

Communication

# FeCl<sub>3</sub>-Mediated Reaction of 1,4-Dilithio-1,3-dienes with Alkynes Affording Benzene Derivatives

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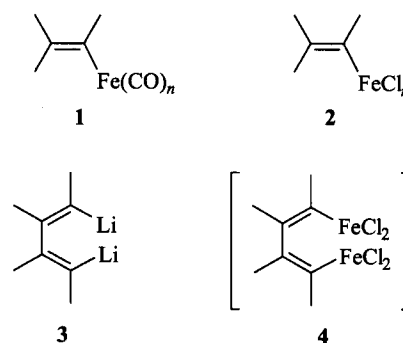
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Unactivated alkynes reacted with 1,4-dilithio-1,3-diene derivatives in the presence of FeCl<sub>3</sub> affording substituted benzene derivatives via a formal [4+2] cycloaddition.

**Keywords** alkenyl iron, alkynes, aromatic compounds, formal [4+2] cycloaddition, 1,4-dilithio-1,3-dienes, organolithium compounds, FeCl<sub>3</sub>

Synthetic methodology based on organometallic compound-mediated C—C bond formation reactions has become one of the most important tools for preparation of complex compounds. Although many of the organometallic compounds have complicated structures and compositions, development of new and synthetically useful methodologies using simple organometallic reagents or catalysts has been always in great demand. For example, among organometallic reactions involving Fe—C bonds,<sup>1</sup> the Fe atoms are in most cases coordinated to CO or more complicated ligands (**1**).<sup>1</sup> Preparation of such compounds (**1**) are usually not easy. Reactive organometallic compounds containing simple ClFe—C or Cl<sub>2</sub>Fe—C bonds (**2**) can be readily prepared. However, few reports have appeared on the study of the reaction chemistry and synthetic applications of simple ClFe—C or Cl<sub>2</sub>Fe—C bonds (**2**). We have recently demonstrated that 1,4-dilithio-1,3-diene derivatives (**3**) are of interesting and synthetically useful reactivities.<sup>2-7</sup> The co-operation or chelation of the two alkenyl lithium moieties in **3** towards coming substrates and the highly electron-rich character of **3** are considered to be critical for the success of these reactions.<sup>2-7</sup> As part of our continuous interest in discovery and development of synthetically useful organometallic reagents, we initiated a project in which the Li—C bonds were transmetalated to Fe—C bonds using very common and simple FeCl<sub>3</sub>. In this paper, we would like to communicate our preliminary results on study of the reaction chemistry of Fe—C bonds shown in **4**.



1,4-Dilithio-1,3-dienes (**3**) did not react with unactivated alkynes such as 4-octyne (Scheme 1). However, interestingly, in the presence of FeCl<sub>3</sub>, 1,4-dilithio-1,3-dienes did react with unactivated alkynes (Scheme 1); benzene derivatives were obtained as the products via a formal [4+2] cycloaddition reaction.<sup>8</sup> To the best of our knowledge, this result represents the first example of such [4+2] cycloaddition. A typical procedure is as follows. To a diethyl ether solution (5 mL) of 1,4-dilithio-1,2,3,4-tetrapropyl-1,3-diene (**3a**), prepared in situ from reaction of its corresponding 1,4-diiodide (1 mmol) with *t*-BuLi (4 mmol),<sup>2</sup> were stepwise added 4-octyne (1.0 mmol) and anhydrous FeCl<sub>3</sub> (0.67 mmol) at -78 °C. The reaction mixture was then warmed up to 0 °C and stirred at the same temperature for 3 h. Hexapropyl benzene (**5a**) was obtained in 51% isolated yield (73% GC yield) after hydrolysis of the reaction mixture with water or aqueous 3 N HCl.<sup>9</sup>

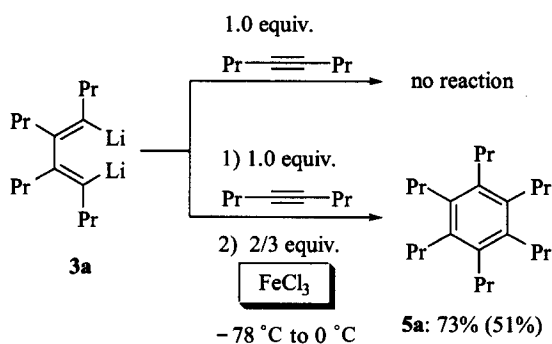
It is noteworthy that, in addition to promoting the above benzene formation reaction, FeCl<sub>3</sub> was found to promote polymerization of the 1,4-dilithio compounds. For example, when 3 equivalents of FeCl<sub>3</sub> were used, **3a** disappeared completely while **5a** was formed in only 8% GC yield; most of the dilithio compound **3a** was polymerized.

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Scheme 1

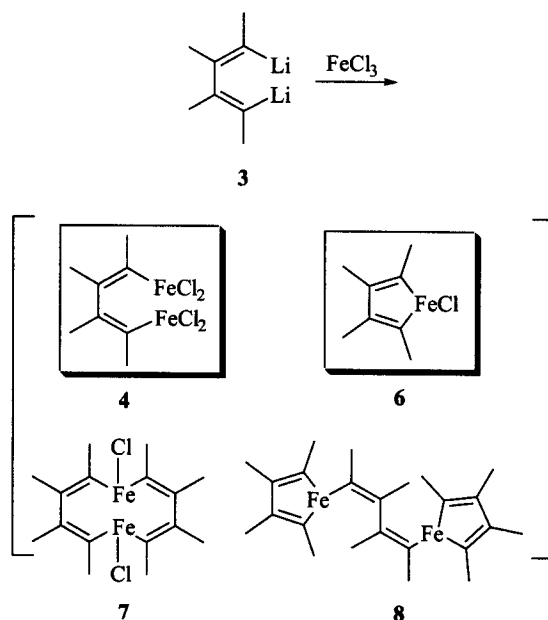


Listed in Table 1 are more examples. Different types of aromatic compounds, such as benzene ring with different substituents (**5b**, **5c**), tetrahydronaphthalene (**5d**) and naphthalene derivative (**5e**) could all be formed in reasonable yields. Therefore, this method provides an alternative way for the preparation of unsymmetrically substituted benzene derivatives.<sup>8e-g</sup> Desilylation took place in the workup procedure of **5b**. A small amount (< 5%) of hexabutyl benzene was formed as by-product in the  $\text{FeCl}_3$ -mediated reaction of **3c** with 5-decyne, obviously via self-cyclotrimerization of 5-decyne. The relatively low yields of formation of benzene derivatives are assumed to be due to competition by the  $\text{FeCl}_3$ -promoted polymerization of dilithio compounds.

Initially, transmetalation of 1,4-dilithio-1,3-dienes (**3**) with  $\text{FeCl}_3$  to form 1,4-diiron-1,3-dienes (**4**) and/or ferrole (**6**) was expected (Scheme 2). However, experimental re-

sults indicated that other intermediates such as **7** and/or **8** might also be involved in the reaction. When 2/3 equivalents of  $\text{FeCl}_3$  were used, best yield of **5a** was formed. Polymerization of 1,4-dilithio compounds was accelerated with an excess amount of  $\text{FeCl}_3$ . Furthermore,  $\text{FeCl}_2$  could also promote the above formal [4 + 2] cycloaddition, but with different reactivities.

Scheme 2



**Table 1** Formation of benzene derivatives by the reaction of 1,4-dilithio-1,3-dienes with unactivated alkynes

Dilithio compound <b>3</b>	Alkyne	Product <b>5</b>	Yield of <b>5</b> <sup>a</sup> (%)
	$\text{Hex}-\text{C}\equiv\text{C}-\text{SiMe}_3$		57 (36)
	$\text{Bu}-\text{C}\equiv\text{C}-\text{Bu}$		69 (51)
	$\text{Bu}-\text{C}\equiv\text{C}-\text{Ph}$		49 (39)
	$\text{Pr}-\text{C}\equiv\text{C}-\text{Pr}$		54 (26)

<sup>a</sup> GC yields. Isolated yields are given in parentheses. <sup>b</sup> Hexabutyl benzene of self-cyclotrimerization of 5-decyne was formed as by-product in <5% GC yield.

In conclusion, we report the first example of formal [4 + 2] cycloaddition of 1,4-dithio compounds with alkynes mediated by FeCl<sub>3</sub>. Preliminary experimental results indicate that (1) novel and reactive organoiron intermediate(s) must be involved in the reactions; and (2) unprecedented reaction chemistry of thus formed Fe—C bonds can be expected. Further investigation into these points is under progress.

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- Characterization data for **5a**: colorless crystals, m.p. 106–107 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 300 MHz) δ: 1.06 (t, *J* = 7.2 Hz, 18H), 1.51–1.59 (m, 12H), 2.49 (t, *J* = 8.4 Hz, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 75 MHz) δ: 15.25 (6C), 24.81 (6C), 32.24 (6C), 136.74 (6C); MS (70 eV) *m/z* (%): 330 (M<sup>+</sup>, 52), 301 (100); HRMS calcd for C<sub>24</sub>H<sub>42</sub> 330.3286, found 330.3281.

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