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Synthesis and Characterization of a Bis(imino)-N-heterocyclic Carbene Analogue to Bis(imino)pyridine Iron Complexes

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Supporting Information

ABSTRACT: New bis(imino)-N-heterocyclic carbene ligands have been synthesized, and the corresponding iron complexes have been isolated and characterized. Whereas imidazole-derived complexes exhibited exclusively bidentate binding modes, 4,5,6trihydropyrimidylidene-based ligands adopted a tridentate pincer conformation analogous to complexes of 2,6-bis(imino)pyridines. Bonding in the five-coordinate bis(imino)-N-heterocyclic carbene complex displayed considerably contracted iron—ligand bond



distances in comparison to those in the analogous bis(imino)pyridine iron complex. Of particular note was an extraordinarily short iron–carbene carbon bond distance (1.812(2) Å). In addition to demonstrating differences in bonding, the isoelectronic structures have different electrochemical properties that reflect the ability of the carbene to stabilize both oxidized and reduced forms of the parent organometallic species.

INTRODUCTION

Over the past 15 years, iron and cobalt complexes bearing 2,6bis(imino)pyridyl ligands have received considerable attention due to their remarkable properties and noteworthy reactivity across a broad range of transformations. In the late 1990s, Gibson, Brookhart, and Bennett introduced the complexes as olefin polymerization catalysts (e.g., 1; Figure 1) with



Figure 1. Bis(imino)pyridine and bis(imino)-N-heterocyclic carbene complexes of iron.

efficiencies that rivaled those of the most potent earlytransition-metal metallocenes.^{1,2} Facile modifications to the redox-active ligand³ enabled the selective production of olefin dimers, oligomers, polymers,⁴ and most recently cyclotrimers⁵ when acetylene was used as the monomer feedstock. Reduction of **1** leads to dinitrogen complexes such as **2** (Figure 1),⁶ which have also been shown to be outstanding catalysts for the hydrogenation⁷ and hydrosilyation⁸ of alkenes, as well as for intermolecular [2 + 2] cycloaddition reactions of alkenes⁹ and dienes.¹⁰

Considering their utility in catalytic reactions, much effort has been devoted to elucidating the structure-activity relationships for iron and cobalt complexes containing such a privileged class of ligand. Whereas most studies have focused on the easily interchangeable imine moieties,⁴ relatively little has been done to explore the steric and electronic implications of the central σ donor.¹¹ Except for a few examples involving para-substituted pyridines,¹² none of the reported variations resulted in fivecoordinate complexes containing a central heterocycle with stronger σ -donating capabilities. Particularly absent from the literature was a tridentate bis(imino)-N-heterocyclic carbene analogue to the bis(imino)pyridine ligand. This finding may be surprising, considering the extensive application of Nheterocyclic carbenes (NHC) in transition-metal-catalyzed processes.¹³ Nevertheless, NHC complexes of iron have remained largely unexplored¹⁴ in comparison to the other transition metals.

More recently, advances in NHC metalation methodology¹⁵ and a renewed interest in non-noble transition-metal catalysis have led to an increase in the number of isolable iron-NHC complexes. In concert with these developments, Lavoie and coworkers reported the synthesis of the first 1,3-bis(imino)imidazol-2-ylidene ligands as potential N-heterocyclic carbene analogues to the bis(imino)pyridine ligands of Brookhart and Gibson (3; Figure 1).¹⁶ Rapid ligand decomposition upon formation of the free carbene¹⁷ was circumvented by treatment of the imidazolium carbene precursor with an in situ generated copper amide reagent. Expanding upon a similar strategy introduced by Danopoulos,¹⁵ the Lavoie group extended this

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Scheme 1. Synthesis of Homologated 1,3-Bis(imino)imidazol-2-ylidene Iron Complexes a



^aReagents and conditions: (i) imidazole, DMF, 23 °C, 76%; (ii) N-(2,6-diisopropylphenyl)acetimidoyl chloride, PhMe, 23 °C, 97%; (iii) 5, CH₃CN, 80 °C, 91%; (iv) 0.25 equiv of [Fe(HMDS)₂]₂, 0.5 equiv of FeCl₂, THF, 23 °C (51% for 9, 35% for 10).



Figure 2. ORTEP plots of 9 (left) and 10 (right) at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

methodology to include the synthesis of iron, cobalt, and chromium bis(imino)-N-heterocyclic carbene complexes.¹⁸ However, crystallographic, computational, and spectroscopic techniques revealed bidentate ligand binding modes for these structures rather than the expected tridentate chelates (e.g., 3; Figure 1).

Concurrent with Lavoie's 2012 report, our research group had also isolated similar tetrahedral bis(imino)-N-heterocyclic carbene complexes of iron. In order to explain why these compounds adopted a four-coordinate geometry, we undertook a systematic investigation of ligand analogues that were sterically and electronically different from the 1,3-bis(imino)imidazol-2-ylidenes. Herein, we report the results of our efforts, which include the synthesis and characterization of a bis-(imino)-N-heterocyclic carbene ligand built upon a 4,5,6trihydropyrimidylidene framework. The iron complex reported is the first example of a pentacoordinate iron structure bearing a tridentate bis(imino)-N-heterocyclic carbene ligand (4; Figure 1), and to the best of our knowledge, it is also the first example of an iron complex bearing the saturated 4,5,6-trihydropyrimidylidene N-heterocyclic carbene moiety.

RESULTS AND DISCUSSION

We hypothesized that the iron complexes containing 1,3bis(imino)imidazol-2-ylidene ligands such as 3^{18} (Figure 1), are four-coordinate complexes for one of two reasons. On the one hand, a tridentate binding mode could be disfavored due to the geometric constraints of a five-membered heterocyclic framework, a hypothesis that has been put forward by both Gibson^{11a} and Mashima¹⁹ when exploring furan- and pyrrole-based ligands. On the other hand, the added electron density from the carbene donor to the iron center may discourage a higher valency complex. The former hypothesis is supported by the constrained $C_{carbene}-N_{imidazole}-C_{amidine}$ angle observed within the chelating ring of 3 in comparison to the analogous angle for the unbound amidine (119.6° vs 125.0°, respectively).¹⁸ We postulated that one-carbon homologation of the amidine arms would allow for tridentate coordination by relieving the angle strain inherent to **3**.

Divergent syntheses of the homologated ligands were efficiently accomplished by iterative N-substitution of imidazole (Scheme 1). Alkylation with α -chloroimine 5 and either amidination or alkylation rapidly delivered the singly homologated 7 or the symmetric, doubly homologated 8 in high yields. Using a protocol similar to that reported by Lavoie,¹⁸ premixing 0.5 equiv. of FeCl₂ and 0.25 equiv. of the dimeric [Fe(HMDS)₂]₂²⁰ in tetrahydrofuran (THF) followed by treatment with the appropriate imidazolium chloride afforded the corresponding NHC complexes 9 and 10 as pale yellow solids. Unfortunately, ¹H NMR spectra were complicated by significant peak broadening, temperature- and concentration-induced chemical shift changes, and missing signals, all features typical of paramagnetic species.²¹ Along these lines, magnetic moments of 5.0 and 5.1 $\mu_{\rm B}$ for 9 and 10, respectively, were measured by the Evans method.²² These values are consistent with similar complexes and correspond to S = 2 high-spin Fe(II) complexes. Crystals suitable for X-ray crystallography were grown from vapor diffusion of pentane into dichloromethane or THF solutions at -40 °C, which revealed that both compounds were tetracoordinate in the solid state (Figure 2).

We were surprised to find that both complexes 9 and 10 crystallized in distorted-tetrahedral geometries, irrespective of ring expansion of one or both amidine fragments on the ligand. Analogously to complex 3, complex 9 binds through the central carbene as well as the amidine, notably preferring the five-membered metallacycle over the possible six-membered chelate. The bond metrics about the iron center are similar to those in complex 3 (Table 1), which indicated that minimal perturbation was imparted on the iron center as a function of the unbound portion of the ligand.

Akin to the bis(imino)-N-heterocyclic carbene compounds 3 and 9, 10 also adopts a distorted-tetrahedral geometry, due to bidentate ligand coordination. The deviation from an ideal

Table 1. Selected Bond Lengths (\AA) and Angles (deg) for 3, 9, and 10

3 ^{<i>a</i>}	9	10
2.091(3)	2.085(2)	2.071(2)
2.240(1)	2.225(1)	2.252(1)
2.244(1)	2.243(1)	2.245(1)
1.369(4)	1.369(3)	1.362(3)
1.350(4)	1.342(3)	1.351(3)
1.256(4)	1.263(3)	1.247(4)
1.269(4)	1.274(3)	1.285(3)
2.145(3)	2.157(2)	2.131(2)
76.9(1)	77.1(1)	87.0(1)
114.9(3)	115.4(2)	120.1(2)
119.6(2)	119.9(2)	124.2(2)
125.0(3)	123.4(2)	124.1(2)
120.37(4)	115.13(3)	121.36(3)
111.7(2)	111.7(1)	119.3(2)
144.6(2)	144.6(2)	137.1(2)
	3^{a} 2.091(3) 2.240(1) 2.244(1) 1.369(4) 1.350(4) 1.256(4) 1.269(4) 2.145(3) 76.9(1) 114.9(3) 119.6(2) 125.0(3) 120.37(4) 111.7(2) 144.6(2)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^{*a*}Data taken from ref 18. ^{*b*}The atom labeled C_6 in complex 3 corresponds to that labeled C_{19} in complex 9 and C_{20} in complex 10. ^{*c*}The atom labeled C_4 in complex 3 corresponds to that labeled C_5 in complex 10. ^{*d*}The atom labeled C_6 in complex 3 corresponds to that labeled C_{18} in the homologated complex 9 and C_{19} in complex 10.

tetrahedral geometry is clearly demonstrated by the C(1)-Fe(1)-N(3) and Cl(1)-Fe(1)-Cl(2) bond angles (87.1(1)) and $121.36(3)^{\circ}$, respectively, for 10 compared to 77.1(1) and $115.13(3)^{\circ}$ for 9). Specific to complex 10, however, is the presence of two homologated imine arms, which necessitate multidentate binding to afford at least one six-membered-ring chelate. This feature inevitably leads to structural differences for 10 in comparison to 3 or 9. Whereas 10 displayed subtle shortening of the Fe(1)-C(1) bond (2.071(2) Å for 10 vs 2.085(2) Å for 9) and modest elongation of the iron-chlorine bonds (2.245(1) and 2.252(1) Å for 10 vs 2.225(1) and 2.2431(1) Å for 9), the most prominent consequence of the expanded chelate was the bond metrics associated with the metallacycle. As mentioned previously, an approximate 5° compression of the C(1)-N(1)-C(4) junction was required for the 1,3-bis(imino)imidazol-2-ylidene ligand to adopt a bidentate binding mode in 3. While a similar compression was observed for 9, the corresponding angles in 10 demonstrated little angle strain associated with bidentate metal chelation (C(1)-N(1)-C(4) and C(1)-N(2)-C(18) are 124.2(4) and $124.1(2)^{\circ}$, respectively).

The lack of strain associated with complex 10 suggested that four-coordinate complexes of bis(imino)-N-heterocyclic carbene ligands could be due to the electronic disparities between NHC's and pyridines. We briefly undertook a study of electrondeficient ligands analogous to 3 but found that the increased electrophilicity of the imidazolium precursors led to cleavage of the amidine arms under metalation reaction conditions. To definitively rule out the steric contribution of the ligand on the observed low-valent iron species, we undertook the synthesis of a 1,3-bis(imino)-N-heterocyclic carbene ligand containing a sixmembered-ring heterocycle. We reasoned that a complex built upon a 4,5,6-trihydropyrimidine N-heterocyclic carbene²³ (e.g., 4; Figure 1) would exhibit $C_{carbene} - N_{pyrimidine} - C_{amidine}$ angles similar to those of the 2,6-bis(imino)pyridines,¹ while still maintaining the potent σ -donating ability of the NHC. A survey of the literature revealed that few saturated N-heterocyclic carbene iron complexes had been reported,²⁴ none of which

contain the 4,5,6-trihydropyrimidine heterocycle. Such complexes would therefore provide fundamental structural and electronic information pertinent to the growing area of iron Nheterocyclic carbene chemistry.

Given the rapid and high-yielding nature of Lavoie's sequential substitution strategy,¹⁶ a similar sequence of transformations was applied to the construction of 1,3-bis(imino)trihydropyrimidinium chloride salt **12** (Scheme 2).

Scheme 2. Synthesis of 1,3-Bis(imino)-4,5,6-

trihydropyrimidinium Chloride 12 and Pentacoordinate Iron Complex $\mathbf{4}^a$



^aReagents and conditions: (i) *n*BuLi, THF, -78 °C, then N-(2,6diisopropylphenyl)acetimidoyl chloride, -78 to 23 °C, 97%; (ii) N-(2,6-diisopropylphenyl)acetimidoyl chloride, PhMe, 23 °C, 74%; (iii) FeCl₂, NaHMDS, THF, -40 to 50 °C, 54%.

Starting with commercially available 1,4,5,6-tetrahydropyrimidine, deprotonation with *n*-butyllithium followed by amidination with *N*-(2,6-diisopropylphenyl)acetimidoyl chloride²⁵ cleanly delivered intermediate 11.²⁶ Subsequent N-substitution in toluene and recrystallization from dichloromethane afforded carbene precursor 12 in multigram quantities.

Unfortunately, attempts to metalate 12 using the previously mentioned procedure resulted in incomplete conversion to the iron–carbene complex. This observation was supported by the isolation of a yellow crystalline solid, which was determined by X-ray crystallography to be a [1,3-bis(imino)-4,5,6-trihydropyrimidinium]FeCl₃ "ate" species (13; see the Supporting Information). Danopoulos and co-workers have previously reported similar ion pairs during metalation reactions of sterically encumbered imidazolium salts with $[Fe(HMDS)_2]_2$, often as the major products when steric constraints prevent the imidazolium precursors from coming into close proximity to the metal center.^{15b} On the basis of their findings, the authors hypothesized that the "ate" complexes are intermediates formed during the metalation process.

Consistent with these observations, we reasoned that ligation of the apparently less reactive 1,3-bis(imino)-4,5,6-trihydropyrimidinium ligands 12 could be driven to the desired complex by simply heating the reaction mixture . We were pleased to find that gentle warming to 50 °C for 24 h converted all of the starting material, including any traces of the "ate" complex, to the new burgundy product 4. In addition to the color change, infrared analysis of the solid product after crystallization yielded amidine stretches at 1612 and 1560 cm⁻¹ for 4, compared to stretches at 1629 and 1587 cm⁻¹ for 13. Interestingly, independently prepared "ate" complex 13 could also be converted to 4 by simple heating in the presence of $[Fe(HMDS)_2]_2$. These observations are consistent with "ate" complexes similar to 13 being intermediates en route to carbene ligation. At this stage in our investigations, however, we

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cannot rule out the possibility that 13 forms as the kinetic product, which is subsequently equilibrated through a pathway different from the more thermodynamically stable 4 under the reaction conditions.

Crystallization of 4 proved particularly challenging, but dark red crystals suitable for X-ray diffraction could be obtained after successive crystallizations from solvent mixtures containing diethyl ether, THF, and dichloromethane. Much to our delight, single-crystal diffraction confirmed the tetragonal structure to be the desired pentacoordinate iron complex 4 (Figure 3). The



Figure 3. ORTEP plot of 4 at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 4: Fe(1)-C(1), 1.812(2); Fe(1)-N(4), 2.028(2); Fe(1)-N(3), 2.023(2); Fe(1)-Cl(1), 2.325(1); Fe(1)-Cl(2), 2.28(1); C(5)-N(4), 1.306(2); C(19)-N(3), 1.305(3); C(1)-N(2)-C(5), 112.0(2); C(1)-N(1)-C(19), 112.0(2); Cl(1)-Fe(1)-Cl(2), 106.40(2).

distorted-square-planar geometry is very similar to that of the bis(imino)pyridine complex 1.¹ However, careful evaluation of the data illuminates some notable differences between the pyridine and the NHC containing molecules. One of the most striking features of the new complex is the Fe(1)-C(1) bond length, which at 1.812(2) Å is on par with the shortest iron-Nheterocyclic carbene bonds ever reported.²⁷ This value is in contrast to the Fe(1)–C(1) bond lengths in 3 (2.091(3) Å)¹⁸ and 9 (2.085(2) Å), which are more typical for 16-electron iron(II) complexes, as well as the iron-pyridine bond in 1 $(2.091(4) \text{ Å})^{-1}$ Additionally, the iron-amidine bond distances (i.e., Fe(1)-N(3) and Fe(1)-N(4)) are also contracted in relation to the analogous iron-imine bond distances of bis(imino)pyridine complex 1 (2.023(2) and 2.028(2) Å for 4 vs 2.222(4) and 2.23(1) Å for 1). In fact, the iron-amidine bonds in 4 are even shorter than the iron-imine bond lengths in the higher oxidation state iron(III) bis(imino)pyridine complexes (average Fe-N length 2.185 Å).28 Despite the closer proximity of the 1,3-bis(imino)trihydropyrimidine ligand to the iron center in 4, the Fe(1)-Cl(1) and Fe(1)-Cl(2)distances are almost equivalent to those in complex 1(2.280(2))and 2.3250(6) Å for 4 vs 2.263(2) and 2.317(2) Å for 1). It is also curious that the C(5)-N(4) and C(19)-N(3) bond lengths in 4 (1.306(2) and 1.305(3) Å) are nearly identical with the analogous bound $C_{\text{imine}}{-}N_{\text{imine}}$ distances in bis(imino)pyridine 1 (1.30(1) and 1.30(1) Å).

The reduced metal-ligand bond distances in 4 have a profound effect on the critical C(1)-N(2)-C(5) and C(1)-N(1)-C(19) amidine arm angles, which are both measured to

be 112.0(2). These values reflect geometries significantly more acute than those in the aforementioned tetrahedral complexes and are more compressed than the analogous angles in complex 1 (114.3(4) and 114.6(1)°). Combined, these structural features result in a less open coordination environment for 4 in comparison to 1, the consequence of which is best reflected by comparing the "wingspan" of the complexes. Defined as the distance between the ipso carbons of the flanking aryl groups, the opening contracts from 6.58 Å for 1 to 6.00 Å for 4. Considering that catalytic processes involving pyridyl-diimine iron catalysts are particularly sensitive to the steric environment of the complex,³ it is anticipated that the structural parameters of 4 will have significant implications for substrate binding and overall reactivity.

In addition to elucidating the structural features of the bis(imino)-N-heterocyclic carbene complex 4, the magnetic and electrochemical properties were also evaluated for comparison to those of the known bis(imino)pyridine complex 1. A magnetic moment (μ_{eff}) of 5.0 μ_{B} was measured for 4 using Evans's method,²² which was consistent with the value determined for 1 and suggests an S = 2 spin state for the complex. Despite this similarity, cyclic voltammograms obtained for the two complexes demonstrated notably different redox properties (Figure 4, Table 2). Consistent with a more



Figure 4. Comparison of the cyclic voltammograms of **1** (red) and **4** (blue). Conditions: 0.01 M acetonitrile solution of analyte; 0.1 M nBu_4NPF_6 as supporting electrolyte; platinum mesh as working electrode; platinum wire as counter electrode; Ag/Ag⁺/I⁻ as reference electrode; scan rate of 100 mV s⁻¹.

electron rich metal center, the $E_{1/2}$ values for the transitions are shifted to lower potential.²⁹ For example, the central transition, which we assign to a Fe(II)–Fe(III) transition,³⁰ is shifted by 137 mV from 0.041 V for 1 to -0.096 V for 4 (vs ferrocene/ ferrocenium, Table 2). Interestingly, the next oxidation wave demonstrates an even more significant cathodic shift of 244 mV. Aside from the Fe(II)–Fe(III) transition, we have not differentiated any of the other redox events as being metal or ligand centered. Nevertheless, the most striking features of the voltammogram of 4 are the four seemingly reversible redox events. This is in great contrast to the single reversible Fe(II)/ Fe(III) redox couple observed for 1. We believe that a combination of the more σ -donating carbene and the low-lying

Table 2. Redox Potentials for 1 and 4

Tuble 2. Redox Fotentials for F and F							
	$E_{1/2}{}^a$						
compd							
1	$-0.707 (ir)^{b}$	-0.496 (ir) ^b	$0.041 (r)^c$	0.566 (qr)			
4		-0.449 (r)	$-0.096 (r)^{c}$	0.322 (r)	0.788 (r)		
^{<i>a</i>} Values in V vs Fc/Fc^+ : r = reversible, ir = irreversible, qr = quasi-reversible. ^{<i>b</i>} Reduction potential shown. ^{<i>c</i>} Fe(II)/Fe(III) transition.							

vacant p orbital may collectively stabilize both oxidized and reduced forms of the parent complex, a feature which may prove greatly beneficial to catalytic applications.

CONCLUSION

In conclusion, we have synthesized the first pentacoordinate iron complex bearing a tridentate 1,3-bis(imino)-4,5,6-trihydropyrimidine carbene ligand (4). Novel homologated ligands based on bis(imino)imidazol-2-ylidenes were also developed, but complexation to iron afforded distorted-tetrahedral complexes similar to structures previously reported.¹⁸ In contrast, tridentate chelation by a bis(imino)-4,5,6-trihydropyrimid-2-ylidene ligand (4) suggests that the steric environment enforced by a central imidazol-2-ylidene is most likely responsible for the observed binding modes to iron. Complex 4 contains one of the shortest iron-N-heterocyclic carbene bonds reported to date, which combined with shortened ironamidine bond lengths leads to a more sterically congested coordination environment relative to that of the parent bis(imino)pyridine complex 1. Additionally, cyclic voltammograms of complex 4 exhibit four reversible, cathode-shifted redox events in comparison to one for complex 1. Explorations into the origin of the unusual electronic and structural properties of complex 4 as well as an evaluation of its catalytic activity are currently underway.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out in oven-dried glassware in a nitrogen atmosphere glovebox or using standard Schlenk line techniques.³¹ Solvents were used after passage through a solvent purification system similar to that reported by Grubbs³² under a blanket of argon and then degassed by briefly exposing the solvent to vacuum. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on spectrometers operating at 500 MHz for ¹H NMR or 125 MHz for ¹³C NMR. Infrared (IR) spectra were recorded on an ATR infrared spectrometer. Magnetic moments were determined by the Evans method²² according to the procedure published by Gibson and co-workers.³³ Elemental analysis was carried out by Robertson Microlit Laboratories (Ledgewood, NJ). Highresolution mass spectra were obtained at the Boston College Mass Spectrometry Facility. Cyclic voltammetry was carried out with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte in acetonitrile. The sample solution was 0.01 M with respect to the analyte. The working electrode was a platinum mesh, the counter electrode was a platinum wire, and the reference electrode was a nonaqueous Ag/Ag⁺/I⁻ electrode. Cyclic voltammograms were measured with scan rates of 100 mV s⁻¹ and were referenced to Fc/ Fc^{+,34} (^{2,6-dipp}PDI)FeCl₂ (1) was prepared according to the procedure of Gibson and co-workers.

Synthesis of 1-Chloro-2-(2,6-diisopropylphenylimino)propane (5). To a solution of chloroacetone (4.79 mL, 59.5 mmol, 1.00 equiv) in dichloromethane (107 mL) was added 2,6diisopropylaniline (11.8 mL, 62.5 mmol, 1.05 equiv), and the mixture was cooled to 0 °C. A solution of titanium tetrachloride (3.30 mL, 29.8 mmol, 0.500 equiv) in dichloromethane (12.0 mL) was added dropwise via cannula, immediately turning the reaction mixture a deep yellow. Triethylamine (33.0 mL, 238 mmol, 4.00 equiv) was then added dropwise, during which time the mixture turned orange-red and cloudy. The reaction was stirred for 1 h at 0 °C and then 3 h at 23 °C. Water (20 mL) was carefully added to quench any remaining titanium tetrachloride, and the mixture was filtered through a pad of Celite. The filtrate was transferred into a separatory funnel containing water (300 mL), and the product was extracted with dichloromethane (3 × 100 mL). The combined organics were dried over magnesium sulfate, filtered, and concentrated. The crude residue was purified by flash column chromatography with 5% diethyl ether in pentane as eluent ($R_{\rm f}$ = 0.47) to deliver the title compound 5 (8.79 g, 59%) as a yellow oil. Spectroscopic data were in agreement with the reported literature values.³⁵

Synthesis of N-1-[2-(2,6-Diisopropylphenylimino)propyl]imidazole (6). A solution of imidazole (1.15 g, 16.8 mmol, 5.00 equiv) in dimethylformamide (DMF, 5.00 mL) was cooled to 0 °C, and a solution of α -chloroimine 5 (848 mg, 3.37 mmol, 1.00 equiv) in DMF (1.70 mL) was added dropwise via cannula. The solution was then gradually warmed to 23 °C and was stirred for 12 h. The mixture was poured into saturated aqueous sodium bicarbonate (20 mL), and the product was extracted with ethyl acetate (3 \times 20 mL). The combined organics were washed with water (30 mL) and brine (30 mL), and then dried over sodium sulfate, filtered, and concentrated. The crude residue was purified by flash column chromatography with 1% triethyl amine and 5% methanol in dichloromethane as eluent ($R_{\rm f}$ = 0.30) to deliver the title compound 6 as a white solid (752 mg, 76%). ¹H NMR (CDCl₃, 500 MHz): δ 7.60 (s, 1H), 7.14 (s, 1H), 7.11-7.03 (m, 3H), 7.00 (s, 1H), 4.87 (s, 2H), 2.66-2.57 (m, 2H), 1.59 (s, 3H), 1.12 (d, J = 6.6 Hz, 6H), 1.10 (d, J = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 165.59, 144.88, 137.86, 135.91, 130.20, 124.13, 123.14, 119.54, 55.20, 28.22, 23.22, 22.93, 17.75. IR (neat): 2960, 2869, 1681, 1663, 1506, 1436, 1328, 1229, 784, 752 662 cm⁻¹. HRMS (ESI+): calcd for $C_{18}H_{26}N_3$ [M + H]⁺ 284.2127, found 284.2113.

Synthesis of N-1-[1-(2,6-Diisopropylphenylimino)ethyl]-N-3-[2-(2,6-diisopropylphenylimino)propyl]imidazolium Chloride (7). In an inert-atmosphere glovebox, N-1-[2-(2,6diisopropylphenylimino)propyl]imidazole (6; 622 mg, 2.19 mmol, 1.00 equiv) was weighed into a vial equipped with a magnetic stirbar. A solution of N-(2,6-diisopropylphenyl)acetimidoyl chloride²⁵ (522 mg, 2.19 mmol, 1.00 equiv) in toluene (4.38 mL) was then added via pipet, and the solution was stirred at 23 °C for 20 min. The solvent was removed in vacuo, and the crude residue was washed with pentane (20 mL) to afford the title compound 7 as an off-white solid, which was used without further purification (1.11 g, 97%). ¹H NMR (CDCl₃, 500 MHz): δ 12.32 (dd, J = 1.5, 1.5 Hz, 1H), 8.28 (dd, J = 2.0, 2.0 Hz, 1H), 7.54 (dd, J = 2.2, 1.5 Hz, 1H), 7.22-7.19 (m, 4H), 7.18-7.14 (m, 2H), 5.92 (s, 2H), 2.70-2.63 (m, 4H), 2.60 (s, 3H), 2.04 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H), 1.23 (d, J = 7.1 Hz, 3H), 1.19 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ 163.65, 148.40, 144.23, 140.67, 139.85, 136.60, 135.78, 125.78, 124.50, 124.22, 123.74, 123.34, 116.76, 55.72, 28.69, 28.43, 23.32, 23.14, 22.92, 22.66, 19.30, 16.90. IR (neat): 2962, 2925, 2868, 1696, 1675, 1577, 1539, 1440, 1377, 1336, 1188, 775, 753 cm⁻¹. HRMS (ESI+): calcd for $C_{32}H_{45}N_4 [M + H]^+$ 485.3644, found 485.3617.

Synthesis of N,N-1,3-Bis[2-(2,6-diisopropylphenylimino)propyl]imidazolium Chloride (8). $N-1-[2-(2,6-Diisopropylphenylimino)propyl]imidazole (6; 567 mg, 2.00 mmol, 1.00 equiv) was weighed into a 25 mL round-bottom flask equipped with a magnetic stirbar and affixed to a 180° adaptor containing ground glass joints and a Teflon stopcock. A solution of <math>\alpha$ -chloroimine 5 (504 mg, 2.00 mmol, 1.00 equiv) in acetonitrile (2.00 mL) was added via cannula transfer, and the flask was sealed and heated to 80 [°]C for 19 h. The solvent was removed in vacuo, and the apparatus was brought into an inert-atmosphere glovebox. The crude residue was washed with pentane (10 mL) to afford the title compound **8** as an off-white solid that was used without further purification (980 mg, 91%). ¹H NMR (CDCl₃, 500 MHz): δ 11.00 (s, 1H), 7.44–7.43 (m, 2H), 7.06–7.00 (m, 6H), 5.50 (s, 4H), 2.51–2.43 (m, 4H), 1.82 (s, 6H), 1.09 (d, *J* = 7.1 Hz, 6H), 0.96 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 163.00, 144.24, 140.06, 135.76, 124.40, 123.17, 122.76, 55.56, 28.32, 23.21, 22.70, 18.92. IR (neat) 3063, 2962, 2870, 1679, 1432, 1359, 1186, 1112, 1045, 784, 771, 751, 643 cm⁻¹. HRMS (ESI +): calcd for $C_{33}H_{47}N_4$ [M + H]⁺ 499.3801, found 499.3798.

Synthesis of [N-1-[1-(2,6-Diisopropylphenylimino)ethyl]-N-3-[2-(2,6-diisopropylphenylimino)propyl]imidazol-2-ylidene]iron(II) Chloride (9). In an inert-atmosphere glovebox, anhydrous iron(II) dichloride (60.8 mg, 0.480 mmol, 0.500 equiv) was weighed into a vial equipped with a magnetic stirbar. A solution of $[Fe(HMDS)_2]_2^{\frac{20}{20}}$ (181 mg, 0.240 mmol, 0.250 equiv) in THF (7.30 mL) was added to the solid iron(II) dichloride via pipet, and the suspension was stirred at 23 °C for 20 min. During this time, the reaction mixture turned light brown and homogeneous. The solution was diluted with additional THF (20.0 mL), and then a suspension of imidazolium chloride 7 (500 mg, 0.959 mmol, 1.00 equiv) in THF (20.8 mL) was added dropwise. Immediately upon addition, the imidazolium salt dissolved and the reaction mixture turned yellow. The solution was stirred for 2 h, and then the solvent was removed in vacuo. The crude yellow solid was dissolved in dichloromethane, lavered with pentane, and cooled to -40 °C. The vellow crystals were filtered, washed with pentane $(3 \times 5 \text{ mL})$, and dried in vacuo to deliver the title complex 9 (297 mg, 51%). Crystals suitable for X-ray crystallography were grown by vapor diffusion of pentane into a solution of 9 in dichloromethane at -40 °C. IR (neat): 2961, 2868, 1678, 1634, 1435, 1394, 1365, 1300, 1253, 1214, 810, 782, 754, 733 cm⁻¹. $\mu_{\rm eff}$ = 5.0 $\mu_{\rm B}$ at 25 °C (Evans method). Anal. Calcd for C32H44Cl2FeN4: C, 62.86; H, 7.25; N, 9.16. Found: C, 62.89; H, 7.35; N, 8.98.

Synthesis of [N,N-1,3-Bis[2-(2,6-diisopropylphenylimino)propyl]imidazol-2-ylidene]iron(II) Chloride (10). In an inertatmosphere glovebox, anhydrous iron(II) dichloride (56.1 mg, 0.466 mmol, 0.500 equiv) was weighed into a vial equipped with a magnetic stirbar. A solution of $[Fe(HMDS)_2]_2^{20}$ (175 mg, 0.233 mmol, 0.250 equiv) in THF (7.90 mL) was added to the solid iron(II) dichloride via pipet, and the suspension was stirred at 23 °C for 20 min. During this time, the reaction mixture turned light brown and homogeneous. The solution was diluted with additional THF (20.0 mL), and then a suspension of imidazolium chloride 8 (500 mg, 0.932 mmol, 1.00 equiv) in THF (19.6 mL) was added dropwise. Immediately upon addition, the imidazolium salt dissolved and the reaction mixture turned a yellow-orange. The solution was stirred for 2 h, and then the solvent was removed in vacuo. The crude yellow solid was dissolved in THF, layered with pentane, and cooled to -40 °C. The yellow crystals were filtered, washed with pentane $(3 \times 5 \text{ mL})$, and dried in vacuo to deliver the title complex 10 (212 mg, 35%). Crystals suitable for X-ray crystallography were grown by vapor diffusion of pentane into a solution of 10 in THF at 23 °C. IR (neat): 2961, 2869, 1666, 1639, 1460, 1438, 1366, 809, 780, 747 cm⁻¹. $\mu_{\rm eff}$ = 5.1 $\mu_{\rm B}$ at 25 °C (Evans method). Anal. Calcd for C33H46Cl2FeN4: C, 63.37; H, 7.41; N, 8.96. Found: C, 62.28; H, 7.17; N, 8.46.³⁶

Synthesis of N-1-[1-(2,6-Diisopropylphenylimino)ethyl]-4,5,6-trihydropyrimidine (11). A solution of 1,4,5,6-tetrahydropyrimidine (0.201 mL, 2.45 mmol, 1.00 equiv) in THF (20.0 mL) was cooled to -78 °C, and *n*-butyllithium in hexanes (1.00 mL, 2.57 mmol, 2.57 M, 1.05 equiv) was added dropwise, during which time a white precipitate formed. The precipitate dissolved upon completion of the addition, and the mixture was stirred for 20 min at -78 °C. To the reaction mixture was then added a solution of *N*-(2,6diisopropylphenyl)acetimidoyl chloride²⁵ (582 mg, 2.45 mmol, 1.00 equiv) in THF (4.0 mL) via cannula transfer. The solution was stirred for 1 h at -78 °C and was then warmed to 23 °C and stirred for another 1 h. The mixture was poured into water (40 mL), and the product was extracted with dichloromethane (3 × 30 mL). The combined organics were dried over sodium sulfate, filtered, and concentrated to afford the title compound **11** as a white solid (677 mg, 97%) that was used without further purification. ¹H NMR (CDCl₃, 500 MHz): δ 7.87 (s, 1H), 7.11–7.08 (m, 2H), 7.02 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.87 (t, *J* = 6.1 Hz, 2H), 3.49 (t, *J* = 4.9 Hz, 2H), 2.77–2.68 (m, 2H), 1.99–1.94 (m, 2H), 1.89 (s, 3H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 152.30, 144.56, 144.20, 137.80, 123.16, 123.09, 44.68, 41.29, 28.32, 23.34, 23.08, 21.27, 15.23. IR (neat): 2957, 2920, 2850, 1620, 1458, 1380, 749 cm⁻¹. HRMS (ESI+): calcd for C₁₈H₂₈N₃ [M + H]⁺ 286.2283, found 286.2279.

Synthesis of N,N-1,3-Bis[1-(2,6-diisopropylphenylimino)ethyl]-4,5,6-trihydropyrimidinium Chloride (12). In an inertatmosphere glovebox, 1-[1-(2,6-diisopropylphenylimino)ethyl]-4,5,6trihydropyrimidine (11; 819 mg, 2.87 mmol, 1.00 equiv) was dissolved in toluene (5.00 mL). A solution of N-(2,6-diisopropylphenyl)acetimidoyl chloride 25 (682 mg, 2.87 mmol, 1.00 equiv) in toluene (4.60 mL) was then added via pipet, and the solution was stirred at 23 °C for 20 min, during which time a white precipitate formed. The solvent was removed in vacuo, and the crude solid was recrystallized from dichloromethane layered with pentane at -40 °C. The colorless crystals were filtered, washed with pentane $(3 \times 10 \text{ mL})$, and dried in vacuo to deliver the title compound 12 as a crystalline white solid (1.188 g, 79%). ¹H NMR (CDCl₃, 500 MHz): δ 9.88 (s, 1H), 7.18– 7.11 (m, 6H), 4.36 (t, J = 5.9 Hz, 4H), 2.78–2.70 (m, 4H), 2.61 (s, 6H), 2.49 (p, J = 5.9 Hz, 2H), 1.21 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz): δ 153.86, 153.34, 141.97, 136.83, 125.07, 123.48, 42.11, 28.49, 23.52, 23.02, 18.79, 16.23. IR (neat): 2960, 2868, 1620, 1586, 1234, 1196, 764, 751 cm⁻¹. HRMS (ESI+): calcd for C₃₂H₄₇N₄ [M]⁺ 487.3812, found 487.3801.

Synthesis of [N,N-1,3-Bis[1-(2,6-diisopropylphenylimino)ethyl]-4,5,6-trihydropyrimid-2-ylidene]iron Chloride (4). In an inert-atmosphere glovebox, anhydrous iron(II) dichloride (79.8 mg, 0.630 mmol, 1.05 equiv) was suspended in THF (6.0 mL) and cooled to -40 °C. To the cold suspension was then added dropwise a precooled (-40 $^{\circ}$ C) solution of sodium hexamethyldisilazane (116 mg, 0.630 mmol, 1.05 equiv) in THF (9.6 mL), and the mixture was held at -40 °C and agitated occasionally for 12 h.37 The mixture was then warmed to 23 $\,^{\circ}\text{C}$ for 20 min, during which time most of the remaining solid dissolved. The orange-brown solution was recooled to -40 °C, filtered through Celite, and added to a precooled (-40 °C) suspension of 12 (312 mg, 0.600 mmol, 1.00 equiv) in THF (6.0 mL). The suspension was gradually warmed to 23 °C, during which time it turned deep orange. The reaction mixture was then transferred to a Schlenk tube, removed from the drybox, and heated to 50 °C for 24 h, during which time the solution turned a dark wine red. The volatiles were removed in vacuo, and the crude solid was brought back into the glovebox. The crude residue was dissolved in a mixture of dichloromethane and THF (ca. 10/1 v/v), filtered through Celite, and concentrated. Recrystallization from THF layered with pentane at -40 °C delivered a burgundy solid (200 mg, 54%). Dark red, X-rayquality crystals were then grown by submitting the collected solid to recrystallization from a mixture of Et₂O, CH₂Cl₂, and THF (2/3/2 v/v) at -40 °C. IR (neat): 2959, 2866, 1612, 1560, 1389, 1322, 1291, 1206, 794, 769 cm⁻¹. $\mu_{\rm eff}$ = 5.0 $\mu_{\rm B}$ at 25 °C (Evans method). Anal. Calcd for C₃₂H₄₆Cl₂FeN₄: C, 62.65; H, 7.56; N, 9.13. Found: C, 61.57; H, 7.48; N, 8.46.³⁶

ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving ¹H NMR spectra of 4, 9, and 10 and crystallographic data for 4, 9, 10, and 13 (CCDC reference numbers 900880–900883), including tables of crystal data and structure refinement, bond lengths, angles, atomic coordinates, equivalent isotropic displacement parameters, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Biographies



This article is based upon a poster presented by Hilan Z. Kaplan (pictured here with Dr. Gladysz, left) at the first Organometallics Symposium at the ACS meeting in Philadelphia, Pennsylvania on August 21, 2012 (see Editor's Page in this issue). Mr. Kaplan received his B.A. (Cum Laude) at the University of Pennsylvania in 2008 and began his graduate studies in the Chemistry Department at Boston College that same year. He is currently working under the direction of Prof. Jeffery A. Byers, the corresponding author of this article. Mr. Kaplan's research interests encompass the development of iron complexes bearing novel classes of N-heterocyclic carbene ligands for polymerization and oxidation catalysis. After his doctoral work is complete, he plans to pursue his enthusiasm for science and technology in an industrial setting, developing processes and products to better mankind. In his free time, Mr. Kaplan enjoys staying productive as an avid painter and writer.

Whereas Prof. Jeffery A. Byers published his first paper in Organometallics in 2008 as a graduate student working in the labs of Prof. John E. Bercaw at the California Institute of Technology, this paper represents his first contribution to the journal as a principal investigator. After a postdoctoral fellowship at the Massachusetts Institute of Technology under the direction of Prof. Timothy F. Jamison, Prof. Byers began his professional career as an assistant professor at Boston College in 2011. His group focuses on the use of organometallic catalysis for synthetic, energetic, and materials applications. In addition to his passion for chemistry, Jeff enjoys classic literature and film, is an avid sports fan, and enjoys spending time outdoors.

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ABBREVIATIONS

NHC, N-heterocyclic carbene; THF, tetrahydrofuran; NaHMDS, sodium bis(trimethylsilyl)amide

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