2,6-Diiminopyridine Iron(II) Dialkyl Complexes. Interaction with Aluminum Alkyls and Ethylene Polymerization Catalysis

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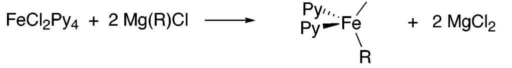
Received July 28, 2005

*Summary: Bis(pyridine)iron dialkyl complexes FeR_2Py_2 ($R = CH_2Ph, CH_2CMe_2Ph$, and CH_2SiMe_3) react with 2,6-diiminopyridine ligands, affording the corresponding organoiron complexes. The complex $Fe(CH_2SiMe_3)_2$-$(C_5H_3N$-2,6-$(C(=N$-mesityl$)Me)_2$, **4a**, becomes an active ethylene polymerization catalyst upon treatment with Al or Zn alkyls. A catalytically active 1:1 Fe/Al adduct has been detected in solution by ^1H and UV−vis spectroscopies.*

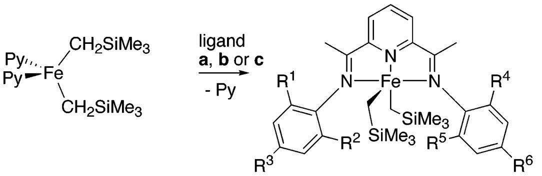
Iron bis(imino)pyridine complexes are extremely active catalysts for ethylene polymerization.[1] The active species involved in the catalysis are Fe(II) alkyl complexes that are generated in situ from the corresponding dihalide complexes and a suitable cocatalyst such as MAO or aluminum trialkyls.[2] However, the isolation of iron alkyl complexes containing bis(imino)pyridine ligands that could serve as a model of the catalytic species has proven elusive until recently.[3,4] Herein we describe the synthesis of three Fe(II) (trimethylsilyl)-methyl complexes containing 2,6-diiminopyridine ligands by means of ligand exchange reactions. During the course of this work, Chirik described the preparation of (diiminopyridine)iron alkyls, by the direct alkylation of the precursor chloro complexes.[4]

We have shown that alkyl complexes of Ni and Pd stabilized by labile pyridine ligands undergo facile ligand exchange reactions with α-diimine and other nitrogen ligands, and therefore they are valuable precursors for the systematic preparation of otherwise difficult to synthesize complexes that are relevant in polymerization chemistry.[5] As a continuation for these investigations, we decided to extend this methodology to iron. Thus, the reaction of $FeCl_2Py_4$ with alkylmagnesium reagents Mg(R)Cl ($R = CH_2SiMe_3$, CH_2Ph, or CH_2CMe_2Ph) in Et_2O gives rise to deep purple solutions that contain the desired dialkyliron complexes (eq 1). A standard workup, followed by crystallization from hexane, allows the isolation of crystals of benzyl (**1**) and neophyl (**2**) complexes of composition FeR_2Py_2. The extreme solubility of the trimethylsilyl derivative **3** prevented its isolation in pure form, but the analysis of the solution contents by ^1H NMR showed paramagnetically shifted resonances corresponding to the $SiMe_3$ (ca. 11.2 ppm) and pyridine ligands (35.5 and 17.4 ppm, for H3 and H4, respectively). The NMR spectra of **1** and **2** display signals corresponding to the pyridine H3 and H4 signals at roughly the same positions as those found in the spectrum of **3**, and other resonances that can be assigned to the benzyl or neophyl groups.[6]



(1)

1, $R = CH_2Ph$
2, $R = CH_2CMe_2Ph$
3, $R = CH_2SiMe_3$



(2)

4a, all R = Me
4b, $R^1 = R^2 = R^4 = R^5 = Me$; $R^3 = R^6 = H$
4c, $R^1 = R^2 = R^3 = Me$; $R^4 = Pr^i$; $R^5 = R^6 = H$

The identity of compounds **1**−**3** has been confirmed by the crystal structure of the neophyl derivative (Figure 1). This compound exhibits a distorted tetrahedral coordination, similar to that found in $Fe(Mes)_2(Py)_2$[7] and

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[6] ^1H NMR data (C_6D_6, 25 °C): **1**, δ −80.28 (116 Hz, 2H, *p*-C*H*$_{ar}$), −58.03 (456 Hz, 4H, *m*-C*H*$_{ar}$), 34.04 (132 Hz, 4H, H3-py), 11.02 (2H, H4-py); **2**, δ 5.42 (48 Hz, *m*-C*H*$_{ar}$), 11.77 (330 Hz, 2H, *p*-C*H*$_{ar}$), 12.92 (117 Hz, 2H, H4-py), 25.23 (462 Hz, 12H, C*Me*$_2$), 35.27 (174 Hz, 4H, H3-py), 119.99 (1350 Hz, 4H, *o*-C*H*$_{ar}$).

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10.1021/om050645d CCC: $30.25

Table 1. Ethylene Polymerization Data[a]

catalyst (μmol)	activator (equiv)	P (bar)	yield (g)	activity[b]	M_n	PDI	Me/1000C	vinyl/1000C	^iPr/1000C
$FeCl_2$·**a** (5)	MMAO (2000)	2	5.34	1600	1840	2.2	9	2.1	5.6
4a (50)[c]	$B(C_6F_5)_3$ (0.90)	3	0.85	19	90300	2.4			
4a (4)	MMAO (1000)	5	3.68	550	4730	2.2	17	1.8	2.5
4a (4)	TiBA (100)	5	5.33	800	3130	25[d]	4.8	1.0	4
4a (4)	TMA(100)	5	4.65	700	9770	10	4.0	1.0	0
4a (4)	TMA (50)	5	4.73	710	14700	5.5	2.7	0.9	0
4a (4)	$ZnMe_2$ (100)	5	0.35	55	6250	9.7	4.6	0.4	0
4a (4)	$AlMe(OAr)_2$ (50)	5	1.14	170	12900	3.0	1.5	1.3	0

[a] Experimental conditions: solvent, toluene, 50 mL, 30 °C, 20 min. [b] kg PE/mol Fe·h·bar. [c] Temperature: −80 °C to RT. [d] Bimodal distribution: M_p = 1200, 20400.

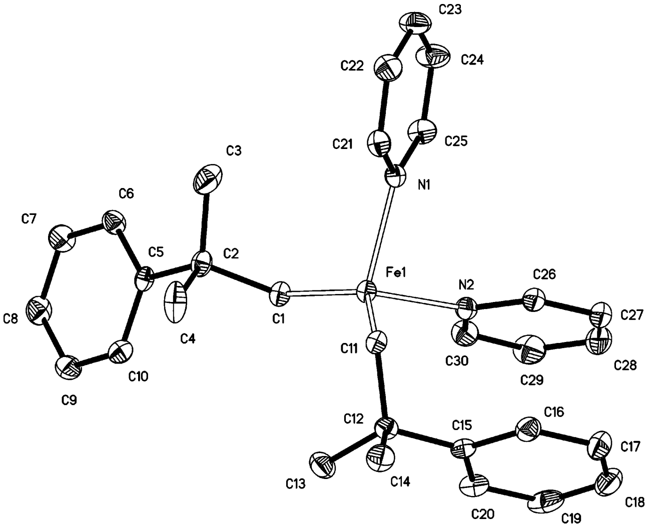

Figure 1. ORTEP view of compound **2**. Selected bond lengths (Å) and angles (deg): Fe(1)−C(1), 2.0905(18); Fe(1)−C(11), 2.0895(19); Fe(1)−N(1), 2.1569(16); Fe(1)−N(2): 2.1414(16); N(1)−Fe−N(2), 91.70(6); C(1)−Fe(1)−C(11), 131.31(8).

in the related amide compound $Fe(N(SiMe_3)_2)_2(Py)_2$.[8] As observed in the latter compound, the angle N−Fe−N formed by the pyridine nitrogen atoms and the metal center is rather acute, approaching 90°. The Fe−C bond lengths (ca. 2.09 Å) are similar to those found in other tetracoordinated Fe(II) alkyls.[9]

Compounds **1**−**3** react rapidly with 2,6-diiminopyridine ligands in hexane at low temperature, but only the bis(trimethylsilyl)methyl derivatives **4a**−**c** have been isolated, as analytically pure dark violet solids (eq 2). They display μ_{eff} values of 5.1 μ_B in the solid state, consistent with a high-spin electronic configuration. The crystal structure of compound **4a** is shown in Figure 1. The iron atom is in a five-coordinated environment, with an approximately square-pyramidal geometry, as observed in the recently reported Fe(II) alkyl complexes with the bulky *N,N′*-bis(2,6-diisopropylphenyl)diiminopyridine ligand.[4b] Despite the fact that the two alkyl groups occupy axial and equatorial positions, the Fe−C distances are virtually identical (ca. 2.077(2) and 2.075(2) Å, respectively). Somewhat surprisingly, the Fe−N bonds are shorter in **4a** than in the electron-poorer FeX_2 complexes of the same tridentate ligand.[1d] The difference is small for the Fe−N(imine) bonds (ca. 0.05 Å shorter in **4a** on average), but more appreciable for the Fe−N(pyridine) bond (2.0056(18) Å in **4a**; 2.110(6) and 2.103(6) Å in the $FeCl_2$ and $FeBr_2$ derivatives, respectively).

Complexes **4a**−**c** give rise to typical paramagnetic ^1H spectra that can be assigned on the basis of the signal intensities and by comparison with those of the analogous halide derivatives. Together with the ligand resonances, they display a single characteristic signal of relative intensity 18 H, corresponding to the two $SiMe_3$ groups. The chemical shifts of the NMR signals of **4a** show the expected linear $1/T$ dependency, but below 258 K, those corresponding to the $SiMe_3$ and the mesityl *o*-methyl groups split in two, indicating that a dynamic process, responsible for their averaging at room temperature, becomes slow at that temperature. This process probably corresponds to the swinging oscillation of the alkyl ligands between the axial and equatorial positions. The coalescence temperatures for the $SiMe_3$ (270 K) and *o*-Me signals (250 K) allow an estimation of ca. 10 kcal/mol for the exchange energy barrier.[10]

The availability of compounds **4a**−**c** led us to investigate the capability of iron alkyls to catalyze the polymerization of ethylene (Table 1). As expected, these high-spin compounds fail to react with ethylene.[9a,11] To convert compound **4a** into a catalytically active species, it was reacted with $B(C_6F_5)_3$ at room temperature under 2 bar of ethylene, but no polymer was formed under these conditions, despite the relatively large load of **4a** (50 μmol) that was used. A marginal polymerization activity was observed when **4a** and $B(C_6F_5)_3$ were mixed at −80 °C and then allowed to warm to room temperature. The use of specially purified ethylene (stored over a solution of triisobutylaluminum (TiBA) for 15 days) did not change these results. However, high catalytic activity levels, comparable to those obtained with the conventional $FeCl_2$ catalyst precursor and MMAO, were recorded in the presence of various aluminum alkyls. Under similar experimental conditions, **4a** becomes catalytically active in the presence of trimethylaluminum (TMA) or triisobutylaluminum (TiBA) at relatively low Fe:Al ratios. $ZnMe_2$, or even the aluminum alkyl−aryloxide $MeAl(OAr)_2$ (Ar $=OC_6H_2Bu^t_3$-2,4,6), considered a good water scavenger but inert as a cocatalyst,[12] also activates the iron complex, albeit not as efficiently as the aluminum alkyls. Not surprisingly, the activity of **4a** in the presence of MMAO is very high, comparable

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(10) At 400 MHz. The chemical shifts of the signals at the coalescence temperature were corrected for their $1/T$ dependence by extrapolation of the values recorded at lower temperatures.

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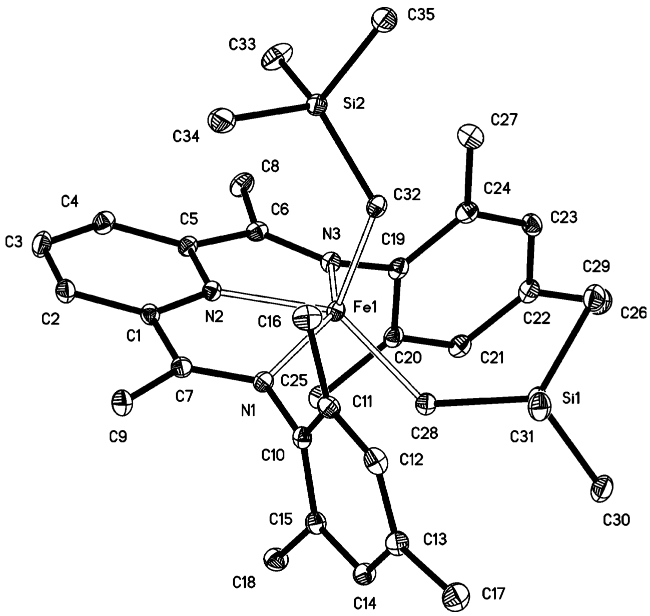

Figure 2. ORTEP view of compound **4a**. Selected bond distances (Å) and angles (deg): Fe(1)−C(28), 2.075(2); Fe(1)−C(32), 2.077(2); Fe(1)−N(1), 2.044(19); Fe(1)−N(3), 2.2284(19); Fe(1)−N(2), 2.0056(18); C(28)−Fe(1)−C(32), 117.23(9); C32−Fe(1)−N(2), 106.11(8); C(28)−Fe(1)−N(2), 136.66(8); N(1)−Fe(1)−N(3), 144.11(7).

to that of the analogous chloro complex. The polymers produced with MMAO and TiBA display isopropyl branches, indicating that Fe−Al chain transfer occurs in the process, as is normally observed with iron catalysts.[1d]

The relatively low number of vinyl terminal groups (systematically less than 1 per molecule) indicates that chain transfer to the cocatalyst competes with β-H elimination as the chain termination processes.

These results prompted us to investigate the interaction of **4a** with trimethyl aluminum, as a functional model of the catalytic reaction. It was noticed that, under the highly diluted conditions used in catalysis (4 μmol Fe in 50 mL of toluene), a minimal Fe:Al ratio of 1:25 is required to generate an active system, even using purified ethylene. However, in more concentrated solutions (ca. 0.02 M), **4a** reacts rapidly with 1 equiv of TMA, with a color change from deep violet to greenish-yellow. If ethylene is bubbled through these solutions, precipitation of PE takes place. The ^{1}H NMR spectrum of a 1:0.9 **4a**/TMA mixture in C_6D_6 shows the formation of a major product (Figure 2) displaying one single signal for the four *ortho*-methyl groups of the aryl substituents, which indicates an effective C_{2v} symmetry. No evidence for fluxional processes was found when the spectra were recorded in the temperature range 300−210 K (toluene-d_8). This feature makes it difficult to propose a specific binding mode for TMA, since alkyl-bridged structures such as those proposed by Bryliakov[13] for the species formed upon reaction of $FeCl_2$(diiminopyridine) complexes with $AlMe_3$ would decrease the molecular symmetry. Even so, the **4a**/TMA spectrum bears some resemblance to the latter. For example, the signal at ca. 36 ppm is almost identical to that assigned to the pendant $AlMe_2$ unit connected to the Fe moiety by bridging Me groups in Bryliakov's system. Measurement of the magnetic moment of this species (Evans' method) afforded values close to 5.0 μ_B in the full temperature range studied by NMR, indicating that the oxidation state of Fe has not changed. These results give support to the occurrence of **4a·**TMA as a high-spin, neutral Fe(II) complex. To examine the species formed in conditions more akin to the real catalysis setup, the ^{1}H NMR spectra of mixtures of **4a** with increasing amounts of TMA (up to 10 equiv) were obtained. These display new signals, indicating the formation of one or more different species, and are significantly broader. Although these spectra are difficult to interpret, the UV−vis spectra of the **4a**/TMA mixtures show no important variations for different Fe:Al ratios, suggesting that the new species formed are structurally similar, probably arising from alkyl exchange processes.

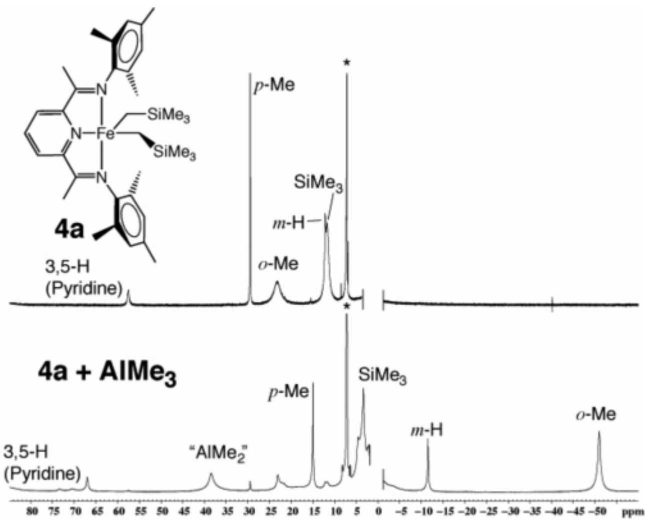

Figure 3. Central section of the ^{1}H NMR spectrum of **4a** and **4a** + 0.9 equiv of $AlMe_3$, displaying the signals corresponding to the mesityl, trimethylsilyl, and Al-Me groups. Signals in the diamagnetic region have been omitted for clarity.

The fact that **4a** develops very low activity levels on treatment with $B(C_6F_5)_3$ (and this only when low temperature is used) is somewhat surprising in view of the recent results of Chirik, who showed that the latter Lewis acid reacts with an Fe(II) dialkyl related to **4a** containing the very bulky *N,N′*-bis(2,6-diisopropylphenyl)-2,6-diiminopyridine ligand, to afford a stable cationic complex that acts as a single-component polymerization catalyst.[4a] A possible explanation for our observation is that the mesityl-based pyridinediimine ligand does not provide enough steric stabilization to such cationic species under the actual polymerization conditions. In any case, the formation of the Fe(II)R_2−AlR_3 adduct is very important under the usual catalysis conditions and contributes to the stabilization of the catalytic species in its resting state. It is conceivable that these adducts could dissociate into Fe(II)$R^+AlR_4^-$ ion pairs, with the anion playing a stabilizing role that can be considered analogous to that of phosphines (or other secondary ligands) in nickel-catalyzed olefin oligomerization or polymerization reactions.[14]

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In summary, we have developed a new method for the preparation of Fe(II) alkyl complexes with nitrogen ligands and showed that these compounds can be employed in the investigation of the mechanism of the Fe-catalyzed ethylene polymerization reactions. Our results suggest that aluminum cocatalysts may have an important role in the stabilization of the catalyst resting state and in the modulation of its activity. We are currently extending our methodology to the synthesis of other types of Fe(II) alkyls that could favor the isolation and characterization of catalytically active Fe−Al complexes.

Acknowledgment. Financial support from the DGI (Project PPQ2003-00975) and Junta de Andalucía is gratefully acknowledged. A.M.N. is grateful for a research fellowship from the Consejo Superior de Investigaciones Científicas (I3P program). We thank Prof. E. Carmona for helpful discussions.

Supporting Information Available: Text giving experimental procedures and characterization data for all new complexes and tables of crystallographic X-ray data for **2** and **4a**, and NMR and UV−vis spectra of **4a** + TMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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