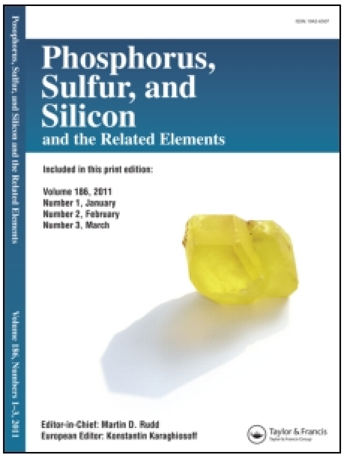

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Shimizu, Rumi , Hayashi, Naoto and Higuchi, Hiroyuki(2010) 'Generation of 1,1'-Diethynylferrocene for Practical Use: One-Pot Synthesis of 1,1'-Bis(Diacetylene)-Connected Ferrocene Derivative', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 5, 952 — 956

To link to this Article: DOI: 10.1080/10426501003769744

URL: http://dx.doi.org/10.1080/10426501003769744

Phosphorus, Sulfur, and Silicon, 185:952–956, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003769744

GENERATION OF 1,1′-DIETHYNYLFERROCENE FOR PRACTICAL USE: ONE-POT SYNTHESIS OF 1,1′-BIS(DIACETYLENE)–CONNECTED FERROCENE DERIVATIVE

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1,1′-Diethynylferrocene was readily generated for practical use from the trimethylsilyl-protected precursor under modified Eglinton conditions. An oxidative coupling reaction of this reactive species with phenylacetylene successively took place to afford the corresponding 1,1′-bis(diacetylene) connected ferrocene derivative.

Keywords Coupling reaction; diacetylene; 1,1′-diethynylferrocene; Eglinton; one-pot reaction

INTRODUCTION

For the development of new organic functional materials, a variety of π-electronic conjugated systems connected with the diacetylene linkage have been intensively investigated, particularly with respect to the advantages of the linkage, which is rigid, has a well defined structure, is sterically less demanding, and provides the possibility of π-conjugation.[1] Thus the characteristics of diacetylene linkages are very closely related to both functionality and processibility of the materials. In the research of functional materials the ferrocene [Cp_2(Fe); Fc], derivatives occupy a unique and characteristic position as a promising candidate for new materials by virtue of their molecular prochirality and electron-donating ability.[2,3] Some diacetylene-connected Fc derivatives have been described, but most of them are derivatives in which the diacetylene linkage is connected to one Cp ring.[4] In practice, no 1,1′-bis(diacetylene)–connected Fc derivatives are known except those which are sterically protected with bulky *tert*-butyl groups on each Cp ring.[5] This can be attributed to the fact that the parent 1,1′-diethynylferrocene (**1**), a useful synthon for the corresponding diacetylene derivatives, is extremely unstable to be handled under normal conditions, spontaneously giving rise to an intermolecular oxidative coupling reaction to form diacetylene connected Fc polymers (**2**) (Scheme 1).[5]

Received 10 November 2008; accepted 24 December 2008.

Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

Financial support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, is gratefully acknowledged.

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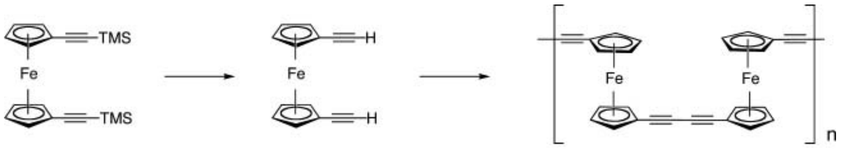

3 1 2

Scheme 1 Spontaneous polymerization of 1-1′-diethynylferrocene **1** to insoluble substance **2**.

These facts strongly stimulated us to develop a methodology for practical use of compound **1**, since we have also been engaged in the studies of diacetylene-connected π-electronic conjugated systems.[6] After several trials, we have succeeded in readily generating **1** from the trimethylsilyl (TMS)-protected precursor **3**[7] and to react it moderately by our conventional but slightly modified method (Scheme 1). In this article, the new method for generating **1** is reported together with its application to an oxidative coupling with phenylacetylene to give compound **4** (Figure 1).

RESULTS AND DISCUSSION

As reported,[5] the usual workup after TMS deprotection of the precursor **3** with potassium carbonate (K_2CO_3)[8] only afforded the insoluble substances **2**. Such highly labile behavior of **1** bearing two reaction sites in the molecule reminds a tandem system under high dilution conditions; thus we tried TMS deprotection of **3** followed by oxidative coupling reaction in one pot. The experimental results are summarized in Table I. Pyridine (Py), MeOH, and/or copper(II) acetate $Cu(OAc)_2$ (oxidative coupling media under Eglinton conditions[9]) were found to be entirely inert to **3**. When a solution of **3** was added to the Eglinton medium in the presence of K_2CO_3, the reaction gradually proceeded to form a linear dimer **5** (runs 4 and 5). $CHCl_3$ was also effective for the present reaction (run 6), probably because it is a good solvent for **5**, which dissolves from the heterogeneous medium somehow. In this reaction, the cyclic Fc dimer **7** was not isolated at all (Scheme 2), but the insoluble substance **2** was predominantly formed in all of runs 4, 5, and 6, similarly to run 1. This fact indicates that the oxidative coupling reaction of **1** proceeds swiftly via a strictly entropy-controlled pathway, in which the two terminal acetylenic sites in **6** exist oppositely far from each other.[5]

According to the above finding, the reaction of **3** with an excessive molar amount (ca. 5 eq.) of phenylacetylene (**8**) was carried out in a mixture of Py, MeOH, and $CHCl_3$ at 50 °C to afford the hetero-coupling product **4** in 38% yield (Scheme 3). To the best of our knowledge, compound **4** is the first example of a 1,1′-bis(diacetylene)–connected Fc derivative with no substituents on both Cp rings. In this reaction, the derivative **9** bearing one

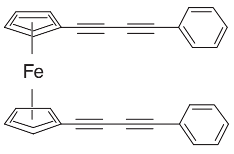

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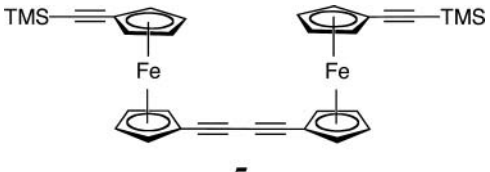
Figure 1 1,1′-Bis(phenyldiacetylene)-connected Fc derivative **4**.

Table I Experimental results of **3** reacted for 10 h under various conditions*

Run	Reagents and media	Temperature	Products
1	K_2CO_3 in $CHCl_3$-MeOH (1:1) [8]	RT	**2**
2	Py-MeOH (l:l)	RT	**3**
3	$Cu(OAc)_2$ in Py-MeOH (1:1) [9]	RT	**3**
4	K_2CO_3-$Cu(OAc)_2$ in Py-MeOH (1:1)	RT	**2** + **3** + **5** (7%)
5	K_2CO_3-$Cu(OAc)_2$ in Py-MeOH (1:1)	50°C	**2** + **3** + **5** (18%)
6	K_2CO_3-$Cu(OAc)_2$ inPy-MeOH-$CHCl_3$ (1:1:1)	50°C	**2** + **5** (34%)

* **3** (0.53 mmol) in a solution (210 mL) containing K_2CO_3 (2.68 mmol) and/or $Cu(OAc)_2$ (5.50 mmol).



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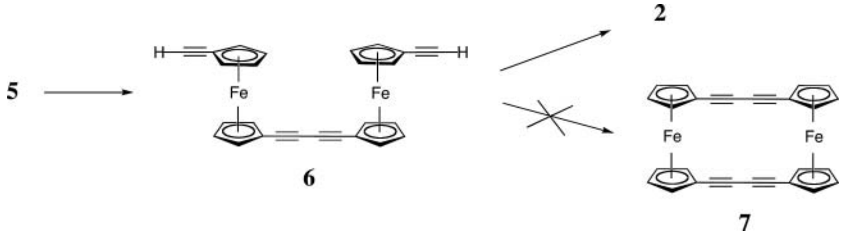
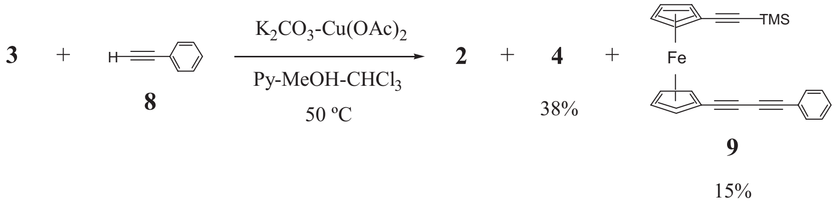


Scheme 2 Intermolecular diacetylene-linkage polymerization preferable to intramolecular diacetylene-linkage cycle dimerization; an entrophy-controlled pathway.



Scheme 3 A hetro-coupling of **3** with phenylacetylene **8** proceeds stepwise.

diacetylene linkage could also be obtained as a byproduct. The isolation of **5** and **9** under the present oxidative coupling conditions apparently indicates that the TMS-deprotection of **3** undergoes stepwise.

In conclusion, a synthetic methodology for 1,1′-bis(diacetylene)–connected Fc derivatives has been successfully developed by employing the tandem system: TMS deprotection of **3** and oxidative coupling reaction of the generated useful synthon **1** with another ethynyl compound in one pot. The present result will extend the research area of 1,1′-bis(diacetylene)–connected Fc derivative system as a precursor of new materials, since each Cp ring carries no substituents and is thus less perturbed both sterically and electronically.[5] Further investigations of **1** in coupling reactions are underway in terms of optimization and limitation.[10]

EXPERIMENTAL

General Procedure, Exemplifying Run 6 in Table I

A solution of **3**[7] (200 mg, 0.53 mmol) in a mixture of Py, MeOH, and $CHCl_3$ (90 mL, 1:1:1) was added to the solution of Py, MeOH, and $CHCl_3$ (120 mL, 1:1:1) containing $Cu(OAc)_2$ (1.0 g, 5.50 mmol) and K_2CO_3 (370 mg, 2.68 mmol) at 50°C with vigorous stirring over 10 h. The reaction mixture was concentrated to ca. one-third of its volume under reduced pressure, poured into water, filtered once to remove insoluble substances (**2**), and extracted with $CHCl_3$. The extracts were shaken with 1M HCl, washed with brine thoroughly, and then dried over $MgSO_4$. The residue obtained after removal of the solvent under reduced pressure was chromatographed on SiO_2 ($\phi 3 \times 15$ cm) with hexane/$CHCl_3$ (1:1) to afford **5** (57 mg, 34%) with recovery of **3** (26 mg). **5**: EI-MS: *m/z* = 634 and 635 (M^+ and $M^+ + 1$) for $C_{36}H_{34}Si_2{}^{56}Fe_2$. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 4.50$–4.48 (m, 8H, Fc-H), 4.29 (m, 4H, Fc-H), 4.27 (m, 4H, Fc-H), 0.25 (s, 18H, CH_3).

Similarly, reaction of **3** with phenylacetylene **8** afforded compounds **4** and **9** in 38% and 15% yield, respectively. **4**: EI-MS: *m/z* = 434 and 435 (M^+ and $M^+ + 1$) for $C_{30}H_{18}{}^{56}Fe$. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.45$ (m, 4H, arom-H), 7.32 (m, 2H, arom-H), 7.25 (m, 4H, arom-H), 4.59 (m, 4H, Fc-H), 4.37 (m, 4H, Fc-H). **9**: EI-MS: m/z 406 and 407 (M^+ and $M^+ + 1$) for $C_{25}H_{22}Si^{56}Fe$. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.51$ (m, 2H, arom-H), 7.37–7.28 (m, 3H, arom-H), 4.52 (m, 2H, Fc-H), 4.50 (m, 2H, Fc-H), 4.29 (broad s, 4H, Fc-H), 0.24 ppm (s, 9H, CH_3).

REFERENCES

1. Only a few articles from the viewpoint of material science are shown. (a) R. Kishi, M. Nakano, S. Yamada, K. Kamada, K. Ohta, T. Nitta, and K. Yamaguchi, *Chem. Phys. Lett.*, **393,** 437 (2004); (b) M. A. Fabre, J. Jaud, and J. J. Bonvoisin, *Inorg. Chim. Acta*, **358**, 2384 (2005); (c) T. Ishida, Y. Marisaki, and Y. Chujo, *Tetrahedron Lett.*, **47**, 5265 (2006).
2. (a) D. Savage, G. Malone, J. F. Gallagher, Y. Ida, and P. T. M. Kenny, *J. Organomet. Chem.*, **690**, 383 (2005); (b) A. Patti and S. Pedotti, *Tetrahedron: Asymmetry*, **16**, 965 (2005); (c) J. B. Heilmann, E. A. Hillard, M.-A. Plamont, P. Pigeon, M. Bolte, G. Jerard, and A. Vessieres, *J. Organomet. Chem.*, **693**, 1716 (2008).
3. (a) H. Imahori, Y. Mori, and Y. Matano, *J. Photochem. Photobio. C: Photochem. Rev.*, **4**, 51 (2003); (b) A. E.-W. A. O. Sarhan, *Tetrahedron*, **61**, 3889 (2005); (c) C. A. Nijhuis, B. J. Ravoo, J. Huskens, and D. N. Reinhouldt, *Coord. Chem. Rev.*, **251**, 1761 (2007).
4. (a) M. Rosenblum, N. Brawn, J. Papenmeier, and M. Applebaum, *J. Organomet. Chem.*, **6**, 173 (1966); (b) K. Kowalski and S. Domagala, *J. Organomet. Chem.*, **692**, 3100 (2007).
5. K. H. H. Fabian, H.-J. Lindner, N. Nimmerfroh, and K. Hafner, *Angew. Chem. Int. Ed.*, **40**, 3402 (2001) and references cited therein.
6. (a) H. Higuchi, T. Ishikura, K. Miyabayashi, M. Miyake, and K. Yamamoto, *Tetrahedron Lett.*, **40**, 9091 (1999); (b) H. Higuchi, T. Ishikura, K. Mori, Y. Takayama, K. Yamamoto, K. Tani, K. Miyabayashi, and M. Miyake, *Bull. Chem. Soc. Jpn.*, **74**, 889 (2001); (c) H. Higuchi, T. Maeda, K. Miyabayashi, M. Miyake, and K. Yamamoto, *Tetrahedron Lett.*, **43**, 3097 (2002); (d) N. Hayashi, T. Matsukihira, K. Miyabayashi, M. Miyake, and H. Higuchi, *Tetrahedron Lett.*, **47**, 5585 (2006); (e) N. Hayashi, T. Nishihara, T. Matsukihira, H. Nakashima, K. Miyabayashi, M. Miyake, and H. Higuchi, *Bull. Chem. Soc. Jpn.*, **80**, 371 (2007).

7. G. Doisneau, G. Balavoine, and T. Fillebeen-Khan, *J. Organomet. Chem.*, **425**, 113 (1992).
8. N. Hayashi, M. Murayama, K. Mori, A. Matsuda, E. Chikamatsu, K. Tani, K. Miyabayashi, M. Miyake, and H. Higuchi, *Tetrahedron*, **60**, 6363 (2004).
9. G. Eglinton and A. R. Galbraith, *Chem. Ind.*, 737 (1956).
10. The results will be reported elsewhere in detail, together with other physical and electronic properties of compounds **4**, **5**, and **9**.