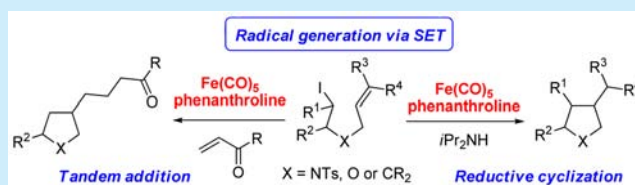


Single-Electron-Transfer Strategy for Reductive Radical Cyclization: $\text{Fe}(\text{CO})_5$ and Phenanthroline SystemJoon Young Hwang,[†] Jong Hwa Baek,[†] Tae Il Shin,[†] Jung Ha Shin,[†] Jae Won Oh,[†] Kwang Pyo Kim,[†] Youngmin You,^{*,‡} and Eun Joo Kang^{*,†}[†]Department of Applied Chemistry, Kyung Hee University, Yongin 17104, Korea[‡]Division of Chemical Engineering and Materials Science, Ewha Womans University, Seoul 03760, Korea

S Supporting Information

ABSTRACT: An electron-transfer strategy using low-valent iron pentacarbonyl $[\text{Fe}(\text{CO})_5]$ to generate radical species from alkyl iodides was achieved. A range of pyrrolidines, tetrahydrofurans, and carbocycles were synthesized via 5-*exo* cyclization reactions of alkyl radical intermediates generated by electron transfer from a system involving $\text{Fe}(\text{CO})_5$, 1,10-phenanthroline, and diisopropylamine. Moreover, tandem addition reactions with Michael acceptors were also explored. Photophysical and electrochemical studies support a mechanism that involves electron transfer from the low-valent Fe reductant to alkyl iodide.



Iron compounds are considered to be green chemicals that are economical and sustainable and have been intensively explored in various kinds of organic reactions as oxygen carriers,¹ Lewis acids,² and cross-coupling catalysts.³ As an alternative coupling catalyst, iron has received substantial attention due to its unprecedented characteristics toward alkyl halide substrates and single-electron-transfer processes in catalytic cycles. These features are not surprising since iron complexes possess rich multivalent states that are stable and easily accessible. For instance, the action of tris(1,10-phenanthroline)iron(III) ($[\text{Fe}(\text{phen})_3]^{3+}$) as a single-electron oxidant can be found in oxidative substitutions of methylarenes,⁴ α - β cleavage of diarylpropanes,⁵ and SOMO cycloaddition reactions.⁶ Additionally, $\text{Fe}(\text{acac})_3$ and FeCl_3 were applied to an oxidative enolate heterocoupling^{7a} and sulfur-directed C-H arene/alkene coupling reactions.^{7b,c} Conversely, reductive single-electron transfer by the $\text{Fe}(\text{II/III})$ couple proceeded with the in situ generated iron(II) complex by external reductants, such as Grignard reagents or silanes, in pinacol coupling and nitroarene addition reactions.⁸ Low-valent iron species have rarely been directly employed as single-electron reductants, while they have been generated in situ in organic reactions. We questioned whether low-valent iron might mediate radical reactions of alkyl halides via a single-electron-transfer process.

Radical cyclization is a well-developed method for C-C bond formation and the efficient elaboration of cyclic compounds. There are two representative reductive radical cyclization methods: chain reaction and nonchain reaction. Radical chain reactions progress using stoichiometric amounts of various alkyl metal/semimetal hydrides, such as tin,⁹ germanium,¹⁰ and silane hydrides¹¹ ($\text{R}_3\text{M-H}$). Other types of metal hydrides have also been reported including HGaCl_2 , HInCl_2 ,¹² $\text{HIn}(\text{OAc})_2$ ¹³ and $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$,¹⁴ which were prepared from metal salts (MX_3) with silane or aluminum hydride reductant. Recently, iron

hydride was shown to participate in an electron transfer process via anionic iron(I) hydrido species ($[\text{HFeCl}(\text{dppe})_2]^-$; $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane), which was generated from iron(II) catalyst and stoichiometric NaBH_4 reductant.¹⁵

Nonchain reactions include the single-electron-transfer (SET) process from a low-valent transition metal, which could be the metal itself,¹⁶ metal salts,¹⁷ or reduced metal species generated by RMgX , RLi , or RSiH_3 .¹⁸ These low-valent transition metals transfer one electron to substrates to afford radical anion intermediates, which are easily transformed into reactive alkyl radical species. Photoactivation methods of Ru, Ir, and Au are usually performed to achieve this type of electron transfer in catalytic systems.¹⁹ However, the methods mentioned above require additives (AIBN or alkylborane) to prepare active metal radical intermediates, hydride reductants to prepare low-valent metal species, and the use of scarce or expensive chemicals. For these reasons, concerted efforts on SET and radical generation have been expended. We questioned whether the commercial low-valent iron might mediate radical reactions, and we describe the first reductive cyclization reactions mediated by iron-phenanthroline complexes.

To examine the possibility of low-valent iron species as single-electron reductants, various iron compounds were tested together with 1,10-phenanthroline monohydrate (phen, 2.0 equiv), triethylamine (2.0 equiv), and ω -iodoalkene **1a** in acetonitrile (0.10 M) (Table 1). In the reaction with iron dichloride, no conversion was observed at room temperature, and the halogen-exchanged product ω -chloroalkene **3a** was detected at 60 °C (entry 1). Other $\text{Fe}(\text{II})$ compounds, including FeF_2 , $\text{Fe}(\text{OAc})_2$, and FeO , did not exhibit noticeable reactivities (entries 2–4). The commercially available $\text{Fe}(\text{0})$ compound iron

Received: August 9, 2016

Published: September 27, 2016

Table 1. Reductive Cyclization with Fe Complex

entry	[Fe]	ligand	amine	yield ^b (%)
1 ^c	FeCl ₂	phen	Et ₃ N	(68)
2 ^c	FeF ₂	phen	Et ₃ N	
3 ^c	Fe(OAc) ₂	phen	Et ₃ N	(38)
4 ^c	FeO	phen	Et ₃ N	
5 ^c	Fe(CO) ₅	phen	Et ₃ N	74
6	Fe(CO) ₅	phen	Et ₃ N	90
7	Fe(CO) ₅	bpy	Et ₃ N	83
8	Fe(CO) ₅	terpy	Et ₃ N	56
9	Fe(CO) ₅	Me ₂ phen	Et ₃ N	72
10	Fe(CO) ₅	phen	TMEDA	89
11	Fe(CO) ₅	phen	<i>i</i> -Pr ₂ NH	92
12	Fe(CO) ₅	phen	<i>c</i> Hex ₂ NH	83
13	Fe(CO) ₅	phen	EtNH ₂	92
14	Fe(CO) ₅	phen	AmylNH ₂	87
15	Fe(CO) ₅	phen	EDA	72
16 ^d	Fe(CO) ₅	phen	<i>i</i> -Pr ₂ NH	95
17 ^e	Fe(CO) ₅	phen	<i>i</i> -Pr ₂ NH	43
18	Fe ₂ (CO) ₉	phen	<i>i</i> -Pr ₂ NH	38
19	Fe ₃ (CO) ₁₂	phen	<i>i</i> -Pr ₂ NH	46
20 ^f	Fe(CO) ₅		<i>i</i> -Pr ₂ NH	8
21 ^g	Fe(CO) ₅	phen		14

^aReaction conditions: **1a** (0.2 mmol), [Fe] (0.2 mmol), ligand (0.4 mmol, 2 equiv), amine (0.4 mmol, 2 equiv), CH₃CN (0.1 M), rt for 6 h under N₂, unless otherwise specified. ^bIsolated yield (yield of **3a** (X = Cl) in parentheses in entry 1; yield of **3b** (X = OAc) in parentheses of entry 3). ^cReaction at 60 °C. ^dReaction with phen (0.6 mmol, 3 equiv). ^eReaction with Fe(CO)₅ (0.1 mmol, 0.5 equiv) and phen (0.3 mmol, 1.5 equiv) resulted in **1a** (25%) and **4** (17%). ^fReaction resulted in **1a** (90%). ^gReaction with phen (0.3 mmol) resulted in **1a** (54%) and **4** (18%). phen = 1,10-phenanthroline monohydrate, bpy = 2,2'-bipyridine, terpy = 2,2':6',2''-terpyridine, Me₂phen = 2,9-dimethyl-1,10-phenanthroline, TMEDA = tetramethylethylenediamine, EDA = ethylenediamine.

pentacarbonyl [Fe(CO)₅] was found to serve as an effective reductant, resulting in 5-*exo* product **2a** in 74% yield (entry 5). Surprisingly, the reaction conditions at ambient temperature improved the product formation to 90% yield. Among a variety of diimine ligands, including bpy, terpy, and Me₂phen, the phen ligand was found to give the best result (entries 6–9). Examination of various tertiary, secondary, and primary amines revealed that diisopropylamine was the optimal choice as a sacrificial electron and hydrogen donor (entries 10–15). Almost 50% of cyclized product **2a** was observed when the reaction was carried out with 0.5 equiv of Fe(CO)₅ in a glovebox (entry 17), indicating a 1:1 stoichiometry of Fe(CO)₅ and **1a**. Changing the Fe(0) complex to Fe₂(CO)₉ and Fe₃(CO)₁₂ reduced the yield to 38–46% (entries 18 and 19). Control experiments performed in the absence of the phen ligand or *i*-Pr₂NH showed recovery of starting material or formation of the atom-transferred iodoalkane byproduct **4** (entries 20 and 21). Additionally, experiments conducted with bromo- and chloroalkenes fail to generate any product.

The scope of the reductive cyclization reaction with respect to ω-iodoalkene substrate was explored using the optimized conditions (entry 16, Table 1).²⁰ Diversely substituted alkene substrates were clearly transformed into the corresponding

pyrrolidines **2a–f** in good yields, and no 6-*endo* products were observed even with the sterically encumbered environment of **1f** (Table 2). Cyclization of a secondary iodide gave the desired

Table 2. Substrate Variations

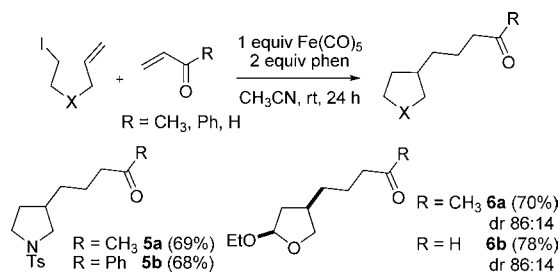
entry	substrate	product (yield, %) ^b
1	1a R = R' = H 1b R = Me; R' = H 1c R = R' = Me 1d R = Ph; R' = H 1e R = CO ₂ Me; R' = H	2a (95) 2b (90) 2c (94) 2d (98) ^c 2e (84) ^c
2	1f	2f (54) ^c
3	1g	2g (85, dr 75:25)
4	1h R = R' = Me 1i R = Ph; R' = H	2h (80, dr 63:37) 2i (80, dr 70:30)
5	1j	2j (73, dr 64:36)
6	1k	2k (75, dr 65:35)
7	1l R = R' = H 1m R = R' = Me 1n R = Ph; R' = H	2l (75, dr 88:12) 2m (73, dr 72:28) 2n (90, dr 71:29)
8	1o	2o (79)
9	1p	2p (84)

^aGeneral conditions: substrate (0.2 mmol), 1,10-phenanthroline monohydrate (0.6 mmol), diisopropylamine (0.4 mmol), Fe(CO)₅ (0.2 mmol) in CH₃CN (0.1 M). ^bIsolated yield. The diastereomeric ratio was determined by ¹H NMR analysis. ^cReaction with 2 equiv of phen.

pyrrolidine **2g** in 85% yield. Various iodoacetals were reacted to afford 2-ethoxytetrahydrofurans (**2h–j**) and hexahydro-2H-furo[2,3-*b*]pyrans (**2k–n**). Oxacycles **2h** and **2l–m** reported previously under other types of radical process also resulted in similar diastereomeric ratios, implying that this strategy afforded a radical process under milder conditions or shorter reaction times. The *cis* ring junction protons in **2k–n** also provide evidence for the radical mechanism, while starting allyloxyiodotetrahydropyrans **1k–n** had *trans* stereochemistry. The cyclization of allyl 2-iodoethyl malonate and 2-iodoethyl phenyl acrylate also gave the carbocycles **2o** and **2p** in high yield.²¹

To apply the cyclized methyl radical intermediate to further C–C bond formation, we accomplished tandem radical cyclization reactions with various electrophilic Michael acceptors, such as methyl vinyl ketone (MVK), phenyl vinyl ketone, and acrolein (Scheme 1). When *i*-Pr₂NH was added in the tandem reaction even with the reduced amount (1 equiv), a tandem product was produced as a minor product (30%) accompanied by the cyclized one **2a** (61%), which indicates that

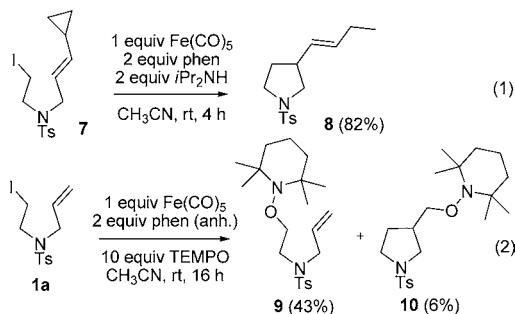
Scheme 1. Tandem Reactions with Michael Acceptors



the hydrogen abstraction of the cyclized methyl radical intermediate is faster than addition to the β -carbon in the α,β -unsaturated carbonyl compound for α -carbonyl radical intermediate formation. According to the previous reports,²² the α -carbonyl radical adducts ($E_{1/2} = -0.59$ to -0.73 V vs SCE) could be reduced with the available electron donor species, such as low-valent iron species, and the resulting enolates would be protonated to afford the tandem addition products. Similarly, in the absence of $i\text{-Pr}_2\text{NH}$, the tandem reactions of vinyl ketones with **1a** resulted in the formation of methyl ketone **5a** and phenyl ketone **5b** in 68–69% yield, indicating the feasibility of reduction by Fe species and proton transfer by hydrated phen ligand.²³ The reaction also works well for the preparation of tetrahydrofuran ketone **6a** and aldehyde **6b**. Tandem addition reactions were very specific to α,β -unsaturated carbonyl compounds, while acrylonitrile, acrylate, and styrene derivatives rarely participated as the radical acceptor.²²

The selective 5-*exo* mode cyclization suggested that the $\text{Fe}(\text{CO})_5$ –phen system promoted one-electron-reductive cleavage of the C–I bond, generating a radical intermediate. To examine this hypothesis, we ran the reactions in the presence of a radical clock or a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy, TEMPO (Scheme 2). The substrate **7** underwent

Scheme 2. Experiments for Mechanistic Investigations



radical cyclization, followed by a cyclopropane ring-opening reaction, affording the allyl group in product **8** with high yield (82%). TEMPO was found to inhibit cyclization of the radical intermediate, as TEMPO-trapped derivatives **9** and **10** were observed in the product mixture.

To investigate the redox processes mediated by the $\text{Fe}(\text{CO})_5$ –phen system, we performed mechanistic studies employing photophysical and electrochemical techniques. The UV–vis absorption spectrum obtained for the reaction solution (1.0 mM **1a**, 1.0 mM $\text{Fe}(\text{CO})_5$, 3.0 mM phen, and 1.0 mM $i\text{-Pr}_2\text{NH}$) exhibited a strong absorption band with a peak wavelength at 508 nm along with shoulders at 476 and 437 nm (Figure 1a). The spectral signatures were consistent with MLCT transition ($\lambda_{\text{obs}} = 508$ nm; $\epsilon = 1.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) of $[\text{Fe}(\text{phen})_3](\text{PF}_6)_2$ that

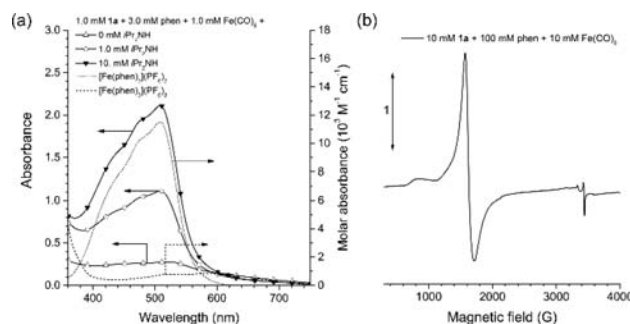


Figure 1. (a) UV–vis absorption spectra of an CH_3CN solution containing 1.0 mM **1a**, 3.0 mM phen, 1.0 mM $\text{Fe}(\text{CO})_5$, and varied concentrations of $i\text{-Pr}_2\text{NH}$ (0, 1.0, 10 mM). (b) Low-temperature EPR spectrum of an CH_3CN solution containing 10 mM **1a**, 100 mM phen, and 10 mM $\text{Fe}(\text{CO})_5$.

was independently prepared.²⁴ When the reaction was performed in the absence of $i\text{-Pr}_2\text{NH}$, UV–vis absorption spectra showed broad and weak absorptions at 527 and 586 nm that were reminiscent of $[\text{Fe}(\text{phen})_3]^{3+}$. Reaction mixtures in CH_3CN or toluene are EPR-silent, irrespective of the presence of $i\text{-Pr}_2\text{NH}$. However, a strong EPR signal was observed when the concentration of phen was increased (10 equiv). The rhombic EPR signature with a g value of 4.2194 is characteristic of a Fe(III) species (Figure 1b).^{25a} An additional weak EPR signal with a g value of 2.0083 was observed, which can be assigned to be a radical anion of phen.^{25b} These results support the mechanism involving electron transfer of $\text{Fe}(\text{CO})_5$ and formation of Fe(III) species.²⁶

To gain more insight into the redox process, we collected cyclic and differential pulse voltammograms of $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$. A reversible one-electron redox process of Fe(II/III) was found at 1.10 V vs SCE in deaerated CH_3CN solutions (Figure S2). An oxidation potential (E_{ox}) of the sacrificial electron donor was less positive [e.g., $E_{\text{ox}}(\text{TEA}) = 0.70$ V vs SCE],²⁷ which supports the notion that Fe(II) was the final oxidation state in the presence of amines. The electron transfer from amines to the Fe(III) species is crucial because the resulting radical cation of amines can provide a hydrogen atom to the radical intermediate of the cyclized products. Further reduction to low-valent Fe species was observed at more negative potentials at -1.33 and -1.46 V vs SCE. Since reduction of **1a** occurred at -1.15 V vs SCE (Figure S2), the low-valent species derived from $\text{Fe}(\text{CO})_5$ would be capable of promoting reductive cleavage of **1a** through exoergic one-electron transfer with a free energy change greater than -0.18 eV. The lack of reactivities by $[\text{Fe}(\text{phen})_3](\text{PF}_6)_2$, $[\text{Fe}(\text{phen})_3](\text{PF}_6)_3$, and their combined system corroborated this hypothesis. Although the electron stoichiometry and an action of the phen ligands in the redox processes require further resolution, the mechanistic studies provided evidence that the $\text{Fe}(\text{CO})_5$ –phen system is an effective reductant for radical generation from alkyl iodide.

Taken together, we propose a mechanism outlined in Figure 2. The Fe–phenanthroline complex generated from $\text{Fe}(\text{CO})_5$ and phenanthroline transfers an electron to alkyl iodide substrates to achieve alkyl radical intermediates (**II**), which undergo the 5-*exo* radical cyclization. The formation of **2a** is completed by a hydrogen atom abstraction from the aminium radical cation species, which was formed by oxidation by $\text{Fe}^{\text{III}}(\text{phen})_n$.

In summary, we have described the $\text{Fe}(\text{CO})_5$ -mediated reductive cyclization of organohalides. Phenanthroline ligand is crucial for a single-electron-transfer system, and amine is

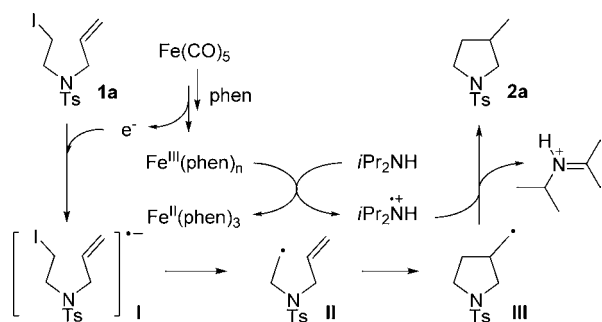


Figure 2. Plausible mechanism for reductive radical cyclizations with an Fe-phenanthroline system.

required as a hydrogen donor in this transformation. We believe that this method is an alternative approach to reductive radical cyclizations and provides a synergistic exploration in iron radical chemistry. Efforts toward expanding the scope of radical precursor as well as developing a catalytic variant are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.6b02375](https://doi.org/10.1021/acs.orglett.6b02375).

Experimental procedures and characterization data for new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: odds2@ewha.ac.kr.

*E-mail: ejkang24@khu.ac.kr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the Ministry of Education, Science and Technology, National Research Foundation (Grant Nos. NRF-2012R1A1A1044770 and NRF-2015R1D1A1A01060349)

■ REFERENCES

- (1) (a) Gu, H.; Shen, L.; Zhong, Z.; Niu, X.; Ge, H.; Zhou, Y.; Xiao, S. *Ind. Eng. Chem. Res.* **2014**, *53*, 13006. (b) Gonzalez-de-Castro, A.; Xiao, J. J. *Am. Chem. Soc.* **2015**, *137*, 8206.
- (2) (a) Mayer, M. F.; Hossain, M. M. *J. Org. Chem.* **1998**, *63*, 6839. (b) Gopalaiah, K. *Chem. Rev.* **2013**, *113*, 3248. (c) Racys, D. T.; Warrilow, C. E.; Pimlott, S. L.; Sutherland, A. *Org. Lett.* **2015**, *17*, 4782.
- (3) (a) Sherry, B.; Furstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500. (b) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417. (c) Bauer, I.; Knolker, H.-J. *Chem. Rev.* **2015**, *115*, 3170.
- (4) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567.
- (5) Harvey, P. J.; Schoemaker, H. E.; Bowen, R. M.; Palmer, J. M. *FEBS Lett.* **1985**, *183*, 13.
- (6) Jui, N. T.; Lee, E. C. Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010**, *132*, 10015.
- (7) (a) Demartino, M. P.; Chen, K.; Baran, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 11546. (b) Cavanagh, C. W.; Aukland, M. H.; Hennessy, A.; Procter, D. J. *Chem. Commun.* **2015**, *51*, 9272. (c) Cavanagh, C. W.; Aukland, M. H.; Laurent, Q.; Hennessy, A.; Procter, D. J. *Org. Biomol. Chem.* **2016**, *14*, 5286.
- (8) (a) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 7117. (b) Gui, J.; Pan, C.-M.; Jin, Y.; Qin, T.; Lo, J. C.; Lee, B. J.; Spergel,

S. H.; Mertzman, M. E.; Pitts, W. J.; La Cruz, T. E.; Schmidt, M. A.; Darvathkar, N.; Natarajan, S. R.; Baran, P. S. *Science* **2015**, *348*, 886.

(9) (a) Malacria, M. *Chem. Rev.* **1996**, *96*, 289. (b) Salom-Roig, X. J.; Denes, F.; Renaud, P. *Synthesis* **2004**, *12*, 1903.

(10) Miura, K.; Ootsuka, K.; Hosomi, A. *Synlett* **2005**, *20*, 3151.

(11) Yamazaki, O.; Yamaguchi, K.; Yokoyama, M.; Togo, H. *J. Org. Chem.* **2000**, *65*, 5440.

(12) Takami, K.; Mikami, S.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2003**, *59*, 6627.

(13) Miura, K.; Tomita, M.; Yamada, Y.; Hosomi, A. *J. Org. Chem.* **2007**, *72*, 787.

(14) Fujita, K.; Nakamura, T.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2001**, *123*, 3137.

(15) Ekomie, A.; Lefevre, G.; Fensterbank, L.; Lacote, E.; Malacria, M.; Ollivier, C.; Jutand, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 6942.

(16) (a) Yanada, R.; Nishimori, N.; Matsumura, A.; Fujii, N.; Takemoto, Y. *Tetrahedron Lett.* **2002**, *43*, 4585. (b) Yanada, R.; Koh, Y.; Nishimori, N.; Matsumura, A.; Obika, S.; Mitsuya, H.; Fujii, N.; Takemoto, Y. *J. Org. Chem.* **2004**, *69*, 2417.

(17) (a) Baldwin, J. E.; MacKenzie Turner, S. C.; Moloney, M. G. *Tetrahedron* **1994**, *50*, 9411. (b) Molander, G. A.; St. Jean, D. J. *J. Org. Chem.* **2002**, *67*, 3861. (c) Millan, A.; Álvarez de Cienfuegos, L. A.; Miguel, D.; Campana, A. G.; Cuerva, J. M. *Org. Lett.* **2012**, *14*, 5984. (d) Szostak, M.; Fazakerley, N. J.; Parmar, D.; Procter, D. J. *Chem. Rev.* **2014**, *114*, 5959.

(18) RMgX: (a) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435. (b) Hatakeyama, T.; Okada, Y.; Yoshimoto, Y.; Nakamura, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 10973. (c) Kim, J. G.; Son, Y. H.; Seo, J. W.; Kang, E. J. *Eur. J. Org. Chem.* **2015**, *2015*, 1781. RLi: (d) Fujita, K.; Yorimitsu, H.; Oshima, K. *Synlett* **2002**, *2002*, 337.

(19) (a) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4*, 854. (b) Kim, H.; Lee, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 12303. (c) Revol, G.; McCallum, T.; Morin, M.; Gagosz, F.; Barriault, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 13342. (d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322.

(20) This condition also proved to be efficient in the hydrodehalogenation reaction of alkyl iodides without a pendent olefin, affording the reduced products in good yield (see Scheme S1).

(21) Iodoalkyne (S3) and iodoallene (S5) also participated as radical acceptors to provide pyrrolidines with side products. See the Supporting Information.

(22) (a) Kohls, P.; Jadhav, D.; Pandey, G.; Reiser, O. *Org. Lett.* **2012**, *14*, 672. (b) Ruiz Espelt, L.; Wiensch, E. M.; Yoon, T. P. *J. Org. Chem.* **2013**, *78*, 4107. (c) Terrett, J. A.; Clift, M. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 6858.

(23) Deuterium experiments were tested with deuterium oxide in tandem reactions (Table S2).

(24) (a) Braterman, P. S.; Song, J. I.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 555. (b) Tribollet, J.; Galle, G.; Jonusauskas, G.; Deldicque, D.; Tondusson, M.; Letard, J. F.; Freysz, E. *Chem. Phys. Lett.* **2011**, *513*, 42.

(25) (a) Petrat, F.; Paluch, S.; Dogruoz, E.; Dorfler, P.; Kirsch, M.; Korth, H.-G.; Sustmann, R.; de Groot, H. J. *Biol. Chem.* **2003**, *278*, 46403. (b) Yi, H.; Jutand, A.; Lei, A. *Chem. Commun.* **2015**, *51*, 545.

(26) The $[\text{Fe}(\text{phen})_3]^{2+}$ formation was checked by ESI-MS and time-dependent UV-vis absorption spectroscopy. See the Supporting Information.

(27) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. J. *Am. Chem. Soc.* **1978**, *100*, 7219.