# Synthesis and Characterization of Homoannularly Disubstituted and Heteroannularly Trisubstituted Ferrocene Derivatives by Arsenic and Silicon or by Arsenic and Tin

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The ferrocene derivatives (**5**−**10**) homoannularly disubstituted and heteroannularly trisubstituted by two different kinds of main-group elements, i.e., arsenic (As) and silicon (Si) or tin (Sn), were synthesized from *N*,*N*-dimethylaminomethylferrocene (**1**) and its diphenylarsino derivative **2** through mono- or dilithiation, followed by substitution with the organo-substituted chlorides $R_mMCl_n$ [R = alkyl, ($m$, $n$) = (2, 2) or (3, 1)] of main-group elements M = As, Si, or Sn. The dimethylaminomethyl ($-CH_2NMe_2$) group of the starting compounds facilitates lithiation of the cyclopentadienyl (Cp) ring and introduces lithium into the *ortho*-position of the $-CH_2NMe_2$ groups by the directing functionality. The efficiency of the subsequent substitution reaction with the organo-substituted chlorides $R_mMCl_n$ is influenced not only by their reactivity but also by the spatial factors of the main-group elements and the ferrocene derivative molecules to be reacted. All products **5**−**10** were identified by elemental analysis, proton nuclear magnetic resonance ($^1$H NMR) spectroscopy, and mass spectrometry (MS). Furthermore, the X-ray crystal structure of **5** was determined. The application of **5**, **6**, and **10** to fungicides for crop plant diseases was examined. The results of the percent inhibition test for fungal growth have indicated that the derivative **10** has high fungicidal activity for early tomato blight.

## Introduction

Ferrocene and ferrocene derivatives are widely used in various areas[1−4] such as asymmetric catalysis, photochemistry, and electrochemistry, due to their unique steric structures and a variety of chemical and physical properties. Therefore, the derivatization of ferrocene has become a significant branch of ferrocene chemistry. To date, many ferrocene derivatives containing main-group elements have been synthesized and characterized, which are of great interest not only in ferrocene chemistry but also in the chemistry of organometallics and main-group elements. Most of the previous reports about the synthesis of ferrocenyl organometallics and ferrocene derivatives substituted by main-group elements refer to mono-[5−12] and 1,1′-disubstitued ferrocenes.[13−17] However, there are only a few research works on the ferrocene derivatives substitued by two different kinds of main-group elements. For example, Ahn et al. have previously synthesized the ferrocene derivatives homoannularly disubstituted by silicon (Si) and phosphorus (P) or Si and sulfur (S), which are introduced into the 2,5-positions of the cyclopentadienyl (Cp) ring substituted by the *ortho*-directing groups.[18] Iftime et al. have synthesized the ferrocene derivatives heteroannularly disubstituted by Si and Sn.[19] Investigations in the field of the ferrocene derivatives of arsenic (As) have been rare since the research by Sollot et al.[20] and Bishop

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et al.[21] Furthermore, there is no report about the synthesis and characterization of disubstituted ferrocene derivatives by As and other main-group elements.

In recent years, we have investigated the ferrocene derivatives substituted by two different main-group elements in the presence of a strongly *ortho*-directing *N*,*N*-dimethylaminomethyl ($-CH_2NMe_2$) functionality. Here we report the synthesis of the ferrocene derivatives (**5** and **6**) homoannularly disubstituted by As and Si or by As and tin (Sn), as well as the dimethylsilicon- and the dibutyltin-bridged bis(diphenylarsinoferrocene) derivatives (**7** and **8**), and the heteroannularly 2,5,1′-trisubstituted derivatives (**9** and **10**) of *N*,*N*-dimethylaminomethylferrocene (**1**). Basically, the homoannularly disubstituted ferrocenes and the bridged ferrocene derivatives were obtained by twice using the well-established monosubstitution reaction of the lithium ferrocenides prepared using *n*-buthyllithium (*n*-BuLi)[22−24] with organotin, organoarsenic, or organosilicon chlorides. Note that organostannyl ferrocenes easily undergo a Sn−Li exchange reaction by organolithium in relatively strong coordinating solvents[25] such as DME, THF, and $Et_2O$, where a tin ate complex, stabilized in the solvent, is proposed as an intermediate for the exchange reaction. Tetraorganylsilanes also form an ate complex with organolithium,[26] which is likely to cause a lowering of the yields of lithiation by unfavorable Si−Li exchange reactions. As mentioned above, Iftime et al. have ably introduced $Bu_3Sn-$ to the 1′-position of ferrocenecarbaldehydes containing trimethylsilyl ($Me_3Si-$) groups in the 2-position by employing the temporary directing group lithium *N*-methylpiperazide, whose amine moiety forms a chelate complex with organolithium reagents to lithiate selectively the 1′-position. This work has tried to introduce Sn and As or Si and As into the same Cp ring. To the best of our knowledge, there has been no report about As−Li exchange reactions and the formation of an arsenic ate complex. Thus, the possibility of the straightforward introduction of two main-group elements to the same Cp ring was examined in the order of As and Sn and As and Si, where the *ortho*-directing $Me_2NCH_2-$ group would also contribute to the selective lithiation of the Cp ring even in the presence of another main-group element by its coordinating ability. In the synthesis of the heteroannularly trisubstituted derivatives, the dilithium ferrocenides obtained using *n*-BuLi and *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA)[27] are used in the heteroannular introduction of main-group elements. The structures of all products **5**−**10** were characterized by elemental analysis, $^1$H NMR, and MS. Furthermore, the X-ray crystal structure of the product **5** was determined.

Transition-metal coordination complexes have been widely studied for the development of effective bioactive agents such as antimicrobial, antibacterial, and antitumor agents.[28−37] In the research field the investigation of antimicrobial and cytotoxic activities of ferrocene-based metal complexes is involved. Haque et al. have reported that the ferrocene derivative manganese complex shows the maximum antibacterial and antifungal activities compared with other cobalt, nickel, copper, and zinc complexes.[38] Different from the research on transition-metal complexes of ferrocene derivatives, we have tried to examine the applicability of the ferrocene derivatives containing two main-group elements of As, Si, and Sn to antifungal agents, because organosilicon, organoarsenic, and organotin compounds exhibit bioactivity such as antimicrobial and fungicidal effects at a certain level. In this work, the fungicidal activity of **5**, **6**, and **10** for crop plants was examined against fusarium head blight of wheat, early blight of tomato, wilt disease of cotton, ring-rot disease of apple, and brown blotch disease of peanut.

## Results and Discussion

**Synthesis of the Ferrocene Derivatives 5−10 Containing Arsenic and Silicon or Tin.** The basic route for the synthesis of ferrocenyl organometallics is the lithiation of ferrocene by *n*-BuLi followed by the substitution reaction of the resulting lithiated ferrocene with organometal chlorides.[39−41] This is also an important route for the introduction of main-group elements into the Cp ring of ferrocenes. In this basic route, however, there are problems: the reaction time of the lithiation is relatively long, the reaction yield of the lithiated ferrocene with the organo-substituted chlorides of main-group elements is low, and the resulting ferrocene derivative is a mixture of monosubstituted and disubstituted ferrocene. In contrast, the introduction of $-CH_2NMe_2$ groups into the Cp ring facilitates the lithiation of ferrocenes to decrease the reaction time (ca. 1 h with *n*-BuLi in diethyl ether).[42] The directing $-CH_2NMe_2$ functionality of *N*,*N*-dimethylaminomethylferrocene (**1**) introduces lithium into the *ortho*-position of the $-CH_2NMe_2$ groups. The introduced lithium probably forms a chelation complex with the amine nitrogen.[42] The resulting 1-dimethylaminomethyl-2-lithioferrocene undergoes substitution by the organo-substituted chlorides of main-group elements to provide the ferrocene derivatives (e.g., compound **2**) containing main-group elements at the *ortho*-positions adjacent to the $-CH_2NMe_2$ group.

Scheme 1 shows the synthetic paths of compounds **5**−**10**. The $-CH_2NMe_2$ group of **2** exhibits the *ortho*-directing functionality similar to that observed in *N*,*N*-dimethylaminomethylferrocene (**1**), as described above. Actually, the lithiation

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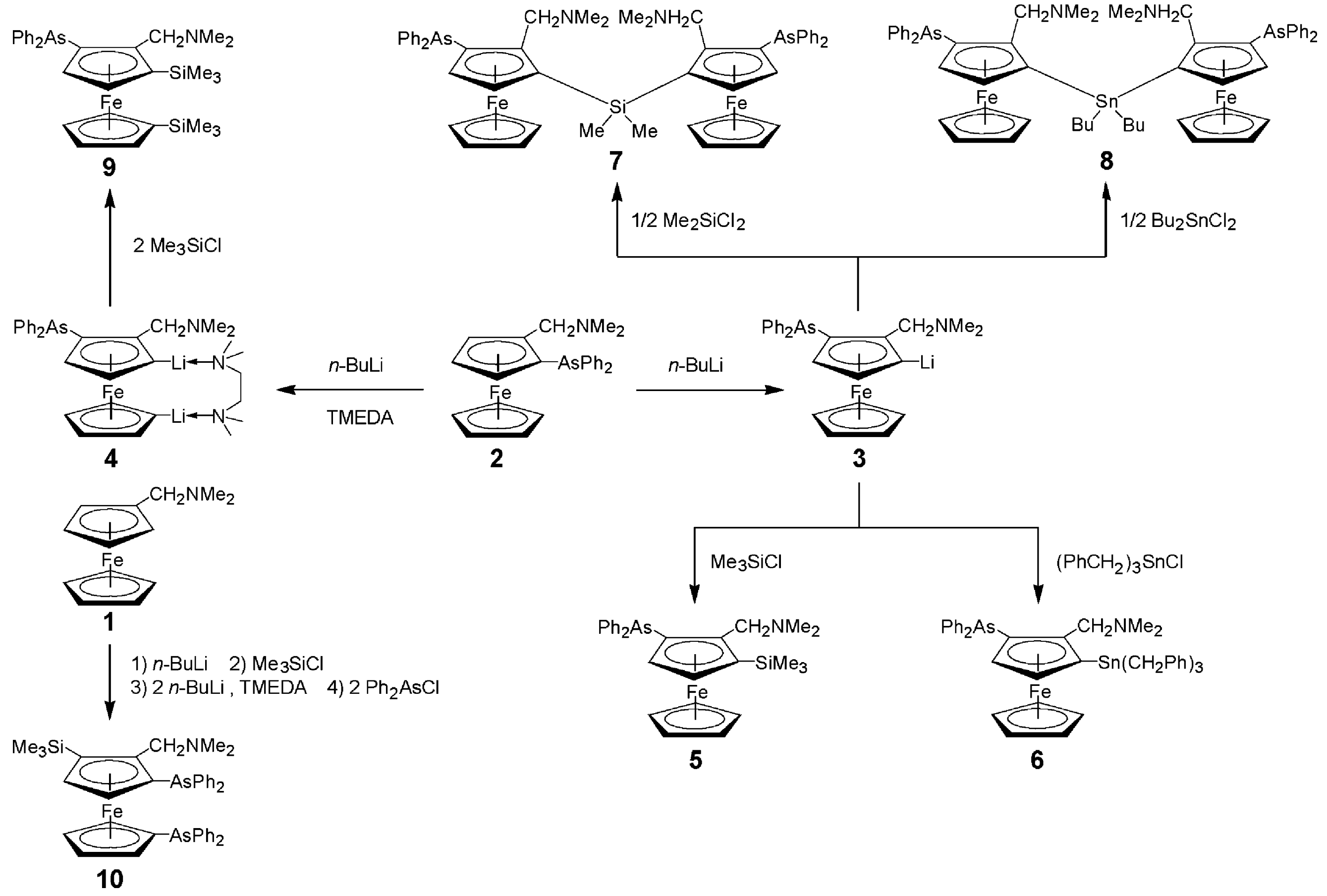
**Scheme 1. Synthetic Paths of Ferrocene Derivatives 5−10**



of **2** introduced lithium into the Cp ring at the *ortho*-position of $-CH_2NMe_2$ groups to provide 1-dimethylaminomethyl-5-lithioferrocene derivative **3**. The substitutions of **3** with equimolar amounts of trimethylchlorosilane ($Me_3SiCl$) and tribenzylstannyl chloride ($(PhCH_2)_3SnCl$) provided the ferrocene derivatives **5** and **6** homoannularly disubstituted by As and Si and by As and Sn in yields of 33% and 47%, respectively. The yield of **5** is comparable to the substitution yield (37%) of 1-(*N*,*N*-dimethylaminomethyl)-2-lithioferrocene with $Me_3SiCl$.[43] In contrast, the substitution of **3** with diphenylarsino chloride ($Ph_2AsCl$) gave a lower yield of 20%.[44]

The substitution of compound **3** with half-equimolar amounts of dimethyldichlorosilane ($Me_2SiCl_2$) and dibutylstannyl dichloride ($Bu_2SnCl_2$) provided the dimethylsilicon- and the dibutyltin-bridged bis(diphenylarsinoferrocene) derivatives **7** and **8** in yields of 18% and 34%, respectively. The dissociation energy of Sn−Cl bonds is smaller than that of Si−Cl bonds.[45,46] Therefore, the higher yields of **8** might result from the more reactive Sn−Cl bond as compared to the Si−Cl bond. Furthermore, the atomic radius of tin is significantly larger than that of silicon, so that the tetrahedral structure formed by tin has more spatial advantage. This also would contribute to the higher yield of **8** than that of **7**. The yields of the half-equimolar substitution are lower than those of the equimolar substitution mentioned above. The substitution of 1-(*N*,*N*-dimethylaminomethyl)-2-lithioferrocene with half-equimolar amounts of $Me_2SiCl_2$ and $Bu_2SnCl_2$ gave yields of 22%[43] and 43%,[47] respectively. The half-equimolar substitution yields from 1-(*N*,*N*-dimethylaminomethyl)-2-lithioferrocene are higher than those from compound **3**, which contains the bulky diphenylarsino group. Therefore, the lowering of the half-equimolar substitution yields from **3** is attributed to the steric hindrance caused by the spatial bulkiness of the substituted ferrocene molecules to be bridged.

The lithiation of **2** by *n*-BuLi in the presence of TMEDA introduces lithium into the 5, 1′-positions to provide the dilithiated ferrocene derivative **4**. The substitution of **4** with two times the equimolar amount of $Me_3SiCl$ gave the trisubstituted derivative **9** containing a diphenylarsino ($-AsPh_2$) group and 5,1′-bis(trimethylsilyl ($= -SiMe_3$)) groups in 33% yield. The yield was much lower than the substitution yield (57%[25]) of 1-(*N*,*N*-dimethylaminomethyl)-5,1′-dilithioferrocene with $Me_3SiCl$. Similarly, compound **10** was synthesized by the *n*-BuLi−TMEDA procedure.[27] First, *N*,*N*-dimethylaminomethylferrocene (**1**) was lithiated and then substituted with $Me_3SiCl$. After the *n*-BuLi−TMEDA dilithiation of the resulting trimethylsilylferrocene derivative, the substitution with two times the equimolar amount of $Ph_2AsCl$ gave the trisubstituted derivative **10** containing a $-SiMe_3$ group and 5,1′-bis($-AsPh_2$) groups in an overall yield of 18% from **1**.

In summary, the ferrocene derivatives (**5**−**10**) homoannularly disubstituted and heteroannularly trisubstituted by As and Si or Sn were synthesized from *N*,*N*-dimethylaminomethylferrocene (**1**) and its diphenylarsino derivative **2** through mono-

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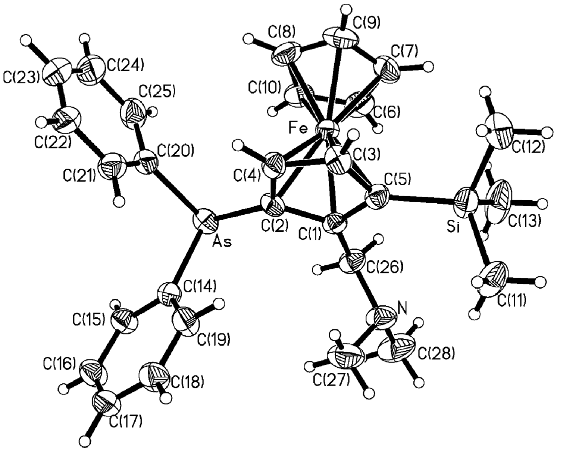

**Figure 1.** ORTEP view of compound **5** with 30% probability thermal ellipsoids.

**Table 1. Crystal Data and Structure Refinement for Compound 5**

| | |
|---|---|
| empirical formula | $C_{28}H_{34}AsFeNSi$ |
| fw (g/mol) | 543.42 |
| temp (K) | 293 |
| cryst size (mm) | 0.8 × 0.8 × 0.6 |
| cryst syst | triclinic |
| space group | *P*1 |
| unit cell dimens | $a = 1.0079(2)$ nm |
| | $b = 1.2213(2)$ nm |
| | $c = 1.2333(2)$ nm |
| | $\alpha = 73.54(3)°$ |
| | $\beta = 70.10(3)°$ |
| | $\gamma = 75.02(3)°$ |
| volume (nm$^3$) | 1.3467(4) |
| *Z* (molecules/cell) | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.340 |
| radiation ($\lambda$, Å) | 0.71073 (Mo Kα) |
| absorp coeff (mm$^{-1}$) | 1.839 |
| *F*(000) | 564 |
| $\theta$ range for data collection (deg) | 2.18−26.00 |
| index ranges | $-12 \leq h \leq 12$ |
| | $-12 \leq k \leq 0$ |
| | $-15 \leq l \leq 14$ |
| no. of reflns collected | 5304 |
| no. of indep reflns | 5043 [$R_{(int)} = 0.0215$] |
| no. of data/restraints/params | 5038/0/289 |
| goodness of fit on $F^2$ | 1.017 |
| final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0462$ |
| | $wR_2 = 0.1143$ |
| *R* indices (all data) | $R_1 = 0.0959$ |
| | $wR_2 = 0.1389$ |
| largest diff peak and hole (e Å$^{-3}$) | 0.497, −0.812 |

and dilithiation and subsequent substitution with the organo-substituted chlorides of main-group elements. The results of this work have indicated that the substitution efficiency is largely influenced by the spatial volumes of the main-group elements and the lithiated ferrocene molecules.

**Structural Characterization of 5−10.** All ferrocene derivatives **5−10** were identified by elemental analysis, $^1$H NMR, and MS. The MS spectrum of **5** gave the molecular ion ($M^+$) peak at $m/z = 543$, which substantiates the validity of the molecular formula of **5**. The $^1$H NMR spectrum of **5** showed a triplet peak of seven protons at 3.83−4.02 ppm, which was not the intrinsic triplet peak split at the intensity ratio of 1:2:1 by spin−spin coupling but the peaks comprised of two weak peaks with almost the same intensity and a singlet peak with high intensity. The apparent triplet peak indicates the presence of trisubstituted and nonsubstituted Cp rings. The tips of the two weak peaks were slightly split, with a coupling constant $^3J = 2.6$ Hz. The observation of the spin−spin coupling indicates that the two Cp protons are adjacent to each other and that the $-AsPh_2$ group and the $-SiMe_3$ group are located in the *ortho*-positions of the $-CH_2NMe_2$ group. The singlet peak of three methyl groups observed at a quite high magnetic field of 0.24 ppm implies that the three methyl groups are magnetically equivalent and exist on the Si atom. The $^1$H NMR of **6** also showed an apparent triplet peak corresponding to the seven protons of trisubstituted and nonsubstituted Cp rings. In the $^1$H NMR spectrum of **7**, a multiplet peak of 14 protons was observed at 4.22−4.55 ppm, in which the outstanding singlet peak corresponding to the nonsubstituted Cp rings was observed at 4.22 ppm. The two methyl groups existing on the Si atom were observed independently at 0.93 and 1.09 ppm. This indicates that the two methyl groups are located under chemically inequivalent conditions caused by the anisotropy of the molecular structure of **7**. In the case of **8**, the two butyl groups existing on the Sn atom are chemically inequivalent and were observed at 0.70−1.66 ppm as a multiplet peak. In the MS spectrum of **9**, the $M^+$ peak was confirmed at $m/z = 615$. The $^1$H NMR spectrum gave two singlet peaks showing the $-SiMe_3$ protons at 0.13 and 0.43 ppm, which indicates that the two $-SiMe_3$ groups are located under chemically inequivalent conditions. Similarly, the $^1$H NMR spectrum of **10** gave two singlet peaks showing the phenyl protons of the chemically inequivalent $-AsPh_2$ groups at 7.20 and 7.26 ppm. The MS analysis of **10** was performed by fast atom bombardment mass spectrometry (FAB-MS). The FAB-MS spectrum did not give the $M^+$ peak but the $m/z = 727$ peak of the fragment ion losing the dimethylamino ($-NMe_2$) group from the molecule.

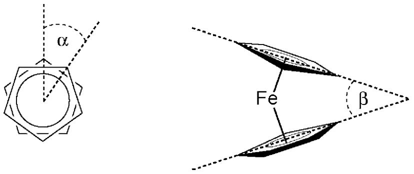

**Figure 2.** Definitions of the torsion (α) and tilt ($\beta$) angles of Cp rings.

**Table 2. Selected Bond Lengths and Angles for Compound 5**

| | |
|---|---|
| Bond Lengths (Å) | |
| Fe−C(1) | 2.039(4) |
| Fe−C(2) | 2.043(4) |
| Fe−C(3) | 2.039(4) |
| Fe−C(4) | 2.034(4) |
| Fe−C(5) | 2.054(4) |
| Fe−C(6) | 2.032(5) |
| Fe−C(7) | 2.036(5) |
| Fe−C(8) | 2.043(5) |
| Fe−C(9) | 2.026(5) |
| Fe−C(10) | 2.045(5) |
| As−C(2) | 1.953(4) |
| As−C(14) | 1.960(4) |
| As−C(20) | 1.966(5) |
| Si-C(5) | 1.866(4) |
| Si-C(11) | 1.849(5) |
| Si-C(12) | 1.870(7) |
| Si-C(13) | 1.870(6) |
| Bond Angles (deg) | |
| C(26)−C(1)−C(2) | 126.2(4) |
| C(26)−C(1)−C(5) | 125.7(4) |
| C(1)−C(5)−Si | 130.6(3) |
| C(1)-C(2)−As | 123.5(3) |
| C(2)−C(1)−C(5) | 108.0(4) |
| Cp-torsion (α) | 12 |
| Cp-tilt ($\beta$) | 0.18 |

**X-ray Structural Analysis of 5.** The crystal data and the structure refinement for **5** are summarized in Table 1. Compound

**Table 3. Percentage of the Growth Inhibition of Crop-Blight-Inducing Fungi by Ferrocene Derivatives**

| product | head blight (wheat) | | early blight (tomato) | | wilt disease (cotton) | | ring rot disease (apple) | | brown blotch disease (peanut) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^a$ | $I^b$ | $R$ | $I$ | $R$ | $I$ | $R$ | $I$ | $R$ | $I$ |
| **5** | 21.5 | 23.8 | 17.1 | 10.6 | 36.8 | 0 | 19.5 | 27.0 | 14.7 | 0 |
| **6** | 21.8 | 22.7 | 16.5 | 16.7 | 20.1 | 45.4 | 17.2 | 35.6 | 14.8 | 0 |
| **10** | 19.5 | 30.9 | 10.7 | 45.9 | 18.9 | 48.6 | 16.9 | 36.7 | 14.6 | 0 |
| $A^c$ | 0 | 100 | 15.6 | 21.2 | 0 | 100 | 0 | 100 | 0 | 100 |

[a] $R$: average diameter (mm) of inhibition zone. [b] $I$: percentage (%) of inhibition. [c] A: 50% carbendazim wettable powder as a control.

**5** crystallizes from anhydrous ethanol as an brownish-yellow crystal in the triclinic space group $P1$. Figure 1 shows the ORTEP diagram of the molecular structure of **5**. Selected bond lengths and angles are listed in Table 2. The distortion of the Cp ring arrangements is defined by Cp torsion ($\alpha$) and Cp tilt ($\beta$) angles in Figure 2. The Cp rings are arranged in a nearly eclipsed conformation with an average torsion angle of $\alpha = 12°$ and have an almost parallel orientation with a tilt angle of $\beta = 0.18°$. The average bond length of Fe−C (Cp1−5) is 2.042 Å, which is comparable to that (2.037 Å) of Fe−C (Cp6−10). Although the Fe−C(5) bond length (2.054 Å) of the carbon atom bearing the $-SiMe_3$ group is slightly longer than the average bond length, the Fe−C(Cp) bond lengths are proved to be not largely influenced by the incorporated $-CH_2NMe_2$, $-AsPh_2$, and $-SiMe_3$ groups. The C(26)−C(C1)−C(C2) and C(26)−C(C1)−C(C5) angles are almost equivalent (126°), which indicates that the C(26)−C(Cp) bond is undistortedly attached on the elongation of the axis connecting C(C1) and the Cp ring center. The C(1)−C(2)−As angle (124°) is slightly bent toward the C(26)−C(Cp) bond, different from the equivalent C(26)−C(Cp)−C(Cp) angles by 2°. In contrast, the C(1)−C(5)−Si angle (131°) is bent in the opposite direction of the C(26)−C(Cp) bond by 5°. The irregularity of the bending directions implies that the distortions in the bond angles of C(1)−C(2)−As and C(1)−C(5)−Si result not from intramolecular steric effects but from the crystal-packing effects.

**Examination of the Fungicidal Activity of 5, 6, and 10 against Fungi that Cause Crop Plant Disease.** Table 3 shows the percent inhibition of fungi growth by the ferrocene derivatives **5**, **6**, and **10** and, for comparison, by a commercial pesticide, carbendazim wettable powder. Compound **5** exhibited low but unambiguous fungicidal activities against fungi bringing on head blight of wheat, early blight of tomato, and ring-rot disease of apple. In contrast, no fungicidal activity was observed for fungi causing wilt disease of cotton and brown blotch disease of peanut. Compound **6** largely improved the percent inhibition of fungi for early blight of tomato, wilt disease of cotton, and ring-rot disease of apple, although no improvement was observed for head blight of wheat and brown blotch of peanut. The ferrocene derivatives **5** and **6** homoannularly disubstituted by organoarsenic and organosilicon or organotin were proved to exhibit fungicidal activity except for wilt disease of cotton and/or brown blotch disease of peanut. However, the absolute fungicidal effects observed for **5** and **6** are lower than those of the carbendazim wettable powder. The ferrocene derivative **10** heteroannularly trisubstituted by organosilicon and organoarsenic further improved the percent inhibition for head blight of wheat and early blight of tomato. Particularly, the percent inhibition (45.9%) for early blight of tomato reaches approximately 3 to 4 times the value observed for **5** and **6**. Furthermore, the fungicidal activity of **10** for early blight of tomato is more than twice that of the carbendazim wettable powder. The results of the percent inhibition test for crop-blight-inducing fungi indicate that the fungicidal activity of the ferrocene derivatives has a close relation to the kind and number of substituted main-group elements and the introduction position of the main-group elements on the Cp rings of ferrocenes.

## Conclusions

We have successfully synthesized the ferrocene derivatives disubstituted (**5** and **6**) and trisubstituted (**9** and **10**) by As and Si or Sn, as well as the dimethylsilicon- and dibutyltin-bridged bis(diphenylarsinoferrocene) derivatives (**7** and **8**). The $-CH_2NMe_2$ group of the diphenylarsinoferrocene derivative **2** (a starting compound of **5**−**9**) facilitates the lithiation of the Cp ring and introduces lithium into the *ortho*-position of the $-CH_2NMe_2$ group by the directing functionality. The monolithiation of **2** provides the 5-lithioferrocene derivative **3** by the *ortho*-directing $-CH_2NMe_2$ functionality. The dilithiation of **2** by the *n*-BuLi−TMEDA procedure provides the 5,1′-dilithioferrocene derivative **4**. The equimolar substitutions of **3** with $Me_3SiCl$ and $(PhCH_2)_3SnCl$ provide the diphenylarsinoferrocene derivatives **5** and **6**, containing Si and Sn, respectively. The substitutions of **3** with half-equimolar amounts of $Me_2SiCl_2$ and $Bu_2SnCl_2$ provide the $Me_2Si$- and the $Bu_2Sn$-bridged bis(diphenylarsinoferrocene) derivatives **7** and **8**. The equimolar and half-equimolar substitutions gave higher yields for Sn than for Si. In addition, the half-equimolar substitutions gave lower yields than those of the equimolar substitutions. It is therefore concluded that the substitution yields are influenced by the spatial factor of the main-group elements (i.e., atomic radius) and the ferrocene molecules (i.e., spatial bulkiness) to be reacted. The substitution of **4** with twice equimolar amounts of $Me_3SiCl$ gave the trisubstituted derivative **9**, containing a $-AsPh_2$ group and 5,1′-bis ($-SiMe_3$) groups. Compound **10** was synthesized from **1** through monolithiation and followed by substitution with $Me_3SiCl$ and then dilithiation and substitution with $Ph_2AsCl$. The substitution of the dilithiated trimethylsilylferrocene derivative with twice equimolar amounts of $Ph_2AsCl$ gave the trisubstituted derivative **10**, containing a $-SiMe_3$ group and 5,1′-bis ($-AsPh_2$) groups. In the application of **5**, **6**, and **10** as fungicides, the derivative **10** exhibited much higher percent inhibition of fungal growth for early blight of tomato, compared with **5** and **6**. The results of the percent inhibition test have indicated that the fungicidal activity of the ferrocene derivatives has a close relation to the kind and number of main-group elements and their introduction position on the Cp rings of ferrocenes.

## Experimental Section

**General Remarks.** All reagents were purchased from Beijing Chemical Reagent Co. and used as received. Solvents were dried and distilled prior to use by standard procedures. 2-(Diphenylarsino)-1-(*N*,*N*-dimethylaminomethyl)ferrocene (**2**),[48] tribenzyltin

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[48] Du, H. H.; Shi, S. J. *Chem. J. Chin. Univ.* **1993**, *14*, 1087.

chloride,[49] dibutyltin dichloride,[50] *N*,*N*-dimethylaminomethylferrocene (**1**),[51] and diphenylchloroarsine[52] were prepared according to the literature. All experiments were performed under an inert atmosphere (prepurified $N_2$) using either standard Schlenk-line techniques[53] or an inert-atmosphere glovebox. Melting points were determined on a microscopic apparatus without correction. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. $^1$H NMR spectra were recorded on a Bruker AC 80 spectrometer, using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a VG70 SE GC/MS gas chromatography mass spectrometer. Crystallographic data were obtained on a Rigaku AFC6S diffractometer (graphite monochromator, Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å). All calculations were performed using the SHELXL-93 program. The structure was solved by direct methods and was refined using full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms, and all hydrogen atoms were included but not refined. Percent inhibition tests of fungal growth by ferrocene derivatives were conducted using a plating method, which was repeated nine times for each sample. The concentration of ferrocene derivatives was 50 ppm in all runs, and 50% carbendazim wettable powder was used as a control.

**General Procedure for the Synthesis of Products 5−9.** Compound **2** and anhydrous diethyl ether ($Et_2O$) were placed into a three-neck round-bottom flask equipped with a dropping funnel, a reflux condenser, and a gas inlet. *n*-BuLi in petroleum ether was transferred to the flask, and the mixture was magnetically stirred at room temperature for 1 h, followed by reflux for 15 min. The anhydrous ether solution of organo-substituted chlorides of main-group elements was added dropwise into the above lithiated solution and then stirred at 34−35 °C for 20 h. After cooling, water was added and the mixture was separated. The obtained aqueous phase was extracted with $Et_2O$ three times. The organic phase was gathered and dried by anhydrous magnesium sulfate ($MgSO_4$). After filtrating and evaporating the solvent, the crude product was purified by alkaline alumina ($Al_2O_3$) column chromatography and/or recrystallization to give **5**−**9**. The products were characterized as follows.

**5-(Trimethylsilyl)-2-(diphenylarsino)-1-(*N*,*N*-dimethylaminomethyl)ferrocene (5).** The product was purified by alkaline $Al_2O_3$ column chromatography with petroleum ether/ethyl acetate (EtOAc) (v/v 20:1) as an eluent and recrystallization from anhydrous ethanol (EtOH) to give **5** as a brownish-yellow crystalline solid. Yield: 33%. Mp: 102.5−104.5 °C. Anal. Calcd for $C_{28}H_{34}NAsSiFe$: C, 61.88; H, 6.31; N, 2.58. Found: C, 61.71; H, 6.26; N, 2.39. $^1$H NMR ($\delta$, ppm): 7.58−7.10 (m, 10H, Ph), 4.02−3.83 (s and d, 7H, Cp), 3.30 (s, 2H, $CH_2$), 1.75 (s, 6H, $NMe_2$), 0.24 (s, 9H, $SiMe_3$). MS (EI): *m/z* (% relative intensity) 543 ($M^+$, 100), 499 (11), 423 (33), 349 (37), 299 (12), 227 (5), 121 (5), 73 (26).

**5-(Tribenzyltin)-2-(diphenylarsino)-1-(*N*,*N*-dimethylaminomethyl)ferrocene (6).** The product was purified by alkaline $Al_2O_3$ column chromatography with petroleum ether/EtOAc (v/v 4:1) as an eluent and recrystallization from anhydrous EtOH to give **6** as a brownish-yellow crystalline solid. Yield: 47%. Mp: 79.5−81.0 °C. Anal. Calcd for $C_{46}H_{46}NAsFeSn$: C, 64.07; H, 5.38; N, 1.62. Found: C, 64.06; H, 5.53; N, 1.44. $^1$H NMR ($\delta$, ppm): 7.34−6.65 (m, 25H, Ph), 4.08−3.54 (m, 7H, Cp), 3.15−2.78 (t, 2H, $CH_2N$), 2.38 (s, 6H, $NMe_2$), 1.88 (s, 6H, $CH_2Ph$).

**Bis[2-(*N*,*N*-dimethylaminomethyl)-3-(diphenylarsino)ferrocenyl]dimethylsilicane (7).** The product was purified by alkaline $Al_2O_3$ column chromatography with petroleum ether/EtOAc (v/v 3:1) as an eluent to give **7** as a yellow solid. Yield: 18%. Mp: 208−214 °C. Anal. Calcd for $C_{52}H_{56}N_2As_2Fe_2Si$: C, 62.54; H, 5.65; N, 2.81. Found: C, 62.32; H, 5.70; N, 2.45. $^1$H NMR ($\delta$, ppm): 7.98−7.42 (m, 20H, Ph), 4.55−4.22 (m, 14H, Cp), 3.87 (s, 4H, $CH_2$), 2.21(s, 12H, $NMe_2$), 1.09, 0.93 (2s, 6H, $SiMe_2$).

**Bis[2-(*N*,*N*-dimethylaminomethyl)-3-(diphenylarsino)ferrocenyl]dibutyltin (8).** The product was purified by alkaline $Al_2O_3$ column chromatography with petroleum ether/EtOAc (v/v 4:1) as an eluent to give **8** as a yellow solid. Yield: 34%. Mp: 208−214 °C (dec). Anal. Calcd for $C_{58}H_{68}N_2As_2Fe_2Sn$: C, 59.37; H, 5.84; N, 2.39. Found: C, 59.09; H, 5.90; N, 2.12. $^1$H NMR ($\delta$, ppm): 7.60−6.93 (m, 20H, Ph), 4.30−3.76 (m, 14H, Cp), 3.33 (s, 4H, $CH_2$), 1.81 (s, 12H, $CH_3$), 1.66−0.70 (m, 18H, Bu).

**2-(Diphenylarsino)-5,1′-bis(trimethylsilyl)-1-(*N*,*N*-dimethylaminomethyl)ferrocene (9).** The product was recrystallized from petroleum ether (60−90 °C) to give **9** as a brownish-yellow crystalline solid. Yield: 33%. Mp: 105.5−106.5 °C. Anal. Calcd for $C_{31}H_{42}NFeSi_2As$: C, 60.48; H, 6.88; N, 2.28. Found: C, 60.63; H, 6.79; N, 2.15. $^1$H NMR ($\delta$, ppm): 7.85−7.37 (m, 10H, Ph); 4.55−3.38 (m, 6H, Cp); 3.53 (s, 2H, $CH_2$); 2.00 (s, 6H, $NMe_2$); 0.43,0.13 (2s, 18H, $SiMe_3$). MS (FAB): *m/z* 615 ($M^+$).

**Synthesis of 2-(Trimethylsilyl)-5,1′-bis(diphenylarsino)-1-(*N*,*N*-dimethylaminomethyl)ferrocene (10).** Compound **1** (0.85 mL, 5.0 mmol) and anhydrous $Et_2O$ (10 mL) were placed into a 100 mL three-neck round-bottom flask. *n*-BuLi in petroleum ether (4.0 mL, 1.3 mol/L, 5.2 mmol) was slowly added to the flask, and the mixture was stirred at room temperature for 1 h, followed by reflux for 15 min. $Me_3SiCl$ (0.65 mL, 5.2 mmol) dissolved in anhydrous $Et_2O$ (10 mL) was added dropwise into the above lithiated solution, and the mixture was stirred at 34−35 °C for 18 h. Then, a *n*-BuLi solution (8.0 mL, 1.3 mol/L, 10.4 mmol) and TMEDA (0.80 mL, 5 mmol) were added, and the mixture was stirred for 5 h. $Ph_2AsCl$ (1.90 mL, 10.2 mmol) dissolved in anhydrous $Et_2O$ (10 mL) was added dropwise into the above reactant solution at 34−35 °C for 24 h. After cooling, water (20 mL) was added and the mixture was separated. The aqueous phase was extracted in anhydrous $Et_2O$ (10 mL) three times. The eluted organic phase was gathered and dried by anhydrous $MgSO_4$. After evaporating the solvent, the crude product was recrystallized from petroleum ether (60−90 °C) to give **10** as a yellow crystalline solid. Yield: 18.0%. Mp: 167−168 °C. Anal. Calcd for $C_{40}H_{43}NAs_2SiFe$: C, 62.27; H, 5.62; N, 1.82. Found: C, 62.28; H, 5.71; N, 1.78. $^1$H NMR ($\delta$, ppm): 7.26−7.20 (2s, 20H, Ph), 4.43−3.35 (m, 6H, Cp), 3.43 (s, 2H, $CH_2$), 1.88 (s, 6H, $NMe_2$), 0.38 (s, 9H, $SiMe_3$). MS (FAB): *m/z* 727 ($M^+ - NMe_2$).

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**Supporting Information Available:** Text giving details of the characterization of **5** and tables and a CIF file giving full crystallographic descriptions of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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