

Development of a Catalytic Electron Transfer System Mediated by Transition Metal Ate Complexes: Applicability and Tunability of Electron-Releasing Potential for Organic Transformations

Masanobu Uchiyama,^{*,†,||} Yotaro Matsumoto,[†] Shinji Nakamura,[†]
Tomohiko Ohwada,[†] Nagao Kobayashi,[§] Natsuno Yamashita,[‡]
Atsushi Matsumiya,[‡] and Takao Sakamoto[‡]

Contribution from the Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Graduate School of Pharmaceutical Sciences and Graduate School of Science, Tohoku University, Aobayama, Aoba-ku, Sendai 980-8578, Japan

Received November 19, 2003; E-mail: uchiyama@mol.f.u-tokyo.ac.jp

Abstract: We have developed a catalytic electron transfer (ET) system composed of a transition metal ate complex ($\text{Me}_3\text{M}(\text{II})\text{Li}$; $\text{M} = \text{Co}(\text{II}), \text{Mn}(\text{II}), \text{Fe}(\text{II})$) and magnesium. This system (catalytic $\text{Me}_3\text{M}(\text{II})\text{Li}/\text{Mg}$) turned out to be effective for various ET reactions, such as the desulfonation of *N*-phenylsulfonyl amides, and others (the chemoselective cleavage of *O*-allyl groups, the reduction of nitro groups, the partial reduction of diketones, and the reductive coupling of diphenyliodonium salt). The ET ability of this system can be tuned by changing the ligands of the ate complexes. This tunability was experimentally and electrochemically demonstrated: alkoxy-ligated and dianion-type ET ate complexes showed attenuated and enhanced reducing abilities, respectively. The modification of the ET abilities was evaluated by means of electrochemical measurements and chemical reactions. These results provide a basis for the design of various tailor-made ET ate complexes.

Introduction

Radical anion species of carbonyl compounds, organic halides, and aromatic rings are among the most important intermediates in organic chemistry.¹ These species are traditionally generated via electron transfer (ET) reactions using alkali metals,² metal amalgams, or low-valent lanthanides.³ However, excessive reactivity, low chemo- and stereoselectivity, and the usual requirement of strictly controlled reaction conditions with stoichiometric (or greater) quantities of the ET reagent have limited the utility of such reactions. Furthermore, there are only a few electron-releasing metal reagents, such as Li, Na, and SmI_2 , and their reductive abilities exhibit significant gaps; while the oxidative potentials of Li and Na are high, that of SmI_2 is much lower in magnitude. In fact, it is very difficult to apply radical anions in synthetic chemistry. There are many cases where Li or Na overreduces substances in undesired side

reactions, while SmI_2 often does not promote the desired reaction.⁴ Thus, the development of simple and practical ET reagents (systems), especially catalytic systems having a range of electron-releasing abilities suitable for selective organic transformations, is required.

In this paper, we report a catalytic ET system composed of transition metal ate complexes and magnesium, in which the ate complexes⁵ accept electrons from magnesium and deliver them to the substrate. These ET abilities of the present ate complexes were evaluated by the measurement of oxidation potentials. This catalytic ET system turned out to be effective for various organic transformations, such as desulfonation of *N*-phenylsulfonyl amides, and other reactions. Examples of the latter include chemoselective deprotection of *O*-protective groups, reduction of nitro groups, partial reduction of carbonyl groups of diketone, and ligand coupling of iodonium salts. Furthermore, modification of the ET ability of this system could be achieved by control of the ligation environment of the ate complexes. The change of the ET ability can be monitored by means of electrochemical measurements and chemical reactions.

[†] The University of Tokyo.

[‡] Graduate School of Pharmaceutical Sciences, Tohoku University.

[§] Graduate School of Science, Tohoku University.

^{||} PRESTO, Japan Science and Technology Agency (JST).

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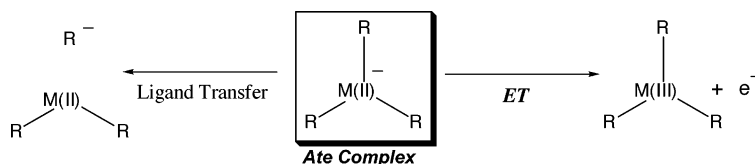


Figure 1. Generalized reaction pathways for ate complexes.

Table 1. Oxidation Potential Data in THF at 0 °C^a

Entry	Metal reagent	E° (V)	Entry	Metal reagent	E° (V)
1	FeCl ₂	+0.15	5	Me ₃ MnLi	-2.56
2	MeFeCl	-1.38	6	Me ₃ CoLi	-2.60
3	Me ₂ Fe	-1.93	7	SmI ₂	-2.33
4	Me ₃ FeLi	-2.50	8	Mg	-3.05

^a Measured in 0.1 M n-Bu₄N⁺ClO₄⁻-THF solution vs Ag/AgCl.

Results and Discussion

Catalytic ET Systems Based on Transition Metal Ate Complexes and Magnesium. Recently, C–C bond-forming reactions using some transition metal ate complexes such as Mn-ates, Fe-ates, and Co-ates have been reported, and ET processes are proposed to be involved in some cases (Figure 1).⁶ We first compared the ET abilities of Mn-ates, Fe-ates, and Co-ates by using in situ attenuated total reflectance (ATR) IR spectroscopy. The transformation of benzophenone to the corresponding ketyl radical by the transition metal ate complexes (Me₃Mn(II)Li, Me₃Fe(II)Li, and Me₃Co(II)Li) or Na was monitored with in situ IR. As the signal at 1663 cm⁻¹, which can be assigned to the C–O stretching vibration of the carbonyl moiety of benzophenone, diminished in intensity, a new band (at 1561 cm⁻¹ (Me₃Co(II)Li), 1555 cm⁻¹ (Me₃Mn(II)Li), 1559 cm⁻¹ (Me₃Fe(II)Li), or 1561 cm⁻¹ (Na)) increased in intensity in all cases (Chart 1). This new absorption can be assigned to the C–O stretching vibration of the newly generated ketyl species.⁷ Therefore, the present in situ IR data strongly support the occurrence of electron-release reactions from Me₃Mn(II)Li, Me₃Fe(II)Li, and Me₃Co(II)Li.

Next, for quantitative estimation of the ET abilities of these ET ate complexes, we applied electrochemical measurements of various kinds of transition metal reagents based on differential pulse voltammograms (DPV). Electrochemical data in THF at 0 °C for transition metal complexes are summarized in Table 1. The Fe^{IV/III} oxidation potentials of Fe(II)Cl₂, MeFe(II)Cl, Me₂Fe(II), and Me₃Fe(II)Li in THF were +0.15, -1.38, -1.93, and -2.50 V, respectively. Similarly, the oxidation potentials of other ET ate complexes, such as Me₃Mn(II)Li (-2.56 V) and Me₃Co(II)Li (-2.60 V), were much more negative than those of the corresponding dichloride derivatives (MnCl₂, +1.10 V; CoCl₂, +1.37 V). The oxidative potentials of SmI₂ and Mg were evaluated as -2.33 and -3.05 V, respectively.⁴ Therefore, the present ET ate complexes have adequately high oxidation potentials intermediate between those of SmI₂ and Mg. Furthermore, the M^{IV/III} oxidation and reduction couples of the ET ate complexes were electrochemically reversible in all cases. Therefore, if a reduction pathway of trivalent to divalent ate

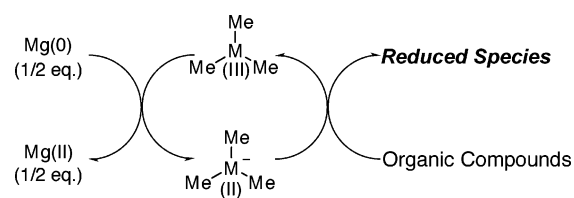


Figure 2. Working model for the catalytic ET system.

complexes also exists in the reaction system, a catalytic ET ate complex cycle should theoretically proceed (Figure 2). The high oxidation potential of Mg raises the possibility that Mg would serve as a reducing agent of the trivalent ET complexes.

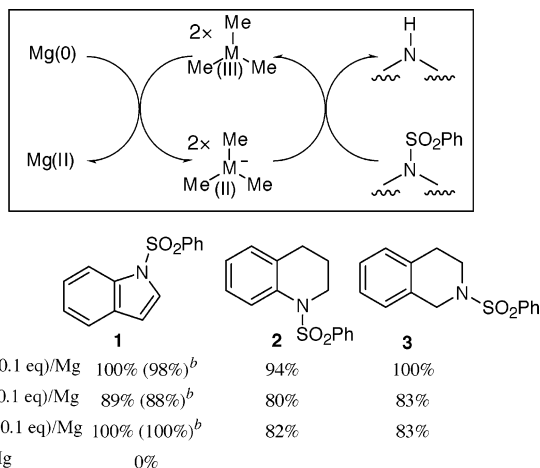
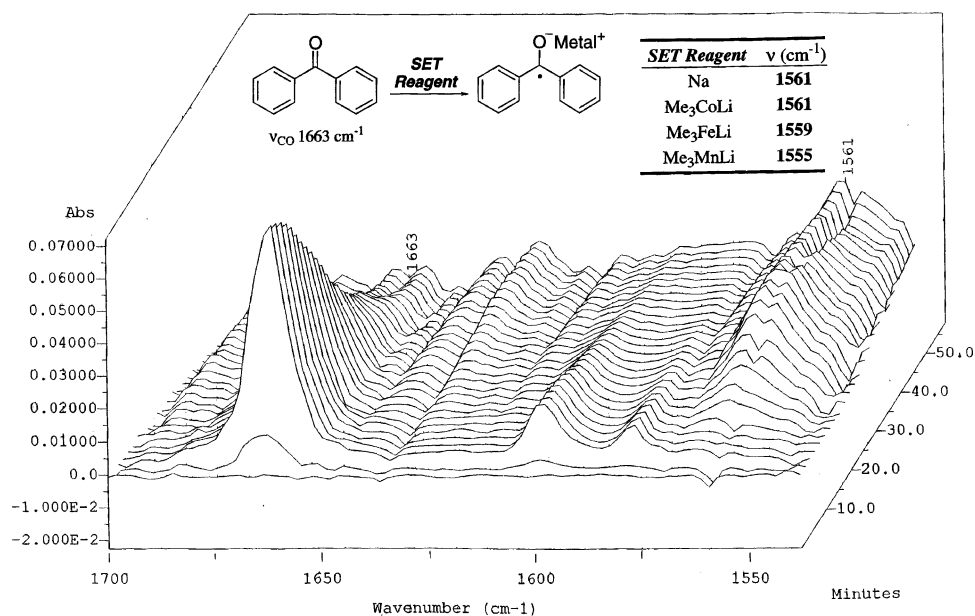
Magnesium has various advantages as an electron store, such as low cost, easy operation, and latent high oxidation potential. Therefore, the development of a catalytic ET system using magnesium as the rereductor would provide a safe and simple catalytic electron transfer system. Moreover, in such a system, electron transfer ability (oxidation potential) and reaction selectivity could in principle be controlled by the choice of mediator. To confirm that the chemical reactivities were consistent with the estimated ET abilities, we applied the present ET system to several chemical reactions.

Although sulfonamides are one of the most important and stable nitrogen protective groups, a general procedure for deprotection that consistently gives high yields is not available.⁸ The sulfonamides can be divided into three types based on the strength of the N–S bond, i.e., less basic arylamine, more basic arylamine, and more basic alkylamine. Sulfonamides of the more basic aryl- and alkylamines are much harder to cleave than those of the less basic amines such as indoles, pyrroles, and imidazoles.⁸ Most sulfonamides are stable to alkaline hydrolysis and to catalytic reduction. They are cleaved under more severe conditions such as Na/NH₃, Na/butanol, sodium naphthalenide, or sodium anthracenide, and by refluxing in acid (48% HBr). However, their usefulness has been limited because various functional groups do not remain intact under such severe deprotection conditions.⁹ Thus, the development of a simple and practical method for the deprotection of the *N*-phenylsulfonyl moiety would be very useful. Initial attempts focused on the development of catalytic reductive desulfonylation of various sulfonamides.¹⁰ As model substrates, we chose *N*-phenylsulfonylindole (less

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Chart 1



^a The catalytic reactions were carried out in THF at room temperature for 12 h. ^b The values in parentheses are the yields of reactions using stoichiometric amounts of ate complexes (without Mg). The stoichiometric reactions were carried out in THF at -78°C for 3 h.

Figure 3. Catalytic deprotection of *N*-phenylsulfonyl moiety using ET ate complexes.

basic arylamine) (**1**), *N*-phenylsulfonyl-1,2,3,4-tetrahydroquinoline (more basic arylamine) (**2**), and *N*-phenylsulfonyl-1,2,3,4-tetrahydroisoquinoline (more basic alkylamine) (**3**) (Figure 3).

First of all, the reaction of **1** using stoichiometric amounts of complexes was investigated (Figure 3, yields in parentheses). While the reaction using Fe(II)Cl₂, MeFe(II)Cl, and Me₂Fe(II) did not occur at all, the reaction using Me₃Fe(II)Li occurred to give the indole in 88% yield. Under the same conditions, the reactions using Me₃Co(II)Li and Me₃Mn(II)Li also proceeded to give the indole in high yields. Since the reduction potential of **1** was -1.96 V under the same measurement conditions used for DPV measurement, it is reasonable that only the ET ate complexes with an adequate oxidation potential are effective for the reductive deprotection of the *N*-phenylsulfonyl moiety (Table 1, entries 1–4). SmI₂ (-2.33 V, Table 1, entry 7) showed moderate reactivity in this reaction under the same conditions, and indole was obtained in 33% yield.

Magnesium was inert in this reductive N–S bond cleavage reaction, presumably due to its insolubility and small surface area, although it has a sufficiently high oxidation potential (-3.05 V, Table 1, entry 8). As a result of evaluation using the deprotection reaction of **1**, the combination of the ET ate complex and Mg metal¹¹ was found to successfully generate a catalytic cycle for ET (Figure 3). Interestingly, this system could be applied to the desulfonylation of aryl (**2**) and alkyl (**3**) sulfonamides, which are stable to alkaline hydrolysis and catalytic reduction. The reduction potentials of **2** and **3** were more negative than that of **1**, being -2.07 and -2.12 V, respectively (under the same measurement conditions used for DPV measurement). In fact, the stoichiometric ET reaction between **2** (or **3**) and SmI₂ (-2.33 V, Table 1, entry 7) did not proceed at all.

The N–S bond cleavage reaction of **2** using catalytic Me₃Fe(III) (prepared from Fe(III)Cl₃ and MeLi (3 eq.))/Mg proceeded smoothly to give 1,2,3,4-tetrahydroquinoline in 85% yield. These results indicate that the neutral Me₃M(III) species successfully underwent reduction by Mg to provide the corresponding Me₃M(II)-ate complex, and this cleavage reaction occurred by ET, not ligand transfer from the ate complex. However, no reaction took place with Mg only, or with the M(II)Cl₂/Mg, MeLi/Mg, or LiCl/Mg system. This rules out the promotion of the pathway by these systems in the absence of the ET ate complexes.

Some representative examples of application of the present ET system to other functionalities such as allyl ethers,¹² haloaromatics,¹³ aromatic nitro groups,¹⁴ carbonyl groups of diketone, and diphenyliodonium compounds¹⁵ are illustrated in Figure 4. The applicability of common ET reagents, such as

- (11) Commercially available Mg turnings were used.
- (12) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1991; Parts 2 and 3.
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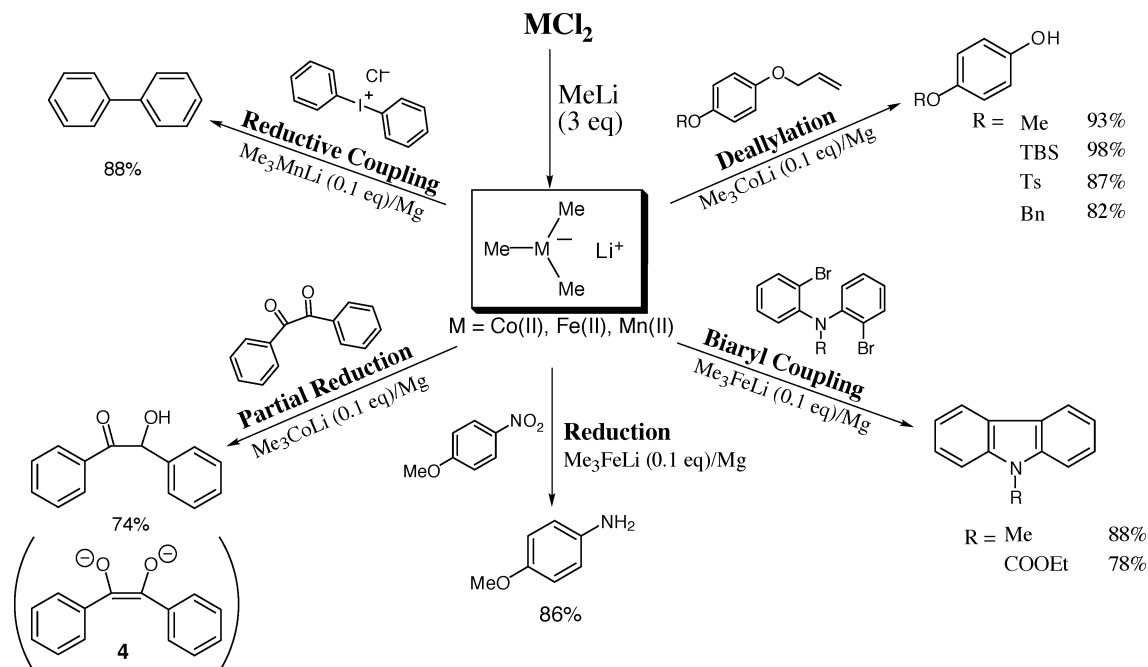


Figure 4. Catalytic ET reactions using transition metal ate complexes.

alkali metals, metal amalgams, and low-valent lanthanides, to these systems has not been well studied.

When 4-allyloxyanisole was treated with this catalytic ET system, the deallylation reaction proceeded smoothly and selectively at room temperature to give 4-methoxyphenol in high yield (the allyl radical is more stable than the methyl radical). Competitive removal of *O*-allyl vs TBDMS, benzyl, and tosyl groups was then examined. Selective deallylation proceeded with more than 98% chemoselectivity: the *tert*-butyldimethylsilyloxy, benzyloxy, and tosyloxy groups remained intact.¹⁶

When bis(2-bromophenyl)methylamine (**5a**) was treated with $\text{Me}_3\text{FeLi}(\text{cat.})/\text{Mg}$, the intramolecular Ullmann-type biaryl coupling reaction smoothly proceeded without a palladium, nickel, or copper catalyst¹³ to afford the desired carbazole derivative in 88% yield. The present cyclization reaction was found to be effective for electrophilic functional group containing dihalogen compounds.

In the reaction of 4-nitroanisole with $\text{Me}_3\text{FeLi}(\text{cat.})/\text{Mg}$, the reduction of the nitro group proceeded at room temperature to give 4-methoxyaniline in 86% yield. The present procedure may provide a new catalytic reduction system for nitro compounds via the anion radical *without* using a co-reducing reagent (e.g., hydrazine or NaBH_4) or hydrogen gas.

Although the half-reduction of 1,2-diketones using metal hydrides is difficult and generally proceeds to the corresponding 1,2-diols, this catalytic ET system turned out to be applicable to the partial reduction of 1,2-diketones to the corresponding α -hydroxy ketones.

In the reaction of diphenyliodonium salt with $\text{Me}_3\text{MnLi}(\text{cat.})/\text{Mg}$, the reductive ligand coupling reaction proceeded smoothly to give biphenyl in 88% yield.¹⁷ Although many reactions using

iodonium salts as highly activated halides that can easily react with nucleophiles have been reported, the ligand coupling reaction was favored over the nucleophilic reaction in this case.

Tunability of the Present Catalytic ET System. To achieve ad hoc matching of the catalyst to a reaction, the ET ability of the mediator (ET ate complex) needs to be fine-tuned for individual reactions because each reaction has unique appropriate oxidation/reduction potentials. Indeed, while all or some of $\text{Me}_3\text{M}(\text{II})\text{Li}$ ($\text{M} = \text{Mn}, \text{Co}, \text{and Fe}$) are effective as mediators for the reactions in the previous section, catalytic pinacol coupling of ketones (or aldehydes) and intramolecular Ullmann-type diaryl coupling of bis(2-chlorophenyl)methylamine (**5b**) using $\text{Me}_3\text{M}(\text{II})\text{Li}$ did not occur, or scarcely occurred. We therefore took Fe(II)-ate complexes as a model and attempted to optimize the ligation environment.

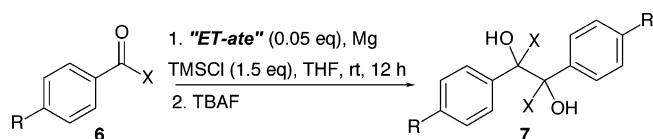
(A) Tuning through the Type of Ligands of the Ate Complex. As mentioned above, although the catalytic pinacol coupling of benzaldehyde using $\text{Me}_3\text{Fe}(\text{II})\text{Li}$ as a mediator was investigated, the desired coupling reactions did not proceed due to side reactions such as overreduction, ligand transfer, etc. Because the $\text{Fe}^{\text{II/III}}$ oxidation potential of $\text{Me}_3\text{Fe}(\text{II})\text{Li}$ is too high (-2.50 V, Table 1, entry 4) compared with the reduction potential of benzaldehyde (-1.73 V), the reaction was considered to be poorly controlled.

To achieve the desired pinacol coupling selectively, the electron-releasing ability of the ET ate complex needs to be tuned down. After several attempts to design and optimize ligands to reduce the ET ability, the *tert*-butoxide ligand, which has a lower σ -donating ability than those of the alkyl ligands, was found to reduce the ET ability of the ferrate appropriately, and the oxidation potential of $(t\text{-BuO})_3\text{Fe}(\text{II})\text{K}$ was measured to be -1.86 V.¹⁹ In fact, catalytic pinacol coupling reactions of

(16) In the reaction of the tosyloxy-containing allyl aryl ether, Me_3MnLi showed completely opposite chemoselectivity from Me_3CoLi or Me_3FeLi . The reaction with Me_3CoLi or Me_3FeLi gave 4-tosyloxyphenol as the sole product, whereas the reaction using Me_3MnLi selectively gave 4-allyloxyphenol. These results clearly indicate that the present catalytic ET reactions can be controlled by the choice of ET ate complex (mediator), not by Mg (Figure 2).

(17) On the other hand, in the case of using $\text{Me}_3\text{Co}(\text{II})\text{Li}$ or $\text{Me}_3\text{Fe}(\text{II})\text{Li}$ instead of $\text{Me}_3\text{Mn}(\text{II})\text{Li}$, the reactions were uncontrolled.

(18) For a review on the pinacol coupling reactions, see: Robertson, G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, Chapter 2.6.



Entry	X	R	"ET-ate"	E° (V) ^a	Yield(%)	TON
1	H	H	Me ₃ FeLi	-2.50	trace	–
2	H	H	(t-BuO) ₃ FeK	-1.86	95	19
3	H	F	(t-BuO) ₃ FeK	-1.86	100	20
4	H	MeO	(t-BuO) ₃ FeK	-1.86	65	13
5	Me	H	(t-BuO) ₃ FeK	-1.86	71	14
6	Me	Me	(t-BuO) ₃ FeK	-1.86	76	15
7	Me	MeO	(t-BuO) ₃ FeK	-1.86	75	15

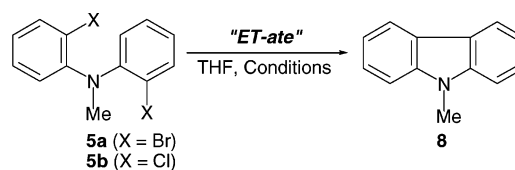
^a Measured in 0.1 M n-Bu₄N⁺ClO₄⁻-THF solution vs Ag/AgCl.

Figure 5. Catalytic pinacol coupling reaction using (t-BuO)₃FeK.

various carbonyl compounds proceeded smoothly with (t-BuO)₃Fe(II)K, and the turnover number (TON, defined as moles of the product per mole of the catalyst) of the coupling reached 13–20 (Figure 5).

(B) Tuning through the Number of Ligands of the Ate Complex. In contrast to the case of the pinacol coupling, the intramolecular Ullmann-type diaryl coupling of bis(2-chlorophenyl)methylamine (**5b**) using Me₃M(II)Li (M = Mn, Co, and Fe) did not occur at all, and almost all of the starting material (**5b**) was recovered. In this case, the electron-releasing ability of ET ate complex needs to be increased. Dianion-type ate complexes, i.e., tuning through a change in the number of ligands (Figure 6) were then examined. The outer shell of the central metal in Me₃Mn(II)Li, Me₃Fe(II)Li, and Me₃Co(II)Li is filled with 11, 12, and 13 electrons, respectively, and there is room (Lewis acidity or vacant orbitals) for an additional ligand to coordinate, which could form dianion-type ate complexes.²⁰

To investigate the difference in reactivity between Me₄Fe(II)Li₂ (dianion-type ferrate) and Me₃Fe(II)Li (monoanion-type ferrate), the reactions were carried out under similar conditions (Figure 6). While the Ullman-type cyclization of the dibromo compound (**5a**) with Me₃FeLi proceeded smoothly at room temperature to give **8** in high yield (entry 1), the reaction at –78 °C was very sluggish (entry 2). However, when Me₄FeLi₂ was used in place of Me₃FeLi, the reaction proceeded even at –78 °C to give **8** in 88% yield (entry 3). Similarly, the dichloro compound (**5b**), treated with Me₄FeLi₂ in THF at room temperature for 12 h, gave **8** in 43% yield, while the reaction



Entry	X	"ET-ate" (2.2 eq.)	E° (V) ^a	Conditions	Yield(%)
1	Br	Me ₃ FeLi	-2.50	rt, 3 h	88
2	Br	Me ₃ FeLi	-2.50	–78°C, 3 h	10
3	Br	Me ₄ FeLi ₂	< -3.50	–78°C, 3 h	88
4	Cl	Me ₃ FeLi	-2.50	rt, 12 h	trace
5	Cl	Me ₄ FeLi ₂	< -3.50	rt, 12 h	43

^a Measured in 0.1 M n-Bu₄N⁺ClO₄⁻-THF solution vs Ag/AgCl.

Figure 6. Intramolecular biaryl coupling reaction using ET ate complexes.

of **5b** with Me₃FeLi hardly proceeded under the same reaction conditions. These results are clearly consistent with a postulate that the oxidation potential (i.e., the ET ability) of the dianion-type ET ate complex was much more negative (i.e., higher) than that of the corresponding monoanion-type ET ate complex.

Conclusion

We have developed a catalytic ET system composed of ET ate complex and magnesium. The ET abilities, evaluated by the electrochemical method, were consistent with the observed chemical reactivities for various chemical transformations. This ET system could be applicable for some representative organic transformations involving anion radicals. Tunability of electron transfer ability of ET ate complex was demonstrated in this paper through changing any of several factors, such as the central metal, the type and number of ligands, and the type of counterions. A theoretical approach toward tailor-made ET reagents with the help of ab initio calculations and spectroscopies, and a study of electron-doping ability²¹ for polymers, are currently under way, together with work on other applications to organic syntheses.

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Supporting Information Available: Experimental procedures and characterizations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) The alkoxide ligated Mn(II)-ates, Co(II)-ates, and Fe(II)-ate are little known; see ref 6a.

(20) In recent publications, we revealed that tetracoordinated dianion-type zincates have a higher transference aptitude for ligands than tricoordinated monoanion-type zincates; see: (a) Uchiyama, M.; Koike, M.; Kameda, M.; Kondo, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 8733–8734. (b) Uchiyama, M.; Kondo, Y.; Miura, T.; Sakamoto, T. *J. Am. Chem. Soc.* **1997**, *119*, 12372–12373. (c) Uchiyama, M.; Kameda, M.; Mishima, O.; Yokoyama, N.; Koike, M.; Kondo, Y.; Sakamoto, T. *J. Am. Chem. Soc.* **1998**, *120*, 4934–4946. (d) Kobayashi, M.; Matsumoto, Y.; Uchiyama, M.; Ohwada, T. *Macromolecules* **2004**, *37*, 4339–4341.