Reactions of Doubly Bridged Bis(cyclopentadienes) with Iron Pentacarbonyl

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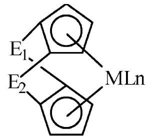
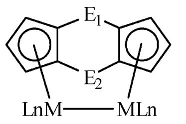
When the doubly bridged bis(cyclopentadiene) ligand $(Me_2C)(Me_2Si)(C_5H_4)_2$ (**1**) reacted with $Fe(CO)_5$ in refluxing toluene, the unusual product $[(C_5H_6)(Me_2C)(Me_2Si)(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**2**) with a hydrogenated double bond in one of the cyclopentadiene ligands, the diiron complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Fe(CO)_2]_2$ (**3**), and the desilylation product **4** were obtained. When the reaction was performed in refluxing xylene, the novel complex $(Me_2C)(\eta^5\text{-}C_5H_3)(\eta^5{:}\eta^1\text{-}C_5H_3)[(Me_2Si)Fe(CO)_2][Fe(CO)_2]$ (**5**) with an Fe−Si bond, which should be accompanied by the cleavage of a C−Si bond in the ligand, was isolated in addition to the complexes **2**∼**4**. When bis(cyclopentadienyl) ligands bridged with R_2C ($R_2C = Me_2C$, $(CH_2)_5C$) and Me_2E (E = Si, Ge) groups were used instead of **1**, the similar novel complexes $(R_2C)(\eta^5\text{-}C_5H_3)(\eta^5{:}\eta^1\text{-}C_5H_3)[(Me_2E)Fe(CO)_2][Fe(CO)_2]$ ($R_2C = Me_2C$, E = Ge (**7**); $R_2C = (CH_2)_5C$, E = Si (**17**), Ge (**21**)) with an Fe−E bond were obtained in addition to the diiron complexes $(R_2C)(Me_2E)[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ ($R_2C = Me_2C$, E = Ge (**8**); $R_2C = (CH_2)_5C$, E = Si (**18**), Ge (**22**)) and the desilylation or degermylation products. When a *tert*-butyl group was introduced into the cyclopentadienyl rings, or two phenyl groups were introduced at the bridging silicon atom instead of two methyl groups in **1**, only the diiron complexes $(Me_2C)(Me_2E)[(\eta^5\text{-}t\text{-}BuC_5H_2)Fe(CO)_2]_2$ (E = Si(**10**), Ge (**13**)) and $(Me_2C)(Ph_2Si)[(\eta^5\text{-}C_5H_3)Fe(CO)_2]_2$ (**15**) were obtained, in addition to the desilylation or degermylation products. When a methylene bridge was used instead of an isopropylene bridge in **1** and **6**, the partially hydrogenated complexes $(Me_2E)(\eta^3\text{-}CHC_5H_6)(\eta^5\text{-}C_5H_3)Fe(CO)_3Fe(CO)_2$ (E = Si (**24**), Ge (**28**)), the diiron complexes $(CH_2)(Me_2E)[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (E = Si (**25**), Ge (**29**)), and the desilylation or degermylation products were obtained. The molecular structures of **2**, **3**, **5**, **7**, **8**, **10**, **11t**, **15**, **17**, **18**, **21**, **24**, **25**, **28**, and **29** were determined by X-ray diffraction.

Introduction

Bridged bis(cyclopentadienyl) transition-metal complexes have been investigated widely in recent years. Bridged bis(cyclopentadienyl) ligands may be used in the synthesis of *ansa*-metallocenes, which are well-known catalyst precursors for stereospecific α-olefin polymerization.[1] Bridged bis(cyclopentadienyl) dinuclear metal complexes in which two reactive metal centers are held in close proximity could potentially exhibit cooperative electronic and chemical effects that would be useful in catalysis.[2] In comparison with singly bridged bis(cyclopentadienyl)metal complexes, doubly bridged bis(cyclopentadienyl) ligands are more rigid, which could result in unique properties in structures and catalysis. Doubly bridged *ansa*-metallocenes (type **A**) may offer a more constrained environment, which represent a new class of stereorigid metallocene catalysts for stereospecific α-olefin polymerization.[3] In dinuclear complexes (types **C** and **D**), the doubly bridged ligands restrict the relative orientation of the two metals, locking the metals on either the same (cis) or opposite (trans) faces of the ligand. Doubly bridged dinuclear group IV metallocene complexes have been investigated extensively as olefin polymerization catalysts.[4] In doubly bridged dinuclear or polynuclear metallocenes (M = Fe, Co, Ni, Cr, V) the intramolecular magnetic and electrostatic interactions between the metal centers have been probed by cyclic voltammetry.[5] Intramolecular electron transfer has also been observed in highly concentrated solutions.[5c]



A



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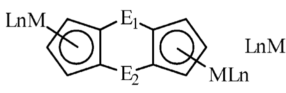
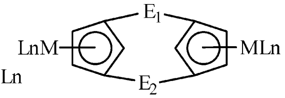


cis* and *trans
C



cis* and *trans
D

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Doubly bridged bis(cyclopentadienyl) dinuclear metal carbonyl complexes have also received considerable attention.[6,7] However, there have only been a few reports of doubly bridged bis(cyclopentadienyl) metal−metal-bonded complexes (type **B**) and they are all limited to the doubly Me_2Si bridged ligand.[5d,6e,7] Recently, we synthesized some doubly bridged bis(cyclopentadienyl) diiron complexes by the reaction of different doubly bridged ligands with $Fe(CO)_5$.[8] Here, we further report the reaction of carbon and silicon or germanium doubly bridged bis(cyclopentadienes) with $Fe(CO)_5$.

Experimental Section

General Considerations. Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. ^1H NMR spectra were recorded on a Bruker AC-P200 instrument, while IR spectra were recorded as KBr disks on a Nicolet560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. $(Me_2C)(C_5H_5)_2$,[9] $(Me_2C)(Me_2Si)(C_5H_4)_2$ (**1**),[9] $(Me_2C)(Me_2Ge)(C_5H_4)_2$ (**6**),[9] $(Me_2C)(t\text{-}BuC_5H_4)_2$,[10] $[(CH_2)_5C](C_5H_4)_2$,[11] and $(CH_2)(C_5H_5)_2$[12] were prepared according to the literature methods.

Reaction of $(Me_2C)(Me_2Si)(C_5H_4)_2$ (1) with $Fe(CO)_5$ in Toluene. A solution of 1.43 g (6.24 mmol) of $(Me_2C)(Me_2Si)(C_5H_4)_2$ (**1**) and 1.8 mL (13.7 mmol) of $Fe(CO)_5$ in 50 mL of toluene was refluxed for 16 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) afforded 0.38 g (9%) of **2** as deep red crystals. The second band (green) gave 0.82 g (29%) of **3** as deep green crystals. The third band (red) afforded 0.12 g (5%) of **4** as deep red crystals. Data for **2** are as follows. Mp: 160 °C dec. Anal. Calcd for $C_{34}H_{42}Fe_2Si_2O_4$: C, 59.83; H, 6.20. Found: C, 59.78; H, 6.23. ^1H NMR ($CDCl_3$): δ 5.00 (s, 2H, C_5H_3), 4.68 (s, 2H, C_5H_3), 3.50 (s, 2H, C_5H_3), 2.44 (m, 8H, $C{=}CCH_2$), 1.77−1.45 (m, 4H, $CH_2C\mathit{H}_2CH_2$), 1.63 (s, 6H, CMe), 1.30 (s, 6H, CMe), 0.55 (s, 6H, SiMe), 0.22 (s, 6H, Si−Me). IR (ν_{CO}, cm^{-1}): 1950 (s), 1938 (s), 1763(s). Data for **3** are as follows. Mp: 281−282 °C. Anal. Calcd for $C_{19}H_{18}Fe_2SiO_4$: C, 50.70; H, 4.03. Found: C, 50.35; H, 4.13. ^1H NMR ($CDCl_3$): δ 4.99 (s, 2H, C_5H_3), 4.80 (s, 2H, C_5H_3), 4.57 (s, 2H, C_5H_3), 1.52 (s, 3H, CMe), 1.43 (s, 3H, CMe), 0.62 (s, 3H, Si−Me), 0.58 (s, 3H, Si−Me). IR (ν_{CO}, cm^{-1}): 1993 (s), 1950 (s), 1929 (s). Data for **4** are as follows.[13] ^1H NMR ($CDCl_3$): δ 5.16 (s, 4H, C_5H_4), 5.07 (s, 4H, C_5H_4), 1.40 (s, 6H, Me). IR (ν_{CO}, cm^{-1}): 1988 (s), 1942 (s), 1774 (s).

Reaction of $(Me_2C)(Me_2Si)(C_5H_4)_2$ (1) with $Fe(CO)_5$ in Xylene. A solution of 2.8 g (12.3 mmol) of **1** and 3.4 mL (26 mmol) of $Fe(CO)_5$ in 80 mL of xylene was refluxed for 10 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (yellow) afforded 0.32 g (6%) of **5** as yellow crystals. The second band afforded 0.55 g (13%) of **2**. The third band gave 1.1 g (29%) of **3**. The fourth band afforded 0.22 g

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(4%) of **4**. Data for **5** are as follows. Mp: 178 °C dec. Anal. Calcd for $C_{19}H_{18}Fe_2SiO_4$: C, 50.70; H, 4.03. Found: C, 50.80; H, 4.29. ^{1}H NMR ($CDCl_3$): δ 5.69 (m, 1H, C_5H_3), 5.40 (m, 1H, C_5H_3), 5.00 (m, 1H, C_5H_3), 4.86 (m, 1H, C_5H_3), 4.40 (m, 1H, C_5H_3), 4.32 (m, 1H, C_5H_3), 1.52 (m, 3H, CMe), 1.42 (s, 3H, CMe), 0.70 (s, 3H, SiMe), 0.62 (s, 3H, Si−Me). IR (ν_{CO}, cm^{-1}): 2017 (s), 1979 (s), 1952 (s), 1920 (s).

Reaction of $(Me_2C)(Me_2Ge)(C_5H_4)_2$ (6) with Fe(CO)$_5$. A solution of 0.6 g (2.2 mmol) of **6** and 0.9 mL (6.8 mmol) of Fe(CO)$_5$ in 30 mL of xylene was refluxed for 10 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (yellow) afforded 0.36 g (26%) of **7** as orange-red crystals. The second band (green) gave 0.12 g (9%) of **8** as black crystals. The third band (red) afforded 0.04 g (4%) of **4**. Data for **7** are as follows. Mp: 185 °C dec. Anal. Calcd for $C_{19}H_{18}Fe_2GeO_4$: C, 46.14; H, 3.67. Found: C, 45.64; H, 3.59. ^{1}H NMR ($CDCl_3$): δ 5.62 (m, 1H, C_5H_3), 5.43 (m, 1H, C_5H_3), 4.97 (m, 1H, C_5H_3), 4.75 (m, 1H, C_5H_3), 4.35 (m, 2H, C_5H_3), 1.53 (s, 3H, CMe), 1.44 (s, 3H, CMe), 0.80 (s, 3H, GeMe), 0.71 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 2016 (s), 1982 (s), 1952 (s), 1924 (s). Data for **8** are as follows. Mp: 160 °C dec. Anal. Calcd for $C_{19}H_{18}Fe_2GeO_4$: C, 46.14; H, 3.67. Found: C, 45.96; H, 4.23. ^{1}H NMR ($CDCl_3$): δ 5.00 (m, 2H, C_5H_3), 4.62 (m, 2H, C_5H_3), 4.60 (m, 2H, C_5H_3), 1.51 (s, 3H, CMe), 1.48 (s, 3H, CMe), 0.81 (s, 3H, GeMe), 0.71 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 1975 (s), 1938 (s), 1770 (s).

Similarly, 0.60 g (2.2 mmol) of **6** reacted with 0.9 mL (6.8 mmol) of Fe(CO)$_5$ in refluxing toluene for 19 h to give 0.11 g (11%) of **8** and small amounts of **7** and **4**.

Preparation of $(Me_2C)(Me_2Si)$(*t*-Bu$C_5H_3)_2$ (9). A 9.5 mL portion of an *n*-BuLi solution in hexane (2.54 M, 24.6 mmol) was added to a solution of 3.5 g (12.3 mmol) of (Me_2C)(*t*-Bu$C_5H_4)_2$ in 100 mL of THF at 0 °C. The mixture was stirred for 24 h at room temperature to give a white suspension of dilithium salts. To the suspension was added slowly 1.6 g (12.3 mmol) of Me_2SiCl_2. After the mixture was stirred for 48 h at room temperature, the solvents were removed under reduced pressure. The residue was extracted with pentane, and the solvent was concentrated; 4.0 g (95%) of **9** was obtained as light yellow crystals. Mp: 128 °C. Anal. Calcd for $C_{23}H_{36}Si$: C, 81.10; H, 10.65. Found: C, 80.75; H, 8.81. ^{1}H NMR ($CDCl_3$): δ 6.20 (s, 2H, C_5H_3), 5.86 (s, 2H, C_5H_3), 3.46 (s, 2H, C_5H_3), 1.57 (s, 3H, CMe), 1.46 (s, 3H, CMe), 1.17 (s, 9H, CMe_3), 1.11 (s, 9H, CMe_3), 0.43 (s, 3H, SiMe), 0.33 (s, 3H, Si−Me).

Reaction of 9 with Fe(CO)$_5$. A solution of 0.6 g (1.8 mmol) of **9** and 0.9 mL (6.8 mmol) of Fe(CO)$_5$ in 30 mL of xylene was refluxed for 10 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (green) gave 0.18 g (18%) of **10** as dark green crystals. The second band (red) afforded 0.02 g (2%) of **11t** as deep red crystals. The third band (red) afforded a trace amount of **11c** as deep red crystals. Data for **10** are as follows. Mp: 220 °C dec. Anal. Calcd for $C_{27}H_{34}Fe_2O_4Si$: C, 57.67; H, 6.09. Found: C, 57.71; H, 6.13. ^{1}H NMR ($CDCl_3$): δ 4.86 (s, 2H, C_5H_2), 4.67 (s, 2H, C_5H_2), 1.48 (s, 3H, CMe), 1.34 (s, 3H, CMe), 1.22 (s, 18H, CMe_3), 0.57 (s, 3H, SiMe), 0.54 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 1997 (s), 1946 (s), 1926 (s), 1902 (m). Data for **11t** are as follows. Mp: 222 °C dec. Anal. Calcd for $C_{25}H_{30}Fe_2O_4$: C, 59.32; H, 5.97. Found: C, 58.88; H, 6.61. ^{1}H NMR ($CDCl_3$): δ 5.08 (s, 2H, C_5H_3), 4.92 (m, 4H, C_5H_3), 1.34 (s, 6H, CMe), 1.32 (s, 18H, CMe_3). IR (ν_{CO}, cm^{-1}): 1977 (s), 1938 (s), 1803 (m), 1763 (s). Data for **11c** are as follows. ^{1}H NMR ($CDCl_3$): δ 5.08 (m, 2H, C_5H_3), 4.92 (m, 2H, C_5H_3), 4.88 (m, 2H, C_5H_3), 1.36 (s, 6H, CMe), 1.32 (s, 18H, CMe_3).

Preparation of $(Me_2C)(Me_2Ge)$(*t*-Bu$C_5H_3)_2$ (12). Using a method similar to that described for **9**, **12** was synthesized from (Me_2C)(*t*-Bu$C_5H_4)_2$, *n*-BuLi, and Me_2GeBr_2 in 91% yield as light yellow crystals. Mp 145 °C. Anal. Calcd for $C_{23}H_{36}Ge$: C, 71.73; H, 9.42. Found: C, 71.50; H, 8.87. ^{1}H NMR ($CDCl_3$): δ 6.33 (m, 2H, C_5H_3), 5.81 (s, 2H, C_5H_3), 3.02 (s, 2H, C_5H_3), 1.43 (s, 6H, CMe), 1.18 (s, 18H, CMe_3), −0.02 (s, 6H, GeMe).

Reaction of 12 with Fe(CO)$_5$. A solution of 0.8 g (2.0 mmol) of **12** and 0.9 mL (6.8 mmol) of Fe(CO)$_5$ in 30 mL of xylene was refluxed for 7 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (green) gave 0.04 g (3%) of **13** as dark green crystals. The second band (red) afforded 0.05 g (5%) of **11t**. **13**: mp 214 °C. Anal. Calcd for $C_{27}H_{34}Fe_2GeO_4$: C, 53.44; H, 5.65. Found: C, 53.60; H, 5.61. ^{1}H NMR ($CDCl_3$): δ 4.86 (s, 2H, C_5H_2), 4.64 (s, 2H, C_5H_2), 1.46 (s, 3H, CMe), 1.39 (s, 3H, CMe), 1.21 (s, 18H, CMe_3), 0.73 (s, 3H, GeMe), 0.67 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 1993 (s), 1942 (s), 1932 (s), 1902 (m).

Preparation of $(Me_2C)(Ph_2Si)(C_5H_4)_2$ (14). To a suspension of dilithium salts of $(Me_2C)(C_5H_5)_2$, prepared from 5.0 g (29.0 mmol) of $(Me_2C)(C_5H_5)_2$ and 58 mmol of an *n*-BuLi hexane solution in 100 mL of THF, was added slowly 7.3 g (29.0 mmol) of Ph_2SiCl_2. After the mixture was refluxed for 2 days, the solvents were removed under reduced pressure. The residue was extracted with pentane. Upon concentration and cooling, 4.2 g (41%) of **14** was obtained as a light yellow solid. Mp: 114−115 °C. Anal. Calcd for $C_{25}H_{24}Si$: C, 85.17; H, 6.86. Found: C, 85.18; H, 6.80. ^{1}H NMR ($CDCl_3$): δ 7.80−7.00 (m, 10H, Ph H), 6.78 (m), 6.61 (m), 6.30−6.20 (m), 3.20 (m), 3.08 (s) (total 8H, C_5H_4), 1.64, 1.48, 1.43 (s, s, s, 6H, CMe).

Reaction of 14 with Fe(CO)$_5$. A solution of 0.8 g (2.3 mmol) of **14** and 0.9 mL (6.8 mmol) of Fe(CO)$_5$ in 30 mL of xylene was refluxed for 7 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (green) gave 0.10 g (8%) of **15** as dark green crystals. The second band (red) afforded 0.20 g (22%) of **4**. Data for **15** are as follows. Mp: 220 °C dec. Anal. Calcd for $C_{27}H_{34}Fe_2O_4Si$: C, 60.65; H, 3.86. Found: C, 61.24; H, 3.59. ^{1}H NMR ($CDCl_3$): δ 7.84 (m, 2H, Ph H), 7.67 (m, 2H, Ph H), 7.45−7.30 (m, 6H, Ph H), 5.26 (m, 2H, C_5H_3), 4.90 (m, 2H, C_5H_3), 4.67 (m, 2H, C_5H_3), 1.43 (s, 3H, CMe), 1.11 (s, 3H, CMe). IR (ν_{CO}, cm^{-1}): 1993 (s), 1942 (s), 1932 (s), 1902 (s).

Preparation of $[(CH_2)_5C](Me_2Si)(C_5H_4)_2$ (16). To a suspension of dilithium salts of $[(CH_2)_5C](C_5H_5)_2$, prepared from 2.0 g (9.4 mmol) of $[(CH_2)_5C](C_5H_5)_2$ and 18.8 mmol of *n*-BuLi hexane solution in 50 mL of THF, was added slowly 1.2 g (9.4 mmol) of Me_2SiCl_2. After the mixture was refluxed for 2 days, the solvents were removed under reduced pressure. The residue was extracted with pentane. After removal of solvent, 1.1 g (43%) of **16** was obtained as a light yellow liquid. ^{1}H NMR ($CDCl_3$): δ 6.50−6.20 (m, 6H, C_5H_3), 3.63 (m, 2H, C_5H_3), 2.20−1.20 (m, 10H, CH_2), 0.50, 0.46 (s, s, total 3H, SiMe), −1.17, −1.20 (s, s, total 3H, SiMe).

Reaction of 16 with Fe(CO)$_5$. A solution of 0.35 g (1.4 mmol) of **16** and 0.6 mL (4.6 mmol) of Fe(CO)$_5$ in 20 mL of xylene was refluxed for 6 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (yellow) afforded 0.10 g (16%) of **17** as orange-red crystals. The second band (green) gave 0.15 g (24%) of **18** as black crystals. The third band (red) afforded 0.05 g (9%) of **19** as deep red crystals. Data for **17** are as follows. Mp: 232 °C dec. Anal. Calcd for $C_{22}H_{22}Fe_2SiO_4$: C, 53.91; H, 4.52. Found: C, 53.50; H, 4.70. ^{1}H NMR ($CDCl_3$) δ: 5.74 (m, 1H, C_5H_3), 5.39 (m, 1H, C_5H_3), 5.10 (m, 1H, C_5H_3), 4.86 (m, 1H, C_5H_3), 4.42 (m, 1H, C_5H_3), 4.31 (m, 1H, C_5H_3), 2.10−1.40 (m, 10H, CH_2), 0.70 (s, 3H, SiMe), 0.61 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 2026 (s), 1981 (s), 1962 (s), 1918 (s). Data for **18** are as follows. Mp: 230 °C dec. Anal. Calcd for $C_{22}H_{22}Fe_2SiO_4$: C, 53.91; H, 4.52. Found: C, 53.25; H, 4.92. ^{1}H NMR ($CDCl_3$): δ 4.99 (m, 2H, C_5H_3), 4.87 (m, 2H, C_5H_3), 4.62 (m, 2H, C_5H_3), 1.90−1.40 (m, 10H, CH_2), 0.61 (s, 3H, SiMe), 0.55 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 2002 (s), 1954 (s), 1934 (s), 1902 (m). Data for **19** are as follows.[14]

^{1}H NMR ($CDCl_3$): δ 5.21 (m, 4H, C_5H_4), 4.95 (m, 4H, C_5H_4), 1.90−1.20 (m, 10H, CH_2). IR (ν_{CO}, cm^{-1}): 1998 (s), 1983 (s), 1777 (s).

Preparation of [$(CH_2)_5C$](Me_2Ge)$(C_5H_4)_2$ (20). To a suspension of 14.1 mmol of dilithium salts of [$(CH_2)_5C$]$(C_5H_5)_2$, prepared in a manner similar to that for **16**, was added slowly 3.7 g (14.1 mmol) of Me_2GeBr_2. After the mixture was refluxed for 2 days, the solvents were removed under reduced pressure. The residue was extracted with pentane. After removal of the solvent 1.3 g (29%) of **20** was obtained as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 6.50−6.20 (m, 6H, C_5H_3), 3.75 (s, 2H, C_5H_3), 2.20−1.20 (m, 10H, CH_2), 0.70 (s, 3H, GeMe), −1.07 (s, 3H, GeMe).

Reaction of 20 with $Fe(CO)_5$. A solution of 0.50 g (1.6 mmol) of **20** and 0.6 mL (4.6 mmol) of $Fe(CO)_5$ in 20 mL of xylene was refluxed for 6 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (yellow) afforded 0.20 g (23%) of **21** as orange-red crystals. The second band (green) gave 0.04 g (5%) of **22** as black crystals. The third band (red) afforded 0.06 g (9%) of **19** as deep red crystals. Data for **21** are as follows. Mp: 240 °C dec. Anal. Calcd for $C_{22}H_{22}Fe_2GeO_4$: C, 49.41; H, 4.15. Found: C, 48.96; H, 3.95. ^{1}H NMR ($CDCl_3$): δ 5.67 (m, 1H, C_5H_3), 5.42 (m, 1H, C_5H_3), 5.07 (m, 1H, C_5H_3), 4.74 (m, 1H, C_5H_3), 4.35 (m, 2H, C_5H_3), 2.10−1.30 (m, 10H, CH_2), 0.79 (s, 3H, GeMe), 0.68 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 2022 (s), 1976 (s), 1956 (s), 1921 (s). Data for **22** are as follows. Mp: 240 °C dec. Anal. Calcd for $C_{22}H_{22}Fe_2SiO_4$: C, 49.42; H, 4.15. Found: C, 49.37; H, 4.20. ^{1}H NMR ($CDCl_3$): δ 5.01 (m, 2H, C_5H_3), 4.91 (m, 2H, C_5H_3), 4.70 (m, 2H, C_5H_3), 2.00−1.20 (m, 10H, CH_2), 0.82 (s, 3H, GeMe), 0.68 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 1973 (s), 1942 (s), 1785 (m), 1767 (s).

Preparation of (CH_2)(Me_2Si)$(C_5H_4)_2$ (23). Using a method similar to that described for **9**, **23** was synthesized from (CH_2)$(C_5H_4)_2$, *n*-BuLi, and Me_2SiCl_2 in 85% yield as light yellow crystals. Mp: 57−58 °C. Anal. Calcd for $C_{23}H_{36}Si$: C, 77.93; H, 9.20. Found: C, 77.40; H, 8.05. ^{1}H NMR ($CDCl_3$): δ 6.33 (m, 4H, C_5H_4), 6.23 (m, 2H, C_5H_4), 3.69 (d, J = 14.2 Hz, 1H, CH_2), 3.59 (d, J = 14.2 Hz, 1H, CH_2), 3.40 (s, 2H, C_5H_4), 0.50 (s, 3H, SiMe), −1.14 (s, 3H, SiMe).

Reaction of 23 with $Fe(CO)_5$. A solution of 0.4 g (2.0 mmol) of **23** and 1.0 mL (7.6 mmol) of $Fe(CO)_5$ in 40 mL of xylene was refluxed for 7 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) afforded 0.12 g (13%) of **24** as red crystals. The second band (black) gave 0.2 g (24%) of **25** as black crystals. The third band (red) afforded 0.08 g (11%) of **26** as deep red crystals. Data for **24** are as follows. Mp: 160−162 °C. Anal. Calcd for $C_{18}H_{16}Fe_2O_5Si$: C, 47.82; H, 3.57. Found: C, 47.56; H, 3.60. ^{1}H NMR ($CDCl_3$): δ 5.10 (m, 1H, C_5H_3), 5.03 (s, 1H, CH), 4.64 (m, 1H, C_5H_3), 4.02 (m, 1H, C_5H_3), 3.10−2.80 (m, 2H, CH_2), 2.20−2.00 (m, 1H, CH_2), 2.00−1.80 (m, 3H, CH_2), 0.35 (s, 3H, Si−Me), 0.02 (s, 3H, Si−Me). IR (ν_{CO}, cm^{-1}): 2010 (s), 1973 (s), 1954 (s), 1934 (s), 1803 (m). Data for **25** are as follows. Mp: 180 °C dec. Anal. Calcd for $C_{17}H_{14}Fe_2O_4Si$: C, 48.38; H, 3.34. Found: C, 47.20; H, 3.25. ^{1}H NMR ($CDCl_3$): δ 5.25 (m, 2H, C_5H_3), 5.20 (m, 2H, C_5H_3), 5.11 (m, 2H, C_5H_3), 3.09 (d, J = 15.2 Hz, 1H, CH_2), 2.86 (d, J = 15.2 Hz, 1H, CH_2), 0.83 (s, 3H, SiMe), 0.24 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 1977 (s), 1926 (s), 1811 (s), 1771 (s). Data for **26** are as follows.[15] Mp: 250 °C dec. Anal. Calcd for $C_{15}H_{10}Fe_2O_4$: C, 49.23; H, 2.75. Found: C, 49.39; H, 2.71. ^{1}H NMR ($CDCl_3$): δ 5.19 (m, 4H, C_5H_4), 4.93 (m, 4H, C_5H_4), 2.61 (s, 2H, CH_2). IR (ν_{CO}, cm^{-1}): 1958 (s), 1926 (s), 1775 (s), 1740 (m).

Preparation of (CH_2)(Me_2Ge)$(C_5H_4)_2$ (27). Using a method similar to that described for **9**, **27** was synthesized from (CH_2)$(C_5H_4)_2$, *n*-BuLi, and Me_2GeBr_2 in 80% yield as light yellow crystals. Mp: 69−70 °C. Anal. Calcd for $C_{23}H_{36}Ge$: C, 63.76; H, 6.59. Found: C, 63.52; H, 7.46. ^{1}H NMR ($CDCl_3$): δ 6.50−6.10 (m, 6H, C_5H_4), 3.70 (d, J = 11.7 Hz, 1H, CH_2), 3.54 (m, 3H, CH_2 and C_5H_4), 0.71 (s, 3H, GeMe), −1.01 (s, 3H, GeMe).

Reaction of 27 with $Fe(CO)_5$. A solution of 0.6 g (2.5 mmol) of **27** and 1.0 mL (7.6 mmol) of $Fe(CO)_5$ in 30 mL of xylene was refluxed for 6 h. After removal of solvent, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (red) afforded 0.05 g (4%) of **28** as red crystals. The second band (black) gave 0.12 g (10%) of **29** as black crystals. The third band (red) afforded 0.08 g (9%) of **26**. Data for **28** are as follows. Mp: 150−152 °C. Anal. Calcd for $C_{18}H_{16}Fe_2O_5Ge$: C, 43.52; H, 3.25. Found: C, 43.46; H, 3.35. ^{1}H NMR ($CDCl_3$): δ 5.08 (m, 2H, CH and C_5H_3), 4.70 (m, 1H, C_5H_3), 4.02 (m, 1H, C_5H_3), 3.10−2.80 (m, 2H, CH_2), 2.20−1.80 (m, 4H, CH_2), 0.52 (s, 3H, GeMe), 0.16 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 2010 (s), 1966 (s), 1946 (s), 1918 (s). Data for **29** are as follows. Mp: 200 °C dec. Anal. Calcd for $C_{17}H_{14}Fe_2O_4Ge$: C, 43.76; H, 3.02. Found: C, 44.00; H, 3.05. ^{1}H NMR ($CDCl_3$): δ 5.33 (m, 2H, C_5H_3), 5.20 (m, 2H, C_5H_3), 5.15 (m, 2H, C_5H_3), 3.12 (d, J = 17.8 Hz, 1H, CH_2), 2.75 (d, J = 17.8 Hz, 1H, CH_2), 1.04 (s, 3H, GeMe), 0.40 (s, 3H, GeMe). IR (ν_{CO}, cm^{-1}): 1973 (s), 1930 (s), 1803 (s), 1771 (s).

Crystallographic Studies. Crystals of complexes **2**, **3**, **5**, **7**, **8**, **10**, **11t**, **15**, **17**, **18**, **21**, **24**, **25**, **28**, and **29** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2 solution. Data collection was performed on a Bruker SMART 1000 except for **7**, which was performed on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation ($\omega-2\theta$ scans, λ = 0.710 73 Å). Empirical absorption corrections were applied for **3** and **5**, and semiempirical absorption corrections were applied for **11t**, **15**, **17**, **18**, **21**, **24**, **25**, **28**, and **29**. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were performed using the SHELXL-97 or Siemens SHELXTL-PC program system. The crystal data and summary of X-ray data collection are presented in Table 1.

Results and Discussion

Reaction of (Me_2C)(Me_2Si)$(C_5H_4)_2$ (1) with $Fe(CO)_5$. The solution of the doubly bridged bis(cyclopentadiene) ligand **1** and $Fe(CO)_5$ in toluene was heated under reflux for 16 h; complexes **2**−**4** were obtained (Scheme 1).

Complex **2** is an intermolecular diiron complex. Its IR spectrum exhibited two strong (1950, 1938 cm^{-1}) terminal carbonyl bands and one bridging carbonyl band (1763 cm^{-1}). Its ^{1}H NMR spectrum displayed three Cp H proton peaks at 5.00 (2H), 4.68 (2H), and 3.50 (2H) and multiplet allyl and alkyl proton peaks at 2.44 (8H) and 1.77−1.45 (4H), respectively. On the basis of the IR and ^{1}H NMR spectra, elemental analysis, and X-ray diffraction analysis, **2** was assigned to be [$(C_5H_6)(Me_2C)(Me_2Si)(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$, an unusual structure with a hydrogenated double bond in the uncoordinated cyclopentadiene ligands. Complex **3** is a normal intramolecular diiron complex. Its ^{1}H NMR spectrum displayed three Cp H proton peaks at 4.99 (2H), 4.80 (2H), and 4.57 (2H) ppm. However, its IR spectrum exhibited only three strong terminal carbonyl bands at 1993, 1950, and 1929 cm^{-1}, indicating that there are no bridging carbonyl groups in the molecule of **3**. This has been further confirmed by X-ray diffraction analysis. **4** was assigned as the desilylation product $(Me_2C)[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$, on the basis of its ^{1}H NMR and IR spectra.[13]

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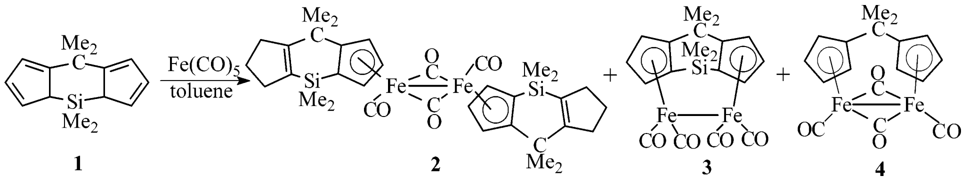
Table 1. Crystal Data and Summary of X-ray Data Collection

	2	**3**	**5**	**7**	**8**	**10**	**11t**	**15**
formula	$C_{17}H_{21}FeO_2Si$	$C_{19}H_{18}Fe_2O_4Si$	$C_{19}H_{18}Fe_2O_4Si$	$C_{19}H_{18}Fe_2GeO_4$	$C_{19}H_{18}Fe_2GeO_4$	$C_{27}H_{34}Fe_2O_4Si$	$C_{25}H_{30}Fe_2O_4$	$C_{29}H_{22}Fe_2O_4Si$
fw	341.28	450.12	450.12	494.64	494.62	562.33	506.19	574.26
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$	$Pbca$	$Pbca$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	19.999(4)	9.1644(10)	16.3299(17)	16.365(3)	9.162(4)	9.429(3)	18.743(6)	8.394(4)
b (Å)	13.788(3)	13.8521(15)	13.3165(14)	13.290(3)	15.227(6)	10.627(3)	13.562(5)	10.097(4)
c (Å)	14.508(3)	15.3075(17)	17.2512(18)	17.228(3)	12.986(5)	28.228(8)	19.554(7)	16.130(7)
α (deg)	90	90	90	90	90	90	90	72.204(7)
β (deg)	123.423(4)	102.103(2)	90	90	91.098(8)	92.313(5)	106.116(6)	79.040(7)
γ (deg)	90	90	90	90	90	90	90	88.160(7)
V (Å^3)	3338.8(12)	1900.0(4)	3751.4(7)	3747(2)	1811.4(12)	2826.2(13)	4775(3)	1277.4(9)
Z	8	4	8	8	4	4	8	2
D_{calcd} (g cm^{-3})	1.358	1.574	1.594	1.754	1.814	1.322	1.408	1.493
μ (mm^{-1})	0.976	1.610	1.631	3.1225	3.250	1.097	1.242	1.216
F(000)	1432	920	1840	1984	992	1176	2112	588
cryst size (mm)	0.1 × 0.15 × 0.4	0.25 × 0.2 × 0.15	0.25 × 0.22 × 0.15	0.35 × 0.35 × 0.40	0.30 × 0.20 × 0.15	0.30 × 0.25 × 0.20	0.40 × 0.22 × 0.20	0.20 × 0.15 × 0.05
max 2θ (deg)	48.84	52.82	50.04	50	50.04	50.06	52.86	50.04
no. of rflns collected	5296	10 993	14 723	3688	6628	11 522	26 953	2425
no. of indep rflns/R_{int}	2585/0.0582	3901/0.0607	3308/0.0963	2999	2925/0.0560	4991/0.0564	9764/0.0978	2333/0.0277
no. of params	190	235	235	235	244	307	576	325
goodness of fit on F^2	1.042	1.019	1.001	1.17 (on F)	1.083	0.952	0.944	1.052
R1, wR2 ($I > 2\sigma$(I))	0.0634, 0.1701	0.0375, 0.0793	0.0352, 0.0492	0.042, 0.045 ($I \geq 3\sigma(I)$)	0.0744, 0.1770	0.0480, 0.0965	0.0554, 0.0865	0.0630, 0.1160
R1, wR2 (all data)	0.0976, 0.1925	0.0587, 0.0858	0.0735, 0.0542		0.0983, 0.1904	0.0921, 0.1082	0.1450, 0.1084	0.1224, 0.1349

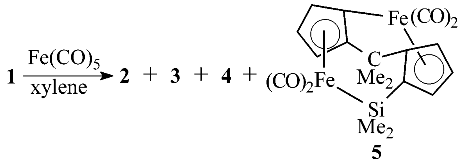
	17	**18**	**21**	**24**	**25**	**28**	**29**
formula	$C_{22}H_{22}Fe_2O_4Si$	$C_{22}H_{22}Fe_2O_4Si$	$C_{22}H_{22}Fe_2GeO_4$	$C_{18}H_{16}Fe_2O_5Si$	$C_{17}H_{14}Fe_2O_4Si$	$C_{36}H_{32}Fe_4Ge_2O_{10}$	$C_{17}H_{14}Fe_2GeO_4$
fw	490.19	490.19	534.69	452.10	422.07	993.20	466.57
cryst syst	orthorhombic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/m$	$P2/c$	$P2_1/n$
a (Å)	10.006(4)	9.505(3)	9.937(3)	7.895(6)	8.300(4)	10.092(4)	10.147(4)
b (Å)	12.069(5)	17.433(6)	12.085(4)	8.874(6)	11.905(5)	12.968(5)	13.971(5)
c (Å)	17.325(8)	13.411(5)	17.485(5)	13.927(10)	9.169(4)	29.395(10)	12.300(5)
α (deg)	90	90	90	104.962(12)	90	90	90
β (deg)	90	109.990(6)	90	90.808(13)	113.149(7)	106.506(12)	104.543(7)
γ (deg)	90	90	90	105.267(13)	90	90	90
V (Å^3)	2092.2(16)	2092.9(12)	2099.8(11)	905.8(11)	833.1(6)	3688(2)	1687.9(11)
Z	4	4	4	2	2	4	4
D_{calcd} (g cm^{-3})	1.556	1.556	1.691	1.658	1.683	1.789	1.836
μ (mm^{-1})	1.470	1.469	2.811	1.693	1.830	3.197	3.482
F(000)	1008	1008	1080	460	428	1984	928
cryst size (mm)	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.25 × 0.20 × 0.18	0.25 × 0.20 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.04	0.26 × 0.20 × 0.16
max 2θ (deg)	50.04	50.06	52.86	50.06	50.04	50.06	52.76
no. of rflns collected	8690	8513	12 101	3693	3451	12 004	7797
no. of indep rflns/R_{int}	3709/0.0255	3701/0.0328	4317/0.0562	3116/0.0485	1551/0.0258	6353/0.0838	3432/0.0497
no. of params	263	262	266	235	123	469	218
goodness of fit on F^2	1.033	1.007	1.004	1.061	1.055	1.007	0.973
R1, wR2 ($I > 2\sigma$(I))	0.0261, 0.0497	0.0320, 0.0749	0.0407, 0.0581	0.0646, 0.1290	0.0284, 0.0617	0.0778, 0.1264	0.0369, 0.0644
R1, wR2 (all data)	0.0338, 0.0520	0.0559, 0.0843	0.0694, 0.0641	0.1285, 0.1519	0.0435, 0.0668	0.1639, 0.1535	0.0720, 0.0731

Scheme 1

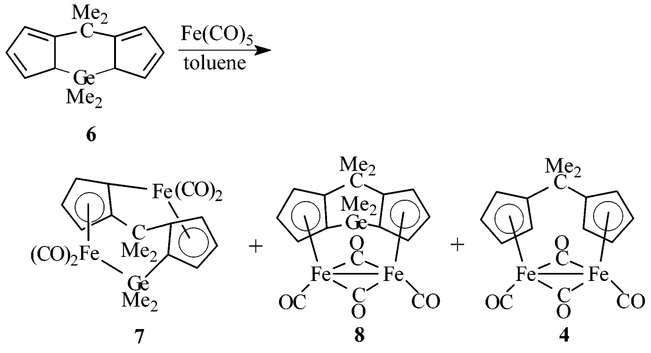


When the reaction was carried out in refluxing xylene, similar phenomena and faster reaction were observed in comparison with the case for toluene. To our surprise, the unexpected yellow complex **5** was isolated in addition to **2**–**4** (Scheme 2), which indicated that the higher temperature favors the formation of **5**. The IR spectrum

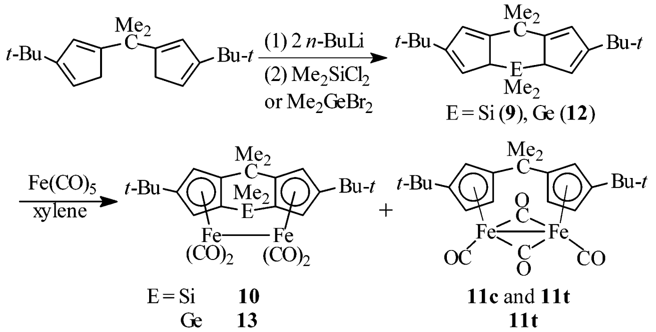
Scheme 2



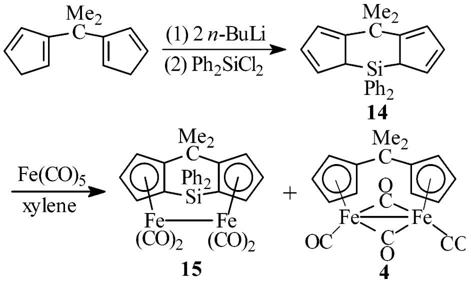
Scheme 3



Scheme 4



Scheme 5



of **5** exhibited only terminal carbonyl bands (2017, 1979, 1952, 1920 cm^{-1}). The ^{1}H NMR spectrum of **5** displayed six Cp H proton peaks at 5.69, 5.40, 5.00, 4.86, 4.40, and 4.31 ppm, indicating the unsymmetrical structure. X-ray diffraction analysis indicates that the novel complex contains an Fe−Si bond, and the other iron atom is coordinated with two cyclopentadienyl ligands in an η^5 and η^1 manner in the meantime, indicating that the formation of **5** should be accompanied by the cleavage of a C−Si bond in the ligand.

We considered whether **3** might be an intermediate to **4** or **5**. However, when a xylene solution of **3** was heated under reflux for 48 h, no **4** , **5**, or any other complex was observed by TLC monitoring. This suggests that complexes **4** and **5** are formed during the reaction and not from complex **3**.

Reaction of $(Me_2C)(Me_2Ge)(C_5H_4)_2$ (6) with Fe(CO)$_5$. The reaction of **1** with Fe(CO)$_5$ gave some unexpected complexes. We sought to establish whether these compounds are the normal result of these reactions or species unique to this ligand. To find the answer, the isopropylene and germylene doubly bridged ligand **6** was used instead of **1**, and it is found that, in both refluxing toluene and xylene, similar products **7**, **8**, and **4** were obtained (Scheme 3). Complex **7** showed five Cp H proton peaks at 5.62, 5.43, 4.97, 4.75, and 4.35 ppm in the ^{1}H NMR spectrum and only terminal carbonyl bands in the IR spectrum (2016, 1982, 1952, 1924 cm^{-1}). X-ray diffraction analysis indicates that, similar to the structure of the silicon analogue **5**, **7** contains an Fe−Ge bond, and the other iron atom is coordinated with two cyclopentadienyl ligands in an η^5 and η^1 manner in the meantime. This suggested that, unlike the case for complex **2**, complexes with this kind of novel structure are not occasional products. Complex **7** can be formed at lower temperature (refluxing toluene), and the yield (26%) of **7** is much higher than that of the silicon analogue **5** (6%), indicating that the weakness of the C−Ge bond may promote the formation of this kind of novel complex. Complex **8** is a normal intramolecular diiron complex with both terminal and bridging carbonyl groups (1975, 1938, 1770 cm^{-1}), differing from the silicon analogue **3**. Complex **4** is the degermylation product in this case.

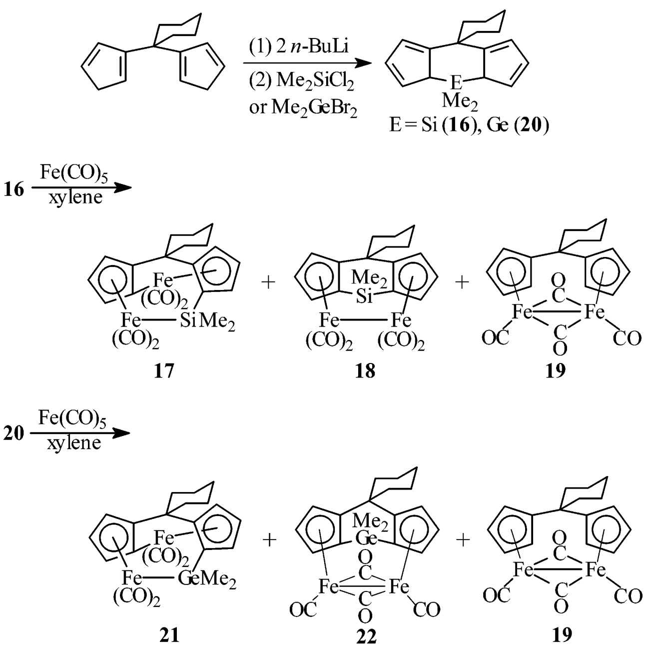
Reaction of $(Me_2C)(Me_2E)(t\text{-}BuC_5H_3)_2$ (E = Si (9), Ge (12)) with Fe(CO)$_5$. To study the steric effect of this reaction, a *tert*-butyl group was introduced onto the cyclopentadienyl ring and ligands **9** and **12** were synthesized. When ligand **9** or **12** and Fe(CO)$_5$ in xylene were heated under reflux, only the corresponding diiron complex **10** or **13** and the desilylation or degermylation product **11** were obtained (Scheme 4).

When the reactions were done in decahydronaphthalene, the same products were obtained, indicating that the bulky *tert*-butyl groups may prevent the formation of the novel complex with an Fe−Si or Fe−Ge bond. Similar to the case for the unsubstituted analogue **3**, the isopropylene and dimethylsilylene doubly bridged bis(cyclopentadienyl) diiron complex **10** has no bridging carbonyl groups (1997, 1946, 1926, 1902 cm^{-1}). However, the isopropylene and dimethylgermylene doubly bridged bis(cyclopentadienyl) diiron complex **13** has also no bridging carbonyl groups (1993, 1942, 1932, 1902 cm^{-1}), which is different from the case for the unsubstituted analogue **8**, indicating that the introduction of the bulky *tert*-butyl groups may increase the steric repulsion between the *tert*-butyl groups, the substituents at bridge atoms, and Fe(CO)$_2$ groups. Complex **11** is a mixture of cis and trans isomers. When the reactions were done in refluxing toluene, no reaction was found.

Reaction of $(Me_2C)(Ph_2Si)(C_5H_4)_2$ (14) with Fe(CO)$_5$. To further study the steric effect of this reaction, two phenyl groups were introduced onto the bridging silicon atom instead of two methyl groups. When ligand **14** and Fe(CO)$_5$ in toluene or xylene were heated under reflux, only the corresponding diiron complexes **15** and the desilylation product **4** were obtained (Scheme 5).

No analogue of **5** was obtained, indicating that the two phenyls at the bridging silicon atom may also prevent the formation of this kind of complex. Similar

Scheme 6



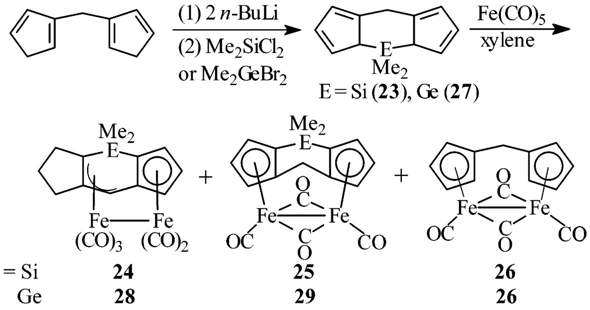
to the case for other carbon and silicon doubly bridged bis(cyclopentadienyl) diiron complexes (**3** and **10**), **15** also has no bridging carbonyl groups (1993, 1942, 1932, 1902 cm^{-1}).

Reaction of [(CH$_2$)$_5$C](Me$_2$E)(C$_5$H$_4$)$_2$ (E = Si (16), Ge (20)) with Fe(CO)$_5$. To further study the steric effect of this reaction, a 1,1-cyclohexylene bridge was introduced instead of an isopropylene bridge and ligands **16** and **20** were synthesized. When ligand **16** or **20** and Fe(CO)$_5$ were heated under reflux in both xylene and toluene, the same products **17** (or **21**), **18** (or **22**), and **19**[14] (Scheme 6) were obtained. Complexes **17** and **21** have unsymmetrical structures similar to those of **5** and **7**. The ^{1}H NMR spectra of **17** and **21** displayed six Cp H proton peaks at 5.74, 5.39, 5.10, 4.86, 4.42, and 4.31 ppm and five Cp H proton peaks at 5.67, 5.42, 5.07, 4.74, and 4.35 ppm, respectively. Complex **17** can be formed at lower temperature (refluxing toluene), and the yield (16%) of **17** is much higher than that of **5** (6%), indicating that the increasing steric effect at the bridging carbon atom may promote the formation of this kind of novel complex.

Similar to other carbon and silicon doubly bridged bis(cyclopentadienyl) diiron complexes (**3**, **10**, and **15**), **18** has no bridging carbonyl groups (2002, 1954, 1934, 1902 cm^{-1}), but the carbon and germanium doubly bridged bis(cyclopentadienyl) diiron complex **22** has both terminal and bridging carbonyl groups (1973, 1942, 1785, 1767 cm^{-1}).

Reaction of (CH$_2$)(Me$_2$E)(C$_5$H$_4$)$_2$ (E = Si (23), Ge (27)) with Fe(CO)$_5$. To further study the steric effect of a bridging carbon atom on the reaction, a methylene bridge was introduced instead of an isopropylene bridge in **1**, and ligands **23** and **27** were synthesized. It is interesting that in the ^{1}H NMR spectra of **23** and **27** the bridging methylene protons were split as two double peaks at 3.69, 3.59 ppm ($\Delta\delta = 0.10$ ppm) and 3.70, 3.54 ppm ($\Delta\delta = 0.16$ ppm) with $J = 14.2$ and 11.7 Hz, respectively. The SiMe protons were also split as two single peaks at 0.50, −1.14 ppm ($\Delta\delta = 1.64$ ppm) for **23** and at 0.71, −1.01 ppm ($\Delta\delta = 1.72$ ppm) for **27**. This suggested that the bridging methylene protons and SiMe protons were situated in different shielding regions by the double bonds due to the decreased repulsion between the substituents at two bridge atoms in comparison with the isopropylene and silylene or germylene doubly bridged ligands.

Scheme 7



When ligand **23** or **27** and Fe(CO)$_5$ in xylene were heated under reflux, similar products **24** (or **28**), **25** (or **29**), and **26**[15] (Scheme 7) were obtained. No similarly novel complex with an Fe−Si or Fe−Ge bond (analogue of **5**) was obtained in these cases, indicating that the decreased steric effect may also not favor forming this kind of novel complex.

The IR spectrum of **24** exhibited four terminal carbonyl bands at 2010, 1973, 1954, and 1934 cm^{-1} and a half-bridging carbonyl band at 1803 cm^{-1}. However, the IR spectrum of **28** exhibited only terminal carbonyl bands at 2010, 1966, 1946, and 1918 cm^{-1}. The ^{1}H NMR spectrum of **24** displayed three Cp H proton peaks at 5.10, 5.03, and 4.64 ppm, one vinyl proton peak at 4.02 ppm, and allyl or alkyl protons at 3.01 (2H), 2.90 (2H), and 2.12 (2H) ppm, indicating the unusual structure. X-ray diffraction analysis shows that the complex contains an Fe−Fe bond. One iron atom is coordinated with cyclopentadienyl ligand in an η^5 manner, and the other iron atom is coordinated in an η^3 manner with the allyl group consisting of the methylene bridge and two bridgehead carbons. The other cyclopentadienyl ring was hydrogenated partially. Complex **28** has a structure and ^{1}H NMR spectrum similar to those of **24**. Complexes **25** and **29** are the normal intramolecular diiron complexes with both terminal and bridging carbonyl groups, differing from the other carbon and silicon doubly bridged analogues **3**, **10**, **15**, and **18**. After complexation with iron carbonyl, the splitting of the bridging methylene protons in ^{1}H NMR spectra was increased ($\Delta\delta = 0.23$ ppm for **25**, 0.37 ppm for **29**), but the splitting of the Si−Me protons was much decreased ($\Delta\delta = 0.59$ ppm for **25**, 0.64 ppm for **29**). This suggests that the Si−Me protons are not situated at the shielding region by the cyclopentadienyl groups again. Complex **26** is the desilylation or degermylation product.[15]

Molecular Structures. The molecular structures of **2**, **3**, **5**, **7**, **8**, **10**, **11t**, **15**, **17**, **18**, **21**, **24**, **25**, **28**, and **29** are shown in Figures 1−15, respectively.

The molecule of **2** has C_i symmetry, consisting of two equivalent moieties linked to each other by an Fe−Fe bond (2.5522(15) Å) (Figure 1). The two ligands take a stable trans conformation, and the two coordinated cyclopentadienyl ring planes are parallel. The C−C bond lengths of the uncoordinated five-membered ring are

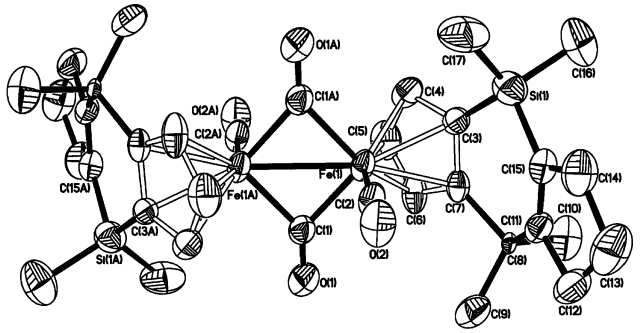


Figure 1. ORTEP diagram of **2**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(1a) = 2.5522(15), C(3)−Si(1) = 1.784(6), C(15)−Si(1) = 1.797(7), C(7)−C(8) = 1.623(7), C(8)−C(11) = 1.623(7), C(11)−C(15) = 1.334(8), C(11)−C(12) = 1.532(9), C(12)−C(13) = 1.512(12), C(13)−C(14) = 1.499(14), C(14)−C(15) = 1.520(8); C(3)−Si(1)−C(15) = 101.7(3), C(7)−C(8)−C(11) = 106.4(3).

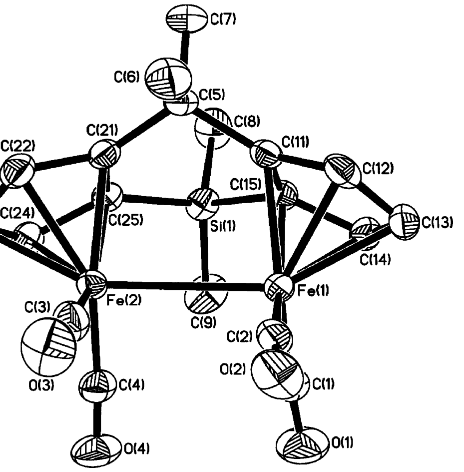


Figure 2. ORTEP diagram of **3**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.7747(6), Fe(1)−C(11) = 2.113(3), Fe(1)−C(15) = 2.099(3), Fe(2)−C(21) = 2.094(3), Fe(2)−C(25) = 2.107(3), Si(1)−C(15) = 1.853(3), Si(1)−C(25) = 1.861(3), C(5)−C(11) = 1.525(4), C(5)−C(21) = 1.511(4); C(21)−C(5)−C(11) = 106.5(2), C(15)−Si(1)−C(25) = 95.73(12).

1.334 Å (C(11)−C(15)), 1.532 Å (C(11)−C(12)), 1.512 Å (C(12)−C(13)), 1.499 Å (C(13)−C(14)), and 1.520 Å (C(14)−C(15)). Among them, only C(11)−C(15) bond is a double bond; the others are single bonds, suggesting that one cyclopentadiene of the doubly bridged ligand was partially hydrogenated to cyclopentene. Whitesides and Shelly investigated the mechanism of the reaction of Fe(CO)$_5$ with cyclopentadiene in detail.[16] Following their suggestion, the doubly bridged ligand may react with an iron hydride intermediate as a hydrogen acceptor to give a double bond hydrogenated ligand which can further react with Fe(CO)$_5$ to form complex **2**.

Complexes **3**, **8**, **10**, **15**, **18**, **25**, and **29** are intramolecular diiron complexes. It is worth noting that the carbon and silicon doubly bridged bis(cyclopentadienyl) diiron complexes **3**, **10**, **15**, and **18** have no bridging carbonyl group and have unusually long Fe−Fe bond distances, because the bridging carbonyl groups tend to shorten metal−metal distances.[19] The Fe−Fe bond distances in these complexes (**3**, 2.7747(6) Å; **10**, 2.7825(9) Å; **15**, 2.766(2) Å; **18**, 2.7522(9) Å) are evidently

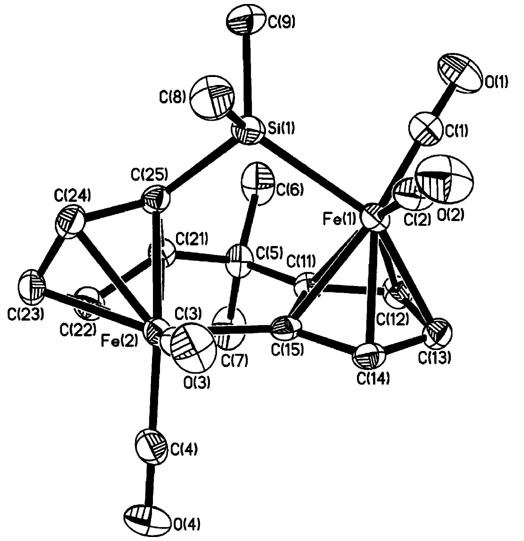


Figure 3. ORTEP diagram of **5**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Si(1) = 2.3222(10), Fe(1)−C(11) = 2.097(3), Fe(1)−C(15) = 2.162(3), Fe(2)−C(15) = 1.974(3), Fe(2)−C(21) = 2.080(3), Fe(2)−C(25) = 2.080(3), C(5)−C(11) = 1.510(4), C(5)−C(21) = 1.532(4), Si(1)−C(25) = 1.891(3); C(25)−Si(1)−Fe(1) = 104.69(10), C(11)−C(5)−C(21) = 102.9(2), C(15)−Fe(2)−C(25) = 87.14(12), C(15)−Fe(2)−C(21) = 79.83(12), Fe(2)−C(15)−Fe(1) = 126.29(14).

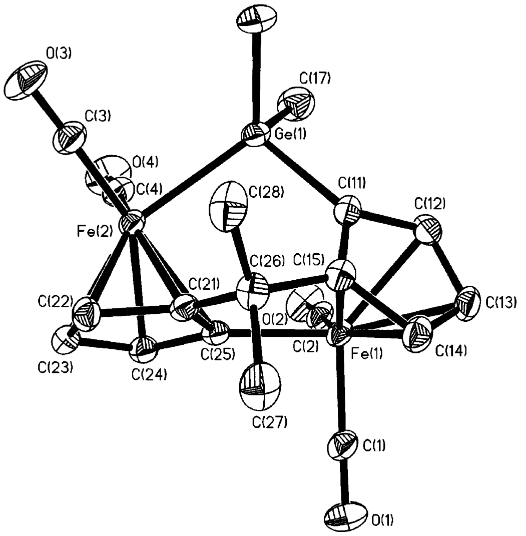


Figure 4. ORTEP diagram of **7**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Ge(1)−Fe(2) = 2.382(1), Fe(1)−C(11) = 2.078(5), Fe(1)−C(15) = 2.085(5), Fe(1)−C(25) = 1.969(5), Fe(2)−C(21) = 2.100(5), Fe(2)−C(25) = 2.161(5), Ge(1)−C(11) = 1.977(6), C(26)−C(15) = 1.523(8), C(26)−C(21) = 1.512(8), C(11)−Ge(1)−Fe(2) = 102.9(2), C(15)−C(26)−C(21) = 103.4(4), C(25)−Fe(1)−C(11) = 88.4(2), C(25)−Fe(1)−C(15) = 80.1(2), Fe(2)−C(25)−Fe(1) = 126.8(3).

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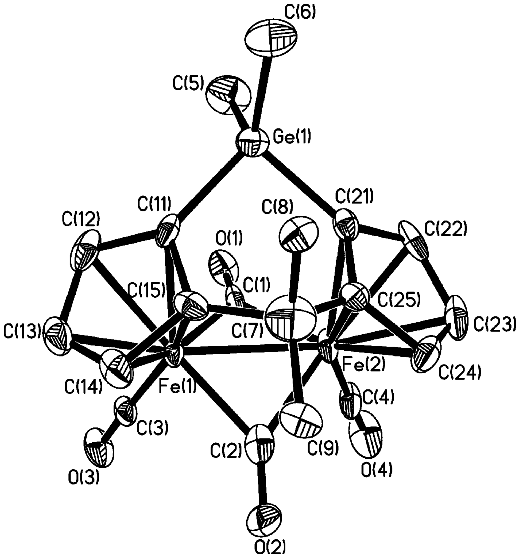

Figure 5. ORTEP diagram of **8**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.4816(18), Fe(1)−C(11) = 2.138(9), Fe(1)−C(15) = 2.121(10), Fe(2)−C(21) = 2.135(9), Fe(2)−C(25) = 2.158(9), Ge(1)−C(11) 1.929(10), Ge(1)−C(21) = 1.903(9), C(7)−C(15) = 1.614(11), C(7)−C(25) = 1.525(10); C(15)−C(7)−C(25) = 102.1(5), C(11)−Ge(1)−C(21) = 92.3(4).

Table 2. Structural Parameter Comparison for Bis(cyclopentadienyl) Diiron Complexes

complex	M−M (Å)	PL−PL (deg)[a]	ref[b]
cis-$[CpFe(CO)]_2(\mu\text{-}CO)_2$	2.531	92.8	17
$Me_2C[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$	2.4836(6)	109.6(1), 109.3(1)	13
$Me_2Si[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$	2.512(3)	97.2	18
$(CH_2)_5C[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$	2.466(1)	108.4	14
trans-$Me_2C[t\text{-}BuC_5H_3Fe(CO)]_2(\mu\text{-}CO)_2$ (**11t**)	2.4876(10)	109.7	tw
	2.4902(12)	109.1	
$(Me_2C)(Me_2Si)[C_5H_3Fe(CO)_2]_2$ (**3**)	2.7747(6)	126.92(9)	tw
$(Me_2C)(Me_2Ge)[C_5H_3Fe(CO)]_2(\mu\text{-}CO)_2$ (**8**)	2.4816(18)	117.03(27)	tw
$(Me_2C)(Me_2Si)[t\text{-}BuC_5H_2Fe(CO)_2]_2$ (**10**)	2.7825(9)	127.17(18)	tw
$(Me_2C)(Ph_2Si)[C_5H_3Fe(CO)_2]_2$ (**15**)	2.766(2)	126.4	tw
$[(CH_2)_5C](Me_2Si)[C_5H_3Fe(CO)_2]_2$ (**18**)	2.7522(9)	125.1	tw
$(CH_2)(Me_2Si)[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$ (**25**)	2.4833(13)	117.5	tw
$(CH_2)(Me_2Ge)[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$ (**29**)	2.4877(11)	117.03	tw
$(Me_2Ge)_2[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$	2.494(2)	110.3	8
$(Me_2SiSiMe_2)_2[C_5H_4Fe(CO)]_2(\mu\text{-}CO)_2$	2.5440(8)	100.26	8

[a] PL = plane of the cyclopentadienyl ring. [b] tw = this work.

greater than those found in other doubly bridged or singly bridged bis(cyclopentadienyl) diiron complexes (Table 2) and are the longest so far reported in the literature for the bis(cyclopentadienyl) diiron complexes. This may be attributed to two factors. At first, all these complexes contain one carbon and one silicon atom double bridge, which is the shortest bridge for the doubly bridged bis(cyclopentadienyl) diiron complexes up to now. The shorter bridges increase the intramolecular nonbonding interactions and make the dihedral angle between two cyclopentadienyl ring planes (125−127°) much larger than for the related analogues with two longer bridges (for example, $(Me_2C)(Me_2Ge)[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**8**) 117.03°, $(Me_2Ge)_2[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ 110.3°,[8] $(Me_2SiSiMe_2)_2[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ 100.26°[8]) or a single bridge (97−110°). Second, at both the bridging carbon and silicon atoms, there are at least two substituent methyl groups. The repulsion between the substituents at the two bridge atoms and that between the substituents with the $Fe_2(CO)_4$ group make the dihedral angle between two cyclopentadienyl ring planes (125−127°) much larger than for the unsubstituted analogues (for example, $(CH_2)(Me_2Si)[(\eta^5\text{-}C_5H_3)Fe(CO)]_2(\mu\text{-}CO)_2$ (**25**), 117.5°) and favors the formation of a long Fe−Fe bond. However, the bulk substituents at two bridge atoms (for example, Ph_2Si or $(CH_2)_5C$) also increase the repulsions between the substituents and two cyclopentadienyl rings, which make the dihedral angle between two cyclopentadienyl ring planes (126.4° for **15**, 125.1° for **18**) and the Fe−Fe distances (2.766(2) Å for **15**, 2.7522(9) Å for **18**) slightly decreasing.[14] The Fe−Fe distance in **10** (2.7825(9) Å) is the longest among the bis(cyclopentadienyl) diiron complexes up to now. Further studies of the effects of the unusually long Fe−Fe bond on the reactivity of these complexes are being continued in our group.

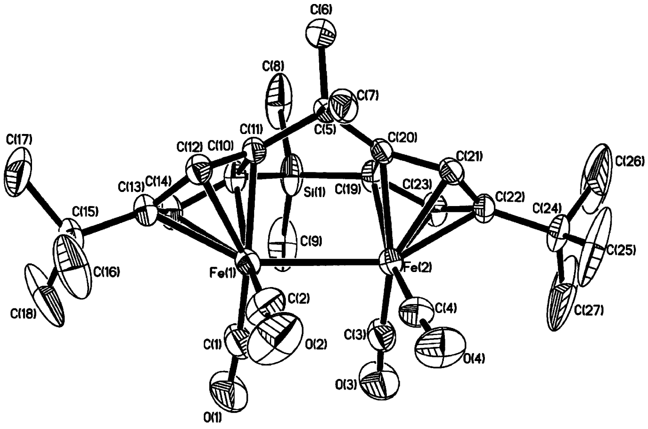

Figure 6. ORTEP diagram of **10**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.7825(9), Fe(1)−C(11) = 2.091(4), Fe(1)−C(10) = 2.110(4), Fe(2)−C(19) = 2.106(4), Fe(2)−C(20) = 2.110(4), Si(1)−C(10) = 1.850(4), Si(1)−C(19) = 1.849(4), C(5)−C(11) = 1.544(5), C(5)−C(20) = 1.520(5); C(11)−C(5)−C(20) = 106.5(3), C(10)−Si(1)−C(19) = 96.32(18).

Complex **11t** is a normal singly bridged bis(cyclopentadienyl) diiron complex. Figure 7 shows that it is a trans isomer, and there are two independent molecules in the ratio of 1/1 (A/B) in the unit cell. The Fe−Fe bond lengths are 2.4876(10) and 2.4902(12) Å, similar to those for other single carbon atom bridged bis(cyclopentadienyl) diiron complexes (Table 2).

Complexes **5**, **7**, **17**, and **21** have similar novel structures: one iron atom is coordinated with a cyclopentadienyl ligand in an η^5 manner, and the other iron atom is coordinated with two cyclopentadienyl ligands in an η^1 and η^5 manner in the meantime. All these complexes contain an Fe−Si or Fe−Ge bond, indicating that the formation of these complexes should be accompanied by the cleavage of a C−Si or C−Ge bond in the ligand. The similar ruthenium complexes $[Ru(CO)_2]_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4)[\mu\text{-}Me_2Si\text{-}(\eta^5\text{-}C_5H_4)]$,[20] $[Ru(CO)_2]_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4)[\mu\text{-}Me_2Si\text{-}(\eta^5\text{-}C_5H_4)]$,[21] and $[(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)$-

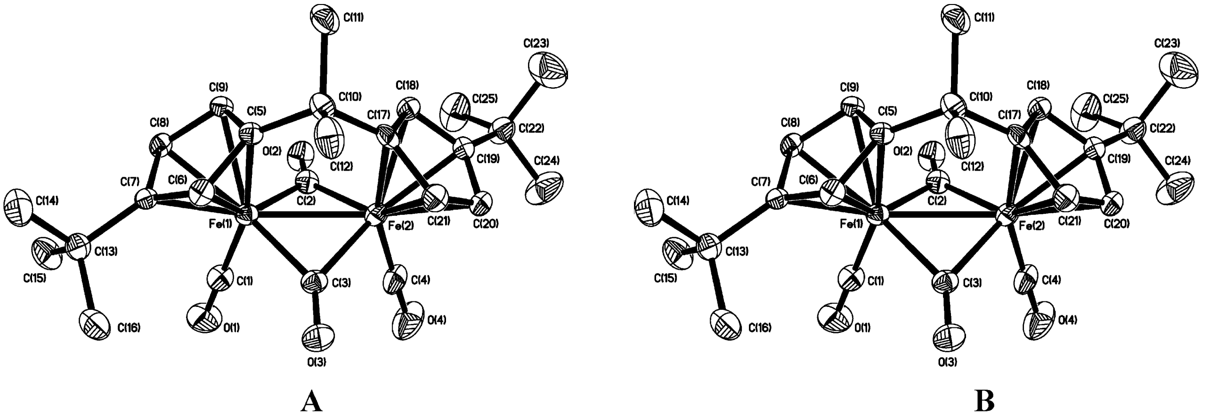

Figure 7. ORTEP diagram of **11t**. Thermal ellipsoids are shown at the 30% level. There are two independent molecules in a ratio of 1/1 (A/B) in the crystal structure. Selected bond lengths (Å) and angles (deg): Fe(1)−C(5) = 2.134(4), Fe(1)−Fe(2) = 2.4876(10), Fe(2)−C(17) = 2.128(4), Fe(3)−C(30) = 2.137(4), Fe(3)−Fe(4) = 2.4902(12), Fe(4)−C(42) = 2.130(4), C(5)−C(10) = 1.512(5), C(10)−C(17) = 1.534(6), C(30)−C(35) = 1.524(6), C(35)−C(42) = 1.525(6); C(5)−C(10)−C(17) = 109.3(3), C(30)−C(35)−C(42) = 110.0(3).

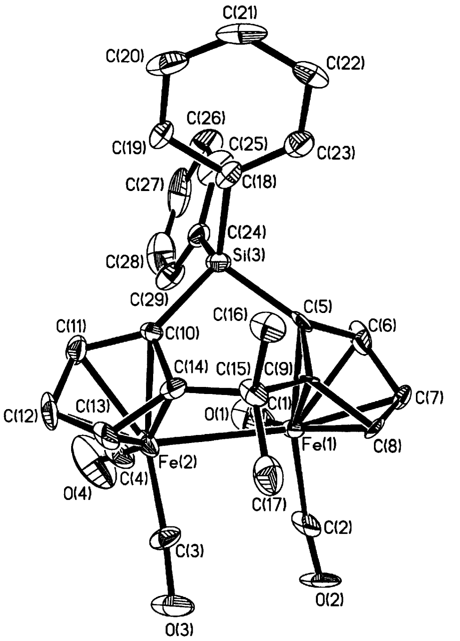

Figure 8. ORTEP diagram of **15**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.766(2), Fe(1)−C(5) = 2.136(9), Fe(1)−C(9) = 2.097(7), Fe(2)−C(10) = 2.127(9), Fe(2)−C(14) = 2.086(8), Si(3)−C(5) = 1.826(11), Si(3)−C(10) = 1.869(11), C(15)−C(9) = 1.569(14), C(15)−C(14) = 1.493(14); C(9)−C(15)−C(14) = 105.9(8), C(5)−Si(3)−C(10) = 96.0(5).

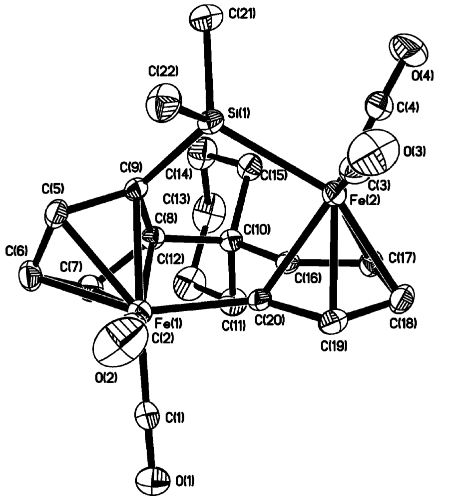

Figure 9. ORTEP diagram of **17**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(2)−Si(1) = 2.3222(12), Fe(1)−C(8) = 2.089(3), Fe(1)−C(9) = 2.096(3), Fe(1)−C(20) = 1.985(3), Fe(2)−C(16) = 2.109(3), Fe(2)−C(20) = 2.159(3), Si(1)−C(9) = 1.898(3), C(10)−C(8) = 1.545(4), C(10)−C(16) = 1.517(4); C(9)−Si(1)−Fe(2) = 105.40(9), Si(1)−Fe(2)−C(16) = 91.20(7), Si(1)−Fe(2)−C(20) = 86.01(7), Fe(2)−C(20)−Fe(1) = 128.53(13), C(8)−C(10)−C(16) = 102.7(2).

$Ru(CO)_2]_2$[22] have been reported from the photolysis of the silyl-bridged complexes $Me_2Si[\eta^5\text{-}C_5H_4Ru(CO)_2]_2$ and $Me_2Si[\eta^5\text{-}C_5Me_4Ru(CO)_2]_2$ and the fulvalene derivative $(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_5H_4C_5H_4)Ru_2(CO)_4$, respectively. The structures of **5**, **7**, **17**, and **21** are also somewhat similar to the rearrangement products $[Me_2E(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (E = Si, Ge).[23] The Fe−Si or Fe−Ge bond lengths in **5**, **7**, **17**, and **21** (2.3222(10), 2.382(1), 2.3222(12), and 2.3749(10) Å) are very close to those in the rearrangement product $[Me_2E(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (Fe−Si = 2.315(2) Å, Fe−Ge = 2.379 Å),[23] and much shorter than those in acyclic molecules of the same type.[24] This is consistent with the thermal stability of **5**, **7**, **17**, and **21**.

Complexes **24** and **28** have similar structures. One iron atom is coordinated with a cyclopentadienyl ligand in an η^5 manner, and the other iron atom is coordinated in an η^3 manner, with the allyl group consisting of the methylene bridge and two bridgehead carbons. Similar to complex **2**, one of the cyclopentadienyl rings of **24** and **28** was hydrogenated partially to cyclopentene. In the molecule of **24** the Fe(2)−C(3)−O(3) angle (156.9(8)°) is

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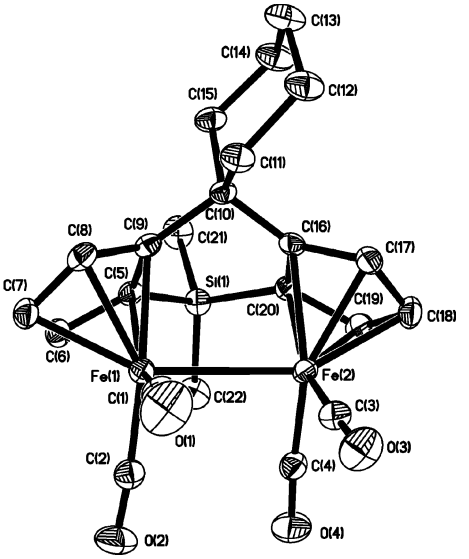


Figure 10. ORTEP diagram of **18**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(2) = 2.7522(9), Fe(1)–C(5) = 2.117(3), Fe(1)–C(9) = 2.103(3), Fe(2)–C(16) = 2.131(3), Fe(2)–C(20) = 2.116(3), Si(1)–C(5) = 1.866(3), Si(1)–C(20) = 1.863(3), C(10)–C(9) = 1.519(4), C(10)–C(16) = 1.524(4); C(9)–C(10)–C(16) = 106.5(2), C(5)–Si(1)–C(20) = 95.42(12).

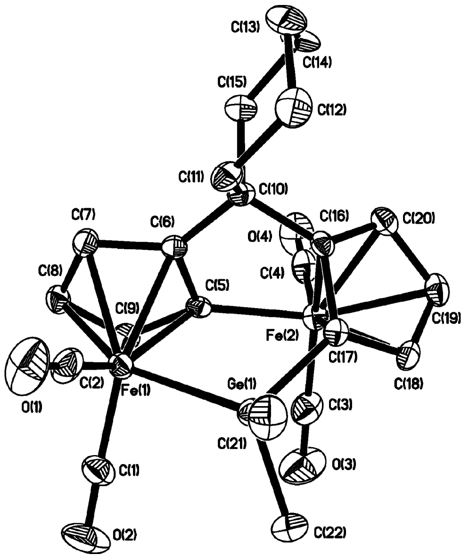


Figure 11. ORTEP diagram of **21**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Ge(1)–Fe(1) = 2.3749(10), Fe(1)–C(6) = 2.116(4), Fe(1)–C(5) = 2.159(4), Fe(2)–C(5) = 1.977(5), Fe(2)–C(16) = 2.077(4), Fe(2)–C(17) = 2.096(4), Ge(1)–C(17) = 1.968(4), C(6)–C(10) = 1.508(6), C(10)–C(16) = 1.536(6); C(17)–Ge(1)–Fe(1) = 103.79(13), Fe(2)–C(5)–Fe(1) = 129.2(2), C(6)–C(10)–C(16) = 103.3(3).

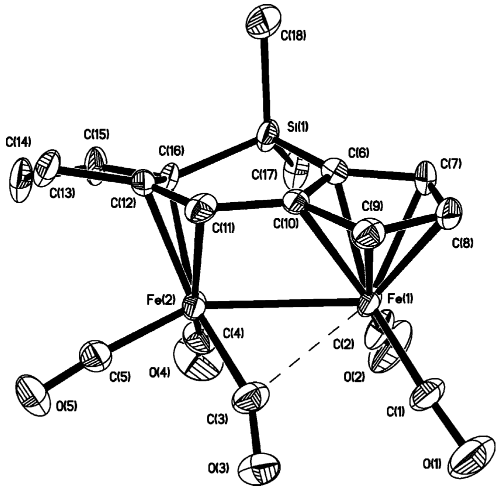


Figure 12. ORTEP diagram of **24**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(2) = 2.771(2), Fe(1)–C(3) = 2.400(10), Fe(1)–C(6) = 2.106(8), Fe(1)–C(10) = 2.133(7), Fe(2)–C(3) = 1.814(9), Fe(2)–C(11) = 2.095(7), Fe(2)–C(12) = 2.107(7), Fe(2)–C(16) = 2.223(8), Si(1)–C(6) = 1.854(8), Si(1)–C(16) = 1.853(8), C(10)–C(11) = 1.448(10), C(11)–C(12) = 1.406(10), C(12)–C(13) = 1.505(10), C(13)–C(14) = 1.511(12), C(14)–C(15) = 1.512(11), C(15)–C(16) = 1.517(10), C(12)–C(16) = 1.387(10); C(12)–C(11)–C(10) = 120.7(7), C(16)–C(12)–C(11) = 122.7(7), C(6)–Si(1)–C(16) = 98.7(4), O(1)–C(1)–Fe(1) = 176.4(10), O(2)–C(2)–Fe(1) = 175.5(8), O(3)–C(3)–Fe(1) = 122.2(7), O(3)–C(3)–Fe(2) = 156.9(8), O(4)–C(4)–Fe(2) = 175.9(9), O(5)–C(5)–Fe(2) = 175.1(8).

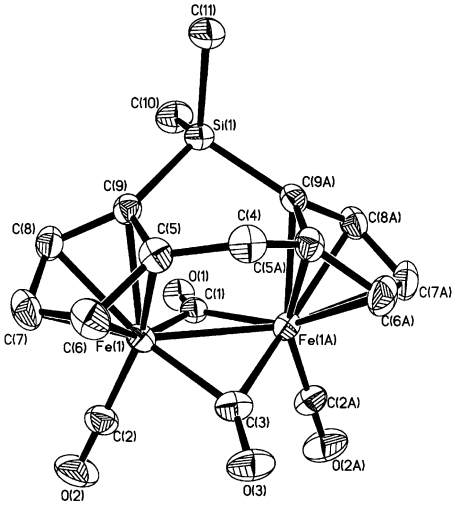
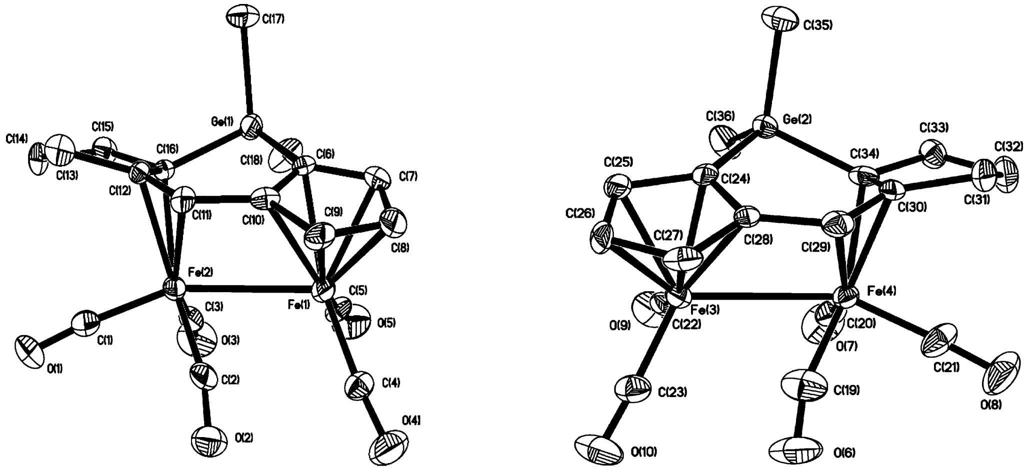


Figure 13. ORTEP diagram of **25**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)–Fe(1A) = 2.4833(13), Fe(1)–C(5) = 2.126(3), Fe(1)–C(9) = 2.145(3), Si(1)–C(9) = 1.869(3), C(4)–C(5) = 1.506(3); C(5)–C(4)–C(5A) = 109.7(3), C(9)–Si(1)–C(9A) = 96.12(16).

much more bent than the others (Fe(1)–C(1)–O(1) = 176.4(10)°, Fe(1)–C(2)–O(2) = 175.5(8)°, Fe(2)–C(4)–O(4) = 175.9(9)°, Fe(2)–C(5)–O(5) = 175.1(8)°). The Fe(1)–C(3) and Fe(2)–C(3) distances are 2.400(10) and 1.814(9) Å, respectively. This suggests that the carbonyl C(3)–O(3) exists as a half-bridging carbonyl, which is consistent with the middle absorption at 1803 cm^{-1} in the IR spectrum. The IR spectrum of **28** shows no bridging carbonyl group (2010, 1966, 1946, 1918 cm^{-1}), but there still is an Fe–C–O bond angle (Fe(2)–C(2)–O(2) = 166.5(9)° for **A**, Fe(4)–C(19)–O(6) = 164.1(13)° for **B**) much more bent than the others, existing as a half-bridging carbonyl. The Fe–Fe bond length in **24** is 2.771(2) Å, which is close to the Fe–Fe bond length in **3** (2.7747(6) Å). There are two independent molecules in the ratio of 1/1 (**A**/**B**) in the unit cell of **28**. The Fe–Fe bond lengths are 2.816(2) and 2.798(2) Å, slightly longer than that in **24** due to the atom radius of germanium being larger than that of silicon. The Fe–



A **B**

Figure 14. ORTEP diagram of **28**. Thermal ellipsoids are shown at the 30% level. There are two independent molecules as a ratio of 1/1 (A/B) in the crystal structure. Selected bond lengths (Å) and angles (deg): (A) Fe(1)−Fe(2) = 2.816(2), Fe(1)−C(6) = 2.110(9), Fe(1)−C(10) = 2.111(9), Fe(2)−C(11) = 2.106(8), Fe(2)−C(12) = 2.104(8), Fe(2)−C(16) = 2.208(9), Ge(1)−C(6) = 1.929(10), Ge(1)−C(16) = 1.931(9), C(10)−C(11) = 1.473(12), C(11)−C(12) = 1.369(13), C(12)−C(13) = 1.518(12), C(13)−C(14) = 1.500(14), C(14)−C(15) = 1.563(12), C(15)−C(16) = 1.548(12), C(12)−C(16) = 1.411(13), C(12)−C(11)−C(10) = 122.6(9), C(11)−C(12)−C(16) = 122.2(8), C(6)−Ge(1)−C(16) = 96.5(4), Fe(2)−C(2)−O(2) = 164.1(13), Fe(2)−C(1)−O(1) = 174.9(10), Fe(2)−C(3)−O(3) = 175.4(10), C(11)−Fe(2)−Fe(1) = 78.9(2), C(12)−Fe(2)−Fe(1) = 105.4(2), C(16)−Fe(2)−Fe(1) = 99.0(2), Fe(1)−C(4)−O(4) = 173.6(10), Fe(1)−C(5)−O(5) = 175.5(10); (B) Fe(3)−Fe(4) = 2.798(2), Fe(3)−C(24) = 2.113(9), Fe(3)−C(28) = 2.129(9), Fe(4)−C(29) = 2.110(9), Fe(4)−C(30) = 2.106(9), Fe(4)−C(34) = 2.218(9), Ge(2)−C(24) = 1.924(9), Ge(2)−C(34) = 1.932(10), C(28)−C(29) = 1.432(13), C(29)−C(30) = 1.433(13), C(30)−C(31) = 1.508(13), C(31)−C(32) = 1.574(15), C(32)−C(33) = 1.490(14), C(33)−C(34) = 1.516(12), C(30)−C(34) = 1.442(14), C(28)−C(29)−C(30) = 123.4(10), C(29)−C(30)−C(34) = 121.2(9), C(24)−Ge(2)−C(34) = 97.1(4), Fe(4)−C(19)−O(6) = 164.1(13), Fe(4)−C(20)−O(7) = 178.7(11), Fe(4)−C(21)−O(8) = 177.0(11), C(29)−Fe(4)−Fe(3) = 78.0(3), C(30)−Fe(4)−Fe(3) = 106.4(3), C(34)−Fe(4)−Fe(3) = 100.1(2), Fe(3)−C(22)−O(9) = 177.2(9), Fe(3)−C(23)−O(10) = 176.8(10).

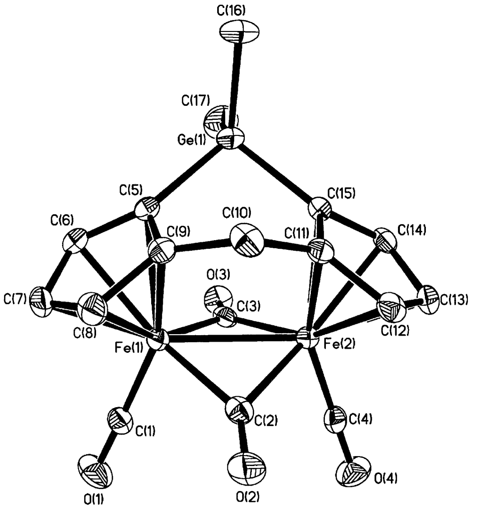


Figure 15. ORTEP diagram of **29**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.4877(11), Fe(1)−C(5) = 2.153(4), Fe(1)−C(9) = 2.117(4), Fe(2)−C(11) = 2.120(3), Fe(2)−C(15) = 2.146(4), Ge(1)−C(5) = 1.952(4), Ge(1)−C(15) = 1.946(4), C(9)−C(10) = 1.511(5), C(11)−C(10) = 1.518(5); C(9)−C(10)−C(11) = 109.8(3), C(5)−Ge(1)−C(15) = 93.50(15).

Fe bond lengths in **24** and **28** are consistent with those found in other molecules with both η^5 and η^3 coordination (for example, 2.782(4) Å for (azulene)$Fe_2(CO)_5$[25]), due to the fact that the very strong (η^3-allyl)−Fe linkage stretches the relatively weak Fe−Fe bond in order to maintain its own optimal geometry.[26]

There have been some reports about the cleavage of the C−Si or C−Ge bond and the migration of the silyl or germyl group.[27−29] When $C_5H_5EMe_3$ (E = Si, Ge, Sn) reacted with $(MeCN)_3M(CO)_3$ (M = Cr, Mo, W), it was found that $GeMe_3$ and $SnMe_3$ can easily migrate to the metal atom to give $C_5H_5(CO)_3M{-}EMe_3$ (M = Cr, Mo, W; E = Ge, Sn) but $SiMe_3$ was much more difficult to transfer.[27a,28,29] The silyl-bridged diruthenium complexes $Me_2Si[\eta^5\text{-}C_5H_4Ru(CO)_2]_2$ and $Me_2Si[\eta^5\text{-}C_5Me_4Ru(CO)_2]_2$ can rearrange to the similar novel complexes $[Ru(CO)_2]_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4)[\mu\text{-}Me_2Si\text{-}(\eta^5\text{-}C_5H_4)]$ and $[Ru(CO)_2]_2(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4)[\mu\text{-}Me_2Si\text{-}(\eta^5\text{-}C_5H_4)]$ with a Ru−Si bond through the silyl single migration under photolysis.[20,21] This allows us to consider that the complexes with an Fe−Si or Fe−Ge bond in this work may be the silyl or germyl single migration products, especially for the complexes with an Fe−Ge bond, due to the weakness of the C−Ge bond. The silyl migration may also occur with a greater intramolecular nonbonding interaction and higher reaction temperature. When bulky substituents were introduced onto the bridging carbon atom (ligand **16** and **20**), silyl or germyl single migration could be promoted due to the increased repulsion with the bulky substituents and complexes with an Fe−Si or Fe−Ge bond were formed in higher yield (**17**, 16%; **21**, 23%). When a methylene bridge was introduced instead of an isopropylene bridge in **1** or **6**, no similar

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complex with an Fe−Si or Fe−Ge bond (analogue of **5**) was obtained, indicating that the larger intramolecular nonbonding interactions may be the driving force of silyl or germyl single migration. The yields of the complexes with an Fe−Ge bond (**7**, 26%; **21**, 23%) are much higher than those with an Fe−Si bond (**5**, 6%; **17**, 16%), which can be attributed to the weakness of the C−Ge bond as compared to the C−Si bond. However, when bulky substituents were introduced onto the cyclopentadienyl rings or the bridging silicon atom (ligand **9**, **12**, and **14**), silyl or germyl single migration is hindered and a complex with an Fe−Si or Fe−Ge bond could not be formed. However, the detailed mechanism needs further studies.

Conclusions

The reactions of carbon and silicon or germanium doubly bridged bis(cyclopentadiene) ligands $(Me_2C)(Me_2E)(C_5H_4)_2$ (E = Si, Ge) with $Fe(CO)_5$ result in the formation of doubly bridged bis(cyclopentadienyl) diiron complexes, as well as novel complexes containing Fe−Si or Fe−Ge bonds. The factors effecting the structures of diiron complexes and the formation of novel complexes were discussed.

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Supporting Information Available: Tables of crystallographic data collection details, final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **2**, **3**, **5**, **7**, **8**, **10**, **11t**, **15**, **17**, **18**, **21**, **24**, **25**, **28**, and **29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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