Studies on Synthesis and Reactions

of Aryldicarbonylcyclopentadienyliron

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Contents

|				
Ac	acetyl	m.p.	melting point
acac	acetylacetonate	*n*	normal
aq.	aqueous	NMR	nuclear magnetic resonance
Ar	aryl	*o*	ortho
bs	broad singlet (spectral)	*p*	para
Bu	butyl	Ph	phenyl
c	cyclo	pin	pinacolato
˚C	degrees Celsius	pp.	page(s)
calcd	calculated	ppm	parts per million (in NMR)
cat.	catalytic	Pr	propyl
cm	centimeter(s)	q	quartet (spectral)
Co.	company	quant.	quantitative
Cp	cyclopentadienyl	ref(s)	reference(s)
δ	chemical shift in parts per million downfield from tetramethylsilane	r.t.	room temperature (25 ± 3 ˚C)
		s (*sec*)	secondary
d	doublet (spectral)	s	singlet (spectral)
DIBAL-H	diisobutylaluminum hydride	sept	septet (spectral)
DPPE (dppe)	1,2-bis(diphenylphosphino)ethane	t	triplet (spectral)
E	*entgegen* (means "opposite")	*t* (*tert*)	tertiary
Ed(s).	editor(s)	TEMPO	2,2,6,6-tetramethylpiperidine *N*-oxyl radical
equiv	equivalent(s)		
Et	ethyl	Tf	trifluoromethanesulfonyl
Fp	Fe(CO)$_2$Cp	THF	tetrahydrofuran
g	gram(s)	TLC	thin-layer chromatography
h	hour(s)	TMEDA	*N,N,N',N'*-tetramethylethylenediamine
Hz	hertz (s^{-1})	TMS	trimethylsilyl
HRMS	high-resolution mass spectrum	Ts	*p*-toluenesulfonyl
i	iso	UV	ultraviolet
i.e.	that is	vide infra	see below
IR	infrared (spectrum)	Vol.	volume
J	coupling constant (in NMR)	X-Phos	dicyclohexyl[2-(2,4,6-triisopropylphenyl)phenyl]phosphine
LDA	lithium diisopropylamide		
m	multiplet (spectral), meter(s), milli		
m	meta		
M	molar (1 M = 1 mol dm^{-3})		
Me	methyl		
mg	milligram(s)		
MHz	megahertz		
min	minute(s)		
mL	milliliter(s)		
mm	millimeter(s)		
mmol	millimole		

General Introduction

1. Organoiron Compounds in Organic Synthesis

Iron is the most abundant and cheapest transition metal on the earth.   Therefore, development of synthetic methods using iron compounds has attracted much attention.   Because of their abundance, not only iron-catalyzed reactions but also reactions employing stoichiometric amounts of iron compounds are of great value.   Generally, various iron salts are used stoichiometrically as Lewis acids or oxidants in organic synthesis.   Iron carbonyl complexes are used as carbonyl sources for carbonyl insertion reactions.[1]   In addition to the reactions using inorganic iron compounds, there are various useful reactions using organoiron compounds. Especially, organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)$_2$R] have been attracting much attention as useful reagents because of their unique properties and have found numerous applications in organic synthesis.[2]   Some important organic reactions of [CpFe(CO)$_2$R] are described below.

1-1. General Synthesis of [CpFe(CO)$_2$R]

In principle, the synthesis of [CpFe(CO)$_2$R] (R = alkyl, allyl, alkenyl, alkynyl, acyl, aryl) can be achieved by one of two processes (Scheme 1).   One is the reaction of [CpFe(CO)$_2$]M (M = Na, K), which is prepared by reduction of [CpFe(CO)$_2$]$_2$ with sodium/mercury amalgam or activated potassium metal, with organic halides.[3]   The other is the reaction of [CpFe(CO)$_2$X] (X = I, Br, Cl), which is prepared by oxidation of [CpFe(CO)$_2$]$_2$ with X$_2$ or HX/O$_2$, with organometallic reagents.[4]
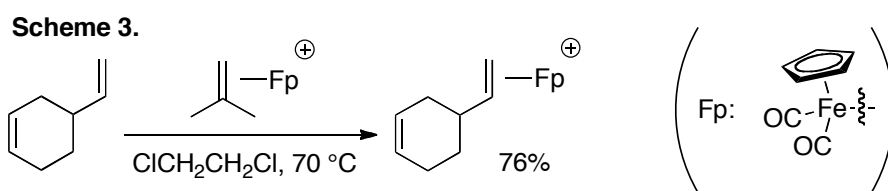
Scheme 1.
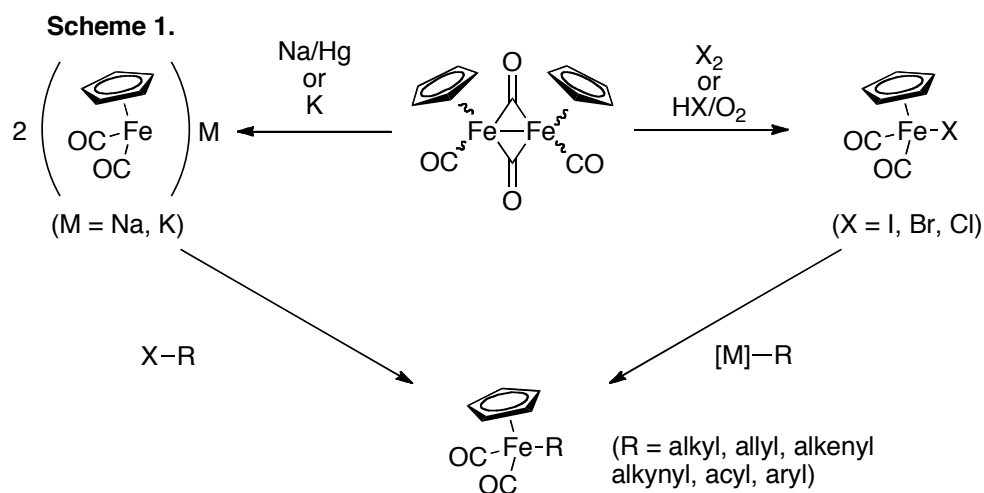
## 1-2. Synthesis and Reactions of Cationic (η^2-Alkene)iron Complexes

In general, a transition metal that is π-bound to an olefinic ligand activates the olefin toward nucleophilic attack. There are many examples of reactions of cationic (η^2-alkene)iron complexes with nucleophiles utilizing this effect.

Generally, cationic (η^2-alkene)iron complexes are synthesized by treatment of allyliron complexes with acids. For example, treatment of methallyliron complex, which is prepared by reactions of [CpFe(CO)$_2$]Na with methallyl chloride, with an acid affords cationic (η^2-isobutene)iron complex (Scheme 2).[2a,5] Moreover, obtained cationic (η^2-isobutene)iron complex can be used to prepare other cationic (η^2-alkene)iron complex by olefin exchange (Scheme 3).[6] The exchange prefers the formation of sterically less encumbered cationic (η^2-alkene)iron complex.
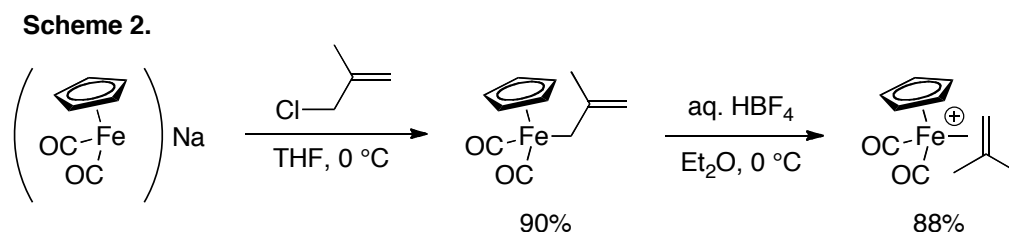
Scheme 2.

Scheme 3.

Various nucleophilic additions to cationic (η^2-alkene)iron complexes proceed with high regioselectivity or stereoselectivity (Schemes 4 and 5).[7] The greater positive charge density at the more highly substituted carbon and the steric hindrance of Fp group (Fp = CpFe(CO)$_2$) lead to these high regioselectivity and stereoselectivity.

Scheme 4.

Scheme 5.
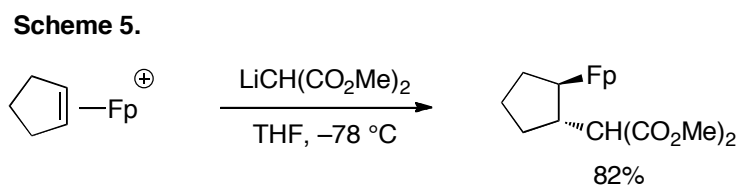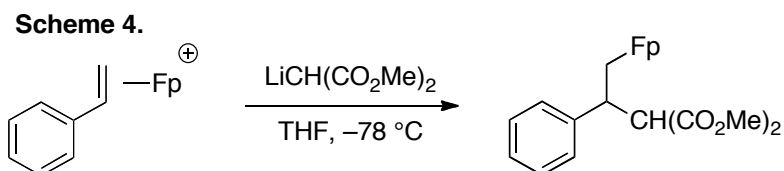
On the other hand, these cationic (η^2-alkene)iron complexes are completely resistant to attack by electrophiles. Therefore, Fp group can be used as a protecting group for an alkene moiety in electrophilic substitutions. One example is shown in Scheme 6.[2a]

Scheme 6.

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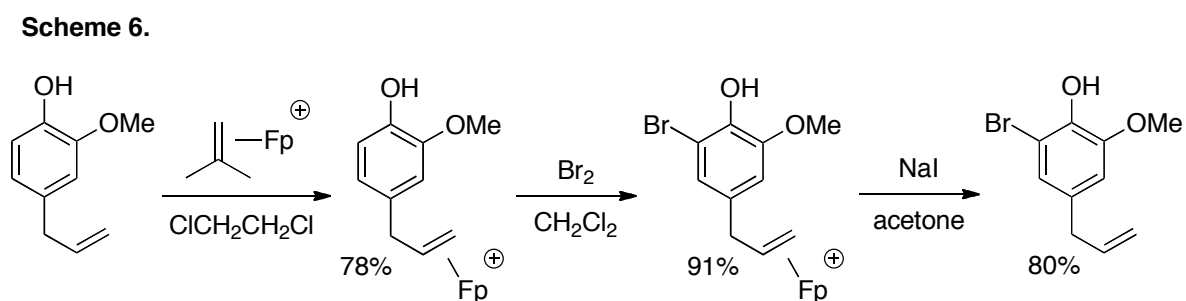
1-3. Synthesis and Reactions of η^1-Allyliron Complexes
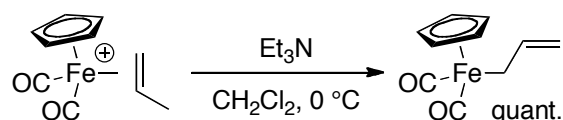
Generally, η^1-allyliron complexes are synthesized by treatment of [CpFe(CO)$_2$]Na with allyl chlorides (Scheme 2) or of cationic (η^2-alkene)iron complexes with bases (Scheme 7).[8]

Scheme 7.

Treatment of η^1-allyliron complexes with electron deficient alkenes results in a tandem electrophile/nucleophile addition sequence to give products corresponding to overall [3+2] cycloaddition (Scheme 8).[2a]

Scheme 8.
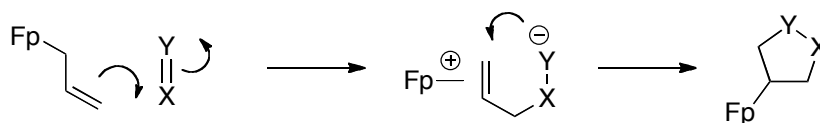
For example, the reaction of η^1-allyliron complex with an electron deficient alkene, such as tetracyanoethylene, affords the corresponding [3+2] cycloaddition product (Scheme 9).[8]

Scheme 9.
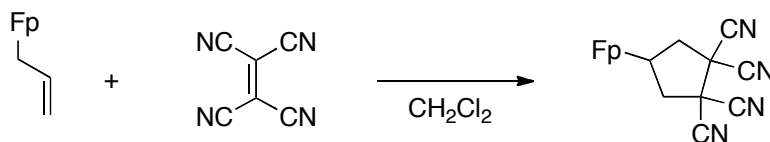
This reaction can be applied to the synthesis of a sarkomycin intermediate (Scheme 10).[9]

Scheme 10.
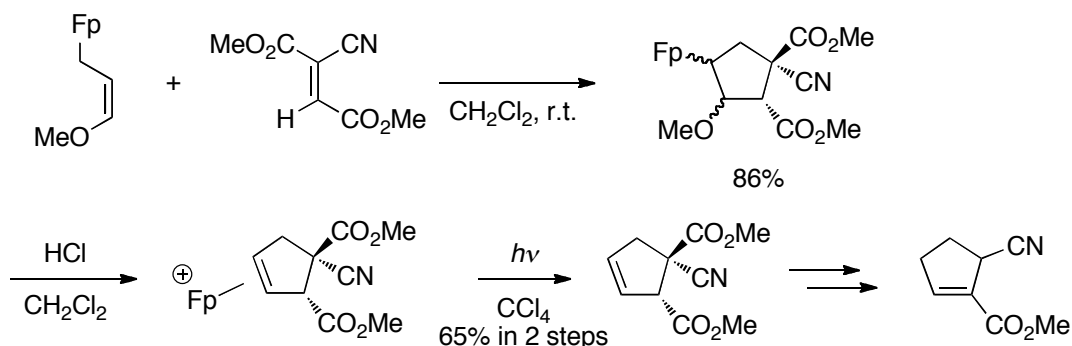
In the presence of Lewis acid, η^1-allyliron complex adds to an aldehyde (Scheme 11).[10] Several transformations including demetalation of the obtained cationic (η^2-alkene)iron complexes are possible.

Scheme 11.
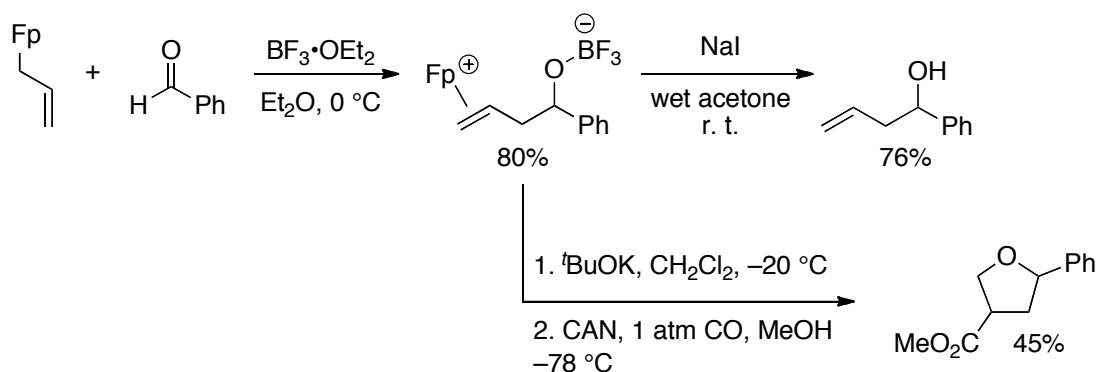
1-4. Synthesis and Reactions of Carbene Complexes of Iron

A carbene complex of iron is generated in situ from a methoxymethyliron complex by treatment with an acid and can be used as a methylene transfer reagent for cyclopropanation of alkenes (Scheme 12).[11]

Scheme 12.
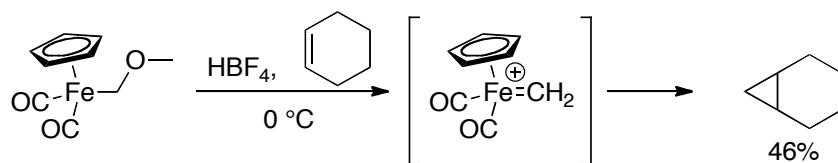
A stereoselective cyclopropanation is also possible by use of a substituted siloxyalkyliron complex (Scheme 13).[12]
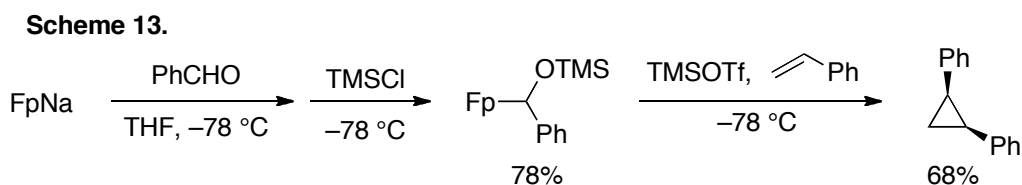
Scheme 13.

1-5.   Synthesis and Reactions of Acyliron Complexes

Generally, acyliron complexes [CpFe(CO)$_2$(COR)] are synthesized by reactions of [CpFe(CO)$_2$]M (M = Na, K) with the corresponding acyl chlorides (Scheme 14).[13]

Scheme 14.
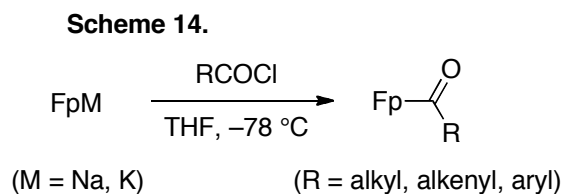
Moreover, the generation and reactions of the lithium enolate of [CpFe(CO)$_2$(COR)] are possible.   Especially, these reactions of the easily accessible acetyliron complex [CpFe(CO)$_2$(COCH$_3$)] have been studied well to open up a route to highly substituted acyliron complexes (Scheme 15).[14]

Scheme 15.

R = CH(CH$_3$)$_2$, 60%
R = CH$_2$–CH=CH$_2$, 54%
R = CH$_2$(*p*-MeOC$_6$H$_4$), 96%
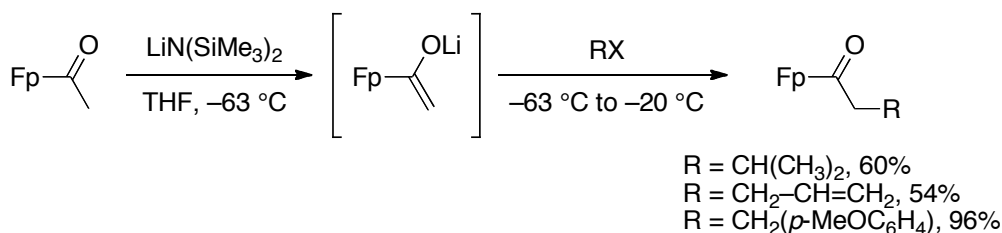
This alkylation of enolates derived from acyliron complexes can be expanded to diastereoselective alkylation by use of the iron complexes in which one carbonyl ligand is substituted by triphenylphosphine. Reaction of [CpFe(CO)$_2$Me], which is prepared from [CpFe(CO)$_2$I] and methyl Grignard reagent, with triphenylphosphine affords racemic [CpFe(CO)(PPh$_3$)(COCH$_3$)] (Scheme 16).[15] Optically pure complexes can be obtained by the resolution of the racemic compounds. In this iron complex, the triphenylphosphine ligand is pushed close to the acyl group. This results in a very effective shielding of one face of the enolate derived from the complex. (Scheme 17).[16]

Scheme 16.
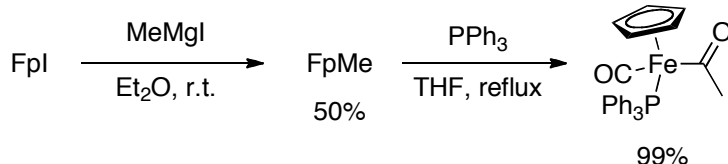
Scheme 17.
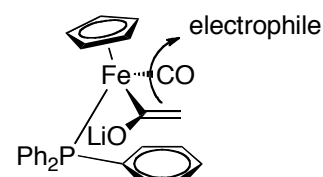
Treatment of the optically pure complex (*R*)-(–)-[CpFe(CO)(PPh$_3$)(COCH$_3$)] with LDA, followed by the addition of MeI affords the methylated complex. Subsequent similar enolate alkylation affords the thioalkylated complex as a single diastereomer. Demetalation by bromine, addition of *L*-proline *t*-butyl ester, and deprotection of the products afford angiotensin converting enzyme inhibitor (–)-captopril (Scheme 18).[17]

Scheme 18.

78%

71%

83%

(−)-captopril
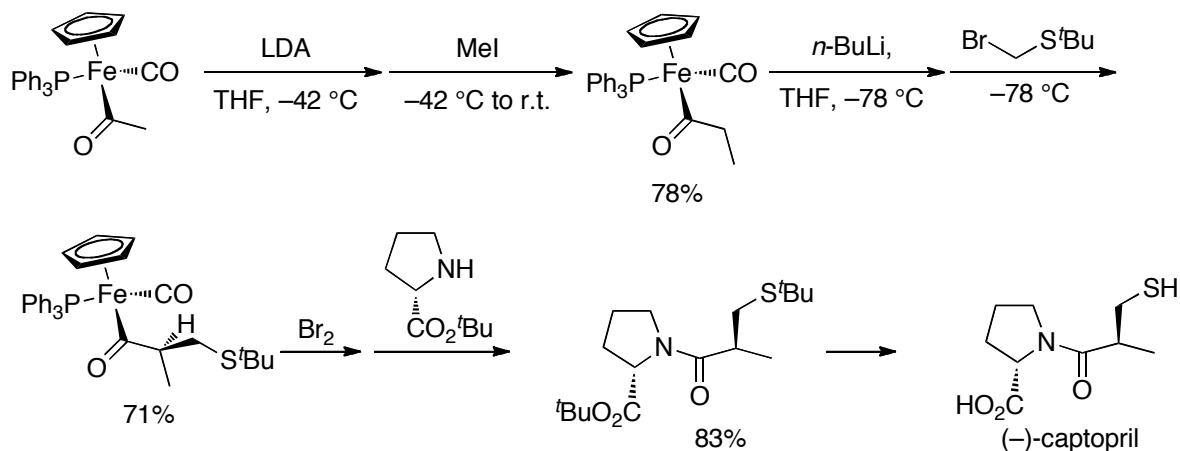
1-6. Synthesis and Reactions of Aryliron Complexes

There are several approaches to aryliron complexes [CpFe(CO)$_2$Ar].[18]   Among them, the most reliable method is shown in Scheme 19.[18b]   Transmetalation between [CpFe(CO)$_2$]Na and zinc chloride affords [CpFe(CO)$_2$]$_2$Zn.   Subsequent palladium-catalyzed reaction of iodobenzene with [CpFe(CO)$_2$]$_2$Zn provides [CpFe(CO)$_2$Ph].

Scheme 19.

68%
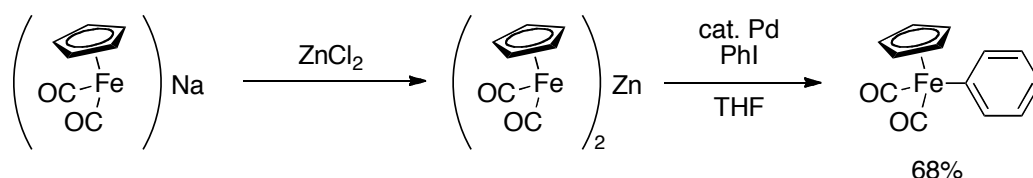
There is only one report on transformation of [CpFe(CO)$_2$Ar] to organic compounds. Treatment of [CpFe(CO)$_2$Ar] with diphenylacetylene affords indenone derivatives (Scheme 20).[19] The postulated mechanism is as follows; (i) insertion of the acetylene into the Fe–Ar bond, (ii) isomerization, (iii) ortho-metalation, (iv) CO migration, and (v) reductive elimination of the metal fragment.

Scheme 20.
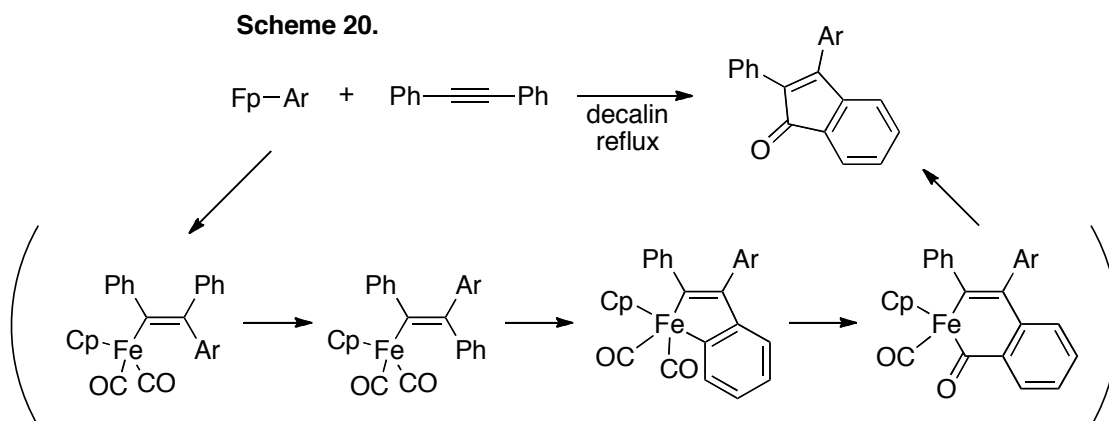
2. Overview of This Thesis

As described above, iron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)$_2$R] have interesting reactivity, and they are usually utilized in organic synthesis. Among them, the chemical reactivity of the corresponding aryliron complexes [CpFe(CO)$_2$Ar] has not been well investigated partly because of the limited availability of [CpFe(CO)$_2$Ar]. Therefore, the development of efficient approaches to [CpFe(CO)$_2$Ar] should lead to the progress of the chemistry of [CpFe(CO)$_2$Ar] which have high potential as useful arylmetal reagents.[20] So the author planned to develop new efficient methods of synthesis of [CpFe(CO)$_2$Ar] under mild conditions and their applications to organic synthesis. After extensive investigation, he found that [CpFe(CO)$_2$Ar] were obtained efficiently by the transmetalation reactions of [CpFe(CO)$_2$I] with various arylmetal reagents in the presence of a catalytic amount of palladium salt or a stoichiometric amount of copper salt. Moreover, he found several reactions of [CpFe(CO)$_2$Ar] with organic compounds.

2-1. Synthesis of [CpFe(CO)$_2$Ar] by Transmetalation between [CpFe(CO)$_2$I] and Arylmetal Reagents (Chapters 1–3)

So far, little is known about the concise synthesis of [CpFe(CO)$_2$Ar]. The author developed new efficient methods for the synthesis of [CpFe(CO)$_2$Ar] utilizing transmetalation

between [CpFe(CO)$_2$I] and arylmetal reagents in the presence of a catalytic amount of palladium salt or a stoichiometric amount of copper salt.

2-1-1. Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis (Chapter 1)

Palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and aryl Grignard reagents affords [CpFe(CO)$_2$Ar] (Scheme 21).
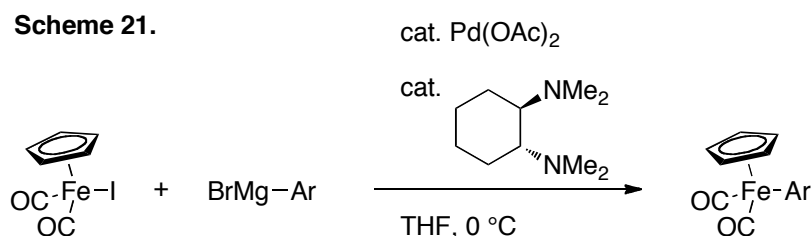
Scheme 21.

The reaction would proceed via a mechanism similar to the conventional cross-coupling reaction, which consists of oxidative addition of [CpFe(CO)$_2$I] to palladium that generates [Cp(CO)$_2$Fe–Pd–I], transmetalation with arylmagnesium bromide, and reductive elimination that forms the aryl–iron bond (Scheme 22).
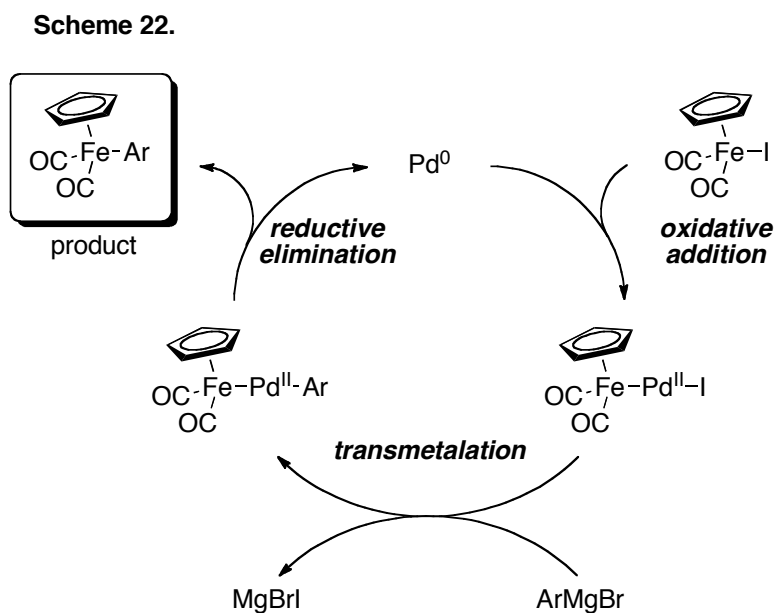
Scheme 22.

The aryliron complexes thus formed are useful arylmetal reagents that become active upon oxidation or UV irradiation (Scheme 23). Oxidative methoxycarbonylations of [CpFe(CO)$_2$Ar] in methanol proceed to form ArCOOMe. [CpFe(CO)$_2$Ar] react with allylic electrophiles under UV irradiation to afford allylarenes.

Scheme 23.
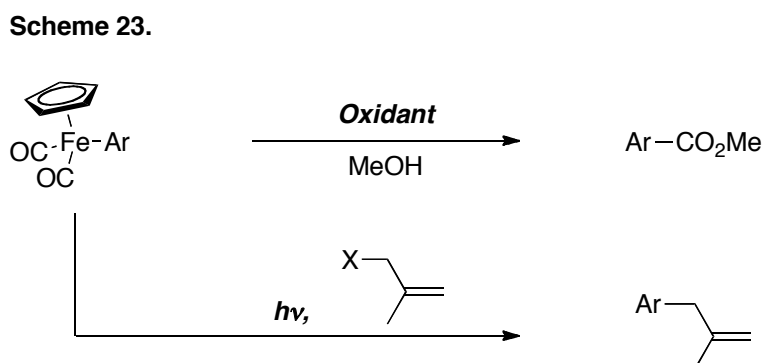
2-1-2. Synthesis of Aryliron Complexes [CpFe(CO)$_2$Ar] by Palladium-Catalyzed Reactions of [CpFe(CO)$_2$I] with Arylzinc, -Boron, or -Indium Reagents (Chapter 2)

Transmetalation between [CpFe(CO)$_2$I] and arylzinc iodide-lithium chloride complexes proceeds in the presence of catalytic amounts of palladium acetate and

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N,N,N',N'-tetramethyl-1,2-cyclohexanediamine to yield the corresponding aryliron complexes [CpFe(CO)$_2$Ar]. Phenylation of [CpFe(CO)$_2$I] also takes place when triphenylindium is used under similar conditions (Scheme 24).
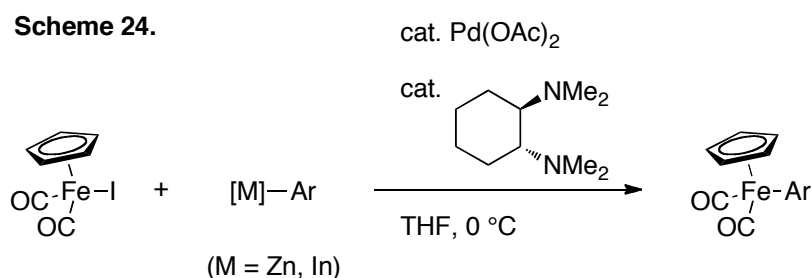
Scheme 24.

[CpFe(CO)$_2$I] undergoes arylation with arylboronic acids in the presence of cesium carbonate and a palladium-*N*-heterocyclic carbene complex, PEPPSI (Scheme 25).

Scheme 25.
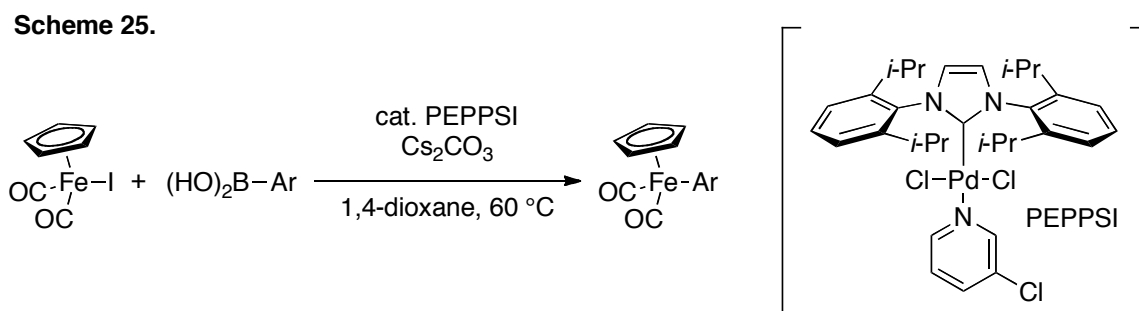
These reactions would proceed via a mechanism similar to the reactions with aryl Grignard reagents. The present methods are useful for the facile synthesis of various functionalized [CpFe(CO)$_2$Ar]. The products [CpFe(CO)$_2$Ar] represent an interesting class of aryl metals that undergo several transformation.

2-1-3. Synthesis of Functionalized Aryliron Complexes [CpFe(CO)$_2$Ar] by Copper-Mediated Transmetalation between [CpFe(CO)$_2$I] and Aryltin Reagents (Chapter 3)

Transmetalation between [CpFe(CO)$_2$I] and aryltin reagents in the presence of copper(I)

trifluoromethanesulfonate yields the corresponding aryliron complexes [CpFe(CO)$_2$Ar]. The high functional group compatibility of this copper-mediated reaction enables the author to obtain [CpFe(CO)$_2$Ar] having an acetyl or formyl group on benzene ring, which can not be prepared by the previous methods with arylzinc or arylboron reagents under palladium catalysis (Scheme 26).

Scheme 26.
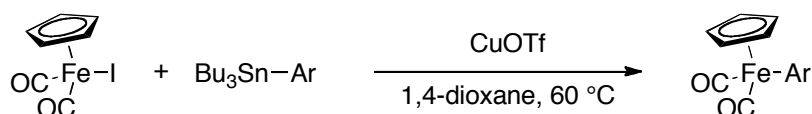
The author assumes that arylcopper species would be generated from CuOTf and the aryltin reagents and would undergo transmetalation with [CpFe(CO)$_2$I] to afford [CpFe(CO)$_2$Ar].

2-2. Transformation of CpFe(CO)$_2$Ar (Chapters 4 and 5)

Although rich coordination chemistry has been reported for [CpFe(CO)$_2$Ar],[20] the chemical reactivity of [CpFe(CO)$_2$Ar] has not been well investigated. The author developed two organic transformations of [CpFe(CO)$_2$Ar].

2-2-1. Use of Aryliron Complexes [CpFe(CO)$_2$Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents To Yield Ketones (Chapter 4)

The reactions of [CpFe(CO)$_2$Ar] with organometallic reagents are rare. The reaction of [CpFe(CO)$_2$Ph] with excess butyllithium in THF at –78 °C was reported, leading to the lithiation of the cyclopentadienyl ring (Scheme 27).[21]

Scheme 27.
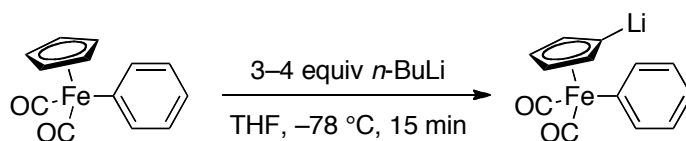
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The author found that a similar reaction at a higher reaction temperature led to a completely different outcome. Treatment of aryliron complexes [CpFe(CO)$_2$Ar] with n-BuLi at –20 °C in THF affords the corresponding ketones n-BuCOAr. Not only BuLi but also other various organolithium reagents lead to the formation of ketones (Scheme 28). The reaction, wherein the aryliron complexes serve as arylcarbonyl cation equivalents, would begin with nucleophilic addition of RLi to one of the carbonyl ligands to form acylferrate [CpFe(CO)(RCO)Ar]Li without lithiation of the Cp ring. The (η^2-ketone)iron complex would be formed via nucleophilic migration of the reactive Ar anion to the acyl carbonyl. The η^2 complexation is not robust, and liberation of ketone would take place upon addition of water.

Scheme 28.
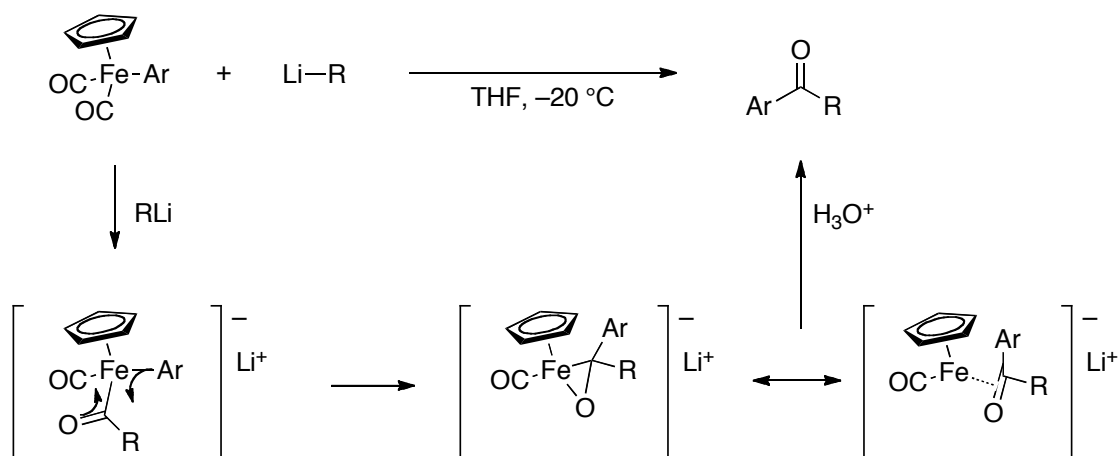
2-2-2. Arylation of Styrenes with Aryliron Complexes [CpFe(CO)$_2$Ar] (Chapter 5)

Insertion of unsaturated bonds into the aryl–iron bonds of [CpFe(CO)$_2$Ar] is well known.[22] However, there is only one example of application of such insertion to useful organic transformation.[19] In Chapter 5, the author describes arylation of styrenes with aryliron complexes [CpFe(CO)$_2$Ar] utilizing the insertion of the C=C bond of styrene into the aryl–iron bond. Treatment of aryliron complexes [CpFe(CO)$_2$Ar] with various styrenes affords the corresponding stilbenes (Scheme 29). The reaction would proceed as follows. Insertion of the

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C=C bond of styrene into the aryl–iron bond would generate the corresponding alkyl–iron complex.   Subsequent β-hydride elimination affords stilbene derivatives.

Scheme 29.
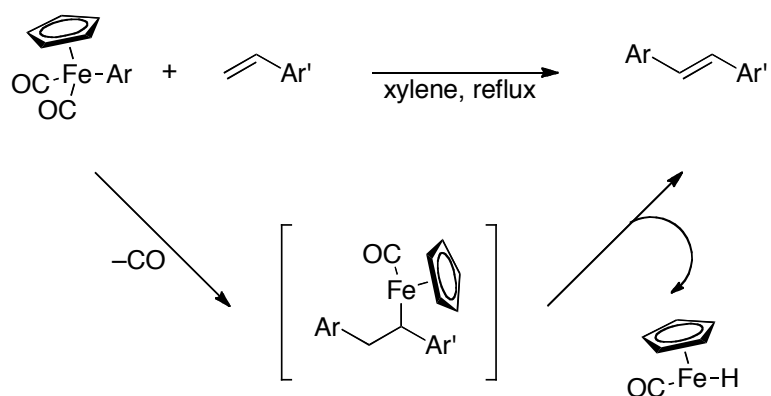
In summary, the author developed the new efficient approaches to aryldicarbonylcyclopentadienyliron [CpFe(CO)$_2$Ar].   Moreover, he found several transformations of [CpFe(CO)$_2$Ar] to organic compounds.   He expects these works will lead to further progress of the chemistry of [CpFe(CO)$_2$Ar].

References and Notes

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Chapter 1

Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis

Palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and aryl Grignard reagents emerges as a new method for the synthesis of [CpFe(CO)$_2$Ar]. The aryliron complexes thus formed are useful arylmetal reagents that become active upon oxidation or UV irradiation.

Introduction

Thanks to the ubiquity of iron, organoiron compounds represent rare organic transition-metal compounds that we can use stoichiometrically in organic synthesis. However, the potential of organoiron compounds have not been fully developed.[1]

Among organoiron compounds, the coordinatively saturated aryldicarbonylcyclopentadienyliron complexes $[CpFe(CO)_2Ar]$ are easy to handle and hence can be useful as arylmetal reagents in organic synthesis. However, little is known about the concise synthesis of $[CpFe(CO)_2Ar]$.[2] In Chapter 1, the author reports a new efficient method for the synthesis of $[CpFe(CO)_2Ar]$ under palladium catalysis. Several transformations of $[CpFe(CO)_2Ar]$ are also disclosed, which will be useful in organic synthesis.[3,4]

Results and Discussion

As reported previously,[2a] the author's attempt at a substitution reaction of $[CpFe(CO)_2I]$ (**1**) with phenylmagnesium bromide in the absence of a catalyst resulted in failure, affording a poor yield of $[CpFe(CO)_2Ph]$ (**2a**), a significant amount of $[CpFe(CO)_2]_2$ (**3**), and recovered **1** (Table 1, entry 1). After extensive screening of the reaction conditions, he found that a combination of palladium acetate and diamine **4** efficiently catalyzed the phenylation reaction (entry 7).[5] The phenylation is regarded as palladium-catalyzed transmetalation between $[CpFe(CO)_2I]$ and phenylmagnesium bromide.

The choice of the ligand is important. The use of phosphine ligands favored the formation of **3** (entries 3–5). The *N*-heterocyclic carbene ligand IPr•HCl[6] did not work well (entry 9). Palladium acetate by itself had high catalytic activity (entry 2). TMEDA and 2,2'-bipyridyl showed slightly lower activity than diamine **4** (entries 6–8). Diamine **4** was so efficient that the reaction went to completion at 0 °C within 15 min with 5 mol% of the palladium catalyst (entry 10).

Table 1. Ligand Effect on Palladium-Catalyzed Arylation of **1**
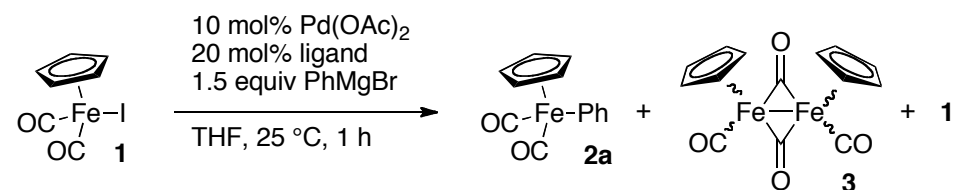
entry	ligand	yield/%		
		2a	**3**	**1**
1[a]		5	51	5
2	none	73	9	6
3	PPh$_3$	32	38	4
4	P(c-C$_6$H$_{11}$)$_3$	15	37	5
5	DPPE[b]	45	31	4
6	TMEDA[c]	73	<1	8
7	**4**	87	7	2
8	2,2'-bipyridyl	81	3	5
9[d]	IPr·HCl[e]	28	<1	59
10[f]	**4**	87	<6	<1

[a] In the absence of Pd(OAc)$_2$. PhMgBr (2.0 equiv) was used.
[b] 1,2-Bis(diphenylphosphino)ethane (10 mol%).
[c] *N,N,N',N'*-Tetramethylethylenediamine. [d] PhMgBr (1.6 equiv) was used.
[e] 12 mol%. [f] 5 mol% of Pd(OAc)$_2$, 6 mol% of **4**, 0 °C, 15 min.
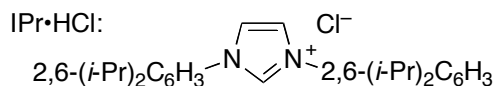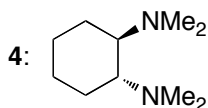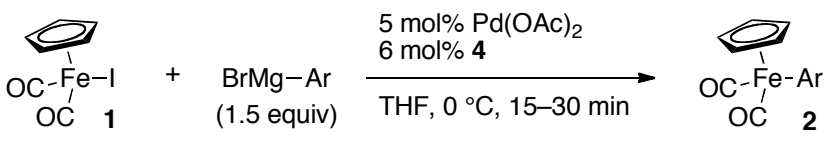
The reaction would proceed via a mechanism similar to the conventional cross-coupling reaction,[5c] which consists of oxidative addition of **1** to palladium that generates [Cp(CO)$_2$Fe–Pd–I], transmetalation with phenylmagnesium bromide, and reductive elimination that forms the phenyl–iron bond (Scheme 1).

Scheme 1.
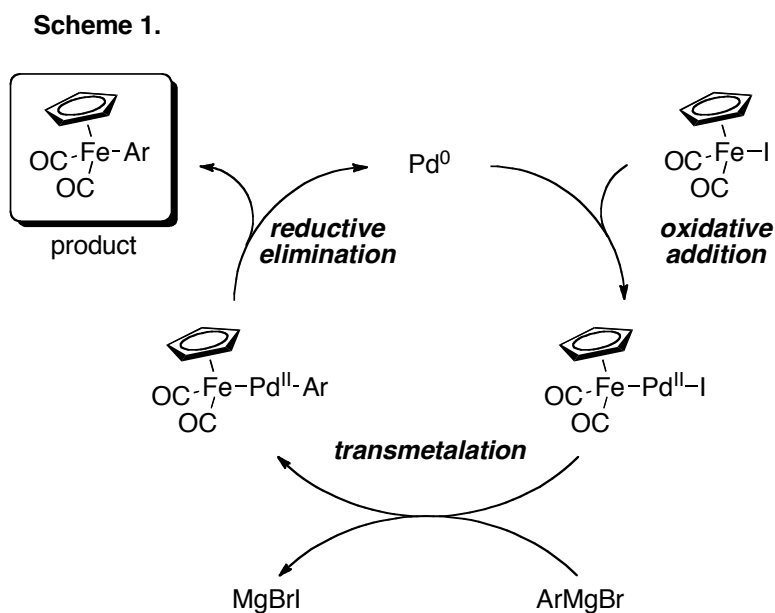
[CpFe(CO)$_2$I] is the best starting material for the preparation of **2a**. The corresponding bromide and chloride were arylated with lower efficiency. The palladium-catalyzed reactions of [CpFe(CO)$_2$Br] and [CpFe(CO)$_2$Cl] afforded **2a** in 53% and 66% yields along with **3** in 24% and 12% yields, respectively. Advantageously, [CpFe(CO)$_2$I] was more stable in air than [CpFe(CO)$_2$Br] and [CpFe(CO)$_2$Cl].

The scope of aryl Grignard reagents is summarized in Table 2. Substituents at the 4-positions of aryl Grignard reagents had little effect on the arylation reaction. An electron-rich [CpFe(CO)$_2$(4-MeOC$_6$H$_4$)] (**2d**) was somewhat sensitive to oxygen, which led to a moderate yield of **2d** after silica gel column purification under air. Unfortunately, the reaction of **1** with (2-methylphenyl)magnesium bromide failed to afford **2g** in reasonable yield, probably for steric reasons.

Table 2. Palladium-Catalyzed Arylation of **1** with ArMgBr

entry	Ar	2	yield/%
1	4-MeC$_6$H$_4$	**2b**	80
2	4-PhC$_6$H$_4$	**2c**	87
3[a]	4-MeOC$_6$H$_4$	**2d**	62 (90[b])
4	4-ClC$_6$H$_4$	**2e**	74
5	4-FC$_6$H$_4$	**2f**	87
6	2-MeC$_6$H$_4$	**2g**	21

[a] Performed at –20 °C for 2 h.
[b] Yield determined by ^{1}H NMR analysis of the crude product.

(4-Bromophenyl)magnesium reagent, prepared from 4-bromoiodobenzene according to the procedure of Knochel,[7] also underwent the arylation reaction at –20 °C, albeit in modest yield and with a higher catalyst loading (Scheme 2).

Scheme 2. Synthesis of Aryliron Complex from ArMgCl·LiCl
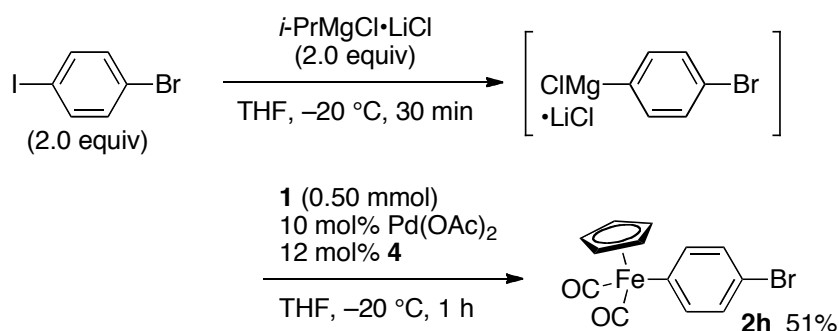
Although rich coordination chemistry has been reported for [CpFe(CO)$_2$Ar],[4] the application of [CpFe(CO)$_2$Ar] to organic synthesis has been almost unknown.[3] Hence, the author examined several transformations of [CpFe(CO)$_2$Ar] which will be useful in organic

synthesis.

Many oxidative alkoxycarbonylations of [CpFe(CO)$_2$R] with ceric ammonium nitrate to form RCOOR' were reported,[8] although there have been no reports on the reaction of [CpFe(CO)$_2$Ar]. He thus optimized conditions for the reaction of [CpFe(CO)$_2$Ar] to find the conditions in Scheme 3. Treatment of **2c** with ceric ammonium nitrate in a methanol–toluene mixed solvent at –78 °C for 30 min provided methyl 4-biphenylcarboxylate (**5**) in 89% yield.

Scheme 3.
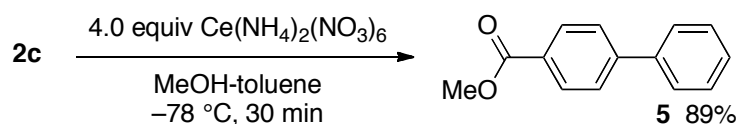
The carbon–iron bond of **2** was robust enough to be compatible under transition-metal-catalyzed conditions. For instance, the palladium-catalyzed borylation[9] of **2h** proceeded smoothly to afford the (borylphenyl)iron complex **2i** (Scheme 4).

Scheme 4.
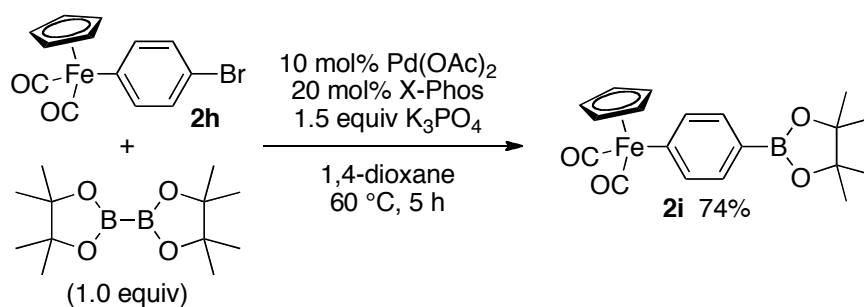
Iron complexes **2** reacted with allylic electrophiles under irradiation with a high-pressure mercury lamp to afford allylarenes **6** (Schemes 5 and 6).

Scheme 5.

2c + (allyl bromide structure with Br, R) (5 equiv) → $\xrightarrow[\text{THF, 25 °C, 1 h}]{h\nu}$ → (biphenyl product)
6a (R = H) 75%
6b (R = Me) 86%

Scheme 6.

2i + (methallyl tosylate, OTs) (5 equiv) → $\xrightarrow[\text{THF, 25 °C, 1 h}]{h\nu}$ → (pinacol boronate product)
6c 71%
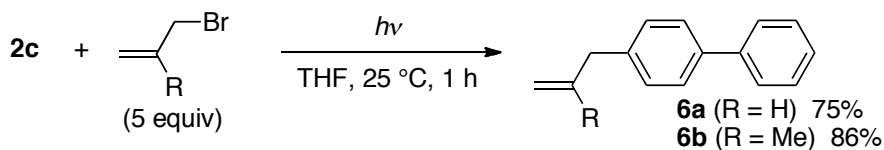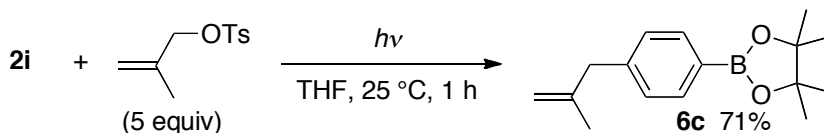
The reaction would proceed as follows (Scheme 7): (1) photoinduced dissociation of a carbonyl ligand,[10–12] (2) coordination of an allylic electrophile followed by migratory insertion,[13] and (3) β-halide elimination.[14]   It is worth noting that the reaction of **2i** with methallyl tosylate occurred selectively at the iron–carbon bond without affecting the boron–carbon bond.   This photoinduced additive-free metal-selective carbon–carbon bond formation opens up a new possibility of organoiron-based organic synthesis that takes advantage of the most ubiquitous transition metal.

Scheme 7.
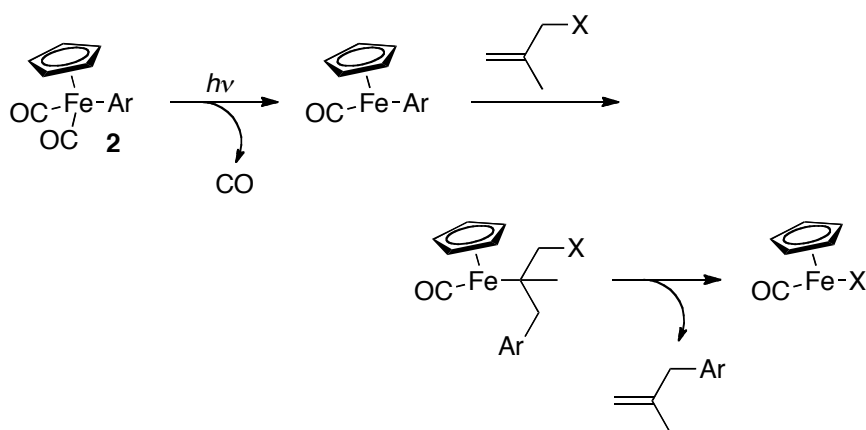
Conclusion

The author has devised an efficient method for the synthesis of the series of iron complexes [CpFe(CO)$_2$Ar]: that is, palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and aryl Grignard reagents. The iron complexes thus synthesized are a useful class of arylmetals of significant stability and become reactive upon oxidation or irradiation.   As notably demonstrated in the reaction of **2i** and methallyl tosylate, the organoiron complexes [CpFe(CO)$_2$Ar] play unique roles as reagents in organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to CDCl$_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Photochemical reactions were conducted with a 100-W high-pressure mercury lamp, SEN LIGHTS Corporation HL100CH-4.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dicarbonylcyclopentadienyliron dimer was purchased from Aldrich. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is.

Procedure for Synthesis of [CpFe(CO)$_2$I]

Dicarbonylcyclopentadienyliron dimer (10.0 g, 28 mmol), chloroform (150 mL), and iodine (8.6 g, 34 mmol) were sequentially added in a 300-mL round-bottomed flask under air. After the mixture was filled with argon, it was refluxed and stirred for 2 h. Then the resulting mixture was cooled to room temperature and quenched with an aqueous solution of sodium thiosulfate. The products were extracted with chloroform (100 mL) three times and the combined organic layer was dried over sodium sulfate and concentrated. Silica gel column purification (eluent: CHCl$_3$) of the crude product provided dicarbonylcyclopentadienyliodoiron (**1**, 16.4 g, 96% yield). Complex **1** was recrystallized from chloroform/hexane prior to use in the following reactions.

Typical Procedure for Palladium-Catalyzed Arylation Reactions of [CpFe(CO)₂I] (Table 1, entry 10)

Dicarbonylcyclopentadienyliodoiron (**1**, 152 mg, 0.50 mmol), palladium(II) acetate (5.6 mg, 0.025 mmol), diamine **4** (6.0 mg, 0.030 mmol), and THF (1.0 mL) were sequentially added in a 20-mL reaction flask under argon. The mixture was cooled to 0 °C and then phenylmagnesium bromide (1.1 M THF solution, 0.68 mL, 0.75 mmol) was added. After the resulting mixture was stirred for 15 min at 0 °C, a saturated ammonium chloride solution (0.2 mL) was added to the reaction mixture. The mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: CS_2) of the crude product provided dicarbonylcyclopentadienylphenyliron[15] (**2a**, 110 mg, 87% yield).

Procedure for Palladium-Catalyzed Arylation Reactions of [CpFe(CO)₂I] with Grignard Reagent Generated in situ by I/Mg Exchange Reaction (Scheme 2)

1-Bromo-4-iodobenzene (283 mg, 1.0 mmol) and THF (1.0 mL) were added in a 20-mL reaction flask under argon. The mixture was cooled to –20 °C and then isopropylmagnesium chloride/lithium chloride complex (1.0 M THF solution, 1.0 mL, 1.0 mmol) was added. After the mixture was stirred for 30 min at –20 °C, palladium(II) acetate (11 mg, 0.050 mmol), diamine **4** (12 mg, 0.060 mmol), and dicarbonylcyclopentadienyliodoiron (**1**, 152 mg, 0.50 mmol) were sequentially added to the reaction mixture. After the resulting mixure was stirred for 1 h at –20 °C, a saturated ammonium chloride solution (0.2 mL) was added to the reaction mixture. The mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: CS_2) of the crude product provided (4-bromophenyl)dicarbonylcyclopentadienyliron (**2h**, 85 mg, 51% yield).

Procedure for Oxidation Reactions of [CpFe(CO)₂Ar] with Ce(IV)(NH₄)₂(NO₃)₆ (Scheme 3)

Diammonium cerium(IV) nitrate (658 mg, 1.2 mmol) and MeOH (6.0 mL) were added in a 50-mL reaction flask under argon. The mixture was cooled to –78 °C and then

(4-biphenylyl)dicarbonylcyclopentadienyliron (**2c**, 99 mg, 0.30 mmol) in toluene (1.0 mL) was added slowly over 1 min.   After being stirred for 30 min at –78 °C, the reaction mixture was quenched with an aqueous solution of sodium thiosulfate and sodium bicarbonate.   The products were extracted with diethyl ether (20 mL) three times and the combined organic layer was dried over sodium sulfate and concentrated.   Silica gel column purification (eluent: hexane/ethyl acetate = 40:1) of the crude product provided methyl 4-biphenylcarboxylate (**5**, 56 mg, 89% yield).

Procedure for Palladium-Catalyzed Borylation Reactions of [CpFe(CO)$_2$(4-BrC$_6$H$_4$)] with Bis(pinacolato)diboron (Scheme 4)

(4-Bromophenyl)dicarbonylcyclopentadienyliron (**2h**, 333 mg, 1.0 mmol), bis(pinacolato)diboron (254 mg, 1.0 mmol), palladium(II) acetate (22 mg, 0.10 mmol), dicyclohexyl[2-(2,4,6-triisopropylphenyl)phenyl]phosphine (95 mg, 0.20 mmol), potassium phosphate (318 mg, 1.5 mmol), and 1,4-dioxane (3.0 mL) were sequentially added in a 30-mL reaction flask under argon.   The reaction mixture was heated at 60 °C and stirred for 5 h.   Then the reaction mixture was cooled to room temperature and filtered through a pad of Florisil, and the filtrate was concentrated.   Silica gel column purification (eluemt: CHCl$_3$) of the crude product provided dicarbonylcyclopentadienyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl]iron (**2i**, 281 mg, 74% yield).

Typical Procedure for Photo-Induced Allylation Reactions of [CpFe(CO)$_2$Ar] with Allylic Electrophiles (Scheme 5, synthesis of 6b)

(4-Biphenylyl)dicarbonylcyclopentadienyliron (**2c**, 99 mg, 0.30 mmol), 3-bromo-2-methylpropene (203 mg, 1.5 mmol), and THF (1.5 mL) were sequentially added in a quartz tube under argon.   The reaction mixture was irradiated by a UV lamp at 25 °C and stirred for 1 h with irradiation.   The distance between the reaction flask and the UV lamp was 2 cm. After irradiation, the mixture was filtered through a pad of Florisil, and the filtrate was

concentrated.　Silica gel column purification (eluent: hexane) of the crude product provided 4-(2-methyl-2-propenyl)biphenyl (**6b**, 54 mg, 86% yield).

Characterization Data

Dicarbonylcyclopentadienylphenyliron (2a)[15]
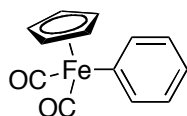
IR (neat) 3052, 2011, 1953, 1564, 1470, 1421, 1054, 1010, 995, 832, 732, 698, 633 cm^{-1};　^{1}H NMR (CDCl$_3$) δ = 4.87 (s, 5H), 6.91–6.94 (m, 1H), 6.97–6.99 (m, 2H), 7.46 (d, J = 7.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 85.77, 122.87, 127.51, 145.07, 145.51, 216.04;　Found: C, 61.46; H, 4.08%.　Calcd for C$_{13}$H$_{10}$FeO$_2$: C, 61.46; H, 3.97%.

Dicarbonylcyclopentadienyl(4-methylphenyl)iron (2b)
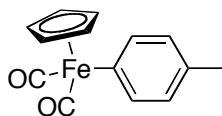
IR (nujol) 2019, 1998, 1968, 1939, 1915, 1480, 1431, 1009, 793, 635, 596 cm^{-1};　^{1}H NMR (CDCl$_3$) δ = 2.24 (s, 3H), 4.86 (s, 5H), 6.84 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H);　^{13}C NMR (CDCl$_3$) δ = 20.51, 85.71, 128.74, 132.23, 139.68, 144.75, 216.14;　Found: C, 62.86; H, 4.52%.　Calcd for C$_{14}$H$_{12}$FeO$_2$: C, 62.72; H, 4.51%.　m.p.: 83–84 °C.

(4-Biphenylyl)dicarbonylcyclopentadienyliron (2c)
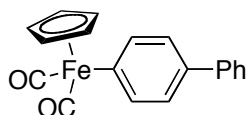
IR (nujol) 2008, 1953, 1938, 1919, 1466, 1443, 1003, 815, 761, 702, 637, 606, 596, 579 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.89 (s, 5H), 7.23–7.29 (m, 3H), 7.38–7.41 (m, 2H), 7.52–7.56 (m, 4H); ^{13}C NMR (CDCl$_3$) δ = 85.82, 126.00, 126.51, 126.72, 128.61, 136.02, 141.49, 145.20, 145.23,

215.99; Found: C, 68.95; H, 4.29%. Calcd for $C_{19}H_{14}FeO_2$: C, 69.12; H, 4.27%. m.p.: 113–115 °C.

Dicarbonylcyclopentadienyl(4-methoxyphenyl)iron (2d)
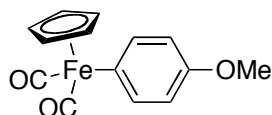
IR (neat) 2834, 2010, 1953, 1581, 1481, 1463, 1420, 1264, 1232, 1181, 1052, 1026, 1000, 812, 634, 593 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 3.74 (s, 3H), 4.85 (s, 5H), 6.68 (d, J = 7.5 Hz, 2H), 7.29 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 55.09, 85.71, 114.27, 131.03, 144.70, 157.04, 216.22; Found: C, 58.83; H, 4.26%. Calcd for $C_{14}H_{12}FeO_3$: C, 59.19; H, 4.26%.

Dicarbonyl(4-chlorophenyl)cyclopentadienyliron (2e)
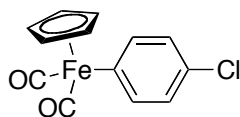
IR (neat) 2016, 1959, 1468, 1432, 1420, 1090, 1034, 1003, 909, 845, 835, 803, 734, 631, 592, 572 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.86 (s, 5H), 6.96 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 85.77, 127.25, 129.85, 143.44, 145.51, 215.70; Found: C, 54.33; H, 3.42%. Calcd for $C_{13}H_9ClFeO_2$: C, 54.12; H, 3.14%.

Dicarbonylcyclopentadienyl(4-fluorophenyl)iron (2f)
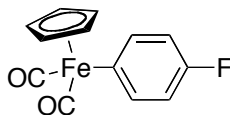
IR (nujol) 2022, 2005, 1971, 1941, 1920, 1477, 1468, 1163, 810, 635, 596, 578 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.85 (s, 5H), 6.74–6.77 (m, 2H), 7.31–7.34 (m, 2H); ^{13}C NMR (CDCl$_3$) δ = 85.75, 114.60 (d, J_{C-F} = 18.6 Hz), 136.99, 144.76 (d, J_{C-F} = 5.8 Hz), 161.46 (d, J_{C-F} = 239.0 Hz), 215.94; Found: C, 57.29; H, 3.32%. Calcd for $C_{13}H_9FFeO_2$: C, 57.39; H, 3.33%. m.p.: 62–63 °C.

Dicarbonylcyclopentadienyl(2-methylphenyl)iron (2g)
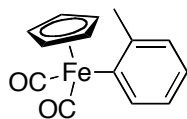
IR (nujol) 2016, 1998, 1965, 1941, 1905, 1448, 826, 741, 635, 592 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.44 (s, 3H), 4.88 (s, 5H), 6.80–6.83 (m, 1H), 6.88–6.91 (m, 1H), 7.03 (d, J = 7.0 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ = 28.15, 86.05, 123.35, 124.59, 129.23, 144.33, 146.80, 148.86, 215.92; Found: C, 62.47; H, 4.42%. Calcd for C$_{14}$H$_{12}$FeO$_2$: C, 62.72; H, 4.51%. m.p.: 68–69 °C.

(4-Bromophenyl)dicarbonylcyclopentadienyliron (2h)
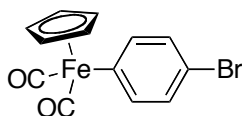
IR (nujol) 2023, 2003, 1973, 1950, 1917, 1456, 1418, 1359, 998, 850, 801, 631, 594 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.88 (s, 5H), 7.11 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 85.77, 117.98, 130.08, 144.51, 146.05, 215.63; Found: C, 47.00; H, 3.10%. Calcd for C$_{13}$H$_9$BrFeO$_2$: C, 46.89; H, 2.72%. m.p.: 104–105 °C.

Dicarbonylcyclopentadienyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]iron (2i)
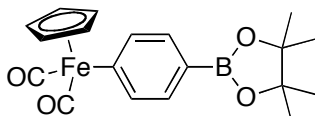
IR (nujol) 2006, 1959, 1577, 1456, 1357, 1143, 1093, 1008, 813, 734, 659 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.33 (s, 12H), 4.87 (s, 5H), 7.40 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 24.85, 83.35, 85.83, 133.07, 144.99, 154.28, 215.80. The borylated carbon could not be observed. Found: C, 60.17; H, 5.56%. Calcd for C$_{19}$H$_{21}$BFeO$_4$: C, 60.05; H, 5.57%. m.p.: 180 °C (decomposed).

4-(2-Methyl-2-propenyl)biphenyl (6b) showed the identical spectra found in the literature.[16]

1-(2-Methyl-2-propenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (6c)
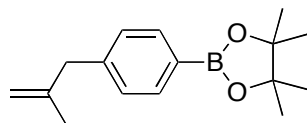
IR (nujol) 1611, 1456, 1398, 1362, 1321, 1272, 1146, 1090, 1023, 963, 891, 861, 659 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.36 (s, 12H), 1.68 (s, 3H), 3.35 (s, 2H), 4.74–4.75 (m, 1H), 4.82–4.83 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 22.28, 25.08, 45.05, 83.87, 112.32, 128.60, 135.04, 143.36, 145.04.   The borylated carbon could not be observed.   Found: C, 74.35; H, 9.11%.   Calcd for C$_{16}$H$_{23}$BO$_2$: C, 74.44; H, 8.98%.   m.p.: 33–34 °C.

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14. Oxidative addition followed by reductive elimination via an unusual Fe(IV) oxidation state is an alternative process for the allylation (Scheme 8).

Scheme 8.
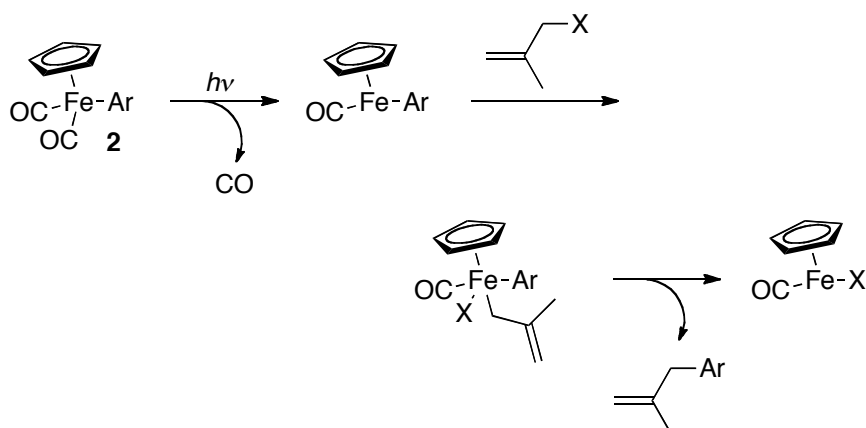
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Chapter 2

Synthesis of Aryliron Complexes [CpFe(CO)$_2$Ar] by Palladium-Catalyzed Reactions of [CpFe(CO)$_2$I] with Arylzinc, -Boron, or -Indium Reagents

Transmetalation between [CpFe(CO)$_2$I] and arylzinc iodide-lithium chloride complexes proceeds in the presence of catalytic amounts of palladium acetate and *N,N,N',N'*-tetramethyl-1,2-cyclohexanediamine to yield the corresponding aryliron complexes [CpFe(CO)$_2$Ar]. Phenylation of [CpFe(CO)$_2$I] also takes place when triphenylindium is used under similar conditions. Arylboronic acids undergo arylation in the presence of cesium carbonate and a palladium-*N*-heterocyclic carbene complex, PEPPSI. The present methods are useful for the facile synthesis of various functionalized [CpFe(CO)$_2$Ar]. The products [CpFe(CO)$_2$Ar] represent an interesting class of arylmetals that undergo several transformations.

Introduction

Aryldicarbonylcyclopentadienyliron complexes [CpFe(CO)$_2$Ar] are important as typical 18-electron organometallics,[1] reagents in organic synthesis,[2] and functional organic materials.[3–5] Despite their importance, there had been few reports of a concise and general synthesis of [CpFe(CO)$_2$Ar].[6–10] In Chapter 1, the author reported catalytic reactions for the synthesis of [CpFe(CO)$_2$Ar]. His report showed that transmetalation between [CpFe(CO)$_2$I] and arylmagnesium reagents proceeds smoothly under palladium catalysis.[11] However, the scope of the reaction is limited due to the high reactivity of arylmagnesium reagents. In Chapter 2, he reports palladium-catalyzed arylation reactions of [CpFe(CO)$_2$I] with arylzinc or arylboron reagents, the mild reactivities of which should ensure high functional group compatibility. Moreover, he demonstrates palladium-catalyzed phenylation reactions of [CpFe(CO)$_2$I] with triphenylindium.

Results and Discussion

1. Reactions of [CpFe(CO)$_2$I] with Arylzinc Reagents

The author initially examined the reaction of [CpFe(CO)$_2$I] (**1**) with commercially available PhZnI (Aldrich) in the presence of 0.25 mol% of palladium acetate and 0.50 mol% of *trans-N,N,N',N'*-tetramethyl-1,2-cyclohexanediamine (Table 1, entry 1). The reaction proceeded to yield the corresponding product **2a** in only 46% yield. A 29% of starting material **1** was recovered, and dimer **3** was detected as the only identifiable byproduct. He then tried to use the more reactive arylzinc reagent reported by Knochel.[12] Treatment of iodobenzene with zinc powder in the presence of lithium chloride at 50 °C for 24 h afforded PhZnI•LiCl. The reaction with PhZnI•LiCl was indeed successful, affording **2a** quantitatively (90% isolated yield) (entry 2). It is worth noting that the reaction of **1** with PhZnI•LiCl proceeded less efficiently in

the absence of the palladium catalyst (25 °C, 30 min) to provide **2a** in only 52% yield.

The use of Knochel's arylzinc reagent was indispensable. The yield of **2a** was low when the author used a phenylzinc reagent prepared by mixing commercially supplied LiCl-free phenylzinc iodide and LiCl just prior to use (entry 3). The complexation of PhZnI and LiCl would not proceed efficiently at ambient temperature, but it proceeded to near completion upon heating a mixture of PhZnI and LiCl at 50 °C for 24 h to ensure sufficient reactivity (entry 4). The use of diphenylzinc prepared from $ZnCl_2$ and 2 equiv of PhMgBr was also effective (entry 5), although he could not prepare functionalized diarylzinc by this method.

Table 1. Reactions of [CpFe(CO)$_2$I] (**1**) with Several Types of Phenylating Reagents
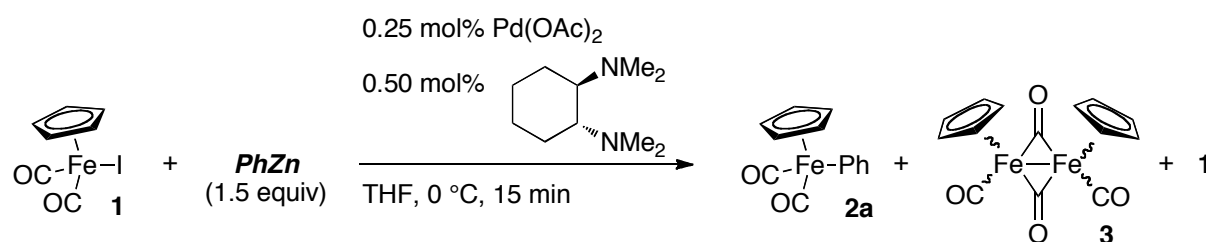
entry	PhZn	yield based on ^{1}H NMR/%		
		2a	**3**	**1**
1	PhZnI	46	15	29
2	PhZnI·LiCl	100(90[a])	0	0
3	PhZnI + LiCl	20	34	35
4	PhZnI + LiCl then 50 °C, 24 h	73	0	17
5	ZnCl$_2$ + 2 PhMgBr	100	0	0

[a] Isolated yield.

The scope of arylzinc reagent is wide, as shown in Table 2. Although the reaction of **1** with sterically demanding aryl Grignard reagent had failed,[11] the present method allowed him to introduce aryl groups bearing a substituent at the 2 position (entries 2, 3, and 6). The electronic nature of arylzinc reagents had little effect on the yield of arylirons (entries 4–10). The modest reactivity of organozinc reagents opened the way for facile preparation of aryliron complexes

having bromo, cyano, and ethoxycarbonyl groups (entries 7–10). However, the reaction with 2-ethoxycarbonylphenylzinc reagent or 4-acetylphenylzinc reagent resulted in recovery of **1** (entries 11 and 12). Thienyliron complex **2m** was obtained in high yield, while no reaction took place with 3-pyridylzinc reagent (entries 13 and 14).

Table 2. Palladium-Catalyzed Arylation of [CpFe(CO)$_2$I] (**1**) with Arylzinc Reagents ArZnI•LiCl

0.25 mol% Pd(OAc)$_2$

0.50 mol%

$$\text{OC}^{-}\underset{\underset{\text{OC}}{|}}{\text{Fe}}\!-\!\text{I} \quad + \quad \text{ArZnI•LiCl} \quad \xrightarrow[\text{THF, 0 °C, 15 min}]{} \quad \text{OC}^{-}\underset{\underset{\text{OC}}{|}}{\text{Fe}}\!-\!\text{Ar}$$

1 (1.5 equiv) **2**

entry	Ar	2	yield/%
1	Ph	**2a**	90
2	1-naphthyl	**2b**	92
3	2-MeC$_6$H$_4$	**2c**	73[a]
4	4-MeOC$_6$H$_4$	**2d**	94
5	3-CF$_3$C$_6$H$_4$	**2e**	94
6	2-FC$_6$H$_4$	**2f**	74
7	4-BrC$_6$H$_4$	**2g**	92
8	4-NCC$_6$H$_4$	**2h**	94
9	4-EtOC(=O)C$_6$H$_4$	**2i**	82
10	3-EtOC(=O)C$_6$H$_4$	**2j**	90
11	2-EtOC(=O)C$_6$H$_4$	**2k**	trace
12	4-MeC(=O)C$_6$H$_4$	**2l**	trace
13	2-thienyl	**2m**	79
14	3-pyridyl	**2n**	trace
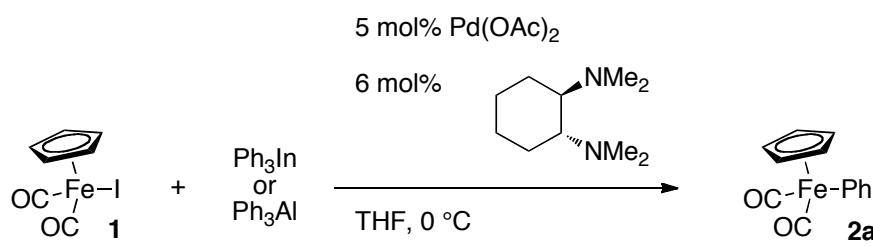
[a] 3.0 equiv of the zinc reagent was used.

A mechanism similar to the conventional cross-coupling reaction would operate[14] in the phenylation, *i.e.*, oxidative addition of **1** to palladium that generates [Cp(CO)$_2$Fe–Pd–I], transmetalation with PhZnI•LiCl, and reductive elimination to yield **2a**.

2. Reactions of [CpFe(CO)₂I] with Triphenylindium or -Aluminum

Triphenylindium, prepared from InCl$_3$ and 3 equiv of PhMgBr, could transfer the phenyl group to **1** under similar conditions (Table 3, entry 1).[14]   The amount of Ph$_3$In could be reduced to 0.50 equiv (entry 2).   However, the yield of **2a** was modest when 0.33 equiv of Ph$_3$In was used (entry 3).   Thus, two of the three phenyl groups on indium would be efficiently transferred.[15]   The reaction of **1** with triphenylaluminum prepared from AlCl$_3$ and 3 equiv of PhMgBr afforded **2a** sluggishly (entry 4).

Table 3. Palladium-Catalyzed Phenylation of [CpFe(CO)₂I] (**1**) with Triphenylindium or -Aluminum

entry	phenylating agent	time/h	yield based on ¹H NMR/%
1	Ph$_3$In (1.5 equiv)	1	92
2	Ph$_3$In (0.50 equiv)	7	83
3	Ph$_3$In (0.33 equiv)	3	56
4	Ph$_3$Al (1.5 equiv)	2	22

3. Reactions of [CpFe(CO)₂I] with Arylboronic Acids

Initially, a number of attempts to perform Suzuki-type arylation of **1** with phenylboronic acid failed to afford the corresponding aryliron **2a** when various phosphine ligands, amine ligands and bases were screened.   The author then found that bulky *N*-heterocyclic carbenes were good ligands.   Especially, a combination of a palladium complex PEPPSI and cesium carbonate proved to provide marked improvement (Table 4, entry 1).[16,17]   A variety of

arylboronic acids underwent the arylation with high efficiency. In case that the arylation was not efficient enough, the addition of copper(I) iodide promoted the reactions (entries 5, 9, 11, 12, and 14).[18–21] He assumes that arylcopper species generated from CuI and arylboronic acids would undergo more efficient transmetalation with the iodopalladium intermediate.[22,23] Notably, the combination of PEPPSI and copper(I) iodide allowed the synthesis of **2k** (entry 12), which could not be prepared from the corresponding arylzinc reagent. Styrene derivative **2r** was prepared from 4-vinylphenylboronic acid in high yield (entries 13 and 14). Unfortunately, the reaction with arylboronic acids having a hydroxy group was sluggish (entry 15).

Table 4. Palladium-Catalyzed Arylation of [CpFe(CO)$_2$I] (**1**) with Arylboronic Acids
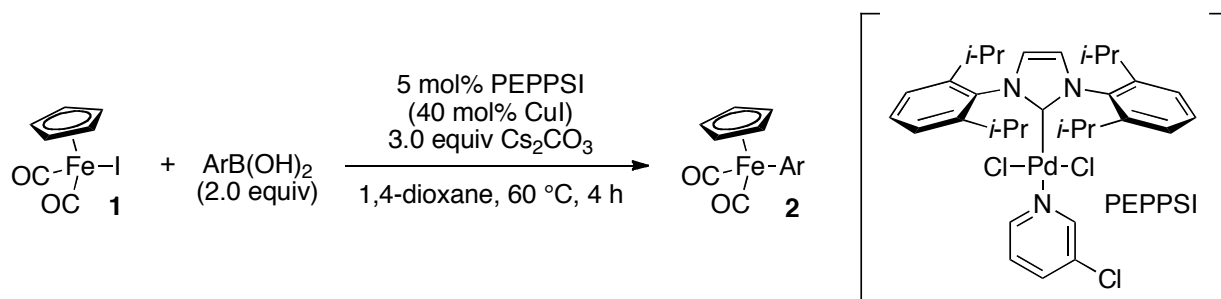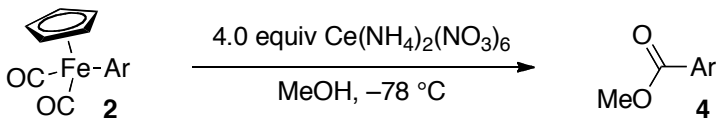
entry	Ar	CuI/mol%	2	yield/%
1	Ph	0	**2a**	88
2	1-naphthyl	0	**2b**	82
3	2-MeC$_6$H$_4$	0	**2c**	76
4	4-MeOC$_6$H$_4$	0	**2d**	68
5	4-MeOC$_6$H$_4$	40	**2d**	82
6	4-CF$_3$C$_6$H$_4$	0	**2o**	80
7	4-MeC$_6$H$_4$	0	**2p**	79
8	4-MeOCH$_2$C$_6$H$_4$	0	**2q**	73
9	4-MeOCH$_2$C$_6$H$_4$	40	**2q**	86
10	4-EtOC(=O)C$_6$H$_4$	0	**2i**	67
11	4-EtOC(=O)C$_6$H$_4$	40	**2i**	87
12	2-EtOC(=O)C$_6$H$_4$	40	**2k**	75
13	4-CH$_2$=CHC$_6$H$_4$	0	**2r**	72
14	4-CH$_2$=CHC$_6$H$_4$	40	**2r**	83
15	4-HOCH$_2$C$_6$H$_4$	0	**2s**	0

4. *Transformation of [CpFe(CO)$_2$Ar]*

In Chapter 1, the author demonstrated oxidative methoxycarbonylation of [CpFe(CO)$_2$(4-biphenylyl)] to afford methyl 4-biphenylcarboxylate.[11,24–26] The methoxycarbonylation proved to be applicable to functionalized [CpFe(CO)$_2$Ar] prepared by the present method, leaving the functional groups untouched (Table 5). The yields of esters are good to excellent.
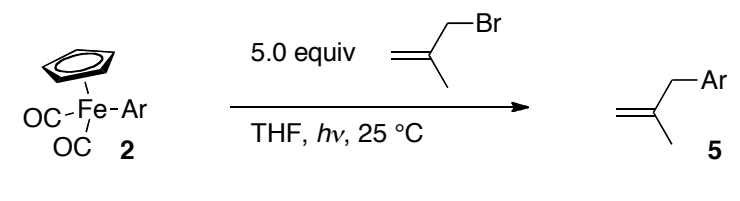
Table 5. Oxidative Methoxycarbonylation of Functionalized Aryliron Complexes

OC–Fe–Ar / OC **2** → (4.0 equiv Ce(NH$_4$)$_2$(NO$_3$)$_6$ / MeOH, −78 °C) → MeO–C(=O)–Ar **4**

entry	2	time/h	4	yield/%
1	**2d**	0.5	**4a**	45
2	**2g**	1	**4b**	61
3	**2h**	4.5	**4c**	59
4	**2i**	2	**4d**	91

The same set of the functionalized aryliron complexes also underwent photoinduced allylation (Table 6).[11] The scope of the allylation is wide, and allylated products **5** were obtained in high yields.

Table 6. Allylation of Functionalized Aryliron Complexes under UV Irradiation

entry	2	time/h	5	yield/%
1	**2d**	2	**5a**	79
2	**2g**	1	**5b**	75
3	**2h**	2	**5c**	78
4	**2i**	15	**5d**	71

Treatment of **2i** with diisobutylaluminum hydride (DIBAL-H) in toluene or butyllithium in THF afforded benzylic alcohol **2t** or **2u**, respectively (Scheme 1).   Nucleophilic attack to the ester moiety proceeded exclusively with the CpFe(CO)$_2$ moiety untouched.

Scheme 1.

2t (R = H) 73% (toluene, 25 °C, 2 h)
2u (R = *n*-Bu) 77% (THF, 0 °C, 0.5 h)
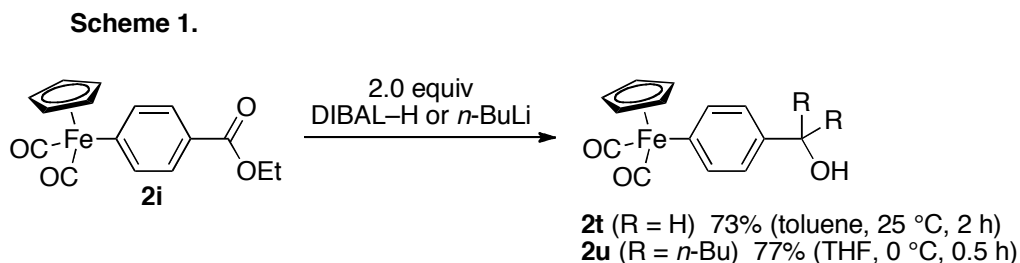
(Vinylphenyl)iron **2r** underwent ruthenium-catalyzed metathesis to expand the diversity of available aryliron complexes (Table 7).[27,28]   Self-metathesis of **2r** afforded (*E*)-stilbene derivative **2v** in excellent yield (entry 1).   A cross-metathesis reaction of **2r** with 3 equiv of ethyl acrylate proceeded smoothly (entry 2).   A cross-metathesis reaction with 1-octene or allyltrimethylsilane required a large excess of the alkene to achieve reasonable efficiency (entries 3 and 4).   All the reactions proceeded with exclusive *E* selectivity.   The aryl–iron bonds were tolerant under the metathesis conditions.

Table 7. Ruthenium-Catalyzed Metathesis of **2r**
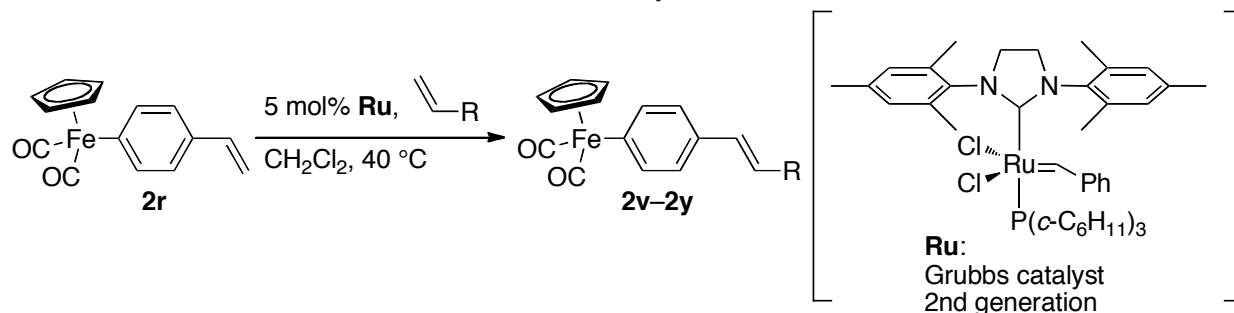
entry	⟋⟋—R	Amt. of 1-alkene	time/h	**2**	yield/%
1	**2r**	–	8	**2v**	91
2	⟋⟋—CO$_2$Et	3	6	**2w**	79
3	⟋⟋—n-C$_6$H$_{13}$	30	8	**2x**	76
4	⟋⟋—SiMe$_3$	10	15	**2y**	33 (66[a])

[a] Yield determined by ^{1}H NMR analysis of the crude mixture.

Conclusion

The palladium-catalyzed arylation of [CpFe(CO)$_2$I] with arylzinc or arylboron reagents offers an efficient method for the synthesis of various functionalized iron complexes. Triphenylindium transfers the phenyl groups under palladium catalysis to arylate [CpFe(CO)$_2$I]. The functionalized aryliron complexes [CpFe(CO)$_2$Ar] undergo carbon–carbon bond formations with cleaving the carbon–iron bonds as well as functional group transformations without cleaving the carbon–iron bonds. The iron complexes thus synthesized can find many applications in material chemistry as well as in organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer or a Varian GEMINI 300 spectrometer, using CDCl$_3$ as solvent with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to CDCl$_3$ at 77.2 ppm for ^{13}C, unless otherwise noted. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Photochemical reactions were conducted with a 100-W high-pressure mercury lamp (SEN LIGHTS Corporation HB100P-1).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF was purchased from Kanto Chemical Co., stored under argon, and used as it is. 1,4-Dioxane was obtained from Wako Pure Chemicals Co. and was stored over slices of sodium. Palladium acetate, cesium carbonate, ceric ammonium nitrate, and copper(I) iodide were obtained from Wako Pure Chemicals Co. PEPPSI and 2nd generation Grubbs catalyst were purchased from Aldrich. Arylzinc iodide-lithium chloride complexes were prepared according to the literature[12] and stored under argon. [CpFe(CO)$_2$I] was prepared according to the literature.[11]

Typical Procedure for Arylation with Arylzinc Reagents (Table 2, entry 1)

THF (1.0 mL) was placed in a 20-mL reaction flask under argon. [CpFe(CO)$_2$I] (**1**, 152 mg, 0.50 mmol), palladium acetate (0.050 M THF solution, 0.025 mL, 0.0013 mmol), *trans-N,N,N',N'*-tetramethyl-1,2-cyclohexanediamine (0.050 M THF solution, 0.050 mL, 0.0025

mmol), and phenylzinc iodide–lithium chloride complex (0.66 M THF solution, 1.14 mL, 0.75 mmol) were sequentially added at 0 °C. After the mixture was stirred for 15 min, a saturated ammonium chloride solution (1 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). Combined organic layer was passed through a pad of anhydrous sodium sulfate/Florisil and concentrated. ^{1}H NMR analysis of the crude product by using 1,1,2,2-tetrabromoethane as an internal standard indicated that **2a** was quantitatively formed. The crude oil was purified in air on silica gel by using carbon disulfide as an eluent to yield **2a** (114 mg, 0.45 mmol, 90%).

Procedure for Phenylation with Triphenylindium (Table 3, entry 1)

Indium trichloride (1.55 g, 7.0 mmol) and THF (2 mL) were placed in a 20-mL reaction flask under argon. Phenylmagnesium bromide (1.03 M THF solution, 20.4 mL, 21 mmol) was added at 0 °C. The resulting mixture was stirred at ambient temperature overnight to prepare a THF solution of triphenylindium (0.31 M). THF (0.60 mL) was placed in another 20-mL reaction flask under argon. [CpFe(CO)$_2$I] (**1**, 91 mg, 0.30 mmol), palladium acetate (3.4 mg, 0.015 mmol), *trans-N,N,N',N'*-tetramethyl-1,2-cyclohexanediamine (3.6 mg, 0.018 mmol), and a THF solution of triphenylindium (0.31 M THF solution, 1.4 mL, 0.45 mmol) were sequentially added at 0 ˚C. After the mixture was stirred for 1 h, a saturated ammonium chloride solution (0.6 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). Combined organic layer was passed through a pad of anhydrous sodium sulfate/Florisil and concentrated. ^{1}H NMR analysis of the crude product by using 1,1,2,2-tetrabromoethane as an internal standard indicated that **2a** was obtained in 92% yield. Chromatographic purification using carbon disulfide as an eluent yielded **2a** (66 mg, 0.26 mmol, 87%).

Typical Procedure for Arylation with Arylboronic Acids (Table 4, entry 1)

[CpFe(CO)$_2$I] (**1**, 152 mg, 0.50 mmol), phenylboronic acid (122 mg, 1.0 mmol), PEPPSI (17 mg, 0.025 mmol), and cesium carbonate (489 mg, 1.50 mmol) were placed in a 20-mL

reaction flask under an atmosphere of argon. 1,4-Dioxane (1.5 mL) was then added, and the resulting mixture was stirred for 4 h at 60 ˚C. The reaction was quenched with a saturated ammonium chloride solution (1 mL). Extractive workup followed by silica gel column purification (eluent: carbon disulfide) afforded **2a** (104 mg, 0.41 mmol) in 88% yield.

Procedure for Oxidative Methoxycarbonylation Reactions of [CpFe(CO)$_2$Ar] with Ce(NH$_4$)$_2$(NO$_3$)$_6$ (Table 5, entry 4)

Diammonium cerium(IV) nitrate (658 mg, 1.2 mmol) and methanol (6.0 mL) were added in a 50-mL reaction flask under argon. The mixture was cooled to –78 °C and then dicarbonylcyclopentadienyl(4-ethoxycarbonylphenyl)iron (**2i**, 98 mg, 0.30 mmol) in methanol (4.0 mL) was added slowly over 1 min. After being stirred for 2 h at –78 °C, the reaction mixture was quenched with an aqueous solution of sodium thiosulfate and sodium bicarbonate. The products were extracted with diethyl ether (20 mL × 3). The combined organic layer was passed through a pad of Florisil and sodium sulfate and concentrated. Silica gel column purification (eluent: hexane/ethyl acetate = 10:1) of the crude product provided ethyl methyl terephthalate (**4d**, 48 mg, 0.27 mmol, 91% yield).

Procedure for Photoinduced Allylation Reactions of [CpFe(CO)$_2$Ar] (Table 6, entry 4)

Dicarbonylcyclopentadienyl(4-ethoxycarbonylphenyl)iron (**2i**, 98 mg, 0.30 mmol), 3-bromo-2-methyl-propene (203 mg, 1.5 mmol), and THF (1.5 mL) were sequentially added in a quartz tube under argon. The reaction mixture was irradiated by a UV lamp at 25 °C and stirred for 2 h with irradiation. The distance between the reaction flask and the UV lamp was 2 cm. After irradiation, the mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: hexane/ethyl acetate = 10:1) provided ethyl 4-(2-methyl-2-propenyl)benzoate (**5d**, 44 mg, 0.21 mmol, 71% yield).

DIBAL-Reduction of 2i (Scheme 1)

Aryliron **2i** (98 mg, 0.30 mmol) was placed in a reaction flask under argon. Toluene (1.5 mL) and DIBAL-H (1.0 M in hexane, 0.60 mL, 0.60 mmol) were sequentially added at 25 °C. After the mixture was stirred for 2 h, a 30% Rochelle salt solution (5 mL) was added slowly at 0 °C. The resulting mixture was stirred overnight. Extractive workup followed by silica gel column purification (eluent: $CS_2/CHCl_3$ = 1:1 to $CHCl_3$ only) provided **2u** (62 mg, 0.22 mmol, 73%).

Reaction of 2i with Butyllithium (Scheme 1)

Aryliron **2i** (98 mg, 0.30 mmol) and THF (1.0 mL) were placed in a reaction flask under argon. Butyllithium (1.66 M in hexane, 0.36 mL, 0.60 mmol) was added dropwise at 0 °C. After the mixture was stirred for 30 min, a saturated ammonium chloride solution (5 mL) was added slowly at 0 °C. Extractive workup followed by silica gel column purification (eluent: $CS_2/CHCl_3$ = 1:1) provided **2v** (92 mg, 0.23 mmol, 77%).

Typical Procedure for Metathesis Reactions of 2r (Table 7, entry 2)

(Vinylphenyl)iron **2r** (84 mg, 0.30 mmol), dichloromethane (1.0 mL), and ethyl acrylate (0.098 mL, 0.90 mmol) were sequentially added in a reaction flask under argon. 2nd Generation Grubbs catalyst (13 mg, 0.015 mmol) was then added. After the mixture was stirred for 6 h at 40 °C, the mixture was passed through a pad of Florisil. The filtrate was concentrated in vacuo. Silica gel column purification (eluent: $CS_2/CHCl_3$ = 2:1) provided **2x** (85 mg, 0.24 mmol, 79%).

Characterization Data

Characterization data for arylirons **2a**,[11] **2b**,[3] **2c**,[11] **2d**,[11] **2g**,[11] **2p**,[11] **2r**,[5] **4a**,[29] **4b**,[30] **4c**,[30] **4d**,[31] **5a**,[32] **5b**,[33] **5c**,[34] and **5d**[35] were available in the literature.

**Dicarbonylcyclopentadienyl(3-trifluoromethylphenyl)iron (2e)**
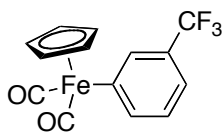
IR (neat) 2016, 1966, 1311, 1183, 1160, 1121, 1096, 1081, 1047, 790, 703, 676, 637, 621 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.89 (s, 5H), 7.05 (dd, J = 7.5, 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.68 (s, 1H); ^{13}C NMR (CDCl$_3$) δ = 86.00, 120.05 (q, J_{C-F} = 3.8 Hz), 124.86 (q, J_{C-F} = 273.8 Hz), 126.98, 129.17 (q, J_{C-F} = 30.2 Hz), 140.37 (q, J_{C-F} = 3.8 Hz), 148.28, 148.41 (q, J_{C-F} = 1.5 Hz), 215.66; Found: C, 52.48; H, 2.91%. Calcd for C$_{14}$H$_9$F$_3$FeO$_2$: C, 52.21; H, 2.82%.

Dicarbonylcyclopentadienyl(2-fluorophenyl)iron (2f)
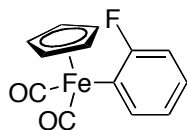
IR (nujol) 2028, 1977, 1454, 1193, 1016, 834, 764, 710, 629 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.91 (s, 5H), 6.80–6.88 (m, 2H), 6.95–6.99 (m, 1H), 7.49–7.52 (m, 1H); ^{13}C NMR (CDCl$_3$) δ = 85.57, 113.79 (d, J_{C-F} = 30.7 Hz), 123.86, 125.26 (d, J_{C-F} = 7.7 Hz), 128.15 (d, J_{C-F} = 38.8 Hz), 146.73 (d, J_{C-F} = 13.0 Hz), 169.62 (d, J_{C-F} = 230.5 Hz), 215.49; Found: C, 57.61; H, 3.41%. Calcd for C$_{13}$H$_9$FFeO$_2$: C, 57.39; H, 3.33%. m.p.: 57–58 °C.
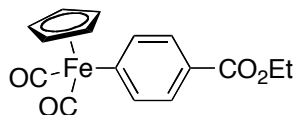
Dicarbonyl(4-cyanophenyl)cyclopentadienyliron (2h)
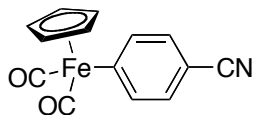
IR (nujol) 2225, 2014, 1964, 1942, 1920, 1575, 1462, 1418, 1042, 1010, 848, 818, 717 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.89 (s, 5H), 7.16 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 86.05, 106.54, 120.32, 129.13, 145.47, 161.07, 215.21; Found: C, 60.22; H, 3.24%.

Calcd for $C_{14}H_9FeNO_2$: C, 60.25; H, 3.25%.   m.p.: 100–101 °C.

Dicarbonylcyclopentadienyl(4-ethoxycarbonylphenyl)iron (2i)

IR (nujol) 2023, 1949, 1708, 1576, 1454, 1283, 1124, 1008, 758 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.36 (t, J = 7.0 Hz, 3H), 4.33 (q, J = 7.0 Hz, 2H), 4.88 (s, 5H), 7.58 (s, 4H); ^{13}C NMR (CDCl$_3$) δ = 14.59, 60.55, 86.04, 125.76, 127.24, 144.96, 159.28, 167.97, 215.61;   Found: C, 58.99; H, 4.43%.   Calcd for $C_{16}H_{14}FeO_4$: C, 58.93; H, 4.33%.   m.p.: 104–106 °C.

Dicarbonylcyclopentadienyl(3-ethoxycarbonylphenyl)iron (2j)
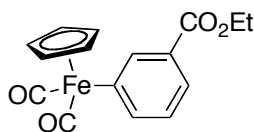
IR (nujol) 2015, 1962, 1944, 1703, 1456, 1367, 1253, 1110, 751 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.38 (t, J = 7.5 Hz, 3H), 4.35 (q, J = 7.5 Hz, 2H), 4.89 (s, 5H), 7.03 (dd, J = 7.5, 7.5 Hz, 1H), 7.58–7.60 (m, 1H), 7.65–7.67 (m, 1H), 8.12–8.13 (m, 1H); ^{13}C NMR (CDCl$_3$) δ = 14.56, 60.80, 86.00, 124.53, 127.03, 129.16, 145.36, 146.63, 149.66, 167.71, 215.82;   Found: C, 58.79; H, 4.45%.   Calcd for $C_{16}H_{14}FeO_4$: C, 58.93; H, 4.33%.   m.p.: 67–68 °C.

Dicarbonylcyclopentadienyl(2-ethoxycarbonylphenyl)iron (2k)
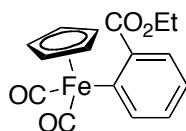
IR (nujol) 2020, 1969, 1945, 1707, 1456, 1377 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.37 (t, J = 7.0 Hz, 3H), 4.32 (q, J = 7.0 Hz, 2H), 4.94 (s, 5H), 6.97–6.99 (m, 2H), 7.44–7.46 (m, 1H), 7.72–7.74 (m, 1H); ^{13}C NMR (CDCl$_3$) δ = 14.48, 60.81, 86.85, 122.95, 128.10, 129.56, 146.55, 147.63,

147.70, 172.04, 215.62;　Found: C, 58.78; H, 4.39%.　Calcd for $C_{16}H_{14}FeO_4$: C, 58.93; H, 4.33%.　m.p.: 64–65 °C.

Dicarbonylcyclopentadienyl(2-thienyl)iron (2m)

IR (neat) 3104, 2854, 2026, 1966, 1420, 1391, 1317, 905, 826, 808, 682 cm^{-1};　^{1}H NMR (CDCl$_3$) δ = 4.98 (s, 5H), 6.83 (d, J = 3.0 Hz, 1H), 7.08 (dd, J = 4.5, 3.0 Hz, 1H), 7.45 (d, J = 4.5 Hz, 1H);　^{13}C NMR (CDCl$_3$) δ = 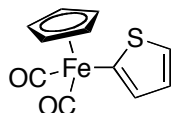85.89, 128.89, 131.31, 134.68, 138.23, 214.72;　Found: C, 50.55; H, 3.23%.　Calcd for $C_{11}H_8FeO_2S$: C, 50.80; H, 3.10%.

Dicarbonylcyclopentadienyl(4-trifluoromethylphenyl)iron (2o)
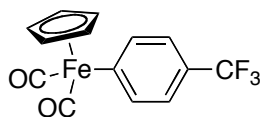
IR (nujol) 2007, 1957, 1588, 1325, 1158, 1072, 1008, 820, 631, 605 cm^{-1};　^{1}H NMR (CDCl$_3$) δ = 4.88 (s, 5H), 7.17 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.5 Hz, 2H);　^{13}C NMR (CDCl$_3$) δ = 86.01, 123.08 (q, $J_{C–F}$ = 3.8 Hz), 125.01 (q, $J_{C–F}$ = 272.3 Hz), 125.71 (q, $J_{C–F}$ = 32.3 Hz), 144.94, 155.28 (q, $J_{C–F}$ = 1.4 Hz), 215.63;　Found: C, 52.07; H, 2.97%.　Calcd for $C_{14}H_9F_3FeO_2$: C, 52.21; H, 2.82%.　m.p.: 72–73 °C.

Dicarbonylcyclopentadienyl(4-methoxymethylphenyl)iron (2q)
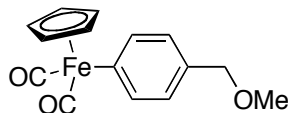
IR (neat) 2920, 2012, 1955, 1480, 1187, 1096, 1042, 1007, 832, 797, 632 cm^{-1};　^{1}H NMR (CDCl$_3$) δ = 3.36 (s, 3H), 4.34 (s, 2H), 4.86 (s, 5H), 6.96 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 2H);　^{13}C NMR (CDCl$_3$) δ = 58.18, 75.02, 85.95, 127.50, 132.88, 145.04, 145.24, 216.19; Found: C, 60.69; H, 4.91%.　Calcd for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73%.

Dicarbonylcyclopentadienyl(4-hydroxymethylphenyl)iron (2t)
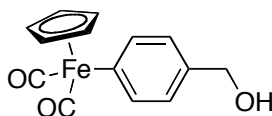
IR (nujol) 3450, 2007, 1952, 1005 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.48 (bs, 1H), 4.57 (d, J = 5.4 Hz, 2H), 4.87 (s, 5H), 7.00 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 65.68, 85.96, 126.75, 135.78, 145.24, 145.61, 216.12;   Found: C, 58.97; H, 4.29%.   Calcd for C$_{14}$H$_{12}$FeO$_3$: C, 59.19; H, 4.26%.   m.p.: 92–93 °C.

Dicarbonylcyclopentadienyl[4-(1-butyl-1-hydroxypentyl)phenyl]iron (2u)
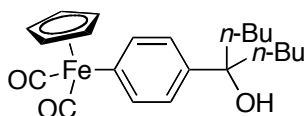
IR (neat) 3480, 2935, 2862, 2016, 1961, 1684, 1456, 1003, 815 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 0.85 (t, J = 7.2 Hz, 6H), 1.10–1.29 (m, 8H), 1.61 (s, 1H), 1.72–1.77 (m, 4H), 4.86 (s, 5H), 6.96 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 14.27, 23.35, 25.95, 42.47, 76.72, 85.95, 124.78, 141.52, 141.93, 144.51, 216.40;   Found: C, 66.91; H, 7.07%.   Calcd for C$_{22}$H$_{28}$FeO$_3$: C, 66.68; H, 7.12%.

[(E)-1,2-Ethenediyldi-4,1-phenylene]bis(dicarbonylcyclopentadienyliron) (2v)
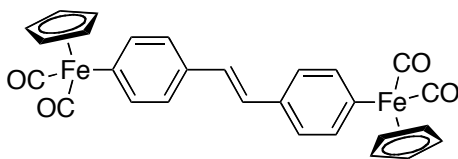
IR (nujol) 2004, 1940, 1001, 964, 815, 725, 634 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.88 (s, 10H), 6.93 (s, 2H), 7.13 (d, J = 8.0 Hz, 4H), 7.43 (d, J = 8.0 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ = 86.03, 125.59, 127.09, 133.20, 145.28, 145.66, 216.19;   HRMS (m/z) Observed: 532.0059.   Calcd for C$_{28}$H$_{20}$Fe$_2$O$_4$: 532.0060.   m.p.: >280 °C.

Dicarbonylcyclopentadienyl[4-((E)-2-ethoxycarbonylethenyl)phenyl]iron (2w)
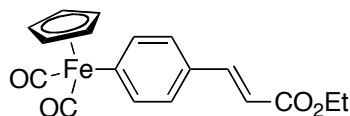
IR (neat) 2016, 1961, 1699, 1627, 1576, 1481, 1309, 1266, 1175, 1044, 1004, 811, 631, 591 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.33 (t, J = 7.5 Hz, 3H), 4.24 (q, J = 7.5 Hz, 2H), 4.88 (s, 5H), 6.34 (d, J = 16.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 16.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ = 14.54, 60.41, 86.00, 115.62, 126.43, 129.69, 145.48, 145.82, 154.35, 167.74, 215.72; HRMS (m/z) Observed: 352.0398. Calcd for C$_{18}$H$_{16}$FeO$_4$: 352.0398.

Dicarbonylcyclopentadienyl[4-((E)-1-octenyl)phenyl]iron (2x)
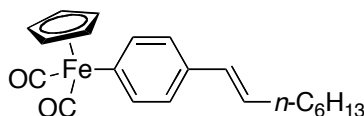
IR (neat) 2927, 2855, 2016, 1958, 1577, 1481, 1044, 1003, 965, 831, 797, 633, 592, 575 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 0.88 (s, 3H), 1.29–1.30 (m, 6H), 1.41–1.43 (m, 2H), 2.16–2.17 (m, 2H), 4.85 (s, 5H), 6.08–6.14 (m, 1H), 6.25–6.28 (m, 1H), 6.99 (d, J = 7.0 Hz, 2H), 7.37 (d, J = 7.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 14.31, 22.84, 29.06, 29.74, 31.97, 33.23, 85.94, 125.28, 129.05, 129.95, 133.21, 144.13, 145.10, 216.18; HRMS (m/z) Observed: 364.1120. Calcd for C$_{21}$H$_{24}$FeO$_2$: 364.1126.

Dicarbonylcyclopentadienyl[4-((E)-3-trimethylsilyl-1-propenyl)phenyl]iron (2y)
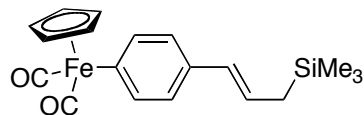
IR (nujol) 2020, 1969, 1002, 862, 830, 799, 589 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 0.03 (s, 9H), 1.63 (dd, J = 5.0, 2.0 Hz, 2H), 4.87 (s, 5H), 6.14 (bs, 2H), 6.97 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = −1.68, 23.88, 85.92, 125.04, 125.39, 128.53, 133.80, 142.97, 145.05, 216.22; m.p.: 66–67 °C.

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Chapter 3

Synthesis of Functionalized Aryliron Complexes [CpFe(CO)$_2$Ar] by Copper-Mediated Transmetalation between [CpFe(CO)$_2$I] and Aryltin Reagents

Transmetalation between [CpFe(CO)$_2$I] and aryltin reagents in the presence of copper salts yields the corresponding aryliron complexes [CpFe(CO)$_2$Ar]. The high functional group compatibility of this copper-mediated reaction makes it possible to synthesize [CpFe(CO)$_2$Ar] having an acetyl or formyl group on benzene ring, which can not be prepared by the methods with arylzinc or arylboron reagents under palladium catalysis.

Introduction

Because of their unique reactivity, organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)$_2$R] have been attracting much attention as useful reagents and have found numerous applications in organic synthesis.[1] Among them, the reactivity of the corresponding aryliron complexes [CpFe(CO)$_2$Ar] has not been fully investigated[2] partly because there are few methods for the synthesis of [CpFe(CO)$_2$Ar].[3] Therefore, the development of efficient approaches to [CpFe(CO)$_2$Ar] should lead to the progress of the chemistry of [CpFe(CO)$_2$Ar] which have high potential as useful arylmetal reagents.[4]

In Chapters 1 and 2, the author demonstrated an easy and efficient method for the synthesis of [CpFe(CO)$_2$Ar], palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and arylmagnesium,[5] arylzinc, or arylboron reagents.[6] Especially, the reactions with arylzinc or arylboron reagents showed high functional group compatibility and allowed him to prepare a wide range of [CpFe(CO)$_2$Ar]. However, the functional group compatibility of these methods was not perfect. For example, [CpFe(CO)$_2$Ar] bearing an acetyl, formyl, or hydroxy group on benzene ring could not be obtained. Therefore, he turned his attention to transmetalation from other organometallic compounds. In Chapter 3, he reports that copper salts can promote arylation reactions of [CpFe(CO)$_2$I] with aryltin reagents, which show a higher functional group compatibility than the methods with arylzinc or arylboron reagents under palladium catalysis.[5,6]

Results and Discussion

After extensive screening of the reaction conditions, the author found that copper(I) trifluoromethanesulfonate efficiently promoted a substitution reaction of [CpFe(CO)$_2$I] (**1**) with tributylphenyltin to afford [CpFe(CO)$_2$Ph] (**2a**) in excellent yield (Table 1, entry 1). Although dinuclear complex [CpFe(CO)$_2$]$_2$ (**3**) was formed as a byproduct in the reactions with arylmagnesium,[5] arylzinc, or arylboron reagents,[6] no formation of **3** was observed in this

copper-mediated reaction. The combination of CuOTf and a catalytic amount of palladium acetate lowered the yield of **2a** (entry 2).[7] The amounts of the copper salt and the tin reagent could be reduced to 1.2 equiv to afford **2a** in slightly lower yield (entry 3). The phenylation reaction did not proceed efficiently in the presence of a catalytic amount of the copper salt (entry 4). Copper(II) trifluoromethanesulfonate and silver(I) trifluoromethanesulfonate showed lower activity (entries 5 and 6). In entries 4–6, the reactions afforded significant amounts of unidentified byproducts other than **1** and **2a**. Copper(I) halide showed no activity (entries 7–9).

Table 1. Optimization of Copper-Mediated Reaction of **1** with PhSn(n-Bu)$_3$[a]

$$\underset{\substack{\text{OC} \\ \text{OC} \quad \mathbf{1}}}{\text{Fe}-\text{I}} \quad \xrightarrow[\text{1,4-dioxane, 60 °C, 1 h}]{\substack{x \text{ equiv PhSn}(n\text{-Bu})_3 \\ y \text{ equiv additive}}} \quad \underset{\substack{\text{OC} \\ \text{OC} \quad \mathbf{2a}}}{\text{Fe}-\text{Ph}}$$

entry	x	additive	y	2a/%	1/%
1	2.0	CuOTf	2.0	97	0
2[b]	2.0	CuOTf	2.0	77	0
3	1.2	CuOTf	1.2	86	0
4	1.2	CuOTf	0.10	4	9
5	1.2	Cu(OTf)$_2$	1.2	27	0
6	1.2	AgOTf	1.2	17	1
7	1.2	CuI	1.2	0	82
8	1.2	CuBr	1.2	0	84
9	1.2	CuCl	1.2	0	47

[a] Yields were determined by ^{1}H NMR analysis of the crude products.
[b] With 10 mol% Pd(OAc)$_2$.

The author assumes that phenylcopper species would be generated from CuOTf and the phenyltin reagents[8] and would undergo transmetalation with **1** to afford **2a**.

The scope of aryltin reagents is summarized in Table 2. Basically, 1.3 equiv of the copper salt and 1.3 equiv of an aryltin reagent were used to complete the reactions. Sterically demanding (2-methylphenyl)tin reagent reacted with **1** to afford **2b** in modest yield (entry 2). The electronic nature of aryltin reagents had little effect on the yields of aryliron complexes, and

an electron-rich aryliron complex **2c** and electron-deficient ones **2d** and **2e** were obtained in high

yields (entries 3–5).   Thanks to the mild reactivity of organotin reagents, aryliron complexes

having a cyano (**2f**), acetyl (**2g**), and formyl (**2h**) group were readily prepared (entries 6–8).   It is

worth noting that aryliron complexes **2g** and **2h** could not be prepared from the corresponding

arylzinc or arylboron reagents under palladium catalysis.[6]   Unfortunately, the reaction of **1** with

(4-hydroxyphenyl)tin reagent failed to afford **2i** in reasonable yield (entry 9).

Table 2. Copper-Mediated Arylation of **1** with $ArSn(n\text{-}Bu)_3$

entry	Ar	2	yield/%
1	Ph	**2a**	86
2	$2\text{-MeC}_6\text{H}_4$	**2b**	68
3[a]	$4\text{-MeOC}_6\text{H}_4$	**2c**	80
4	$4\text{-FC}_6\text{H}_4$	**2d**	89
5	$3\text{-CF}_3\text{C}_6\text{H}_4$	**2e**	92
6	$4\text{-NCC}_6\text{H}_4$	**2f**	69
7	$4\text{-MeC(=O)C}_6\text{H}_4$	**2g**	91
8	$4\text{-HC(=O)C}_6\text{H}_4$	**2h**	84
9[b]	$4\text{-HOC}_6\text{H}_4$	**2i**	14

[a] $4\text{-MeOC}_6\text{H}_4\text{SnMe}_3$ was used. Performed for 5 min.
[b] With 2.0 equiv of tin reagent and 2.0 equiv of Cu salt. Performed for 20 min.

Conclusion

CuOTf has proven to mediate transmetalation between $[CpFe(CO)_2I]$ and aryltin reagents,

which represents an efficient method for the synthesis of various functionalized aryliron

complexes.   As notably demonstrated in the synthesis of **2g** and **2h**, this method shows a higher

functional group compatibility than the palladium-catalyzed arylation reaction with arylzinc or

arylboron reagents demonstrated in Chapter 2.   The iron complexes would be useful in various

fields of organic chemistry.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ [using tetramethylsilane (for ^{1}H, δ = 0.00 ppm) and CDCl$_3$ (for ^{13}C, δ = 77.2 ppm) as an internal standard] or C$_6$D$_6$ [using C$_6$H$_6$ (for ^{1}H, δ = 7.15 ppm) and C$_6$D$_6$ (for ^{13}C, δ = 128.6 ppm) as an internal standard]. IR spectra were determined on a JASCO IR-810 spectrometer. Mass spectra (EI) were determined on a JEOL Mstation 700 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 1,4-Dioxane was obtained from Wako Pure Chemicals Co. and was stored over slices of sodium. Copper(I) trifluoromethanesulfonate was purchased from Aldrich. Aryltin reagents were prepared according to the literature[9] and stored under argon. [CpFe(CO)$_2$I] was prepared according to the literature.[5] Silica gel (Wakogel 200 mesh) was used for column chromatography.

Typical Procedure for Copper-Mediated Arylation Reactions of [CpFe(CO)$_2$I] (Table 2, entry 1)

Dicarbonylcyclopentadienyliodoiron (**1**, 152 mg, 0.50 mmol), copper(I) trifluoromethanesulfonate/benzene complex (164 mg, 0.65 mmol), tributylphenyltin (239 mg, 0.65 mmol), and 1,4-dioxane (1.7 mL) were sequentially added in a 30-mL reaction flask under argon. The mixture was heated to 60 °C and stirred for 1 h. Then the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. After evaporation, silica gel column purification (eluent: CS$_2$) of the crude product provided dicarbonylcyclopentadienylphenyliron (**2a**, 109 mg, 0.43 mmol, 86% yield).

Characterization Data

The spectral data of the products **2a–2d**,[5] **2e** and **2f**,[6] can be found in the literature.

**Dicarbonylcyclopentadienyl(4-acetylphenyl)iron (2g)**
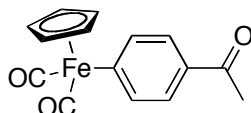
IR (nujol) 2022, 2007, 1943, 1672, 1356, 1275, 1006, 810 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ = 2.24 (s, 3H), 3.98 (s, 5H), 7.51 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H); ^{13}C NMR (C$_6$D$_6$) δ = 26.62, 86.33, 127.10, 134.40, 145.74, 159.77, 197.60, 216.66;   Found: C, 60.85; H, 4.46%.   Calcd for C$_{15}$H$_{12}$FeO$_3$: C, 60.84; H, 4.08%.   m.p.: 82–84 °C.

Dicarbonylcyclopentadienyl(4-formylphenyl)iron (2h)
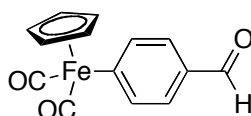
IR (nujol) 2283, 2014, 1964, 1943, 1685, 1573, 1546, 1179, 1037, 1008, 834, 813 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ = 3.94 (s, 5H), 7.42 (d, J = 5.5 Hz, 2H), 7.51 (d, J = 5.5 Hz, 2H), 9.84 (s, 1H); ^{13}C NMR (C$_6$D$_6$) δ = 86.34, 127.89, 134.19, 146.13, 163.74, 192.40, 216.42;   Found: C, 59.62; H, 3.73%.   Calcd for C$_{14}$H$_{10}$FeO$_3$: C, 59.61; H, 3.57%.   m.p.: 98–100 °C.

Dicarbonylcyclopentadienyl(4-hydroxyphenyl)iron (2i)
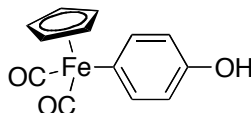
IR (nujol) 2013, 1942, 1583, 1534, 1365, 1289, 1236, 1187, 1146, 875, 845, 656 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.92 (s, 5H), 6.46 (bs, 1H), 6.85 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 86.44, 114.83, 129.64, 143.84, 158.75, 214.28;   HRMS (m/z) Observed: 269.9977 (Δ = –0.9 ppm).   Calcd for C$_{13}$H$_{10}$FeO$_3$: 269.9979.   m.p.: 75 °C (decomposition).

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Chapter 4

Use of Aryliron Complexes [CpFe(CO)$_2$Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents to Yield Ketones

Treatment of aryliron complexes [CpFe(CO)$_2$Ar] with organolithium reagents RLi in THF affords the corresponding ketones RCOAr.   The reaction, wherein the aryliron complexes serve as arylcarbonyl cation equivalents, would begin with nucleophilic addition of RLi to one of the carbonyl ligands to form acyliron [CpFe(CO)(RCO)Ar] without lithiation of the Cp ring.

Introduction

Dicarbonylcyclopentadienylorganoiron complexes [CpFe(CO)$_2$R] represent an important class of organometallic compounds due to their rich coordination chemistry.[1] The corresponding aryliron complexes [CpFe(CO)$_2$Ar] are fundamental 18-electron arylmetals, and several reliable methods for the synthesis of the aryliron complexes have been reported.[2] On the other hand, the chemical reactivity of the aryliron complexes has not been well investigated.[3–8] Thanks to the ubiquity and abundance of iron as a transition metal, the author has envisioned that [CpFe(CO)$_2$Ar] would serve as interesting arylating agents in organic synthesis and has been studying the reactivity and utility of [CpFe(CO)$_2$Ar].[2e–2g]

The reactions of [CpFe(CO)$_2$Ar] with organometallic reagents are rare. The reaction of [CpFe(CO)$_2$Ph] with excess butyllithium in THF at –78 °C was reported, leading to the lithiation of the cyclopentadienyl ring (Scheme 1).[9,10]
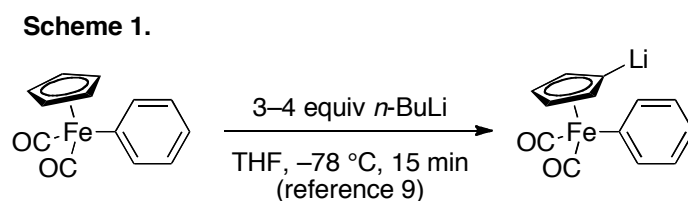
Scheme 1.

The author found that a similar reaction at a higher reaction temperature led to a completely different outcome. Iron complex [CpFe(CO)$_2$Ar] behaved as an arylcarbonyl cation equivalent to react with butyllithium. In Chapter 4, the author describes this reaction in detail.

## Results and Discussion

Treatment of [CpFe(CO)$_2$(4-tolyl)] (**1a**) with 2 equiv of butyllithium at –20 °C afforded butyl 4-tolyl ketone (**2a**) in 59% yield (Table 1, entry 1). Whereas bulky secondary and tertiary

butyllithiums reacted with **1a** to afford the corresponding ketones in modest yields (entries 2 and 3), methylation proceeded smoothly (entry 4).   The reaction of **1a** with phenyllithium furnished phenyl 4-tolyl ketone (**2e**) in excellent yield (entry 5).   The use of a smaller amount, 1.2 equiv, of phenyllithium diminished the yield of **2e** (entry 6).   Grignard reagents were ineffective for the formation of ketone, even at an elevated temperature (entry 7).

Other aryllithium reagents, prepared by bromine–lithium exchange, also engaged in the reaction (entries 8–14).   Despite their steric hindrance, bulky 2-tolyllithium and 1-naphthyllithium converted **1a** smoothly to the corresponding ketones in high yields (entries 8 and 9).   Although 4-methoxyphenyllithium reacted efficiently (entry 10), electron-deficient aryllithium reagents were less reactive (entries 11–13).

Table 1. Reactions of [CpFe(CO)$_2$(4-tolyl)] with Organolithium Reagents
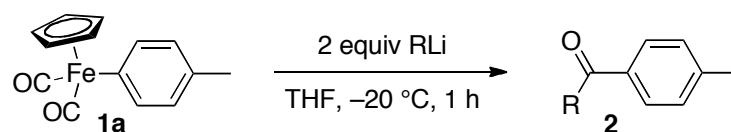
| entry	R	2	yield/%
1	*n*-Bu	**2a**	59
2	*s*-Bu	**2b**	37
3	*t*-Bu	**2c**	36
4	Me	**2d**	63
5	Ph	**2e**	91
6[a]	Ph	**2e**	68
7[b]	Ph	**2e**	4
8[c]	2-MeC$_6$H$_4$	**2f**	71
9[c]	1-naphthyl	**2g**	75
10[c]	4-MeOC$_6$H$_4$	**2h**	65
11[c]	4-FC$_6$H$_4$	**2i**	52
12[c,d]	4-CF$_3$C$_6$H$_4$	**2j**	47
13[c]	4-ClC$_6$H$_4$	**2k**	46
14[c]	4-PhC$_6$H$_4$	**2l**	79

[a] 1.2 equiv of PhLi. [b] Instead of PhLi, PhMgBr was used at 25 °C.
[c] The aryllithium reagent was prepared from 2 equiv of the corresponding aryl bromide and 4 equiv of *tert*-butyllithium at −20 °C.
[d] The aryllithium reagent was prepared at −78 °C and reacted with **1a** at −20 °C.

The reactions of various aryliron complexes with phenyllithium were investigated (Table 2). Sterically demanding arylirons **1d** and **1f** were available for use (entries 3 and 5), while the 1-naphthyl group of **1d** retarded the reaction. Halophenylirons **1g**–**1i** and electron-deficient aryliron **1j** underwent the reaction to afford the corresponding benzophenone derivatives in high yields (entries 6–9). The reaction of electron-rich 4-methoxyphenyliron **1k** was slow, requiring a higher temperature to obtain **2v** in moderate yield (entry 10). The methoxy group lowered the electrophilicity of **1k**.

Table 2. Scope of Aryliron Complexes
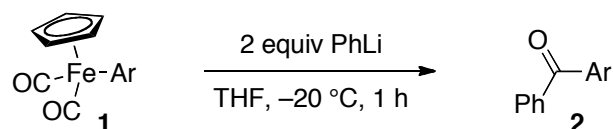
entry	Ar	1	2	yield/%
1	4-PhC$_6$H$_4$	**1b**	**2m**	74
2	2-naphthyl	**1c**	**2n**	86
3[a]	1-naphthyl	**1d**	**2o**	65
4	4-t-BuC$_6$H$_4$	**1e**	**2p**	91
5	2-MeC$_6$H$_4$	**1f**	**2q**	76
6	4-ClC$_6$H$_4$	**1g**	**2r**	85
7	4-FC$_6$H$_4$	**1h**	**2s**	83
8	4-BrC$_6$H$_4$	**1i**	**2t**	68
9	3-CF$_3$C$_6$H$_4$	**1j**	**2u**	89
10[b]	4-MeOC$_6$H$_4$	**1k**	**2v**	59

[a] Performed at 25 °C. [b] Performed at 0 °C.

The reaction of iron complex **1l**, bearing an ester group, with 2.5 equiv of phenyllithium resulted in selective nucleophilic addition at the ester moiety, providing iron complex **1m** (Scheme 2). The reactivity of the carbonyl ligands proved to be lower than that of the ester carbonyl. With 4 equiv of phenyllithium, the aryliron moiety acted as an arylcarbonyl cation equivalent to yield ketone **2w**.

Scheme 2. Reaction of (Ethoxycarbonylphenyl)iron Complex **1l**
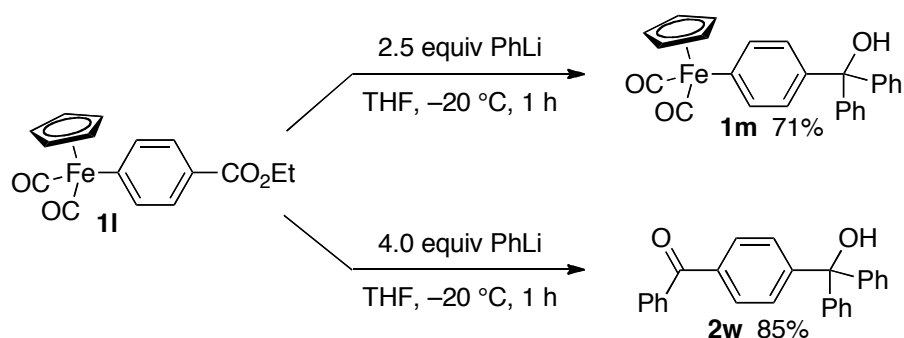
The author had initially proposed a draft mechanism as shown in Scheme 3. The reaction would begin with nucleophilic addition of Ar'Li to the carbonyl group of [CpFe(CO)$_2$Ar] (**1**) to form acylferrate [CpFe(CO)(Ar'CO)Ar]Li (**3**).[11] Acylferrate **3** might undergo reductive elimination to yield ketone **2**.

Scheme 3. Draft Mechanism
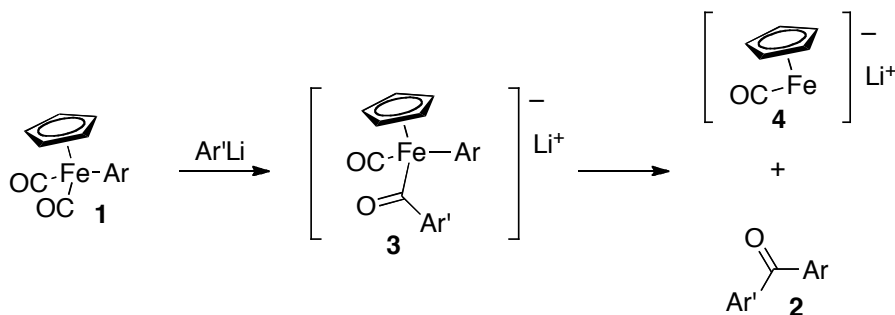
However, there are two issues to be addressed. While the mechanism in Scheme 3 should require only 1 equiv of PhLi in principle, the higher yield of **2e** was obtained when 2 equiv of PhLi was used (Table 1, entry 5 vs entry 6). It is also worth noting that no further nucleophilic attack of organolithium to ketone **2** was observed despite the use of 2 equiv of organolithium.

To gain more information about the reaction mechanism, he examined the following experiment. Treatment of **1a** with 2 equiv of PhLi in THF at –20 °C for 1 h was followed by an addition of 4-isopropylbenzaldehyde (**5**, 1.0 equiv) (Scheme 4). After quenching with water, the

reaction afforded (4-isopropylphenyl)(phenyl)methanol (**6**) in 27 % yield along with an 80% yield of **2e** and a 30% recovery of the aldehyde **5**. The formation of **6** and the absence of triarylmethanol **7** suggest that ketone **2e** is protected from the nucleophilic attack of organolithium under the reaction conditions.

Scheme 4. Attempt To Trap PhLi with Aldehyde **5**
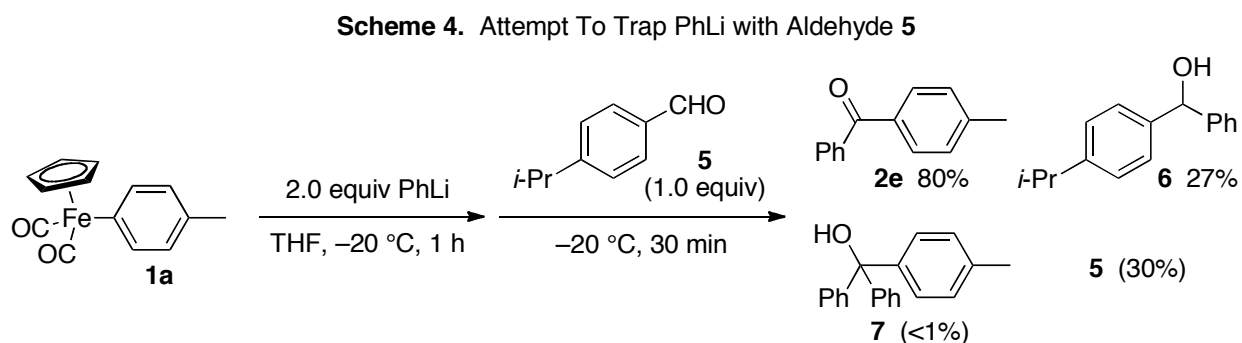
He presumes that ketone **2e** exists in the resonance of **8** and **8'** (Scheme 5).[12] The (η^2-ketone)iron complex would be formed via nucleophilic migration of the reactive Ar anion to the acyl carbonyl.[13] The η^2 complexation is not robust, and liberation of ketone **2** would take place upon addition of water.

The formation of **6** clarifies that 1.7 equiv of phenyllithium was consumed before the addition of **5** and suggests that 0.7 equiv of aryllithium might attack the second carbonyl ligand to yield diacylferrate **9** (Scheme 5). The Ar group of the higher order ferrate **9** would be more reactive than that of **3** and undergo smoother migration to yield a hybrid of **10** and **10'**. The subsequent protonolysis would afford **2**.[14]

Scheme 5. Detailed Plausible Reaction Mechanism
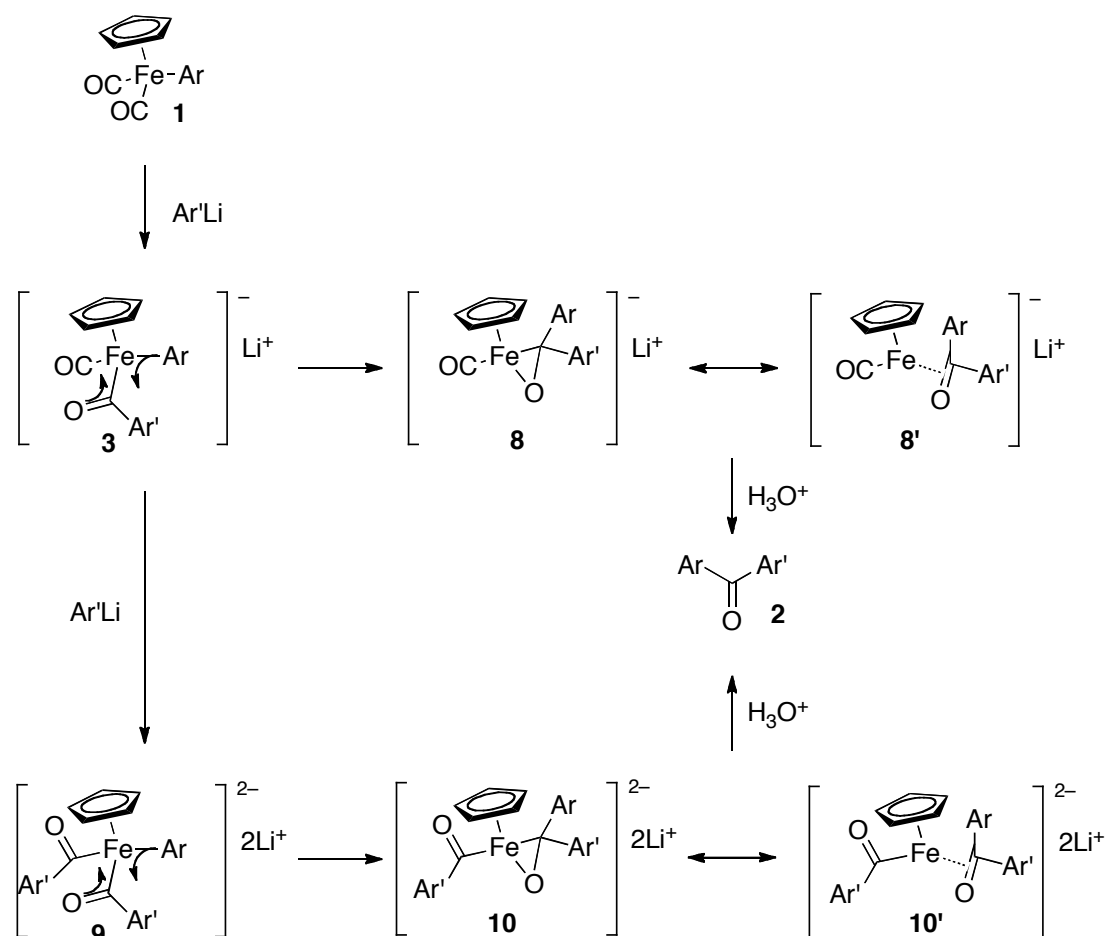
The following experiments verified that the lithiation of the Cp ring by the excess amount of RLi[9,10] did not occur under the present conditions. Treatment of **1a** with only 1.0 equiv of PhLi was followed by quenching with D_2O (Scheme 6). The reaction afforded **2e** in 62% yield, and **1a** was recovered in 25% yield. The recovered **1a** had only the natural abundance of deuterium. The use of 1.0 equiv of *n*-BuLi at –20 °C also resulted in no deuterium incorporation (47% of **2a** and 37% of **1a**). Given that the lithiation of the Cp ring is irreversible, the lithiation would predominate kinetically at –78 °C and the nucleophilic attack would occur under kinetic control at –20 °C.

Scheme 6.
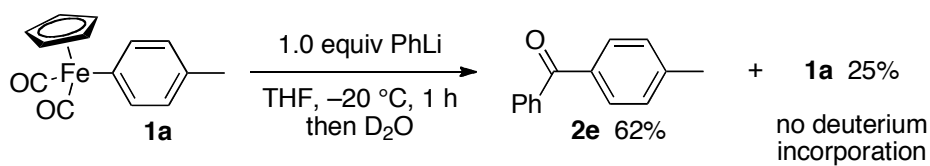
Conclusion

[CpFe(CO)₂Ar] complexes have emerged as arylcarbonyl cation equivalents in the reaction with organolithium reagents. In contrast to the previous report on the reaction of [CpFe(CO)₂Ar] with organolithium, no metalation of the Cp ring was observed. This finding represents a new chemical reactivity of [CpFe(CO)₂Ar] toward organometallic reagents and will be applicable to organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ [using tetramethylsilane (for ^{1}H, δ = 0.00 ppm) and CDCl$_3$ (for ^{13}C, δ = 77.2 ppm) as an internal standard] or C$_6$D$_6$ [using C$_6$H$_6$ (for ^{1}H, δ = 7.15 ppm) and C$_6$D$_6$ (for ^{13}C, δ = 128.6 ppm) as an internal standard]. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. [CpFe(CO)$_2$Ar] were synthesized by palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and arylmetal reagents according to the methods reported in Chapters 1–3.[2e–2g] THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Organolithium reagents were commercially available or prepared as described below.

Typical Procedure for Reactions of [CpFe(CO)$_2$Ar] with Organolithium Reagents (Table 1, entry 5)

Dicarbonylcyclopentadienyl(4-methylphenyl)iron (**1a**, 80 mg, 0.30 mmol) and THF (1.5 mL) were added in a 20-mL reaction flask under argon. The mixture was cooled to –20 °C and then phenyllithium (1.1 M cyclohexane/Et$_2$O solution, 0.55 mL, 0.60 mmol) was added. After being stirred for 1 h at –20 ˚C, saturated ammonium chloride solution (0.13 mL) was added to the reaction mixture. The mixture was filtered through a pad of silica gel, and the filtrate was concentrated. Silica gel column purification (eluent: hexane/ethyl acetate = 40:1) of the crude

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product provided phenyl 4-tolyl ketone (**2e**, 53 mg, 0.27 mmol, 91% yield).

Typical Procedure for Reactions of [CpFe(CO)₂(4-tolyl)] with Aryllithium Reagents Generated in situ by Br/Li Exchange Reactions (Table 1, entry 14)

4-Bromobiphenyl (140 mg, 0.60 mmol) and THF (1.0 mL) were added in a 20-mL reaction flask under argon. The mixture was cooled to –20 °C and then *t*-butyllithium (1.6 M pentane solution, 0.75 mL, 1.2 mmol) was added. After being stirred for 30 min at –20 °C, dicarbonylcyclopentadienyl(4-methylphenyl)iron (**1a**, 80 mg, 0.30 mmol) in THF (1.0 mL) was added to the reaction mixture. After being stirred for 1 h at –20 ˚C, saturated ammonium chloride solution (0.26 mL) was added to the reaction mixture. The mixture was filtered through a pad of silica gel, and the filtrate was concentrated. Silica gel column purification (eluent: hexane/ethyl acetate = 40:1) of the crude product provided 4-biphenylyl phenyl ketone (**2l**, 65 mg, 0.24 mmol, 79% yield).

Procedure for Reaction of [CpFe(CO)₂(4-tolyl)] with Phenyllithium and Subsequent Trap of Phenyllithium with 4-Isopropylbenzaldehyde (Scheme 4)

Dicarbonylcyclopentadienyl(4-methylphenyl)iron (**1a**, 80 mg, 0.30 mmol) and THF (1.5 mL) were added in a 20-mL reaction flask under argon. The mixture was cooled to –20 °C and then phenyllithium (1.1 M cyclohexane/Et₂O solution, 0.55 mL, 0.60 mmol) was added. After being stirred for 1 h at –20 ˚C, 4-isopropylbenzaldehyde (**5**, 44 mg, 0.30 mmol) was added to the reaction mixture. After being stirred for 30 min at –20 ˚C, saturated ammonium chloride solution (0.13 mL) was added to the reaction mixture. The mixture was filtered through a pad of silica gel, and the filtrate was concentrated. The yields of phenyl 4-tolyl ketone (**2e**), (4-isopropylphenyl)(phenyl)methanol (**6**), (4-methylphenyl)diphenylmethanol (**7**), and 4-isopropylbenzaldehyde (**5**) were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard. The formation of (4-isopropylphenyl)(phenyl)methanol (**6**) was confirmed by the comparison with the ¹H NMR chart of an authentic sample of

(4-isopropylphenyl)(phenyl)methanol (**6**) synthesized by the reaction of 4-isopropylbenzaldehyde (**5**) with phenyllithium.

Characterization Data

The product **2p** showed the spectra identical to that of the commercially available authentic sample.   The spectral data of the products **1a**,[2c] **1b**,[2c] **1d**,[2f] **1f–1l**,[2e–2g] **2a**,[15] **2b**,[15] **2c**,[16] **2d**,[17] **2e**,[15] **2f**,[15] **2g**,[17] **2h**,[15] **2i**,[15] **2k**,[17] **2m**,[18] **2n**,[17] **2o**,[16] **2q**,[17] **2r**,[16] **2s**,[17] **2t**,[17] and **2v**[16] can be found in the literature.

**Dicarbonylcyclopentadienyl(2-naphthyl)iron (1c)**
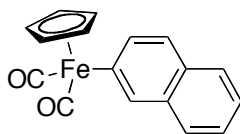
IR (nujol) 2342, 2021, 1998, 1970, 1944, 1574, 1456, 1419, 813, 745, 644, 628 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 4.90 (s, 5H), 7.28 (dd, J = 7.5, 7.0 Hz, 1H), 7.36 (dd, J = 8.0, 7.0 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.55–7.59 (m, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.93 (s, 1H); ^{13}C NMR (CDCl$_3$) δ = 86.14, 124.08, 125.51, 125.53, 125.94, 127.73, 131.09, 134.20, 143.07, 143.30, 143.90, 216.27; Found: C, 67.11; H, 3.94%.   Calcd for C$_{17}$H$_{12}$FeO$_2$: C, 67.14; H, 3.98%.   m.p.: 94–95 °C.

**Dicarbonylcyclopentadienyl(4-*t*-butylphenyl)iron (1e)**
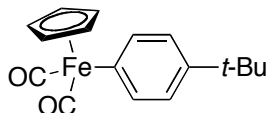
IR (nujol) 2002, 1966, 1945, 1917, 1479, 1464, 1362, 1116, 1004, 809, 729, 632, 594 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.27 (s, 9H), 4.86 (s, 5H), 7.02 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 31.44, 33.80, 85.70, 124.83, 139.89, 144.45, 145.60, 216.21;   Found: C, 65.57; H, 5.75%.   Calcd for C$_{17}$H$_{18}$FeO$_2$: C, 65.83; H, 5.85%.   m.p.: 106–107 °C.

## Dicarbonylcyclopentadienyl(4-(hydroxydiphenylmethyl)phenyl)iron (1m)
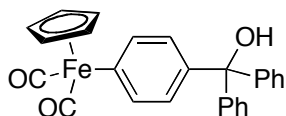
IR (nujol) 3548, 2022, 1970, 1957, 1448, 1157, 998, 818, 757, 700 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ = 2.41 (s, 1H), 4.01 (s, 5H), 7.03–7.06 (m, 2H), 7.09–7.11 (m, 6H), 7.42 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 7.5 Hz, 4H); ^{13}C NMR (C$_6$D$_6$) δ = 82.67, 86.27, 127.67, 128.57, 128.91, 129.14, 143.46, 144.97, 145.23, 148.85, 217.27; Found: C, 71.31; H, 4.52%. Calcd for C$_{26}$H$_{20}$FeO$_3$: C, 71.58; H, 4.62%. m.p.: 116–117 °C.

4-Tolyl 4-trifluoromethylphenyl ketone (2j)
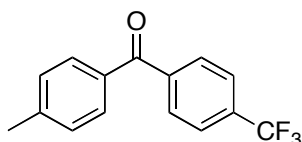
IR (nujol) 1647, 1605, 1407, 1329, 1171, 1136, 1110, 1067 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.46 (s, 3H), 7.30–7.32 (m, 2H), 7.71–7.73 (m, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 22.07, 124.04 (q, J_{C-F} = 271.1 Hz), 125.63 (q, J_{C-F} = 3.9 Hz), 129.58, 130.36, 130.69, 133.83 (q, J_{C-F} = 32.5 Hz), 134.40, 141.46, 144.44, 195.64; Found: C, 68.13; H, 4.35%. Calcd for C$_{15}$H$_{11}$F$_3$O: C, 68.18; H, 4.20%. m.p.: 136–137 °C.

4-Biphenylyl 4-tolyl ketone (2l)
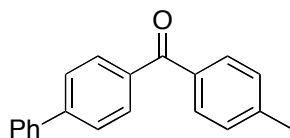
IR (nujol) 1644, 1604, 1275, 933, 855, 826, 776, 739, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.46 (s, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.39–7.42 (m, 1H), 747–7.50 (m, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 9.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 22.01, 127.25, 127.64, 128.47, 129.30, 129.35, 130.60, 130.95, 135.37, 136.94, 140.40, 143.54,

145.33, 196.47;   Found: C, 88.29; H, 5.94%.   Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.   m.p.: 122–124 °C.

Phenyl 3-trifluoromethylphenyl ketone (2u)
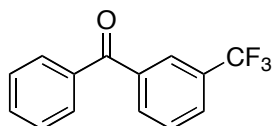
IR (nujol) 1654, 1337, 1266, 1170, 1118, 1073, 725, 715, 691, 660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.50–7.54 (m, 2H), 7.62–7.65 (m, 2H), 7.79–7.81 (m, 2H), 7.85 (d, J = 7.5 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR (CDCl$_3$) δ = 123.91 (q, J_{C-F} = 271.1 Hz), 126.90 (q, J_{C-F} = 3.9 Hz), 128.78, 129.03 (q, J_{C-F} = 3.4 Hz), 129.16, 130.23, 131.22 (q, J_{C-F} = 32.3 Hz), 133.22, 133.32, 136.98, 138.51, 195.41;   Found: C, 67.24; H, 3.37%.   Calcd for $C_{14}H_9F_3O$: C, 67.20; H, 3.63%.   HRMS (m/z) Observed: 250.0603 (Δ = –1.0 ppm). Calcd for $C_{14}H_9F_3O$: 250.0605. m.p.: 48–49 °C.

4-(Hydroxydiphenylmethyl)phenyl phenyl ketone (2w)
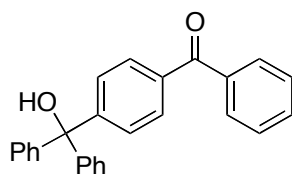
IR (neat) 3444, 1658, 1599, 1447, 1405, 1318, 1279, 764, 732, 701, 680 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ = 2.51 (s, 1H), 7.06–7.19 (m, 9H), 7.33 (d, J = 7.5 Hz, 4H), 7.38 (d, J = 9.0 Hz, 2H), 7.71–7.75 (m, 4H); ^{13}C NMR (C$_6$D$_6$) δ = 82.55, 128.19, 128.53, 128.71, 128.93, 128.97, 130.51, 130.79, 132.64, 137.43, 138.83, 147.68, 152.12, 196.01;   Found: C, 85.67; H, 5.66%.   Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%.

(4-Isopropylphenyl)(phenyl)methanol (6)
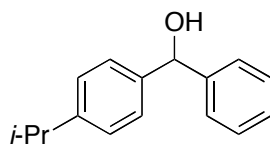

^{1}H NMR (CDCl$_3$) δ = 1.22 (d, *J* = 7.0 Hz, 6H), 2.29 (d, *J* = 8.0 Hz, 1H), 2.88 (sept, *J* = 7.0 Hz, 1H), 5.79 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.23–7.26 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.30–7.33 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 24.17, 33.99, 76.33, 126.67, 126.77, 126.79, 127.64, 128.62, 141.47, 144.08, 148.47.

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12. Complexes having an open structure such as **8"** are also conceivable.

OC–Fe(Ar)(Ar')(OLi)   **8"**
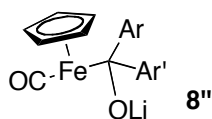
13. The conventional reductive elimination process may provide the same complex.

14. Although the protonolysis is likely to yield aldehyde Ar'CHO, none of the aldehyde was detected.   Prior to the protonolysis of the (arylcarbonyl)iron moiety Ar'C(=O)Fe, decarbonylation could occur to yield Ar'Fe(CO), which then undergoes protonolysis.

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# Chapter 5

Arylation of Styrenes with Aryliron Complexes [CpFe(CO)$_2$Ar]

Treatment of aryliron complexes [CpFe(CO)$_2$Ar] with styrenes in boiling xylene affords the corresponding stilbenes.

Introduction

Organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)$_2$R] are utilized as useful organometallic reagents in organic synthesis.[1]   Among them, the reactions of the corresponding aryliron complexes [CpFe(CO)$_2$Ar] are still unexplored.[2–8]   Studies on chemical reactivity of [CpFe(CO)$_2$Ar] would provide useful organic reactions because they are expected to show different reactivity from other arylmetal reagents.   Recently, the author has developed the efficient synthesis of [CpFe(CO)$_2$Ar] and has been pursuing their synthetic utility as useful arylmetal reagents.[9,10]   In the course of these studies, he now reports that [CpFe(CO)$_2$Ar] react with styrenes to yield the corresponding stilbenes.[11]   The reaction would begin with insertion of the C=C bond of styrene into the aryl–iron bond.   Insertion of unsaturated bonds into aryl–iron bonds of [CpFe(CO)$_2$Ar] is well known.[2,3]   However, there has been only one report on application of such insertion to useful organic transformation.[2]

Results and Discussion

Treatment of [CpFe(CO)$_2$(4-tolyl)] (**1a**) with 2 equiv of styrene in refluxing xylene afforded 4-methylstilbene (**3a**) in 79% yield (Table 1, entry 1).   The high temperature is essential.   The yield of **3a** was much lower when the similar reaction was performed at a lower temperature (entry 2).   Electron-rich styrene **2b** and electron-deficient ones **2c** and **2d** reacted with **1a**, although the yields of the corresponding products were modest (entries 3–5).   The reactions with styrenes having a bromo (**2e**) and acetoxy (**2f**) group proceeded to afford **3e** and **3f** in modest yields, leaving the functional groups untouched (entries 6 and 7).   Unfortunately, alkenes other than styrenes were much less reactive in the reactions.   For examples, the reactions with ethyl acrylate (**2g**) and vinyl boronate **2h** were sluggish (entries 8 and 9).   In all cases, some amounts of hydridoiron complex [CpFe(CO)$_2$H] was formed as a byproduct.

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Table 1. Reactions of [CpFe(CO)$_2$(4-tolyl)] with Various Styrenes
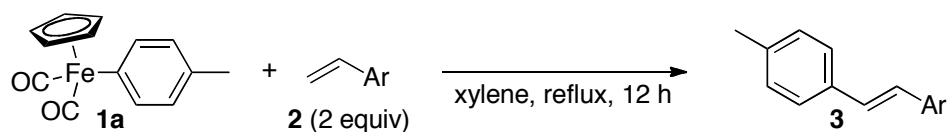
entry	Ar	2	3	yield/%
1	Ph	**2a**	**3a**	79
2[a]	Ph	**2a**	**3a**	23
3	4-MeOC$_6$H$_4$	**2b**	**3b**	59
4	4-FC$_6$H$_4$	**2c**	**3c**	71
5	4-ClC$_6$H$_4$	**2d**	**3d**	58
6	4-BrC$_6$H$_4$	**2e**	**3e**	53
7	4-AcOC$_6$H$_4$	**2f**	**3f**	50
8	(CH$_2$=CHCO$_2$Et)	**2g**	**3g**	15[b]
9	(CH$_2$=CHB(pin))	**2h**	**3h**	10[b]

[a] Performed in refluxing toluene.
[b] Yield determined by ^{1}H NMR analysis of the crude product.

This arylation reaction with [CpFe(CO)$_2$Ar] was much affected by steric effects. Unfortunately, the reactions of **1a** with sterically demanding α-methylstyrene (**2i**) and β-methylstyrene (**2j**) failed to afford the corresponding stilbene derivatives **3i** and **3j** in reasonable yields (Schemes 1 and 2).

Scheme 1.
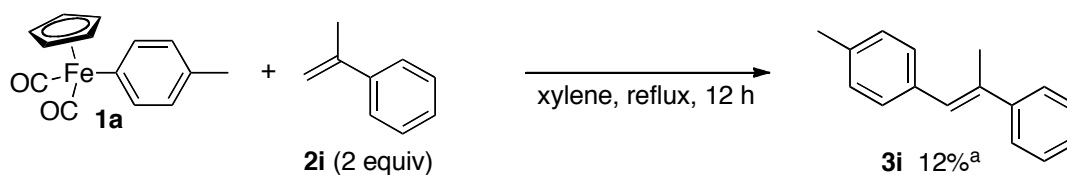
Scheme 2.
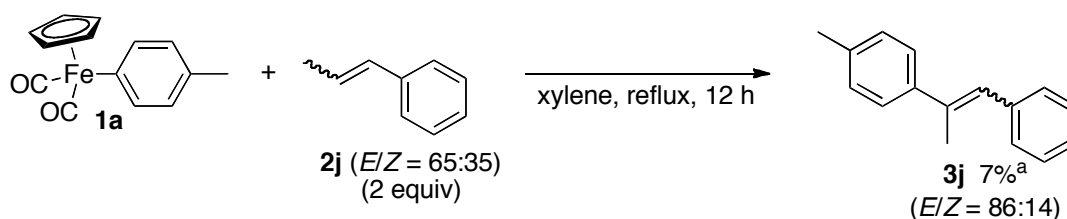
[a] Yield determined by ^{1}H NMR analysis of the crude product.

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The reactions of various aryliron complexes with styrene were investigated (Table 2). The reaction of 2-naphthyliron **1b** afforded **3k** in slightly lower yield than the case of **1a** (entry 1). The reaction of sterically demanding aryliron **1c** was sluggish (entry 2). Electron-rich aryliron **1d**, halophenylirons **1e–1g,** and electron-deficient aryliron **1h** underwent the reaction to afford the corresponding stilbene derivatives in modest yields (entries 3–7). The reaction of arylirons having an ester (**1i**) and a boron (**1j**) moiety occurred selectively at the iron–carbon bond without affecting the functional groups (entries 8 and 9).

Table 2. Scope of Aryliron Complexes

2a (2 equiv)   xylene, reflux, 12 h
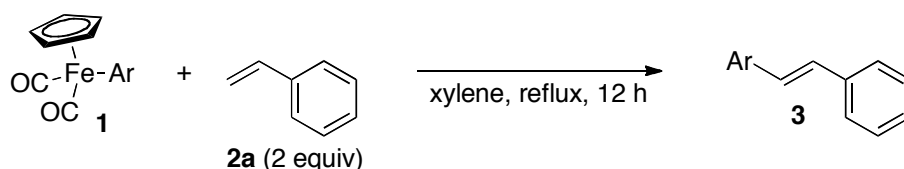
entry	Ar	1	3	yield/%
1	2-Naphthyl	**1b**	**3k**	69
2	2-MeC$_6$H$_4$	**1c**	**3l**	32
3	4-MeOC$_6$H$_4$	**1d**	**3m**	53
4	4-FC$_6$H$_4$	**1e**	**3n**	57
5	4-ClC$_6$H$_4$	**1f**	**3o**	58
6	4-BrC$_6$H$_4$	**1g**	**3p**	58
7[a]	3-CF$_3$C$_6$H$_4$	**1h**	**3q**	58
8	4-EtOC(=O)C$_6$H$_4$	**1i**	**3r**	70
9[a]	4-(pin)BC$_6$H$_4$	**1j**	**3s**	84

[a] Performed for 24 h.

The reaction would proceed as shown in Scheme 3. Insertion of the C=C bond of styrene into the aryl–iron bond would generate the corresponding alkyliron complex. Subsequent β-hydride elimination affords the stilbene derivative.[12]

Scheme 3.
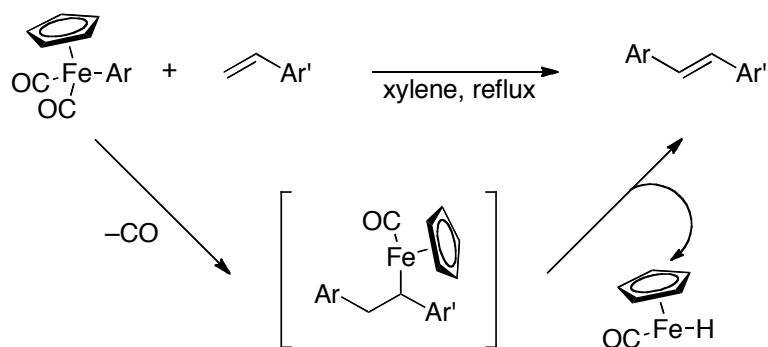
The author assumed another mechanism that Ar radical generated in situ would participate in the reaction. Therefore, he carried out the reaction of **1a** with **2a** in the presence of radical inhibitor, TEMPO. The reaction proceeded to afford **3a** in 45% yield, although the yield was lower than the case in the absence of TEMPO (vs. Table 1, entry 1). This result rules out the mechanism in which Ar radical reacts with styrene to yield the product.

Conclusion

[CpFe(CO)$_2$Ar] complexes have emerged as arylating agents in the reaction with styrenes. This reaction utilizes insertion of the C=C bond of styrene into the aryl–iron bond, representing a new chemical reactivity of [CpFe(CO)$_2$Ar] toward carbon–carbon multiple bonds. The reaction will be applicable to organic synthesis.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to CDCl$_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. [CpFe(CO)$_2$Ar] were synthesized by palladium-catalyzed transmetalation between [CpFe(CO)$_2$I] and arylmetal reagents according to the methods reported in Chapters 1–3.[9a–c,9e] Xylene was purchased from Nacalai Tesque. and was stored over slices of sodium.

Typical Procedure for Reactions of [CpFe(CO)$_2$Ar] with Styrenes (Table 1, entry 1)

Dicarbonylcyclopentadienyl(4-methylphenyl)iron (**1a**, 80 mg, 0.30 mmol), styrene (62 mg, 0.60 mmol), and xylene (1.5 mL) were sequentially added in a 30-mL reaction flask under argon. The mixture was heated at reflux for 12 h. Then the reaction mixture was cooled to room temperature and filtered through a pad of silica gel. After evaporation, silica gel column purification (eluent: hexane) of the crude product provided 4-methylstilbene (**3a**, 46 mg, 0.24 mmol, 79% yield).

Characterization Data

The spectral data of the products **3a**,[13] **3b**,[14] **3d**,[13] **3e**,[15] **3g**,[16] **3h**,[17] **3i**,[18] **3j**,[19] **3k**,[20] **3l**,[13] **3m**,[21] **3o**,[13] **3p**,[21] **3q**,[22] **3r**,[23] and **3s**[24] can be found in the literature.

### (*E*)-4-Fluoro-4'-methylstilbene (3c)
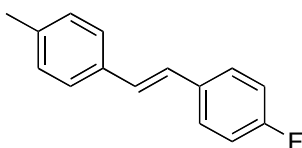
IR (nujol) 1507, 1233, 1210, 972, 829, 719 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.36 (s, 3H), 7.00 (d, *J* = 4.0 Hz, 2H), 7.02–7.05 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.44–7.47 (m, 2H); ^{13}C NMR (CDCl$_3$) δ = 21.46, 115.78 (d, J_{C-F} = 21.5 Hz), 126.57, 126.71, 128.04 (d, J_{C-F} = 8.1 Hz), 128.64 (d, J_{C-F} = 2.4 Hz), 129.63, 133.92 (d, J_{C-F} = 3.4 Hz), 134.61, 137.79, 162.43 (d, J_{C-F} = 245 Hz);   Found: C, 84.63; H, 6.28%.   Calcd for C$_{15}$H$_{13}$F: C, 84.88; H, 6.17%.   m.p.: 125–126 °C.

(*E*)-4-[2-(4-Methylphenyl)ethenyl]phenyl acetate (3f)
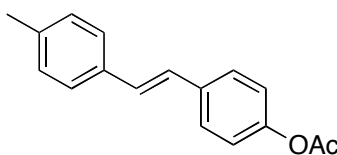
IR (nujol) 1752, 1701, 1685, 1507, 1223, 1196, 1013, 972, 915 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 2.30 (s, 3H), 2.36 (s, 3H), 7.03 (s, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 21.35, 21.46, 121.96, 126.63, 126.87, 127.49, 129.09, 129.62, 134.60, 135.57, 137.83, 150.10, 169.67;   Found: C, 80.69; H, 6.46%.   Calcd for C$_{17}$H$_{16}$O$_2$: C, 80.93; H, 6.39%.   m.p.: 157–159 °C.

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(*E*)-4-Fluorostilbene (3n)
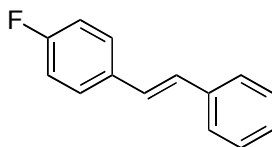
IR (nujol) 1030, 964, 824, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 6.99–7.08 (m, 4H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.45–7.50 (m, 4H); ^{13}C NMR (CDCl$_3$) δ = 115.82 (d, *J*$_{C-F}$ = 22.0 Hz), 126.65, 127.70, 127.87, 128.19 (d, *J*$_{C-F}$ = 7.8 Hz), 128.71 (d, *J*$_{C-F}$ = 2.4 Hz), 128.92, 133.74 (d, *J*$_{C-F}$ = 3.4 Hz), 137.39, 162.55 (d, *J*$_{C-F}$ = 245.8 Hz);   Found: C, 84.82; H, 5.55%.   Calcd for C$_{14}$H$_{11}$F: C, 84.82; H, 5.59%.   m.p.: 118–119 °C.

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Appendix

## Vanadium-Catalyzed Cross-Coupling Reactions of Alkyl Halides with Aryl Grignard Reagents

Vanadium(III) chloride catalyzed cross-coupling reactions of alkyl halides with arylmagnesium bromides. Various arylmagnesium bromides, except for an ortho-substituted arylmagnesium reagent, could be used for the reaction.   Among alkyl halides tested, cyclohexyl halides and primary alkyl halides were good substrates. The reactions likely proceed via carbon-centered radical intermediates.

Introduction

Transition-metal-catalyzed cross-coupling reactions are useful in organic synthesis, and recently, cross-coupling reactions of alkyl halides with organometallic reagents have attracted increasing attention.[1,2]   To achieve this rather difficult transformation, copper, palladium, nickel, manganese, iron, and cobalt have been used as the catalysts.   Herein, the author reports the catalytic activity of vanadium for the cross-coupling reactions of alkyl halides with aryl Grignard reagents.

Results and Discussion

Treatment of bromocyclohexane with phenylmagnesium bromide in the presence of a catalytic amount of vanadium(III) chloride in THF afforded cyclohexylbenzene (**1a**) in high yield (Table 1, entry 1).   *p*-Methoxy- and *p-tert*-butylphenylmagnesium bromides also reacted with bromocyclohexane smoothly (entries 2 and 3).   The reaction with *p*-fluorophenylmagnesium bromide gave the corresponding coupling product **1d** in good yield, although the reaction required a higher temperature (entry 4).   An aryl Grignard reagent having a trifluoromethyl group at the meta position reacted less efficiently to yield product **1e** in modest yield (entry 5). When an aryl Grignard reagent had a substituent at the ortho position, the coupling reaction was completely suppressed (entry 6).   In all cases, except for entry 6, bromocyclohexane was completely consumed.

Table 1. Vanadium-Catalyzed Reactions of Bromocyclohexane with Arylmagnesium Bromide[a]
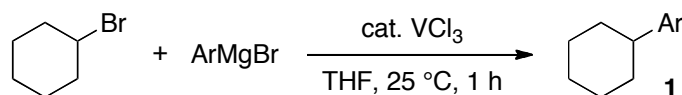
entry	Ar	yield/%
1	Ph	**1a**, 75
2	p-MeOC$_6$H$_4$	**1b**, 68
3	p-(t-Bu)C$_6$H$_4$	**1c**, 67
4	p-FC$_6$H$_4$	**1d**, 69[b]
5	m-CF$_3$C$_6$H$_4$	**1e**, 49[b,c]
6	o-MeC$_6$H$_4$	**1f**, 0[b,c,d]

[a] Conditions: Bromocyclohexane (0.50 mmol), ArMgBr (1.0 mmol, 1 M THF solution), VCl$_3$ (0.050 mmol, 0.050 M THF solution).
[b] Performed at reflux. [c] Performed for 3 h.
[d] Bromocyclohexane (15%) was recovered.

Not only bromocyclohexane but also its iodo and chloro analogues reacted with phenylmagenesium bromide in the presence of VCl$_3$ (Table 2, entries 1 and 2). Halocyclohexanes are exceptionally good substrates for the vanadium-catalyzed reaction. The reactions of bromocyclopentane and bromocycloheptane afforded the corresponding products in 37% and 8% yields, respectively, in refluxing THF (entries 3 and 4). The reactions of acyclic secondary alkyl halides were not efficient. Namely, 2-bromododecane and 2-iodobutane were converted to the corresponding phenylated products in low yields (entries 5 and 6). In contrast, primary alkyl iodide, 1-iododecane, reacted smoothly at room temperature (entry 7). The reaction of 1-bromodecane was slow and required an elevated temperature (entry 8). *tert*-Butyl bromide did not undergo the coupling reaction, and, instead, 2-methylpropene and isobutane were produced.

Table 2. Vanadium-Catalyzed Reactions of Various Alkyl Halides with Phenylmagnesium Bromide[a]

$$R-X \quad + \quad PhMgBr \quad \xrightarrow[\text{THF, 25 °C, 1 h}]{\text{cat. VCl}_3} \quad R-Ph$$

entry	R–X	yield/%
1	Iodocyclohexane	**1a**, 75
2	Chlorocyclohexane	**1a**, 62[b,c]
3	Bromocyclopentane	**2a**, 37[b]
4	Bromocycloheptane	**2b**, 8[b,c]
5	2-Bromododecane	**2c**, 34[d]
6	2-Iodobutane	**2d**, 21
7	1-Iododecane	**2e**, 74
8	1-Bromodecane	**2e**, 66[b]

[a] Conditions: Haloalkane (0.50 mmol), PhMgBr (1.0 mmol, 1 M THF solution), VCl$_3$ (0.050 mmol, 0.050 M THF solution).
[b] Performed at reflux. [c] Performed for 5 h.
[d] 1-Dodecene (39%), 2-dodecene (14%), and dodecane (10%) were formed.

It is worth noting that the reactions in diethyl ether, instead of THF, afforded none of the phenylated products, although the starting material was fully converted. Cyclohexane and cyclohexene were formed instead. Dioxane was equally effective as THF as a solvent. Namely, the reactions in dioxane gave the coupling products in yields similar to those in THF. A variety of additives (0.050 mmol), such as *N,N,N',N'*-tetramethylethylenediamine, 4-(dimethylamino)pyridine, *N*-methylmorpholine, triphenylphosphine, trimethylphosphine, tricyclohexylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, and *N*-heterocyclic carbene ligands, had no effects on the reactions. Addition of 2,2'-bipyridyl suppressed the reaction completely. Other vanadium compounds such as VO(acac)$_2$ and V(acac)$_3$ also exhibited catalytic activity, although their activities were modest (49% and 45% yields, for the reaction of chlorocyclohexane with phenylmagnesium bromide, respectively). Cp$_2$VCl$_2$ did not show any catalytic activity.

Treatment of 6-bromo-1-hexene with phenylmagnesium bromide in the presence of a catalytic amount of VCl$_3$ afforded benzylcyclopentane (**3**) in 50% yield, in addition to a trace

amount of 5-hexenylbenzene (<2%) (Scheme 1). It is well known that 5-hexenyl radical isomerizes into cyclopentylmethyl radical rapidly.[3] The formation of **3** strongly supports the intermediacy of 5-hexenyl radical.

**Scheme 1.** Reaction of 6-Bromo-1-hexene with Phenylmagnesium Bromide
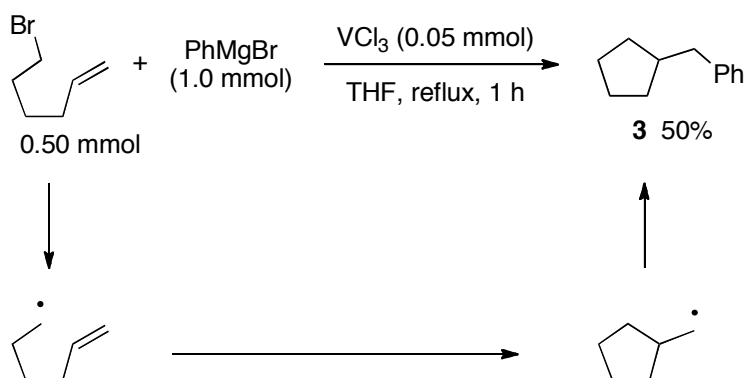
The experimental fact that the phenylations of *endo-* and *exo-*2-bromonorbornane yielded the corresponding phenylated product **4** with the same *endo/exo* selectivity also suggests a radical pathway (Scheme 2). The stereochemical outcome of the reaction indicates the existence of a planar carbon center with no original stereochemical information,[2j,4] that is, 2-norbornyl radical. These experiments indicate that the vanadium-catalyzed reaction proceeds via carbon-centered radical intermediates. The mechanism should be similar to the cobalt-catalyzed coupling reactions of alkyl halides with aryl Grignard reagents (vide infra).[1e]

Scheme 2. Reactions of *exo*- and *endo*-2-Bromonorbornane with Phenylmagnesium Bromide
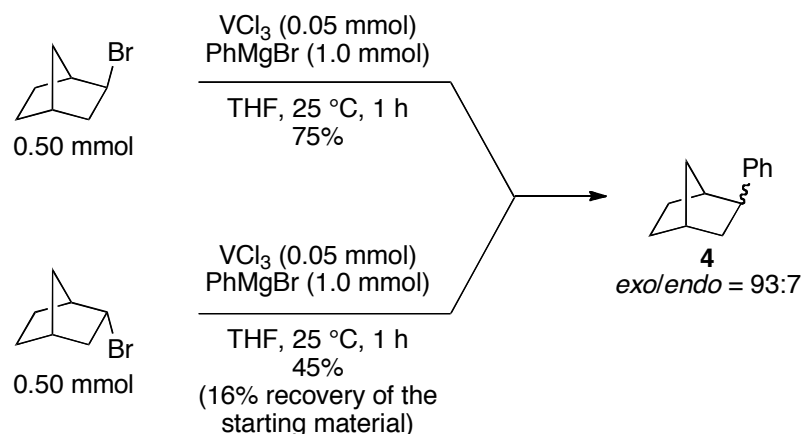
The vanadium-catalyzed phenylation exhibited interesting reactivity (Scheme 3). Treatment of *cis*-1-bromo-4-*tert*-butylcyclohexane with phenylmagnesium bromide under the conditions for the vanadium-catalyzed reaction yielded coupling product **5** in moderate yield. On the other hand, no reaction took place when its *trans* isomer was subjected to the reaction. The reason for the marked difference has not been determined.

Scheme 3. Reactions of *cis*- and *trans*-1-Bromo-4-*tert*-butylcyclohexane with Phenylmagnesium Bromide
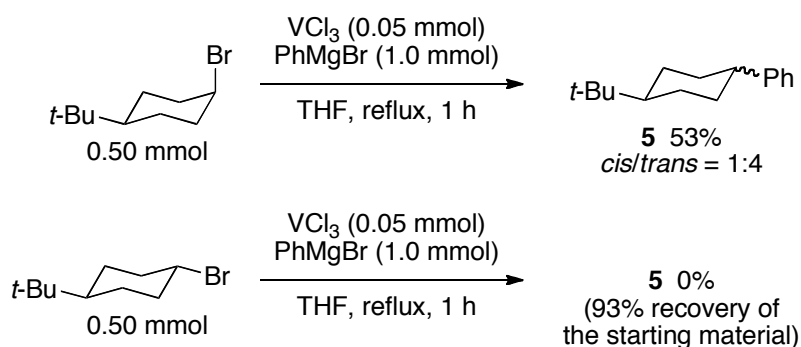
To gain further information about the reaction mechanism and the actual vanadium species that is responsible for the coupling reaction, the reaction of bromocyclohexane with PhMgBr in the presence of a stoichiometric amount of VCl_3 was examined with different amounts of

PhMgBr (Table 3). Treatment of bromocyclohexane (0.50 mmol) with a vanadium complex, prepared from 0.50 mmol of VCl_3 and 1.0 mmol of PhMgBr, gave a trace amount of **1a** (entry 1). About half of the bromocyclohexane was recovered. Product **1a** formed when three molar amounts of PhMgBr were used (entry 2), and using larger amounts of PhMgBr increased the yields of the product (entries 3–5). The yield markedly increased when four molar amounts of PhMgBr were used (entry 3). However, the yield did not increase when seven molar amounts of PhMgBr were used (entry 6). It is worth noting that only a small amount of biphenyl was formed in each case, implying that trivalent vanadium species plays a key role in the reaction. It is well known that lithium teraarylvanadates, $[Ar_4VLi]$, readily form upon treatment of VCl_3 with four molar amounts of ArLi.[5,6] Hence, in the catalytic reaction, vanadate complexes such as $[Ar_4VMgBr]$ should serve as an active species.

Table 3. Reactions of Bromocyclohexane with Various Phenylvanadium Reagents

entry	n	yield/%	c-$C_6H_{11}Br$ recovered/%
1	1.0	<1	52
2	1.5	22	38
3	2.0	58	0
4	2.5	69	0
5	3.0	76	0
6	3.5	76	0

The author proposes the following mechanism for the catalytic reaction (Scheme 4). The reaction of VCl_3 with four molar amounts of ArMgBr gives $[Ar_4VMgBr]$. The vanadate complex undergoes single electron transfer to the alkyl halide to yield the anion radical of the

alkyl halide, [Ar$_4$V],[5d] and MgBr$^+$. Immediate loss of bromide from the anion radical affords the corresponding alkyl radical intermediate R•, and [Ar$_4$V] then captures the carbon-centered radical to form [RAr$_4$V]. The pentavalent organovanadium complex should be so unstable that it should undergo rapid reductive elimination to afford the coupling product and [Ar$_3$V], which is reconverted into [Ar$_4$VMgBr] by reacting with the remaining ArMgBr.

Scheme 4. Plausible Mechanism
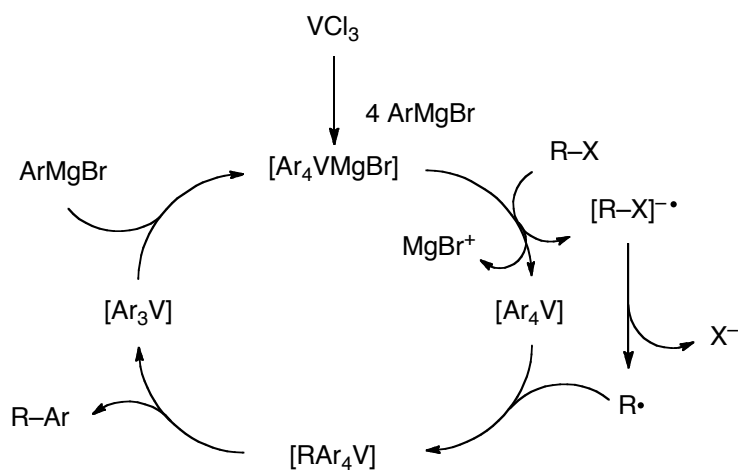
Conclusion

The author showed the catalytic activity of vanadium(III) chloride in the cross-coupling reactions of alkyl halides with aryl Grignard reagents. Vanadium catalysts are rarely used for carbon–carbon bond-formation reactions.[7] The results herein will open up new possibilities for using vanadium catalysts.

Experimental Section

Instrumentation and Chemicals

^{1}H NMR (500 and 300 MHz) and ^{13}C NMR (125.7 and 75.3 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and a Varian GEMINI 300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to CDCl$_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a JASCO IR-810 spectrometer. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous VCl$_3$•THF was purchased from Aldrich and was diluted to prepare a 0.050 M THF solution. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Silica gel (Wakogel 200 mesh) was used for column chromatography.

Typical Procedure for Vanadium-Catalyzed Arylation Reactions of Alkyl Halides (Table 1, entry 1)

Vanadium(III) chloride (0.050 M THF solution, 1.0 mL, 0.050 mmol) and phenylmagnesium bromide (1.0 M THF solution, 1.0 mL, 1.0 mmol) were sequentially added to a 20-mL reaction flask under argon. The mixture was stirred for about 20 min at room temperature. Bromocyclohexane (0.082 g, 0.50 mmol) was added to the reaction mixture at 25 °C. While the Grignard reagent was being added, the mixture turned dark-brown. After stirring for 1 h at 25 °C, a saturated ammonium chloride solution (0.2 mL) was added to the reaction mixture. The mixture was filtered through a pad of Florisil, and the filtrate was concentrated. Silica gel column purification (eluent: hexane) of the crude product provided cyclohexylbenzene (**1a**, 61 mg, 0.38 mmol, 75% yield).

Characterization Data

The following products are well known compounds or found in the literature: **1b**,[8] **2b**,[4] **2c**,[9] **3**,[10] **4**,[11] and **5**.[12]

## 1- *tert*-Butyl-4-cyclohexylbenzene (1c)
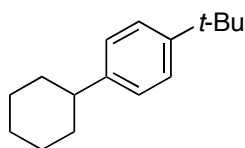
IR (neat) 2925, 2852, 1521, 1507, 1461, 1448, 1362, 1270, 1109, 825, 570 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.21–1.29 (m, 1H), 1.31 (s, 9H), 1.36–1.45 (m, 4H), 1.72–1.75 (m, 1H), 1.82–1.88 (m, 4H), 2.45–2.49 (m, 1H), 7.13 (d, J = 6.5 Hz, 2H), 7.31 (d, J = 6.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ = 26.49, 27.25, 31.71, 34.58, 34.76, 44.26, 125.37, 126.67, 145.27, 148.67; Found: C, 88.58; H, 11.38%. Calcd for C$_{16}$H$_{24}$: C, 88.82; H, 11.18%.

1- Cyclohexyl-4-fluorobenzene (1d)
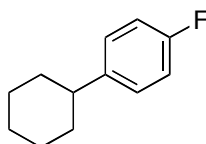
IR (neat) 2927, 2853, 1605, 1511, 1448, 1159, 827, 807 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.19–1.28 (m, 1H), 1.32–1.43 (m, 4H), 1.71–1.76 (m, 1H), 1.80–1.88 (m, 4H), 2.44–2.50 (m, 1H), 6.94–6.98 (m, 2H), 7.13–7.16 (m, 2H); ^{13}C NMR (CDCl$_3$) δ = 26.33, 27.09, 34.88, 44.07, 115.12 (d, $J_{C–F}$ = 20.6 Hz), 128.28 (d, $J_{C–F}$ = 7.8 Hz), 143.94 (d, $J_{C–F}$ = 3.4 Hz), 161.35 (d, $J_{C–F}$ = 241.5 Hz); Found: C, 80.91; H, 8.49%. Calcd for C$_{12}$H$_{15}$F: C, 80.86; H, 8.48%.

1- Cyclohexyl-3-trifluoromethylbenzene (1e)
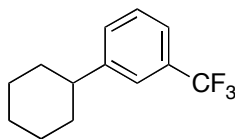
IR (neat) 2928, 2855, 1491, 1451, 1437, 1333, 1277, 1232, 1198, 1163, 1125, 1074, 799, 702, 668 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.24–1.31 (m, 1H), 1.35–1.47 (m, 4H), 1.74–1.78 (m, 1H), 1.84–1.90 (m, 4H), 2.53–2.58 (m, 1H), 7.37–7.40 (m, 2H), 7.41–7.44 (m, 1H), 7.44–7.46 (m, 1H); ^{13}C NMR (CDCl$_3$) δ = 25.99, 26.73, 34.27, 44.42, 122.62 (q, J_{C-F} = 3.9 Hz), 123.50 (q, J_{C-F} = 3.4 Hz), 124.37 (q, J_{C-F} = 270.6 Hz), 128.63, 130.26, 130.28, 130.50 (q, J_{C-F} = 31.5 Hz); Found: C, 68.57; H, 6.67%. Calcd for C$_{13}$H$_{15}$F$_3$: C, 68.41; H, 6.62%.

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Publication List

I. Parts of the present thesis have been published in the following journals.

Chapter 1   Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Organometallics **2008**, *27*, 4025–4027.

Chapter 2   Synthesis of Aryliron Complexes [CpFe(CO)$_2$Ar] by Palladium-Catalyzed Reactions of [CpFe(CO)$_2$I] with Arylzinc, -Boron, or -Indium Reagents
Shigeo Yasuda, Yoshihiro Asada, Hideki Yorimitsu, and Koichiro Oshima
Materials **2009**, *2*, 978–991.
Synthesis of Functionalized Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)$_2$I] and Arylzinc or Arylboron Reagents
Yoshihiro Asada, Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Organometallics **2008**, *27*, 6050–6052.

Chapter 3   Synthesis of Functionalized Aryliron Complexes [CpFe(CO)$_2$Ar] by Copper-Mediated Transmetalation between [CpFe(CO)$_2$I] and Aryltin Reagents
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Organometallics **2010**, *29*, 273–274.

Chapter 4   Use of Aryliron Complexes [CpFe(CO)$_2$Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents to Yield Ketones
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Organometallics **2009**, *28*, 4872–4875.

Chapter 5   Arylation of Styrenes with Aryliron Complexes [CpFe(CO)$_2$Ar]
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
To be submitted.

Appendix   Vanadium-Catalyzed Cross-Coupling Reactions of Alkyl Halides with Aryl
Grignard Reagents
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Bull. Chem. Soc. Jpn. **2008**, *81*, 287–290.

II.   Other publication not included in this thesis.

Synthesis   of   (1-Alkynyl)dicarbonylcyclopentadienyliron   Complexes   by
Palladium-Catalyzed Sonogashira-Type Carbon–Iron Bond Formation.
Ryotaro Nakaya, Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Tetrahedron Lett. **2009**, *50*, 5274–5276.

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