<table>
<thead>
<tr>
<th>Title</th>
<th>Studies on Synthesis and Reactions of Aryldicarbonylcyclopentadienyliron (Dissertation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Yasuda, Shigeo</td>
</tr>
<tr>
<td>Citation</td>
<td>Kyoto University</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2010-03-23</td>
</tr>
<tr>
<td>URL</td>
<td><a href="https://doi.org/10.14989/doctor.k15387">https://doi.org/10.14989/doctor.k15387</a></td>
</tr>
<tr>
<td>Type</td>
<td>Thesis or Dissertation</td>
</tr>
<tr>
<td>Textversion</td>
<td>author</td>
</tr>
</tbody>
</table>

Kyoto University
Studies on Synthesis and Reactions

of Aryldicarbonylcyclopentadienyliiron

Shigeo Yasuda
2010
Contents

General Introduction .................................................................................................................................. 1

Chapter 1
Synthesis of Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)₂I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis ........................................................................................................................... 19

Chapter 2
Synthesis of Aryliron Complexes [CpFe(CO)₂Ar] by Palladium-Catalyzed Reactions of [CpFe(CO)₂I] with Arylzinc, -Boron, or -Indium Reagents ............................................................................................................................... 37

Chapter 3
Synthesis of Functionalized Aryliron Complexes [CpFe(CO)₂Ar] by Copper-Mediated Transmetalation between [CpFe(CO)₂I] and Aryltin Reagents ........................................................................................................... 57

Chapter 4
Use of Aryliron Complexes [CpFe(CO)₂Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents to Yield Ketones ..................................................................................................... 65

Chapter 5
Arylation of Styrenes with Aryliron Complexes [CpFe(CO)₂Ar] ........................................................................ 81

Appendix
Vanadium-Catalyzed Cross-Coupling Reactions of Alkyl Halides with Aryl Grignard Reagents ........................................................................................................................................................................ 93

Publication List ........................................................................................................................................ 107

Acknowledgment ....................................................................................................................................... 109
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. In addition to the reactions using inorganic iron compounds, there are various useful reactions using organoiron compounds. Especially, organoiron complexes bearing a dicarbonylcyclopentadienyliron moiety \([\text{CpFe(CO)}_2\text{R}]\) have been attracting much attention as useful reagents because of their unique properties and have found numerous applications in organic synthesis. Some important organic reactions of \([\text{CpFe(CO)}_2\text{R}]\) are described below.

1-1. General Synthesis of \([\text{CpFe(CO)}_2\text{R}]\)

In principle, the synthesis of \([\text{CpFe(CO)}_2\text{R}]\) (R = alkyl, allyl, alkenyl, alkynyl, acyl, aryl) can be achieved by one of two processes (Scheme 1). One is the reaction of \([\text{CpFe(CO)}_2\text{]}\text{M (M} = \text{Na, K), which is prepared by reduction of [CpFe(CO)}_2\text{]}_2\text{ with sodium/mercury amalgam or activated potassium metal, with organic halides. The other is the reaction of [CpFe(CO)}_2\text{]}\text{X (X} = \text{I, Br, Cl), which is prepared by oxidation of [CpFe(CO)}_2\text{]}_2\text{ with X}_2\text{ or HX/O}_2\text{, with organometallic reagents.}
1-2. Synthesis and Reactions of Cationic (η²-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 (η²-alkene)iron complexes with nucleophiles utilizing this effect.

Generally, cationic (η²-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 (η²-isobutene)iron complex (Scheme 2).<sup>2a,5</sup> Moreover, obtained cationic (η²-isobutene)iron complex can be used to prepare other cationic (η²-alkene)iron complex by olefin exchange (Scheme 3).<sup>6</sup> The exchange prefers the formation of sterically less encumbered cationic (η³-alkene)iron complex.
Various nucleophilic additions to cationic ($\eta^2$-alkene)iron complexes proceed with high regioselectivity or stereoselectivity (Schemes 4 and 5). 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.

On the other hand, these cationic ($\eta^2$-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.
1-3. Synthesis and Reactions of $\eta^1$-Allyliron Complexes

Generally, $\eta^1$-allyliron complexes are synthesized by treatment of [CpFe(CO)$_2$]Na with allyl chlorides (Scheme 2) or of cationic ($\eta^2$-alkene)iron complexes with bases (Scheme 7).$^8$

![Scheme 7.][1]

Treatment of $\eta^1$-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.][2]

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

![Scheme 9.][3]

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). 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).
A stereoselective cyclopropanation is also possible by use of a substituted siloxyalkyliron complex (Scheme 13).\(^\text{12}\)

1-5. Synthesis and Reactions of Acyliron Complexes

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

Moreover, the generation and reactions of the lithium enolate of \([\text{CpFe(CO)}_2(\text{COR})]\) are possible. Especially, these reactions of the easily accessible acetyliron complex \([\text{CpFe(CO)}_2(\text{COCH}_3)]\) have been studied well to open up a route to highly substituted acyliron complexes (Scheme 15).\(^\text{14}\)
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 $[\text{CpFe(CO)}_2\text{Me}]$, which is prepared from $[\text{CpFe(CO)}_2\text{I}]$ and methyl Grignard reagent, with triphenylphosphine affords racemic $[\text{CpFe(CO)(PPh}_3\text{(COCH}_3\text{)}])$ (Scheme 16).\textsuperscript{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).\textsuperscript{16}

Treatment of the optically pure complex $(R)$-$(\text{--})$-[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 $(\text{--})$-captopril (Scheme 18).\textsuperscript{17}
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].

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.
2. Overview of This Thesis

As described above, iron complexes bearing a dicarbonylcyclopentadienyliron moiety [CpFe(CO)₂R] have interesting reactivity, and they are usually utilized in organic synthesis. Among them, the chemical reactivity of the corresponding aryliron complexes [CpFe(CO)₂Ar] has not been well investigated partly because of the limited availability of [CpFe(CO)₂Ar]. Therefore, the development of efficient approaches to [CpFe(CO)₂Ar] should lead to the progress of the chemistry of [CpFe(CO)₂Ar] which have high potential as useful arylmetal reagents.²⁰ So the author planned to develop new efficient methods of synthesis of [CpFe(CO)₂Ar] under mild conditions and their applications to organic synthesis. After extensive investigation, he found that [CpFe(CO)₂Ar] were obtained efficiently by the transmetalation reactions of [CpFe(CO)₂I] 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)₂Ar] with organic compounds.

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

So far, little is known about the concise synthesis of [CpFe(CO)₂Ar]. The author developed new efficient methods for the synthesis of [CpFe(CO)₂Ar] 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](image)

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

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

Transmetalation between \([\text{CpFe(CO)}_2\text{I}]\) and arylzinc iodide-lithium chloride complexes proceeds in the presence of catalytic amounts of palladium acetate and
12

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

\[ \text{Scheme 24.} \]

\[
\begin{align*}
\text{OC:Fe-I} & \quad + \quad [M]-\text{Ar} \\
& \quad \text{cat. Pd(OAc)}_2 \\
& \quad \text{cat. } \begin{array}{c}
\text{NMe}_2 \\
\text{THF, 0 °C}
\end{array} \\
& \quad \text{OC:Fe-Ar} \\
(M = \text{Zn, In})
\end{align*}
\]

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

\[ \text{Scheme 25.} \]

\[
\begin{align*}
\text{OC:Fe-I} & \quad + \quad (\text{HO})_2\text{B}-\text{Ar} \\
& \quad \text{cat. PEPPSI} \\
& \quad \text{cat. } \begin{array}{c}
\text{Cs}_2\text{CO}_3 \\
1,4\text{-dioxane, 60 °C}
\end{array} \\
& \quad \text{OC:Fe-Ar} \\
\end{align*}
\]

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 \([\text{CpFe(CO)}_2\text{Ar}]\). The products \([\text{CpFe(CO)}_2\text{Ar}]\) represent an interesting class of aryl metals that undergo several transformation.

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

Transmetalation between \([\text{CpFe(CO)}_2\text{I}]\) and aryltin reagents in the presence of copper(I)
trifluoromethanesulfonate yields the corresponding aryliron complexes \([\text{CpFe(CO)}_2\text{Ar}]\). The high functional group compatibility of this copper-mediated reaction enables the author to obtain \([\text{CpFe(CO)}_2\text{Ar}]\) 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.](image)

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

2-2. Transformation of \(\text{CpFe(CO)}_2\text{Ar}\) (Chapters 4 and 5)

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

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

The reactions of \([\text{CpFe(CO)}_2\text{Ar}]\) with organometallic reagents are rare. The reaction of \([\text{CpFe(CO)}_2\text{Ph}]\) with excess butyllithium in THF at \(-78 \, ^\circ\text{C}\) was reported, leading to the lithiation of the cyclopentadienyl ring (Scheme 27).
The author found that a similar reaction at a higher reaction temperature led to a completely different outcome. Treatment of aryliron complexes \([\text{CpFe(CO)}_2\text{Ar}]\) with \(n\text{-BuLi}\) at \(-20^\circ\text{C}\) in THF affords the corresponding ketones \(n\text{-BuCOAr}\). Not only \(\text{BuLi}\) 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 \(\text{RLi}\) to one of the carbonyl ligands to form acylferrate \([\text{CpFe(CO)(RCO)Ar}]\text{Li}\) without lithiation of the \(\text{Cp}\) ring. The \((\eta^2\text{-ketone})\text{iron}\) complex would be formed via nucleophilic migration of the reactive \(\text{Ar}\) anion to the acyl carbonyl. The \(\eta^2\) complexation is not robust, and liberation of ketone would take place upon addition of water.

Scheme 28.

\[
\begin{align*}
\text{OC}_2\text{Fe}\cdots\text{Ar} & \quad + \quad \text{Li}\cdots\text{R} \\
\text{OC} & \quad \text{THF, } -20^\circ\text{C} \\
\text{Ar} & \quad \text{H}_3\text{O}^+ \\
\text{OC}\cdots\text{Fe} & \quad \text{Li}^+ \\
\text{R} & \quad \text{Li}^+ \\
\text{OC}\cdots\text{Fe} & \quad \text{Li}^+ \\
\text{OC}\cdots\text{Fe} & \quad \text{Li}^+
\end{align*}
\]

2-2-2. Arylation of Styrenes with Aryliron Complexes \([\text{CpFe(CO)}_2\text{Ar}]\) (Chapter 5)

Insertion of unsaturated bonds into the aryl–iron bonds of \([\text{CpFe(CO)}_2\text{Ar}]\) is well known. However, there is only one example of application of such insertion to useful organic transformation. In Chapter 5, the author describes arylation of styrenes with aryliron complexes \([\text{CpFe(CO)}_2\text{Ar}]\) utilizing the insertion of the \(\text{C}=\text{C}\) bond of styrene into the aryl–iron bond. Treatment of aryliron complexes \([\text{CpFe(CO)}_2\text{Ar}]\) with various styrenes affords the corresponding stilbenes (Scheme 29). The reaction would proceed as follows. Insertion of the
C=C bond of styrene into the aryl–iron bond would generate the corresponding alkyl–iron complex. Subsequent $\beta$-hydride elimination affords stilbene derivatives.

**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


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 \([\text{CpFe(CO)}_2\text{Ar}]\) are easy to handle and hence can be useful as arylmetal reagents in organic synthesis. However, little is known about the concise synthesis of \([\text{CpFe(CO)}_2\text{Ar}]\).\(^2\) In Chapter 1, the author reports a new efficient method for the synthesis of \([\text{CpFe(CO)}_2\text{Ar}]\) under palladium catalysis. Several transformations of \([\text{CpFe(CO)}_2\text{Ar}]\) 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 \([\text{CpFe(CO)}_2\text{I}]\) (1) with phenylmagnesium bromide in the absence of a catalyst resulted in failure, affording a poor yield of \([\text{CpFe(CO)}_2\text{Ph}]\) (2a), a significant amount of \([\text{CpFe(CO)}_2]_2\) (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 \([\text{CpFe(CO)}_2\text{I}]\) 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 \(\text{IPr}^\text{HCl}\) 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).
The reaction would proceed via a mechanism similar to the conventional cross-coupling reaction,\textsuperscript{5c} which consists of oxidative addition of \textbf{1} to palladium that generates [Cp(CO)\textsubscript{2}Fe–Pd–I], transmetalation with phenylmagnesium bromide, and reductive elimination that forms the phenyl–iron bond (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.
(4-Bromophenyl)magnesium reagent, prepared from 4-bromoiodobenzene according to the procedure of Knochel,\textsuperscript{7} also underwent the arylation reaction at \(-20^\circ\text{C}\), albeit in modest yield and with a higher catalyst loading (Scheme 2).

**Scheme 2. Synthesis of Aryliron Complex from ArMgCl\(\cdot\)LiCl**

\[
\text{I-Br} \quad \text{THF, \(-20^\circ\text{C}, 30\text{ min}\)} \quad [\text{ClMg-Br} \quad \text{-LiCl}]
\]

\[
\text{1 (2.0 equiv)} \quad \text{1 (0.50 mmol)} \quad \text{10 mol\% Pd(OAc)}_2 \quad \text{12 mol\% 4}
\]

\[
\text{OC-Fe-I} \quad \text{OC} \quad \text{OC-Fe-Ar} \quad \text{OC}
\]

\[
\begin{array}{cccc}
\text{entry} & \text{Ar} & \text{2} & \text{yield/\%} \\
1 & 4\text{-MeC}_6\text{H}_4 & \text{2b} & 80 \\
2 & 4\text{-PhC}_6\text{H}_4 & \text{2c} & 87 \\
3^a & 4\text{-MeOC}_6\text{H}_4 & \text{2d} & 62 (90^b) \\
4 & 4\text{-ClC}_6\text{H}_4 & \text{2e} & 74 \\
5 & 4\text{-FC}_6\text{H}_4 & \text{2f} & 87 \\
6 & 2\text{-MeC}_6\text{H}_4 & \text{2g} & 21 \\
\end{array}
\]

\text{a} Performed at \(-20^\circ\text{C}\) for 2 h.

\text{b} Yield determined by \(^1\text{H}\) NMR analysis of the crude product.

Although rich coordination chemistry has been reported for [CpFe(CO)]\(_2\)Ar,\textsuperscript{4} the application of [CpFe(CO)]\(_2\)Ar to organic synthesis has been almost unknown.\textsuperscript{3} Hence, the author examined several transformations of [CpFe(CO)]\(_2\)Ar which will be useful in organic
Many oxidative alkoxy carbonylations of [CpFe(CO)₂R] with ceric ammonium nitrate to form RCOOR’ were reported, although there have been no reports on the reaction of [CpFe(CO)₂Ar]. He thus optimized conditions for the reaction of [CpFe(CO)₂Ar] 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](image)

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

![Scheme 4](image)

Iron complexes 2 reacted with allylic electrophiles under irradiation with a high-pressure mercury lamp to afford allylarenes 6 (Schemes 5 and 6).
The reaction would proceed as follows (Scheme 7): (1) photoinduced dissociation of a carbonyl ligand,\textsuperscript{10–12} (2) coordination of an allylic electrophile followed by migratory insertion,\textsuperscript{13} and (3) β-halide elimination.\textsuperscript{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.
Conclusion

The author has devised an efficient method for the synthesis of the series of iron complexes [CpFe(CO)₂Ar]: that is, palladium-catalyzed transmetalation between [CpFe(CO)₂I] 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)₂Ar] 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 ($\delta$) 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)$_2$I] (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)$_2$I] 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 mixture 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)$_2$Ar] with Ce(IV)(NH$_4$)$_2$(NO$_3$)$_6$ (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-biphenyl)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-BrC₆H₄)] 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 (eluent: CHCl₃) 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)₂Ar] with Allylic Electrophiles (Scheme 5, synthesis of 6b)

(4-Biphenyl)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)**

IR (neat) 3052, 2011, 1953, 1564, 1470, 1421, 1054, 1010, 995, 832, 732, 698, 633 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta = 4.87\) (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\(_3\)) \(\delta = 85.77, 122.87, 127.51, 145.07, 145.51, 216.04\); 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\(_3\)) \(\delta = 2.24\) (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\(_3\)) \(\delta = 20.51, 85.71, 128.74, 132.23, 139.68, 144.75, 216.14\); 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\(_3\)) \(\delta = 4.89\) (s, 5H), 7.23–7.29 (m, 3H), 7.38–7.41 (m, 2H), 7.52–7.56 (m, 4H); \(^13\)C NMR (CDCl\(_3\)) \(\delta = 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 C₁₀H₁₄FeO₂: C, 69.12; H, 4.27%. m.p.: 113–115 °C.

Dicarboxylycyclopentadienyl(4-methoxyphenyl)iron (2d)

![Structure](image)

IR (neat) 2834, 2010, 1953, 1581, 1463, 1420, 1264, 1232, 1181, 1052, 1026, 1000, 812, 634, 593 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ = 55.09, 85.71, 114.27, 131.03, 144.70, 157.04, 216.22; Found: C, 58.83; H, 4.26%. Calcd for C₁₄H₁₉FeO₂: C, 59.19; H, 4.26%.

Dicarboxylycyclopentadienyl(4-chlorophenyl)cyclopentadienyliron (2e)

![Structure](image)

IR (neat) 2016, 1959, 1468, 1432, 1420, 1090, 1034, 1003, 909, 845, 835, 803, 734, 631, 592, 572 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.86 (s, 5H), 6.96 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H); ¹³C NMR (CDCl₃) δ = 85.77, 127.25, 129.85, 143.44, 145.51, 215.70; Found: C, 54.33; H, 3.42%. Calcd for C₁₃H₁₂ClFeO₂: C, 54.12; H, 3.14%.

Dicarboxylycyclopentadienyl(4-fluorophenyl)iron (2f)

![Structure](image)

IR (nujol) 2022, 2005, 1971, 1941, 1920, 1477, 1468, 1163, 810, 635, 596, 578 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.85 (s, 5H), 6.74–6.77 (m, 2H), 7.31–7.34 (m, 2H); ¹³C NMR (CDCl₃) 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 C₁₀H₁₀FFeO₂: 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\(_3\)) \(\delta = 2.44\) (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); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta = 28.15, 86.05, 123.35, 124.59, 129.23, 144.33, 146.80, 148.86, 215.92\); 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\(_3\)) \(\delta = 4.88\) (s, 5H), 7.11 (d, \(J = 8.0\) Hz, 2H), 7.32 (d, \(J = 8.0\) Hz, 2H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta = 85.77, 117.98, 130.08, 144.51, 146.05, 215.63\); 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\(_3\)) \(\delta = 1.33\) (s, 12H), 4.87 (s, 5H), 7.40 (d, \(J = 8.0\) Hz, 2H), 7.55 (d, \(J = 8.0\) Hz, 2H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta = 24.85, 83.35, 85.83, 133.07, 144.99, 154.28, 215.80\). The borylated carbon could not be observed. Found: C, 60.17; H, 5.56%. Calcd for C\(_{19}\)H\(_{21}\)BFeO\(_3\): 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$_3$) $\delta = 1.36$ (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$_3$) $\delta = 22.28, 25.08, 45.05, 83.87, 112.32, 128.60, 135.04, 143.36, 145.04$. 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.
References and Notes


4. The coordination chemistry of [CpFe(CO)2Ar] has been summarized: Kerber, R. C. In


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


Chapter 2

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

Transmetalation between $[\text{CpFe(CO)}_2\text{I}]$ 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 $[\text{CpFe(CO)}_2\text{Ar}]$. Phenylation of $[\text{CpFe(CO)}_2\text{I}]$ 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 $[\text{CpFe(CO)}_2\text{Ar}]$. The products $[\text{CpFe(CO)}_2\text{Ar}]$ 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 arylimagnesium reagents proceeds smoothly under palladium catalysis.¹¹ However, the scope of the reaction is limited due to the high reactivity of arylimagnesium 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.

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.

**Table 1. Reactions of [CpFe(CO)$_2$I] (1) with Several Types of Phenylating Reagents**

<table>
<thead>
<tr>
<th>entry</th>
<th>PhZn</th>
<th>yield based on $^1$H NMR/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2a</td>
</tr>
<tr>
<td>1</td>
<td>PhZnI</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>PhZnI•LiCl</td>
<td>100(90$^a$)</td>
</tr>
<tr>
<td>3</td>
<td>PhZnI + LiCl</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>PhZnI + LiCl then 50 °C, 24 h</td>
<td>73</td>
</tr>
<tr>
<td>5</td>
<td>ZnCl$_2$ + 2 PhMgBr</td>
<td>100</td>
</tr>
</tbody>
</table>

$^a$ 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] (1) with Arylzinc Reagents ArZnI•LiCl

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>2</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>2a</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>1-naphthyl</td>
<td>2b</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>2-MeC₆H₄</td>
<td>2c</td>
<td>73ᵃ</td>
</tr>
<tr>
<td>4</td>
<td>4-MeOC₆H₄</td>
<td>2d</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>3-CF₃C₆H₄</td>
<td>2e</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>2-FC₆H₄</td>
<td>2f</td>
<td>74</td>
</tr>
<tr>
<td>7</td>
<td>4-BrC₆H₄</td>
<td>2g</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>4-NCC₆H₄</td>
<td>2h</td>
<td>94</td>
</tr>
<tr>
<td>9</td>
<td>4-EtOC(=O)C₆H₄</td>
<td>2i</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>3-EtOC(=O)C₆H₄</td>
<td>2j</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td>2-EtOC(=O)C₆H₄</td>
<td>2k</td>
<td>trace</td>
</tr>
<tr>
<td>12</td>
<td>4-MeCl(=O)C₆H₄</td>
<td>2l</td>
<td>trace</td>
</tr>
<tr>
<td>13</td>
<td>2-thienyl</td>
<td>2m</td>
<td>79</td>
</tr>
<tr>
<td>14</td>
<td>3-pyridyl</td>
<td>2n</td>
<td>trace</td>
</tr>
</tbody>
</table>

ᵃ 3.0 equiv of the zinc reagent was used.

A mechanism similar to the conventional cross-coupling reaction would operate¹⁴ in the phenylation, *i.e.*, oxidative addition of 1 to palladium that generates [Cp(CO)₂Fe–Pd–I], transmetalation with PhZnI•LiCl, and reductive elimination to yield 2a.
2. Reactions of [CpFe(CO)$_2$I] with Triphenylinidium or -Aluminum

Triphenylinidium, prepared from InCl$_3$ and 3 equiv of PhMgBr, could transfer the phenyl group to 1 under similar conditions (Table 3, entry 1). 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. 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)$_2$I] (1) with Triphenylinidium or -Aluminum |
|---|---|---|---|
| entry | phenylating agent | time/h | yield based on $^1$H 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)$_2$I] 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). 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). He assumes that arylcopper species generated from CuI and aryloboronic acids would undergo more efficient transmetalation with the iodopalladium intermediate. 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 aryloboronic acids having a hydroxy group was sluggish (entry 15).

Table 4. Palladium-Catalyzed Arylation of [CpFe(CO)_2] (1) with Arylboronic Acids

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>Cul/mol%</th>
<th>2</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>0</td>
<td>2a</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>1-naphthyl</td>
<td>0</td>
<td>2b</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>2-MeC_6H_4</td>
<td>0</td>
<td>2c</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>4-MeOC_6H_4</td>
<td>0</td>
<td>2d</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>4-MeOC_6H_4</td>
<td>40</td>
<td>2e</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>4-CF_3C_6H_4</td>
<td>0</td>
<td>2o</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>4-MeC_6H_4</td>
<td>0</td>
<td>2p</td>
<td>79</td>
</tr>
<tr>
<td>8</td>
<td>4-MeOCH_2C_6H_4</td>
<td>0</td>
<td>2q</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>4-MeOCH_2C_6H_4</td>
<td>40</td>
<td>2q</td>
<td>86</td>
</tr>
<tr>
<td>10</td>
<td>4-EtOC(=O)C_6H_4</td>
<td>0</td>
<td>2i</td>
<td>67</td>
</tr>
<tr>
<td>11</td>
<td>4-EtOC(=O)C_6H_4</td>
<td>40</td>
<td>2i</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>2-EtOC(=O)C_6H_4</td>
<td>40</td>
<td>2k</td>
<td>75</td>
</tr>
<tr>
<td>13</td>
<td>4-CH_2=CHC_6H_4</td>
<td>0</td>
<td>2r</td>
<td>72</td>
</tr>
<tr>
<td>14</td>
<td>4-CH_2=CHC_6H_4</td>
<td>40</td>
<td>2r</td>
<td>83</td>
</tr>
<tr>
<td>15</td>
<td>4-HOCH_2C_6H_4</td>
<td>0</td>
<td>2s</td>
<td>0</td>
</tr>
</tbody>
</table>
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 |
|---------------------------------|----------------|-------------|-------------|
| 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

<table>
<thead>
<tr>
<th>entry</th>
<th>2</th>
<th>time/h</th>
<th>5</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2d</td>
<td>2</td>
<td>5a</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>2g</td>
<td>1</td>
<td>5b</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>2h</td>
<td>2</td>
<td>5c</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>2i</td>
<td>15</td>
<td>5d</td>
<td>71</td>
</tr>
</tbody>
</table>

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.

(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.
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 aryiron 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 ($\delta$) 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-cyclohexanediadmine (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. ^1H 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)₂I] (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. ^1H 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)₂I] (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)2Ar] with Ce(NH4)2(NO3)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 dicarboxylcyclopentadienyl(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)2Ar] (Table 6, entry 4)**

Dicarboxylcyclopentadienyl(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: CS₂/CHCl₃ = 1:1 to CHCl₃ 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: CS₂/CHCl₃ = 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: CS₂/CHCl₃ = 2:1) provided 2x (85 mg, 0.24 mmol, 79%).

Characterization Data

Characterization data for arylirons 2a, 2b, 2c, 2d, 2g, 2p, 2r, 4a, 4b, 4c, 4d, 5a, 5b, 5c, and 5d were available in the literature.
Dicarbonylcyclopentadienyl(3-trifluoromethylphenyl)iron (2e)

IR (neat) 2016, 1966, 1311, 1183, 1096, 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\textsubscript{14}H\textsubscript{9}FeNO\textsubscript{2}: C, 60.25; H, 3.25%. m.p.: 100–101 °C.

**Dicarbonylcyclopentadienyl(4-ethoxycarbonylphenyl)iron (2i)**

![Chemical structure](image)

IR (nujol) 2023, 1949, 1708, 1576, 1454, 1283, 1124, 1008, 758 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.36\) (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\(_3\)) \(\delta = 14.59, 60.55, 86.04, 125.76, 127.24, 144.96, 159.28, 167.97, 215.61\); Found: C, 58.99; H, 4.43%. Calcd for C\textsubscript{16}H\textsubscript{14}FeO\textsubscript{4}: C, 58.93; H, 4.33%. m.p.: 104–106 °C.

**Dicarbonylcyclopentadienyl(3-ethoxycarbonylphenyl)iron (2j)**

![Chemical structure](image)

IR (nujol) 2015, 1962, 1944, 1703, 1456, 1367, 1253, 1110, 751 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.38\) (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\(_3\)) \(\delta = 14.56, 60.80, 86.00, 124.53, 127.03, 129.16, 145.36, 146.63, 149.66, 167.71, 215.82\); Found: C, 58.79; H, 4.45%. Calcd for C\textsubscript{16}H\textsubscript{14}FeO\textsubscript{4}: C, 58.93; H, 4.33%. m.p.: 67–68 °C.

**Dicarbonylcyclopentadienyl(2-ethoxycarbonylphenyl)iron (2k)**

![Chemical structure](image)

IR (nujol) 2020, 1969, 1945, 1707, 1456, 1377 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta = 1.37\) (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\(_3\)) \(\delta = 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)**

![Diagram](image)

IR (neat) 3104, 2854, 2026, 1966, 1420, 1391, 1317, 905, 826, 808, 682 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 4.98$ (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$_3$) $\delta = 85.89$, 128.89, 131.31, 134.68, 138.23, 214.72; Found: C, 50.55; H, 3.23%. Calcd for C$_{11}$H$_8$FeO$_2$: C, 50.80; H, 3.10%.

**Dicarbonylcyclopentadienyl(4-trifluoromethylphenyl)iron (2o)**

![Diagram](image)

IR (nujol) 2007, 1957, 1588, 1325, 1158, 1072, 1008, 820, 631, 605 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 4.88$ (s, 5H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.59 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta = 86.01$, 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$_9$F$_3$FeO$_2$: C, 52.21; H, 2.82%. m.p.: 72–73 °C.

**Dicarbonylcyclopentadienyl(4-methoxymethylphenyl)iron (2q)**

![Diagram](image)

IR (neat) 2920, 2012, 1955, 1480, 1187, 1096, 1042, 1007, 832, 797, 632 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 3.36$ (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$_3$) $\delta = 58.18$, 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ = 65.68, 85.96, 126.75, 135.78, 145.24, 145.61, 216.12; Found: C, 58.97; H, 4.29%. Calcd for C₁₄H₁₂FeO₃: 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₂H₂₈FeO₃: 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ = 86.03, 125.59, 127.09, 133.20, 145.28, 145.66, 216.19; HRMS (m/z) Observed: 532.0059. Calcd for C₂₈H₂₈Fe₂O₄: 532.0060. m.p.: >280 °C.
Dicarboxycyclopentadienyl[4-((E)-2-ethoxycarbonylvinyl)phenyl]iron (2w)

IR (neat) 2016, 1961, 1699, 1627, 1576, 1481, 1309, 1266, 1175, 1044, 1004, 811, 631, 591 cm⁻¹;
¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₈H₁₆FeO₄: 352.0398.

Dicarboxycyclopentadienyl[4-((E)-1-octenyl)phenyl]iron (2x)

IR (neat) 2927, 2855, 2016, 1958, 1577, 1481, 1003, 965, 831, 797, 633, 592, 575 cm⁻¹;
¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₁H₂₄FeO₂: 364.1126.

Dicarboxycyclopentadienyl[4-((E)-3-trimethylsilyl-1-propenyl)phenyl]iron (2y)

IR (nujol) 2020, 1969, 1002, 862, 830, 799, 589 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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.
References and Notes

2768–2813.


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 \([\text{CpFe}(\text{CO})_2R]\) 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 \([\text{CpFe}(\text{CO})_2\text{Ar}]\) has not been fully investigated\(^2\) partly because there are few methods for the synthesis of \([\text{CpFe}(\text{CO})_2\text{Ar}]\).\(^3\) Therefore, the development of efficient approaches to \([\text{CpFe}(\text{CO})_2\text{Ar}]\) should lead to the progress of the chemistry of \([\text{CpFe}(\text{CO})_2\text{Ar}]\) 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 \([\text{CpFe}(\text{CO})_2\text{Ar}]\), palladium-catalyzed transmetalation between \([\text{CpFe}(\text{CO})_2\text{I}]\) 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 \([\text{CpFe}(\text{CO})_2\text{Ar}]\). However, the functional group compatibility of these methods was not perfect. For example, \([\text{CpFe}(\text{CO})_2\text{Ar}]\) 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 \([\text{CpFe}(\text{CO})_2\text{I}]\) 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 \([\text{CpFe}(\text{CO})_2\text{I}]\) (1) with tributylphenyltin to afford \([\text{CpFe}(\text{CO})_2\text{Ph}]\) (2a) in excellent yield (Table 1, entry 1). Although dinuclear complex \([\text{CpFe}(\text{CO})_2]_2\) (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).

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

<table>
<thead>
<tr>
<th>entry</th>
<th>x</th>
<th>additive</th>
<th>y</th>
<th>2a/%</th>
<th>1/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>CuOTf</td>
<td>2.0</td>
<td>97</td>
<td>0</td>
</tr>
<tr>
<td>2(^b)</td>
<td>2.0</td>
<td>CuOTf</td>
<td>2.0</td>
<td>77</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>CuOTf</td>
<td>1.2</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>CuOTf</td>
<td>0.10</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>Cu(OTf)(_2)</td>
<td>1.2</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1.2</td>
<td>AgOTf</td>
<td>1.2</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>CuI</td>
<td>1.2</td>
<td>0</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>CuBr</td>
<td>1.2</td>
<td>0</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>1.2</td>
<td>CuCl</td>
<td>1.2</td>
<td>0</td>
<td>47</td>
</tr>
</tbody>
</table>

\(^a\) Yields were determined by \(^1\)H NMR analysis of the crude products.

\(^b\) With 10 mol\% Pd(OAc)\(_2\).
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. 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-Bu)\(_3\)

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>2</th>
<th>yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>2a</td>
<td>86</td>
</tr>
<tr>
<td>2</td>
<td>2-MeC(_6)H(_4)</td>
<td>2b</td>
<td>68</td>
</tr>
<tr>
<td>3(^a)</td>
<td>4-MeOC(_6)H(_4)</td>
<td>2c</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>4-FC(_6)H(_4)</td>
<td>2d</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>3-CF(_3)C(_6)H(_4)</td>
<td>2e</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>4-NCC(_6)H(_4)</td>
<td>2f</td>
<td>69</td>
</tr>
<tr>
<td>7</td>
<td>4-MeC(=O)C(_6)H(_4)</td>
<td>2g</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>4-HC(=O)C(_6)H(_4)</td>
<td>2h</td>
<td>84</td>
</tr>
<tr>
<td>9(^b)</td>
<td>4-HOC(_6)H(_4)</td>
<td>2i</td>
<td>14</td>
</tr>
</tbody>
</table>

\(^a\) 4-MeOC\(_6\)H\(_4\)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)\(_2\)I] 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, $\delta = 0.00$ ppm) and CDCl$_3$ (for $^{13}$C, $\delta = 77.2$ ppm) as an internal standard] or C$_6$D$_6$ [using C$_6$H$_6$ (for $^1$H, $\delta = 7.15$ ppm) and C$_6$D$_6$ (for $^{13}$C, $\delta = 128.6$ 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)**

![Chemical structure of 2g]

IR (nujol) 2022, 2007, 1943, 156, 1275, 1006, 810 cm⁻¹; ¹H NMR (C₆D₆) 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); ¹³C NMR (C₆D₆) 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 C₁₅H₁₂FeO₃: C, 60.84; H, 4.08%. m.p.: 82–84 °C.

**Dicarbonylcyclopentadienyl(4-formylphenyl)iron (2h)**

![Chemical structure of 2h]

IR (nujol) 2283, 2014, 1964, 1943, 1685, 1573, 1546, 1179, 1037, 1008, 834, 813 cm⁻¹; ¹H NMR (C₆D₆) 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); ¹³C NMR (C₆D₆) δ = 86.34, 127.89, 134.19, 146.13, 163.74, 192.40, 216.42; Found: C, 59.62; H, 3.73%. Calcd for C₁₄H₁₀FeO₃: C, 59.61; H, 3.57%. m.p.: 98–100 °C.

**Dicarbonylcyclopentadienyl(4-hydroxyphenyl)iron (2i)**

![Chemical structure of 2i]

IR (nujol) 2013, 1942, 1583, 1534, 1365, 1289, 1236, 1187, 1146, 875, 845, 656 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₃H₁₀FeO₃: 269.9979. m.p.: 75 °C (decomposition).
References and Notes


Chapter 4

Use of Aryliron Complexes [CpFe(CO)_2Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents to Yield Ketones

Treatment of aryliron complexes [CpFe(CO)_2Ar] 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).$^9$,$^{10}$

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-tolylolithium 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

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>2</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-Bu</td>
<td>2a</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>s-Bu</td>
<td>2b</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>t-Bu</td>
<td>2c</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>2d</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>Ph</td>
<td>2e</td>
<td>91</td>
</tr>
<tr>
<td>6ᵃ</td>
<td>Ph</td>
<td>2e</td>
<td>68</td>
</tr>
<tr>
<td>7ᵇ</td>
<td>Ph</td>
<td>2e</td>
<td>4</td>
</tr>
<tr>
<td>8ᶜ</td>
<td>2-MeC₆H₄</td>
<td>2f</td>
<td>71</td>
</tr>
<tr>
<td>9ᶜ</td>
<td>1-naphthyl</td>
<td>2g</td>
<td>75</td>
</tr>
<tr>
<td>10ᶜ</td>
<td>4-MeOC₆H₄</td>
<td>2h</td>
<td>65</td>
</tr>
<tr>
<td>11ᶜ</td>
<td>4-FC₆H₄</td>
<td>2i</td>
<td>52</td>
</tr>
<tr>
<td>12ᶜᵈ</td>
<td>4-CF₃C₆H₄</td>
<td>2j</td>
<td>47</td>
</tr>
<tr>
<td>13ᶜ</td>
<td>4-ClC₆H₄</td>
<td>2k</td>
<td>46</td>
</tr>
<tr>
<td>14ᶜ</td>
<td>4-PhC₆H₄</td>
<td>2l</td>
<td>79</td>
</tr>
</tbody>
</table>

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.

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.

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>1</th>
<th>2</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-PhC₆H₄</td>
<td>1b</td>
<td>2m</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>2-naphthyl</td>
<td>1c</td>
<td>2n</td>
<td>86</td>
</tr>
<tr>
<td>3a</td>
<td>1-naphthyl</td>
<td>1d</td>
<td>2o</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>4-t-BuC₆H₄</td>
<td>1e</td>
<td>2p</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>2-MeC₆H₄</td>
<td>1f</td>
<td>2q</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>4-ClC₆H₄</td>
<td>1g</td>
<td>2r</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>4-FC₆H₄</td>
<td>1h</td>
<td>2s</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>4-BrC₆H₄</td>
<td>1i</td>
<td>2t</td>
<td>68</td>
</tr>
<tr>
<td>9</td>
<td>3-CF₃C₆H₄</td>
<td>1j</td>
<td>2u</td>
<td>89</td>
</tr>
<tr>
<td>10b</td>
<td>4-MeOC₆H₄</td>
<td>1k</td>
<td>2v</td>
<td>59</td>
</tr>
</tbody>
</table>

a Performed at 25 °C. b Performed at 0 °C.
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)₂Ar] (1) to form acylferrate [CpFe(CO)(Ar’CO)Ar]Li (3). Acylferrate 3 might undergo reductive elimination to yield ketone 2.

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 triaryl methanol 7 suggest that ketone 2e is protected from the nucleophilic attack of organolithium under the reaction conditions.

He presumes that ketone 2e exists in the resonance of 8 and 8’ (Scheme 5). The $(\eta^2$-ketone)iron complex would be formed via nucleophilic migration of the reactive Ar anion to the acyl carbonyl. The $\eta^2$ 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.
The following experiments verified that the lithiation of the Cp ring by the excess amount of \( \text{RLi}^{9,10} \) did not occur under the present conditions. Treatment of \( \text{1a} \) with only 1.0 equiv of PhLi was followed by quenching with \( \text{D}_2\text{O} \) (Scheme 6). The reaction afforded \( \text{2e} \) in 62% yield, and \( \text{1a} \) was recovered in 25% yield. The recovered \( \text{1a} \) had only the natural abundance of deuterium. The use of 1.0 equiv of \( n\text{-BuLi} \) at \(-20 \) °C also resulted in no deuterium incorporation (47% of \( \text{2a} \) and 37% of \( \text{1a} \)). 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.
Conclusion

[CpFe(CO)$_2$Ar] 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)$_2$Ar] with organolithium, no metalation of the Cp ring was observed. This finding represents a new chemical reactivity of [CpFe(CO)$_2$Ar] 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, $\delta = 0.00$ ppm) and CDCl$_3$ (for $^{13}$C, $\delta = 77.2$ ppm) as an internal standard] or C$_6$D$_6$ [using C$_6$H$_6$ (for $^1$H, $\delta = 7.15$ ppm) and C$_6$D$_6$ (for $^{13}$C, $\delta = 128.6$ 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. 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
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/Et\_2O 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 \(^1\)H 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 \(^1\)H 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–11,2e–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 2v16 can be found in the literature.

**Dicarboxylicdipentadienyl(2-naphthyl)iron (1c)**

![Chemical Structure](image)

IR (nujol) 2342, 2021, 1998, 1970, 1454, 1456, 1419, 813, 745, 644, 628 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₇H₁₂FeO₂: C, 67.14; H, 3.98%. m.p.: 94–95 °C.

**Dicarboxylicdipentadienyl(4-t-butylphenyl)iron (1e)**

![Chemical Structure](image)

IR (nujol) 2002, 1966, 1945, 1917, 1479, 1464, 1362, 1116, 1004, 809, 729, 632, 594 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₇H₁₈FeO₂: 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; ¹H NMR (C₆D₆) 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); ¹³C NMR (C₆D₆) 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 C₂₆H₂₀FeO₃: 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₅H₁₁F₃O: 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; ¹H NMR (CDCl₃) δ = 2.46 (s, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.39–7.42 (m, 1H), 7.47–7.50 (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); ¹³C NMR (CDCl₃) 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<sub>20</sub>H<sub>16</sub>O: C, 88.20; H, 5.92%. m.p.: 122–124 °C.

**Phenyl 3-trifluoromethylphenyl ketone (2u)**

![Structural formula](image)

IR (nujol) 1654, 1337, 1266, 1170, 1073, 725, 715, 691, 660 cm<sup>–1</sup>; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ = 123.91 (q, J<sub>C–F</sub> = 271.1 Hz), 126.90 (q, J<sub>C–F</sub> = 3.9 Hz), 128.78, 129.03 (q, J<sub>C–F</sub> = 3.4 Hz), 129.16, 130.23, 131.22 (q, J<sub>C–F</sub> = 32.3 Hz), 133.22, 133.32, 136.98, 138.51, 195.41; Found: C, 67.24; H, 3.37%. Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>O: C, 67.20; H, 3.63%. HRMS (m/z) Observed: 250.0603 (Δ = −1.0 ppm). Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>O: 250.0605.

m.p.: 48–49 °C.

**4-(Hydroxydiphenylmethyl)phenyl phenyl ketone (2w)**

![Structural formula](image)

IR (neat) 3444, 1658, 1599, 1447, 1405, 1318, 1279, 764, 732, 701, 680 cm<sup>–1</sup>; ¹H NMR (C<sub>6</sub>D₆) 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); ¹³C NMR (C<sub>6</sub>D₆) 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<sub>26</sub>H<sub>20</sub>O₂: C, 85.69; H, 5.53%.
(4-Isopropylphenyl)(phenyl)methanol (6)

\[
\text{\includegraphics[width=0.1\textwidth]{image.png}}
\]

$^1$H NMR (CDCl$_3$): $\delta = 1.22$ (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$_3$): $\delta = 24.17$, 33.99, 76.33, 126.67, 126.77, 126.79, 127.64, 128.62, 141.47, 144.08, 148.47.
References and Notes


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

![8’’](image)

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.


Chapter 5

Arylation of Styrenes with Aryliron Complexes [CpFe(CO)₂Ar]

Treatment of aryliron complexes [CpFe(CO)₂Ar] 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.
This arylation reaction with [CpFe(CO)$_2$(4-tolyl)] was much affected by steric effects. Unfortunately, the reactions of 1a with sterically demanding $\alpha$-methylstyrene (2i) and $\beta$-methylstyrene (2j) failed to afford the corresponding stilbene derivatives 3i and 3j in reasonable yields (Schemes 1 and 2).

**Table 1. Reactions of [CpFe(CO)$_2$-(4-tolyl)] with Various Styrenes**

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>2 (2 equiv)</th>
<th>3 (2 equiv)</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>2a</td>
<td>3a</td>
<td>79</td>
</tr>
<tr>
<td>2$^a$</td>
<td>Ph</td>
<td>2a</td>
<td>3a</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>4-MeOC$_2$H$_4$</td>
<td>2b</td>
<td>3b</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>4-FC$_6$H$_4$</td>
<td>2c</td>
<td>3c</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>4-ClC$_6$H$_4$</td>
<td>2d</td>
<td>3d</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>4-BrC$_6$H$_4$</td>
<td>2e</td>
<td>3e</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>4-AcOC$_6$H$_4$</td>
<td>2f</td>
<td>3f</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>(CH$_2$=CHCO$_2$Et)</td>
<td>2g</td>
<td>3g</td>
<td>15$^b$</td>
</tr>
<tr>
<td>9</td>
<td>(CH$_2$=CHB(pin))</td>
<td>2h</td>
<td>3h</td>
<td>10$^b$</td>
</tr>
</tbody>
</table>

$^a$ Performed in refluxing toluene.

$^b$ Yield determined by $^1$H NMR analysis of the crude product.

$^a$ Yield determined by $^1$H NMR analysis of the crude product.
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).

![Scheme 3.](image)

**Table 2.** Scope of Aryliron Complexes

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>1</th>
<th>3</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-Naphthyl</td>
<td>1b</td>
<td>3k</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>2-MeC₆H₄</td>
<td>1c</td>
<td>3l</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>4-MeOC₆H₄</td>
<td>1d</td>
<td>3m</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>4-FC₆H₄</td>
<td>1e</td>
<td>3n</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>4-ClC₆H₄</td>
<td>1f</td>
<td>3o</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>4-BrC₆H₄</td>
<td>1g</td>
<td>3p</td>
<td>58</td>
</tr>
<tr>
<td>7a</td>
<td>3-CF₃C₆H₄</td>
<td>1h</td>
<td>3q</td>
<td>58</td>
</tr>
<tr>
<td>8</td>
<td>4-EtOC(=O)C₆H₄</td>
<td>1i</td>
<td>3r</td>
<td>70</td>
</tr>
<tr>
<td>9a</td>
<td>4-(pin)BC₆H₄</td>
<td>1j</td>
<td>3s</td>
<td>84</td>
</tr>
</tbody>
</table>

*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 $\beta$-hydride elimination affords the stilbene derivative.$^{12}$
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)\textsubscript{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)\textsubscript{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. 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\(_3\)) \(\delta = 2.36\) (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\(_3\)) \(\delta = 21.46, 115.78\) (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\(_3\)) \(\delta = 2.30\) (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\(_3\)) \(\delta = 21.35, 21.46, 121.96, 126.63, 126.87, 127.49, 129.09, 129.62, 134.60, 135.57, 137.83, 150.10, 169.67\);  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.
(E)-4-Fluorostilbene (3n)

IR (nujol) 1030, 964, 824, 690 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₄H₁₁F: C, 84.82; H, 5.59%. m.p.: 118–119 °C.
References and Notes


11. The reaction of [CpFe(CO)$_2$H] with $\alpha$-cyclopropylstyrene has been reported: Bullock, R. M.; Samsel, E. G. J. Am. Chem. Soc. 1990, 112, 6886–6898.


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.\textsuperscript{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). \textit{p}-Methoxy- and \textit{p}-\textit{tert}-butylphenylmagnesium bromides also reacted with bromocyclohexane smoothly (entries 2 and 3). The reaction with \textit{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

\[
\begin{align*}
\text{Br} & \quad + \quad \text{ArMgBr} \quad \xrightarrow{\text{cat. VCl}_3} \quad \text{Ar} \\
\text{THF, 25 °C, 1 h} & \quad \xrightarrow{} \quad \text{1}
\end{align*}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>Ar</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>1a, 75</td>
</tr>
<tr>
<td>2</td>
<td>(p)-MeOC(_6)H(_4)</td>
<td>1b, 68</td>
</tr>
<tr>
<td>3</td>
<td>(p)-(t-Bu)C(_6)H(_4)</td>
<td>1c, 67</td>
</tr>
<tr>
<td>4</td>
<td>(p)-FC(_6)H(_4)</td>
<td>1d, 69(^b)</td>
</tr>
<tr>
<td>5</td>
<td>(m)-CF(_3)C(_6)H(_4)</td>
<td>1e, 49(^b,c)</td>
</tr>
<tr>
<td>6</td>
<td>(\alpha)-MeC(_6)H(_4)</td>
<td>1f, 0(^b,c,d)</td>
</tr>
</tbody>
</table>

\(^a\) 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 phenylmagnesium 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-bromododecane 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$^a$

$$R-X + \text{PhMgBr} \xrightarrow{\text{cat. VCl}_3; \text{THF}, 25 \degree C, 1 \text{ h}} R-\text{Ph}$$

<table>
<thead>
<tr>
<th>entry</th>
<th>R–X</th>
<th>yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iodocyclohexane</td>
<td>1a, 75</td>
</tr>
<tr>
<td>2</td>
<td>Chlorocyclohexane</td>
<td>1a, 62$^{b,c}$</td>
</tr>
<tr>
<td>3</td>
<td>Bromocyclopentane</td>
<td>2a, 37$^b$</td>
</tr>
<tr>
<td>4</td>
<td>Bromocycloheptane</td>
<td>2b, 8$^{b,c}$</td>
</tr>
<tr>
<td>5</td>
<td>2-Bromododecane</td>
<td>2c, 34$^d$</td>
</tr>
<tr>
<td>6</td>
<td>2-Iodobutane</td>
<td>2d, 21</td>
</tr>
<tr>
<td>7</td>
<td>1-Iododecane</td>
<td>2e, 74</td>
</tr>
<tr>
<td>8</td>
<td>1-Bromododecane</td>
<td>2e, 66$^b$</td>
</tr>
</tbody>
</table>

$^a$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 $N,N,N',N'$-tetramethylethlenediamine, 4-(dimethylamino)pyridine, $N$-methylmorpholine, triphenylphosphate, trimethylphosphate, 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. The formation of 3 strongly supports the intermediacy of 5-hexenyl radical.

**Scheme 1.** Reaction of 6-Bromo-1-hexene with Phenylmagnesium Bromide

![Reaction Scheme]

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, 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).
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.

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 VCl₃ 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$_4$VLi], 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$_4$VMgBr] should serve as an active species.

<table>
<thead>
<tr>
<th>entry</th>
<th>$n$</th>
<th>yield/%</th>
<th>$c$-C$<em>8$H$</em>{11}$Br recovered/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>&lt;1</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>22</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>58</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>69</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>76</td>
<td>0</td>
</tr>
</tbody>
</table>

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

**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. 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: \(1b, 2b, 4c, 3, 10, 4, 11\) and \(5.\)

1- \textit{tert}-Butyl-4-cyclohexylbenzene (1c)

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

1- Cyclohexyl-4-fluorobenzene (1d)

\[
\text{IR (neat) 2927, 2853, 1605, 1511, 1448, 1159, 827, 807 cm}^{-1}; \quad \text{\(^1\)H NMR (CDCl}_3\) \(\delta = 1.19–1.28 \text{ (m, 1H)}, 1.32–1.43 \text{ (m, 4H)}, 1.71–1.76 \text{ (m, 1H)}, 1.80–1.88 \text{ (m, 4H)}, 2.44–2.50 \text{ (m, 1H)}, 6.94–6.98 \text{ (m, 2H)}, 7.13–7.16 \text{ (m, 2H)}; \quad \text{\(^{13}\)C NMR (CDCl}_3\) \(\delta = 26.33, 27.09, 34.88, 44.07, 115.12 \text{ (d, } J_{C\text{-F}} = 20.6 \text{ Hz)}, 128.28 \text{ (d, } J_{C\text{-F}} = 7.8 \text{ Hz)}, 143.94 \text{ (d, } J_{C\text{-F}} = 3.4 \text{ Hz)}, 161.35 \text{ (d, } J_{C\text{-F}} = 241.5 \text{ Hz}); \quad \text{Found: C, 80.91; H, 8.49\%. Calcd for C}_{12}H_{13}F: \text{C, 80.86; H, 8.48\%.}
\]
1- Cyclohexyl-3-trifluoromethylbenzene (1e)

IR (neat) 2928, 2855, 1491, 1437, 1333, 1277, 1232, 1198, 1163, 1125, 1074, 799, 702, 668 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = 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%.
References and Notes


6. Formations of higher-order vanadates, [Ar₅VLi₂] and [Ar₆VLi₃] were reported, although they are rare cases: (a) Helmut, D. Z. Chem. 1975, 15, 451. (b) Ref. 5d.


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)₂I] and Aryl Grignard Reagents and Their Chemistry Directed toward Organic Synthesis
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima

Chapter 2  Synthesis of Aryliron Complexes [CpFe(CO)₂Ar] by Palladium-Catalyzed Reactions of [CpFe(CO)₂I] with Arylzinc, -Boron, or -Indium Reagents
Shigeo Yasuda, Yoshihiro Asada, Hideki Yorimitsu, and Koichiro Oshima
Synthesis of Functionalized Aryliron Complexes by Palladium-Catalyzed Transmetalation between [CpFe(CO)₂I] and Arylzinc or Arylboron Reagents
Yoshihiro Asada, Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima

Chapter 3  Synthesis of Functionalized Aryliron Complexes [CpFe(CO)₂Ar] by Copper-Mediated Transmetalation between [CpFe(CO)₂I] and Aryltin Reagents
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima
Organometallics 2010, 29, 273–274.

Chapter 4  Use of Aryliron Complexes [CpFe(CO)₂Ar] as Arylcarbonyl Cation Equivalents in the Reactions with Organolithium Reagents to Yield Ketones
Shigeo Yasuda, Hideki Yorimitsu, and Koichiro Oshima

Chapter 5  Arylation of Styrenes with Aryliron Complexes [CpFe(CO)₂Ar]
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

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
Acknowledgment

The studies described in this thesis have been carried out under the direction of Professor Koichiro Oshima at Kyoto University from April, 2007 to March, 2010.

Professor Koichiro Oshima always encouraged and advised the author with a warm and generous heart. The author was helped by Professor Oshima’s valuable suggestions and interesting ideas many times. The author wishes to express his grateful acknowledgment to Professor Oshima. Associate Professor Hideki Yorimitsu kindly gave practical ideas about this work and cared the author with a generous heart. The author is deeply thankful to him.

The author wishes to show his gratitude to Professor Tamejiro Hiyama and Professor Seijiro Matsubara for their helpful suggestions. The author is also thankful to Associate Professor Masaki Shimizu, Dr. Yoshiaki Nakao, and Dr. Takuya Kurahashi for their generous help.

It is his great pleasure to express his appreciation to all the members of Oshima group for their active and helpful discussions.

Professor Eiichi Nakamura and Professor Masaharu Nakamura taught the author the fundamentals of organic chemistry at The University of Tokyo. The author wishes to express his acknowledgement to them. He equally wishes to thank Professor Yutaka Matsuo, Professor Hiroyuki Isobe, Dr. Naohiko Yoshikai. The author is also thankful to Dr. Yoichiro Kuninobu for helpful discussions.

Professor Paul Knochel gave the author the precious opportunity to stay and study in his laboratory for about two months. The author wishes to express his grateful acknowledgment to Professor Knochel.

Financial support from JSPS, Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists, was indispensable, and the author sincerely appreciates the support.

Finally, the author would like to express his sincere appreciation to his father, Shin-etsu Yasuda and his mother, Kayoko Yasuda and his sister, Akiko Yamaki for their encouragement and continuous assistance.

Shigeo Yasuda