ambiguous behavior has obvious implications as far as the oxidation state of the metal in the catalytically active species is concerned.

The question at the basis of the unusually high catalytic activity of these derivatives is what is the type of polymerization mechanism followed by these complexes while activated by the Al cocatalysts (MAO, $AlMe_3$, or $AlEt_3$). It is debated whether the role of the Al cocatalyst in this system is that of an alkylating agent, a reductant, a cationizing agent or a combination of these. Studies on the Co system show that the first step of the activation is reduction from Co^{II} to Co^{I},[15] thus entertaining the possibility that the primary role of the cocatalyst may be that of an alkylating/reducing agent, as observed in the cases of V,[2] Cr,[3] and Mn.[3] This, however, does not exclude the possibility that a low-valent species might be cationized in a subsequent step by the same cocatalyst also acting as a Lewis acid. In the case of the Fe derivative,[1c,d] the most active and performing in this series of catalyst precursors, the situation is even more complex. Recent NMR and MS studies specifically targeting the interaction of the Fe catalyst with MAO and AlR_3 have shown that the nature of the activator determines whether cationic or neutral divalent species are formed.[16] Other recent studies have established that alkylating agents may initially reduce the Fe metal toward either a zero[17]- or monovalent[18] state, which can still be activated by MAO for polymerization. On the other hand, formation of a cationic organo−Fe(II) species has also been demonstrated to be a viable possibility for producing catalytically active species.[19]

Scheme 1



[X = Cl, CH_2SiMe_3, Ar = 2,6-i-Pr_2Ph]   [X = Cl, Ar = 2,6-i-Pr_2Ph]

Therefore, we have herein studied the reaction of the Fe complex with MAO and R_3Al [R = Me, Et]. The reactions of $LFeCl_2$ (L= {2,6-[2,6-(^{i}Pr)$_2$PhN=C(CH_3)]$_2$(C_5H_3N)}) with the Al alkylating agents (10 equiv) were carried out in toluene at −35 °C (Scheme 1).[20] Unfortunately, in the case of MAO (the preferred activator), efforts have only led to ill-defined species. In the case of Me_3Al, the color changed instantly to purple upon mixing and then to green while reaching room temperature. Under identical conditions, LFe(CH_2SiMe_3)$_2$ was also reacted with Me_3Al, leading to a dark-orange solution.[20] After workup, both reaction mixtures afforded the same orange and paramagnetic $LAlMe_2$ (**1**) derivative [$\mu_{eff} = 1.73\ \mu_{BM}$] which was isolated in significant yield (38 and 39% respectively).

The crystal structure of **1** (Figure 1) shows a Me_2Al unit bound to the apparently unperturbed ligand with the Al in a distorted trigonal bipyramidal coordination environment without any special structural features.

The appearance of this complex as a divalent Al species is obviously deceiving, given the established ability of this ligand system to embark on electron-transfer interactions.[11−14] Thus, **1** is more appropriately described as $[(L^{-1})Al^{III}(Me)_2]$, with the unpaired electron mainly centered on the one-electron-reduced diiminepyridine radical anion. Accordingly, the EPR spectrum of **1** (Figure 2) shows the complexity expected for an organic radical. A satisfactory simulation of the experimental spectrum was obtained using parameters consistent with a substantial delocalization of the

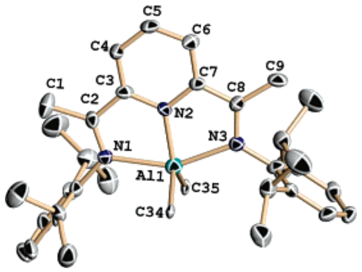


Figure 1. Thermal ellipsoid plot of **1**. Ellipsoids drawn at 30% probability. Selected bond distance (Å) and angles (deg): Al−N(1) = 2.212(8), Al−N(2) = 1.892(8), Al−N(3) = 2.163(8), Al−C(34) = 1.982(4), Al−C(35) = 2.007(4), N(1)−Al−N(3) = 153.1(3), N(2)−Al−C(35) = 126.2(3), N(2)−Al−C(34) = 119.0(3), C(34)−Al−C(35) = 114.72(18).

[†] University of Ottawa.
[‡] Radboud University.
[§] University of Manitoba.

10.1021/ja056135s CCC: $30.25 © 2005 American Chemical Society

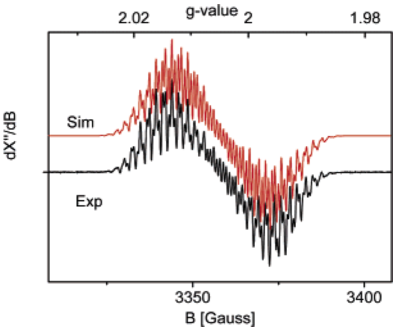


Figure 2. Solution X-band EPR spectrum of **1** in toluene at 293 K. Conditions: frequency = 9.4228 GHz, modulation amplitude = 0.01 mT, microwave power = 0.998 mW. The simulation was obtained with the parameters included and explained in the text.

Table 1. Experimental and DFT-EPR Properties of **1**[a]

	nuclear spin I^b	exp. (sim.)	ORCA (b3-lyp)	ADF (BP86)
g_{iso}		2.0047	2.0031	2.0034
A^{Al}	$^5/_2$	13.39	20.90	17.40
$A^{1\text{N}}$	1	15.45	9.90	7.20
$A^{2\text{N}}$	1	5.50	4.60^c	3.20^c
$A^{1\text{H}}$	$^1/_2$	17.81	15.80	13.10
$A^{2\text{H}}$	$^1/_2$ (2)	4.94	4.50^c	1.70^c
$A^{6\text{H}}$	$^1/_2$ (6)	7.50	6.50^c	0.48^c
A^{Me}	$^1/_2$ (6)	<0.5	0.11^c	0.03^c

[a] Absolute values of the HFCs in MHz. [b] Number of equivalent nuclei in brackets. [c] Average of nonequivalent atoms in the static DFT structure.

spin density over the diiminepyridine part, with hyperfine couplings (HFCs) to aluminum (A^{Al}), the pyridine nitrogen ($A^{1\text{N}}$), two equivalent imine nitrogens ($A^{2\text{N}}$), the pyridine ring proton in *para* position ($A^{1\text{H}}$), two equivalent *meta* protons ($A^{2\text{H}}$), and a set of six equivalent protons ($A^{6\text{H}}$) corresponding to the two equivalent imine methyl groups (see Figure 2 and Table 1).

The possibility that A^{H6} could also stem from coupling with the six equivalent protons of the two aluminum-bound methyls was clearly ruled out by DFT calculations.[21−23] From the optimized geometry[23] of **1**, the EPR parameters were calculated with both ORCA[21] and ADF.[24] ORCA gave the most satisfactory results, in good agreement with the experimental parameters (Table 1).[22]

The SOMO consists mainly of the diiminepyridine π^* orbital of L^{-1}, with small antibonding contributions from σ^* Al−C orbitals, and nearly zero contribution from aluminum itself (Figure S1, Supporting Information). The LUMO of **1** consists of a different diiminepyridine π^* orbital, without any other significant contributions (Figure S2). Substantial delocalization of the spin density over the diiminepyridine part of **1** is clear from a spin density plot (Figure S3).

Complex **1** provides the second case of a crystallographically characterized paramagnetic Al species, the first having been very recently obtained with the series of (bis-imine)acenaphthene derivatives (dpp-BIAN)AlR_2 (dpp-BIAN = 1,2-bis[(2,6-^{i}$Pr_2C_6H_3$)imino]-acenaphthene; R = Me, Et, ^{i}Bu).[25] According to the procedure reported by Schumann for the preparation of those species,[25] **1** could also be conveniently synthesized (79%) via reduction of the ligand L in THF with Na followed by addition of Me_2AlCl in toluene.[20]

The reaction of $LFeCl_2$ with Et_3Al (10 equiv) was also carried out in toluene at −35 °C (Scheme 1).[20] After workup, the reaction mixture afforded the paramagnetic dark-orange complex [η^4-LAl_2Et_3(μ-Cl)]Fe−(η^6-C_7H_8) (**2**) which was isolated in significant yield (41%). Complex **2** is paramagnetic with a rather low value of the magnetic moment at room temperature in both solid state and solution [$\mu_{\text{eff}} = 1.41$ and 1.48 μ_{BM} (Evan's method)]. The ^{1}H NMR spectrum[20] consists of broad features in the range normally expected for diamagnetic species. The resonances of the nonequivalent ethyl groups attached to the aluminum atoms can tentatively be assigned to two broad singlets at −0.3, 0.9, 0.17, and 0.32 ppm. Also clearly recognizable were the resonances of the nonequivalent ^{i}Pr substituents at 3.5 (*ipso* H) and 1.4 ppm (Me groups).

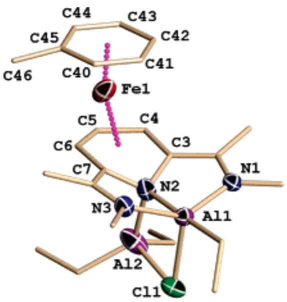


Figure 3. Thermal ellipsoid plot of one of two independent molecules of **2**. Ellipsoids drawn at 30% probability. Selected bond distance (Å) and angles (deg): Al−N(1) = 1.996(4), Al(1)−N(2) = 1.993(4), Al(1)−N(3) = 2.035(5), Al(2)−N(2) = 1.970(5); Al(1)−Cl = 2.430(2), Fe(1)−C(3) = 2.254(6); Fe(1)−C(4) = 1.748(10); Fe(1)−C(5) = 1.905(9); Fe(1)−C(6) = 2.146(7; Al(1)−Cl−Al(2) = 82.73(8).

The crystal structure of **2** (Figure 3) shows a Et_2Al(μ-Cl)AlEt unit bound to the N atoms of the folded ligand. The major distortion is observable around the pyridine ring which adopts an η^4-bonding mode with an Fe atom (disordered over two positions and alternatively η^4-coordinating one or the other side of the pyridine ring). In turn, Fe is η^6-coordinated to a molecule of toluene. The pyridine N atom deviates from the plane defined by the C atoms and is tetrahedrally bound to two Al.

Given the established ability of the π-system of this ligand to accept up to three electrons,[8] there is no doubt that even in this case the two Al atoms are in their trivalent state and that the ligand is dianionic, thus being the recipient of two of the *four* electrons necessary for the formation of **2**. In this event, the Fe atom may be regarded as being present in its *formal* zerovalent state. However, there is the realistic possibility that the ligand may actually be carrying *three* electrons and that Fe may be in the formal monovalent state.

DFT calculations[23] were carried out on different spin states of a model compound having Me groups instead of the Et and ^{i}Pr groups of **2**, and benzene instead of toluene. In both singlet and triplet states the ligand has accepted two electrons from the Al_2Et_3Cl fragment bound to it. In the singlet state, these electrons are located in an orbital that is a 1:1 mixture of the original two ligand π^* orbitals. This orbital mixing results in a localization of the imine single and double bonds, and in a concentration of the LAl_2Et_3Cl HOMO on one side of the pyridine ring. Interaction with the iron-containing fragment then results in a regular 18-electron (arene)-$Fe^{(0)}$(butadiene)-like coordination environment, in good agreement with the crystal structure (Figure S1). The LAl_2Et_3Cl moiety is calculated to be a *poorer* donor for Fe than real butadiene by about 17 kcal/mol.[26]

The structure calculated for the triplet state has C_s symmetry, with a mirror plane through the pyridine nitrogen, the Al, and Fe atoms. The Fe atom is η^3-bound to the pyridine ring and approximately η^4-bound to the arene ring. The bonding situation is complex and is best described starting from a *triplet* ligand dianion (both π^* orbitals singly occupied) and high-spin (arene)$Fe^{(0)}$ (also a triplet). Of the pairwise interactions between the unpaired fragment electrons, one is antiferromagnetic and one is ferromagnetic, leading to the triplet state for the molecule[27] (the quintet state is much higher in energy). Due to the high-spin nature of $Fe^{(0)}$, its coordination number is lower than in the singlet state.

The calculations predict the energy of the triplet to be ca. 6 kcal/mol lower than that of the singlet. However, the observed X-ray structure agrees much better with the singlet than with the triplet. Spin-state energies are notoriously difficult to calculate with high accuracy. It is not clear at present whether the apparent disagreement is due to the choice of functional and basis set, to the simplifications used to model the system, or to packing forces in the crystal. The most reasonable interpretation seems to be that for the real complex **2** the singlet and triplet states are very close in energy, that the X-ray structure corresponds to the singlet state, and that the observed magnetism (too low for a pure triplet, but clearly not in agreement with a pure singlet) is due to thermal population of the triplet state.

Both **1** and **2** are catalytically inactive even upon further treatment with MAO or with other aluminum alkyls. Therefore, their formation is a catalyst deactivation pathway. The formation of **1** from the reaction of the Fe catalyst with the Me_3Al activator is the result of both ligand transmetalation and reduction. Although we observed that traces of **1** ($\leq$0.5%) may be formed upon addition of $AlMe_3$ to a solution of the free ligand in toluene, the reactivity of $AlMe_3$ with the free ligand is well understood and does not involve redox transformations in a significant amount.[5,7] Therefore, an obvious question arises about the source of the electron necessary for the formation of **1**. It is unlikely to be provided by the homolytic cleavage of the Al−Me bond of the hypothetical $LAlMe_3$ intermediate (as possibly arising from a simple transmetalation). Conversely, the possibility that the Fe center may be rapidly reduced during alkylation processes has been recently substantiated.[6,17,18] The fact that **1** is also formed by the reaction of $LFe(CH_2SiMe_3)_2$ with Me_3Al entertains the possibility that an unstable FeR_2 species might be extruded first, followed by decomposition toward a transient low-valent organo−Fe complex. This species might have sufficient reducing power to form **1**.

The formation of **2,** although conceptually different (it involves a four-electron reduction), is related to the formation of **1** and provides a mechanistic insight into how the strong terdentate ligand loses its metal. Regardless of how the oxidation states of Al and Fe are assigned in **2**, the formation of this species is the result of a *four-electron reduction*. The fact that the reduction appears to be more extensive than in the case of **1** (which required only one or perhaps three electrons, depending on the unknown fate of the Fe atom) can be only related to the lower stability of the Fe−Et bond of intermediate species in comparison to the Fe−Me bond. In other words, it is not unreasonable to expect that the lower stability of an Fe−Et-containing moiety may no longer provide a lifetime sufficiently long to enable its migration from the ligand system. As a result, the ligand transmetalation appears to have been arrested halfway, with the Fe atom remaining π-coordinated to the ligand.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada and by the Radboud University Nijmegen and the University of Manitoba.

Supporting Information Available: Crystallographic data (CIF), and details of the DFT calculations (including spin density plots) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) For comparison, 1,2-dihydropyridine and 2-methylene-1,2-dihydropyridine are calculated to bind more weakly than butadiene to the (benzene)$Fe^{(0)}$ fragment by 8 and 15 kcal/mol, respectively.

(27) The calculated UHF electronic structure is not a pure triplet ($\langle S^2 \rangle = 2.36$). The high value can be attributed to singlet-biradical character of the antiferromagnetic interaction.

JA056135S