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^{57}Fe-Mössbauer and ^{13}C-CP-MAS NMR Spectroscopic Studies of the Reaction Products of Ferrocene Derivatives with Mercury(II) Salts

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The unstable adducts of ferrocene and methylferrocene and the stable adducts of biferrocene, diferrocenylmethane, 1,2-diferrocenylethane, and [*n*]ferrocenophane (n=2, 3) with HgX_2 (X=Cl, Br, I, and BF_4) were studied by means of ^{57}Fe-Mössbauer and high-resolution solid-state ^{13}C NMR spectroscopies. The large quadrupole splitting (Q. S.) values in the ^{57}Fe-Mössbauer and the large low-field shifts in the ^{13}C-CP-MAS NMR, spectroscopy suggest the presence of a direct chemical bond between the Fe and Hg atoms.

All attempts to prepare a stable $HgCl_2$ adduct of ferrocene have been unsuccessful and have given green-colored paramagnetic ferrocenium-type salts after standing for a day. However, stable light-colored diamagnetic adducts of biferrocene, diferrocenylmethane, and 1,2-diferrocenylethane with $HgCl_2$ could be prepared.[1,2] It was shown in our previous reports that [2]ferrocenophane derivatives give much more stable adducts in reactions with Lewis acids, $SnCl_4$, $HgCl_2$, $CdCl_2$, and I_2,[3–6] whereas binuclear ferrocene derivatives could be oxidized to their ferrocenium-type salts in reactions with Lewis acids other than $HgCl_2$. These results can be explained by assuming that [2]ferrocenophanes have less steric hindrance in donating e_{2g} electrons than ferrocene and binuclear ferrocene derivatives, on the basis of ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopics, which provide direct information concerning the iron and tin atoms concerned with bond formation. X-Ray diffraction studies of the I_2 adduct with 1,1,2,2-tetramethyl[2]ferrocenophane show that the Fe atoms squeezed out of the tilted cyclopentadienyl (Cp) structure have I atoms at a short distance (2.675 Å),[6] much shorter than the sum of the van der Waals radii of the Fe and I atoms. Applications of ^{13}C-CP-MAS NMR spectroscopy to the reaction products of ferrocene and ruthenocene derivatives with various Lewis acid adducts have proved its sensitivity to the changes in structural distortion caused by adduct formation and have provided additional information; e.g., the large low-field shift of peaks ascribed to Cp rings of the ruthenocene suggests the formation of direct chemical bonds between the Ru atom and the Lewis acids (I^+, Hg^{2+}, and Sn^{4+}) in the adducts, as has already been verified by means of X-ray diffraction[8,9] and ^{119}Sn-Mössbauer spectroscopic studies.[10] The present studies were carried out in order to cross-examine the bond formation between the metal atoms in ferrocene derivative adducts with HgX_2 and the structural distortion associated with adduct formation by using both ^{57}Fe-Mössbauer spectroscopy and high-resolution ^{13}C-CP-MAS NMR spectroscopy.

Experimental

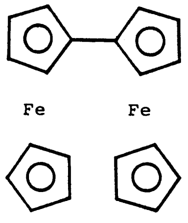
Materials: The reaction products of ferrocene,[8] biferrocene,[1] diferrocenylmethane,[2] 1,2-diferrocenylethane,[2] and [2]ferrocenophane[4] with $HgCl_2$ were prepared by the previously reported methods. The $HgCl_2$ adducts of methylferrocene and [3]ferrocenophane were first prepared by a method similar to that used in the case of ferrocene-7$HgCl_2$ adduct.[8] The purities of the adducts were confirmed by elemental analysis. Found: C, 7.03; H, 0.75%. Calcd for methylferrocene-6$HgCl_2$, $C_{11}H_{12}FeHg_6Cl_{12}$: C, 7.22; H, 0.66%. Found: C, 8.54; H, 0.84%. Calcd for [3]ferrocenophane-6$HgCl_2$, $C_{13}H_{14}FeHg_6Cl_{12}$: C, 8.42; H, 0.76%. Adducts of [2]ferrocenophane with $HgBr_2$ and HgI_2 were prepared in diethyl ether and benzene solution, respectively, by a method similar to that used in the preparation of [2]ferrocenophane-3$HgCl_2$ adduct.[4] A red-orange precipitate was filtered, washed with diethyl ether, and dried under vacuum. Found: C, 12.57; H, 1.16%. Calcd for [2]ferrocenophane-2.5$HgBr_2$, $C_{12}H_{12}FeHg_{2.5}Br_5$: C, 12.93; H,1.08%. Found: C, 11.86; H, 1.02%. Calcd for [2]ferrocenophane-2.2HgI_2, $C_{12}H_{12}FeHg_{2.2}I_{4.4}$: C, 11.89; H, 0.99%.

Measurements: ^{57}Fe-Mössbauer spectroscopic measurements were carried out by using a ^{57}Co(Rh) source moving in a constant acceleration mode. The isomer shift (I. S.) value for the ^{57}Fe-Mössbauer spectroscopic measurements was taken with respect to metallic iron; the experimental error of the I. S. and Q. S. values was estimated to be within ±0.02 mm s^{-1}.

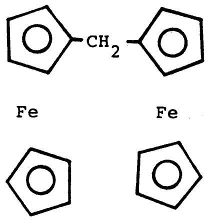
The ^{13}C-CP-MAS NMR spectra were obtained under the same conditions as in the case of our previous reports.[7] The chemical-shift values were measured with respect to external adamantane and then converted to the shift values from TMS. Both the ^{1}H and ^{13}C NMR spectra in solution were measured by using a JEOL FX-200 spectrometer at 200.0 and 50.1 MHz, respectively, using TMS as a standard. The assignment of the ^{13}C signals of the metallocenes was carried out by selective proton decoupling experiments.

Results and Discussion

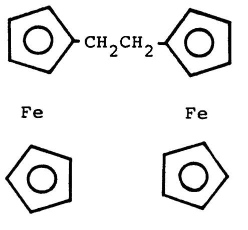
It has already been known that ferrocene gives an unstable orange-yellow diamagnetic ferrocene-7$HgCl_2$ adduct in a reaction with $HgCl_2$ in diethyl ether.[9] No ^{1}H NMR signals of the ferrocene-7$HgCl_2$ adduct could be obtained in acetonitrile solution because of oxida-



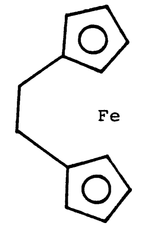
Biferrocene



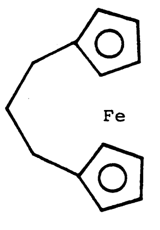
Diferrocenylmethane



1,2-Diferrocenylethane



[2]Ferrocenophane



[3]Ferrocenophane

tion to the ferrocenium salt of the adduct. This smaller stability of the adduct in solution is one of the large differences from that of ruthenocene-3HgCl$_2$ adduct (i.e., the HgCl$_2$ adduct of ruthenocene is stable in the acetonitrile, giving a large low-field shift ($\Delta\delta$) for the ^{1}H signal ($\Delta\delta$; 0.84 ppm)[7] caused by the direct chemical bond between the Ru and Hg atoms as already verified from X-ray diffraction studies[8]). In order to avoid the experimental difficulties associated with the lower stability of the ferrocene-7HgCl$_2$ adduct in solution, ^{13}C-CP-MAS NMR spectroscopic measurements of the solid adduct were carried out in the present studies.

A π-C$_5$H$_5$ ring carbon signal (δ) in the ferrocene appears at δ=69.8, while a broader signal of the HgCl$_2$ adduct appears at δ=79.7, as shown in Figs. 1-a, and b and Table 1. A large low-field shift ($\Delta\delta$; 9.9 ppm) has been found in ferrocene-7HgCl$_2$ adduct, as in the case of ruthenocene-3HgCl$_2$ adduct ($\Delta\delta$; 8.0 ppm).[7] On the other hand, no low-field shift has been observed for the chloromercurioferrocene, (C$_5$H$_5$)(C$_5$H$_4$HgCl)Fe, in which a chloromercurio group (HgCl) is attached to the Cp-ring.[11] The ^{13}C chemical-shift value of the Cp-ring in the chloromercurioferrocene (δ=70.5) is very similar to that of ferrocene itself (δ=69.8) in the solid state, as can be seen in Figs. 1-a and c. These facts clearly indicate that the large low-field shift observed in the ferrocene-7HgCl$_2$ adduct can be ascribed to a chemical bond formed between the Fe and Hg atoms, as previously indicated on the basis of the anomalously large Q. S. value (3.09 mm s^{-1} at 80 K) in the

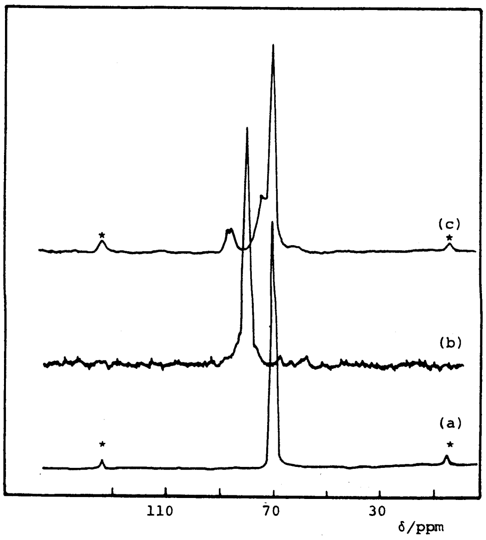


Fig. 1. ^{13}C-CP-MAS NMR spectra of ferrocene(a), its 7HgCl$_2$(b) adduct, and chloromercurioferrocene(c). The sample spinning side band (SSB) is represented by * in the Figure.

Table 1. ^{13}C-Chemical Shift Values of Ferrocene Derivatives and Their Mercury(II) Halides Adducts

Compound	Chemical shift value δ/ppm
Ferrocene	69.8(C$_5$H$_5$)
Ferrocene-7HgCl$_2$	79.7(C$_5$H$_5$)
Biferrocene	84.8(C$_1$) 70.7(C$_5$H$_5$) 67.1(C$_{2,5}$, C$_{3,4}$)
Biferrocene-2HgCl$_2$	79.7(C$_5$H$_5$) 71.4(C$_{2,5}$, C$_{3,4}$)
Diferrocenylmethane	91.3, 86.6(C$_1$) 70.1(C$_5$H$_5$) 31.3(CH$_2$)
Diferroceneylmethane-6HgCl$_2$	91.4(C$_1$) 78.9(C$_5$H$_5$, C$_{2,5}$, C$_{3,4}$) 31.0(CH$_2$)
1,2-Diferrocenylethane	90.1(C$_1$) 70.0(C$_5$H$_5$, C$_{2,5}$, C$_{3,4}$) 36.6(CH$_2$CH$_2$)
1,2-Diferrocenylethane-6HgCl$_2$	91.9(C$_1$) 78.4(C$_5$H$_5$, C$_{2,5}$, C$_{3,4}$) 31.7(CH$_2$CH$_2$)
[2]Ferrocenophane	92.6(C$_1$) 75.0(C$_{2,5}$) 70.8(C$_{3,4}$) 35.3(CH$_2$CH$_2$)
[2]Ferrocenophane-3HgCl$_2$	114.2(C$_1$) 78.6(C$_{2,5}$, C$_{3,4}$) 35.1(CH$_2$CH$_2$)
[2]Ferrocenophane-2.5HgBr$_2$	119.6(C$_1$) 83.0(C$_{2,5}$) 77.2(C$_{3,4}$) 35.6(CH$_2$CH$_2$)
[2]Ferrocenophane-2.2HgI$_2$	116.7(C$_1$) 81.8(C$_{2,5}$,C$_{3,4}$) 36.3(CH$_2$CH$_2$)
[2]Ferrocenophane-0.5Hg(BF$_4$)$_2$	118.8, 117.3(C$_1$) 81.8, 75.0(C$_{2,5}$, C$_{3,4}$) 34.1(CH$_2$CH$_2$)
[3]Ferrocenophane	86.6(C$_1$) 70.5(C$_{2,5}$, C$_{3,4}$) 36.0(CH$_2$CH$_2$*CH$_2$) 25.4(CH$_2$*CH$_2$CH$_2$*)
[3]Ferrocenophane-6HgCl$_2$	110.7(C$_1$) 78.8—72.6(C$_{2,5}$, C$_{3,4}$) 35.7(CH$_2$CH$_2$*CH$_2$) 24.6(CH$_2$*CH$_2$CH$_2$*)

^{57}Fe-Mössbauer spectrum of the $HgCl_2$ adduct.[12]

It is suggested that an enhanced ligand-to-metal donation of the electrons from the Cp-ring associated with the Fe-Hg or Ru-Hg bond formation should result in a decreased in the electron density around Cp-ring carbons in the adducts, giving the large low-field shift of the Cp-ring observed in the adducts.

Similar Fe-Hg bond formation has also been found for the $HgCl_2$ adduct of methylferrocene. Methylferrocene reacts with $HgCl_2$ in diethyl ether and gives an orange-yellow $HgCl_2$ adduct, expressed as methylferrocene-6$HgCl_2$ on the basis of an elemental analysis. The $HgCl_2$ adduct is less stable than the ferrocene-7$HgCl_2$ adduct; i.e., its color changes to green for a few hours at room temperature, suggesting the oxidation of methylferrocene, while the color of the ferrocene-7$HgCl_2$ remains unchanged for a slightly longer period than that of methylferrocene-6$HgCl_2$. Attempts to obtain a clear ^{13}C-CP-MAS NMR spectrum of the methylferrocene-6$HgCl_2$ adduct have been unsuccessful, probably because of the formation of paramagnetic oxidized species. However, an anomalously large Q. S. value (3.02 mm s^{-1} at 78 K) is actually found in the ^{57}Fe-Mössbauer spectroscopy of the methylferrocene- 6$HgCl_2$ adduct. These facts indicate the presence of a less-stable bond formed between the Fe and Hg atoms in the adduct.

The $HgCl_2$ adduct of biferrocene has been found to be much more stable than the ferrocene-7$HgCl_2$ adduct; i.e., its color remains unchanged for more than 200 days upon standing at room temperature.[1] The ^{13}C chemical-shift values of the biferrocene in $CDCl_3$ solution have been found to be δ=83.9 (C_1), 69.2 (C_5H_5), 67.6 ($C_{3,4}$), and 66.4 ($C_{2,5}$), as illustrated in Fig. 2-c. Relatively sharp signals are observed for the biferrocene in the solid state and broader signals for the $HgCl_2$ adduct, as shown in Fig. 2-b. The signals of $C_{2,5}$, $C_{3,4}$, and C_1 of the $HgCl_2$ adduct cannot be well-resolved, being superimposed on the main C_5H_5-ring signal. Therefore, only the low-field shift values of π-C_5H_5 will be discussed. The large low-field shift of the main C_5H_5-ring signal ($\Delta\delta$; 9.0 ppm) is observed and the value is a little smaller than that of ferrocene-7$HgCl_2$ ($\Delta\delta$; 9.9 ppm). The result of ^{13}C-CP-MAS NMR spectroscopy is in line with that of the ^{57}Fe-Mössbauer study; i.e., the Q. S. value of the biferrocene-2$HgCl_2$ adduct (2.93 mm s^{-1} at 78 K) is a little smaller than that of the ferrocene-7$HgCl_2$ adduct (3.09 mm s^{-1} at 80 K).[12] Both results indicate that the chemical bond between the Fe and Hg atoms in the biferrocene-2$HgCl_2$ adduct is slightly weaker than that of

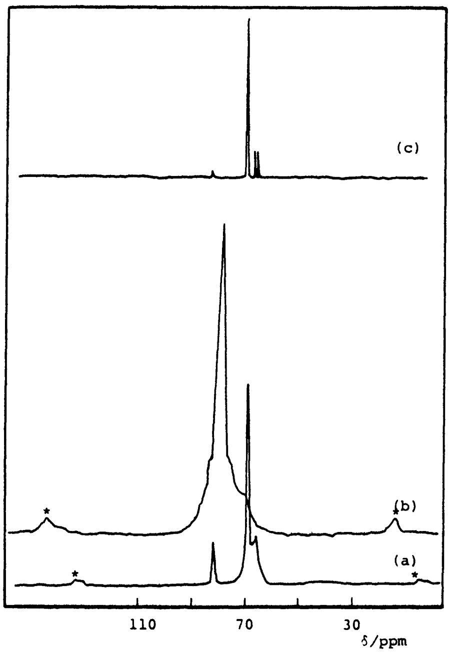


Fig. 2. ^{13}C-CP-MAS NMR spectra of biferrocene(a), its 2$HgCl_2$(b) adduct, and ^{13}C NMR spectrum of biferrocene(c) in chloroform solution.

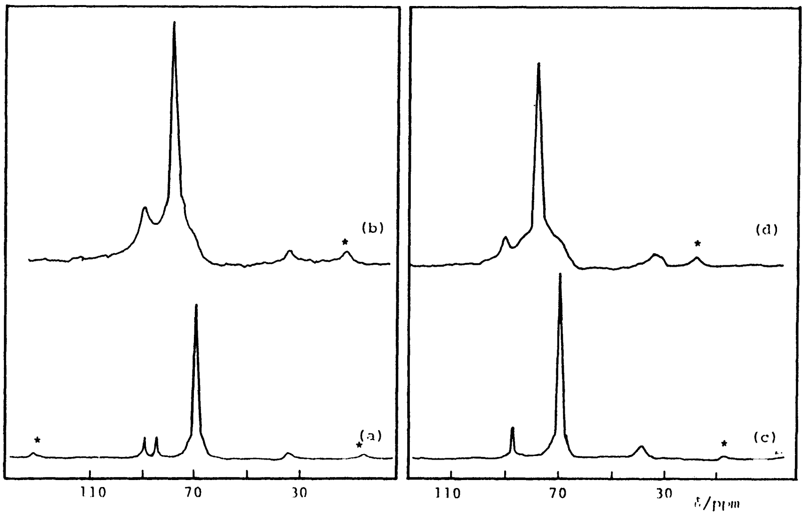


Fig. 3. ^{13}C-CP-MAS NMR spectra of diferrocenylmethane(a), its 6$HgCl_2$(b), 1,2-diferrocenylethane(c), and its 6$HgCl_2$(d) adduct.

the ferrocene-7$HgCl_2$ adduct. One of the possible explanations for the much larger stability of the biferrocene-2$HgCl_2$ adduct, than the ferrocene-7$HgCl_2$ adduct, can be given by assuming that biferrocene reacts with a mercury(II) atom as a chelating agent, such as $[(C_5H_5)(\overline{C_5H_4)Fe \rightarrow HgCl_2 \leftarrow Fe(C}_5H_4)(C_5H_5)]$.

Similar large Q. S. components (3.02 and 3.00 mm s^{-1} both at 78 K) have been observed for diferrocenylmethane-6$HgCl_2$ and 1,2-diferrocenylethane-6$HgCl_2$ adducts, respectively,[2] suggesting a chemical bond formation between the Fe and Hg atoms in the adducts. Slightly smaller but similar $\Delta\delta$ values of the Cp-rings have been observed ($\Delta\delta$; 8.8 and 8.4 ppm for the $HgCl_2$ adducts of diferrocenylmethane and 1,2-diferrocenylethane, respectively) compared with the value for biferrocene-2$HgCl_2$ adduct ($\Delta\delta$; 9.0 ppm). The slightly smaller $\Delta\delta$ values of these Cp-rings may be expected for a slightly weaker bond between the Fe and Hg atoms in the adducts. Changes in the color of the diferrocenylmethane and 1,2-diferrocenylethane-6$HgCl_2$ adducts from orange-yellow to blue-green within several days at room temperature after preparation also suggest a less-stable Fe-Hg bond formation.

All of the above-mentioned results lead us to the conclusion that there is a direct interaction between the Fe and Hg atoms in the $HgCl_2$ adducts of ferrocene, methylferrocene, biferrocene, diferrocenylmethane, and 1,2-diferrocenylethane. The smaller stability of the adducts of diferrocenylmethane and 1,2-diferrocenylethane, compared with that of biferrocene-2$HgCl_2$ adduct, may be ascribed to a larger distance between the Fe-Fe atoms for chelation in the adducts.

Table 2. ^{57}Fe-Mössbauer Parameters of Ferrocene Derivatives and Their Mercury(II) Salt Adducts

Compound	Temperature K	Q. S. mm s^{-1}	I. S. mm s^{-1}
Ferrocene	78	2.41	0.52
Ferrocene-7$HgCl_2$[a)]	80	3.09	0.53
Methylferrocene	78	2.42	0.52
Methylferrocene-6$HgCl_2$	78	3.02	0.50
Biferrocene	78	2.33	0.53
Biferrocene-2$HgCl_2$	78	2.93	0.55
Diferrocenylmethane	78	2.38	0.52
Diferrocenylmethane-6$HgCl_2$	78	3.02	0.53
1,2-Diferrocenylethane	78	2.40	0.50
1,2-Diferrocenylethane-6$HgCl_2$	78	3.00	0.50
[2]Ferrocenophane	78	2.41	0.49
	300	2.34	0.42
[2]Ferrocenophane-3$HgCl_2$	78	3.29	0.49
[2]Ferrocenophane-2.5$HgBr_2$	78	3.08	0.52
[2]Ferrocenophane-2.2HgI_2	78	3.12	0.52
[2]Ferrocenophane-0.5$Hg(BF_4)$	78	3.11	0.53
	300	3.10	0.46
[3]Ferrocenophane	78	2.29	0.52
[3]Ferrocenophane-6$HgCl_2$	78	2.93	0.53

a) Date was taken from Ref. 12.

As mentioned in the introduction, [2]ferrocenophane gives stable adducts with some Lewis acids. The adducts were investigated by means of the same methods used for the binuclear ferrocene derivative-Lewis acid adducts for the sake of comparison. Slightly smaller Q. S. values for [2]ferrocenophane-HgX_2 (3.08 and 3.12 mm s^{-1} at 78 K for $HgBr_2$ and HgI_2, respectively) than the value of the $HgCl_2$ adduct (3.29 mm s^{-1} at 78 K) were found, but these values are much larger than the value of [2]ferrocenophane itself (2.41 mm s^{-1} at 78 K), as can be seen in Table 2. These facts indicate the presence of a stable bond between the Fe and Hg atoms in the $HgBr_2$ and HgI_2 adducts, as in the case of the $HgCl_2$ adduct.

The ^{13}C chemical shift values of [2]ferrocenophane in $CDCl_3$ were found to be δ=91.2 (C_1), 72.2 ($C_{2,5}$), 67.9 ($C_{3,4}$), and 33.7 (CH_2CH_2). The assignment of the carbon signals was made by using the same method as that in the case of biferrocene on the basis of the results of [n]ferrocenophane (n=1,2) derivatives.[13] Relatively sharp signals have been found for [2]ferrocenophane and broader signals for the HgX_2 adducts in the solid state. The ^{13}C chemical-shift values of $C_{2,5}$ and $C_{3,4}$ for the $HgCl_2$ adduct (δ=78.6) are almost the same as those of the $HgCl_2$ adducts of ferrocene (δ=79.7) and biferrocene (δ=79.7). One of the most striking features is the low-field shift value of the C_1 signal (about $\Delta\delta$; 21.6) in the adduct. This value is anomalously large in com-

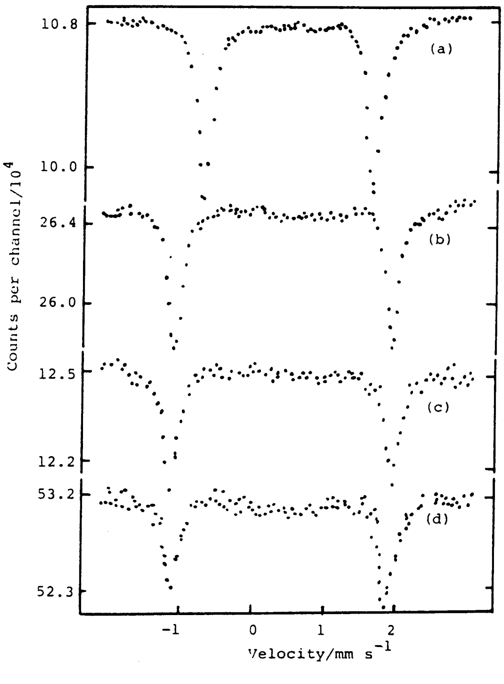


Fig. 4. ^{57}Fe-Mössbauer spectra of [2]ferrocenophane(a), its 2.5$HgBr_2$(b), 2.2HgI_2(c) adducts, and [3]ferrocenophane-6$HgCl_2$(d) adducts.

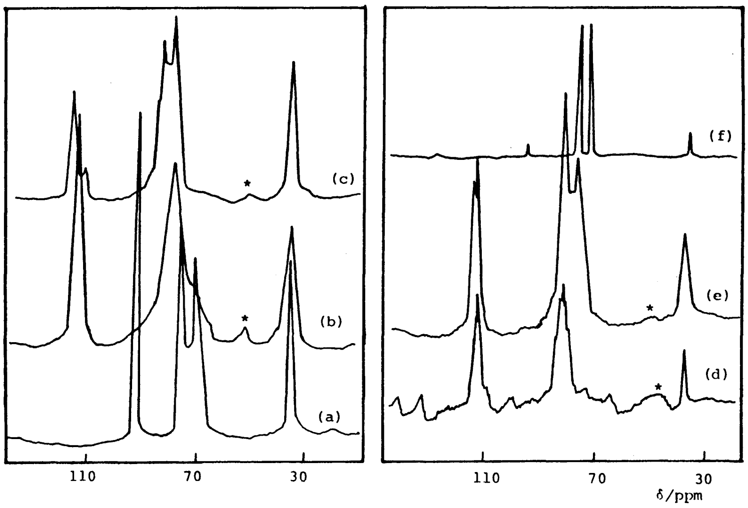


Fig. 5. ^{13}C-CP-MAS NMR spectra of [2]ferrocenophane(a), its $3HgCl_2$(b), $2.5HgBr_2$(c), $2.2HgI_2$(d), $0.5Hg(BF_4)_2$(e) adducts, and ^{13}C NMR spectrum of [2]ferrocenophane(f) in chloroform solution.

parison with the values of most adducts of ferrocene and ruthenocene derivative; i.e., most low-field shift values of the $HgCl_2$ adducts of ferrocene and ruthenocene derivatives are within the range 8.0 to 10.0 ppm.[7] Anomalously large low-field shifts of the C_1 signal were also observed for other [2]ferrocenophane-$2.5HgBr_2$ and -$2.2HgI_2$ adducts ($\Delta\delta$; 27.0 and 24.1 ppm, respectively). Moreover, the splittings (δ=118.8 and 117.3) and large low-field shifts of the C_1 signal ($\Delta\delta$; 26.2 and 24.7 ppm), shown in Fig. 5-f for a [2]ferrocenophane-$0.5Hg(BF_4)_2$ adduct, suggest the presence of two kinds of conformations of the Cp rings in the $Hg(BF_4)_2$ solid adduct.

A large low-field shift of the C_1 signal was also observed in the [3]ferrocenophane-$6HgCl_2$ adduct. [3]Ferrocenophane gives a less stable $HgCl_2$ adduct than the adduct of [2]ferrocenophane in a reaction with $HgCl_2$ in diethyl ether; i.e., the color of the [3]ferrocenophane-$6HgCl_2$ adduct was found to change to green within several days at room temperature. A slightly smaller Q. S. value of the $HgCl_2$ adduct (2.93 mm s^{-1} at 78 K) than the value of the [2]ferrocenophane-$3HgCl_2$ adduct (3.29 mm s^{-1} at 78 K) was found using ^{57}Fe-Mössbauer spectroscopy; however, this value (2.93 mm s^{-1}) is much larger than the value for [3]ferrocenophane, itself (2.29 mm s^{-1}). This fact suggests that the bond formed between the Fe and Hg atoms is weaker than the bond of the [2]ferrocenophane-$3HgCl_2$ adduct, as in the case of the ferrocenophane-$7HgCl_2$ adduct. The reason why [3]ferrocenophane forms a less-stable adduct with $HgCl_2$ has been interpreted on the basis of the fact that the Cp-rings in [3]ferrocenophane are only slightly inclined (ca. 9°) from each other;[14] i.e., the Fe-Hg bond is less stabilized by an increased steric hindrance of Cp-rings, while the Cp-rings in [2]ferrocenophane are greatly tilted (22.2°) from each other.[15] Relatively sharp signals (δ=86.6, 70.5, 36.0, and 25.4) have been found for [3]ferrocenophane and three broader signals (δ=78.8—72.6 for $C_{2,5}$ and $C_{3,4}$; δ=35.7 and 24.6 for methylene group's carbon) and a relatively strong, sharp signal (δ=110.7 for C_1) have been observed in the $HgCl_2$ adduct, as illustrated in Fig. 6. The spectral line shape and position of the methylene group in the [3]ferrocenophane-$6HgCl_2$ adduct correspond to those of [3]ferrocenophane, itself; however, those of the Cp-rings are much different from those of [3]ferrocenophane.

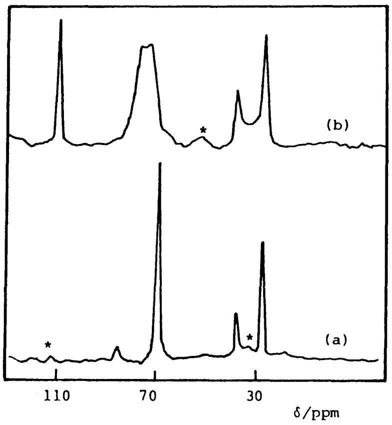


Fig. 6. ^{13}C-CP-MAS NMR spectra of [3]ferrocenophane(a) and its $6HgCl_2$(b) adduct.

The $\Delta\delta$ values (26.0—24.0) of the C_1 signal in [n]ferrocenophane (n=2,3) adducts with Hg(II) are much larger than the values of the ferrocenylmethane and 1,2-diferrocenylethane adducts with Hg(II). The structural distortion at the C_1 atoms of the [2]ferrocenophane-$n$$HgX_2$ (X=Cl, Br, I, and BF_4) and [3]ferrocenophane-$6HgCl_2$ adducts, caused by Fe-Hg bond formation, may be responsible for the large $\Delta\delta$ values in the C_1 signal in the [n]ferrocenophane adducts, although further structural investigations are required in order to confirm these conclusions.

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