**COMMUNICATION**

**C$_7$-symmetric $\beta$-Diketiminatoiron(II) Complexes for Hydroamination of Primary Alkenylamines**

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Received: (will be filled in by the editorial staff)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201####. (Please delete if not appropriate)

**Abstract.** The synthesis and solid-state characterization of an array of well-defined low-coordinate $C_7$-symmetric $\beta$-diketiminatoiron(II) alkyl complexes $B_3-B_6$, featuring steric and electronic variations on one of the $N$-aryl substituents of the $\beta$-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 advantageous $ortho$-methoxy substituent on one of the $N$-aryl rings of the $\beta$-diketiminate skeleton, in conjunction with a more crowded 2,6-disopropylphenyl group on the other, affords a far more active catalyst ($B_3$) than our previously reported $C_2$-symmetric $\beta$-diketiminatoiron(II)alkyl complex $B$ ($Ar'=Ar''=2,4,6-(Me)C_6H_3$)/cyclooctylamine system. Comparative studies let us postulate that this superior activity of $B_3$, when compared with $B_2-B_6$, is likely arising from steric effects and/or the coordinating ability of the $ortho$-methoxy substituent. The scope and limitations of this novel $C_7$-symmetric $\beta$-diketiminatoiron(II) alkyl complex $B_3$ are also presented.

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

In the last decades, the catalytic alkene hydromamination 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 prompted the development of hydromamination 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 been 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$^{[2c,4b-e]}$ or hydrogen-atom$^{[2f,3a]}$ transfer. Although these formal approaches have significantly broadened 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 $\beta$-diketiminometal 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$^{[2c]}$ and a precedent DFT study,$^{[7]}$ we have synthesized and herein report well-defined $C_7$-symmetric $\beta$-diketiminometal alkyl complexes with significantly improved catalytic activity and hydromamination 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.
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-diketiminateiron(II) alkyl complex B (Ar'$_1$=Ar'$_2$=2,4,6-(Me)$_2$C$_6$H$_3$ 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 cyclopentamylene to the reaction media. As underscored by our depth mechanistic studies, the reaction selectivity likely results from the competition of pathways for rate-limiting amination (that affords the hydroamination product) and β-H elimination (that leads to the formation of the oxidative amination product and the reduced starting material). This selectivity enhancement may originate from the participation of the non-cyclizable amine addition in the turnover-limiting amination step.

![Figure 1](image1.png)

**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. 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. 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](image2.png)

**Scheme 2.** General two-step metathetic procedure of well-defined iron(II) alkyl complexes [L$_2$FeCH$_2$SiMe$_3$(THF)] (B$_{2,6}$) from 1,3-diketimines ligands H$_2$A$_{2,6}$. Reaction conditions: 1. a) nBuLi (1 equiv), THF, −78 °C to 25°C, b) FeCl$_2$ (1 equiv), 25 °C; 2. a) LiCH$_2$SiMe$_3$ (1 equiv), Et$_2$O, 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$_2$ all the attempts to obtain the corresponding alkyl complex B$_2$ were unsuccessful. Indeed, room-temperature metathesis reaction of A$_2$ with LiCH$_2$SiMe$_3$ leads to the isolation of homogeneous 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).

![Figure 2](image3.png)

**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. To address the ligand redistribution reactivity observed during the complex synthesis, we
turned our attention to the preparation of iron(II) alkyl complex B₃ stabilized by a Cₛ-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 FeCl₂ and the lithium salt of ligand HL₃ (Figure 1) affords the ate complex A₃ as confirmed by X-ray diffraction analysis.[⁶] To our delight, subsequent metathesis reaction of A₃ with LiCH₂SiMe₃ results, after cold recrystallization, in the isolation of red crystals of B₃ in 45% yield. X-ray diffraction analysis of a single crystal of B₃ shows a four-coordinate iron atom having a trigonal-pyramidal coordination geometry, similarly to our previously reported complex B⁵⁺ (Ar¹=Ar²=2,4,6-(Me₃)C₆H₂ in Scheme 1) (Figure 3).[⁸]

**Figure 3.** ORTEP diagram of complex B₃ showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

The catalytic efficiency of B₃ was next evaluated in the cyclization of benchmark aminoalkene 1a (Scheme 3). As clearly shown in Figure 4, B₃ performs distinctly better than Cₛ-symmetric β-diketimatoiron(II) alkyl complex B₁ 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 B₃, whereas merely a 42% yield is reached with B₁ (Figure 4).

It is worth noting that our previously reported complex B (Ar¹=Ar²=2,4,6-(Me₃)C₆H₂) affords under these conditions similar yield to B₃. This underlines the improvement of efficiency achieved with Cₛ-symmetric β-diketimatoiron(II) alkyl complex B₃ bearing one *ortho*-methoxyphenyl ring over our previous Cₛ-symmetric family of complexes. To gain more insight upon the impact of the electronic/steric ligand effects on the catalyst efficiency, complexes B₄ and B₅ 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 A₄,5 were confirmed by X-ray crystallography.[⁸] As revealed from Figure 4, complexes B₄ and B₅ perform similarly, but somewhat inferior as B₃, 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 (B₄) upon the catalyst performance relative to B₃ without a methoxy substituent may seem counter-intuitive. A closer look at the solid-state structure of complex B₄ reveals that the *para*-methoxyphenyl ring is almost perpendicularly aligned to the β-diketimatoiron 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 B₄ and B₅. A comparable catalytic efficiency was also observed for alkyl complex B₆ 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 B₃, when compared with B₄,₆, 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 B₃,₄,₅ and B₁. Selectivity towards the hydroamination product (%)=[2a (%) / (2a (%) + 3a(%) + 4a (%))] in parentheses at >90% conversion.
Encouraged by the better ability of B₃ to selectively promote the cyclization of benchmark substrate 1a, the cyclohydroamination of various primary aminoaalkenes 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 aminoaalkenes 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 B₃ to observe a comparable cyclization outcome than with our previously reported catalytic system B/cyclopentylamine,²⁷ as it was observed for the reaction of 1a.

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<th>Table 1. Scope of the cyclohydroamination of primary aminoaalkenes promoted by $C_1$-symmetric $\beta$-diketiminoiron(II) complex B₃,a,b</th>
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a) Reaction conditions: B₃ (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 aminoaalkenes 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]₂/HNEt₃Cl catalytic system.¹² As mentioned early on and in contrast to previously reported [Ir(COD)Cl]₂/HNEt₃Cl¹² and [Rh(COD)₂BF₃/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 aminoaalkene was not detected during the cyclization of other substrates promoted by $\beta$-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 (R¹ = Ph, R² = Me, R³ = H for 1 in Table 1) promoted by our various catalytic systems. To the best of our knowledge, the cyclohydroamination of this class of aminoaalkenes 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 aminoaalkenes as it is also well-suited for the exo-cyclization of primary aminoaalkenes. 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 $\beta$–diketiminatoiron(II) alkyl complexes B₃-B₇ featuring steric and electronic variations on one of the N-aryl substituents of the $\beta$–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 (B₄) 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/cyclopentamylene to reach such high selectivity under similar reaction conditions. Comparative studies let us postulate that this superior reactivity of B₄ when compared with B₄,h might 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 [LFe(µ-Cl)Li(THF)]₂ (A₄):** n-BuLi (1.3 mL, 3.25 mmol) was added to a stirred solution of 2-(2,6-diisopropylphenylimino)-4-(2-methoxyphenylimino)pentane (H₁Lₐ) (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 FeCl₂ 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 EtO (2 x 10 mL). The brown solution was concentrated and cooled to −20 °C to afford A₄ as yellow crystals (0.915 g, 1.43 mmol, 44%). Anal. Calcld for C₆H₉Cl₂FeLi₂O₂: C, 59.92; H, 7.39; N, 4.58. Found: C, 59.7; H, 6.15; N, 4.5. 1H NMR (300 MHz, THF-d₈, 298 K): 10.9 (s, 2H, CH₂), 8.3 (s, 2H, THF), -40.7 (br s, 3H, Me), -10.6 (s, 3H, Me). 1H NMR (500 MHz, THF-d₈, 298 K): 8.5 (s, 2H, CH₂), 8.3 (s, 2H, THF), -40.7 (br s, 3H, Me), -10.6 (s, 3H, Me).

**Synthesis of complex [L₂Fe(CH₃TMS-THF)]₂ (B₄):** LiClCH₂TMS (0.147 g, 1.56 mmol) was added as a solid to a stirred yellow solution of A₄ (1.0 g, 1.56 mmol) in Et₂O (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 B₄ as red crystals (0.467 g, 0.807 mmol, 52%). Anal. Calcld for C₈H₁₀Fe₂N₂O₂Si: C, 66.42; H, 8.82; N, 5.11. Found: C, 65.93; H, 8.61; N, 5.05. Evans μₐ (THF-d₈, 298 K) = 5.6 μB. 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. 1H NMR (250 MHz, CD₂Cl₂, RT) δ 112.9 (br s, 1H, CH). 79.3 (br s, 3H, Me), 74.7 (br s, 3H, Me), 40.4 (br s, 9H, SiMe₃), 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, CH₂Me₂), −67.3 (s, 1H, p-H Ar), −92.9 (br s, 6H, CH₂Me₂), −128.8 (br s, 2H, o-H Ar).

**General procedure for the catalytic cyclohydroamination of primary alkyleneamines catalyzed by complex B₄:** 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·d⁶. 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 1H 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**

Financial supports from MENSUR, Univ Paris Sud and the CNRS, are gratefully acknowledged

**References**


[8] CCDC 1874107, 1571108-1571111, 1571113-1571116 & 1812907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.


[10] Complex C2 (10 mol%) is inefficient to catalytically promote the cyclization of 1a at 90°C as only starting material was recovered after 24 h of reaction.


[14] For rare examples of noble late-transition metal systems suitable for the cyclization of internal alkenes see references 12 and 13.

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