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Spin Transitions in Bis(amidinato)-N-Heterocyclic Carbene Iron(II) and Iron(III) Complexes

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In contrast to high spin pyridyl diimine iron(II) dichloride complexes, analogous bis(amidinato)-N-heterocyclic carbene iron(II) and iron(III) complexes demonstrate complex magnetic behaviour. In the solid state, they are best described as intermediate spin complexes at low temperatures that demonstrate gradual spin transitions beginning near or below room temperature. Treating the bis(amidinato)-N-heterocyclic carbene iron(II) complex with an aryl azide revealed enhanced reactivity compared to analogous complexes supported by pyridyl diamidine ligands.

Since being discovered independently by Brookhart and Gibson as exceptionally active and selective ethylene polymerization catalysts, the chemistry of iron complexes bearing pyridyl diimine (PDI) ligands (e.g. 1, Figure 1) has been of considerable interest to organometallic chemists. In addition to ethylene oligomerization, alkylene cyclotrimerization, atom transfer radical polymerization (ATRP), and lactide polymerization reactions that have been developed using iron(II) halide or alkoxide catalyst precursors, Chirik and co-workers have discovered that reduced PDI iron complexes lead to excellent catalysts for the hydrogenation, hydroboration and hydroformylation of olefins as well as the [2+2] cycloaddition of olefins and dienes.

Inspired by the breadth of reactions catalysed by PDI iron complexes, our research group recently synthesized the first analogous pentacoordinate iron complex bearing a novel bis(amidinato)-N-heterocyclic carbene ligand (2a, Figure 1). Henceforth, we will refer to this ligand as carbenodiamidine, CDA. Noteworthy is the central trihydropyrimid-2-ylidene donor of CDA, which is a class of N-heterocyclic carbenes (NHCs) that had never been reported for iron complexes. We surmised that replacing the central pyridine of PDI ligands with a sterically similar, but electronically different NHC would significantly alter electronic structure and reactivity compared to 1. Initial structural data and catalytic reactions supported this hypothesis. For example, deviations from typical metal–ligand bond distances were observed, including one of the shortest iron–carbene bond lengths observed to date (1.812(2) Å at 100 K). Additionally, the electron donating capabilities of CDA ligands were exploited for the generation of an exceptionally active iron catalyst for lactide polymerization. Coupled with the need to better understand iron–NHC bonding, these findings prompted a more thorough inquiry into the electronic structure of iron complexes containing the CDA ligand. Moreover, the enhanced reactivity of CDA iron complexes compared to PDI iron complexes is illustrated by reactions between analogous iron(II) complexes and an aryl azide.

Figure 1. pyridyl diimine (1) and carbenodiamidine (2) complexes of iron.

Previously, we reported the synthesis of (CDAFeCl (2a)). A high spin iron(II) configuration was assigned to the complex based on the solution magnetic moment (μB) of 5.0 μB (χT = 3.1 cm³K/mol) in THF and 4.6 μB (χT = 2.7 cm³K/mol) in CH₂Cl₂ at 25 °C using Evans’ method. One electron oxidation of 2a was possible using acetylferrocenium tetrafluoroborate in CH₂Cl₂ to form [(CDAFeCl₂)BF₄ (3). The magnetic moment of 5.0 μB (χT = 3.1 cm³K/mol) in THF at 25 °C is too low for a high spin iron(III) complex and too high for an intermediate spin iron(III) complex.

To further investigate the magnetic properties of 2a and 3, solid-state dc-magnetic susceptibility data were obtained from 2 K to 300 K (Figure 2). The samples demonstrated complex magnetic behaviour as a function of temperature. At low temperatures, both complexes had low magnetic moments that increased rapidly to a plateau at intermediate temperatures. Upon further heating, the magnetic moments underwent a gradual increase until the samples reached the maximum temperature achievable by the instrument.

The low magnetic moments observed at low temperatures for both 2a and 3 are consistent with contributions from zero-field splitting, which is common for iron(II) and iron(III) complexes. The plateau in χT for 2a occurred from 30 K to 150 K and at 1.00
Figure 2. Variable temperature solid-state de-magnetization data for 2a and 3 using SQUID magnetometry. Filled symbols represent experimental data, and the solid line for 2a represents the simulation obtained by combining two models: below 100 K, the data were fit to intermediate spin iron complexes with significant contributions from zero-field splitting (for S = 1 in 2a: \( g_{	ext{iso}} = 2.01 \), |\( D \) = 26 cm\(^{-1} \), |\( E \) = 6 cm\(^{-1} \); for S = 3/2 in 3 (fit shown in ESI): \( g_{	ext{iso}} = 2.01 \), |\( D \) = 3.4 cm\(^{-1} \), |\( E \) = 2.0 cm\(^{-1} \)) and above 100 K, the data were fit using \( x = 1/[1 + \exp((\Delta H/RT)(1/T_0 −1/T)) \) (Figure S1). This value is significantly lower than the spin-only value expected for an S = 3/2 state at 199 K. When the high temperature data (>100 K) was modelled with the Sorai domain model, the best fit was for a spin state change at 199 K from an S = 3/2 state to a higher spin state characterized by \( \chi T = 3.13 \) cm\(^2\)K/mol (Figure S1). This value is significantly lower than the spin only value expected for a high spin S = 3/2 iron(III) centre (4.39 cm\(^2\)K/mol), which suggests that a spin equilibrium model may be inappropriate. As such, the fit was not included in Figure 2. Attempts to provide some clarity were made by evaluating 2a by EPR spectroscopy. However, solid state spectra collected at 10 K were complicated and suggested the presence of multiple S = 3/2 species (Figure S2).

To gain further insight, 2a and 3 were analysed by variable temperature zero-field \(^{57}\)Fe Mössbauer spectroscopy (Figures 3 and S2). At 90 K, the Mössbauer spectrum of \((\text{CDA}^{\text{Fe}})\text{FeCl}\_2\)BF\(_4\) (2a) features an isomer shift of 0.31 mm/s and a quadrupole splitting of 2.14 mm/s (Figure 3). These values are consistent with an intermediate spin (S = 1) iron(II) centre as suggested by the SQUID measurements. Also consistent with the SQUID measurements were minimal changes in the Mössbauer spectrum between 100 and 150 K and significant changes upon warming to 295 K. The latter were characterized by a noticeable increase in the isomer shift (\( \delta = 0.41 \) mm/s) and a slight decrease in the quadrupole splitting (\( \Delta E_Q = 1.93 \) mm/s). Although the changes observed in the Mössbauer spectrum are consistent with a change in spin state, the observation of one rather than two quadrupole doublets suggests either rapid interconversion between spin states or a quantum admixed S = 1,2 spin state at elevated temperatures. We currently favour the former explanation because the latter has little precedence in ferrous compounds, and the SQUID expected data could be fit using a spin equilibrium model with magnetic moments for high and intermediate spin states that are within the range expected for S = 1 and S = 2 spin states (Figure 2).

Similar to 2a, the Mössbauer spectrum of \((\text{CDA}^{\text{Fe}})\text{FeCl}\_2\)BF\(_4\) (3) demonstrated isomer shifts at 100 K that were more consistent with an intermediate spin S = 3/2 iron(III) species (\( \delta = 0.18 \) mm/s) than a high spin S = 5/2 complex (Figure S2). As the temperature was raised, a single quadrupole doublet was observed and a steady reduction in the quadrupole splitting from 2.21 mm/s to 1.62 mm/s occurred. As was the case with \((\text{CDA}^{\text{Fe}})\text{FeCl}\_2\) (2a), the presence of one quadrupole doublet is atypical for conventional spin equilibrium behaviour and may be better explained by an S = 3/2,5/2 quantum admixture. Quantum admixed S = 3/2,5/2 spin states have precedence in iron porphyrin complexes and are believed to be important in many biological systems, but examples such as this one that does not involve porphyrin ligands are uncommon. The existence of an admixed spin state in 3 is further supported by the high temperature SQUID data, which begin to saturate towards magnetic moments that were too low for a pure S = 5/2 spin state.

As a final experiment directed towards understanding the spin transitions that appear to occur in these complexes, variable temperature X-ray crystallographic experiments were carried out. Consistent with a change in spin state were considerable changes in metal-ligand bond distances in 2a and 3 upon increasing the temperature (Table 1 and ESI for more temperatures). For example, the iron–carbene bond length in 2a elongated from the abnormally short 1.812(2) Å to 1.882(3) Å and the average iron–amidine bond distances extended from 2.026(4) Å to 2.104(4) Å at 100 K and 250 K, respectively. Increases in bond length on the order of 0.07–0.08 Å are common for complexes of iron that undergo spin transitions.

To corroborate our experimental results, we carried out unrestricted DFT calculations on both 2a and 3. Intermediate (S = 1 and 3/2) and high spin (S = 2 and 5/2) configurations were calculated to be close in energy (ca. 5 kcal/mol) for both 2a and 3, but a low spin state configuration (S = 1/2) considered for 3 was significantly higher in energy (>15 kcal/mol). These findings are consistent with the small enthalpies (\( \Delta H \)) obtained from fitting the SQUID data for 3.

Figure 3. Zero-field \(^{57}\)Fe Mössbauer spectra of 2a. Simulation yields the following parameters: \( \delta, |\Delta E_Q| \) at 90 K: 0.31, 2.14 (I) = 0.15 mm/s, at 295 K: 0.40, 1.93 (I) = 0.16 mm/s, where \( \Gamma \) = half width at half height.
An alternative mechanism that may be operative is the iron-catalysed decomposition of aryl azide to form free triplet nitrene, which then undergoes rapid dimerization to form a diazene. Two pieces of experimental evidence are inconsistent with this mechanism. Firstly, p-tolylazide was irradiated with UV light and subjected to the reaction conditions. Since this procedure produces free triplet nitrene, we reasoned that the product distribution would be similar to the iron-catalysed processes if both reactions proceed through a common triplet nitrene intermediate. During photolysis, diazene (54%) was observed as the major product, but unlike the iron-catalysed processes, no p-toluclidine was produced and hydrazine (28%) was observed as an additional product (Table 2, entry 7). These data suggest that the photolysis and iron-catalysed processes do not proceed through a common intermediate. Further contradicting a mechanism involving a free nitrene were differences in reactivity observed for reactions between p-tolylazide and 1-octene at 50 °C (Table S1). Unlike reactions catalysed by 1a, 1b, or 2a, reactions catalysed by 2b resulted in the formation of aziridine as the major product (28%) with diazene being formed as a minor byproduct (5%). Once again, reactions carried out under photolysis demonstrated a different product distribution leading to diazene as the major product (25%) with aziridine being formed as a minor by-product (10%). Unfortunately, the formation of significant quantities of unidentified by-products precluded the use of 2b as catalysts for the aziridination of olefins. Nevertheless, the reactivity of 2b compared to 1b demonstrates the potential benefit of iron complexes supported by CDA ligands.

Table 1. Selected bond lengths (Å) and Mössbauer parameters (\(|\Delta E|/\sigma\)) for 2a and 3. See ESI for additional bond lengths and temperatures.

<table>
<thead>
<tr>
<th></th>
<th>(CDA(^{\text{np}}))FeCl(_2) (2a) Exp.</th>
<th>Calc.</th>
<th>(CDA(^{\text{np}}))FeCl(_2)BF(_4) (3) Exp.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-carbene</td>
<td>100 K 250 K</td>
<td>S = 1</td>
<td>80 K 298 K</td>
<td>S = 5/2</td>
</tr>
<tr>
<td>Fe-amidine</td>
<td>1.812(2) 1.882(3)</td>
<td>1.823</td>
<td>2.024</td>
<td>1.908(2) 2.033(2)</td>
</tr>
<tr>
<td>δ</td>
<td>2.02(4) 2.104(4)</td>
<td>2.071</td>
<td>2.284</td>
<td>2.031(9) 2.142(12)</td>
</tr>
<tr>
<td></td>
<td>0.31 b</td>
<td>0.40</td>
<td>0.42</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>2.14 1.93</td>
<td>2.17</td>
<td>1.43</td>
<td>2.21 d</td>
</tr>
</tbody>
</table>

*Reported as an average. *Measured at 90 K. *Measured at 295 K. *Measured at 100 K.

Table 2. Catalytic homocoupling of p-tolylazide.

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>selectivity*</th>
<th>(k_{\text{obs}} \times 10^{-5} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>0°</td>
<td>0°</td>
</tr>
<tr>
<td>2</td>
<td>FeCl(_2)</td>
<td>1.20</td>
<td>0.906</td>
</tr>
<tr>
<td>3</td>
<td>(PDI(^{\text{np}}))FeCl(_2) (1a)</td>
<td>3:1:0</td>
<td>4.18</td>
</tr>
<tr>
<td>4</td>
<td>(CDA(^{\text{np}}))FeCl(_2) (2a)</td>
<td>4:1:0</td>
<td>5.18</td>
</tr>
<tr>
<td>5</td>
<td>(PDI(^{\text{Me}}))FeCl(_2) (1b)</td>
<td>6:1:0</td>
<td>4.51</td>
</tr>
<tr>
<td>6</td>
<td>(CDA(^{\text{np}}))FeCl(_2) (2b)</td>
<td>10:1:0</td>
<td>20.2</td>
</tr>
<tr>
<td>7</td>
<td>hv</td>
<td>2:0:1</td>
<td>3.09</td>
</tr>
</tbody>
</table>

*Selectivity = diazene/p-toluidine/hydrazine. *Conv. = 0 %.

Considering the renewed interest in base metals for chemical catalysis and the usefulness that N-heterocyclic carbene ligands have demonstrated for organotransition metal catalysis, the investigations presented above have provided insight into the electronic consequences that may result by ligating NHC ligands to iron. Furthermore, a comparison of the CDA ligands to analogous PDI complexes highlight the importance of the electron-donating capabilities of the central neutral donor in this class of pincer-type complexes.
ligands. Although promiscuous reactivity have precluded the use of 2b in aziridination reactions, the differences observed between 2b and catalysts containing PDI ligands is encouraging for the development of unique catalytic reactions that bear CDA ligands. Our future efforts will be directed towards discovering such reactions by applying these complexes as catalysts for a variety of reactions involving multiple oxidation states of iron. The results from these investigations will be forthcoming.

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Notes and references
* This paper is dedicated in memoriam to Gregory L. Hillhouse.
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‡ Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts, 02138.
△ Electronic Supplementary Information (ESI) available: CIF files for complex 2a (CCDC 900881, 927786 – 927788) and 3 (CCDC 927790 - 927794), general considerations, computational methods, synthetic procedures and characterization for all new complexes. See DOI: 10.1039/c000000x/

12 A similar complex was reported almost simultaneously, but the structure was not confirmed crystallographically: J. A. Thagfi and G. G. Lavoie, *Organometallics* 2012, *31*, 7351.
18 Solution and solid state magnetic moments for 2a differed, which likely reflects a different distribution of spin states in the solid and solution state. Solvent dependent magnetic moments are consistent with this hypothesis, which coincidently results in identical magnetic moments for 2a and 3.
20 Quantum admixed spin states are characterized by only one set of Mössbauer quadrupole doublets and a decrease in quadrupole splitting (|e\(\Delta Q_0\)|) as the temperature is increased. (a) M. M. Maltempo, *J. Chem. Phys.* 1974, *61*, 2540; (b) H. D. Dolfi, J. R. Sams and T. B. Tsin, *Inorg. Chem.* 1977, *16*, 711.