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^{57}Fe-Moessbauer and ^{13}C-CP-MAS NMR Spectroscopic Studies of the Reaction Products of Ruthenocene Derivatives with Lewis Acids

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Adducts of ruthenocene with Lewis acids, such as $HgCl_2$, $SnCl_4$, and I_2, are studied mainly by means of high resolution solid state ^{13}C NMR spectroscopy and ^{57}Fe-Moessbauer spectroscopy. The large low-field shifts found in the ^{13}C-CP-MAS NMR spectroscopy suggest the presence of a direct chemical bond between the ruthenium and the Lewis acids. Ferrocenylruthenocene and biruthenocene give stable adducts with $HgCl_2$ and I_2. ^{57}Fe-Moessbauer and ^{13}C-CP-MAS NMR spectroscopic studies suggest the presence of a chemical bond, such as Ru–Hg, Ru–I, in the adducts.

The basicity of the nonbonding e_{2g} electrons around the iron and ruthenium atoms in ferrocene and ruthenocene derivatives respectively has been studied in the reaction of ferrocene and ruthenocene derivatives with protons in a solution, such as $CHCl_3$, CX_3COOH (X=Cl, F), and H_2SO_4.[1,2] Especially, [2]ferrocenophanes react with an appropriate Lewis acid species, such as $HgCl_2$, $SnCl_4$, and I_2, to give diamagnetic stable adducts with a direct chemical bond between the iron atom and the Lewis acids.[3–5] Ruthenocene also reacts with the Lewis acids and it gives much more stable adducts than ferrocene because ruthenocene has less steric hindrance in donating e_{2g} electrons than does ferrocene. Although [2]ferrocenophane and ruthenocene are well-soluble in most organic solvents, the adducts are less soluble in the solvents. Thus far, all attempts to obtain a single crystal of [2]ferrocenophane-$3HgCl_2$ and -$1.5SnCl_4$ have been unsuccessful, while a few adducts, such as ruthenocene-$3HgCl_2$ and -$1.8HgBr_2$, [2]ferrocenophane-$2I_2$, were obtained as single crystals in which direct metal-metal chemical bonds (Ru–Hg and Fe–I respectively) have been found on the basis of the results of X-ray diffraction studies.[5,6]

Recently, improvements in sensitivity, in the resolution in cross-polarization (CP), in dipolar decoupling, and in magic-angle-spinning (MAS) techniques have made it possible to obtain a high-resolution ^{13}C NMR spectrum, even in the solid state.[7–10] The present studies were undertaken to clarify the structure of some ruthenocene derivative-Lewis acid adducts, such as $HgCl_2$, $SnCl_4$, and I_2, by means of ^{57}Fe-Moessbauer and high-resolution ^{13}C-CP-MAS NMR spectroscopy.

Experimental

Materials: The ferrocenylruthenocene was prepared by the Ullmann coupling of bromoruthenocene and bromoferrocene, instead of iodoruthenocene and iodoferrocene, at 120 °C for 12 h.[11] Biruthenocene was prepared by the same method using bromoruthenocene. ^{1}H NMR ($CDCl_3$); δ=4.79(t)($H_{2,5}$), 4.54(t)($H_{3,4}$), 4.44(s)(π-C_5H_5) for the ruthenocene group, δ=4.23(t)($H_{2,5}$), 4.09(t)($H_{3,4}$), 4.05(s)(π-C_5H_5) for the ferrocene group in ferrocenylruthenocene, δ=4.69(t)($H_{2,5}$), 4.47(t)($H_{3,4}$) and 4.50(s)(π-C_5H_5) for biruthenocene. Ferrocenyl ruthenocenyl ketone was prepared by following the previously reported method.[12] The purity of the metallocenes was confirmed by elemental analysis. Adducts of ruthenocene with $HgCl_2$, $SnCl_4$, and I_2 were prepared by following the methods in the previous reports.[6,13,14] Adducts of ferrocenylruthenocene, biruthenocene, and ferrocenyl ruthenocenyl ketone with $HgCl_2$ were prepared in diethyl ether by a method similar to that used in the case of the ruthenocene-$3HgCl_2$ adduct. Found: C, 14.17; H, 1.27%. Calcd for ferrocenylruthenocene-$5HgCl_2$, $C_{20}H_{18}FeRu$-$5HgCl_2$: C, 13.55; H, 1.07%. Found: C, 17.02; H, 1.48%. Calcd for biruthenocene-$3.5HgCl_2$, $C_{20}H_{18}Ru_2$-$3.5HgCl_2$: C, 17.02; H, 1.29%. Found: C, 18.01; H, 1.50%. Calcd for ferrocenyl ruthenocenyl ketone-$3.5HgCl_2$, $C_{21}H_{18}OFeRu$-$3.5HgCl_2$: C, 18.10; H, 1.30%, respectively. Adducts of ferrocenylruthenocene and biruthenocene with I_2 were prepared by mixing I_2 with the metallocenes in a dry benzene–hexane mixture. Found: C, 26.00; H, 1.91%. Calcd for ferrocenylruthenocene-$2I_2$, $C_{20}H_{18}FeRu$-$2I_2$: C, 26.03; H, 1.97%. Found: C, 24.88; H, 1.98%. Calcd for biruthenocene-$2I_2$, $C_{20}H_{18}Ru_2$-$2I_2$: C, 24.81; H, 1.87%.

Measurements: The ^{13}C-CP-MAS NMR spectra were obtained at the frequency of 50.18 MHz using a JEOL FX-200 Fourier Transform NMR Spectrometer. Four thousands datum points at a sweep width setting of 20 kHz were collected by following a spin-locking cross-polarization sequence. Both the ^{1}H- and ^{13}C-rf field strengths were 50 kHz. Magic angle sample spinning rates of 3 to 3.5 kHz were achieved by using Kel-F rotors. The chemical shifts were measured with respect to external adamantane and then converted to the shifts from TMS. The ^{1}H and ^{13}C NMR spectra in solution were measured with the same spectrometer at 199.56 and 50.18 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.

The ^{57}Fe-Moessbauer spectroscopic measurements were carried out by using a ^{57}Co(Rh) source moving in a constant acceleration mode. All the isomer-shift (I. S.) values for the ^{57}Fe-Moessbauer spectra are given relative to metallic iron; the experimental errors of the I. S. and quadrupole-splitting (Q. S.) values are estimated to be within ± 0.02 mm s^{-1}.

Results and Discussion

Figure 1 shows the ^{13}C-CP-MAS NMR spectra of the ruthenocene (a) and its -3HgCl$_2$(b), -1.5SnCl$_4$(c), and -2I$_2$(d) adducts; the ^{13}C chemical-shift (δ) values of the adduct and related compounds are listed in Table 1. The π-C$_5$H$_5$ ring carbon signal in the ruthenocene appears at δ=73.2, and its adducts, at δ=81.2, 89.1, and 93.4 for the -3HgCl$_2$, -1.5SnCl$_4$, and -2I$_2$ adducts, respectively. These large low-field shifts ($\Delta\delta$=8.0, 15.9, and 20.2 for the -3HgCl$_2$, -1.5SnCl$_4$, and -2I$_2$ adducts respectively) can be attributed to the Ru–Hg, Ru–Sn, and Ru–I bond formation in the adducts as has already been verified by means of X-ray-diffraction[6,13] and ^{119}Sn-Moessbauer spectroscopic studies.[4] The increasing values of the low-field shift in the Lewis acid adducts suggest that the interaction between the ruthenocene and the Lewis acids increases in the order of HgCl$_2$<SnCl$_4$<I$_2$. As has previously been mentioned, [2]ferrocenophane–Lewis acid adducts give large Q. S. values (3.29, 3.49, and 3.65 mm s^{-1}, for the -3HgCl$_2$, -1.5SnCl$_4$, and -2I$_2$ adducts, respectively) in their ^{57}Fe-Moessbauer spectra.[3–5] The fact that the order of the increase in

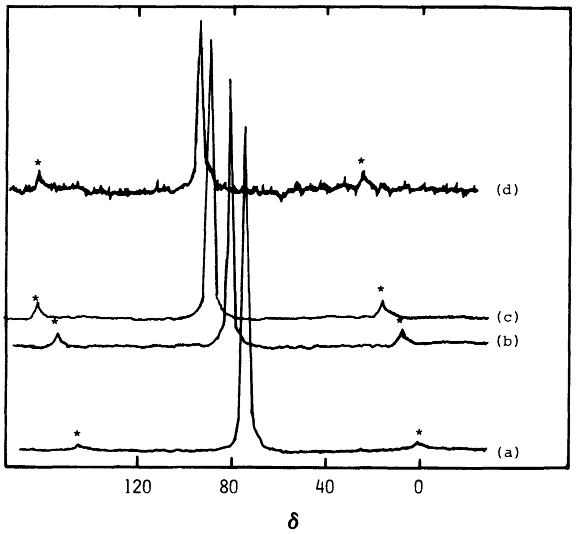


Fig. 1. ^{13}C-CP-MAS NMR spectra of the ruthenocene (a) and its -3HgCl$_2$(b), -1.5SnCl$_4$(c), and -2I$_2$ (d) adducts.
The sample spinning side band (SSB) is represented by * in the Figure.

Table 1. ^{13}C Chemical-Shifts of Ruthenocene and Related Compounds in the Solid State and in a Chloroform Solution

Compound	Ruthenocene δ	Ferrocene δ	
Ruthenocene	73.2		
Ruthenocene-3HgCl$_2$	81.2		
Ruthenocene-1.5SnCl$_4$	89.1		
Ruthenocene-2I$_2$	93.4		
Ferrocenylruthenocene	88.5(C$_1$) 72.9(π-C$_5$H$_5$)	84.6(C$_1$) 71.3(π-C$_5$H$_5$) 67.9(C$_{2.5}$)	
Ferrocenylruthenocene-3HgCl$_2$	81.4(π-C$_5$H$_5$)	79.1(π-C$_5$H$_5$)	
Ferrocenylruthenocene-2I$_2$	93.6(π-C$_5$H$_5$)	76.5(π-C$_5$H$_5$)	
Biruthenocene	87.5(C$_1$) 72.3(π-C$_5$H$_5$) 69.1(C$_{3.4}$)		
Biruthenocene-3.5HgCl$_2$	81.2(π-C$_5$H$_5$)		
Biruthenocene-2I$_2$	92.9(π-C$_5$H$_5$) 77.4(π-C$_5$H$_5$)		
Ferroceny ruthenocenyl Ketone	86.0(C$_1$) 72.7(π-C$_5$H$_5$)	80.7(C$_1$) 71.3(π-C$_5$H$_5$)	197.9(CO)
Ferrocenyl ruthenocenyl Ketone-3.5HgCl$_2$	81.0(π-C$_5$H$_5$)	72.6(π-C$_5$H$_5$)	195.2(CO)
Ferrocenylruthenocene*	87.9(C$_1$) 71.0(π-C$_5$H$_5$) 69.9(C$_{2.5}$) 69.6(C$_{3.4}$)	83.5(C$_1$) 69.2(π-C$_5$H$_5$) 67.4(C$_{3.4}$) 67.2(C$_{2.5}$)	
Biferrocene*		83.9(C$_1$) 69.2(π-C$_5$H$_5$) 67.6(C$_{3.4}$) 66.4(C$_{2.5}$)	
Biruthenocene*	87.5(C$_1$) 70.9(π-C$_5$H$_5$) 71.3(C$_{2.5}$) 69.6(C$_{3.4}$)		

*: Stands for a CD$_3$Cl solution.

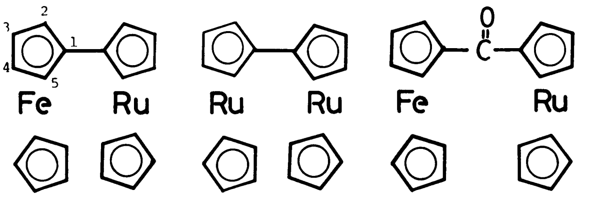
the low-field shifts of the ruthenocene-Lewis acids adducts is similar to that of the Q. S. values of the [2]-ferrocenophane-Lewis acid adducts suggests that the effect of Lewis acids on the ruthenium atoms in ruthenocene is similar to that on the iron atoms in [2]ferrocenophane.

Similar large low-field shifts are also observed for the ^{1}H NMR spectra of the ruthenocene-Lewis acid adducts in CD_3CN. The ^{1}H NMR spectra of the adducts are shown in Fig. 2, while their chemical shift values are summarized in Table 2. The fact that the decreasing shift ($\Delta\delta=1.50$) for the ruthenocene-$2I_2$ adduct is much larger than that of the -$3HgCl_2$ adduct ($\Delta\delta=0.84$), as in the case of the ^{13}C-CP-MAS NMR spectra, shows that the ruthenium atom interacts with the iodine atom more strongly than with the mercury atom in the solution.

Table 2. ^{1}H NMR Chemical-Shifts of Ruthenocene and Related Compounds in Acetonitrile

Compound	Chemical shift δ
Ruthenocene	5.37
Ruthenocene-$3HgCl_2$	6.21
Ruthenocene-$1.5SnCl_4$	5.35
Ruthenocene-$2I_2$	6.87
Biruthenocene	5.53($H_{2,5}$) 5.30($H_{3,4}$) 5.32(π-C_5H_5)
Biruthenocene-$2I_2$	6.90($H_{2,5}$) 6.54($H_{3,4}$) 6.65(π-C_5H_5)

Although the ruthenocene-$2I_2$ and $3HgCl_2$ adducts are stable in acetonitrile, the -$1.5SnCl_4$ adduct is unstable in the solution; i.e., the yellow solution of the -$1.5SnCl_4$ adduct dissociates in acetonitrile, becoming colorless in a few minutes after the dissolution, while the electronic spectrum becomes the same as that of ruthenocene itself. The ^{1}H chemical-shift observed in the ruthenocene-$1.5SnCl_4$ adduct ($\delta=5.35$) in the solution corresponds well to that of the ruthenocene ($\delta=5.37$), also indicating the dissociation of the -$1.5SnCl_4$ adduct in acetonitrile. It seems very reasonable to conclude that the structure of the -$1.5SnCl_4$ adduct can be expressed as $[(C_5H_5)_2Ru\text{-}SnCl_2\text{-}Ru(C_5H_5)_2]^{2+}(SnCl_5^-)_2$, on the basis of the ^{13}C-CP-MAS NMR data, as has already been proposed by Mann et al. based on their infrared spectroscopic study[14] and by us based on our ^{119}Sn-Moessbauer spectroscopic study.[4]



Ferrocenylruthenocene Biruthenocene Ferrocenyl ruthenocenyl ketone

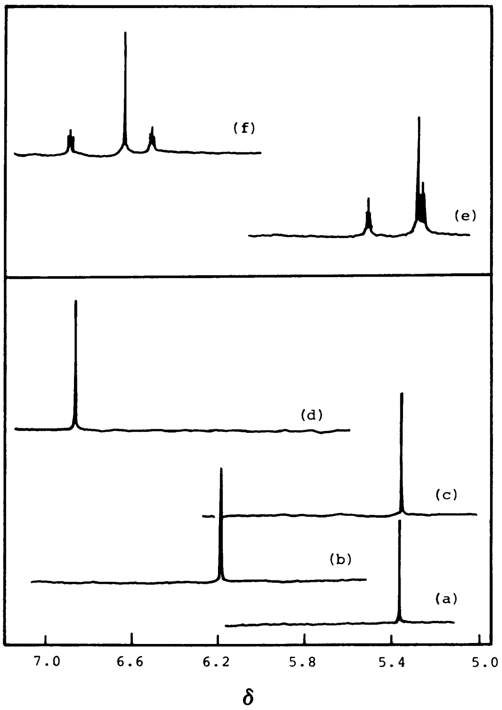


Fig. 2. ^{1}H NMR spectra of the ruthenocene(a), ruthenocene-$3HgCl_2$(b), ruthenocene-$1.5SbCl_4$(c), ruthenocene-$2I_2$(d), biruthenocene(e), biruthenocene-$2I_2$(e) compounds in the acetonitrile solution.

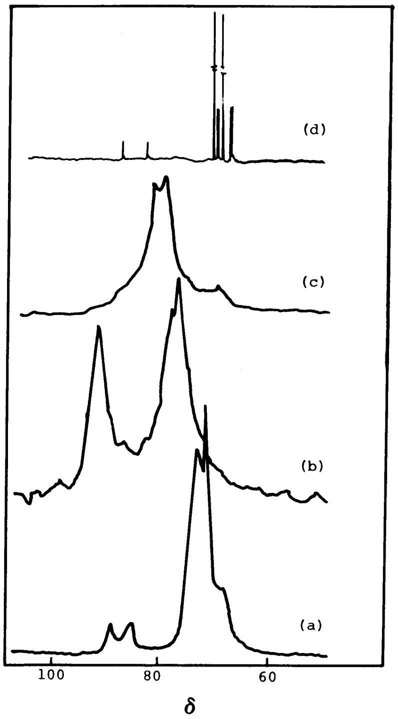


Fig. 3. ^{13}C-CP-NAS NMR spectra of ferrocenylruthenocene(a), and its -$2I_2$(b), -$5HgCl_2$(c) adducts and ^{13}C NMR spectrum of ferrocenylruthenocene(d) in chloroform solution.

Ferrocenylruthenocene was first synthesized by the reaction of the Ullmann coupling of iodoruthenocene with a large excess of iodoferrocene by Neuse in 1981.[11] In the present study, ferrocenylruthenocene is found to react with I_2 and $HgCl_2$ to give stable diamagnetic precipitates, which have been analyzed as ferrocenylruthenocene-$2I_2$ and ferrocenylruthenocene-$5HgCl_2$ adducts.[15] Figure 3 shows the ^{13}C-CP-MAS NMR spectra of the original metallocene(a) and its -$2I_2$(b), -$5HgCl_2$(c) adducts, together with the higher-resolution ^{13}C NMR spectrum of the metallocene in the $CDCl_3$ solution(d).

As is shown in Fig. 3(d), the two groups of resonances for the ferrocene and ruthenocene moieties are separately observed; i.e., the ferrocene signals appear at a higher field than do the ruthenocene signals, and these signals are in good agreement with the ^{13}C NMR spectra of biferrocene and biruthenocene in the same solution, as is shown in Table 1. The carbon signals were assigned by using selective proton decoupling experiments based on the results of previous reports.[11,16]

The broad ^{13}C-CP-MAS NMR spectra of ferrocenylruthenocene(a) cannot, however, be resolved into individual carbon signals. The ^{13}C chemical-shift values of the metallocene in the solid state are shown in Table 1. The signals of $C_{3,4}$ and $C_{2,5}$ for the ruthenocene moiety and of $C_{3,4}$ for the ferrocene moiety are not well resolved, being superimposed on by large and broad π-C_5H_5 signals in the ^{13}C-CP-MAS NMR spectra. Therefore, only the low-field shift values of π-C_5H_5 will be discussed. As is shown in Fig. 3-c, the two broad π-C_5H_5 ring signals (δ=81.4 for the ruthenocene moiety and δ=79.1 for the ferrocene moiety) are found in the ferrocenylruthenocene-$5HgCl_2$ adduct. The former value agrees with the value of the ruthenocene-$3HgCl_2$ adduct (δ=81.2). The observed low-field shifts ($\Delta\delta$=7.8 and 8.5 for the ferrocene and ruthenocene moieties respectively) are similar to that of ruthenocene-$3HgCl_2$ adduct ($\Delta\delta$=8.0). This fact shows the presence of two kinds of direct chemical bondings, Fe–Hg and Ru–Hg, in the -$5HgCl_2$ adduct.

On the other hand, broader signals (δ=93.6 for the ruthenocene moiety and δ=76.5 for the ferrocene moiety) are found for the ferrocenylruthenocene-$2I_2$ adduct (3-b). Although a small low-field shift in the ferrocene moiety ($\Delta\delta$=5.2) is found, a relatively large shift ($\Delta\delta$=20.7) is found for the ruthenocene moiety. The latter value is quite similar to that of the ruthenocene-$2I_2$ adduct ($\Delta\delta$=20.2). These facts indicate that only the ruthenium atom is bound with the iodine atom in the ferrocenylruthenocene-$2I_2$ adduct.

Figure 4 shows the ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene(a) and its -$5HgCl_2$(b), -$2I_2$(c) adducts. An anomalously large Q. S. value (2.99 mm s^{-1} at 78 K) is found in the -$5HgCl_2$ adduct, showing direct chemical Fe–Hg bond formation, while a slightly smaller Q. S. value (2.16 mm s^{-1}) than that of the original metallocene (2.36 mm s^{-1}) is found in the -$2I_2$ adduct. The smaller Q. S. value may be caused by the decreased e_{2g} electrons of the iron atom in the -$2I_2$ adduct containing the Ru–I bond. The absence of a large Q. S. line, as in the case of the -$5HgCl_2$ adduct, shows that the iron atom is not bound to the iodine atom in the ferrocenylruthenocene-$2I_2$ adduct. The ^{57}Fe-Moessbauer results are in

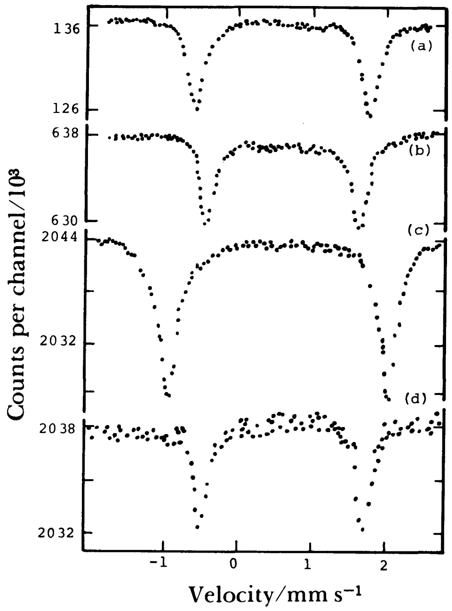


Fig. 4. ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene(a) and its -$2I_2$(b), -$5HCl_2$(c) adducts and ferrocenyl ruthenocenyl ketone-$3.5HgCl_2$ adduct(d), all at 78 K.

Table 3. ^{57}Fe-Moessbauer Parameters of Ferrocenylruthenocene and Related Compounds

Compound	Temperature/K	Q. S./mm s^{-1}	I. S./mm s^{-1}
Ferrocenylruthenocene	78	2.36	0.53
	300	2.29	0.46
Ferrocenylruthenocene-$5HgCl_2$	78	2.99	0.57
Ferrocenylruthenocene-$2I_2$	78	2.16	0.52
	300	2.16	0.43
Ferrocenyl ruthenocenyl ketone	78	2.29	0.54
Ferrocenyl ruthenocenyl ketone-$3.5HgCl_2$	78	2.29	0.54

accordance with those of the ^{13}C-CP-MAS NMR spectroscopic studies of the ferrocenylruthenocene–$2I_2$ and –$5HgCl_2$ adducts. All the results obtained in the present studies indicate that the –$2I_2$ adduct may be expressed as $[(C_5H_5)(C_5H_4)Fe(C_5H_4)(C_5H_5)Ru\text{–}I]^+I_3^-$ in the solid state,[15] which is in accord with the elemental analysis datum.

The –$2I_2$ adduct is found to be unstable; that is, when the adduct is dissolved in acetonitrile, it turns green and an electronic absorption peak characteristic of a ferrocenium (λ_{max}=640 nm) increases rapidly, suggesting that the ferrocene moiety is rapidly oxidized in acetonitrile, giving ferrocenium-type cations. The fact that there is no evidence for Ru–I bond formation in the ferrocenylruthenocene–$2I_2$ adduct in acetonitrile in the studies done by means of ^{1}H and ^{13}C NMR agrees with the magnetic data, which show paramagnetism for the acetonitrile solution of the ferrocenylruthenocene–$2I_2$ adduct.

It is found that the ferrocenylruthenocene–$5HgCl_2$ adduct has two kinds of chemical bonds (Ru–Hg and Fe–Hg), while the ferrocenylruthenocene–$2I_2$ adduct has only a Ru–I bond in the solid state. These results can be explained on the basis of the fact that the van der Waals radius of iodine is much larger than that of the mercury atom. It is known that the Cp-rings are separated by 3.32 Å in ferrocene[17] and by 3.68 Å in ruthenocene.[18] The longer separation between the Cp-rings in the ruthenocene moiety may explain why only the ruthenocene moiety in ferrocenylruthenocene reacts with iodine, giving a stable Ru–I bond, while a ferrocene moiety does not give such a stable bond with an iodine atom bacause of van der Waals repulsion between Cp and the iodine atom.

Biruthenocene reacts with $HgCl_2$ and I_2, giving two stable adducts, analyzed as biruthenocene–$3.5HgCl_2$ and –$2I_2$ respectively. The ^{13}C-CP-MAS NMR spectra of the metallocene(a) and its –$3.5HgCl_2$(b), –$2I_2$(c) adducts are shown in Fig. 5, while the ^{13}C-chemical-shift values are shown in Table 1. A broad signal is found for the –$3.5HgCl_2$ adduct with the chemical-shift value of π-C_5H_5 ring (δ=81.2). This value corresponds to that of the ruthenocene–$3HgCl_2$ adduct (δ=81.2), and the relatively large low-field shift ($\Delta\delta$=8.9) shows the chemical-bond formation between the ruthenium and mercury atoms. These facts indicate that the two ruthenium atoms in the biruthenocene–$3.5HgCl_2$ adduct are bound equivalently to the mercury atoms.

On the other hand, two kinds of broad signals (δ= 92.9 and 77.4) are found for the –$2I_2$ adduct, as is shown in Fig. 5-c. The former value corresponds to that of the ruthenocene–$2I_2$ adduct(δ=93.4), and the latter to that of original biruthenocene itself (δ=72.3). The fact that two kinds of low-field shift values ($\Delta\delta$=20.6 and 5.1) are found indicates that only one of the ruthenium atoms in a biruthenocene molecule is bound with the iodine atom; the adduct may be expressed as $[(C_5H_5)(C_5H_4)Ru(C_5H_4)(C_5H_5)Ru\text{–}I]^+I_3^-$ in the solid state, which is in good agreement with the elemental analysis data.

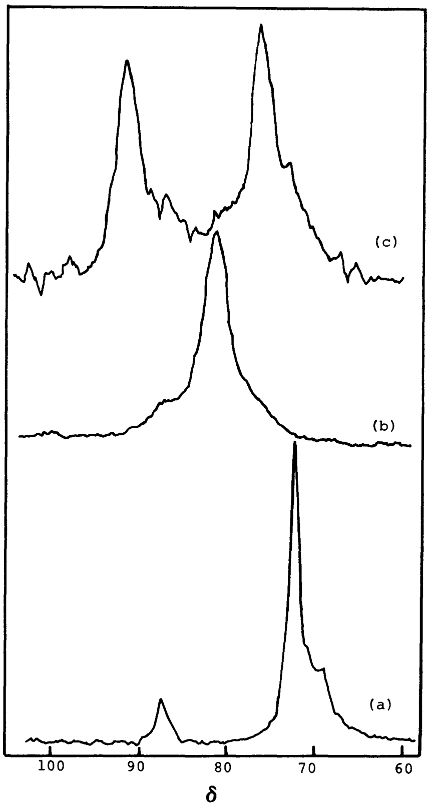


Fig. 5. ^{13}C-CP-MAS NMR spectra of biruthenocene (a) and its –$2I_2$(b), –$3.5HgCl_2$(c) adducts.

Although biruthenocene–$3.5HgCl_2$ is hardly soluble in acetonitrile, the –$2I_2$ adduct is well-soluble in acetonitrile. The ^{1}H NMR spectrum of the adduct is shown in Fig. 2(f), while the ^{1}H chemical-shift values of ruthenocene and biruthenocene in an acetonitrile solution are shown in Table 2. As in the case of the ^{13}C-CP-MAS NMR spectrum, large low-field shifts are found in the ^{1}H NMR spectra of the iodine adducts of the metallocenes in the acetonitrile. The smaller low-field shift of the Cp ring's ^{1}H chemical-shift of the biruthenocene–$2I_2$ adduct ($\Delta\delta$=1.33) compared to that of ruthenocene–$2I_2$ ($\Delta\delta$=1.50) was observed. The fact that the chemical states of the two ruthenocene moieties of the –$2I_2$ adduct are equivalent in the solution, while the chemical states are different in the solid state, suggests the possibility of a rapid exchange of the iodine between the two ruthenium atoms, $[Ru(C_5H_5)(C_5H_4)(C_5H_4)(C_5H_5)Ru\text{–}I]^+I_3^- \rightleftharpoons [I\text{–}Ru\text{–}(C_5H_5)(C_5H_4)\text{–}(C_5H_4)(C_5H_5)]Ru]^+I_3^-$, in acetonitrile.

Ferrocenyl ruthenocenyl ketone was first prepared by Rausch et al. by means of the reaction of ferrocenyl chloride with ruthenocene in the presence of aluminum chloride.[12] Ferrocenyl ruthenocenyl ketone is one of the most suitable compounds for the present studies. Recently, Clemance et al. have reported that diacetylferrocene reacts with a Lewis acid species, such as $AlCl_3$, $SnCl_4$, or $TiCl_4$, to give adducts. All the adducts show smaller Q. S. values (2.10—2.05 mm s^{-1} at 78 K) than the value of the original diacetylferrocene (2.14 mm s^{-1} at 78 K).[19] The results of the ^{57}Fe-Moessbauer spectroscopic studies indicate the absence of chemical bonding between the iron atom and the central metal atom of the Lewis acids, and it has been proposed that the central metal atoms of the Lewis acids are bound to the carbonyl oxygen atoms in the adducts.[19]

Ferrocenyl ruthenocenyl ketone reacts with $HgCl_2$ under the same conditions as those used in the preparation of the ferrocenylruthenocene–$5HgCl_2$ adduct, giving a stable diamagnetic adduct, expressed as ferrocenyl ruthenocenyl ketone-$3.5HgCl_2$ on the basis of the elemental analysis. The color of the adduct is purple, although most $HgCl_2$ adducts with ruthenocene or ferrocene derivatives are yellow or orange respectively. The ^{57}Fe-Moessbauer parameters of the adduct (I. S.=0.54 mm s^{-1}, Q. S.=2.29 mm s^{-1} at 78 K) are the same as those of the original ferrocenyl ruthenocenyl ketone, as is shown in Table 3 and Fig. 4(d). These facts suggest that there is no direct interaction between the mercury and iron atoms in the adduct.

The ^{13}C-CP-MAS NMR spectra of the metallocene(a) and its -$3.5HgCl_2$(b) adduct are shown in Fig. 6, while and the ^{13}C chemical-shift values of the metallocene and its adducts are shown in Table 1. The signals of $C_{2,5}$ and $C_{3,4}$ are overlapped with the π-C_5H_5 ring main peaks. Two kinds of broad signals (δ=81.0 for ruthenocene and δ=72.6 for ferrocene) are found for the -$3.5HgCl_2$ adduct. The latter value is very similar to that of the original compound ($\Delta\delta$=0.9), whereas a relatively large low-field shift is observed for the former ($\Delta\delta$=8.3), its value corresponding to that of ruthenocene-$3HgCl_2$ ($\Delta\delta$=8.0). The carbonyl carbon signal appears at δ=195.2. This value is almost the same as that of the original metallocene (δ=197.9). The infrared spectrum for the original metallocene shows a strong band at 1610 cm^{-1} which can be assigned to a C=O stretching mode; this band is almost the same in position and intensity as that of the -$3.5HgCl_2$ adduct (1600 cm^{-1}). These facts indicate that there is only one kind of chemical bonding between the ruthenium and mercury atoms in the -$3.5HgCl_2$ adduct.

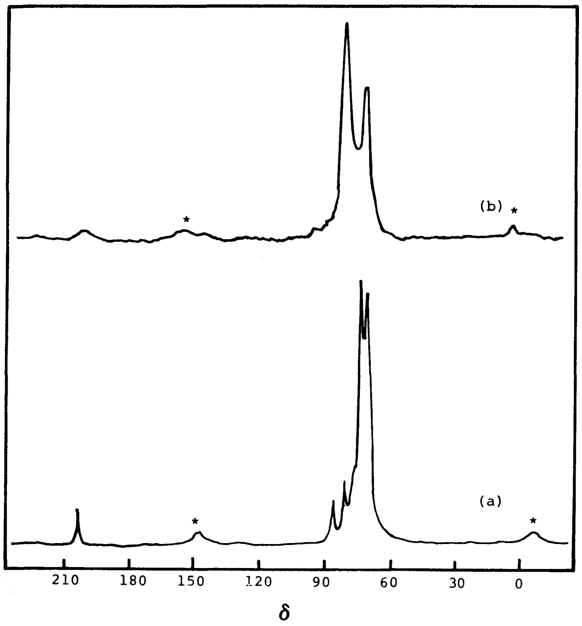


Fig. 6. ^{13}C-CP-MAS NMR spectra of ferrocenyl ruthenocenyl ketone(a) and its -$3.5HgCl_2$ adduct(b).

The absence of the chemical bonding between the iron and mercury atoms in the $HgCl_2$ adduct can be explained as follows; the steric hindrance in the ferrocene moiety makes it impossible to form a chemical bond between the iron and mercury atoms in the -$3.5HgCl_2$ adduct, whereas the ruthenocene moiety can form a chemical bond between the ruthenium and mercury atoms because it has less steric hindrance.

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