

Graphical Abstract

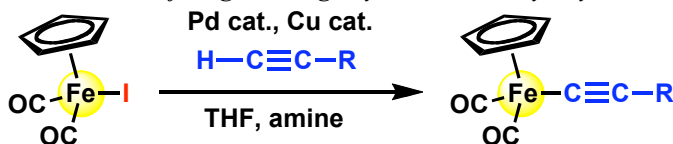
To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

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

Ryotaro Nakaya, Shigeo Yasuda, Hideki Yorimitsu*, and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Leave this area blank for abstract info.





Pergamon

TETRAHEDRON
LETTERS

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

Ryotaro Nakaya, Shigeo Yasuda, Hideki Yorimitsu^{*}, and Koichiro Oshima^{*}

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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

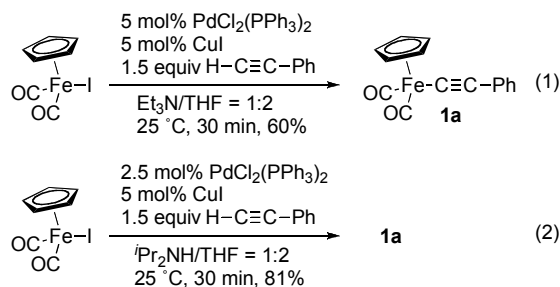
Dicarbonylcyclopentadienylorganoiron complexes $[\text{CpFe}(\text{CO})_2\text{R}]$ have been attracting considerable attention in the field of coordination chemistry.¹ Among them, the corresponding (1-alkynyl)iron complexes $[\text{CpFe}(\text{CO})_2(\text{C}\equiv\text{CR})]$ are interesting not only 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



^{*} Corresponding author. Tel.: +81-75-383-2441; fax: +81-75-383-2438; e-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp; oshima@orgrxn.mbox.media.kyoto-u.ac.jp.

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

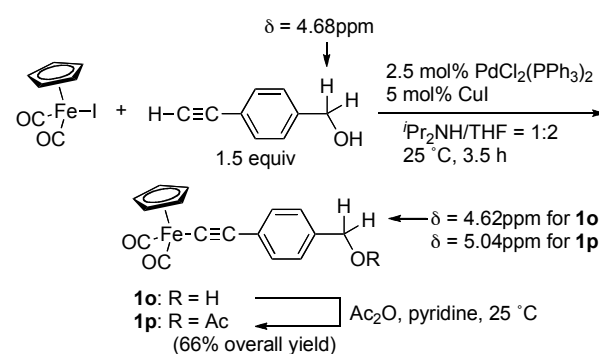
^a Conditions A: 2.5 mol% $[\text{PdCl}_2(\text{PPh}_3)_2]$, 5 mol% CuI, ⁱPr₂NH; Conditions B: 5 mol% $[\text{PdCl}_2(\text{PPh}_3)_2]$, 2.5 mol% CuI, ⁱPr₂EtN. ^b At 50 °C for 1 h. ^c Based on NMR analysis of a crude mixture.

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

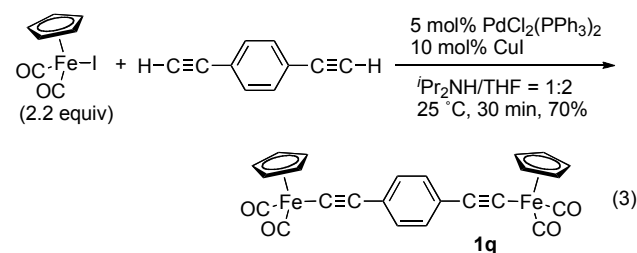
not isolated efficiently in our hands due to the instability under air.¹³

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.

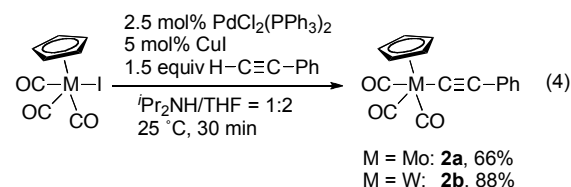
Scheme 1. Chemoselective reaction of 4-ethynylbenzyl alcohol



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.

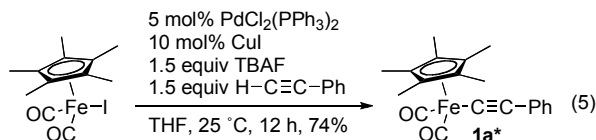


Not only iodoiron complexes but also similar molybdenum and tungsten complexes underwent alkynylation under Conditions A (Eq 4).

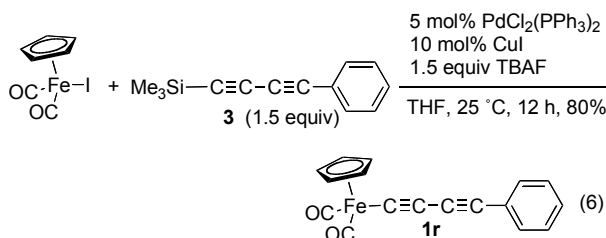


The Sonogashira-type reaction was applicable to the alkynylation of $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}]$ (Eq 5). Due to the more bulky and electron-donating Cp* group, $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}]$ was less reactive. The reaction required larger catalyst

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.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research and GCOE Research from JSPS. H.Y. thanks financial support from The Kurata Memorial Hitachi Science and Technology Foundation. S.Y. acknowledges JSPS for financial support.

References

1. Kerber, R. C. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A. Wilkinson, G. Eds.; Elsevier: Oxford, U.K., 1995; Volume 7, Chapter 2.
2. (a) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (b) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8–C12.
3. (a) Medei, L.; Orian, L.; Semeikin, O. V.; Peterleitner, M. G.; Ustynyuk, N. A.; Santi, S.; Durante, C.; Ricci, A.; Lo Sterzo, C. *Eur. J. Inorg. Chem.* **2006**, 2582–2597. (b) Akita, M.;

- Koike, T. *Dalton Trans.* **2008**, 3523–3530. (c) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586–2617.
- (a) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404–406. (b) Akita, M.; Terada, M.; Oyama, S.; Moro-oka, Y. *Organometallics* **1990**, *9*, 816–825. (c) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276–3285. (d) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1991**, *405*, 333–345.
- (a) Lo Sterzo, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1989–1990. (b) Crescenzi, R.; Lo Sterzo, C. *Organometallics* **1992**, *11*, 4301–4305. (c) Ricci, A.; Angelucci, F.; Bassetti, M.; Lo Sterzo, C. *J. Am. Chem. Soc.* **2002**, *124*, 1060–1071 and references cited therein. (d) Lo Sterzo, C. *Synlett* **1999**, 1704–1722.
- Selected examples: (a) Bruce, M. I.; Humphrey, M. G.; Matison, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955–1961. (b) Szesni, N.; Drexler, M.; Maurer, J.; Winter, R. F.; de Montigny, F.; Lapinte, C.; Steffens, S.; Heck, J.; Weibert, B.; Fischer, H. *Organometallics* **2006**, *25*, 5774–5787. (c) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539–3549. (d) Butler, P.; Gallagher, J. F.; Manning, A. R. *Inorg. Chem. Commun.* **1998**, *1*, 343–345. (e) Bruce, M. I.; Hall, B. C.; Low, P. J.; Smith, M. E.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2000**, *300*–302, 633–644. (f) Powell, C. E.; Cifuentes, M. P.; McDonagh, A. M.; Hurst, S. K.; Lucas, N. T.; Delfs, C. D.; Stranger, R.; Humphrey, M. G.; Houbrechts, S.; Asselberghs, I.; Persoons, A.; Hockless, D. C. R. *Inorg. Chim. Acta* **2003**, *352*, 9–18.
- The reaction of $[\text{Cp}^*\text{Fe}(\text{dppe})\text{Cl}]$ with terminal acetylene in the presence of NH_4PF_6 followed by deprotonation with $t\text{BuOK}$ provides the corresponding alkynyliron complex efficiently. (a) Connelly, N. G.; Gamasa, M. P.; Gimeno, J.; Lapinte, C.; Lastra, E.; Maher, J. P.; Le Narvor, N.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1993**, 2575–2578. (b) Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 4240–4251. (c) Denis, R.; Weyland, T.; Paul, F.; Lapinte, C. *J. Organomet. Chem.* **1997**, *545*–546, 615–618.
- Review for the synthesis of alkynylmetal complexes: (a) Li, C.-L.; Liu, R. S. *Chem. Rev.* **2000**, *100*, 3127–3161. (b) Reference 3c.
- (a) Yasuda, S.; Yorimitsu, H.; Oshima, K. *Organometallics* **2008**, *27*, 4025–4027. (b) Asada, Y.; Yasuda, S.; Yorimitsu, H.; Oshima, K. *Organometallics* **2008**, *27*, 6050–6052.
- The palladium-catalyzed Sonogashira carbon–carbon bond formation reactions of $[\text{Cp}^*\text{Fe}(\text{dppe})(\text{C}\equiv\text{CH})]$ with aryl halides were reported. See references 3 and 8.
- Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664.
- Experimental procedure:** An iodoiron complex $[\text{CpFe}(\text{CO})_2\text{I}]$ (152 mg, 0.50 mmol), CuI (4.8 mg, 0.025 mmol), and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (8.8 mg, 0.013 mmol) were placed in a 20-mL reaction flask under argon. THF (1.0 mL), phenylacetylene (82 μL , 0.75 mmol), and diisopropylamine (0.50 mL) were sequentially added at 25 °C. The resulting mixture was stirred for 30 min at the same temperature. The mixture was then passed through a pad of silica gel by using ethyl acetate as an eluent. The filtrate was concentrated in vacuo. Chromatographic purification on silica gel (carbon disulfide/chloroform = 1:1) provided **1a** (112 mg, 0.40 mmol) in 81% yield.
- We believe that purification in a glovebox filled with inert gas would allow isolation of these unstable complexes.
- The reactions of iodoiron complexes with polyynyllithium were reported: Sakurai, A.; Akita, M.; Moro-oka, Y.

Organometallics **1999**, *18*, 3241–3244 and references cited therein.

15. (a) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321. (b) Sugiyama, J. Tomita, I. *Eur. J. Org. Chem.* **2007**, 4651–4653.
16. West, K.; Wang, C.; Batsanov, A. S.; Bryce, M. R. *J. Org. Chem.* **2006**, *71*, 8541–8544 and references cited therein.

Supplementary Material

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