

NHC Effects on Reduction Dynamics in Iron-Catalyzed Organic Transformations**

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Abstract: The high abundance, low toxicity and rich redox chemistry of iron has resulted in a surge of iron-catalyzed organic transformations over the last two decades. Within this area, N-heterocyclic carbene (NHC) ligands have been widely utilized to achieve high yields across reactions including cross-coupling and C–H alkylation, amongst others. Central to the development of iron-NHC catalytic methods is the understanding of iron speciation and the propensity of these species to undergo reduction events, as low-valent iron species can be advantageous or undesirable from one system

Introduction

The last 20 years have seen a surge in the development of ironcatalyzed organic transformations as the high abundance, low cost, minimal toxicity, and rich redox chemistry of iron make it an attractive, sustainable alternative to precious metals in catalysis.[1-11] Central to the reactivity observed in iron-catalyzed transformations are the ligands and additives utilized in these reactions.^[12] Although a variety of ligands and additives such as phosphines, amines, and N-methylpyrrolidone (NMP) have been used to promote a range of reactions,^[13] amplifying yields and selectivities, N-heterocyclic carbene ligands (NHCs) have arguably been one of the most widely utilized.^[4] Examples illustrating the scope of iron-catalyzed reactions which use NHCs as an essential component include hydrogenation,^[14,15] cross-coupling,^[16,17] carbometallation,^[18] C-H alkylation,^[19] and hydroalkynylation.^[20,21] As the development of these catalytic methods continues, a fundamental understanding of the reaction mechanism, active iron species, and decomposition pathways present is essential to improving and designing new methodologies.

First introduced by Bedford and co-workers in 2006,^[22] the use of iron salts, NHCs and Grignard reagents is a combination that has been quite effective, resulting in the development of cross-coupling and C–H alkylation reactions in recent years

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 [**] NHC=N-heterocyclic carbene.

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to the next. This study highlights the importance of the identity of the NHC on iron speciation upon reaction with EtMgBr, where reactions with SIMes and IMes NHCs were shown to undergo β -hydride elimination more readily than those with SIPr and IPr NHCs. This insight is vital to developing new iron-NHC catalyzed transformations as understanding how to control this reduction by simply changing the NHC is central to improving the reactivity in iron-NHC catalysis.

(Scheme 1). Towards gaining a fundamental understanding of the reactivity in iron-NHC catalysis, the Neidig group recently reported a mechanistic study of the alkyl-alkyl iron-NHCcatalyzed cross-coupling method reported by Cárdenas and coworkers in 2013 (Scheme 1).^[23,24] Unique to this method is the requirement of a Grignard reagent with an acetal group. Detailed synthetic and spectroscopic studies of this system



 $\label{eq:scheme1.Selected examples of iron-catalyzed organic transformations which utilize NHC ligands.^{[19,23,27]}$

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determined that the acetal group was key to the prevention of β -hydride elimination, as one of the oxygen moieties on each of the two alkyl ligands was found to chelate to the iron, stabilizing the intermediate. It was also found that simply altering the saturation on the NHC backbone resulted in a drastic decrease in product yield in this system. Additional studies by the Neidig group determined that the steric requirement of the saturated backbone of SIPr would not allow for the chelation of both of the acetal oxygens, instead only allowing for one of the alkyl ligands to chelate, drastically decreasing the efficacy of this iron intermediate.^[25]

While answering many questions about this specific alkylalkyl cross-coupling reaction, the fundamental mechanistic insight into iron-NHC reactivity provided by the system published by Cárdenas posed an obvious question: what iron species are produced (and any associated effect of the NHC on this) upon reaction with a simple $\beta\mbox{-hydrogen-containing alkyl}$ Grignard reagent such as EtMgBr? A review of the literature produces limited but notable examples of iron-NHC reactions which use alkyl Grignard reagents.^[25,32] Simultaneously, understanding the iron species which form in these reactions is vital for the potential development of alkyl-alkyl cross-coupling methodologies with simple alkyl Grignard reagents. Insight into what iron species form, and their propensity to undergo β hydride elimination, is critical towards controlling a process that, while often regarded as an unwanted side-reaction in cross-coupling, is a key step in other reactions such as C-H alkylation.[19]

In this study, we report four iron-NHC complexes isolated from the reaction of Fe(OAc)₂, NHC, and the β -hydrogen containing Grignard reagent, EtMgBr. Under identical reaction conditions it was found that when the diisopropylphenyl NHCs (SIPr or IPr, Scheme 1) were used, the resulting products were Fe(II) alkyl species, vastly different from when the mesityl NHCs (SIMes or IMes, Scheme 1) were used and Fe(0) alkene species were formed. The four complexes have been characterized using single crystal X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy and magnetic circular dichroism (MCD) spectroscopy. The Fe(0) complexes were determined to have a rare high spin (S =1) ground-state and were further characterized using density functional theory (DFT) calculations. In addition, stoichiometric reactivity of the insitu generated bis-ethyl species were performed to determine their efficacy towards formation of cross-coupled product. Overall, this study highlights the ligand effects on β -hydride elimination in iron-NHC complexes and correlates this propensity for reduction with observed stoichiometric rates of product formation across the two ligand variants.

Results

Isolation and characterization of three-coordinate NHC iron (II) bis-ethyl species

Initial studies focused on the reaction of $Fe(OAc)_2$ with one equivalent of the chloride salt of each NHC precursor (SIPr, IPr,

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SIMes, or IMes) and 4 equivalents of EtMgBr. The solid $Fe(OAc)_2$ and NHC precursor were cooled to $-78\,^{\circ}C$ for 15 minutes and then placed at $-5\,^{\circ}C$ where the EtMgBr in THF was added and the mixture allowed to stir for 20 minutes at this temperature. The reaction was then cooled to $-78\,^{\circ}C$ for 1 h. In situ ^{57}Fe Mössbauer spectroscopy of this reaction mixture showed different major species for SIPr and IPr than that for SIMes and IMes (Figure S1). Crystallization at $-80\,^{\circ}C$ of the reactions with SIPr and IPr resulted in the formation of yellow-orange blocks and yellow-green needles, respectively. Single-crystal X-ray diffraction studies identified these species as (SIPr)Fe(ethyl)₂ (1) and (IPr)Fe(ethyl)₂ (2) (Figures 1A and 2 A). Both complexes 1 and 2 are highly temperature and air sensitive, decomposing readily above the crystallization temperature of $-80\,^{\circ}C$.

While a few examples of three-coordinate Fe(II)-NHC-alkyl complexes have been previously reported, they have historically



Figure 1. X-ray crystal structure with representative bond distances and angles (A), 80 K solid Mössbauer spectrum (B), 5 K, 7 T NIR MCD spectrum (C) and saturation magnetization data (D) for complex 1.

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been prepared by blocking the β -hydrogen position to circumvent β -hydride elimination. Notable examples include the (NHC) Fe(CH₂SiMe₃)₂ complexes reported by Danopoulos and coworkers, and derivatized by Tonzetich and co-workers, as well as the (NHC)Fe(CH₂Ph)₂ reported by Tonzetich and coworkers.^[29-31] The bis-ethyl iron-NHC species reported herein are the first examples of non-stabilized three-coordinate iron-NHCalkyl complexes. In addition, the ethyl nucleophile is commonly utilized in cross-coupling unlike those which are sterically encumbered, allowing for investigation into speciation more relevant to catalysis. To compare the electronic structures of these high-spin Fe(II) species to those previously reported, ⁵⁷Fe Mössbauer spectroscopy and magnetic circular dichroism (MCD) spectroscopy were employed.

The 80 K ⁵⁷Fe Mössbauer spectrum of a solid sample of 1 (Figure 1B) was obtained and fit as two species. The major species in the solid-state sample (orange) has Mössbauer parameters $\delta = 0.24$ mm/s and $\Delta E_0 = 1.42$ mm/s, which are consistent with previously reported three-coordinate high-spin Fe(II) species.^[31-33] The minor species in the solid-state sample (purple), with parameters $\delta\!=\!0.42$ mm/s and $\Delta E_{\text{Q}}\!=\!2.87$ mm/s is the major species observed in situ (Figure S1). The parameters of this species are consistent with other high-spin Fe(II) tetrahedral species (Table S1), suggesting the presence of a THF adduct (1.THF). To further probe this, the solid Mössbauer sample was re-dissolved in THF at low temperature and the solution ⁵⁷Fe Mössbauer spectrum collected (Figure S2). This showed a change in speciation, where the species with the wider quadrupole splitting ($\delta = 0.42$ mm/s and $\Delta E_0 = 2.87$ mm/ s, purple) was now the major species and the species with the smaller quadrupole ($\delta = 0.24$ mm/s and $\Delta E_0 = 1.42$ mm/s, orange) was the minor species, further supporting the formation of a THF adduct. This is also consistent with the major species in situ being 1.THF, as the reaction is performed in THF.

To further evaluate the electronic structure of 1, MCD spectroscopy was performed on mull samples prepared from crystalline material. The 7 T, 5 K near infrared (NIR) MCD spectrum exhibits two field-dependent transitions (Figure S4), a positive transition centered around 7000 cm⁻¹ followed by a negative transition around 9500 cm⁻¹ (Figure 1C). From previously reported MCD spectra of three- and four-coordinate iron-NHC complexes,^[31] the spectrum appears to contain a mixture of both the three- and four-coordinate species, as observed in the ⁵⁷Fe Mössbauer spectrum. To determine the coordination environment corresponding to these two transitions, as well as the spin-state of the iron centers involved, variable temperature-variable field (VTVH) MCD spectroscopy was utilized. The saturation magnetization behavior of the sample collected at 7143 cm⁻¹ is well described by a S=2 negative zero-field split (-ZFS) non-Kramers doublet with ground-state spin-Hamiltonian parameters of $\delta = 1.6 \pm 0.2$ cm⁻¹, $D = -11 \pm 2 \text{ cm}^{-1}$, and $E/D = 0.22 \pm 0.06$ (Figure S5). These parameters are consistent with a distorted tetrahedral, high-spin Fe(II) species (Table S1).^[25,31,34,35] The saturation magnetization behavior of the sample collected at 9542 cm⁻¹ is well described by a S=2 negative zero-field split (-ZFS) non-Kramers doublet with ground-state spin-Hamiltonian parameters of $\delta = 1.7 \pm$



0.2 cm⁻¹, $D = -19 \pm 2$ cm⁻¹, and E/D = 0.18 \pm 0.06 (Figure 1D). These parameters are consistent with previously reported threecoordinate high-spin Fe(II) NHC species (Table S1).^[31] These MCD studies are consistent with the assignment of a fourcoordinate solvent adduct (**1-THF**) as well as the threecoordinate species (**1**) in the ⁵⁷Fe Mössbauer spectrum. The UVvis MCD spectrum was also obtained and is consistent with an overlapping mixture of both the three- and four-coordinate high-spin Fe(II) species (Figure S4).

The same spectroscopic techniques were used to investigate the electronic structure of the analogous IPr complex **2** (Figure 2). The ⁵⁷Fe Mössbauer spectrum of a solid sample of **2** also fit to two species, with the major species (green) having parameters $\delta = 0.23$ mm/s and $\Delta E_Q = 1.42$ mm/s, consistent with the major species observed in **1** and assigned as the three-coordinate (IPr)Fe(ethyl)₂ (Figure 2B). The minor species, with



Figure 2. X-ray crystal structure with representative bond distances and angles (A), 80 K solid Mössbauer spectrum (B), 5 K, 7 T NIR MCD spectrum (C) and saturation magnetization data (D) for complex 2.

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parameters $\delta = 0.45$ mm/s and $\Delta E_0 = 2.65$ mm/s is consistent with the minor species (blue) in the solid spectrum of 1 and is assigned as the four-coordinate species (IPr)Fe(ethyl)₂THF (2-THF). Consistent with this assignment is that once again, the blue species is the major species in the insitu reaction performed in THF. The 7 T, 5 K NIR MCD of 2 has just one negative transition centered around 9500 cm⁻¹ (Figure 2C). This suggests that the MCD sample of 2 contained only the threecoordinate (IPr)Fe(ethyl)₂ species. To confirm this, VTVH MCD was performed. The saturation magnetization behavior of the sample collected at 9345 cm^{-1} is well described by a S=2 negative zero-field split (-ZFS) non-Kramers doublet with ground-state spin-Hamiltonian parameters of $\delta = 1.7 \pm 0.2$ cm⁻¹, $D = -19 \pm 2 \text{ cm}^{-1}$, and E/D = 0.18 \pm 0.06 cm⁻¹ (Figure 2D). This is consistent with the negative transition in 1 and other threecoordinate high-spin Fe(II) species. The discrepancy between Mössbauer speciation, which identifies a mixture, and the MCD speciation, which identifies a singular species, is due to the size of the sample required for each method. MCD spectroscopy requires much less sample than ⁵⁷Fe Mössbauer spectroscopy so fewer crystals need to be utilized, increasing the chance for a more pure sample to be obtained though both species crystallize under identical conditions.

Isolation and characterization of three-coordinate NHC iron (0) bis-ethylene species

As previous reports have shown the effects of the identity of the NHC on the catalytic reactivity both in cross-coupling and C–H alkylation reactions,^[19,22,25,36] the use of NHCs with mesityl wingtips was explored to determine if analogous species to the isopropyl-NHC complexes could be isolated. Towards this, the analogous reaction of Fe(OAc)₂, EtMgBr, and either the SIMes or IMes imidazolium salt, resulted in drastically different speciation

observed in situ by ⁵⁷Fe Mössbauer spectroscopy. While the minor species had Mössbauer parameters consistent with the four-coordinate species 1.THF and 2.THF (see above) the major species observed was not consistent with any species isolated with the SIPr or IPr ligands. With that in mind, isolation of the major species observed in situ reaction was targeted. Crystallization at -80°C of reactions containing the SIMes or IMes NHCs resulted in the formation of blue-green plates and blue blocks, respectively. Single-crystal X-ray diffraction identified these as the Fe(0) species (SIMes)Fe(ethylene)₂ (3) and (IMes) Fe(ethylene)₂ (4) (Figure 3A and 3E). As the synthetic procedures utilized for the isolation of 3 and 4 are identical to those for 1 and 2, the different rates of reduction observed are likely due to the ability of the NHC ligand to stabilize the Fe(II) dialkyl species initially formed. This reduction of a ligand-supported Fe(II) complex to form an Fe(0)-alkene complex in the presence of EtMgBr has been previously observed by Fürstner and coworkers but in the presence of very different ligands (bisphosphine vs. NHC reported herein) and in the presence of excess ethylene.[37,38]

While NHC-Fe(0)-alkene species have previously been reported, they are isolated in the presence of a bulky alkene source and chemical reductant.^[39–42] The method herein highlights the propensity of iron-alkyl species to undergo β -hydride elimination, resulting in a reduction to the Fe(0) species. While Fe(0)-NHC complexes may complicate reactivity in cross-coupling, they have been proposed as active intermediates in iron catalyzed C–H activation reactions.

To confirm that theseFe(0)-ethylene complexes were the species observed in situ, ⁵⁷Fe Mössbauer samples of solid **3** and **4** were prepared. The parameters obtained were consistent with the major species observed in situ, with parameters $\delta = 0.37$ mm/s and $\Delta E_Q = 3.20$ mm/s for **3** and $\delta = 0.37$ mm/s and $\Delta E_Q = 3.24$ mm/s for **4** (Figure 3B and F). These parameters are also consistent with previously reported Fe(0)-NHC



Figure 3. X-ray crystal structure with representative bond distances and angles (A), 80 K solid Mössbauer spectrum (B), 5 K, 7 T NIR MCD spectrum (C) and saturation magnetization data (D) for complex 3 and X-ray crystal structure with representative bond distances and angles (E), 80 K solid Mössbauer spectrum (F), 5 K, 7 T NIR MCD spectrum (G) and saturation magnetization data (H) for complex 4. For peak fit MCD spectra and assignments of transitions for 3 and 4 see Figure S7 and Table S2.

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complexes.^[39,40] When characterizing these species by ¹H NMR spectroscopy, resonances were observed in the paramagnetic region which suggested a high-spin (S = 1) ground state (Figures S11 and S12). To confirm this, Evans method NMR was performed. The magnetic moment of 3 was determined to be 3.7(2) B.M. while that of 4 was 3.9(2) B.M. These values are consistent with the assignment of a S=1 ground state but deviate significantly from the spin-only value of 2.83 B.M. These deviations are often observed in transition metal S=1 $\mathsf{complexes}^{\scriptscriptstyle[43-45]}$ and suggest the ligand environments in these species result in large spin-orbit couplings. As examples and electronic structure and magnetization data for S = 1 iron systems are limited,^[46,47] we employed MCD and density functional theory (DFT) to further investigate the electronic structure of these complexes.

Spin unrestricted DFT calculations were performed on both high-spin Fe(0) complexes 3 and 4. Geometry optimization with PBE0/def2-TZVP^[48,49] and the GD3BJ dispersion correction^[50] yielded overall structure features, bond lengths, and angles in good agreement with those observed crystallographically (Table S4). TD-DFT calculations were performed to assign the transitions observed in the MCD spectra. Molecular orbitals in the gas phase were also explored, focusing on the occupied and unoccupied frontier molecular orbitals (FMOs) of the β orbital manifold to determine major bonding contributions. The calculated FMO energy diagrams for the β manifolds of **3** are outlined in Figure 4. Both complexes share the same FMO ordering and composition around the HOMO/LUMO gap (Figure S13). Both complexes show the Fe-NHC σ -bonding interactions significantly below the energy of the LUMO and have a ground state consisting of three occupied FMOs. For 3, these are the $\beta109$ (d $_{x}^{2}$ $_{y}^{2}$, 42 %), $\beta110$ (d $_{xy}$, 54 %), and $\beta111$ (d $_{z}^{2}$, 83 %) orbitals and for 4, these are the β 108 (d_{x-y}², 41%), β 109 (d_{xy}, 54%), and β 110 (d_z², 83%) orbitals. In both complexes, the HOMO d_z^2 orbital is composed primarily of iron d orbital character. The LUMO in both complexes are NHC π^* orbitals on the mesityl rings. The lowest energy orbitals which have significant d-character in 3 and 4, β 116 (48%) and β 115 respectively, are the d_{yz} orbitals. Due to mixing in these complexes, there are two MOs with significant d_{yz} character. The second d_{vz} MO in **3** is the β 119 orbital (45%) and in **4** is the β 118 (37%). The d_{xz} orbital lies between the mixed d_{yz} orbitals in energy and is assigned as β 117 (89%) in **3** and β 116 (77%) in 4.

MCD spectra of Fe(0) complexes are rare,^[51] likely due to the propensity for this oxidation state to be low-spin and therefore diamagnetic. As such, TD-DFT calculations using B3LYP/ def2TZVP were performed and the resulting absorption spectra were used to assign the transitions observed in the experimental MCD spectra. The 5 K, 7 T NIR MCD spectra of 3 and 4 are very similar with just minor changes in the energies of the three observed transitions (Figure 3C and G). The peak fit spectra and summary of assignments can be found in Figure S7 and Table S2, respectively. The theoretical absorption spectrum of 3 consists of ten transitions across the NIR/UV-vis region (Figure S8). The first six transitions, which are paired into three groupings, are assigned as ligand-field transitions (d_z² to d_{yz} and





Figure 4. The calculated FMO energy level diagram of 3 and all d-orbitals depictions.

 $d_z^{\ 2}$ to $d_{xz\prime}\ d_{x^{\ -y}}^{\ 2}$ to d_{yz} and $d_{x^{\ -y}}^{\ 2}$ to $d_{xz\prime}$ and $d_z^{\ 2}$ to d_{yz} and $d_z^{\ 2}$ to d_{xz}). The lowest energy transition is not observed in the 5 K, 7 T experimental MCD spectrum as it is below the energy limits of the spectrometer.

The next three transitions in the calculated absorption spectrum are assigned to a series of metal to ligand (MLCT) and ligand to metal (LMCT) charge transfer transitions. In the experimental MCD spectrum these transitions are observed as the broad signal centered at 25000 cm⁻¹. The final predicted transition is centered at 30073 cm⁻¹ and is assigned as ligandbased transitions. Due to the lack of d-orbital contributions to this transition, it is not observed in the experimental MCD spectrum. Similar transitions and assignments have been made for 4, and are outlined in Table S2.

VTVH MCD was performed on both species to determine the ground-state spin-Hamiltonian parameters. The saturation magnetization behavior of 3 collected at 12500 cm⁻¹ is well

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described by a S=1 +ZFS non-Kramers doublet with groundstate spin-Hamiltonian parameters $D=27\pm5$ cm⁻¹, E/D=0.10 \pm 0.05 and g=2.25 \pm 0.05 (Figure 3D). Similarly, the saturation magnetization behavior of 4 collected at 11905 cm⁻¹ is well described by a S=1 positive zero-field split (+ZFS) non-Kramers doublet with ground-state spin-Hamiltonian parameters $D=27\pm5$ cm⁻¹, E/D=0.10 \pm 0.05 and g=2.25 \pm 0.05 (Figure 3H). While there are very few examples of saturation magnetization data for S=1 ground states of iron, the large D value observed here is consistent with those previously reported.^[46,47,51]

Reactivity studies of in situ generated (NHC)Fe(ethyl)₂ species

With the identification of the (NHC)Fe(ethyl)₂ species, we wanted to investigate their competency towards cross-coupling under stoichiometric reaction conditions and determine if there was a correlation between the reactivity observed and the propensity for reduction across the series. To test the reactivity, it was first necessary to determine if the (NHC)Fe(ethyl)₂ species could be generated in situ. Although the identity of the species formed after warming to -5 °C for 20 minutes show a significant difference depending on the NHC used, we sought to obtain further detail into the evolution of this speciation. These studies were carried out with IMes and IPr, as representative examples. In situ ⁵⁷Fe Mössbauer spectroscopy of reactions after warming for only 5 minutes showed that the species formed with both the IMes and IPr ligands were a mixture of the three-coordinate (NHC)Fe(ethyl)₂ and fourcoordinate (NHC)Fe(ethyl)₂THF species (Figure S3). This data clearly demonstrates that irrespective of the NHC used, the Fe (II)-NHC bis-alkyl species are initially formed but the identity of the NHC ligand determines the rate at which reduction occurs. This observed reduction to the Fe(0)-ethylene species is in contrast to what has been observed in previously reported three-coordinate Fe(II)-diketiminate-alkyl species which can undergo reversible β -H elimination.^[52,53] While various attempts towards isolating the IMes and SIMes Fe(II)-ethyl species were made, reduction to the Fe(0) species was observed even at −80 °C.

With the ability to generate the (IMes)Fe(ethyl)₂ and (IPr) Fe(ethyl)₂ species in situ we set out to determine whether the inherent reactivity of these Fe(II) bis-ethyl species would manifest in other reactions, such as with an electrophile. The substrate chosen to test reactivity was methyl-4-chlorobenzoate, which has frequently been shown to form cross-coupled product with alkyl Grignard reagents using iron.[26-28] In order to target the formation of the (NHC)Fe(ethyl)₂THF species, Fe(OAc)₂ and either IMes or IPr were cooled to $-78\,^\circ\text{C}$ in THF. The solution was then moved to -5 °C where 3 equivalents of EtMgBr was added dropwise and the reaction was allowed to stir for 5 minutes, which ⁵⁷Fe Mössbauer spectroscopy confirmed resulted in the formation of the Fe(II) diethyl species. After this time, 2 equivalents of methyl-4-chlorobenzoate was added as a THF solution and reaction time points taken (Table 1).



Over a 1-minute reaction time, drastically different reactions rates were observed for the formation of methyl-4-ethylbenzoate, depending on the NHC used. While forming the lessstable iron-ethyl species, the IMes NHC resulted in a much faster rate of reaction with 80% cross-coupled product observed by GC after 1 minute. Conversely, the IPr NHC, which forms the more stable Fe(II) diethyl species, was much slower with only 14% cross-coupled product formed after 1 minute. After 10 minutes, the IMes reaction started to perform a second turnover with 138% product formed while the IPr reaction had not completed a single turnover at 66% yield (Table 1). It is also important to note that the only other trace observed in the GC of these reactions is unreacted electrophile. These deviations in reactivity observed across these iron-NHC complexes suggest that the enhanced stability of the IPr-ethyl species may actually hinder the formation of cross-coupled product, at least under stoichiometric reaction conditions.

As cross-coupled product was observed under stoichiometric reaction conditions, albeit with relatively slow turnovers, we wanted to see whether this could be translated to a catalytic method and how the identity of the NHC would play out under these conditions. These experiments were carried out using Fe(OAc)₂, NHC, and EtMgBr with methyl-4-chlorobenzoate as the electrophile once again. Despite varying the concentration and nucleophile addition rate, the yield of cross-coupled product only ever reached 30%. This yield was also consistent across both IMes and IPr NHCs, but likely for very different reasons. In the stoichiometric reaction with IMes, the rate is much faster than that observed with IPr, but it is also known that this species is more prone to reduction. With this in mind it is highly likely that the reaction cannot proceed to higher yields due to decomposition of the active Fe(II) species. For the IPr species, the stoichiometric rate was much slower. In this case, the stability of the Fe(II) species and added steric hindrance of the NHC likely results in a slower catalytic rebound to form cross-coupled product.

Discussion and Conclusion

The use of iron in combination with NHC ligands and Grignard reagents has proved successful across both cross-coupling and C–H alkylation reactions. As both of these reactions display fundamentally different underlying reactivity, proposed reactive intermediates and oxidation states, despite similar reaction



conditions, we were motivated to study the speciation which can occur under these conditions. Based on previously reported electronic structure studies of both iron and cobalt-NHC species, it has been found that the electronic effect of the NHC ligand has little effect on the metal center, and instead it is the sterics of the wingtip substitution that determines the stability of species.^[25,31,54] With that in mind it was determined herein that it is the sterics of the NHC wingtips that play a key role in the species formed.

While the Fe(II)-NHC dialkyl species are initially formed in all NHC ligand variants, the stability of these species towards reduction is vastly different. When the NHC wingtips bore diisopropylphenyl (Dipp) groups, the Fe(II) bis-ethyl species were stabilized enough to be isolated. Conversely, when the NHCs with mesityl (Mes) wingtips were used, the Fe(II) diethyl species were not isolable even at low temperatures and instead resulted in formation of the reduced Fe(0) bis-ethylene complexes. It is also of note that these complexes are rare examples of high-spin Fe(0) species, which herein have been studied thoroughly with regards to their electronic structure. Additionally, this highlights the drastically different species which can be isolated under analogous reaction conditions and what may be considered as relatively minor changes to the NHC ligand. This type of insight is essential for designing new methods, where targeting specific types of species and oxidation states of iron is important.

Furthermore, understanding the evolution of speciation and the kinetics of such processes is invaluable, rather than interpreting results purely based on what is formed that is stable enough to be easily isolated. This dichotomy of stability and reactivity is well-illustrated by these Fe(II)-NHC dialkyl species reported herein. While the complexes with mesityl wingtips are significantly less stable to β -hydride elimination, this also manifests in greater reactivity towards a prototypical electrophile, reacting significantly faster than the analogous species with Dipp wingtips. Despite the poor catalytic reactivity under the scope of conditions reported herein, it is still possible in the future that these Fe(II)-alkyl species, if properly targeted, might be utilized for effective catalysis. This remains true despite the instability of the Fe(II)-alkyl species, as the Neidig group has reported several unstable intermediates which have been shown to be catalytically relevant.[32,33,55-57] The effects of the NHC ligand on both speciation and reactivity of the resulting iron species reported herein provide a platform on which further reaction development can be designed and interpreted.

Experimental Section

Crystal-structure analysis: Deposition Numbers 2075488 (4), 2075489 (2), 2075490 (1), and 2075491 (3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cross-coupling • electronic structure • iron catalysis • N-heterocyclic carbenes

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FULL PAPER



Upon reaction of Fe(OAc)₂, NHC, and EtMgBr, it was found that the NHC utilized determined the rate of β hydride elimination. Fe(0)-ethylene and Fe(II)-ethyl species were isolated and characterized by X-ray crystallography, ⁵⁷Fe Mössbauer, and MCD spectroscopy. The Fe(0)-ethylene complexes were found to have a rare S = 1 ground state. The Fe(II)-ethyl species were found to form crosscoupled product under stoichiometric reaction conditions.

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NHC Effects on Reduction Dynamics in Iron-Catalyzed Organic Transformations

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