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Iron Catalysis

Well-Defined Four-Coordinate Iron(II) Complexes For Intramolecular Hydroamination of Primary Aliphatic Alkenylamines[**]

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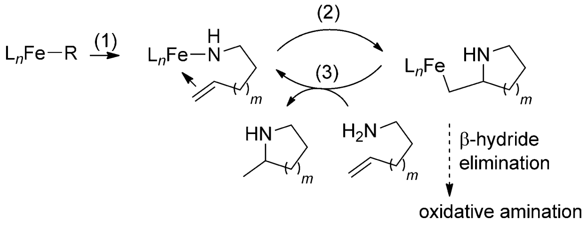
Abstract: *Despite the growing interest in iron catalysis and hydroamination reactions, iron-catalyzed hydroamination of unprotected primary aliphatic amines and unactivated alkenes has not been reported to date. Herein, a novel well-defined four-coordinate β-diketiminatoiron(II) alkyl complex is shown to be an excellent precatalyst for the highly selective cyclohydroamination of primary aliphatic alkenylamines at mild temperatures (70–90°C). Both empirical kinetic analyses and the reactivity of an isolated iron(II) amidoalkene dimer, [LFe(NHCH$_2$CPh$_2$CH$_2$CH=CH$_2$)]$_2$ favor a stepwise σ-insertive mechanism that entails migratory insertion of the pendant alkene into an iron–amido bond associated with a rate-determining aminolysis step.*

The development of more efficient, cost-effective and environmentally friendly methodologies for the synthesis of alkylamines is a major goal in modern chemistry. In this respect, catalytic alkene hydroamination is a key approach since it offers a waste-free process with 100% atom efficiency from relatively inexpensive and easily available amines and olefins.[1] The quest for broader substrate scope and polar functional-group tolerance has stimulated the development of hydroamination catalysts based on late-transition metals.[2] While significant progress has been made in the field, the reaction of unprotected primary amines, arguably the most versatile amines to start an "ideal synthesis",[3] remains problematic.[4,5] To date, only few research groups have tacked this challenging issue, but the systems reported so far are limited in scope and/or based on noble metals of limited availability, high price and considerable toxicity.[6] Thus, truly efficient and sustainable hydroamination catalysts for the preparation of unprotected secondary nitrogen-compounds are still in demand. As part of our research program, we raise the challenge to develop such catalysts based on iron as a low-cost, non-toxic, and abundant metal. To our knowledge, despite the growing interest in iron catalysis,[7] only iron(III) chloride has been reported for the hydroamination of electron-deficient amines.[8] This Lewis acid assisted methodology would be incompatible with the use of primary aliphatic amines, because these having a greater binding affinity than electron-deficient amines towards the metal center. Herein, we report the syntheses of well-defined low-coordinate iron(II) complexes and their remarkable activities in the cyclohydroamination of primary aliphatic alkenylamines, as the first example of iron-catalyzed hydroamination of electronically unbiased amines.

We hypothesized that well-defined and low-coordinate iron(II) alkyl complexes stabilized by β-diketiminate ligands were likely to show a unique reactivity for the selective hydroamination of primary aliphatic alkenylamines (Scheme 1).[9] The predilection for electronegative ligands demonstrated by these coordinatively and electronically unsaturated complexes should drive the preferential formation of a Fe–N bond over a Fe–C bond (Scheme 1, step (1)) and consequently promote catalyst turnover (step (3)).[9b] Even if no direct evidence of alkene insertion into a Fe–N bond (step (2)) has been reported so far,[10] some related alkyl complexes containing β-hydrogen atoms on the alkyl ligand may undergo a rapid alkyl isomerization at room temperature by a reversible β-hydrogen-elimination/alkene reinsertion process.[11] This process likely proceeds through the formation of a four-coordinate alkene hydride intermediate complex. Additionally, the easily electronically and sterically tunability of β-diketiminate ligands[12] is essential for a fine-tuning of the metal reactivity and a possible control of the selectivity for the hydroamination over oxidative amination pathway (Scheme 1).



Scheme 1. Working hypothesis. L$_n$Fe-R represents β-diketiminato-iron(II) alkyl complexes. For details of steps 1–3 see text.

Initially, we synthesized a novel low-coordinate iron(II) alkyl complex **2a**·THF containing the 2,4-bis(2,4,6-trimethylphenylimino)pent-3-yl ligand L by a two-step metathesis procedure (Scheme 2). Reaction between the lithium salt of 2,4-bis(2,4,6-trimethylphenylimino)pentane HL and anhydrous iron(II) chloride leads to the isolation of yellow crystals of the four-coordinate tetrahedral ate complex [LFe(μ-Cl)$_2$Li-

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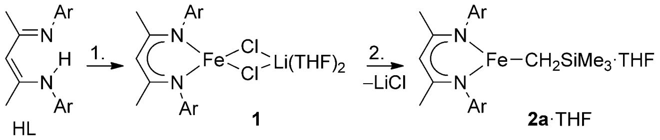


Ar = 2,4,6-(Me)$_3$C$_6$H$_2$

Scheme 2. Synthesis of **2a**·THF. Reaction conditions: 1. a) *n*BuLi (1.01 equiv), THF, −78 °C to 25 °C, 2 h, b) FeCl$_2$ (1.01 equiv), 25 °C, 16 h, 74% (two steps); 2. LiCH$_2$SiMe$_3$ (1 equiv), Et$_2$O, 25 °C, 16 h, 72%.

(THF)$_2$] (**1**; Scheme 2). The proposed structure for **1** was unambiguously determined by X-ray diffraction.[13,14] Subsequent metathesis reaction of **1** with LiCH$_2$SiMe$_3$ affords [LFeCH$_2$SiMe$_3$·THF] (**2a**·THF) in 72% yield as an orange air-sensitive crystalline solid (Scheme 2). Complex **2a**·THF is soluble in Et$_2$O, THF, and toluene and slightly soluble in hexane. It can be stored in crystalline state or in a [D$_6$]benzene solution at room temperature for weeks without noticeable decomposition.

Solid-state analysis of a single-crystal of **2a**·THF[14] reveals that the iron center is four-coordinate and adopts a trigonal-pyramidal geometry in which the apical position is occupied by the THF ligand (Figure 1). No agostic interactions are evident as the shortest relevant Fe···H contact distance is over 3.6 Å. The two Fe–N(diketiminate) bonds are slightly different (Fe–N(1) 2.0273(9) Å, Fe–N(2) 2.0072(8) Å) but are, despite the higher coordination number, similar to those observed in closely related three-coordinate complexes as is the bite angle of the bidentate ligand.[15] The Fe–C bond (Fe–C(9) 2.0492(11) Å) is consistent with that of three- and four-coordinate iron(II) β-diketiminate containing a sp^3-hybridized hydrocarbyl ligand.[11b,15a]

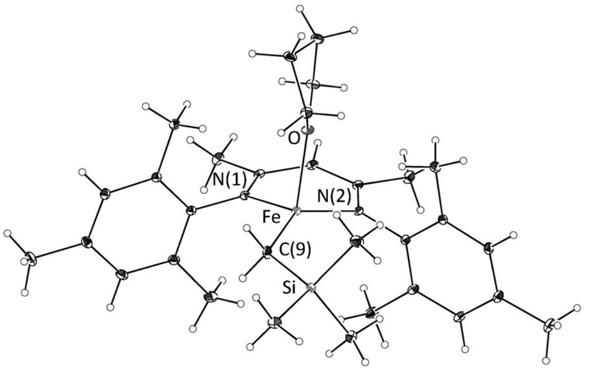
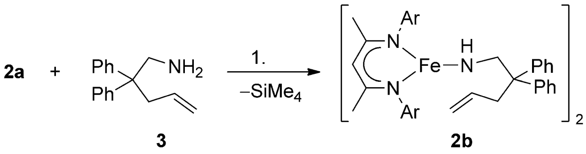


Figure 1. ORTEP drawing of four-coordinate β-diketiminatoiron(II) alkyl complex **2a**·THF. Thermal ellipsoids are set at 30% probability. Selected bond lengths [Å] and bond angles [°]: N(1)–Fe 2.0273(9), N(2)–Fe 2.0072(8), Fe–O 2.2257(8), C(9)–Fe 2.0492(11); N(2)-Fe-N(1) 93.07(4), N(2)-Fe-C(9) 139.74(4), N(1)-Fe-C(9) 116.58(4), N(2)-Fe-O 95.76(3), N(1)-Fe-O 98.68(3), C(9)-Fe-O 105.20(4).

To test the reactivity of **2a** on primary aliphatic amines, the stoichiometric reaction of **2a** and 2,2-diphenylpent-4-en-1-amine (**3**) was carried out (Scheme 3). Room temperature addition of a yellow solution of **2a** to **3** results in the immediate formation of a dark-red solution, from which red-orange crystals can be isolated in 75% yield. The X-ray structure of a single-crystal reveals a centrosymmetric dimer [LFe(NHCH$_2$CPh$_2$CH$_2$CH=CH$_2$)]$_2$ (**2b**) in the solid state, in which two iron atoms are bridged by two amido ligands from two molecules of **3** (Figure 2).[14] Each iron atom has a distorted tetrahedral geometry and the iron–amido bond lengths (Fe–N(3)$^{(i)}$ 2.0665(15) Å, Fe–N(3) 2.0698(14) Å) are longer than those encountered in related monomeric complexes, possibly because of the highly crowded nature of both metal centers.[16] Dimer **2b** which is insoluble in Et$_2$O and hexane, and sparingly soluble in THF and toluene, can be stored as a solid at room temperature for weeks without any evident decomposition. This experiment demonstrates **2a** is sufficiently basic to deprotonate primary aliphatic amines and that in presence of such amines, the amido complex **2b** (or its monomer in solution) will be favored.



Scheme 3. Room temperature stoichiometric reactivity of **2a** and **3**. Reaction conditions: 1. toluene, 25 °C, 3 days, 75%.

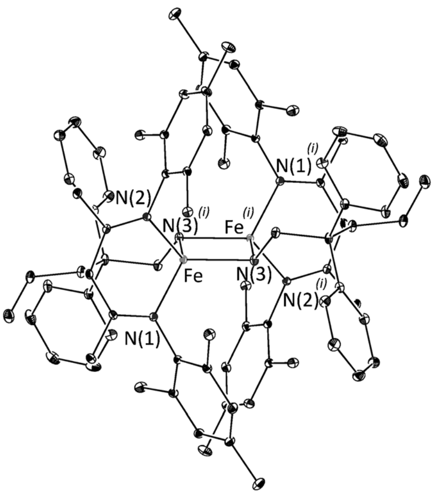
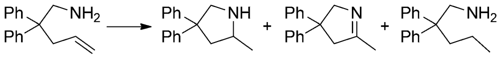


Figure 2. ORTEP drawing of **2b**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: N(1)–Fe 2.0459(14), N(2)–Fe 2.0267(13), N(3)$^{(i)}$–Fe 2.0665(15), N(3)–Fe 2.0698(14), Fe–Fe$^{(i)}$ 2.7828(8); N(2)-Fe-N(1) 92.72(5), N(2)-Fe-N(3)$^{(i)}$ 110.21(6), N(1)-Fe-N(3)$^{(i)}$ 125.88(5), N(2)-Fe-N(3) 120.81(5), N(1)-Fe-N(3) 114.11(5), N(3)-Fe-N(3)$^{(i)}$ 95.44(5). Symmetry transformation used to generate equivalent atoms: (i) = $-x$; $1-y$; $2-z$.

To assess the viability of an intramolecular alkene insertion reaction, **2b** was heated in toluene at 90 °C. GC analysis of the crude reaction shows the presence of the starting amine **3**, 2-methylpyrrolidine (**4**), imine **5** and 2,2-

Table 1: Influence of the catalyst, temperature, concentration, solvent and additive on the efficiency of the cyclohydroamination reaction of **3**.[a]



3 **4** **5** **6**

Entry	Catalyst (mol %)	Additive (mol %)[b]	*T* [°C]	**3** [%][c]	**4** [%][c]	**5** [%][c]	**6** [%][c]
1[d]	**2b** (100)	–	90	9	16	58	18
2	**2b** (5)	–	90	2	82	12	4
3	**2a**·THF (10)	–	90	1	73	14	13
4	**2a**·THF (10)	–	50	94	6	0	0
5[e]	**2a**·THF (10)	–	90	1	80	10	9
6[f]	**2a**·THF (10)	–	90	3	80	10	6
7[f,g]	**2a**·THF (10)	–	70	7	87	5	2
8[f]	$[Fe\{N(SiMe_3)_2\}_2]$ (10)	–	90	19	2	5	6
9[f,h]	**2a**·THF (10)	**7** (20)	90	6	89	2	3
10[f,h]	**2a**·THF (10)	**7** (10)	90	2	94	3	1
11[f]	**2c** (10)	–	90	3	94	1	2

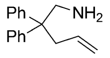
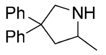
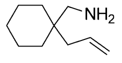
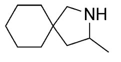
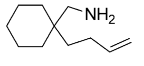
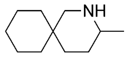
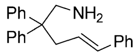
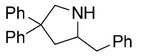
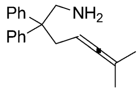
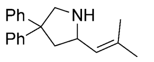
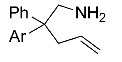
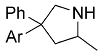
[a] Reaction conditions: [**3**] = 0.56 M, toluene, 24 h unless otherwise stated. [b] **7** = cyclopentylamine. [c] Determined by GC analysis. [d] Without **3**. [e] THF as solvent. [f] [**3**] = 0.96 M. [g] 68 h (unoptimized). [h] 48 h.

diphenylpentan-1-amine (**6**) in a 9:16:58:18 ratio respectively (Table 1, entry 1).[17] The formation of the hydroamination product **4**, the oxidative amination product **5**, and the reduced product **6** are reminiscent of an intramolecular migratory insertion of the carbon–carbon double bond into the iron–amido bond of **2b** (or its monomer, Scheme 1).[18] The reactivity of **2b** is a rare illustration of the migratory insertion of an alkene into the metal–amido bond of a well-defined and isolated metal amido complex.[19]

Encouraged by these initial stoichiometric results, we evaluated the ability of dimer **2b** to catalytically promote the reaction of **3**. To our delight, only 5 mol% of **2b** leads to almost complete conversion of **3** into **4**, **5**, and **6** with a 82% yield in **4** (Table 1, entry 2). In contrast with other late-transition-metal catalytic systems, no olefin isomerization product was detected.[6f–h] Furthermore, comparable reactivity and hydroamination selectivity[20] can be achieved with the use of the monomeric iron alkyl complex **2a**·THF instead of **2b** as precatalyst (Table 1, entry 3). Conducting the reaction at 50 °C results in red-orange crystals after 12 h (which persist during the remaining reaction time) and a poor conversion of 6% after 24 h (Table 1, entry 4). X-ray analysis of a single crystal reveals that the crystals were **2b**, demonstrating the formation of complex **2b** from precatalyst **2a**·THF under catalytic conditions. Gratifyingly, reactions could also be run in the coordinating solvent THF with a positive outcome (Table 1, entry 5 versus 3), which indicates catalyst tolerance of Lewis basic functional groups in the starting amines (see below). A slight improvement in yield of **4** is obtained by either an about twofold increase in the substrate concentration in toluene (Table 1, entry 6 versus 3) or a decrease of the reaction temperature to 70 °C (Table 1, entry 7). It is worth noting the β-diketiminate ligand plays a crucial role in the catalyst control of the selectivity of the reaction, as $[Fe\{N(SiMe_3)_2\}_2]$[21] affords the olefin isomerization product as the main product under identical reaction conditions (entry 8). A plot of the reaction selectivity[20] (%) versus the conversion (%) in the cyclization of **3** by **2a**·THF (10 mol%) shows that the selectivity evolves with the degree of conversion.[13] The selectivity remains high (> 93%) until a 66% conversion then decreases to 83% at full conversion. This observation suggests that the selectivity might be dependent on the concentration of primary amine present in the reaction medium. To maintain a minimum concentration in primary amine, cyclopentylamine (**7**) was added as noncyclizable primary amine. The addition of 20 mol% of **7** preserves the high selectivity, as only traces of **5** and **6** are detected (Table 1, entry 9). Moreover, only 10 mol% of cyclopentylamine was enough to obtain **4** in 94% GC yield as an almost single product (entry 10).

Our catalytic system is efficient for the selective formation of five- and six-membered rings from primary alkenylamines (Table 2). The *exo*-cyclization can occur in good yields with a 1,2-disubstituted alkene bearing a phenyl group, a dimethylsubstituted allene, or even a coordinating methoxy group without noticeable catalyst deactivation (Table 2, entries 4–6). However, the cyclohydroamination does not proceed without a *geminal* disubstitution on the tether or with 1,2-dialkylsubstituted alkenes.[22]

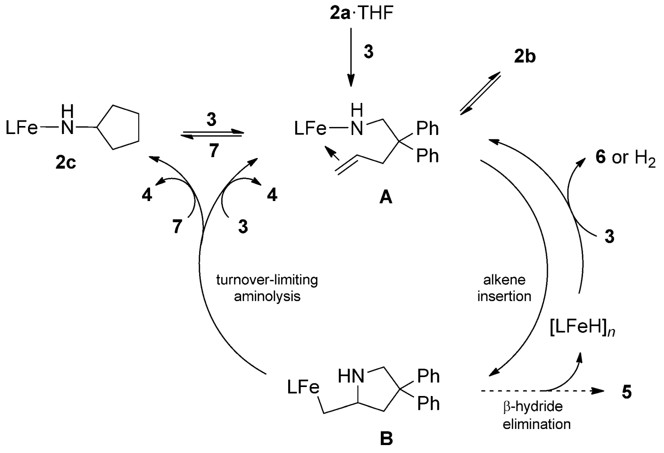
Table 2: Intramolecular hydroamination of primary amines.[a]

Entry	Alkenylamines	Product	Yield [%][b]
1	 **3**	 **4**	94[c] (85)
2			89[d]
3			85[d]
4			> 95[d]
5			91[d] (75)
6	 Ar = *p*-OMeC$_6$H$_4$		98[d,e] (78)

[a] Reaction conditions: **2a**·THF (10 mol%), cyclopentylamine **7** (10 mol%), [D$_8$]toluene, 90 °C, 48 h. [b] Yield of isolated product in parenthesis. [c] Determined by GC analysis [d] Determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv) as internal standard. [e] d.r = 1:1.

To gain a better insight into the reaction mechanism, kinetic measurements[13] were conducted. Monitoring the concentration of **3** over the course of the reaction reveals apparent first-order kinetics up to at least 90% conversion and over a threefold initial concentration range ([**3**] = 0.56–1.65 M).[23] Nevertheless, the observed first-order rate constant decreases with increasing initial substrate concentration, which is consistent with an inverse order dependence of the reaction rate on **3** concentration.[2b,6d,h,24] Over the course of 2–3 half-lives, the hydroamination of **3** is first order with respect to **2a**·THF concentration over a fourfold range ([**2a**·THF] = 0.048–0.192 M). These data suggest the involvement of a monomeric iron species in the rate-determining step of the catalytic cycle. As expected, the transformation also exhibits an inverse rate dependence on the concentration in cyclopentylamine **7**.[25] Additionally, kinetic analysis of the reaction of *N*-proteo-amine **3** versus *N*-deutero-amine [D_2]-**3** yields a kinetic isotope effect (KIE) of $k_H/k_D = 3$ (90 °C).[6d,j,26] This is highly reminiscent of a primary isotope effect, which reflects N−H(D) bond cleavage during the turnover-limiting step.

On the basis of these kinetic data and the observed stoichiometric and catalytic reactivities of isolated dimer **2b**, a stepwise σ-insertive mechanism[1,27] for the iron-catalyzed cyclohydroamination of primary alkenylamines is proposed (Scheme 4). Initial σ-bond metathesis between the coordinatively unsaturated **2a**·THF and basic amine **3** would lead to the formation of catalytically active iron amido species **A**, which in solution would be in rapid equilibrium with dimer **2b**. Subsequent rapid alkene insertion into the Fe−N bond would give iron alkyl intermediate **B**, which might undergo two related pathways. Turnover-limiting aminolysis of **B** with either **3** or **7** would liberate the hydroamination product **4** and give species **A** or **2c**, respectively. An equilibrium between **2c** and **A** might account for the regeneration of the active species **A** from **2c**. To probe this, **2c**[28] was independently synthesized[13] and its catalytic behavior was evaluated in the cyclohydroamination of **3**. Complete conversion of **3** occurs within 24 h using 10 mol% of isolated **2c**, affording the hydroamination product in 94% yield, which is consistent with an equilibrated process (Table 1, entry 11). The evolution of **B** through an undesired but slower β-hydride elimination process would explain the formation of **5** and **6** as minor side-products.[29]



Scheme 4. Proposed stepwise σ-insertive mechanism for alkenylamine **3** (see text for details).

In summary, we have demonstrated that novel well-defined four-coordinated β-diketiminatoiron(II) alkyl complex **2a**·THF is an excellent precatalyst for the highly selective cyclohydroamination of primary aliphatic alkenylamines at mild temperatures (70–90 °C). Reactivity study of isolated iron(II) amidoalkene dimer complex **2b** has indicated that alkene migratory insertion into the iron–amido bond occurs without the assistance of an additional amine. This study, supported by preliminary kinetic measurements, features a stepwise σ-insertive mechanism with aminolysis as the turnover-limiting step of the catalytic cycle. To our knowledge, this work establishes for the first time that well-defined iron complexes are viable catalysts for the selective hydroamination of unprotected primary amines with great binding affinity and polar functional groups. Further studies are currently ongoing to attain a deeper understanding of the mechanism.

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Keywords: alkenes · amines · homogeneous catalysis · hydroamination · iron

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Communications

Iron Catalysis

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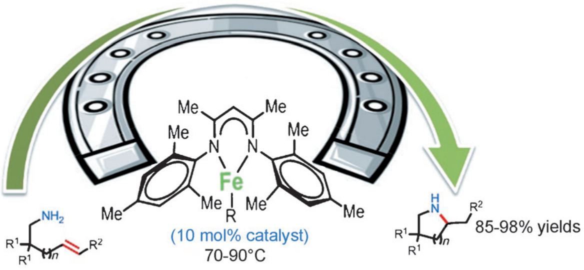
Well-Defined Four-Coordinate Iron(II) Complexes For Intramolecular Hydroamination of Primary Aliphatic Alkenylamines



Iron horseshoe: A well-defined four-coordinate β-diketiminatoiron(II) alkyl complex is a precatalyst for the highly selective cyclohydroamination of primary aliphatic alkenylamines at mild temperatures. Its mechanism is also elucidated.