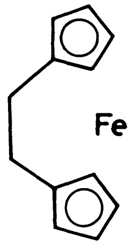
July, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *59*, *2109—2113 (1986)* 2109

Mössbauer Spectroscopic Studies of Tin(IV) Halide Adducts with Ruthenocene and with [2]Ferrocenophanes

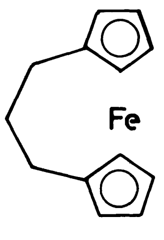
Masanobu Watanabe, Izumi Motoyama, and Hirotoshi Sano*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukasawa, Setagaya-ku, Tokyo 158

(Received Junuary 13, 1986)

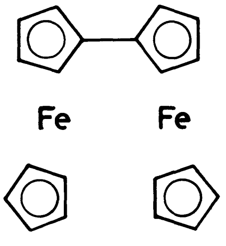
Adducts of tin(IV) halide with [2]ferrocenophane were prepared by treating SnX_4 (X=Cl or Br) with [2]ferrocenophane in hexane. The adducts were studied by means of ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopy and other physicochemical measurements. Anomalously large quadrupole splittings (3.49 mm s^{-1} for [2]ferrocenophane-1.5$SnCl_4$ adduct and 3.47 mm s^{-1} for [2]ferrocenophane-1.5$SnBr_4$ adduct, both at 78 K) found in the ^{57}Fe-Mössbauer spectroscopy and organotin(IV) species (e.g., isomer shift value, 2.14 mm s^{-1} for the [2]-ferrocenophane-1.5$SnCl_4$ adduct and 2.10 mm s^{-1} for the [2]ferrocenophane-1.5$SnBr_4$ adduct, both at 78 K) found from the ^{119}Sn-Mössbauer spectroscopy suggest that a direct chemical bonding between Fe and Sn atoms is formed in the [2]ferrocenophane adducts, as the Ru–Sn bonding in the ruthenocene-1.5$SnCl_4$ adduct (isomer shift value, 2.08 mm s^{-1} at 78 K).



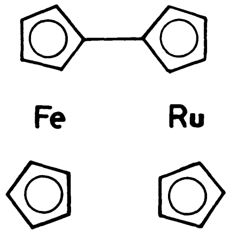
[2]Ferrocenophane



[3]Ferrocenophane



Biferrocene



Ferrocenylruthenocene

Mann et al. reported that yellow-colored ruthenocene-tin(IV) halide adducts are prepared by the reaction of ruthenocene with $SnCl_4$ or $SnBr_4$ in a CCl_4 solution under nitrogen.1) Based on the results of the IR spectra of these adducts, they proposed that the probable formula for the yellow products is $[(Cp)_2Ru\text{-}SnX_2\text{-}Ru(Cp)_2]^{2+}(SnX_5^-)_2$, where X=Cl or Br and Cp=C_5H_5, although no information was given about the ^{119}Sn-Mössbauer spectroscopy. The yellow SnX_4 adducts of ruthenocene are not as stable as the HgX_2 adducts of ruthenocene, in which Hg–Ru bonding is observed in X-ray analytical measurements.2)

All attempts to prepare stable adducts of ferrocene with tin(IV) halide have been unsuccessful; e.g., ferrocene reacts with $SnCl_4$ giving not an adduct but only a paramagnetic ferricinium salt.

It has been shown in our recent reports that [2]ferrocenophanes react with various Lewis-acid species such as Hg^{2+}, Cd^{2+}, H^+, I^+, and Cl^+, giving their adducts by ligating electrons of iron atoms to the Lewis acids.3–6) For instance, ^{57}Fe-Mössbauer spectroscopic studies of the [2]ferrocenophane-3$HgCl_2$ adduct show an anomalously large quadrupole splitting (Q.S.) value (3.29 mm s^{-1} at 78 K), suggesting a direct chemical bond between Fe^{2+} and Hg^{2+} atoms. The stability of [2]ferrocenophane-3$HgCl_2$ is ascribed to "naked" electrons around the iron atoms because the cyclopentadienyl rings are inclined by a bridged structure. In the case of the [2]ferrocenophane-$I^+I_3^-$ adduct, a direct interaction was verified by a single-crystal X-ray structural analysis; a similarly large Q.S. value is found in this adduct.6)

From the similarity to ruthenocene-1.5SnX_4 adducts, it is expected that [2]ferrocenophane derivatives can provide a stable adduct of $SnCl_4$. The present study was planned to clarify the structure of the stable adducts of [2]ferrocenophane with SnX_4 (X=Cl or Br) and to provide further information about the chemical state of iron and tin by means of ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopy.

Experimental

Materials. Biferrocene,7) [2]ferrocenophane,8) and [3]ferrocenophane9) were prepared by the methods previously reported. The adduct of tin chloride with [2]ferrocenophane was prepared by the following method. To a solution of [2]ferrocenophane dissolved in dry hexane, a hexane solution of $SnCl_4$ was added in a nitrogen-filled dry box equilibrated with P_4O_{10}, and the produced red-orange precipitates were filtered, washed with a large excess of hexane, and dried under vacuum. The purity of the adduct was confirmed by elemental analysis: Found; C, 23.41; H, 2.77; Sn, 29.07%. Calcd for [2]ferrocenophane$(SnCl_4)_{1.5}$-(H_2O), $C_{12}H_{14}FeSn_{1.5}Cl_6O$: C, 23.19; H, 2.25; Sn, 28.67%. The red-orange product of [2]ferrocenophane with $SnBr_4$

was obtained by the same conditions as in the case of $SnCl_4$ adduct. The $SnBr_4$ adduct is very hygroscopic. Found: C, 16.21; H, 1.92%. Calcd for [2]ferrocenophane–$(SnBr_4)_{1.5}$-$(H_2O)_3$, $C_{12}H_{18}FeSn_{1.5}Br_6O_3$: C, 15.59; H, 1.95%. Reaction products of [3]ferrocenophane, biferrocene and ferrocene were obtained by the same procedure as described in the case of [2]ferrocenophane–1.5$SnCl_4$ adduct, but the color of the precipitates was dark-green characteristic of ferricinium salts. All the products prepared in the reactions of [2]-, [3]ferrocenophane and ferrocene with tin halides are so hygroscopic that the elemental analysis and IR spectroscopic data show an appreciable amount of water in each final product (as described in each empirical formula), even after keeping the samples in a desiccator. Found: C, 27.43; H, 2.93; Sn, 26.13%. Calcd for [3]ferrocenophanium-$(SnCl_4)_{1.25}(H_2O)_{1.5}$, $C_{13}H_{17}FeSn_{1.25}Cl_5O_{1.5}$: C, 26.96; H, 2.94; Sn, 25.64%. Found: C, 30.67; H, 2.44%. Calcd for biferrocenium$(SnCl_4)_{1.75}$, $C_{20}H_{18}Fe_2Sn_{1.75}Cl_7$: C, 29.07: H, 2.20%. Found: C, 20.10; H, 2.05; Sn, 28.85%. Calcd for ferricinium$(SnCl_4)_{1.5}(H_2O)_2$, $C_{10}H_{14}FeSn_{1.5}Cl_6O_2$: C, 19.58; H, 2.28; Sn, 29.05%. The adducts of [2]ferrocenophane–1.5$SnCl_4$ are hardly soluble in most organic solvents but are soluble in *N*,*N*-dimethylformamide. The solution shows only an absorption spectrum of [2]ferrocenophane, while the other precipitates such as [3]ferrocenophane–1.25$SnCl_4$ are soluble in *N*,*N*-dimethylformamide. The resulting green-colored solution gives an absorption spectra similar to that of the ferricinium salts.

Ruthenocene reacts with a large excess of $SnCl_4$ in dry hexane under nitrogen giving a yellow adduct. Found: C, 20.28; H, 1.78%. Calcd for ruthenocene$(SnCl_4)_{1.5}$, $C_{10}H_{10}RuSn_{1.5}Cl_6$: C, 19.29; H, 1.61%.

Measurements. ^{57}Fe-Mössbauer measurements were carried out by using a ^{57}Co(Pt) source moving in a constant acceleration mode, while ^{119m}Sn-Mössbauer spectra were measured against a $Ca^{119m}SnO_3$ source. The velocity calibration was made by the resonance lines of an ^{57}Fe-enriched metallic-iron absorber against the ^{57}Co(Pt) source. The isomer shift (I.S.) for ^{57}Fe was taken with respect to metallic iron and that for ^{119}Sn was descrided with respect to a $BaSnO_3$ absorber. The experimental error of the I.S. and Q.S. values were estimated to be within ±0.02 mm s^{-1}.

Results and Discussion

The ruthenocene–1.5$SnCl_4$ adduct is not very stable and the yellow color gradually changes into green-yellow upon standing at room temperature for several days in air after preparation. The adduct is soluble in CH_3CN and gives a yellow solution. An absorption band at 360 nm in its fresh solution rapidly decreases in intensity while standing in air, and an absorption band characteristic of ruthenocene appears at 310 nm within a few minutes after preparing the solution. This is ascribed to a dissociation of the adduct into ruthenocene and $SnCl_4$.

The ^{119}Sn-Mössbauer parameters of the adducts and related compounds are listed in Table 1 and typical ^{119}Sn-Mössbauer spectra of $Ru(Cp)_2$–1.5$SnCl_4$ and related compounds are shown in Fig. 1. Measure-

Table 1. ^{119}Sn-Mössbauer Parameter for [2]Ferrocenophane–Tin Halide Adduct and Related Compounds

Compound	Temperature K	I.S. mm s^{-1}
[2]Ferrocenophane$(SnCl_4)_{1.5}(H_2O)$	4.2	0.54
		2.11
	40	0.53
		2.10
	78	0.54
		2.14
	97	0.53
		2.14
	138	0.51
		2.11
[3]Ferrocenophane$(SnCl_4)_{1.25}(H_2O)_{1.5}$	78	0.25
		0.77
		3.99
Ferrocene$(SnCl_4)_{1.5}(H_2O)_2$	78	0.18
		0.80
		4.07
Biferrocene$(SnCl_4)_{1.75}$	78	0.22
		0.86
		4.01
Ruthenocene$(SnCl_4)_{1.5}$	78	0.56
		2.08

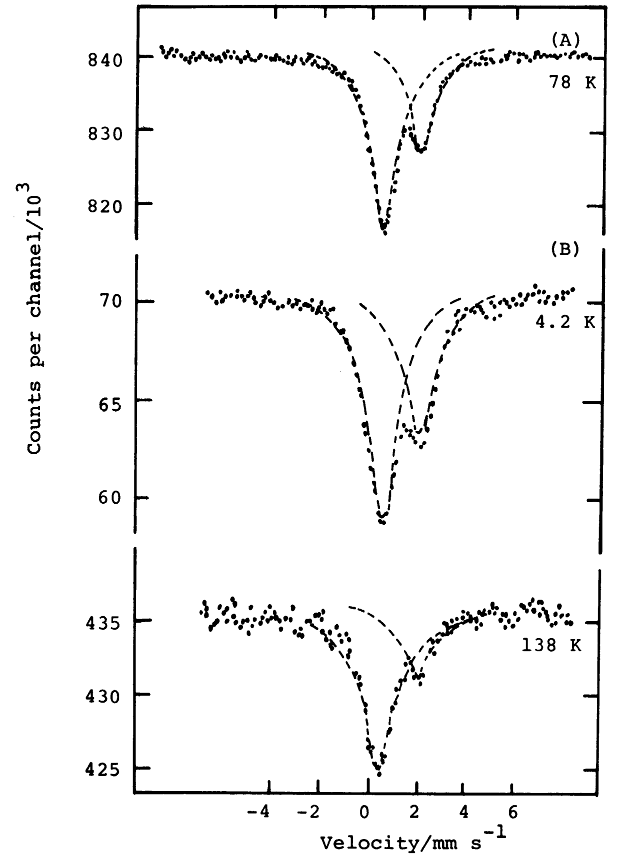


Fig. 1. ^{119}Sn-Mössbauer spectra of (A) ruthenocene–$SnCl_4$ adduct and (B) [2]ferrocenophane–$SnCl_4$ adduct, at indicated temperatures.

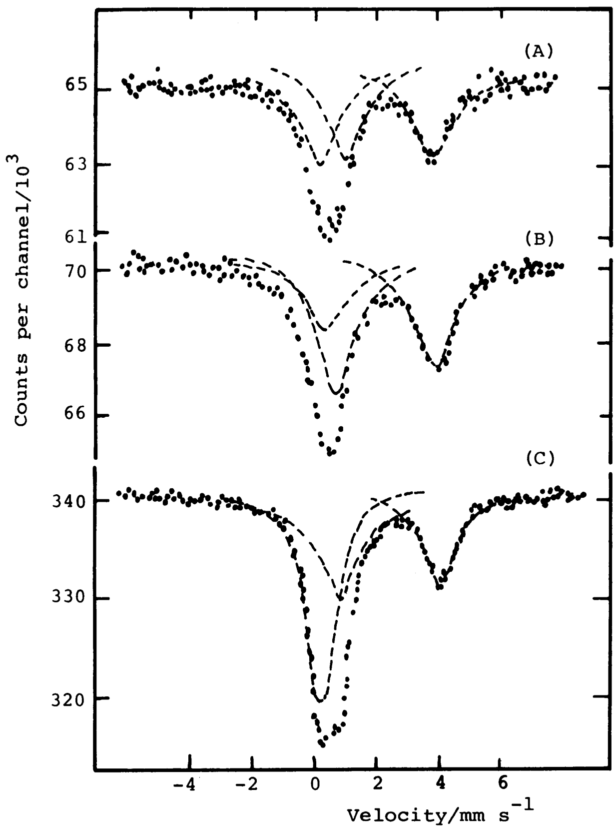


Fig. 2. ^{119}Sn-Mössbauer spectra of (A) reaction products with $SnCl_4$ and ferrocene, (B) [3]ferrocenophane, and (C) biferrocene, all at 78 K.

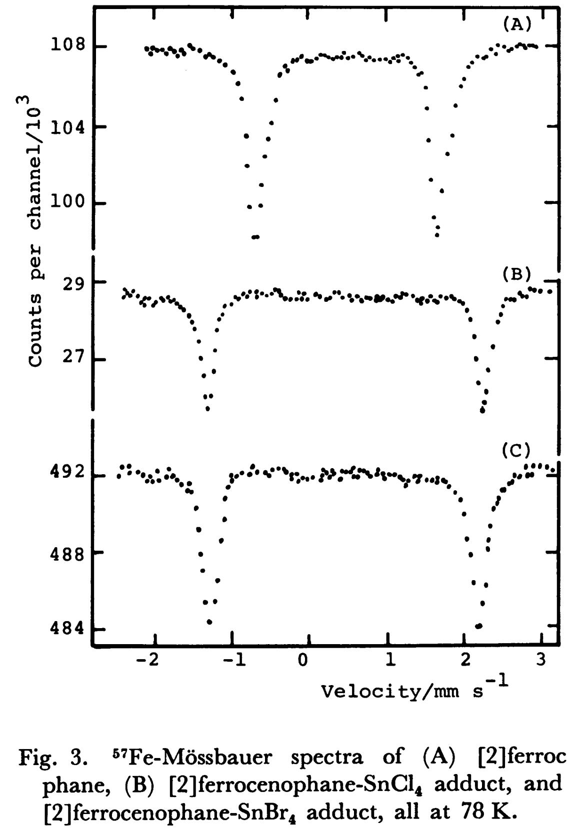


Fig. 3. ^{57}Fe-Mössbauer spectra of (A) [2]ferrocenophane, (B) [2]ferrocenophane-$SnCl_4$ adduct, and (C) [2]ferrocenophane-$SnBr_4$ adduct, all at 78 K.

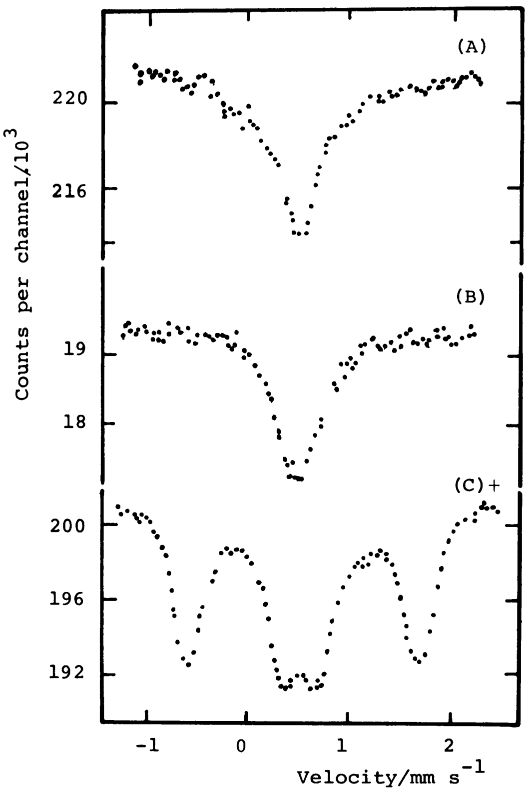


Fig. 4. ^{57}Fe-Mössbauer spectra of (A) reaction products with $SnCl_4$ and ferrocene, (B) [3]ferrocenophane, and (C) biferrocene, all at 78 K.

ments of the ^{119}Sn-Mössbauer spectra for the $SnCl_4$ adducts were limited to within a temperature range below 150 K because of their small recoil-free fraction. In the spectrum measured at 78 K of $Ru(CP)_2$-$1.5SnCl_4$, two kinds of chemical states of the tin(IV) species (I.S., 0.56 and 2.08 mm s^{-1}) were observed. The component with a higher I.S. value (2.08 mm s^{-1}) was ascribed to an organotin(IV) species and the other broad component with a lower I.S. value (0.56 mm s^{-1}) to a rather ionic $SnCl_5^-$ species, respectively. This was based on the systematics of the ^{119}Sn-Mössbauer spectroscopic parameters found in tetravalent organotin or organometallic tin chlorides and hexachlorotin(IV) species.

Mann et al. has already proposed $[(Cp)_2Ru$-$SnCl_2$-$Ru(Cp)_2]^{2+}(SnCl_5^-)_2$ as one of the probable structures for the yellow adduct on the basis of the IR spectroscopic studies.[1] In an analogy to the conclusion, it was also confirmed from the results of a ^{119}Sn-Mössbauer spectroscopic study that the component having a higher I.S. value is ascribable to a tin(IV) species of $(Cp)_2Ru$-$SnCl_2$-$Ru(Cp)_2$ and the lower one to $SnCl_5^-$.

Ferrocene reacts with $SnCl_4$ giving paramagnetic green precipitates. The ^{119}Sn- and ^{57}Fe-Mössbauer spectra of the product are shown in Figs. 2 and 4, respectively. In the ^{57}Fe-Mössbauer spectrum of this product, a broad singlet peak observed indicates the

Table 2. ^{57}Fe-Mössbauer Parameters for the [2]Ferrocenophane-Tin Halides Adducts and Related Compounds

Compound	Temperature K	Q.S. mm s^{-1}	I.S. mm s^{-1}
[2]Ferrocenophane	78	2.41	0.49
[2]Ferrocenophane-$(SnCl_4)_{1.5}(H_2O)$	4.2	3.53	0.52
	78	3.49	0.50
	300	3.40	0.41
[2]Ferrocenophane-$(SnBr_4)_{1.5}(H_2O)_3$	78	3.47	0.51
1,1,2,2-Tetramethyl[2]ferrocenophane$(SnCl_4)_{1.5}(H_2O)$	78	3.43	0.50
	200	3.37	0.46
Ferrocene$(SnCl_4)_{1.5}(H_2O)_2$	78	0.0	0.54
[3]Ferrocenophane-$(SnCl_4)_{1.25}(H_2O)_{1.5}$	78	0.0	0.52
Biferrocene$(SnCl_4)_{1.75}$	78	0.29	0.54
		2.26	0.50

presence of the ferricinium-like iron atoms as expected from the dark-green color of the product. The ^{119}Sn-Mössbauer spectrum shows that there are three components ascribed to two kinds of Sn(IV) species (I.S., 0.18 and 0.80 mm s^{-1}) and to a kind of Sn(II) species (I.S., 4.07 mm s^{-1}) at 78 K. The presence of Sn(II) peak suggests that ferrocene may be oxidized by $SnCl_4$ giving ferricinium salt, expressed as $[(Cp)_2Fe^+]_2(SnCl_3^-)(SnCl_5^-)(SnCl_4)(H_2O)_4$ in accord with the elemental analysis data.

Biferrocene, one of the typical binuclear ferrocene derivatives, is also known to react with $HgCl_2$ giving a more stable adduct than that of ferrocene. Biferrocene reacts with $SnCl_4$ in a hexane solution giving green-black paramagnetic precipitates. ^{57}Fe-Mössbauer spectroscopic measurements indicate that there are two kinds of iron atoms, one of which is ferrocene-like (Q.S., 2.26, I.S., 0.50 mm s^{-1}) and the other is ferricinium-like (Q.S., 0.29, I.S., 0.54 mm s^{-1}, at 78 K), showing a trapped-valence state. ^{119}Sn-Mössbauer spectroscopic measurements show that there are three components ascribed to two kinds of Sn(IV) species, ($SnCl_5^-$ and $SnCl_4\cdot nH_2O$: I.S., 0.86 and 0.22 mm s^{-1} at 78 K, respectively) and to a kind of Sn(II) species ($SnCl_3^-$: I.S., 4.01 mm s^{-1} at 78 K). The spectral shape is similar to that of ferrocene–$1.5SnCl_4(H_2O)_2$. The product is expressed by a formula, $(\text{biferrocenium}^+)_2(SnCl_3^-)(SnCl_5^-)(SnCl_4)_{1.5}$, based on an elemental analysis.

It is reported that cyclopentadienyl rings are separated by 3.32 Å from each other in ferrocene molecules, and by 3.68 Å in ruthenocene molecules.[10,11)] The larger separation of the Cp rings in ruthenocene provides a good explanation for the fact that ruthenocene can easily donate the e_{2g} electrons of the ruthenium atom to a Lewis acid, such as $SnCl_4$, $HgCl_2$, giving a stable coordination compound.[1,2,12)]

Recently, the structure of the [2]ferrocenophane was investigated by an X-ray analysis and it was found that the crystals of [2]ferrocenophane are orthorhombic with a=12.444(2), b=19.969(4), c=7.467(1), space group, P_{bca}. The two five-membered rings are tilted 22.2° with respect to one another. The cyclopentadienyl rings are largely separated by 3.60 Å (in maximum) from each other,[13)] and this value corresponds to that of ruthenocene (3.68 Å).[11)]

[2]Ferrocenophane reacts with a large excess of $SnCl_4$ in dry hexane under the same condition as in the case of ruthenocene–$1.5SnCl_4$, giving an orange-yellow adduct with a formula of [2]ferrocenophane–$1.5SnCl_4(H_2O)$. This adduct is not as stable as the ruthenocene–$1.5SnCl_4$ adduct and its color gradually changes into dark-blue (ferricinium salt) upon standing in air at room temperature for a few hours, while the ruthenocene–$1.5SnCl_4$ adduct keeps its color for several days. The adduct of [2]ferrocenophane with $SnCl_4$ is soluble in *N,N*-dimethylformamide giving a solution exhibiting the original absorption spectrum of [2]ferrocenophane. This suggests a dissociation of the adduct into [2]ferrocenophane and $SnCl_4$.

The ^{119}Sn- and ^{57}Fe-Mössbauer spectra of this adduct are illustrated in Figs. 1, and 3, respectively. Anomalously large Q.S. values (3.49 mm s^{-1} at 78 K, 3.40 mm s^{-1} 300 K) are observed for the [2]ferrocenophane–$1.5SnCl_4$ adduct compared with that of [2]ferrrocenophane itself (2.41 mm s^{-1} at 78 K). The anamalously large Q.S. values are good evidence for a direct interaction between Fe and Sn atoms in this adduct, as already verified in the $HgCl_2$, I_2, $CdCl_2$ adducts with [2]ferrocenophane.[3–6)]

The ^{119}Sn-Mössbauer spectra of [2]ferrocenophane–$1.5SnCl_4$ (Fig. 1) exhibit two peaks corresponding to two kinds of chemical states of the tin(IV) species (I.S., 0.54 mm s^{-1} and 2.14 at 78 K). Based on the assumption that the recoil-free fraction of both the tin atoms should become approximately equal at lower temperatures, the value of the areal intensity of the lower I.S. component is about two times larger than that of the higher I.S. component at 40 K to 4.2 K. Therefore, it seems reasonable to ascribe the component with higher I.S. (2.14 mm s^{-1}) to $(Cp')_2Fe$–$SnCl_2$–$Fe(Cp')_2$–type tin(IV) species and the other broad component with a lower one (I.S., 0.54 mm s^{-1} at 78 K) to a rather ionic $SnCl_5^-$-type tin(IV) species, in the ^{119}Sn-Mössbauer spectroscopic study of ruthenocene–$1.5SnCl_4$ adduct. A similar conclusion is obtained for [2]ferrocenophane–$1.5SnBr_4$ adduct. [2]Ferrocenophane reacts with directly $SnBr_4$ in hexane solution to give orange-yellow precipitates, with a formula of [2]ferrocenophane$(SnBr_4)_{1.5}(H_2O)_3$. Both the [2]ferrocenophane–tin(IV) halide adducts are hygroscopic. The $SnBr_4$ adduct is more hygroscopic than the $SnCl_4$ adduct and its orange-yellow color changes into black in an hour on standing in air at room temperature.

^{57}Fe- and ^{119}Sn-Mössbauer spectroscopic studies on the $SnBr_4$ adduct show an anomalously large quadrupole splitting (3.47 mm s^{-1} at 78 K, see in Fig. 3) for the iron atom and the presence of two kinds of chemical states of tin(IV) atoms (I.S., 0.92 mm s^{-1} for $SnBr_5^-$-type and 2.10 mm s^{-1} for $[(Cp')_2Fe-SnBr_2-Fe(Cp')_2]^{2+}$-type, at 78 K), respectively.

1,1,2,2-Tetramethyl[2]ferrocenophane also reacts with $SnCl_4$, giving an orange-yellow adduct. An anomalously large Q.S. value (3.43 mm s^{-1} at 78 K) is also observed by means of ^{57}Fe-Mössbauer spectroscopy, and two kinds of chemical state of tin(IV) species are found by means of ^{119}Sn-Mössbauer spectroscopy for this adduct.

These ^{119}Sn-Mössbauer results of [2]ferrocenophane–1.5$SnCl_4$ or –1.5$SnBr_4$ adducts are very similar to that of the $SnCl_4$ adduct of ruthenocene. Therefore, these adducts may be expressed as $[(Cp')_2Fe-SnX_2-Fe(Cp')_2]^{2+}(SnX_5^-)_2$, where X=Cl or Br. Similar direct chemical bonds between Fe and Sn atoms (Fe–Sn–Fe) were previously reported in $[Fe(Cp)(CO)_2]_2^{2+}(SnCl_2^{2-})$ by O'Connor and Corey.[14]

The magnetic susceptibility measurement shows that the adducts of [2]ferrocenophane–1.5$SnCl_4$ and –1.5$SnBr_4$ are diamagnetic at temperatures from 78 to 300 K, indicating no possibility of an oxidation of [2]ferrocenophane to a [2]ferrocenophanium cation. However, the color of these adducts gradually changes from orange-yellow to black upon standing at room temperature. These black substances are paramagnetic, probably because [2]ferrocenophane is oxidized by SnX_4 forming [2]ferrocenophanium cations.

On the other hand, [3]ferrocenophane, in which the two Cp rings are slightly inclined to each other (ca., 9°), reacts with $SnCl_4$ giving green-black precipitates. The effective magnetic moment (μ_{eff}) for these precipitates was found to be 2.60 BM; this is a characteristic value for normal ferricinium salts. The ^{57}Fe-Mössbauer spectrum of this salt is shown in Fig. 4-B, where a broad singlet peak is observed (I.S., 0.52 mm s^{-1} at 78 K), and the ^{119}Sn-Mössbauer spectrum (see in Fig. 2-B) also suggests the presence of three types of tin species, ascribed to two kinds of Sn(IV) components (I.S., 0.25 and 0.77 mm s^{-1}, assigned to $SnCl_4 \cdot nH_2O$ and $SnCl_5^-$, respectively) and to a kind of Sn(II) component (I.S., 3.99 mm s^{-1}, assigned to $SnCl_3^-$). The results indicate that the reaction product with [3]ferrocenophane with $SnCl_4$ is expressed as $[(C_5H_4)_2C_3H_6Fe^+]_4(SnCl_3^-)_2(SnCl_5^-)_2(SnCl_4)(H_2O)_6$, in accord with elemental analysis data.

All the results obtained in the present study lead to the conclusion that ruthenocene and [2]ferrocenophanes give adducts with SnX_4, containing coordination bonds between the ruthenium or iron atoms in metallocene and tin atoms. The coordination bonds may be stabilized by a decreased steric hindrance of Cp-rings both in ruthenocene and [2]ferrocenophanes; that is, the longer separation between the Cp-rings both in ruthenocene and [2]ferrocenophane than in ferrocene will make the e_{2g}-electrons of the metallocene easier to be ligated to SnX_4.

Lauher and Hoffmann suggested that the energy levels of frontier orbitals such as e_{2g}, a_{1g}, and e_{1g} in ferrocene depend on the bending angle of the molecule around iron atoms, ∠Cp–Fe–Cp.[15] For instance, one of the split e_{1g} levels goes down while the a_{1g} level and one of the split e_{2g} levels go up, as the angle decreases from 180°. It is not unreasonable to assume that the energy levels cross each other more dramatically if the iron atoms are involved in the ligation to a Lewis acid, giving an increased Q.S. value compared with that of the original [2]ferrocenophane.

References

1) K. R. Mann, W. H. Morrison, Jr., and D. N. Hendrickson, *Inorg. Chem.*, **13**, 1180 (1974).

2) W. H. Morrison, Jr. and D. N. Hendrickson, *Inorg. Chem.*, **11**, 2912 (1972).

3) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, *Bull. Chem. Soc. Jpn.*, **56**, 3291 (1983).

4) M. Watanabe, I. Motoyama, and H. Sano, *J. Radioanal. Nucl Chem. Lett.*, **96**, 585 (1985).

5) H. Sano, M. Watanabe, and I. Motoyama, *Hyperfine Interactions*, **28**, 833 (1986).

6) M. Watanabe, K. Sato, I. Motoyama, and H. Sano, *Chem. Lett.*, **1983**, 1775.

7) M. D. Raush, *J. Org. Chem.*, **26**, 1802 (1961).

8) H. Lenzner and W. H. Watts, *Tetrahedron*, **27**, 4343 (1971).

9) M. B. Laing and K. N. Trueblood, *Acta, Crystallogr.*, **19**, 373 (1965).

10) J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta. Crystallogr.*, **9**, 373 (1956).

11) G. L. Herdgrove and D. H. Templeton, *Acta. Crystallogr.*, **12**, 28 (1959).

12) D. N. Hendrickson, Y. S. Sohn, W. H. Morrison, Jr., and H. B. Gray, *Inorg. Chem.*, **11**, 808 (1972).

13) T. Ito, Private communication.

14) J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967).

15) J. W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, **98**, 1729 (1976).