*J. Org. Chem.* **2001,** *66,* 3533−3537

# Synthesis of Ferrocenyl Alkenes, Dienes, and Enynes via Samarium Diiodide Promoted Tandem Addition and Dehydration of Ferrocenyl Carbonyls with Halides

Shean-Jeng Jong and Jim-Min Fang*

*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China*

*jmfang@mail.ch.ntu.edu.tw*

*Received February 4, 2001*

A practical method for preparation of ferrocenyl alkenes, dienes, and enynes from ferrocenyl carbonyls was explored. A one-pot operation using samarium diiodide to promote the condensation reactions of ferrocenecarboxaldehyde, acetylferrocene, benzoylferrocene, and butanoylferrocene with benzyl bromides, allyl bromide, propargyl bromide, and 1-bromo-3-chlorobutane gave the olefinic products in very high yields. The condensation reactions were also achieved by using catalytic amounts of $SmI_2$ with magnesium to regenerate the divalent samarium reducing agent.

## Introduction

Ferrocenyl alkenes and dienes are important substrates for applications in material science.[1−3] For example, 1-ferrocenyl-2-(4-nitrophenyl)ethane and the related ferrocenyl alkenes exhibit large optical nonlinearities useful for the development of optical information processing.[1] Ferrocenyl 1,3-butadiene is an important substrate for manufacturing copolymers and homopolymers,[2] which are employed as the coating material for aerospace transportation to enhance resistance against photodegradation. Ferrocene-1,3-butadiene can also be used as an enhancement fuel in solid propellants.[2]

Three general methods have been utilized in the preparation of ferrocenyl alkenes and dienes: (i) using Wittig reactions,[4] (ii) using organometallic addition reactions,[5] and (iii) using Heck coupling reactions.[6] A preparation of ferrocenyl Wittig reagent is to activate (dimethylamino)methylferrocene by MeI and subsequently react with $Ph_3P$ and BuLi.[4] The resulting phophorus ylide can couple with aromatic aldehydes and conjugated aldehydes to give ferrocenyl alkenes and dienes. Alternatively, using ferrocenylcarboxaldehyde and the phosphorus ylides generated from organic halides can also afford ferrocenyl alkenes and dienes.[4] The drawbacks of Wittig reactions are that it takes two steps to prepare phosphorus ylides and the byproduct of phosphine oxides often causes problem in separation from the ferrocenyl products. The Wittig reaction of acetylferrocene with phosphorus ylides is complicated by the aldol reaction as the side route.[2e]

The addition reactions of ferrocenyl carbonyl compounds with organolithium,[2a] organomagnesium,[5a−c] and organozinc[5d] reagents have been studied in method ii. For example, allyllithium and allylmagnesium bromide react with ferrocenecarboxaldehyde to afford an addition product, 1-ferrocenyl-3-buten-1-ol. To obtain 1-ferrocenyl-1,3-butadiene, a subsequent dehydration is required, either by using large amounts of dehydrating agents (e.g., $CuSO_4$ and acidic $Al_2O_3$) or by refluxing azeotropically with a strong acid. An allylzinc reagent has been prepared by treating allyl bromide with ultrafine zinc powders supported on graphite. Using such active allyl-

---

[1] (a) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. *J. Nature* **1987**, *330*, 360. (b) Ghosal, S.; Samoc, M.; Prasad, P. N.; Tufariello, J. J. *J. Phys. Chem.* **1990**, *94*, 2847. (c) Calabrese, J. C.; Cheng, L. T. *J. Am. Chem. Soc.* **1991**, *113*, 7227. (d) Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Polyhedron* **1992**, 11, 1489. (e) Kott, K. L.; NcMahon, R. J. *J. Org. Chem.* **1992**, 57, 3097. (f) Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 6050. (g) Togni, A.; Rihs, G. *Organometallics* **1993**, *12*, 3368. (h) Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Cross, G. *J. Organomet. Chem.* **1994**, *464*, 225. (i) Alain, V.; Blanchard-Desce, M.; Chen, C.-T.; Marder, S. R.; Fort, A.; Barzoukas, M. *Synth. Met.* **1996**, *81*, 133. (j) Mata, J.; Uriel, S.; Peris, E.; Llusar, R.; Houbrechts, S.; Persoons, A. *J. Organomet. Chem.* **1998**, *562*, 197. (k) Herrmann, R.; Pedersen, B.; Wagner, G.; Youn, J.-H. *J. Organomet. Chem.* **1998**, *571*, 261. (l) Balavoine, G. G. A.; Daran, J.-C.; Iftime, G.; Lacroix, P. G.; Manoury, E.; Delaire, J. A.; Maltey-Fanton, I.; Nakatani, K.; Bella, S. Di *Organometallics* **1999**, *18*, 21.

[2] (a) Ponder, B. W.; Barnhill, C. W. US Patent 3739004, 1973. (b) Huskins, C. W.; Van Landuyt, D. C. US Patent 3843426, 1974. (c) Gauiter, J. C. C.; Raynal, S. F. US Patent 4661608, 1987. (d) Gautier, J. C. C.; Fontanille. M. H.; Raynal, S. F. US Patent 4647628, 1987. (e) Miller, E. J.; Weigelt, C. A.; Serth, J. A.; Rusyid, R.; Brenner, J.; Luck, L. A.; Godlewski, M. *J. Organomet. Chem.* **1992**, *440*, 91. (f) Grevels, F.-W.; Kuran, A.; Ozkar, S.; Zora, M. *J. Organomet. Chem.* **1999**, *587*, 122.

[3] For incorporation of ferrocenyl alkenes in charge-transfer complexes, porphyrins, crown ethers, see: (a) Togin, A.; Hobi, M,; Rihs, G.; Rist, G.; Albinati, A, *Organometallics* **1994**, 73, 1224. (b) Andrews, M. P.; Blackburn, C.; McAleer, J. F.; Pater, V. D. *J. Chem. Soc. Chem. Commun.* **1987**, 1122. (c) Burrell, A. K.; Campbell, W.; Officer, D. L. *Tetrahedron Lett.* **1997**, *38*, 1249. For spectroscopic and binding studies of ferrocene alkenes and polyenes, see: (d) Bochmann, M.; Lu, J.; Cannon, R. D. *J. Organomet. Chem.* **1996**, *518*, 97. (e) Solcaniova, E.; Toma, S.; Liptaj, T. *Collect. Czech. Chem. Commun.* **1986**, *51*, 670. (f) Liu, J.; Castro, R.; Abboud, K. A.; Kaifer, A. E. *J. Org. Chem.* **2000**, *65*, 6973. For use as an analogue of anticancer drug Tamoxifen, see: (g) Top, S.; Tang, J.; Vessieres, A., Carrez, D.; Provot, C.; Jaouen, G. *Chem. Commun.* **1996**, 955.

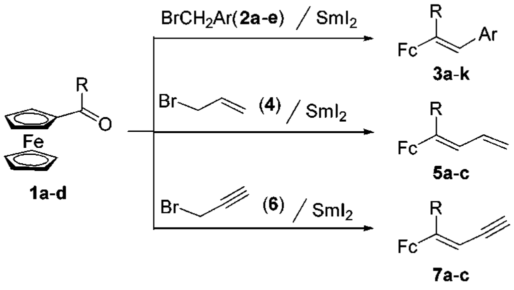
[4] In addition to refs 1d,f,i,j, 2e, and 3a,e, see: (a) Osgerby, J. M.; Pauson, P. L. *J. Chem. Soc.* **1961**, 4604. (b) Ponder, B. W.; Kneisel, R. C.; Lewis, D. H. *Org. Prep. Proc. Int.* **1971**, *3*, 171. (c) Lewis, D. H.; Neal, M. C.; Ponder, B. W. *Synth. Commun.* **1972**, *2*, 93. For a similar reaction using arsonium salts, see: (d) You, X.; Sun, H.; Peng, X.; Yue, C.; Li, C.; Wu, H. *Inorg. Chim. Acta* **1995**, *234*, 139.

[5] In addition to ref 2a, see: (a) Van Landuyt, D. C. US Patent 3751441, 1973. (b) Stephens, W. D.; Willis, T. C.; Combs, C. S. US Patent 3847871, 1974. (c) Duran, M.; Konstantinovic, S.; Pavlovic, V.; Predojevic, J.; Ratkovic, Z.; Rufinska, A.; Simova, S. *J. Serb. Chem. Soc.* **1995**, *60*, 737. *Chem. Abst. 124*, 56207. (d) Qiu, C.; Zhang, Y. *Huaxue Shiji* **1992**, *14*, 104.

[6] (a) Koenig, B.; Zieg, H.; Bubenitschek, P.; Jones, P. G. *Chem. Ber.* **1994**, *127*, 1811. (b) Qian, Y. *Huagong Shikan* **1998**, *12*, 11. (c) Naskar, D.; Das, S. K.; Giribabu, L.; Maiya, B. G.; Roy, S. *Organometallics* **2000**, *19*, 1464.

10.1021/jo015557r CCC: \$20.00

**Scheme 1. $SmI_2$-Promoted One-Pot Formation of Ferrocenyl Alkenes, Dienes, and Enynes**



R = H, $CH_3$, Ph and *n*-Pr
Ar = Ph, *p*-$NCC_6H_4$, *m*-$MeOC_6H_4$, 2-naphthyl, *p*-$F_3CC_6H_4$

zinc reagent to react with ferrocenecarboxaldehyde gives directly 1-ferrocenyl-1,3-butadiene in 85% yield. However, the yield decreases drastically if the zinc powder is not fine enough. As preparation of such active zinc powders involves mixing of melted potassium powders (highly active) with graphite and $ZnCl_2$, one must take precautions during this hazardous operation.

Palladium-catalyzed Heck-type reactions for preparation of ferrocenyl alkenes have appeared in two reports.[6] One paper shows the coupling reactions of vinylferrocene with aromatic and heteroaromatic halides by the catalysis of $Pd(OAc)_2$, giving (1-ferrocenyl-2-aryl)ethenes. The drawback of this method is that vinylferrocene is not readily available and susceptible to polymerization. On the other hand, ferrocene is treated with $HgCl_2$ to give ferrocenylmercury chloride, which undergoes coupling reactions with conjugated olefins $H_2C{=}CHZ$ (Z representing CHO, $CO_2Me$, CN, and 4-pyridyl) by the catalysis of $Li_2PdCl_4$. This method is limited to the synthesis of ferrocenyl alkenes (FcCH=CHZ) with electron-withdrawing groups. Synthesis of ferrocenyl 1,3-dienes by Heck-type coupling reactions has not yet been realized.

Kagan and co-workers have shown that $SmI_2$ exhibits a high reducing power to convert alkyl bromides and iodides into the corresponding organosamarium halides with high efficiency.[7] Barbier-type reactions of the resulting organosamarium reagents with carbonyl compounds afford the addition products of secondary and tertiary alcohols.

## Results and Discussion

We demonstrate herein that condensation reactions of ferrocene carbonyls (**1a**−**d**) with benzyl bromides, allyl bromide, and propargyl bromide were achieved in a single step by the promotion of $SmI_2$ (Scheme 1). A series of ferrocenyl alkenes (**3a**−**j**), dienes (**5a**−**c**), and enynes (**7a**−**c**) were obtained in high yields (Table 1).

The reaction was simply carried out by stirring a ferrocene carbonyl with an excess bromide in the presence of a stoichiometric amount of $SmI_2$. The ferrocene carbonyls examined in this study included ferrocenecarboxaldehyde (**1a**), acetylferrocene (**1b**), benzoylferrocene (**1c**) and butanoylferrocene (**1d**). The $SmI_2$-promoted condensation reactions were clean, without pinacolic coupling[8] of carbonyls or Wurtz coupling[9] of bromides. The cyano, methoxy, and trifluoromethyl substituents on the phenyl rings of benzyl bromides **2b**, **2c**, and **2e** were retained under such reaction conditions (entries 2, 3, and 7, Table 1). Compounds **3a**,[3e] **3b**,[1c] and **5a**[4a,b] are known compounds, whereas the structures of others products were determined by spectral methods. The products **3a**−**k** and **5a**−**c** consistently had (*E*)-configurations as characterized by the large coupling constants (ca. 16 Hz) between olefinic protons in their $^1$H NMR spectra. The stereochemistry of **3g** and **3i** was further confirmed by X-ray diffraction analyses. Enynes **7a**−**c** existing as mixtures of (*E*)- and (*Z*)-isomers with preponderance of the (*E*)-isomers (82−95%). An NOESY study of **7b** isomers supported their structural assignments. Thus, the vinyl proton of (*E*)-**7b** occurring at $\delta$ 6.00 showed an NOE correlation with the ferrocenyl protons, whereas that of (*Z*)-**7b** appearing at $\delta$ 5.58 had an NOE correlation with the phenyl protons.

**Table 1. Reactions of Ferrocene Carbonyls (1a−d) with Benzyl Bromides (2a−d), Allyl Bromide, and Propargyl Bromide Using Stoichiometric Amounts of $SmI_2$ (Scheme 1)[a]**

| entry | ferrocene | halide | product (yield, %)[b] |
|---|---|---|---|
| 1 | **1a**, R = H | **2a**, Ar = Ph | **3a** (95)[c] |
| 2 | **1a** | **2b**, Ar = 4-$NCC_6H_4$ | **3b** (95)[c] |
| 3 | **1a** | **2c**, Ar = 3-$MeOC_6H_4$ | **3c** (90)[c] |
| 4 | **1a** | **2d**, Ar = 2-naphthyl | **3d** (75)[c] |
| 5 | **1b**, R = $CH_3$ | **2a** | **3e** (98)[c] |
| 6 | **1b** | **2b** | **3f** (99)[c] |
| 7 | **1b** | **2e**, Ar = 4-$F_3CC_6H_4$ | **3g** (98)[c] |
| 8 | **1c**, R = Ph | **2a** | **3h** (98)[c] |
| 9 | **1c** | **2b** | **3i** (99)[c] |
| 10 | **1c** | **2c** | **3j** (92)[c] |
| 11 | **1c** | **2d** | **3k** (88)[c] |
| 12 | **1a** | allyl bromide (**4**) | **5a** (98)[c] |
| 13 | **1b** | **4** | **5b** (99)[c] |
| 14 | **1c** | **4** | **5c** (99)[c] |
| 15 | **1b** | propargyl bromide (**6**) | **7a** (98)[d] |
| 16 | **1c** | **6** | **7b** (96)[e] |
| 17 | **1d**, R = *n*-Pr | **6** | **7c** (99)[f] |

[a] Under an atmosphere of argon, an appropriate halide (2.0 mmol in 5 mL of THF) and ferrocene carbonyl (1.2 mmol in 5 mL of THF) were added consecutively to a freshly prepared $SmI_2$ solution (1.8 mmol in 20 mL of THF) at 0 °C. The mixture was stirred for 0.5−2 h. The septum was removed, and the mixture was stirred at room temperature for an additional 15−24 h to give the desired products. [b] The yields are reported on the basis of the molar quantity of the ferrocenyl reagents. [c] The product had (*E*)-configuration. [d] Enyne **7a** contained (*E*)- and (*Z*)-isomers in a ratio of 90:10. [e] Enyne **7b** contained (*E*)- and (*Z*)-isomers in a ratio of 82:18. [f] Enyne **7c** contained (*E*)- and (*Z*)-isomers in a ratio of 95:5.

The $SmI_2$-promoted reaction of ferrocenyl carbonyl with halides conceivably proceeded with a Barbier-type addition intermediate, as exemplified by alkoxide **A** derived from the reaction with allylsamarium. Indeed, the alkoxide intermediate **A** was hydrolyzed to give the corresponding alcohol (**8a**−**c**) by quenching with water (Scheme 2). Elimination of $HOSmI_2$ would lead to the conjugated ferrocenyl dienes **5a**−**c**. This process was presumably promoted by trivalent samarium ion (as a Lewis acid) generated in situ. Formation of a transient α-carbonium ion could be facilitated by the adjacent ferrocenyl moi-

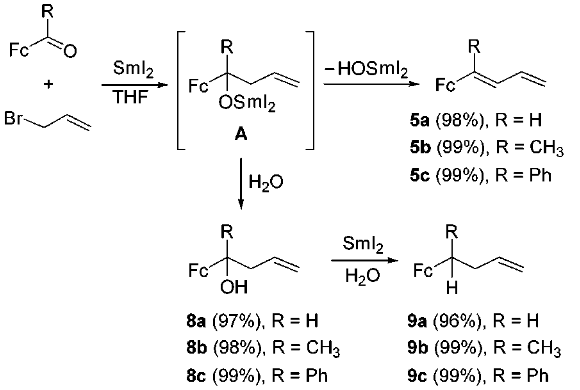
---

(7) (a) Girard, P.; Namy, J.-L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (b) Hamann-Gaudinet, B.; Namy, J.-L.; Kagan, H. B. *Tetrahedron Lett.* **1997**, *38*, 6585.

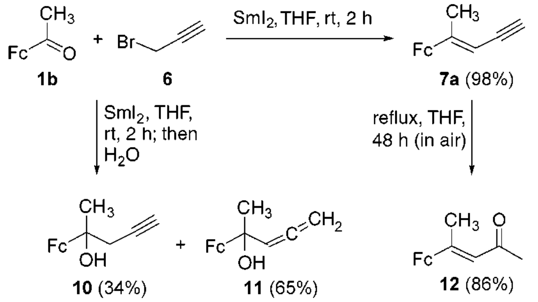
(8) For $SmI_2$-mediated pinacol coupling reactions of ferrocenyl carbonyls, see: (a) Taniguchi, N.; Uemura, M. *Tetrahedron* **1998**, *54*, 12775. (b) Jong, S.-J.; Fang, J.-M.; Lin, C.-H. *J. Organomet. Chem.* **1999**, *590*, 42. (c) Christensen, Torben B.; Riber, D.; Daasbjerg, K.; Skrydstrup, T. *Chem. Commun.* **1999**, 2051.

(9) In the absence of carbonyl compounds, treatment of benzyl bromide with $SmI_2$ leads to a Wurtz coupling product, 1,2-diphenylethane. See refs 7 and 15e.

**Scheme 2. Reactions of Ferrocenyl Carbonyls with Allyl Bromide**



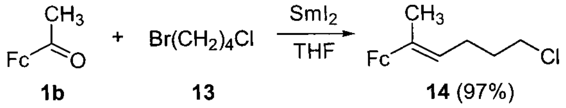
**Scheme 3. Reactions of Acetylferrocene with Propargyl Bromide**



ety.[10] We also carried out a deoxygenation of alcohols **8a**−**c**, giving excellent yields of **9a**−**c**, by treatment with $SmI_2$ in refluxing THF using $H_2O$ (5.5 equiv) as the proton source.[8b, 11]

The $SmI_2$-promoted reaction of acetylferrocene and propargyl bromide yielded a mixture of alkynyl alcohol **10** (34%) and allenyl alcohol **11** (65%) on quenching with water (Scheme 3).[12] A conjugated ketone **12** was obtained in 86% yield[13] when the reaction mixture was further refluxed in THF without rigorous exclusion of moisture. The facile hydration of alkynyl and allenyl groups was attributable to the promotion of trivalent samarium ions. Indeed, enyne **7a** was converted in part to enone **12** on a silica gel column. Isolation of enyne **7a** was realized by chromatography on neutral alumina or on the silica gel pretreated with $Et_3N$.

As $SmI_2$ in THF hardly reduces alkyl chloride without using other activations (e.g., using a polar cosolvent HMPA or light irradiation),[14] we were able to synthesize 2-ferrocenyl-6-chloro-2-hexene (**14**) in 97% yield from 1-bromo-3-chloropropane by the $SmI_2$-promoted condensation with acetylferrocene (eq 1). Such selective transformation would not be feasible by the previous methods using organolithium or Grignard reagents.



There are several reports on using catalytic amounts of $SmI_2$ with an in situ regenerated system.[15] Excess amounts of samarium,[15a] maganesium,[15b,d] zinc amalgam[15c] and mischmetall (cerium mixed metal)[15e] have been employed with sub-stoichiometric amounts of $SmI_2$ to effect a number of reactions, such as coupling of halides with ethynylsilanes,[15a] pinacolic coupling reactions of carbonyl compounds,[15b,e] coupling of imines,[15d] coupling of acid chlorides,[15e] deoxygenation of oxiranes,[15c] reduction of iodoalkanes and benzyl bromides,[15e] cyclization of 1-iodo-6-phenyl-5-hexyne, radical $\pi$-cyclization of ketones with acrylate esters to form $\gamma$-lactones,[15c] and Barbier-type reactions.[15c] In some cases, stoichiometric amounts of $Me_3SiCl$[15b] or $Me_3SiOTf$[15c] are required for cleavage of O−Sm(III) alkoxide bond to facilitate the reaction cycle.

A $SmI_2$-promoted Barbier-type reactions of benzaldehydes with allyl bromide has been conducted by irradiation with high-pressure mercury lamp to regenerate Sm(II) species,[16] presumably using the solvent THF as the reducing agent. The scope of this method is rather limited due to low yields and complication of side products. Aliphatic aldehydes and cinnamaldehyde also failed to react with allyl bromide under such photochemical conditions.

We also tested the feasibility of using magnesium metal to regenerate divalent samarium reducing agent in the transformation of ferrocenyl carbonyl with halides (Table 2). In the absence of $SmI_2$, treatment of acetylferrocene with the Grignard reagents of benzyl bromide and allyl bromide afforded only the addition products **15** and **8b** (entries 1 and 8, Table 2). By using substoichiometric amounts of $SmI_2$ (0.18−0.54 molar proportions) in the absence of Mg metal, the yields of **15** and **8b** were low ($\leq$15%) (entries 2 and 9, Table 2). Combined use of excess Mg (2−3 molar proportions) with substoichiometric amounts of $SmI_2$ (0.18−0.54 molar proportions) increased the yields of **15** (63%) and **8b** (89−99%) to great extent (entries 3, 10, and 11). The reaction mixture in THF solution was thus refluxed for the indicated period to furnish the dehydration to give ferrocenyl alkene **3e** and diene **5b** in nearly quantitative yields (entries 4, 12, and 13, Table 2).

4-Cyanobenzyl bromide did not react with acetylferrocene in the presence of Mg (entry 5, Table 2). However,

---

(10) The ferrocenyl group is known to stabilize the α-carbocation. For formation of ferrocenyl α-carbocations from the corresponding alcohols and dienes, see: (a) Siglmueller, F.; Herrmann, R.; Ugi, I. *Tetrahedron* **1986**, *42*, 5931. (b) Ortaggi, G. *Gazz. Chim. Ital.* **1987**, *117*, 75. (c) Zou, C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7578. (d) Klimova, E. I.; Klimova, T. B.; Martinez, M. G.; Meleshonkova, N. N.; Ruis, L. R. *Mendeleev Commun.* **1997**, 233.

(11) (a) Nesmeyanov, A. N.; Perevalova, E, G. *Izyest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1961**, 1982. This paper reports a preparation of 4-ferrocenyl-1-butene (compound **9a**) in <50% yield by subsequent treatments of (*N*,*N*-dimethylamino)methylferrocene with iodomethane and allylmagnesium bromide. For compound **9c**, see: (b) Mayr, H.; Rau, D. *Chem. Ber.* **1994**, *127*, 2493.

(12) The $SmI_2$-promoted Barbier reaction of propargyl bromide and 2-octanone gives 4-methyl-1-decyn-4-ol (37%) and 4-methyl-1,2-decadien-4-ol (35%). See ref 7a.

(13) Condensation of ferrocene with 2,4-pentanedione in $H_2SO_4$ or $POCl_3/HClO_4$ gives compound **12** in less than 35% yield. See: Temerov, S. A.; Sachivko, A. V.; Tverdokhleov, V. P.; Tselinskii, I V.; Frolova, G. M. *Zh. Org. Khim.* **1991**, 27, 918.

(14) (a) Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485. (b) Ogawa, A.; Sumino, Y.; Nanke, T.; Ohya, S.; Sonoda, N.; Hirao, T. *J. Am. Chem. Soc.* **1997**, *119*, 2745. (c) Shabangi, M.; Flowers, R. A., II. *Tetrahedron Lett.* **1997**, *38*, 1137.

(15) (a) Murakami, M.; Hayashi, M.; Ito, Y. *Synlett* **1994**, 757. (b) Nomura, **R.;** Matsuno, T.; Endo, T. *J. Am. Chem. Soc.* **1996**, *118*, 11666. (c) Corey, E. J.; Zhang, G. Z. *Tetrahedron Lett.* **1997**, *38*, 2045. (d) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Raimondi, L. *Tetrahedron Lett.* **1998**, *39*, 3333. (e) Helion, F.; Namy, J.-L. *J. Org. Chem.* **1999**, *64*, 2944.

(16) Kondo, T.; Akazome, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 757.

**Table 2. Reactions of Acetylferrocene (1b) with Benzyl Bromides (2a,b), Allyl Bromide, and Propargyl Bromide Using Mg and Substoichiometric Amounts of $SmI_2$ (Figure 1)**[a]

| entry | halide | halide/Mg/$SmI_2$ molar proportions[b] | reaction conditions ($T$ (°C), time (h)) | product (yield, %)[c] |
|---|---|---|---|---|
| 1 | $PhCH_2Br$ | 1.5:2:0 | 25, 5[d] | **15** (28) |
| 2 | $PhCH_2Br$ | 1.5:0:0.54 | 25, 3[d] | **15** (15) |
| 3 | $PhCH_2Br$ | 1.5:2:0.54 | 25, 3[d] | **15** (63) |
| 4 | $PhCH_2Br$ | 1.5:2:0.54 | 25, 5;[e] 68, 48 | **3e** (99) |
| 5 | $4\text{-}NCC_6H_4CH_2Br$ | 1.5:2:0 | 68, 8 | no reaction |
| 6 | $4\text{-}NCC_6H_4CH_2Br$ | 1.5:0:0.54 | 25, 15;[e] 68, 2 | **3f** (16) |
| 7 | $4\text{-}NCC_6H_4CH_2Br$ | 1.5:2:0.54 | 25, 15;[e] 68, 2 | **3f** (52) |
| 8 | $CH_2{=}CHCH_2Br$ | 1.5:2:0 | 25, 10 min[d] | **8b** (60) |
| 9 | $CH_2{=}CHCH_2Br$ | 1.5:0:0.18 | 25, 10 min[d] | **8b** (11) |
| 10 | $CH_2{=}CHCH_2Br$ | 1.5:2:0.18 | 25, 10 min[d] | **8b** (89) |
| 11 | $CH_2{=}CHCH_2Br$ | 1.5:3:0.20 | 25, 1[d] | **8b** (99) |
| 12 | $CH_2{=}CHCH_2Br$ | 1.5:3:0.20 | 25, 1;[e] 68, 72 | **5b** (99) |
| 13 | $CH_2{=}CHCH_2Br$ | 1.5:3:0.54 | 25, 1;[e] 68, 2 | **5b** (99) |
| 14 | propargyl bromide | 1.5:3:0.45 | 25, 15;[e] 68, 12 | **12** (59) |

[a] The reaction was conducted by using 1 mmol of acetylferrocene in THF solution. [b] Based on the molar quantity of acetylferrocene. [c] The yields are reported based on the molar quantity of the ferrocenyl reagents. [d] After which, the reaction was quenched by addition of water. [e] After which, the septum was removed, and the reaction mixture was refluxed for the indicated period.

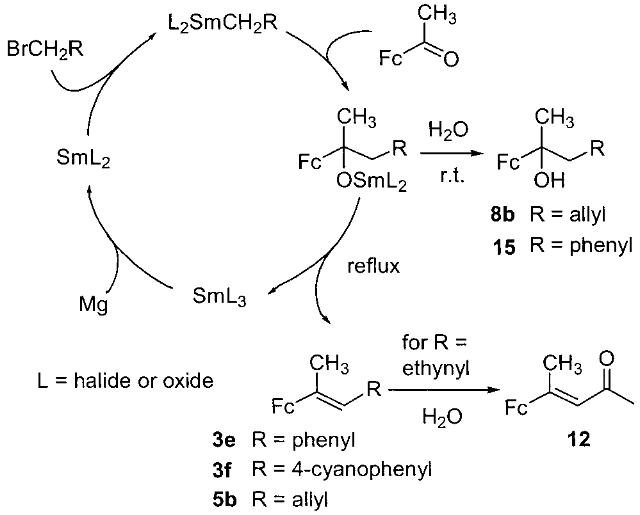


**Figure 1.** Proposed catalytic cycle for the reaction of acetylferrocene with halides in the presence of Mg and $SmI_2$. The ligand L represents halide or oxide.

a modest yield (52%) of alkene **3f** was obtained by reflux in the presence of Mg and $SmI_2$ (entry 7, Table 2). The reaction of acetylferrocene and propargyl bromide was similarly carried out by using Mg (3 molar proportions) and $SmI_2$ (0.45 molar proportions) to give a 59% yield of enone **12** (entry 14, Table 2).

By analogy to the previously proposed reaction mechanisms,[15a,d] the above experimental results could be explained by a reaction cycle as depicted in Figure 1. Reduction of a bromide ($RCH_2Br$) with $SmI_2$ (or the related divalent samarium species) gave an organosamarium reagent ($RCH_2SmBrL$, L is halide or oxide). The Barbier-type addition reaction with acetylferrocene led to an alkoxide intermediate, which could undergo either hydrolysis to give alcohols (e.g., **8b** and **15**) or elimination to give alkenes (e.g., **3e**, **3f** and **5b**). The released trivalent samarium species ($SmI_2OH$ and analogues) could be reduced by Mg to regenerate divalent $SmL_2$ for the next cycle of reactions.

In summary, we have developed a simple and expedient method for the preparation of ferrocenyl alkenes, dienes, and enynes from ferrocenyl carbonyls and halides by using $SmI_2$ in one-pot operation. The $SmI_2$-promoted reaction proceeded with a Barbier-type addition followed by elimination of $HOSmI_2$ to furnish the desired products in very high yields. The condensation reactions were also achieved by using catalytic amounts of $SmI_2$ with excess magnesium to regenerate the divalent samarium reducing agent. No silyl reagents such as $Me_3SiCl$ or $Me_3SiOTf$ were required in this regenerating system. Our present method is superior to previous methods in the sense of simple operation and high yields.

## Experimental Section

Melting points are uncorrected. Chemical shifts are reported relative to $CHCl_3$ ($\delta_H$7.26) and $CDCl_3$ [$\delta_C$ (central line of t) 77.0]. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of nitrogen. Syringes and needles for the transfer of reagents were dried at 120 °C and allowed to cool in a desiccator over $P_2O_5$ before use. Ethers were distilled from sodium benzophenone ketyl, and (chlorinated) hydrocarbons from $CaH_2$. Column chromatography was generally carried out on Kieselgel 60 (40−63 $\mu$m) unless specified. Merck silica gel 60F sheets were used for analytical thin-layer chromatography.

**Representative Procedure for the Reactions of Ferrocene Carbonyls with Halides Using Stoichiometric Amounts of $SmI_2$ (Table 1).** Under an atmosphere of argon, a deep blue $SmI_2$ solution (0.1 M) was prepared by treatment of Sm (331 mg, 2.2 mmol) with 1,2-diiodoethane (507 mg, 1.8 mmol) in anhydrous THF (20 mL) for 1.5 h at room temperature. To the $SmI_2$ solution (cooled in an ice bath) were added consecutively an appropriate halide (benzyl bromide **2a**−**d**, allyl bromide, propargyl bromide, or 1-bromo-4-chlorobutane, 2.0 mmol in 5 mL of THF) and ferrocene carbonyl (**1a**−**d**, 1.2 mmol in 5 mL of THF). The mixture was stirred for 0.5−2 h. The septum was removed, and the mixture was stirred at room temperature for an additional 15−24 h. The mixture was concentrated and chromatographed by elution with gradients of EtOAc/hexane (2:98 up to 1:1) to give the desired condensation products (**3a**−**j**, **5a**−**c**, **7a**−**c**, and **14**). The yields were reported based on the molar quantity of the ferrocenyl reagents. Silica gel was generally used for chromatography, but neutral alumina was preferable for isolation of enynes **7a**−**c**.

**Representative Procedure for the Reactions of Acetylferrocene with Halides Using Mg and Substoichiometric Amounts of $SmI_2$ (Table 2).** Under an atmosphere of argon, Mg powders (48 mg, 2 mmol) were placed in a round-bottomed flask. A freshly prepared $SmI_2$ solution (0.1 M) in anhydrous THF (2 mL) was added. A mixture of acetylferrocene (229 mg, 1 mmol) and an appropriate halide (allyl bromide, benzyl bromide, 4-cyanobenzyl bromide, or propargyl bromide, 1.5 mmol in 20 mL of THF) was added. The deep blue color of

$SmI_2$ discharged. After stirring for a certain period (10 min to 15 h), the light blue color resumed. The septum was removed, and a reflux column was applied. The mixture was refluxed for 2−72 h, cooled, concentrated, and chromatographed by elution with gradients of EtOAc/hexane to give the desired condensation products.

**4-Ferrocenyl-1,3-pentadiene (5b).** According to the representative procedure, the $SmI_2$-promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and allyl bromide (242 mg, 2.0 mmol) gave the title compound (302 mg, 99% yield): orange solid, 55 °C; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.08 (3 H, s, $CH_3$), 4.10 (5 H, s, Fc), 4.23 (2 H, s, Fc), 4.40 (2 H, s, Fc), 5.07 (1 H, d, $J = 11.0$ Hz), 5.19 (1 H. d. $J = 16.7$ Hz), 6.29 (1 H, d, $J = 11.0$ Hz), 6.67 (1 H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 15.7, 65.6 (2×), 68.8 (2×), 69.1 (5×), 115.0, 123.6, 133.5, 135.3; FAB-MS $m/z$ 252 ($M^+$). Anal. Calcd for $C_{15}H_{16}Fe$: C, 71.45; H, 6.40. Found: C, 71.57; H, 6.71.

**4-Ferrocenyl-3-hepten-1-yne (7c).** According to the representative procedure, the $SmI_2$-promoted condensation of butanoylferrocene (307 mg, 1.2 mmol) and propargyl bromide (238 mg, 2.0 mmol) gave the title compound (333 mg, 99% yield) as a mixture of (*E*)- and *Z*)-isomers (95:5) after chromatography on neutral $Al_2O_3$: red-brown oil; IR (KBr) 2084, 1641 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.02 (3 H, t, $J = 7.7$ Hz)/0.99, 1.68−1.58 (2 H, m), 2.60 (2 H, t, $J = 7.7$ Hz), 3.22 (1 H, d, $J = 2.4$ Hz), 4.12 (5 H, s), 4.29 (2 H, m), 4.41 (2 H, m)/4.96, 5.70 (1 H, d, $J = 2.4$ Hz)/5.42; $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 14.4, 23.2, 34.7, 66.1 (2×), 69.4 (7×), 81.4, 82.7, 100.9, 154.7; FAB-MS $m/z$ 278 ($M^+$); HRMS calcd for $C_{17}H_{18}Fe$ 278.0758, found 278.0754.

**2-Ferrocenyl-4-buten-2-ol (8b).** The $SmI_2$-promoted addition reaction of allyl bromide (242 mg, 2.0 mmol) to acetylferrocene (274 mg, 1.2 mmol), by a procedure similar to that for **8a**, gave the title compound (316 mg, 98% yield): orange oil; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.46 (3 H, s), 2.16 (1 H, br s, OH), 2.33 (1 H, dd, $J = 13.7$, 7.5 Hz), 2.46 (1 H, dd, $J = 13.7$, 7.1 Hz), 4.07−4.21 (9 H, m), 5.01 (2 H, m), 5.75 (1 H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.0, 48.3, 65.3, 66.6, 67.5, 67.7, 68.2 (5×), 70.4, 99.3, 117.7, 134.4; FAB-MS $m/z$ 270 ($M^+$); HRMS calcd for $C_{15}H_{18}FeO$ 270.0707, found 270.0693.

**4-Ferrocenyl-1-pentene (9b).** Reduction of alcohol **8b** (270 mg, 1.0 mmol), by a procedure similar to that for **9a**, gave the title compound (252 mg, 99% yield): brown oil; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.20 (3 H, d, $J = 6.8$ Hz), 2.04−2.12 (1 H, m), 2.31−2.39 (1 H, m), 2.51−2.58 (1 H, m), 4.05 (4 H, s), 4.11 (5 H, s), 4.97−5.03 (2 H, m), 5.71−5.85 (1 H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 20.0, 29.7, 33.0, 43.1, 65.9, 66.8, 66.9, 67.0, 68.3 (5×), 95.4, 115.7, 137.4; IR (KBr) 1640 cm$^{-1}$; FAB-MS $m/z$ 254 ($M^+$); HRMS calcd for $C_{15}H_{18}Fe$ 254.0758, found 254.0755. Anal. Calcd for $C_{15}H_{18}Fe$: C, 70.89; H, 7.14. Found: C, 71.19; H, 7.54.

**2-Ferrocenyl-4-propyn-2-ol (10) and 2-Ferrocenyl-3,4-pentadien-2-ol (11).** The $SmI_2$-promoted addition reaction of propargyl bromide (238 mg, 2.0 mmol) to acetylferrocene (274 mg, 1.2 mmol), by a procedure similar to that for **8a**, gave a mixture of alkynyl alcohol **10** and allenyl alcohol **11** in a ratio of 66:34 (320 mg, 99% total yield): red-brown oil; IR (KBr) 3450, 1958, 1660 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz, for compound **10**) $\delta$ 1.60 (3 H, s, $CH_3$). 2.06 (1 H, t, $J = 2.7$ Hz), 2.36 (2 H, br s, OH), 2.53 (1 H, dd, $J = 2.7$, 16.6 Hz), 2.64 (1 H, dd, $J = 2.7$, 16.6 Hz), 4.38−4.08 (18 H, m); $^1$H NMR ($CDCl_3$, 300 MHz, for part of compound **11**) $\delta$ 1.56 (3 H, s), 4.91 (2 H, d, $J = 6.6$ Hz), 5.56 (1 H, t, $J = 6.6$ Hz); FAB-MS $m/z$ 268 ($M^+$); HRMS calcd for $C_{15}H_{16}FeO$ 268.0551, found 268.0548.

**4-Ferrocenyl-3-penten-2-one (12).**[13] Under an atmosphere of argon, a solution of propargyl bromide (238 mg, 2.0 mmol) in THF (10 mL) was added to a freshly prepared $SmI_2$ solution (0.1 M) in THF (20 mL) followed by the addition of a solution of acetylferrocene (274 mg, 1.2 mmol) in THF (10 mL). The mixture was stirred for 30 min at room temperature. The septum was removed, and the mixture was stirred for 2 h at room temperature and refluxed for 12 h to give the title compound (276 mg, 86% yield) after chromatography on a silica gel column eluted with EtOAc/hexane (1:1): red-brown solid; mp 80−82 °C; IR (KBr) 1670, 1593 cm$^{-1}$; $^1$H NMR ($CDC1_3$, 300 MHz) $\delta$ 2.18 (3 H, s), 2.45 (3 H, s), 4.12 (5 H, s), 4.38 (2 H, m), 4.51 (2 H, m), 6.38 (1 H, s); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 17.7, 32.0, 67.0 (2×), 69.3 (5×), 70.5 (2×), 85.2, 119.4, 155.1, 197.7; FAB-MS ($C_{15}H_{16}FeO$) $m/z$ 268 ($M^+$).

**2-Ferrocenyl-6-chloro-2-hexene (14).** According to the representative procedure, the $SmI_2$-promoted condensation of acetylferrocene (274 mg, 1.2 mmol) and 1-bromo-4-chlorobutane (656 mg, 3.0 mmol) gave the title compound (350 mg, 97% yield): red-brown oil; IR (KBr) 1674 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.89 (2 H, m), 1.98 (3 H, Me), 2.26 (2 H, m), 3.56 (2 H, t, $J = 6.5$ Hz), 4.13 (5 H, s), 4.21 (2 H, m), 4.33 (2 H, m), 5.58 (1 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 15.4, 25.4, 32.3, 44.5, 65.1 (2×), 68.2 (2×), 68.9 (5×), 89.1, 121.5, 132.9; FAB-MS $m/z$ 302 ($M^+$); HRMS calcd for $C_{16}H_{19}ClFe$ 302.0525, found 302.0523.

**Acknowledgment.** We thank the National Science Council for financial support.

**Supporting Information Available:** Additional experimental procedures and spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015557R