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

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A B S T R A C T

Treatment of [$CpFe(CO)_2I$] 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 [$CpFe(CO)_2(C\equiv CR)$] in good yields.

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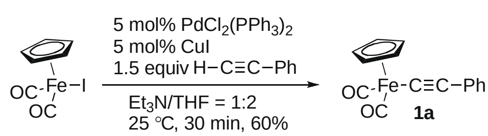
Dicarbonylcyclopentadienylorganoiron complexes [$CpFe(CO)_2R$] have been attracting considerable attention in the field of coordination chemistry.[1] Among them, the corresponding (1-alkynyl)iron complexes [$CpFe(CO)_2(C\equiv CR)$] are interesting not only as fundamental organometallic compounds[2] but also as potentially useful precursors for molecular electronic devices.[3]

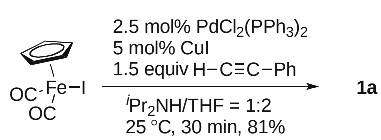
The synthesis of the (1-alkynyl)iron complexes often employs the reactions of [$CpFe(CO)_2X$] (X = halogen) with lithium or magnesium acetylides, which lack generality and functional group compatibility.[4] Although palladium-catalyzed Migita–Kosugi–Stille-type reactions of [$CpFe(CO)_2I$] with (1-alkynyl)stannanes offer an alternative route,[5] preparation of the tin reagents and removal of tin impurities would be troublesome. Copper-catalyzed reactions of [$CpFe(CO)_2X$] (X = Cl or Br) with terminal acetylenes providing [$CpFe(CO)_2(C\equiv CR)$] are most useful at present due to their reasonable scope and efficiency.[4d,6] However, the yields heavily depended on the alkynes used and [$CpFe(CO)_2I$] would not react under the copper-catalyzed conditions. More efficient and versatile methods for the synthesis of [$CpFe(CO)_2(C\equiv CR)$] are hence awaited.[7,8]

Recently, we have developed easy and efficient methods for the synthesis of [$CpFe(CO)_2Ar$], the palladium-catalyzed Kumada–Tamao–Corriu-,[9a] Negishi-,[9b] and Suzuki–Miyaura-type[9b] reactions of [$CpFe(CO)_2I$] with arylmetal reagents. Here we report the synthesis of [$CpFe(CO)_2(C\equiv CR)$] by palladium-catalyzed Sonogashira-type carbon–iron bond formation.[10]

Treatment of [$CpFe(CO)_2I$] with phenylacetylene in the presence of catalytic amounts of CuI and [$PdCl_2(PPh_3)_2$] in a triethylamine/THF mixed solvent afforded [$CpFe(CO)_2(C\equiv CPh)$][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]



(1)



(2)

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 [$PdCl_2(PPh_3)_2$] and CuI were changed from 2.5 mol % and 5 mol % to 5 mol % and 2.5 mol %, respectively. For instance, treatment of [$CpFe(CO)_2I$] 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

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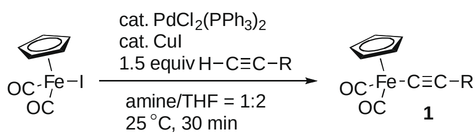
Table 1
Scope of alkynes



Entry	R	Conditions[a]	1	Yield (%)
1	4-MeC_6H_4	A	**1b**	85
2	4-$MeOC_6H_4$	A	**1c**	76
3	2-MeC_6H_4	A	**1d**	88
4	4-FC_6H_4	A	**1e**	77[b]
5	4-$CF_3C_6H_4$	A	**1f**	13
6	4-NCC_6H_4	A	**1g**	23
7	4-$CF_3C_6H_4$	B	**1f**	86
8	4-NCC_6H_4	B	**1g**	84
9	2-NCC_6H_4	B	**1h**	91
10	4-ClC_6H_4	B	**1i**	75
11	4-BrC_6H_4	B	**1j**	74
12	4-MeOC(=O)C_6H_4	B	**1k**	85[c]
13	$^nC_4H_9$	A	**1l**	34[c]
14	$^tC_4H_9$	A	**1m**	66[c]
15	Me_3Si	A	**1n**	73[c]

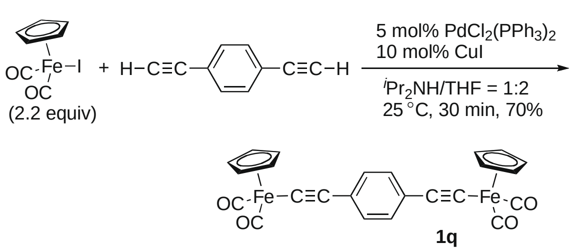
[a] Conditions A: 2.5 mol % $[PdCl_2(PPh_3)_2]$, 5 mol % CuI, $^iPr_2NH$; conditions B: 5 mol % $[PdCl_2(PPh_3)_2]$, 2.5 mol % CuI, $^iPr_2EtN$.
[b] At 50 °C for 1 h.
[c] Based on NMR analysis of a crude mixture.

yield (entry 12) although **1k** was unstable under air and decomposed during chromatographic purification on silica gel.[13]

Although the reaction of $[CpFe(CO)_2I]$ with aliphatic terminal acetylene or trimethylsilylacetylene proceeded under Conditions A (entries 13–15), products **1l**–**n** were not isolated efficiently in our hands due to the instability under air.[13]

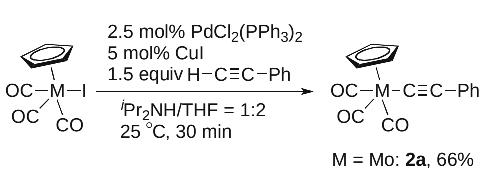
The Sonogashira-type reaction is so chemoselective that 4-ethynylbenzyl alcohol underwent smooth carbon–iron bond formation without affecting the hydroxy group (Scheme 1). To verify that the hydroxy group remained intact, the hydroxy group of **1o** was acetylated to yield **1p**. The benzylic protons 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.

The reaction of $[CpFe(CO)_2I]$ with 1,4-diethynylbenzene afforded dinuclear iron complex **1q** in high yield (Eq. 3), highlighting the efficiency of the carbon–iron bond formation.

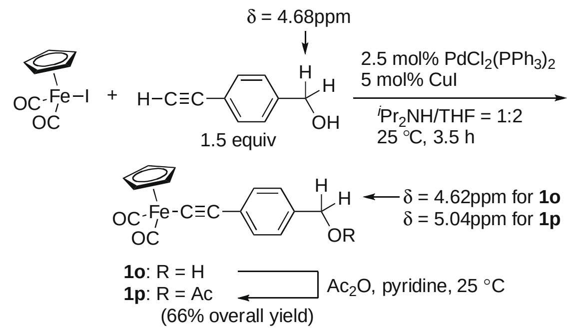


(3)

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

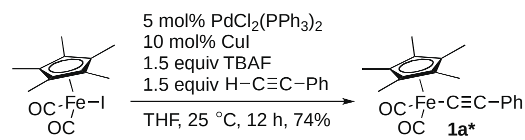


(4)



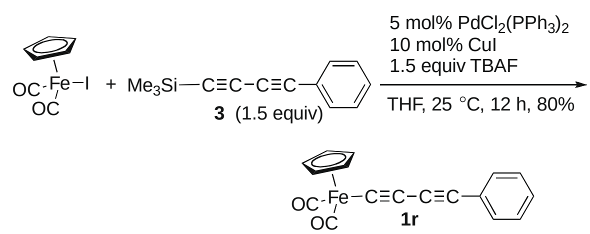
Scheme 1. Chemoselective reaction of 4-ethynylbenzyl alcohol.

The Sonogashira-type reaction was applicable to the alkynylation of $[Cp^*Fe(CO)_2I]$ (Eq. 5). Due to the more bulky and electron-donating Cp^* group, $[Cp^*Fe(CO)_2I]$ 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 precedented copper-catalyzed alkynylation of $[Cp^*Fe(CO)_2Br]$ is low-yielding.[6b]



(5)

The TBAF-mediated alkynylation conditions were also effective for the alkynylation with diynylsilane **3**, which represents a model synthesis of oligoynylirons as molecular electronic devices[3] (Eq. 6). Diynylsilane **3** reacted with $[CpFe(CO)_2I]$ in the presence of TBAF and the $[PdCl_2(PPh_3)_2]$/CuI catalyst to yield diynyliron complex **1r** in 80% yield.[14] It is worth noting that **3** is readily available[15] and stable whereas phenylbutadiyne is difficult to synthesize and to handle.[16]



(6)

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 $[CpFe(CO)_2(C{\equiv}CR)]$. The iron complexes will find many applications in advanced material sciences as well as coordination chemistry and organic synthesis.

Acknowledgments

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Supplementary data

Supplementary data (characterization data of the products) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.005.

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