Insertion of SnCl$_2$ into the metal–metal bonds in bridged binuclear complexes (Me$_2$E)[(η^5-C$_5$H$_4$)M(CO)]$_2$(μ-CO)$_2$ (E = Si, Ge; M = Fe, Ru). The molecular structure of (Me$_2$Ge)[(η^5-C$_5$H$_4$)Fe(CO)$_2$]$_2$SnCl$_2$

Yongqiang Zhang, Shansheng Xu, Gonglu Tian, Wei Zhang, Xiuzhong Zhou *

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Abstract

The synthesis of bridged binuclear complexes (Me$_2$E)[(η^5-C$_5$H$_4$)M(CO)]$_2$(μ-CO)$_2$ [E = Si, M = Ru (3); E = Ge, M = Fe (2), M = Ru (4)] is described. Insertion of SnCl$_2$ into the metal–metal bonds in these complexes affords a type of hetero-nuclear cyclic metallic complexes (Me$_2$E)[(η^5-C$_5$H$_4$)M(CO)$_2$]$_2$SnCl$_2$ [E = Si, M = Ru (7); E = Ge, M = Fe (6), M = Ru (8)]. Complex 6 reacts with Grignard reagents RMgX to yield alkyl (or aryl)-substituted analogues (Me$_2$Ge)[(η^5-C$_5$H$_4$)Fe(CO)$_2$]$_2$SnR$_2$ [R = Me (9); R = Ph (10)]. All of the complexes were characterized by IR, ^{1}H NMR and elementary analysis. Both 6 and 8 are still characterized by ^{119}Sn NMR. The molecular structure of 6 has been determined by X-ray diffraction. Crystals of 6 are orthorhombic, space group Pcab with a = 13.499(2) Å, b = 16.883(6) Å, c = 18.368(4) Å, V = 4168(3) Å^3, Z = 8, Dx = 2.044 g cm^{-3}, R (R_w) = 0.044 (0.059). © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Iron; Insertion reaction; Metal carbonyl; Bridged complexes

1. Introduction

Although the insertion of SnCl$_2$ into metal–metal bonds in binuclear transition metal complexes (M = Fe, Ru, Ni, Co, Cr, Mo, W) was reported earlier [1–5], much less effort has been devoted to related complexes in which either the two cyclopentadienyl ligands are linked by a bridge or the metal–metal bonds are connected by a bridging diphosphine ligand. Field et al. [6] have prepared [Ru$_2$(μ-SnCl$_2$)(CO)$_4$(μ-(RO)$_2$PN(Et)P(OR)$_2$)$_2$] via the insertion of SnCl$_2$ into the Ru–Ru bond in complex Ru$_2$(CO)$_4$(μ-(RO)$_2$PN(Et)P(OR)$_2$)$_2$. We recently reported the synthesis of (Me$_3$Si)[(η^5-C$_5$H$_4$)Fe(CO)$_2$]$_2$SnCl$_2$ (5) via insertion of SnCl$_2$ into Fe–Fe bond in complex (Me$_3$Si)[(η^5-C$_5$H$_4$)Fe(CO)]$_2$(μ-CO)$_2$ (1) [7]. These are rather limited to understand the features of the insertion reaction in bridged binuclear complexes deeply. Thus, a systematic study on this type of complexes appears rather essential. We herein report some recent studies on the insertion of SnCl$_2$ into the M–M bonds in

complexes (Me$_2$E)[(η^5-C$_5$H$_4$)M(CO)]$_2$(μ-CO)$_2$ (E = Si, Ge; M = Fe, Ru).

2. Experimental details

Schlenk and vacuum line technique were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, heptane, benzene, toluene and xylene were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use. C$_5$H$_5$Me$_2$SiC$_5$H$_5$ [8], C$_5$H$_5$Me$_2$GeC$_5$H$_5$ [9] (Me$_2$Si)[(η^5-C$_5$H$_4$)Ru(CO)]$_2$(μ-CO)$_2$ (3) [10] were prepared according to literature methods. Proton (^{1}H NMR) spectra were obtained on a BRUKER AC-P200 spectrometer using CHCl$_3$ (δ: 7.24) or DMSO (δ: 2.49) as an internal standard. ^{119}Sn NMR was also recorded on a BRUKER AC-P200 spectrometer using SnMe$_4$ as an external standard. Elemental analyses were performed by a Perkin-Elmer 240C spectrometer. Infrared spectra were obtained as KBr disk (or in CH$_2$Cl$_2$) and recorded on a Nicolet 5DX FT-IR spectrometer.

* Corresponding author. Fax: +86 22 2350 4843.

2.1. Preparation of $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)]_2(\mu-CO)_2$ (2)

A solution of 2.00 g (8.6 mmol) of $C_5H_5Me_2GeC_5H_5$ and 3.52 g (18.0 mmol) of $Fe(CO)_5$ in 30 mL of xylene was refluxed for 10 h. The solvent was removed under vacuum giving dark-red crude product which was then introduced to an alumina column in the minimum amount of dichloromethane. Elution with petroleum ether:dichloromethane (3:1) gave a red band which afforded 1.35 g (34%) of violet–red crystals of 2: Mp 220 – 1°C. Anal. Calc. for $C_{16}H_{14}Fe_2GeO_4$: C, 42.28; H, 3.10. Found: C, 42.41; H, 2.85.

2.2. Preparation of $(Me_2Ge)[(\eta^5-C_5H_4)Ru(CO)]_2(\mu-CO)_2$ (4)

A solution of 1.64 g (7.04 mmol) of C_5H_5-$Me_2GeC_5H_5$ and 1.00 g (1.56 mmol) of Ru_3-$(CO)_{12}$ in 50 mL of heptane was refluxed for 7 h. The solvent was removed under vacuum to give dark oil which was then dissolved in the minimum amount of dichloromethane. Preparative TLC (developer: petroleum ether:dichloromethane (3:2)) was employed to purify the oil. A yellow band afforded 0.13 g (10%) of orange–yellow crystals of 4: Mp 158–160°C. Anal. Calc. for $C_{16}H_{14}GeO_4Ru_2$: C, 35.26; H, 2.59. Found: C, 35.35; H, 2.59. ^{13}C NMR (CDCl$_3$) δ: –3.37 (GeMe), 88.7 (Cp), 89.6 (ipso Cp), 97.6 (Cp), 218.7 (Ru–CO).

2.3. Preparation of $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)_2]_2SnCl_2$ (6)

A solution of 0.85 g (1.87 mmol) of $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)]_2(\mu-CO)_2$ and 0.43 g (1.90 mmol) of $SnCl_2 \cdot 2H_2O$ in 40 mL of THF was refluxed for 12 h. The solvent was removed under vacuum to give a yellow crude product. The yellow solid was recrystallized from a mixed solvent of CH_2Cl_2 and petroleum

ether affording 0.86 g (71%) of orange crystals of 5: Mp 240 – 1°C. Anal. Calc. for $C_{16}H_{14}Fe_2GeO_4$: C, 29.83; H, 2.19. Found: C, 29.71; H, 2.12. ^{119}Sn NMR (CDCl$_3$) δ: –160.6.

2.4. Preparation of $(Me_2Si)[(\eta^5-C_5H_4)Ru(CO)_2]_2SnCl_2$ (7)

A solution of 0.30 g (0.60 mmol) of $(Me_2Si)[(\eta^5-C_5H_4)Ru(CO)]_2(\mu-CO)_2$ and 0.14 g (0.61 mmol) of $SnCl_2 \cdot 2H_2O$ in 30 mL of THF was refluxed for 20 h. The solvent was removed under vacuum to give a pale-yellow crude product. The solid was first washed several times with dichloromethane and hexane respectively, and then recrystallized from a mixed solvent of THF and CH_2Cl_2 affording 0.15 g (36%) of pale-yellow solids of 5: Mp > 300°C. Anal. Calc. for $C_{16}H_{14}Cl_2O_4Ru_2SiSn$: C, 27.85; H, 2.04. Found: C, 27.51; H, 2.01.

2.5. Preparation of $(Me_2Ge)[(\eta^5-C_5H_4)Ru(CO)_2]_2SnCl_2$ (8)

A solution of 0.10 g (0.18 mmol) of $(Me_2Ge)[(\eta^5-C_5H_4)Ru(CO)]_2(\mu-CO)_2$ and 43 mg (0.19 mmol) of $SnCl_2 \cdot 2H_2O$ in 20 mL of THF was refluxed for 11 h. The solvent was removed under vacuum to give a pale-yellow crude product. The solid was directly recrystallized from a mixed solvent of THF and CH_2Cl_2 affording 0.12 g (91%) of pale-yellow solids of 8: Mp 174 – 6°C. Anal. Calc. for $C_{16}H_{14}Cl_2GeO_4Ru_2Sn$: C, 26.16; H, 1.92. Found: C, 25.88; H, 1.80. ^{119}Sn NMR (DMSO) δ: 18.0.

2.6. Preparation of $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)_2]_2SnR_2$ [R = Me (9), R = Ph (10)]

A diethyl ether solution of CH_3MgI was prepared by adding 0.71 g (5.00 mmol) of CH_3I dissolved in 10 mL

Table 1
^{1}H NMR and IR spectral data for all of complexes

Compd.	^{1}H NMR δ, ppm ^{a} CDCl$_3$			IR ν(CO), cm^{-1} ^{b} (KBr disc)			
1 ^{c}	0.50 (s, 6H, SiMe)	5.1 (d, 4H, Cp)	5.9 (d, 4H, Cp)	1990	1950	1782	
2	0.51 (s, 6H, GeMe)	4.98 (t, 4H, Cp)	5.45 (t, 4H, Cp)	1986(s)	1937(m)	1800(w)	1761(s)
3 ^{d}	0.42 (s, 6H, SiMe)	5.19 (t, 4H, Cp)	5.71 (t, 4H, Cp)	2010(s)	1963(m)	1938(m)	1774(m)
4	0.57 (s, 6H, GeMe)	5.22 (t, 4H, Cp)	5.79 (t, 4H, Cp)	1998(s)	1960(w)	1942(w)	1772(s)
5 ^{e}	0.48 (s, 6H, SiMe)	5.14 (s, 8H, Cp)		2000(s)	1959(s)		
6	0.61 (s, 6H, GeMe)	5.01 (t, 4H, Cp)	5.10 (t, 4H, Cp)	2000(s)	1965(s)	1953(s)	
7	0.51 (s, 6H, SiMe)	5.57 (s, 4H, Cp)	5.82 (s, 4H, Cp)	2041(sh, s)	2016(s)	1959(s)	
8	0.65 (s, 6H, GeMe)	5.58 (s, 4H, Cp)	5.78 (s, 4H, Cp)	2041(sh, s)	2016(s)	1967(s)	
9	0.49 (s, 6H, GeMe)	0.58 (s, 6H, SnMe)	4.87 (t, 4H, Cp) 5.06 (t, 4H, Cp)	1979(m)	1961(s)	1922(m)	1902(s)
10	0.53 (s, 6H, GeMe)	4.99 (t, 4H, Cp)	5.22 (t, 4H, Cp) 7.22–7.45 (m, 10H, Ph)	1977(s)	1927(s)		

^{a} Data for 7 and 8 in DMSO-d_6.
^{b} Data for 3 and 4 in CH_2Cl_2.
^{c} Ref. [13].
^{d} Ref. [10].
^{e} Ref. [7].

of diethyl ether dropwise, with stirring, to 0.10 g (4.16 mmol) of Mg suspended in 10 mL of diethyl ether until the metal magnesium had completely disappeared. This was then added to 0.40 g (0.62 mmol) of complex **6** dissolved in 10 mL of THF and the mixture was stirred at room temperature for 2 h, and subsequently refluxed for an additional hour. 50 mL of water containing 1 mL of acetic acid was added to the mixture. The aqueous layer was separated from the oil layer and extracted twice with 20 mL of ether. The oil and ether extracts were combined and dried with sodium sulfate overnight. The solvent was removed under reduced pressure and the residue was isolated by preparative TLC, yielding 40 mg (11%) of orange crystals of **9**: Mp 165 – 6°C. Anal. Calc. for $C_{18}H_{20}Fe_2GeO_4Sn$: C, 35.83; H, 3.34. Found: C, 35.94; H, 2.91.

Complex **10** was similarly prepared in 20% yield by using Grignard reagent PhMgBr instead of CH_3MgI. For **10**: Mp 185 – 6°C. Anal. Calc. for $C_{23}H_{24}Fe_2GeO_4Sn$: C, 46.23; H, 3.33. Found: C, 46.18; H, 3.45.

All of the complexes previously unreported were characterized by IR, ^1H NMR and elementary analysis. The characterized data are in good agreement with their formulation. ^1H NMR and IR data for carbonyl stretching region of all of complexes are shown in Table 1.

Table 2
Crystallographic data for complex **6**

	6
Formula	$C_{18}H_{14}Cl_2Fe_2GeO_4Sn$
Formula weight	644.17
Space group	Pcab
Crystal system	orthorhombic
Z	8
a (Å)	13.499(2)
b (Å)	16.883(6)
c (Å)	18.368(4)
α, deg	90
β, deg	90
γ, deg	90
Volume (Å³)	4186(3)
d_{calc} (g cm⁻¹)	2.044
Crystal size (mm)	0.20 × 0.30 × 0.30
Radiation (Å³)	MoK α (0.71073)
μ, cm⁻¹	18.33
Data collection method	ω/2θ
Max. 2θ, deg	46
Total no. of observns	3286
No. of unique data, $I > 3\sigma(I)$	1829
Final no. of variables	235
Max. residual density, e⁻/Å³	0.68
R ᵃ	0.044
R_w ᵇ	0.059
Goodness-of-fit	1.485

ᵃ $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.
ᵇ $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$.

Table 3
Selected bond lengths (Å) and angles (deg) for **6**

Bond distances			
Sn(1)–Cl(1)	2.384(3)	C(1)–O(1)	1.14(1)
Sn(1)–Cl(2)	2.413(3)	C(2)–O(2)	1.16(1)
Sn(1)–Fe(1)	2.494(2)	C(3)–O(3)	1.13(2)
Sn(1)–Fe(2)	2.486(2)	C(4)–O(4)	1.15(1)
Fe(1)–C(1)	1.77(1)	Ge(1)–C(5)	1.94(1)
Fe(1)–C(2)	1.75(2)	Ge(1)–C(6)	1.95(1)
Fe(1)–Cp(1)	1.7092 ᵃ	Ge(1)–C(11)	1.94(2)
Fe(2)–C(3)	1.77(2)	Ge(1)–C(21)	1.91(1)
Fe(2)–C(4)	1.74(1)		
Fe(2)–Cp(2)	1.7006 ᵃ		
Bond angles			
Cl(1)–Sn(1)–Cl(2)	95.6(1)	Sn(1)–Fe(1)–C(11)	96.8(4)
Fe(1)–Sn(1)–Fe(2)	124.64(6)	Sn(1)–Fe(2)–C(21)	95.8(3)
C(1)–Fe(1)–C(2)	94.6(6)	C(11)–Ge(1)–C(21)	113.3(4)
C(3)–Fe(2)–C(4)	94.9(6)	C(5)–Ge(1)–C(6)	114.5(7)
Ge(1)–C(11)–Fe(1)	128.0(5)		
Ge(1)–C(21)–Fe(2)	133.7(6)		

ᵃ The distance from the centroid of Cp ring to the linked Fe atom.

which includes the data of some previously reported complexes for comparison.

2.7. Crystallographic studies

A summary of the crystallographic results is presented in Table 2. Crystals of **6** suitable for X-ray diffraction were obtained from hexane/dichloro-

Table 4
Atomic coordinates and thermal parameters for **6** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Sn(1)	0.23393(6)	0.02655(5)	0.42690(5)	2.31(1)
Cl(1)	0.1282(3)	-0.0406(2)	0.5106(2)	4.72(9)
Cl(2)	0.3445(3)	-0.0838(2)	0.4077(2)	4.79(9)
Ge(1)	0.2512(1)	0.24305(8)	0.3295(8)	3.09(3)
Fe(1)	0.1413(1)	0.0482(1)	0.3111(1)	2.46(3)
Fe(2)	0.3243(1)	0.1316(1)	0.4946(1)	3.10(4)
C(1)	0.102(1)	-0.0517(9)	0.3147(9)	4.5(4)
O(1)	0.076(1)	-0.116(6)	0.3163(8)	7.5(3)
C(2)	0.2499(9)	0.0276(8)	0.2625(8)	3.4(3)
O(2)	0.3212(7)	0.0151(7)	0.2289(6)	6.2(3)
C(3)	0.213(1)	0.1576(9)	0.5393(9)	4.6(4)
O(3)	0.1400(9)	0.176(9)	0.5644(7)	8.1(4)
C(4)	0.359(1)	0.0608(9)	0.5584(8)	4.0(3)
O(4)	0.3814(8)	0.1456(6)	0.6014(6)	5.5(3)
C(5)	0.199(1)	0.3443(8)	0.361(1)	5.4(4)
C(6)	0.327(1)	0.247(1)	0.2391(9)	6.1(4)
C(11)	0.1401(9)	0.1723(7)	0.3153(7)	2.6(3)
C(12)	0.1063(8)	0.1452(8)	0.2434(8)	3.1(3)
C(13)	0.0217(9)	0.0973(9)	0.2536(8)	3.6(3)
C(14)	-0.001(1)	0.0940(9)	0.3297(8)	3.8(3)
C(15)	0.0729(9)	0.1414(8)	0.3674(7)	3.1(3)
C(21)	0.339(1)	0.2094(8)	0.4051(8)	3.7(3)
C(22)	0.363(1)	0.2498(9)	0.473(9)	5.4(4)
C(23)	0.441(1)	0.211(1)	0.5081(9)	6.4(4)
C(24)	0.471(1)	0.146(1)	0.465(1)	6.8(5)
C(25)	0.412(1)	0.144(1)	0.4008(9)	5.0(4)

methane solution. All data sets were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα: radiation. A total of 3286 independent reflections was collected in the range of $2° \le \theta \le 23°$ by $\omega/2\theta$ scan technique at room temperature, of which 1829 reflections with $I \ge 3\sigma(I)$ were considered to be observed and used for subsequent refinement. The corrections ($T_{min} = 0.857$, $T_{max} = 1.213$) for empirical absorption was applied to intensity data [11].

The structure was solved by a direct phase determination method. From E-map, two Fe atoms and one Sn atom were located. The other nonhydrogen atoms were found by successive difference Fourier syntheses. The hydrogen atoms were not included in the refinement and calculations of structure factors. The final refinement by full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms converged to unweighted and weighted agreement factors (R and R_w) of 0.044 and 0.059. The final difference Fourier map showed residual peaks of -1.53 e/$\overset{\circ}{\text{A}}{}^{-3}$ associated with Sn atom. All calculations were performed on a PDP 11/14 computer using the SDP-PLUS program system.

Selected bond lengths and bond angles are shown in Table 3, and atom coordinates are presented in Table 4.

3. Results and discussion

3.1. Synthesis and characterization of complexes 2, 3 and 4

Synthesis of the diiron complex (Me$_2$Si)[(η^5-C$_5$H$_4$)Fe(CO)]$_2$(μ-CO)$_2$ (1) via heating a solution of Fe(CO)$_5$ and C$_5$H$_5$Me$_2$SiC$_5$H$_5$ in xylene was reported twenty years ago [12,13]. The same approach is successful for (Me$_2$Ge)[(η^5-C$_5$H$_4$)Fe(CO)]$_2$(μ-CO)$_2$ (2). Thus, when the ligand C$_5$H$_5$Me$_2$GeC$_5$H$_5$ and a slight excess of Fe(CO)$_5$ was heated in boiling xylene for 14 h, a 34% yield of 2 was obtained. Complex 2 is an air-stable violet–red solid but air-sensitive in solution. Therefore, its solution must not be exposed to air for a long period of time. Complex 2 has very similar ^{1}H NMR spectrum to 1, even with germanium methyls exhibiting almost identical chemical shift to silicon methyls of 1. The IR spectrum of 2 exhibits two absorptions of bridged carbonyls different from one absorption in 1.

We recently reported that complex (Me$_2$Si)[(η^5-C$_5$H$_4$)Ru(CO)]$_2$(μ-CO)$_2$ (3) can be prepared in good yield (60%) by heating Ru$_3$(CO)$_{12}$ with a fourfold excess of C$_5$H$_5$Me$_2$SiC$_5$H$_5$ in heptane for 7 h [10]. An alternative route [14], in which the dithallium salt, Tl$_2$(C$_5$H$_4$Me$_2$SiC$_5$H$_4$) is treated with [Ru$_2$Cl$_4$(CO)$_6$], is much less efficient, affording only a 7% yield of 3. The same method is also used for the synthesis of
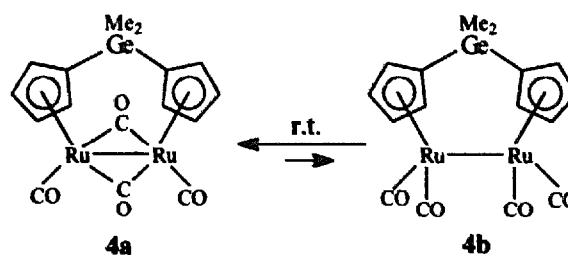
complex (Me$_2$Ge)[(η^5-C$_5$H$_4$)Ru(CO)]$_2$(μ-CO)$_2$ (4). However, the result is less successful than that we expected. Only when the preparative TLC is employed, rather pure complex 4 can be obtained in 10% yield. It is confusing that the yield decreases greatly when a silicon bridge is substituted by a germanium bridge. Some related work is still in progress.

Complex 3 and 4 are air-stable yellow solids but slightly air-sensitive in solution. Their ^{1}H NMR spectra are rather similar, with [AB]$_2$ systems for the protons of the C$_5$H$_4$ rings and singlets for silicon methyls. It should be noted that the IR spectrum of 4 in CH$_2$Cl$_2$ solution indicates that both isomers 4a (bridged form) and 4b (non-bridged form) are present, with the former dominant (Scheme 1)[1].

This is consistent with the results of IR spectral study on 3 [10]. In addition, the phenomenon that two isomers exist simultaneously in solution has also been observed in their analogues [(η^5-C$_5$H$_5$)Ru(CO)]$_2$(μ-CO)$_2$ [15] and (CH$_2$)[(η^5-C$_5$H$_4$)Ru(CO)]$_2$(μ-CO)$_2$ [16]. The carbonyl groups in ^{13}C NMR of 4 only exhibit a singlet (218.7 ppm). This is consistent with a rapid carbonyl scrambling process (bridging-terminal site exchange) [17] which interconverts 4a and 4b, and renders the averaging of the carbonyl ligands.

3.2. Insertion of SnCl$_2$ into M–M (M = Fe, Ru) bonds

We recently reported that SnCl$_2$ could be inserted into the Fe–Fe bond in complex 1 to afford a cyclic complex (Me$_2$Si)[(η^5-C$_5$H$_4$)Fe(CO)$_2$]$_2$SnCl$_2$ (5) [7]. The same treatment is successful for other bridged binuclear analogues. When 2, 3 and 4 and a slight excess of SnCl$_2$·2H$_2$O were heated under reflux in

Scheme 1.

The IR spectrum of complex 4 is very similar to those of complex 3 and (CH$_2$)[(η^5-C$_5$H$_4$)Ru(CO)]$_2$(μ-CO)$_2$ [16] in CH$_2$Cl$_2$ solution (see Table 1). Three absorption bands [1998(s), 1942(w), 1772(m)] are assigned to bridged isomer 4a, while the remaining absorption peak [1960(w)] is assignable to non-bridged isomer 4b. The assignment to the carbonyl absorption bands is made by comparing IR spectrum of 4 in CH$_2$Cl$_2$ solution with that in KBr disc [1991(s), 1941(s), 1805(w), 1766(s)]. Although non-bridged isomer 4b only exhibit one absorption peak according to the assignment, it is possible that the other weak absorption of 4b is hidden in the strong absorption of 4a [1998(s)].
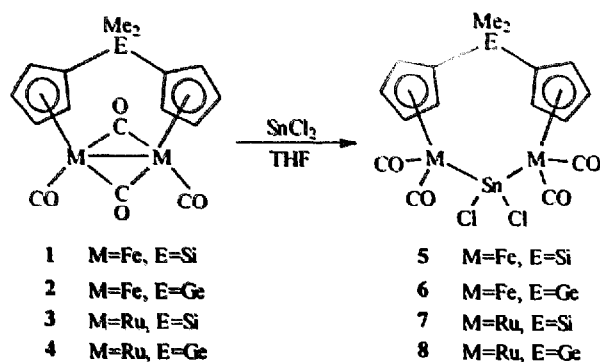
Scheme 2.
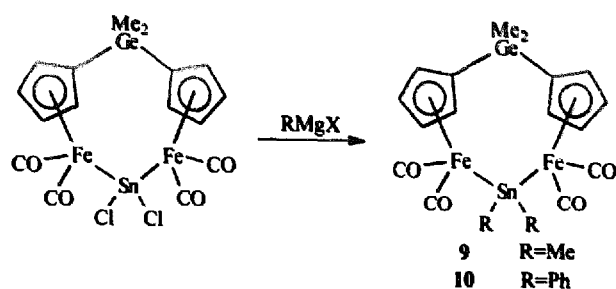

Scheme 3.

THF for 12–24 h. Cyclic complexes $(Me_2E)[(\eta^5-C_5H_4)M(CO)_2]_2SnCl_2$ [E = Ge, M = Fe (6); E = Si, M = Ru (7); E = Ge, M = Ru (8)] were obtained in yields (36% ~ 91%) (Scheme 2). Like 5, complex 6 is orange–yellow solids and rather stable in the solid state as well as in solution at room temperature. Complexes 7 and 8 are pale-yellow and sufficiently air stable to be handled in the air for a long time without the occurrence of noticeable decomposition. The insertion of the moiety $SnCl_2$ greatly lowers their solubility (7 and 8) in CH_2Cl_2 and $CHCl_3$. However, they are well soluble in aprotic solvents such as THF and acetone so that DMSO can be used for the solvent for ^1H NMR detection. In order to probe the structural details of this type of complexes X-ray diffraction was undertaken on 6.

Complexes 5–8 show smaller chemical shift differences between α and β protons of cyclopentadienyl rings than parent complexes, indicating that the chemical inequivalence of $\alpha\beta$ protons is weakened with the insertion of $SnCl_2$. In addition, the silicon (or germanium) methyls are shifted downfield to a certain extent relative to those in parent complexes, which is attributable to stronger electron-withdrawing ability of the moiety $SnCl_2$. The IR spectra of all these complexes only exhibit terminal carbonyl absorption which is in accord with their formulation. The ^{119}Sn NMR singal for 6 and 8 changes from − 160.6 to 18.0 ppm, indicating the difference of electronic effects between iron and ruthenium atoms. The ^{119}Sn chemical shift of 6 is rather different to that (329.7 ppm) of its analogue $[(\eta^5-C_5H_5)Fe(CO)_2]_2SnMe_2$ [18], but very close to that (− 150 ppm) of $SnCl_4$ [19]. This also supports the conclusion that minor molecular structual and electronic changes in ^{119}Sn NMR spectra are magnified into unpredictable δ changes of tens of ppm [20].

To examine the relation between the length of bridges and the insertion reaction, we expanded our investigation to $Me_2SiSiMe_2$ [21] and $Me_2SiOSiMe_2$ [22] bridged biscyclopentadienyl analogues. In no case could the reaction take place even if several solvents with differ-

ent boiling points and polarity were used as reaction media. This may be explained by the fact that the Me_2Si (or Me_2Ge) bridged complexes form a stable six-membered ring (discussed below in the crystal structure) after the insertion of $SnCl_2$, decreasing the strain force of the five-membered ring existing in their parent analogues, while it is uneasier for the $Me_2SiSiMe_2$ (or $Me_2SiOSiMe_2$) bridged analogue to form a seven (or eight)-membered ring.

A further study on the ring-substituted analogues $(Me_2Si)[(\eta^5-C_5H_3R)Fe(CO)]_2(\mu-CO)_2$ (R = t-Bu, t-heptyl) indicated that the insertion reaction of $SnCl_2$ did not proceed either. It is natural that this is attributed to the steric effects of bulky substituted groups. The synthesis and related reactions of the two compounds will be reported separately together with other tert-butyl substituted analogues.

3.3. Reactivity of complex 6

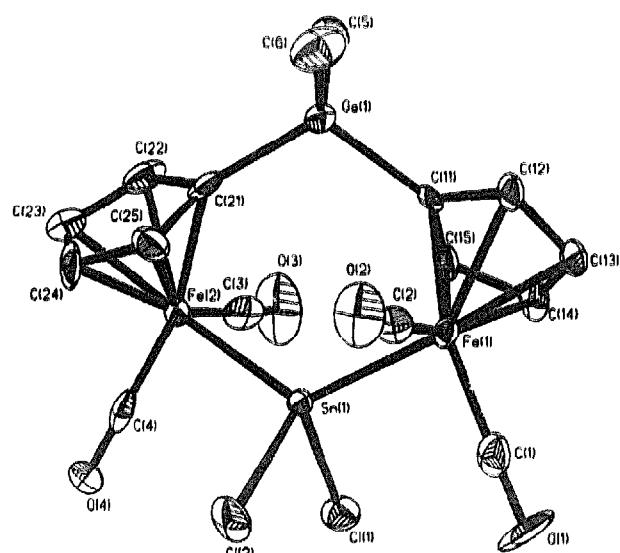Complex 6 displays the same reactivity as $(CH_3)_2SnCl_2$ (or Ph_2SnCl_2) towards Grignard reagents.

Fig. 1. Molecular structure of $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)_2]_2SnCl_2$ (6).

Two chlorine atoms can be rather readily substituted by two alkyls (or aryls) on treatment with CH_3MgI (or PhMgBr) affording $(Me_2Ge)[(\eta^5-C_5H_4)Fe(CO)_2]_2SnR_2$ [R = CH_3 (9); R = Ph (10)] in low yield (Scheme 3).

Complex 9 and 10 are orange, crystalline, and air-stable. The germanium methyls in 9 are strongly shifted upfield relative to complex 6 and even more upfield than that in 2, which may be due to the conformational change of the complex induced by larger size of methyl groups than chlorine atoms. The same factor may be utilized to account for the result that the germanium methyls in 10 exhibit smaller chemical shift (0.53 ppm) than that (0.61 ppm) in parent complex 6.

3.4. Crystal and molecular structures of complex 6

The molecular structure of 6 is presented in Fig. 1. The molecule of 6 consists of two $[(\eta^5-C_5H_4)Fe(CO)_2]$ moieties linked by one Me_2Ge bridge and one $SnCl_2$ bridge. 6 has an approximate C_2 axis passing through the Ge and Sn atoms, and the six-membered ring Sn(1)–Fe(1)–C(11)–Ge(1)–C(21)–Fe(2) constituting the molecular framework adopts a twist boat conformation. The Sn–Fe bond length of mean 2.490 Å is almost equal to that in non-bridged analogue $[(\eta^5-C_5H_4)Fe(CO)_2]_2SnCl_2$ [23] and shorter than many reported tin to iron bonds: e.g., 2.536 Å for $[(\eta^5-C_5H_5)Fe(CO)_2]SnPh_3$ [24], 2.670 and 2.651 Å for $[(C_5H_5)_2SnFe(CO)_4]_2$ [25], 2.605 Å for $[(\eta^5-C_5H_5)Fe(CO)_2]_2SnMe_2$ [26]. The Sn–Cl bond distance of mean 2.399 Å is longer than the Sn–Cl length of 2.31 ~ 2.37 Å found in the series of compounds $(CH_3)_nSnCl_{4-n}$ ($n = 0 - 3$) [27,28]. The Fe(1)–Sn(1)–Fe(2) and Cl(1)–Sn(1)–Cl(2) angles (124.64° and 95.6°) are close to those (128.6° and 94.1°) in non-bridged analogue $[(\eta^5-C_5H_4)Fe(CO)_2]_2SnCl_2$. The above observations can be reasonably accounted for by increased s character in the hybrid orbitals used in Sn–Fe bond formation and increased p character in the orbitals utilized in Sn–Cl bond formation [29].

The dihedral angle between two Cp ring planes is 81.53°. The Ge(1) deviates from the linked cyclopentadienyl planes by 0.0685 Å and 0.2128 Å respectively, indicating that molecules of 6 adopt a completely twist conformation.

References

[1] F. Bonati, G. Wilkinson, J. Chem. Soc. (1964) 179.
[2] T. Blackmore, J.D. Cotton, M.I. Bruce, F.G.A. Stone, J. Chem. Soc. A 12 (1968) 2931.
[3] J.K. Ruff, Inorg. Chem. 6 (1967) 2080.
[4] F. Bonati, S. Cenini, D. Morelli, R. Ugo, J. Chem. Soc. A (1966) 1052.
[5] D.J. Patmore, W.A.G. Graham, Inorg. Chem. 5 (1966) 1405.
[6] F.S. Field, R.J. Haines, M.W. Stewart, J. Sundermeyer, S.F. Woollam, J. Chem. Soc. Dalton Trans. (1993) 947.
[7] W. Hua, X. Zhou, S. Xu, R. Wang, H. Wang, Chem. J. Chin. Univ. 16 (1995) 387.
[8] K.C. Frisch, J. Am. Chem. Soc. 75 (1953) 6050.
[9] H. Kopf, W. Kalh, J. Organomet. Chem. 64 (1974) C37.
[10] X. Zhou, Y. Zhang, S. Xu, G. Tian, B. Wang, Inorg. Chim. Acta, in press.
[11] N. Walker, D. Stuart, Acta Cryst. A39 (1983) 158.
[12] J. Weaver, P. Woodward, J. Chem. Soc. Dalton Trans. (1973) 1439.
[13] P.A. Wegner, V.A. Uski, R.P. Kiester, S. Dabestani, V.W. Day, J. Am. Chem. Soc. 99 (1977) 4846.
[14] T.E. Bitterwolf, M.B. Leonard, P.A. Horine, J.E. Shade, A.L. Rheingold, D.J. Staley, G.P.A. Yap, J. Organomet. Chem. 512 (1996) 11.
[15] F.A. Cotton, G. Yagupsky, Inorg. Chem. 6 (1967) 15.
[16] S.A.R. Knox, K.A. Macpherson, A.G. Orpen, M.C. Rendle, J. Chem. Soc. Dalton Trans. (1989) 1807.
[17] J.G. Bullitt, F.A. Cotton, T.J. Marks, Inorg. Chem. 11 (1972) 671.
[18] S. Sharma, J. Cervantes, J.L. Mata-Mata, M.C. Brun, F. Cervantes-Lee, K.H. Pannell, Organometallics 14 (1995) 4269.
[19] M. Garralda, V. Garcia, M. Kretschmer, P.S. Pregosin, H. Ruegger, Helv. Chim. Acta 64 (1981) 1150.
[20] W.F. Howard Jr., W.H. Nelson, R.W. Crevely, Inorg. Chem. 24 (1985) 2204.
[21] H. Sun, S. Xu, X. Zhou, R. Wang, H. Wang, J. Organomet. Chem. 444 (1993) C41.
[22] M. Moran, I. Cuadrado, J.R. Masaguer, J. Losada, J. Chem. Soc. Dalton Trans. (1988) 833.
[23] J.E. Oconnor, E.R. Corey, Inorg. Chem. 6 (1967) 968.
[24] R.F. Bryan, J. Chem. Soc. A (1967) 192.
[25] P.G. Harrison, T.J. King, J.A. Richards, J. Chem. Soc. Dalton Trans. (1975) 2097.
[26] B.P. Biryukov, Y.T. Struchkov, J. Struct. Chem. 9 (1968) 412.
[27] R.L. Livingston, C.N.R. Rao, J. Chem. Phys. 30 (1959) 339.
[28] H.A. Skinner, L.E. Sutton, Trans. Faraday Soc. 40 (1944) 164.
[29] H.A. Bent, Chem. Rev. 61 (1961) 275.