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# Rhodium- and ruthenium-complex-catalyzed condensation of ferrocene-containing dithiols and diols with diarylsilanes to give silaferrocenophanes and ferrocene polymers

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**1,1′-Ferrocenedithiol reacts with di(4-methoxyphenyl)silane, diphenylsilane, and di(4-fluorophenyl)silane in the presence of $RhCl(PPh_3)_3$ catalyst to give mixtures of 2,2-diaryl-1,3-dithia-2-sila[3]ferrocenophanes (1a–3a) and —(Fc—S—$SiAr_2$—S)$_n$— (Fc = 1,1′-ferrocenylene; 1b: Ar = $C_6H_4OMe$-4; 2b: Ar = Ph; 3b: Ar = $C_6H_4F$-4). The products are isolated and characterized by NMR spectroscopy and elemental analyses. The polymers 1b–3b, obtained from a toluene-soluble fraction of the products, show GPC elution patterns corresponding to $M_n$ values of 2700–4600 (polystyrene standards). The UV–vis spectra of the ferrocenophanes and polymers exhibit a *d–d* transition peak at about 440 nm, while the polymers show a $\pi$–$\pi^*$ transition peak at 320–330 nm. The cyclic voltammograms of 3a (Ar = $C_6H_4F-4$) and 3b show a reversible redox of the iron center at 0.27 V and 0.35 V ($Ag^+$/Ag) respectively. Reaction of 1,1′-ferrocenedimethanol with diphenylsilane in the presence of $RuCl_2(PPh_3)_3$ catalyst results in selective formation of 3,3-diphenyl-2,4-dioxa-3-sila[5]ferrocenophane (4), whose structure was determined by X-ray crystallography.** 

**Keywords: condensation; ferrocenophane; organometallic polymer**

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## INTRODUCTION

Transition-metal complex-catalyzed silicon–heteroatom bond-forming reactions are used for preparation of polymers or oligomers containing these bonds in the main chain. For example, transition metal complexes catalyze reactions of Si—H-containing organosilanes with amines and those of cyclic oligosilanes with benzoquinone to afford poly(silazane)s[1–5] and poly(siloxane)s polymers,[6] respectively. In contrast to many reports on polymers having Si—O or Si—N bonds in the main chain, preparation of polymers containing Si—S bonds is limited due to instability of the bond against moisture and to a smaller number of Si—S bond-forming reactions. Since $RhCl(PPh_3)_3$-catalyzed dehydrocoupling of hydrosilanes with thiols to give (thiolato)silanes takes place without addition of base, which promotes undesired hydrolysis of the product,[7] it was applied to polycondensation of diarylsilanes with benzenedithiols to give the polymers containing Si—S bonds in the main chain.[8]

Based on our recent studies on preparation of ferrocene-containing polymers[9] and ferrocenophanes,[10] we have planned condensation of ferrocene dithiol with diorganosilane with expectation of formation of new ferrocene polymers whose monomer units are bonded with Si—S bonds and/or ferrocenophanes containing Si—S bonds in the side arm. The ferrocene polymers have been regarded as potential materials for electrochemical and optical uses, and strained ferrocenophanes are converted to

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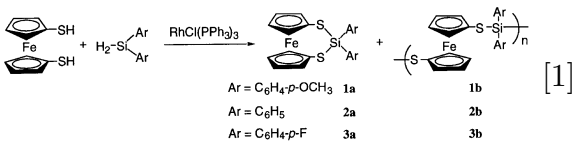
the ferrocene-containing polymers via thermally induced ring-opening polymerization.[11]

Here we report rhodium- or ruthenium-complex-catalyzed reactions of 1,1′-ferrocenedithiol and 1,1′-ferrocenedimethanol with diarylsilanes. The structures and physical properties of the ferrocenophanes and polymers obtained are also mentioned.

## RESULTS AND DISCUSSION

Reactions of 1,1′-ferrocenedithiol with diarylsilanes in the presence of $RhCl(PPh_3)_3$ catalyst in toluene give mixtures of 2,2-diaryl-1,3-dithia-2-sila[3]ferrocenophanes (**1a–3a**) and polymers —(Fc—S—$SiAr_2$—S)$_n$— (Fc = 1,1′-ferrocenylene; **1b**: Ar = $C_6H_4OMe$-4; **2b**: Ar = Ph; **3b**: Ar = $C_6H_4F$-4) as shown in Eqn [1]. The ferrocenophanes are separated as a toluene-insoluble solid from the reaction mixture, whereas the polymers are obtained from a toluene-soluble fraction of the products. Table 1 summarizes yields and analytical data of the products isolated.

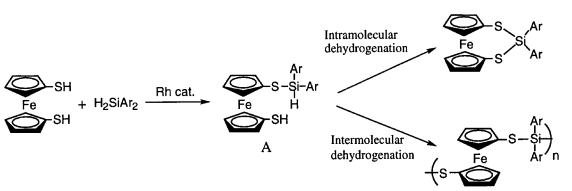


[1]

The ferrocenophanes **1a–3a** are characterized by NMR spectroscopy. For example, the $^1$H NMR spectrum of **1a** exhibits peaks due to the hydrogen atoms of phenylene and the cyclopentadieyl (Cp) groups are observed at reasonable positions ($\delta$ 7.72 and 6.98, and $\delta$ 4.13 and 3.93 respectively) in an equal intensity. The $^{13}C\{^1H\}$ NMR spectrum also gives the signals at the positions expected from the proposed structure. These NMR data are included in Table 2.

The polymers **1b–3b** are soluble in $CHCl_3$, THF, and toluene and have $M_n$ values of 2700–4600, in GPC analyses, as shown in Table 1. The polymers show essentially the same IR spectra as the corresponding ferrocenophanes and give no absorption peaks assignable to $\nu$(S—H) and $\nu$(Si—H) of the starting materials. Exposure of the polymers **1b** and **3b** to air for 1 month does not change their IR spectra, indicating high stability of the polymers towards air and moisture. This is in contrast to most of the already reported Si—S-bond-containing organic compounds and polymers, which undergo partial hydrolysis at room temperature in air in a few days. Figure 1 depicts the $^1$H NMR spectrum of **1b**, which exhibits the signals of phenylene group hydrogen atoms ($\delta$ 7.72 and 6.80) and Cp hydrogen atoms ($\delta$ 4.19 and 4.01) at different positions from **1a**. Multiplicity of the $OCH_3$ hydrogen atoms can be ascribed to the presence of a different conformation about the —S—Si—S— linkage within the polymer chain. Small signals at $\delta$ 2.74 and at $\delta$ 7.54 and 6.85 are due to the SH hydrogen and phenylene group hydrogen atoms of the terminal group of the polymer. Polymer **2b** also shows the Cp and phenyl hydrogen signals, as well as the SH hydrogen peak of the terminal group ($\delta \approx 2.8$). The peak area ratio between the SH hydrogen and the Cp hydrogen atoms of **2b** is consistent with the molecular weight determined by GPC, $M_n$ = 3500 (polystyrene standard).

Scheme 1 illustrates a plausible reaction pathway for formation of the ferrocenophanes and polymers. The rhodium complex promotes initial dehydrogenative coupling of a thiol group of 1,1′-ferrocenedithiol with diarylsilane to produce an intermediate compound, **A**, having both Si—H and S—H groups in the molecule. The subsequent intramolecular and intermolecular dehydrogenative coupling of intermediate **A** gives the ferrocenophanes and ferrocene-containing polymers respectively. The mechanism of the dehydrogenative condensation was studied in detail by using $PMe_3$-coordinated silyl(thiolato)rhodium complexes as a model of the intermediate.[12] Another route to the polymer via a ferrocenophane intermediate may be considered, because strained ferrocenophanes were reported to undergo thermally induced ring-opening polymerization to give ferrocene-containing polymers.[11] However, toluene solutions of the isolated ferrocenophanes, **1a–3a**, did not cause any ring-opening reaction under the polymerization conditions. So the product ratios in the reaction in Eqn [1] depend on the relative reactivity of intermediate **A** toward intermolecular and intramolecular condensation of the Si—H and S—H groups.




**Scheme 1** A plausible reaction mechanism for the present reaction.

**Table 1** Products of the reactions of 1,1′-ferrocenedithiol with diarylsilanes ($H_2SiAr_2$)

| Ar | Ferrocenophane | | | | | | Polymer | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield (%)[a] | Analysis (%)[b] | | | Absorption (nm)[d] | | Yield (%)[a] | Analysis (%)[b] | | | | Absorption (nm)[d] |
| | | | C | H | N | *d*— *d* | | | C | H | N | $M_n$ ($M_w/M_n$)[c] | $\pi$–$\pi$* | *d*–*d* |
| $C_6H_4$-*p*-OMe | **1a** | 39 | 58.35 (58.77) | 4.52 (4.52) | 13.10 (13.07) | 441 | **1b** | 49 | 58.91 (58.77) | 4.36 (4.52) | 13.12 (13.07) | 4600 (1.6) | 330 | 441 |
| $C_6H_5$ | **2a** | 22 | 60.79 (61.39) | 4.41 (4.21) | 15.42 (14.90) | 439 | **2b** | 51 | 61.88 (61.39) | 4.37 (4.21) | 15.50 (14.90) | 3500 (1.4) | 325 | 439 |
| $C_6H_4$-*p*-F | **3a** | 41 | 56.51 (56.65) | 3.58 (3.46) | 13.67 (13.75) | 440 | **3b** | 37 | 57.18 (56.65) | 3.47 (3.46) | 12.85 (13.75) | 2700 (1.6) | 320 | 440 |

[a] Isolated yield.
[b] Required values are in parentheses.
[c] Determined by GPC (eluent: $CHCl_3$, polystyrene standards).
[d] In chloroform.

**Table 2** $^1$H NMR data of ferrocenophanes and polymers in $CDCl_3$

| | Benzene ring | Cp ring | Me |
|---|---|---|---|
| **1a** | 6.98 (d, $J$ = 8 Hz), 7.72 (d, $J$ = 8 Hz) | 3.93 (t, $J$ = 2 Hz), 4.13 (t, $J$ = 2 Hz) | 3.85 (s) |
| **1b** | 6.80 (br), 7.72 (br) | 4.01 (br), 4.19 (br) | 3.78 (s) |
| **2a** | 7.19–7.82 (m) | 3.96 (t, $J$ = 2 Hz), 4.14 (t, $J$ = 2 Hz) | |
| **2b** | 7.11–7.68 (m) | 3.95 (br), 4.13 (br) | |
| **3a** | 7.16 (t, $J$ = 8 Hz), 7.78 (t, $J$ = 8 Hz) | 3.92 (t, $J$ = 2 Hz), 4.16 (t, $J$ = 2 Hz) | |
| **3b** | 6.95–7.52 (m) | 3.92 (br), 4.16 (br) | |
| **4** | 7.81 (d, $J$ = 7 Hz), 7.45 (d, $J$ = 7 Hz) | 4.16 (s), 4.26 (s) | |

Physical properties of the products, including results of the optical and electrochemical measurements, are mentioned below. Figure 2 compares the UV–vis spectra of ferrocenophane **3a** and polymer **3b**. Both compounds show a peak assignable to a *d–d* transition in the ferrocene unit at about 440 nm whose position is similar to that of ferrocene (438 nm).[13] In addition, the polymer exhibited an absorption peak due to a $\pi$–$\pi$* transition at 330 nm, whereas the corresponding peak of ferrocenophanes is not observed, possibly due to the transition in a higher-energy region. Figure 3 depicts a cyclic voltammogram of ferrocenophane **3a** in a DMSO solution and of polymer **3b** in a cast film on a platinum surface. They show $E_{1/2}$ potentials at 0.27 V and 0.35 V respectively, whereas the difference between $E_{pa}$ and $E_{pc}$ of **3b** (0.25 V) is significantly larger than that of **3a** (0.14 V). Thermogravimetric analysis (TGA) indicates that polymers **1b–3b** show thermal losses of the sample of 10 wt% at 260 °C, 240 °C, and 270 °C, respectively.

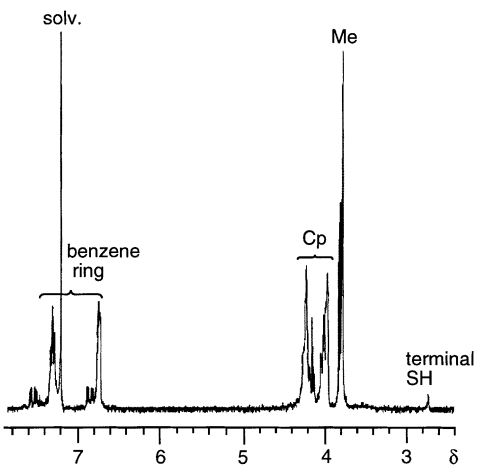
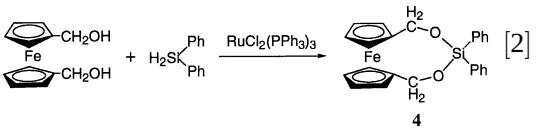



**Figure 1** $^1$H (400 MHz) NMR spectrum of **1b** in $CDCl_3$.

Reaction of 1,1′-ferrocenedimethanol with diphenylsilane in the presence of $RuCl_2(PPh_3)_3$ catalyst gives 3,3-diphenyl-2,4-dioxa-3-sila[5]ferrocenophane (**4**) in 67% yield (Eqn [2]). Although $RuCl_2(PPh_3)_3$ catalyzes reaction of 1,1′-ferrocenedimethanol with primary amines to give aza[3]ferrocenophanes,[10] similar dehydration does not occur in the present reaction.




[2]

**4**

Figure 4 shows the molecular structure of **4** determined by X-ray crystallography. Si—O bond lengths of **4** are 1.627 and 1.632 Å, which are similar to those of the previously reported Si—O-bond-containing compounds.[14] The two five-membered Cp rings are at staggered positions due to flexible $CH_2OSiOCH_2$ linkage, whereas the more strained [3] and [4]ferrocenophanes usually have two eclipsed Cp ligands.[10,15] $^1$H and $^{13}$C{$^1$H} NMR spectra and analytical data agree with the above formula.

The present study provided new organometallic polymers containing ferrocenylene units and Si—S

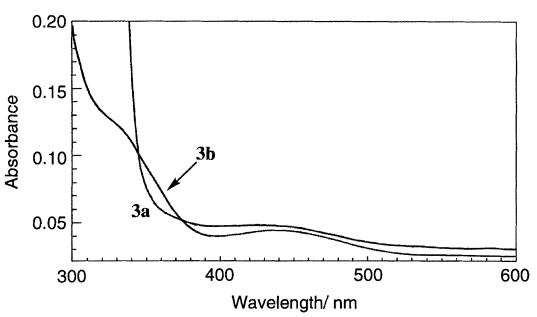



**Figure 2** UV–vis spectra of **3a** (in acetone) and **3b** (in $CHCl_3$).

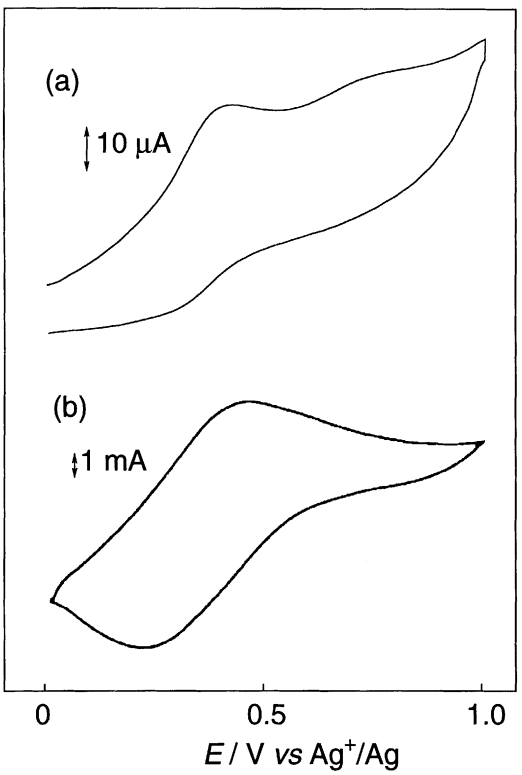



**Figure 3** Cyclic voltammogram of (a) **3a** in DMSO solution containing 0.1 M $[Et_4N]BF_4$ and (b) **3b** in a cast film on a platinum plate using acetonitrile solution containing 0.1 M $[Et_4N]BF_4$. Scan rate was 100 mV $s^{-1}$.

linkages in the main chain. They are easily separated from concomitantly formed silaferrocenophane. The ferrocenylene group of the products seems to stabilize the Si—S bond and to make hydrolysis of the compounds slower. The ferrocenophanes with the siloxane group are also obtained from the ruthenium-complex-catalyzed condensation, which does not cause polycondensation at all.

## EXPERIMENTAL

### General, measurements and materials

All the manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled by the usual method and stored under nitrogen. $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$ and

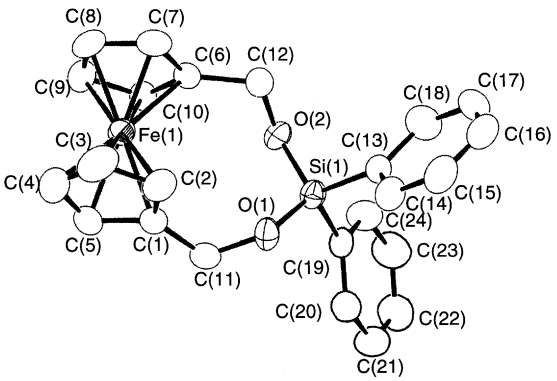



**Figure 4** Molecular structure of **4**. Selected bond lengths (Å) and angles (deg): Si(1)—O(1) 1.632(2), Si(1)—O(2) 1.627 (2), Si(1)—C(13) 1.842(3), Si(1)—C(19) 1.858(3), O(1)—C(11) 1.426(4), O(2)—C(12) 1.426(4), C(1)—C(11) 1.485(5), C(6)—C(12) 1.530(4), O(1)—Si(1)—O(2) 113.4(1), O(1)—Si(1)—C(13) 103.5(1), O(1)—Si(1)—C(19) 117.1(1), O(2)—Si(1)—C(13) 110.4(1), O(2)—Si(1)—C(19) 105.4(1), C(13)—Si(1)—C(19) 112.6(1), C(1)—C(11)—O(1) 112.6(3), C(6)—C(12)—O(2) 111.9(3), Si(1)—O(1)—C(11) 124.2(2), Si(1)—O(2)—C(12) 122.4(2).

1,1′-ferrocenedimethanol were prepared according to literature procedures,[16,17] and other organic chemicals were purchased and used as received. IR spectra were recorded on a JASCO-IR 810 spectrophotometer. NMR spectra were obtained on a JEOL EX-400 spectrometer. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder. GPC analyses were performed by a Shimadzu liquid chromatography system with a Shodex 80M column and a 6A refractive index detector using $CHCl_3$ as the eluent and polystyrene as the standard. TGA was undertaken on a Shimadzu TGA-50 under nitrogen atmosphere with a heating ratio of 10 °C $min^{-1}$. X-ray data were collected at 23 °C on a Rigaku AFC-5R automated diffractometer and monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cyclic voltammetry was carried out in solution containing 0.1 M $[Et_4N]BF_4$ with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator.

### Reaction of di(4-methoxyphenyl)silane with 1,1′-ferrocenedithiol catalyzed by $RhCl(PPh_3)_3$

To a toluene (2 ml) solution of $RhCl(PPh_3)_3$ (9 mg,

0.010 mmol) was added di(4-methoxyphenyl)silane (190 mg, 0.80 mmol) and 1,1′-ferrocenedithiol (200 mg, 0.80 mmol) at room temperature. Stirring of the reaction mixture at 100 °C for 6 h under nitrogen caused precipitation of a yellow–brown solid, which was collected by filtration, washed with hexane to give **1a** as an orange crystalline solid (190 mg, 49%). The filtrate was poured into hexane (*ca* 200 ml) and the resulting precipitate was collected and dried in vacuo to give **1b** as an orange solid (160 mg, 39%). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) data of **1a**: $\delta$ 161.9, 137.2, 123.9, 113.9 (Ph), 81.8, 76.7, 69.0 (Cp), 55.1.

Reactions of 1,1′-ferrocenthiol with di(4-methoxyphenyl)silane and with di(4-fluorophenyl)silane were carried out in a similar manner.

## Reaction of diphenylsilane with 1,1′-ferrocenedimethanol catalyzed by $RuCl_2(PPh_3)_3$

To a 1-methyl-2-pyrrolidinone (5 ml) solution of $RuCl_2(PPh_3)_3$ (66 mg, 0.070 mmol) was added 1,1′-ferrocenedimethanol (490 mg, 2.0 mmol) and diphenylsilane (380 mg, 2.0 mmol) at room temperature. After the reaction mixture was stirred at 100 °C for 24 h under nitrogen, the solvent was removed by evaporation under high vacuum. The resulting brown paste was purified by column chromatography (silica gel; eluent: ethyl acetate) to give **4** as a yellow solid (590 mg, 67%, $R_f = 0.84$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 134.4, 132.7, 130.4, 128.0 (Ph), 90.0, 67.6, 65.8 (Cp), 61.3 ($CH_2$). Anal. Calc. for $C_{24}H_2Fe_2O_2Si$: C, 67.61; H, 5.20. Found: C, 67.85; H, 4.84%.

## X-ray structure determination of 4

Crystal data: $C_{24}H_{22}O_2SiFe$, $M_r = 426.37$, monoclinic, $P2_1/c$ (no. 14), $a = 8.892(4)$, $b = 17.136(1)$, $c = 13.908(3)$ Å, $V = 2013(1)$ Å$^3$, $\beta = 108.14(2)$ °, $Z = 4$, $\mu = 8.24$ cm$^{-1}$, $F(000) = 888$, $D_{calcd} = 1.406$ Mg m$^{-3}$; no. of unique reflections: 4785; no. of reflections used ($I > 3\sigma(I)$): 2996; no. of variables: 253. The final $R(F_o)$ and $R_w(F_o)$ values were 0.041 and 0.033 respectively; $R = \sum||F_o| - |F_o| / \sum|F_o|$; $R_w = [\sum_w|F_o - F_c|^2 / \sum_w|F_o|^2]^{1/2}$; weighting scheme $w = [\{\sigma(F_o)^2\}]^{-1}$. Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication no. CCDC 149318. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## REFERENCES

1. (a) Laine RM, Blum YD, Tse D, Glaser R. In *Inorganic and Organometallic Polymers*, ACS Symposium Series 360, Zeldin M, Wynne KI, Allcock HR (eds.). American Chemical Society: Washington, DC, 1988; 124. (b) Seyferth D. In *Silicon-Based Polymer Science. A Comprehensive Resources*, Advances in Chemistry Series 224, Ziegler JM, Fearon FW (eds.). American Chemical Society: Washington, DC, 1990; 565. (c) Peukert M, Vaahs T, Bück M. *Adv. Mater.* 1990; **2**: 398.
2. (a) Zoeckler MT, Laine RM. *J. Org. Chem.* 1983; **48**: 2539. (b) Blum Y, Laine RM. *Organometallics* 1986; **5**: 2081.
3. Seyferth D, Schwark JM, Stewart RM. *Organometallics* 1989; **8**: 1980.
4. (a) Liu HQ, Harrod JF. *Organometallics* 1992; **11**: 822. (b) He J, Liu HQ, Harrod JF, Hynes R. *Organometallics* 1994; **13**: 336.
5. Choong Kwet Yive NS, Corriu RJP, Leclerco D, Mutin H, Vioux A. *Chem. Mater.* 1992; **4**: 141.
6. Reddy NP, Yamashita H, Tanaka M. *J. Am. Chem. Soc.* 1992; **114**: 6596.
7. (a) Ojima I, Nihonyanagi M, Nagai Y. *J. Organomet. Chem.* 1973; **50**: C26. (b) Nagai Y, Ojima I. Japan Kokai, 7 475 537, 1975; *Chem. Abstr.* 1975; **82**: 57923a.
8. Baruah JB, Osakada K, Yamamoto T. *Organometallics* 1996; **12**: 128.
9. (a) Yamamoto T, Morikita T, Maruyama T, Kubota K, Katada M. *Macromolecules* 1997; **30**: 5390. (b) Morikita T, Maruyama T, Yamamoto T, Kubota K, Katada M. *Inorg. Chim. Acta* 1998; **269**: 310. (c) Yamaguchi I, Osakada K, Yamamoto T, Katada M. *Bull. Chem. Soc. Jpn.* 1999; **72**: 2557.
10. (a) Yamaguchi I, Sakano T, Ishii H, Osakada K, Yamamoto T. *J. Organomet. Chem.* 1999; **584**: 213. (b) Sakano T, Ishii H, Yamaguchi I, Osakada K, Yamamoto T. *Inorg. Chim. Acta* 1999; **296**: 176.
11. (a) Manners I. *Adv. Organomet. Chem.* 1995; **37**: 131. (b) Manners I. *Polyhedron* 1996; **15**: 4311. (c) Manners I. *Can. J. Chem.* 1998; **76**: 371.
12. (a) Osakada K, Hataya K, Yamamoto T. *J. Chem. Soc. Chem. Commun.* 1996; 2315. (b) Osakada K, Hataya K, Yamamoto T. *Bull. Chem. Soc. Jpn.* 1998; **71**: 2853.
13. Gonsalves KE, Chen X. In *Ferrocenes*, Togni A, Hayashi T (eds). VCH: Weinheim, 1995.
14. Auner N, Weis J (eds). *Organosilicon Chemistry*. VCH: Weinheim, 1996.
15. (a) Batail P, Grandjean D, Astruc D, Dabard R. *J. Organomet. Chem.* 1975; **102**: 79. (b) Lacomte C,

 

Dusausoy Y, Protas J, Moise RE, Richards JH. *Acta Crystallogr. Sect. B* 1965; **19**: 330. (c) Lacomte C, Dusausoy Y, Potas J, Moise C, Tirouflet J. *Acta Crystallogr. Sect. B* 1973; **29**: 488.

16. Hallman PS, Stephenson TA, Wilkinson G. *Inorg. Synth.* 1970; **12**: 237.
17. Carlstrom A-S, Frejd T. *J. Org. Chem.* 1990; **55**: 4175.

 