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Synthesis of (1-alkynyl)dicarbonylcyclopentadienyliron complexes by palladium-catalyzed Sonogashira-type carbon–iron bond formation

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Synthesis of (1-alkynyl)dicarbonylcyclopentadienyliron complexes by palladium-catalyzed Sonogashira-type carbon–iron bond formation

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Abstract—Treatment of $[\text{CpFe}(\text{CO})_2\text{I}]$ with terminal alkynes in the presence of catalytic amounts of dichlorobis(triphenylphosphine)palladium and copper iodide in aliphatic amine/THF results in Sonogashira-type carbon–iron bond formation to yield $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ in good yields. © 2010 Elsevier Science. All rights reserved

Dicarbonylcyclopentadienylorganoiron complexes $[\text{CpFe}(\text{CO})_2\text{R}]$ have been attracting considerable attention in the field of coordination chemistry.¹ Among them, the corresponding (1-alkynyl)iron complexes $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ are interesting not only as fundamental organometallic compounds² but also as potentially useful precursors for molecular electronic devices.³

The synthesis of the (1-alkynyl)iron complexes often employs the reactions of $[\text{CpFe}(\text{CO})_2\text{X}]$ (X = halogen) with lithium or magnesium acetylides, which lack generality and functional group compatibility.⁴ Although palladium-catalyzed Migita-Kosugi-Stille-type reactions of $[\text{CpFe}(\text{CO})_2\text{I}]$ with (1-alkynyl)stannanes offer an alternative route,⁵ preparation of the tin reagents and removal of tin impurities would be troublesome. Copper-catalyzed reactions of $[\text{CpFe}(\text{CO})_2\text{X}]$ (X = Cl or Br) with terminal acetylenes providing $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ are most useful at present due to their reasonable scope and efficiency.^{4d,6} However, the yields heavily depended on the alkynes used and $[\text{CpFe}(\text{CO})_2\text{I}]$ would not react under the copper-catalyzed conditions. More efficient and versatile methods for the synthesis of $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ are hence awaited.^{7,8}

Recently, we have developed easy and efficient methods for the synthesis of $[\text{CpFe}(\text{CO})_2\text{Ar}]$, the palladium-catalyzed Kumada-Tamao-Corriu-,^{9a} Negishi-,^{9b} and

Suzuki-Miyaura-type^{9b} reactions of $[\text{CpFe}(\text{CO})_2\text{I}]$ with arylmetal reagents. Here we report the synthesis of $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ by palladium-catalyzed Sonogashira-type carbon–iron bond formation.¹⁰

Treatment of $[\text{CpFe}(\text{CO})_2\text{I}]$ with phenylacetylene in the presence of catalytic amounts of CuI and $[\text{PdCl}_2(\text{PPh}_3)_2]$ in a triethylamine/THF mixed solvent afforded $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CPh})]$ ¹¹ (**1a**) in 60% yield (Eq 1). The combination of CuI and the palladium catalyst is important. The reaction was sluggish when copper iodide (11% yield) or the palladium complex (18%) was omitted. After screening reaction conditions, we found that diisopropylamine is the most effective base (Eq 2). The reaction in a diisopropylamine/THF mixed solvent at 25 °C for 30 min afforded **1a** in 81% yield, albeit with a smaller amount, 2.5 mol%, of the palladium catalyst.¹²

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The scope of alkynes is summarized in Table 1. A methyl or methoxy group at the 4 position of the arylacetylene had little influence on the reaction (entries 1 and 2). The steric effect of a 2-methyl group was also negligible (entry 3). On the other hand, electron-withdrawing groups retarded the reaction. The reaction with 4-fluorophenylacetylene required a higher temperature and a longer reaction time to attain a satisfactory result (entry 4). More disappointingly, very inefficient conversions were observed in the reactions of 4-trifluoromethyl- and 4-cyanophenylacetylene (entries 5 and 6).

We thus reexamined the conditions for the reactions with electron-deficient arylacetylenes. To our delight, ethyldiisopropylamine proved to be effective. In addition, the amounts of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI were changed from 2.5 mol% and 5 mol% to 5 mol% and 2.5 mol%, respectively. For instance, treatment of $[\text{CpFe}(\text{CO})_2\text{I}]$ with 4-trifluoromethylphenylacetylene under the reoptimized conditions (Conditions B) furnished the corresponding alkynyliron **1f** in 86% yield (entry 7). Cyano or halo-substituted arylacetylenes were also transformed efficiently (entries 8–11). Iron complex **1k** bearing a carbonyl group was obtained in high yield (entry 12) although **1k** was unstable under air and decomposed during chromatographic purification on silica gel.¹³

Table 1. Scope of alkynes

entry	R	conditions ^a	1	yield / %
1	4-MeC ₆ H ₄	A	1b	85
2	4-MeOC ₆ H ₄	A	1c	76
3	2-MeC ₆ H ₄	A	1d	88
4	4-FC ₆ H ₄	A	1e	77 ^b
5	4-CF ₃ C ₆ H ₄	A	1f	13
6	4-NCC ₆ H ₄	A	1g	23
7	4-CF ₃ C ₆ H ₄	B	1f	86
8	4-NCC ₆ H ₄	B	1g	84
9	2-NCC ₆ H ₄	B	1h	91
10	4-ClC ₆ H ₄	B	1i	75
11	4-BrC ₆ H ₄	B	1j	74
12	4-MeOC(=O)C ₆ H ₄	B	1k	85 ^c
13	ⁿ C ₄ H ₉	A	1l	34 ^c
14	^t C ₄ H ₉	A	1m	66 ^c
15	Me ₃ Si	A	1n	73 ^c

^a Conditions A: 2.5 mol% $[\text{PdCl}_2(\text{PPh}_3)_2]$, 5 mol% CuI, ⁱPr₂NH; Conditions B: 5 mol% $[\text{PdCl}_2(\text{PPh}_3)_2]$, 2.5 mol% CuI, ⁱPr₂EtN. ^b At 50 °C for 1 h. ^c Based on NMR analysis of a crude mixture.

Although the reaction of $[\text{CpFe}(\text{CO})_2\text{I}]$ with aliphatic terminal acetylene or trimethylsilylacetylene proceeded under Conditions A (entries 13–15), products **1l–1n** were

not isolated efficiently in our hands due to the instability under air.¹³

The Sonogashira-type reaction is so chemoselective that 4-ethynylbenzyl alcohol underwent smooth carbon–iron bond formation without affecting the hydroxy group (Scheme 1). To verify that the hydroxy group remained intact, the hydroxy group of **1o** was acetylated to yield **1p**. The benzylic protons of the starting alcohol and **1o** appeared around 4.6–4.7 ppm in ¹H NMR analysis, whereas those of **1p** appeared at a clearly different chemical shift of 5.04 ppm. These NMR analyses strongly support the inertness of the hydroxy group under the palladium catalysis.

Scheme 1. Chemoselective reaction of 4-ethynylbenzyl alcohol

The reaction of $[\text{CpFe}(\text{CO})_2\text{I}]$ with 1,4-diethynylbenzene afforded dinuclear iron complex **1q** in high yield (Eq 3), highlighting the efficiency of the carbon–iron bond formation.

Not only iodoiron complexes but also similar molybdenum and tungsten complexes underwent alkynylation under Conditions A (Eq 4).

The Sonogashira-type reaction was applicable to the alkynylation of $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}]$ (Eq 5). Due to the more bulky and electron-donating Cp* group, $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}]$ was less reactive. The reaction required larger catalyst

loadings and a longer reaction time. Tetrabutylammonium fluoride (TBAF) served as a base more efficiently than ethyldiisopropylamine and diisopropylamine. It is worth noting that the preceded copper-catalyzed alkynylation of $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{Br}]$ is low-yielding.^{6b}

The TBAF-mediated alkynylation conditions were also effective for the alkynylation with diynylsilane **3**, which represents a model synthesis of oligoynylirons as molecular electronic devices³ (Eq 6). Diynylsilane **3** reacted with $[\text{CpFe}(\text{CO})_2\text{I}]$ in the presence of TBAF and the $[\text{PdCl}_2(\text{PPh}_3)_2]/\text{CuI}$ catalyst to yield diynyliron complex **1r** in 80% yield.¹⁴ It is worth noting that **3** is readily available¹⁵ and stable whereas phenylbutadiyne is difficult to synthesize and to handle.¹⁶

In summary, we have applied an important carbon–carbon bond forming reaction, the Sonogashira reaction, to the construction of carbon–iron bonds. We have thus developed a method for the synthesis of 1-alkynyliron complexes $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$. The iron complexes will find many applications in advanced material sciences as well as coordination chemistry and organic synthesis.

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Supplementary Material

Characterization data of the products. Supplementary data associated with this article can be found in the online version.