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C_1-symmetric β-Diketiminatoiron(II) Complexes for Hydroamination of Primary Alkenylamines

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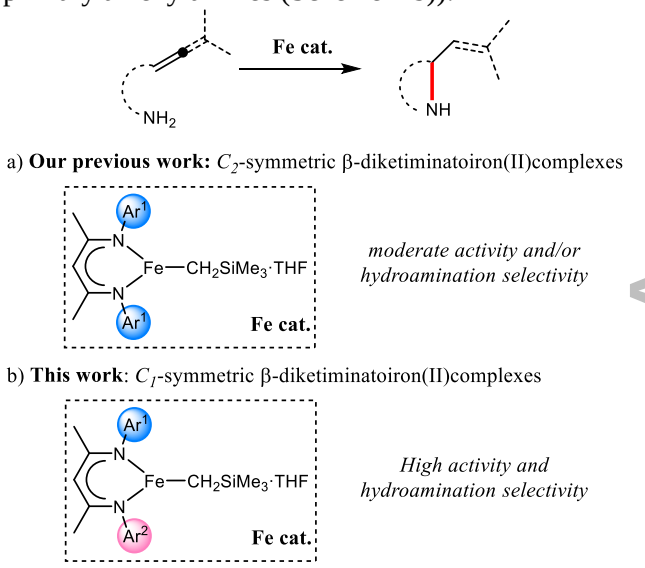
Abstract. The synthesis and solid-state characterization of an array of well-defined low-coordinate C_1-symmetric β–diketiminatoiron(II) alkyl complexes **B_3-B_6** featuring steric and electronic variations on one of the *N*-aryl substituents of the β–diketiminate ligand scaffold are reported. All complexes display unique catalytic abilities of promoting the selective *exo*-cyclohydroamination of unprotected 2,2-diphenylpent-4-en-1-amine (**1a**) under mild reactions conditions. The incorporation of a potentially coordinative *ortho*-methoxy substituent on one of the *N*-aryl rings of the β-diketiminate skeleton, in conjunction with a more crowded 2,6-diisopropylphenyl group on the other, affords a far more active catalyst (**B_3**) than our previously reported C_2-symmetric β-diketiminatoiron(II)alkyl complex **B** (Ar^1=Ar^2=2,4,6-$(Me)_3C_6H_2$)/cyclopentylamine system. Comparative studies let us postulate that this superior activity of **B_3**, when compared with **B_4-B_6**, is likely arising from steric effects and/or the coordinating ability of the *ortho*-methoxy substituent. The scope and limitations of this novel C_1-symmetric β–diketiminatoiron(II) alkyl complex **B_3** are also presented.

Keywords: Hydroamination; Iron; Alkenes; Amines; Catalyst Design

In the last decades, the catalytic alkene hydroamination reaction has emerged as an appealing methodology for the synthesis of important *N*-containing building blocks from relative inexpensive and ubiquitous amines and alkenes as starting materials.[1] The recent interest for sustainable catalysis has prompt the development of hydroamination catalytic systems based on first row late transition metal of high availability, low price and relatively low toxicity. At present, noteworthy advances in this nascent field have be gained by systems derived from iron,[2] cobalt,[3] copper[4] and zinc[5] metal thanks to classical N-H addition and alternative formal approaches such as electrophilic amination[2e,4b-e] or hydrogen-atom[2f-h,3a] transfer. Although these formal approaches have significantly broaden the reaction scope and unlocked some unresolved issues, the requirement for sophisticated electrophilic amine partners and/or the use of a large excess of reducing agent are detrimental to the step and atom efficiency of the overall process. Therefore there is still a need to tackle the search for efficient earth-abundant, first-row late transition metal catalysts for direct N-H bond addition of simple amines on alkenes under functional group-free manipulation and co-reagent-free conditions. In this context, our group has reported the first examples of iron(II)- and cobalt(II)-mediated alkene *exo*-cyclohydroamination of electronically unbiased primary amines using structurally-defined C_2-symmetric low-coordinate β-diketiminatometal alkyl complexes under mild reaction conditions (Scheme 1 a) for iron).[2c,d,3b,6] Inspired by our comprehensive mechanistic investigations conducted recently on iron systems[2d] and a precedent DFT study,[7] we have synthesized and herein report well-defined C_1-symmetric β-diketiminatometal alkyl complexes with significantly improved catalytic activity and hydroamination selectivity in the cyclization of primary alkenylamines (Scheme 1 b)).



Scheme 1. Previous work on iron-catalyzed N-H addition on unactivated alkenes and this work.

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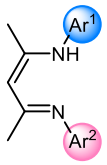
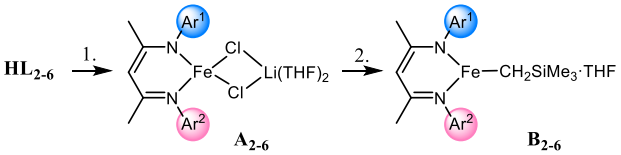
In the course of our investigations towards the development of efficient and selective iron-based hydroamination catalysts, we established that the selectivity of the cyclohydroamination reaction catalyzed by our designed C_2-symmetric β-diketiminatoiron(II) alkyl complex **B** (Ar^1=Ar^2=2,4,6-$(Me)_3C_6H_2$ in Scheme 1) could be enhanced, in favor of the hydroamination product, by the addition of a catalytic amount of a noncyclizable primary amine, such as cyclopentylamine to the reaction media.[2c] As underscored by our depth mechanistic studies, the reaction selectivity likely results from the competition of pathways for rate-limiting aminolysis (that affords the hydroamination product) and β-H elimination (that leads to the formation of the oxidative amination product and the reduced starting material).[2d] This selectivity enhancement may originate from the participation of the non-cyclizable amine addition in the turnover-limiting aminolysis step.



HL_1 Ar^1 = Ar^2 = 2,6-$(iPr)_2C_6H_3$
HL_2 Ar^1 = Ar^2 = 2-$(OMe)C_6H_4$
HL_3 Ar^1 = 2,6-$(iPr)_2C_6H_3$, Ar^2 = 2-$(OMe)C_6H_4$
HL_4 Ar^1 = 2,6-$(iPr)_2C_6H_3$, Ar^2 = 4-$(OMe)C_6H_4$
HL_5 Ar^1 = 2,6-$(iPr)_2C_6H_3$, Ar^2 = C_6H_5
HL_6 Ar^1 = 2,6-$(iPr)_2C_6H_3$, Ar^2 = 3,5-$(CF_3)_2C_6H_3$

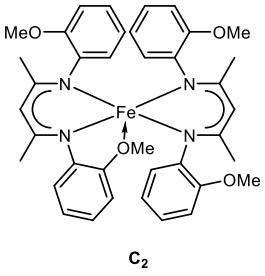
Figure 1. 1,3-diketimines ligands used in this study.

However, although the usage of this additive was effective to achieve high selectivity, it was done at the expense of the catalyst performance as a prolonged reaction time was needed to reach full conversion. To circumvent this drawback in catalyst reactivity, we have explored an alternative strategy based on the rational modification of the structure of the ligand to preserve the high hydroamination selectivity. Our goal was to seek for modification of the β-diketiminate structure that results in the inhibition of the unwanted β-hydride elimination. As demonstrated by our comprehensive DFT mechanistic investigations, the rival and facile β-H elimination pathway evolves through two-spin crossover transitions, from both reactant and product adopting a pseudo-tetrahedral geometry in a high (quintet) spin state.[2d] The β-H elimination requires a pseudo quasi-planar geometry around the metal center in the transition state. The first spin-crossover to a lower (triplet) spin state will deliver the mandatory empty d orbital to accept the incipient hydride's two electrons. A previous computational study has revealed that the increase in steric demands around the metal center disfavors the crucial low spin transition state structure energetically.[7] With these considerations in mind, we envisioned to explore the coordinative ability of the β-diketiminate ligand aimed at enhancing steric bulk around the iron center.



Scheme 2. General two-step metathetic procedure of well-defined iron(II) alkyl complexes [$L_{2\text{-}6}FeCH_2SiMe_3(THF)$] (**$B_{2\text{-}6}$**) from 1,3-diketimines ligands **$HL_{2\text{-}6}$**. Reaction conditions: 1. a) *n*BuLi (1 equiv), THF, −78 °C to 25°C, b) $FeCl_2$ (1 equiv), 25 °C; 2. a) $LiCH_2SiMe_3$ (1 equiv), Et_2O, 25 °C, b) recrystallization hexane/THF, isolated yields for **B_2** (0%), **B_3** (45%), **B_4** (52%), **B_5** (47%), **B_6** (72%).

Our initial efforts were focused on the two-step metathesis synthesis of complex **B_2** stabilized by the β-diketiminate ligand **L_2** (Figure 1) bearing *ortho*-methoxy substituents on the *N*-aryl rings as potentially coordinating groups (Scheme 2). However, despite the formation and solid-state characterization of the ate complex intermediate **A_2**,[8] all the attempts to obtain the corresponding alkyl complex **B_2** were unsuccessful.[9] Indeed, room-temperature metathesis reaction of **A_2** with $LiCH_2SiMe_3$ leads to the isolation of homoleptic complex **C_2** (Figure 2) as red crystals in 35% yield (from 50% theoretical yield) after cold recrystallization. Solid-state analysis of a single crystal reveals a five-coordinated iron atom adopting a distorted square pyramid geometry and in-plane coordinated by one methoxy group of the *N*-aryl rings (Figure 2).[8,10]



C_2

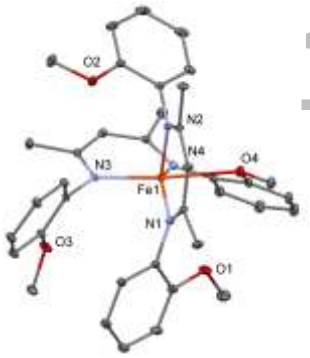


Figure 2. Structure of homoleptic complex **C_2** and its ORTEP diagram showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Although the synthesis of complex **B_2** was not reached, the solid-state structure of **C_2** highlights the ability of the *ortho*-methoxy substituents of the *N*-aromatic groups to bind to the metal center and potentially increase its coordination number. The formation of **C_2** may arise from a ligand redistribution resulting from the poor bulkiness of the β-diketiminate ligand **L_2**. Such phenomenon has been previously observed during the course of the synthesis of β-diketiminatometal complexes bearing low substituted phenyl rings on the ligand nitrogen atoms.[11] To address the ligand redistribution reactivity observed during the complex synthesis, we

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turned our attention to the preparation of iron(II) alkyl complex **B$_3$** stabilized by a C_1-symmetric β-diketiminate ligand having an *ortho*-methoxyphenyl ring on one *N* atom and the more crowded 2,6-diisopropylphenyl group on the other (Scheme 2). Reaction of $FeCl_2$ and the lithium salt of ligand **HL$_3$** (Figure 1) affords the ate complex **A$_3$** as confirmed by X-ray diffraction analysis.[8] To our delight, subsequent metathesis reaction of **A$_3$** with $LiCH_2SiMe_3$ results, after cold recrystallization, in the isolation of red crystals of **B$_3$** in 45% yield. X-ray diffraction analysis of a single crystal of **B$_3$** shows a four-coordinate iron atom having a trigonal-pyramidal coordination geometry, similarly to our previously reported complex **B**[2c] (Ar^1=Ar^2=2,4,6-$(Me_3)C_6H_2$ in Scheme 1) (Figure 3).[8]

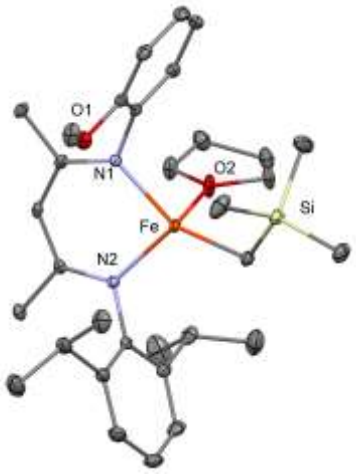
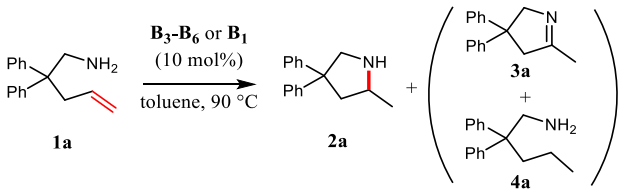


Figure 3. ORTEP diagram of complex **B$_3$** showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The catalytic efficiency of **B$_3$** was next evaluated in the cyclization of benchmark aminoalkene **1a** (Scheme 3). As clearly shown in Figure 4, **B$_3$** performs distinctly better than C_2-symmetric β-diketiminatoiron(II) alkyl complex **B$_1$** having only 2,6-diisopropyl substituents on both *N*-aryl groups of the ligand as far as activity and selectivity towards the hydroamination product (defined as (%)=[**2a** (%) / (**2a** (%) + **3a**(%) + **4a** (%)] are concerned. Indeed, a cycloamine yield of 93% with a selectivity of 95% can be achieved after only 250 min for **B$_3$**, whereas merely a 42% yield is reached with **B$_1$** (Figure 4).



Scheme 3. Cyclization of benchmark aminoalkene **1a** into **2a** catalyzed by complexes **B$_3$**-**B$_6$** and **B$_1$**.

It is worth noting that our previously reported complex **B** (Ar^1=Ar^2=2,4,6-$(Me_3)C_6H_2$) affords under these conditions similar yield to **B$_1$**.[2c,d] This underlines the improvement of efficiency achieved with C_1-symmetric β-diketiminatoiron(II) alkyl complex **B$_3$** bearing one *ortho*-methoxyphenyl ring over our previous C_2-symmetric family of complexes. To gain more insight upon the impact of the electronic/steric ligand effects on the catalyst efficiency, complexes **B$_4$** and **B$_5$** featuring *para*-methoxyphenyl and phenyl groups, respectively, on one of the β-diketiminate N centers have been synthesized (Scheme 2). Their molecular solid-state structures and those of intermediates **A$_{4-5}$** were confirmed by X-ray crystallography.[8] As revealed from Figure 4, complexes **B$_4$** and **B$_5$** perform similarly, but somewhat inferior as **B$_3$**, whilst the hydroamination selectivity achieved at >90 % conversion is comparable in all three cases. At first glance, the apparent absence of a noticeable electronic effect of the *para*-methoxy substituent (**B$_4$**) upon the catalyst performance relative to **B$_5$** without a methoxy substituent may seem counter-intuitive. A closer look at the solid-state structure of complex **B$_4$** reveals that the *para*-methoxyphenyl ring is almost perpendicularly aligned to the β-diketiminatoiron core.[8] As a consequence, there is no real prospect of conjugative π-orbital interactions between the *para*-methoxyphenyl ring and the nitrogen nonbonding π-orbital. This may give rise to a rather small electronic perturbation caused by the *para*-methoxy substituent and thus rationalizing the similar catalytic behavior of **B$_4$** and **B$_5$**. A comparable catalytic efficiency was also observed for alkyl complex **B$_6$** with a strong electronic-withdrawing 3,5-bis(trifluoromethyl)phenyl substituent on one of its nitrogen atoms (Figure 4). Based upon these observations, we postulate that the superior activity of **B$_3$**, when compared with **B$_{4-6}$**, is likely arising from steric effects and/or the coordinating ability of the *ortho*-methoxy substituent.

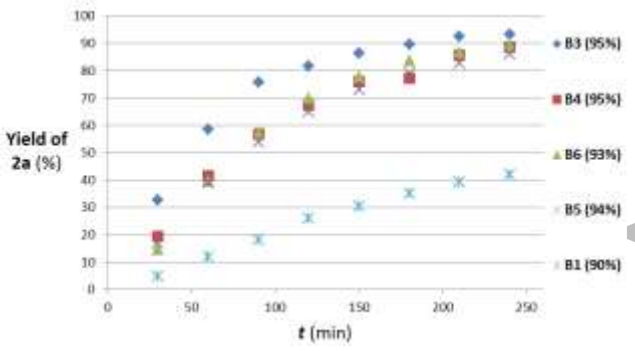


Figure 4. Dependence of the conversion (%) over time for the cyclization of **1a** catalyzed by complexes **B$_{3-6}$** and **B$_1$**. Selectivity towards the hydroamination product (%)=[**2a** (%) / (**2a** (%) + **3a**(%) + **4a** (%)] in parentheses at > 90% conversion.

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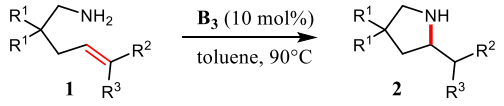
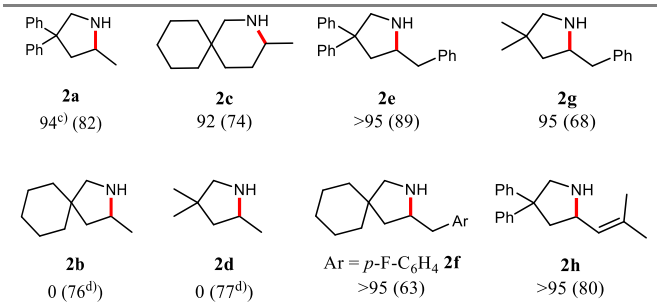
Encouraged by the better ability of **B$_3$** to selectively promote the cyclization of benchmark substrate **1a**, the cyclohydroamination of various primary aminoalkenes featuring different substitution patterns on the alkyl chain and the alkene component or an auxiliary functional group was examined. This substrate scope study was performed as described in Table 1. Under our optimized reaction conditions (90 °C, toluene, 24 h), a variety of *gem*-disubstituted aminoalkenes were suitably converted into the corresponding five- and six-membered rings which were isolated in moderate to excellent yields. In almost all cases studied (excluded **1b** and **1d**), shorter reaction times (24 h) are needed with **B$_3$** to observe a comparable cyclization outcome than with our previously reported catalytic system **B**/cyclopentylamine,[2c] as it was observed for the reaction of **1a**.

Table 1. Scope of the cyclohydroamination of primary aminoalkenes promoted by *C$_1$*-symmetric β–diketiminatoiron(II) complex **B$_3$**.[a,b]





a) Reaction conditions: **B$_3$** (10 mol%), 24 h unless otherwise stated. b) RMN yield determined by in situ ^{1}H NMR spectroscopy using ferrocene (0.4 equiv) as internal standard and isolated yields in parentheses unless otherwise stated. c) Determined by GC analysis. d) NMR yield of isomerization of starting material.

While our methodology is efficient for the selective cyclohydroamination of *gem*-disubstituted aminoalkenes having a less pronounced Thorpe-Ingold effect substitution than with diphenyl such as substrates **1c**, **1f** or **1g**, more challenging substrates unbiased toward cyclization by the chain substituents, such as 5-phenylpent-4-en-1-amine are not converted under our reaction conditions. This observation is in keeping with other late d-block catalytic systems compatible with primary amines such as the [Ir(COD)Cl][12] or the Cu(OtBu)/Xantphos[4a] systems. To our knowledge, the late-transition metal-mediated hydroamination of this class of primary aminoalkenes lacking geminal disubstitution on the alkyl backbone is limited to a single report using the [Rh(COD)$_2$]BF$_4$/Xantphos-based ligand combination and featuring the cyclization of 1-aminopentene and 1-aminohexene in 76 and 77% NMR yield respectively.[13] This isolated example highlights the challenge associated with the hydroamination of this type of substrates. The presence of a *para*-fluoro substituent on a phenyl group attached on the alkene moiety as in **1f** does not influence the outcome of the cyclization affording the corresponding products with high conversion. Surprisingly, and in contrast to **B**/cyclopentylamine catalytic systems,[2c] complex **B$_3$** does not provide pyrrolidine **2b** during the cyclization of (1-allylcyclohexyl)methanamine (**1b**) and only the product resulting from alkene isomerization of the starting material was detected. To a lesser extent, such alkene isomerization was also detected during the cyclization of **1b** promoted by [Ir(COD)Cl]$_2$/HNEt$_3$Cl catalytic system.[12] The same event is also observed with 2,2-dimethylpent-4-en-1-amine (**1d**). This alternative isomerization reactivity has been previously noticed by others as the major reactivity when the cyclohydroamination was not favored.[13] As mentioned early on and in contrast to previously reported [Ir(COD)Cl]$_2$/HNEt$_3$Cl[12] and [Rh(COD)$_2$]BF$_4$/Xantphos-based ligand[13] combination, which are part of the rare examples of late d-block metal hydroamination catalysts compatible with unprotected primary amines, trace of olefin isomerization of the starting aminoalkene was not detected during the cyclization of other substrates promoted by β-diketiminatoiron(II) complexes. In the quest to establish the scope and limitations of our current systems, we turned our attention to the cyclization of another challenging class of substrates that are primary amines tethered to 1,2-di-substituted alkenes. Unfortunately, despite our numerous efforts, no trace of product was detected during the course of the reaction of 2,2-diphenylhex-4-en-1-amine (R^1 = Ph, R^2 = Me, R^3 = H for **1** in Table 1) promoted by our various catalytic systems. To the best of our knowledge, the cyclohydroamination of this class of aminoalkenes has never been reported by a first-row late transition metal catalyst, and rarely been accomplished by noble metal catalytic systems compatible with primary amines.[14,15] Our iron-based methodology is not restricted to primary aminoalkenes as it is also well-suited for the *exo*-cyclization of primary aminoallenes. Indeed, under the reaction conditions, the hydroamination of 6-methyl-2,2-diphenylhepta-4,5-dien-1-amine (**1h**) occurs efficiently affording the corresponding products (**2h**) in 80% isolated yield. This substrate offers the advantage of featuring a C-C double bond which is set for further potential functionalization.

In summary, we have reported the synthesis and solid-state characterization of a variety of well-defined low-coordinate *C$_1$*-symmetric β–diketiminatoiron(II) alkyl complexes **B$_3$**-**B$_6$** featuring steric and electronic variations on one of the *N*-aryl substituents of the β–diketiminate ligand scaffold. All these low-coordinate complexes exhibit abilities of mediating the selective

cyclohydroamination of 2,2-diphenylpent-4-en-1-amine (**1a**) under mild reactions conditions. This study has shown that introducing a potentially coordinative *ortho*-methoxy substituent on one of the *N*-aryl rings of the β-diketiminate skeleton, in conjunction with a more crowded 2,6-diisopropylphenyl group on the other, provides a noteworthy more active and selective iron catalyst (**B_3**) for the cyclization of benchmark substrate **1a**. Indeed, a hydroamination selectivity of 95% is reached at 93% conversion of **1a** after only 250 min of reaction with this catalyst. A prolonged reaction time (up to 48h) was previously required with our formerly reported catalytic system **B**/cyclopentylamine to reach such high selectivity under similar reaction conditions. Comparative studies let us postulate that this superior reactivity of **B_3**, when compared with **$B_{4\text{-}6}$**, may arise from the coordinating ability and/or steric bulk of the *ortho*-methoxy substituent. This study will provide foundations to design more efficient first-row late transition metal catalysts for direct N-H bond addition of unprotected primary amines on unactivated alkenes by further rational modification of the β–diketiminate ligand scaffold. Further work to do so are ongoing.

Experimental Section

Synthesis of complex [$L_3Fe(\mu\text{-}Cl)_2Li(THF)_2$] ($A_3$): *n*-BuLi (1.3 mL, 3.25 mmol) was added to a stirred solution of 2-(2,6-diisopropylphenylimino)-4-(2-methoxy phenylimino)pentane (**HL_3**) (1.184 g, 3.25 mmol) in THF (10 mL) at −78 °C. The cooling was removed 30 min after addition. The resulting light yellow solution was stirred for 2 h at room temperature and $FeCl_2$ was added (0.412 g, 3.25 mmol). The solution was stirred overnight and the solvent was removed until dryness. The resulting brown solid was washed with hexane (2 x 10 mL) and extracted with Et_2O (2 x 10 ml). The brown solution was concentrated and cooled to −20 °C to afford **A_3** as yellow crystals (0.915 g, 1.43 mmol, 44%). Anal. Calcd for $C_{32}H_{47}Cl_2FeLiN_2O_3$: C, 59.92; H, 7.39; N, 4.58. Found: C, 59.73; H 6.15; N 4.54. Evans μ_{eff} (THF-d_8, 298 K) = 5.9 μ_B. UV-vis (toluene, nm): 339 (ε = 17 $mM^{-1}.cm^{-1}$), 427 (ε = 2.1 $mM^{-1}.cm^{-1}$), 474 (ε = 0.53 $mM^{-1}.cm^{-1}$). IR (cm^{-1}): 3011, 2961, 2866, 1525, 1490, 1439, 1392, 1359, 1245, 1211, 1046, 743. ^{1}H NMR (250 MHz, C_6D_6-50 µL THF-d_8, RT) δ 19.5 (s, 1H, *m-H Ar*), 16.9 (s, 2H, *m-H Ar*), 16.0 (s, 1H, *m-H Ar*), 4.4 (s, 8H, *THF*), 1.7 (s, 8H, *THF*), 0.9 (br s, 6H, CH*Me*Me), −10.6 (s, 3H, *MeO Ar*), −20.8 (br s, 6H, CHMe*Me*), −40.7 (br s, 3H, Me_2CH and C*H*), −49,7 (s, 1H, *p-H Ar*), −55,3 (s, 1H, *p-H Ar*), −70.1 (s, 3H, *Me*), −70.4 (s, 3H, *Me*), −119.4 (br s, 1H, *o-H Ar*). ^{7}Li NMR (117 MHz, C_6D_6-50µL THF-d_8, RT) δ 266.6 (br s).

Synthesis of complex [$L_3FeCH_2TMS\cdot THF$] (B_3): $LiCH_2TMS$ (0.147 g, 1.56 mmol) was added as a solid to a stirred yellow solution of **A_3** (1.0 g, 1.56 mmol) in Et_2O (5 mL) at 25 °C. The solution turns red immediately and a white precipitate appeared. After overnight stirring, the solvent was removed under reduced pressure. The red brown solid was extracted with hexane (2 x 5 mL). The red solution was concentrated and cooled to −20 °C after THF addition (0.1 mL) to afford **B_3** as red crystals (0.467 g, 0.807 mmol, 52%). Anal. Calcd for $C_{32}H_{50}FeN_2O_2Si$: C, 66.42; H, 8.82; N, 5.11. Found: C, 65.93; H 8.61; N 5.05. Evans μ_{eff} (THF-d_8, 298 K) = 5.6 μ_B. UV-vis (toluene, nm): 291 (ε = 9.9 $mM^{-1}.cm^{-1}$), 333 (ε = 15.3 $mM^{-1}.cm^{-1}$), 377 (ε = 5.6 $mM^{-1}.cm^{-1}$), 440 (ε = 0.94 $mM^{-1}.cm^{-1}$), 496 (ε = 0.6 $mM^{-1}.cm^{-1}$). IR (cm^{-1}): 3009, 2961, 2865, 1500, 1437, 1375, 1241, 1179, 1037, 885, 850. ^{1}H NMR (250 MHz, C_6D_6, RT) δ 112.9 (br s, 1H, C*H*), 79.3 (br s, 3H, *Me*), 74.7 (br s, 3H, *Me*), 40.4 (br s, 9H, $SiMe_3$), 3.0 (br s, 2H, *THF*), 2.2 (s, 2H, *THF*), 1.3 (s, 2H, *THF*), 0.9 (s, 2H, *THF*), −4.8 (br s, 3H, *MeO Ar*), −7.8 (s, 2H, *m-H Ar*), −10.2 (s, 2H, *m-H Ar*), −15.5 (s, 6H, CH*Me*Me), −67.3 (s, 1H, *p-H Ar*), −92.9 (br s, 6H, CHMe*Me*), −128.8 (br s, 2H, *o-H Ar*).

General procedure for the catalytic cyclohydroamination of primary alkenylamines catalyzed by complex B_3: To a screw-capped tube equipped with a stir-bar were added the appropriate amine (0.18 mmol), ferrocene (13.4 mg, 0.072 mmol) and complex (0.018 mmol). The volume of the tube was completed to 190 µL by toluene-d^8. The screw-capped tube was placed in an oil bath at 90 °C for 24 h and next exposed to air. The yield was determined by ^{1}H NMR spectroscopy analysis of an aliquot of the reaction using ferrocene as internal standard. The appropriate amine was purified as described in the Supporting Information.

Acknowledgements

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