Bis(imino)pyridine iron complexes for catalytic carbene transfer reactions†

Ban Wang, Isaac G. Howard, Jackson W. Pope, Eric D. Conte and Yongming Deng‡*

The bis(imino)pyridine iron complex, for the first time, is developed as an effective metal carbene catalyst for carbene transfer reactions of donor–acceptor diazo compounds. Its broad catalytic capability is demonstrated by a range of metal carbene reactions, from cyclopropanation, cyclopropenation, epoxidation, and Doyle–Kirmse reaction to O–H insertion, N–H insertion, and C–H insertion reactions. The asymmetric cyclopropanation of styrene and methyl phenyldiazoacetate was successfully achieved by the new chiral bis(imino)pyridine iron catalyst, which delivers a new gateway for the development of chiral iron catalysis for metal carbene reactions.

Introduction

Transition-metal-catalyzed carbene transfer reactions occurring through metal carbene intermediates encompass a vast array of reactants and catalysts to achieve novel and selective strategies for organic synthesis.1 The reactive carbeneoid intermediates can be catalytically generated from diazo compounds by metal-catalyzed dinitrogen extrusion,2 and their reactions extend from addition and insertion to cycloaddition and ylide formation.3 Dirhodium complexes have been established as the most successful catalysts for carbene transfer reactions of diazo compounds;4 great achievements have also been accomplished recently by copper and other precious metal catalysts (e.g. ruthenium, palladium, gold).5 Iron, the second most abundant metal, with its particular biological relevance, is emerging as an important metal for catalytic metal carbene reactions.6 However, iron catalysis is comparatively underdeveloped, with the enduring dominance of precious metal catalysis in metal carbene chemistry.

Since the launch of iron porphyrin-catalyzed cyclopropanation by Woo,7 various carbene transfer processes of diazo compounds, including cyclopropanation, heteroatom–hydrogen bond insertions, and intramolecular C–H inversion, have been achieved by porphyrin and related macrocyclic iron complexes; however, these generally occur with active α-hydrogen-diazocarbonyl compounds, diazoalkanes, or the corresponding precursors.8 The spiro-bisoxazoline iron complexes developed by Zhou’s group have exhibited high catalytic activities and selectivities for heteroatom–hydrogen bond insertions and intramolecular cyclopropanation reactions of α-diazoesters.9 Despite these achievements, iron has not been developed as a catalyst to the same extent as other late transition metals, particularly for usage in metal carbene reactions. The advancement of iron catalysis for general carbene transfer reactions with broad substrate schemes, especially asymmetric processes and under mild reaction conditions, remains a wide-open field for discovery and innovation. We report here, for the first time, bis(imino)pyridine iron complexes serving as effective catalysts for a range of metal carbene reactions under mild reaction conditions (at room temperature or 40 °C), including cyclopropanation/cyclopropenation, epoxidation, Doyle–Kirmse reaction, O–H insertion, N–H insertion, and C–H insertion (Scheme 1). To the best of our knowledge, this bis(imino)pyridine iron catalyst represents the most broad-ranging catalytic activity towards metal carbene reactions of diazo compounds over the previously reported iron catalysis system.10

Scheme 1  (a) Selected iron catalysis for metal carbene reactions. (b) This research: bis(imino)pyridine iron catalyzed metal carbene reactions.
The bis(imino)pyridine iron-catalyzed cyclopropanation proceeds on a wide range of aryl diazoacetates, vinyl diazoacetates, styrenes and phenylacetylene. Notably, a new chiral bis(imino)pyridine ligand derivatized from L-valine methyl ester has been synthesized, and the corresponding enantiopure, C₄-symmetric iron catalyst enabled the asymmetric cyclopropanation of styrene and phenyl diazoacetate.

In the past decade, bis(imino)pyridine chelated iron complexes have emerged as an effective class of catalysts for ethylene polymerization, olefin hydrogenation, hydrosilation, and [2π + 2π]-cycloaddition reactions.⁶ Owing to its ease of preparation, the bis(imino)pyridine ligand is easily modifiable, allowing versatility in ligand design, synthesis, and screening.⁶,⁷ However, catalytic metal carbene reactions by bis(imino)pyridine iron complexes have not been achieved. Recently, Chirik reported the formation of a bis(imino)pyridine iron carbene complex B from a stoichiometric amount of bis(imino)pyridine iron dinitrogen complex A and diphenylketoxime by dinitrogen extrusion (Fig. 1).⁸ However, the attempts towards metal carbene reactions, such as cyclopropanation and C–H insertion, were unsuccessful with this bis(imino)pyridine iron carbene complex.⁹,¹⁰

We hypothesized that one reason for the lack of reactivity for bis(imino)pyridine iron carbene complex B in the carbene transfer process is due to the charge delocalization induced by the diphenyl group. To address this issue, we predicted that augmenting the electrophilicity of the disubstituted diazo compound would increase the reactivity of the corresponding iron carbene; thus, it could more readily engage in carbene transfer reactions.³,²,¹¹ It has been documented that the donor-acceptor metal carbene, which can be produced from donor-acceptor diazo compound by metal-catalyzed dinitrogen extrusion, exhibited higher reactivity than the one from diphenylketoxime due to its stronger electrophilicity.¹¹,¹²,¹³ Herein, a donor–acceptor diazo compound, aryldiazoacetate, was selected as the carbene precursor to investigate the bis(imino)pyridine iron-catalyzed metal carbene reactions. Additionally, recent computational studies of bis(imino)pyridine iron complexes for C–H functionalization of donor–acceptor diazo compound also suggest feasibility.¹⁴

The catalytic cycle for the conversion of a diazo compound to a metal-stabilized carbene intermediate is initiated from the metal-catalyzed dinitrogen extrusion of nucleophilic diazo compound. We predicted that compared to the formal iron(0) complex A, the more electrophilic bis(imino)pyridine iron(II) complexes would exhibit higher reactivity towards the nucleophilic diazo compound and facilitate the subsequent metal carbene transfer. Therefore, we aimed to electronically and sterically tune the bis(imino)pyridine iron(n) complexes to achieve the carbene transfer reactions of the donor–acceptor diazo compound under mild reaction conditions.

**Results and discussion**

As a starting point, we focused on evaluating a series of bis(imino)pyridine iron(n) catalysts for the cyclopropanation reaction of styrene 2a with methyl phenyldiazoacetate 1a (Table 1). As proposed, in the presence of 5 mol% of bis(aryl imino)pyridine iron(n) dichloride complexes (entries 1 and 2), the reaction of 2a and phenyl diazoacetate 1a afforded the cyclopropanation product 3a, however, in low yields with predominately recovered starting material. To improve the catalytic activity of the iron complexes, examination of the noncoordinating counterions was performed. The employment of more electrophilic iron complexes with hexafluorooctanitratimolate ([SbF₆]⁻) as counterions (entries 3 and 4) led to a marked increase in yield. The combination of [(PrPDI)FeCl₂] and NaBF₄ also delivered 3a with enhanced yield (48%, Table S1). [(PrPDI)Fe(C₂H₅CN)₂][SbF₆] was isolated product 3a with yield 65% under optimized conditions.

![Fig. 1 Formation of a bis(imino)pyridine iron carbene from bis(aryl imino)pyridine iron dinitrogen complexes and diphenylketoxime.](image)

**Table 1** Screening of iron catalysts for cyclopropanation

| Entry | Catalyst | T (°C) | Yield |
|-------|----------|-------|-------|
| 1     | [(MePDI)FeCl₂] | 50    | 14    |
| 2     | [(PrPDI)FeCl₂] | 50    | 18    |
| 3     | [(PrPDI)Fe(CH₂CN)₂][SbF₆] | rt   | 65    |
| 4     | [(PrPDI)Fe(C₂H₅CN)₂][SbF₆] | rt   | 86    |
| 5     | [(APDI)Fe(C₂H₅CN)₂][SbF₆] | rt   | 68    |
| 6     | [(APDI)Fe(CH₂CN)₂][SbF₆] | 50    | 8     |
| 7     | [(APDI)Fe(CH₂CN)₂][SbF₆] | 50    | 5     |
| 8     | FeCl₂/PyBOX | 50    | 5     |
| 9     | FeCl₂/PyBOX | 50    | 5     |
| 10    | FeCl₂/OIP | 50    | 9     |

a Reaction condition unless otherwise noted: 1a (0.20 mmol, 1.0 equiv.) in dry DCE (1.0 ml) was added to 1.0 mL DCE solution of 2a (1.0 mmol, 5.0 equiv.) and catalyst (0.01 mmol) under N₂ within 1 hour. b Yield of isolated product 3a based on the limiting reagent 1a. c The reaction was performed with 1a : 2a = 1 : 1 (1,2-dichloroethane = DCE).
bearing bulky 2,6-diisopropylphenyl substituents was identified as the best catalyst, which catalyzed the cyclopropanation under room temperature, generating 3a in 86% yield with excellent diastereoselectivity (dr > 20 : 1). A lower yield of 3a (entry 5, 68%) was obtained when the reaction was performed with 1a : 2a = 1 : 1 in the presence of [[(iPrPDI)Fe(CH3CN)2](SbF6)2]. To reveal the imino-substituents' effect on the catalyst, iron complexes containing N-alkyl substituents were examined. However, they resulted in low catalytic activity with recovery of starting material (entries 6 and 7), which could be due to electronic and/or steric constraints from the imino-aryl groups. Additionally, neither iron complexes of pyridine bis(oxazoline) ligands nor oxazoline iminopyridine iron complexes were effective catalysts for this transformation (entries 8 to 10). These results demonstrate the indispensability of the imino-aryl substituent in the ligand frame to conduct active iron catalysis in metal carbene reactions of donor-acceptor diazo compounds.

Under the optimized condition, we investigated the scope of this bis(arylimino)pyridine iron-catalyzed cyclopropanation across a range of aryl diazoacetates and styrene derivatives (Table 2). As indicated by entries 1 to 5, aryl diazoacetates with electron-rich, halogen para-substituents and 2-naphthyl group all reacted smoothly with styrene, generating the corresponding cyclopropanes in good yields (81–88%, 3b–3f) with excellent diastereoselectivities (dr > 20 : 1). However, no reaction occurred with the electron-deficient system, even at 40 °C (1g, entry 6). Reactions of aryl diazoacetates 1h and 1j bearing ortho-substituents on the aromatic ring resulted in lower yields (entries 7 and 8). We rationalize that such lower reactivity can be attributed to a higher kinetic barrier for the generation of corresponding iron carbene intermediate, which is caused by the increased steric hindrance between the ortho-substituent and the bulky bis(arylimino)pyridine ligand frame. The cyclopropanes 3j–3l derived from styrene derivatives 2b–2d were obtained in yields ranging from 88 to 91%, whereas moderate yield (67%, entry 12) was obtained with 4-(trifluoromethyl)styrene 2e. Disubstituted styrenes, including 2-phenylstyrene 2f and trans-β-methylstyrene 2g, were also ideal reagents for this iron-catalyzed cyclopropanation, producing products 3n and 3o in good yields.

In addition to the styrene derivatives, the reaction of 1,3-cyclohexadiene and 1a was also effectively catalyzed by [[(iPrPDI)Fe(CH3CN)2](SbF6)2], affording the cyclopropane product 3p in 80% yield with dr > 20 : 1 (eqn (1)). Furthermore, as shown in eqn (2), [[(iPrPDI)Fe(CH3CN)2](SbF6)2] catalyzed the cyclopropanation of cyclohexene, and 1a was also successfully achieved, affording the desired product 3q in 72% yield. To further probe the diazo substrate generality, vinyl-diazoacetate 1j was subjected to bis(arylimino)pyridine iron-catalyzed cyclopropanation with styrene (eqn (3)). Gratifyingly, the cyclopropane 3r was obtained in 84% yield, which demonstrates the catalytic capability of bis(arylimino)pyridine iron for a broader scope of donor-acceptor diazo compounds. Remarkably, [[(iPrPDI)Fe(CH3CN)2](SbF6)2] was also capable of catalyzing the cyclopropanation of 1a and phenylacetylene, furnishing the product 3s in 61% yield at 40 °C (eqn (4)), which has not been achieved by other reported iron catalysts.

With the accomplishment of achiral bis(arylimino)pyridine iron-catalyzed cyclopropanation, we have sought to modify the ligand architecture to generate a chiral iron catalyst for asymmetric cyclopropanation. Our catalyst screening (Table 1) indicated that the N-aryl substituent in bis(arylimino)pyridine ligand is indispensable for the effective catalytic activity of iron.

Table 2 Scope of bis(arylimino)pyridine iron-catalyzed cyclopropanation

| Entry | 1     | 2     | Yieldb |
|-------|-------|-------|--------|
| 1     | 1b, 4-MeC6H4 | 2a, Ph, H, H | 3b, 81 |
| 2     | 1c, 4-MeOC6H4 | 2a, Ph, H, H | 3e, 83 |
| 3     | 1d, 4-ClC6H4 | 2a, Ph, H, H | 3d, 88 |
| 4     | 1e, 4-BrC6H4 | 2a, Ph, H, H | 3e, 83 |
| 5     | 1f, 2-naphthyl | 2a, Ph, H, H | 3f, 81 |
| 6a    | 1g, 4-NO2C6H4 | 2a, Ph, H, H | 3g, <5 |
| 7     | 1h, 2-MeOC6H4 | 2a, Ph, H, H | 3h, 52 |
| 8     | 1i, 2-CICH2C6H4 | 2a, Ph, H, H | 3i, 58 |
| 9     | 1a, Ph       | 2b, 4-MeC6H4, H, H | 3j, 91 |
| 10    | 1a, Ph       | 2c, 4-MeOC6H4, H, H | 3k, 88 |
| 11    | 1a, Ph       | 2d, 4-ClC6H4, H, H | 3l, 90 |
| 12    | 1a, Ph       | 2e, 4-CH2C6H4, H, H | 3m, 67 |
| 13    | 1a, Ph       | 2f, Ph, Ph, H, H | 3n, 73 |
| 14    | 1a, Ph       | 2g, Ph, H, CH3 | 3o, 70 |

a For experimental details, see ESI. b Isolated yield. c Reactions were performed at 40 °C.
complexes. Guided by these experimental results and Bianchini’s original design of chiral bis(imino)pyridine ligand, we synthesized an enantiopure, C_{1}-symmetric chiral bis(imino) pyridine ligand [(S)-VMEPDI] (Scheme 2), in which one imine is “anchored” by a 2,6-diisopropylphenyl group (activating element) and the other is prepared from L-valine methyl ester (chiral element). To our delight, the asymmetric cyclopropanation reaction of 1a and styrene was successfully achieved by in situ prepared chiral iron catalyst from (S)-VMEPDI, FeCl$_2$, and AgSbF$_6$ at room temperature. The cyclopropane product 1a was isolated in 78% yield with 67% enantiomeric excess. Although with moderate enantioselectivity, the success of this asymmetric cyclopropanation reaction provides a strong basis for the development of a new chiral bis(imino)pyridine iron catalyst for metal carbene reactions.

Encouraged by the success of bis(arylimino)pyridine iron(II)-catalyzed cyclopropanation, we then sought to examine the generality of this iron catalyst for metal carbene reactions. As depicted in Scheme 3, a range of metal carbene reactions of phenyldiazoacetate 1a, including epoxidation, Doyle–Kirmse reaction, N–H insertion, C–H insertion, and O–H insertion, were all successfully catalyzed by [(iPrPDI)Fe(CH$_3$CN)$_2$](SbF$_6$)$_2$.

As documented, bis(imino)pyridines have been recognized as radical-based, redox non-innocent ligands that can directly participate in the electronic structure of metal complexes. Chirik’s study demonstrated that a carbene radical is engaged in bis(arylimino)pyridine iron carbene complex A, which is obtained from a formal iron(0) complex (Scheme 2). Therefore, considering the redox activity of the bis(imino)pyridine ligand, radical tapping experiments were conducted to address whether a radical carbene involved in this bis(arylimino)pyridine iron(II) catalyzes carbene transfer reactions. As shown in Scheme 4a, the addition of the radical scavenger TEMPO (2,2,6,6-tetramethylpiperidine N-oxide) did not harm the [(iPrPDI)Fe(CH$_3$CN)$_2$](SbF$_6$)$_2$-catalyzed cyclopropanation reactions of 1a or vinyl diazoacetate 1j, and the corresponding products were isolated with similar yields to those from the reactions in the absence of TEMPO. These results reveal the unlikely involvement of the carbene radical intermediate in [(iPrPDI)Fe(CH$_3$CN)$_2$](SbF$_6$)$_2$-catalyzed cyclopropanation reactions. Moreover, the achievement of C–H insertion reaction of 1a with N,N-dimethylaniline

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**Scheme 2** Chiral bis(imino)pyridine iron-catalyzed cyclopropanation.

**Scheme 3** Bis(arylimino)pyridine iron-catalyzed: (a) epoxidation; (b) Doyle–Kirmse reaction; (c) N–H insertion; (d) C–H insertion; and (e) O–H insertion.

**Scheme 4** (a) Mechanism study. (b) Proposed mechanism of bis(arylimino)pyridine iron(II)-catalyzed cyclopropanation.
(Scheme 3d) implies the likely generation of donor–acceptor iron(u) carbene intermediate.1,6 Based on the obtained experimental results and mechanism study, we propose that the donor–acceptor diazo compound was decomposed by the bis(arylimin)pyridine iron(u) catalyst to generate an iron(u) carbene intermediate, which readily undergoes cyclopropanation of olefins to afford the cyclopropane product (Scheme 4b).

Conclusions

In summary, the effective catalytic activity of bis(arylimin) pyridine iron(u) complexes for carbene transfer reactions of donor–acceptor diazo compounds has been demonstrated by a range of metal carbene transformations from cyclopropanation and insertions to ylide formation. Notably, the asymmetric cyclopropanation of methyl phenylidiazacacetate and styrene has been achieved by a new chiral iron catalyst based on the bis(imino)pyridine ligand derivatized from l-valine methyl ester. Future studies will be aimed at developing new asymmetric bis(imino)pyridine iron catalysts for highly enantioselective metal carbene reactions, as well as elucidating the mechanism of such process and the nature of the iron carbene intermediate.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Support for this research from Western Kentucky University and the National Science Foundation under Cooperative Agreement No. 1355438 (OIA-1355438-3200000271-19-136) is gratefully acknowledged. Dedicated to Professor Michael P. Doyle on the occasion of the 50th anniversary of his academic career.

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