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⁵⁷Fe-MOESSBAUER AND ¹³C-CP-MAS NMR SPECTROSCOPIC STUDIES OF REACTION PRODUCTS OF FERROCENYL RUTHENOCENE WITH LEWIS ACIDS

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Abstract Adducts of ferrocenylruthenocene (I), ferrocenylruthenocenylnmethane (II) and biruthenocene (III) with Lewis acids were studied by means of ¹³C-CP-MAS NMR and ⁵⁷Fe- and ¹¹⁹Sn-Moessbauer spectroscopies. Large low-field shifts found in the ¹³C-CP-MAS NMR and large quadrupole splittings (Q. S.) found in the ⁵⁷Fe-Moessbauer and covalently bonded tin(IV) species found in the ¹¹⁹Sn-Moessbauer spectroscopic studies on the adducts suggest the presence of a direct chemical bonding between the central metal atoms in the metallocenes and the Lewis acids.

Keywords: Ferrocenylruthenocene, Lewis Acids

INTRODUCTION

It has recently been shown in our previous reports that ferrocenylruthenocene reacts with Lewis acids, such as HgCl₂, SnCl₄, I₂, giving diamagnetic stable adducts. ⁵⁷Fe-Moessbauer spectroscopic studies of the adducts show that an anomalously large Q. S. value is found for the HgCl₂ adduct, whereas relatively smaller Q. S. values than that of ferrocenylruthenocene are found for the I₂ and SnCl₄ adducts.¹⁻³ The results indicate a direct bond formation between the Fe and Hg atoms in the HgCl₂ adduct but no bond formation in the case of I₂ and SnCl₄ adducts. The question, however, has remained whether the Ru atoms of ferrocenylruthenocene could be ligated to the Lewis acid (Hg²⁺, I⁺ and Sn⁴⁺) as in the case of ruthenocene-Lewis acid adducts,⁴ because of lack of Moessbauer spectroscopic information on Ru atoms. Present studies

aim to provide information on the chemical state of metal atoms by means of ^{57}Fe -Moessbauer and ^{13}C -CP-MAS NMR spectroscopies.

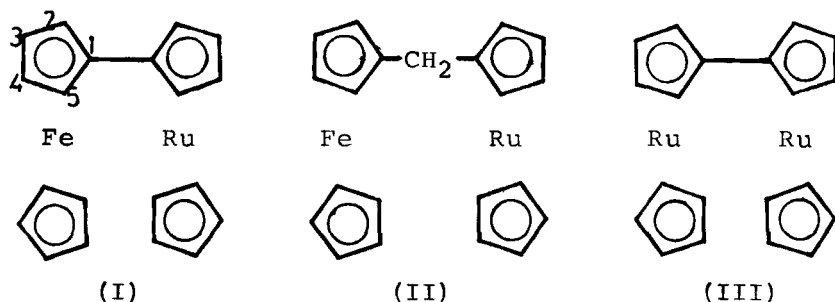
2. EXPERIMENTAL

The reaction products of ferrocenylruthenocene, ferrocenylruthenocenylmethane and biruthenocene with HgCl_2 , SnCl_4 and I_2 were prepared by the methods reported previously.¹⁻³ ^{13}C -CP-MAS NMR spectra were obtained at the same conditions as in the case of previous report.⁵ Chemical shifts were measured with respect to external adamantane and were converted to the shifts from TMS. The assignments of the ^{13}C signals of the metallocenes were carried out using the proton decoupling experiments.

^{57}Fe -Moessbauer spectroscopic measurements were carried out using a $^{57}\text{Co}(\text{Rh})$ source moving in a constant acceleration mode, while ^{119}Sn -Moessbauer spectra were measured against a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source. The isomer shift (I. S.) value for ^{57}Fe was taken with respect to metallic iron and that for ^{119}Sn was described with respect to a BaSnO_3 absorber. The experimental error of the I. S. and Q. S. values was estimated within $\pm 0.02 \text{ mm s}^{-1}$.

3. RESULTS AND DISCUSSION

It has been already reported that ferrocenylruthenocene reacts with HgCl_2 , SnCl_4 and I_2 , giving diamagnetic precipitates which are analyzed as ferrocenylruthenocene- 5HgCl_2 , $-2.5\text{SnCl}_4(\text{H}_2\text{O})$ and -2I_2 , respectively. Figure 1 shows ^{57}Fe -



Moessbauer spectra of ferrocenylruthenocene (a) and its adduct with 5HgCl₂(b), 2.5SnCl₄(H₂O) (c) and 2I₂ (d), and ferrocenylruthenocenylnmethane (e) and its reaction products with HgCl₂ (f) and I₂ (g). Although a large Q. S. value (2.99 mm s⁻¹ at 78 K) is found in the HgCl₂ adduct showing direct chemical bond formation between the Fe and Hg atoms, relatively smaller values (2.25 and 2.16 mm s⁻¹ for the SnCl₄ and I₂ adducts, respectively, both at 78 K) than that of ferrocenylruthenocene (2.36 mm s⁻¹ at 78 K) are observed in the ⁵⁷Fe-Moessbauer spectroscopic studies showing no bond formation between the Fe and Sn or I atoms.

Figure 2 shows ¹³C-CP-MAS NMR spectra of the ferrocenylruthen-

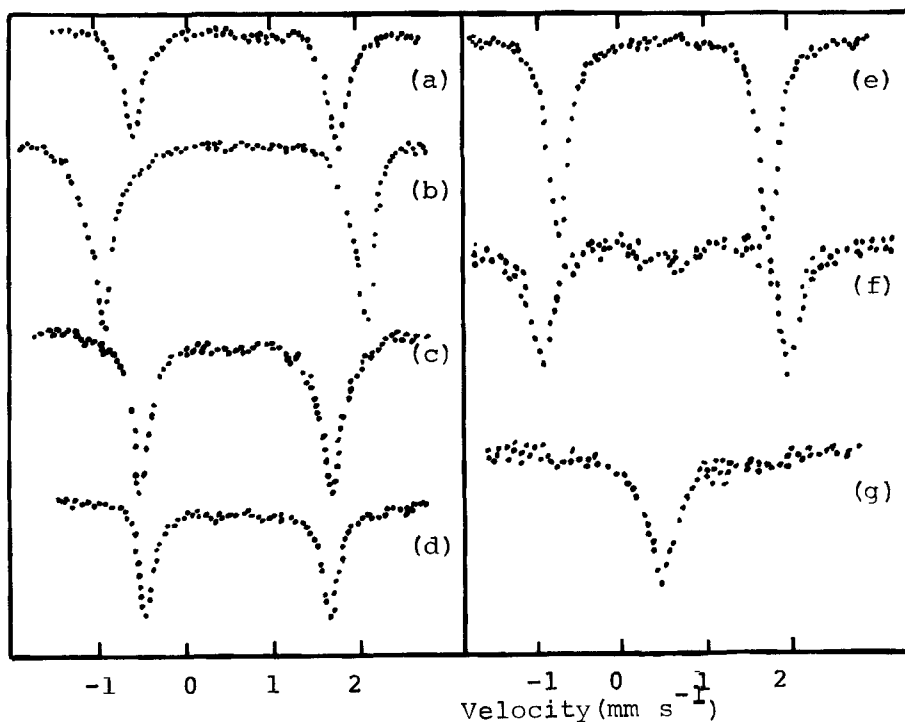


FIGURE 1 ⁵⁷Fe-Moessbauer spectra of (I) (a) and its HgCl₂ (b), SnCl₄ (c), I₂ (d) adducts and (II) (e) and reaction products of (II) with HgCl₂ (f) I₂ (g), all at 78 K.

nocene (a) and its adducts with 5HgCl_2 (b) and 2I_2 (c). The peaks were assigned based on the results of ^{13}C -NMR spectroscopy on the starting material in CDCl_3 . ^{13}C -chemical shift values of ferrocenylruthenocene (a) giving two main peaks are found to be 72.9 ppm for ruthenocene and 71.3 ppm for ferrocene moieties. The values of 88.5 and 84.6 ppm are assigned to C_1 atoms of ruthenocene and ferrocene, respectively. Although the values of $\text{C}_{2,5}$ and $\text{C}_{3,4}$ are found to be 69.9 and 69.6 ppm for ruthenocene and 67.2 and 67.4 ppm for ferrocene moiety in CDCl_3 in the present studies, respectively, these peaks are hidden in the Cp-ring's main peaks in the solid state. Therefore, only the low-field shift values of Cp-ring carbon are discussed.

The Cp-ring's chemical shift values of the ferrocenylrutheno-

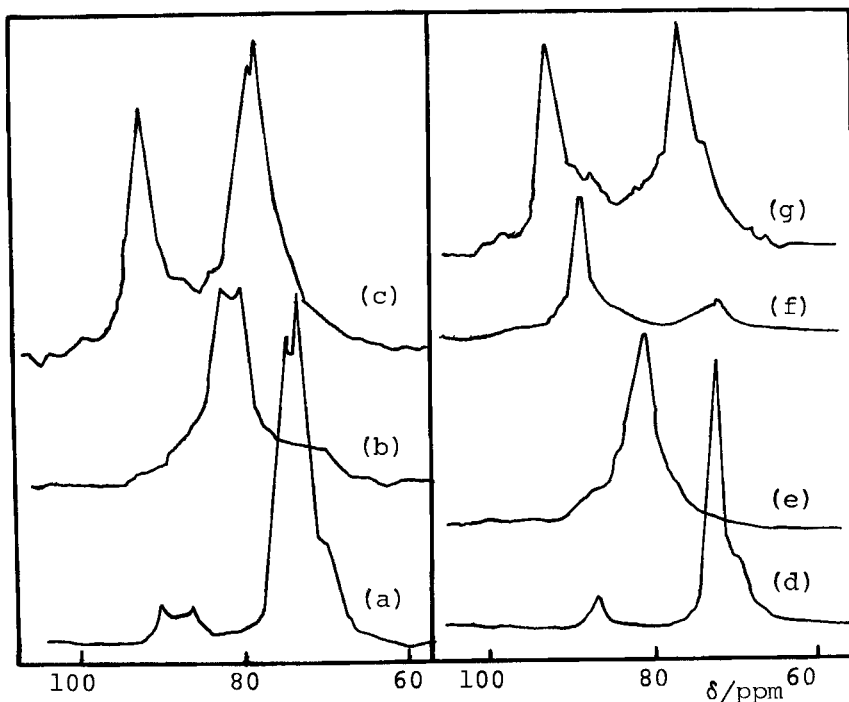


FIGURE 2 ^{13}C -CP-MAS NMR spectra of (I) (a) and its HgCl_2 (b), I_2 (c) and (III) (d), its HgCl_2 (e), SnCl_4 (f), I_2 (g) adducts.

cene-5HgCl₂ adduct are found to be 81.4 ppm for ruthenocene and 79.1 ppm for ferrocene moieties, decreasing by 8.5 and 7.8 ppm from the values of 72.9 and 71.3 ppm, respectively. The low-field shift value of ruthenocene moiety (8.5 ppm) is in good agreement with the value of ruthenocene-3HgCl₂ adduct (8.0 ppm)⁵ but the value of ferrocene moiety (7.8 ppm) is slightly smaller than that of ferrocene-7HgCl₂ (9.9 ppm) in the present studies. This fact suggests that the interaction between the Fe and Hg atoms in ferrocenyl-ruthenocene-5HgCl₂ is slightly smaller than that in ferrocene-7HgCl₂. The conclusion is well supported by the results of the ⁵⁷Fe-Moessbauer spectroscopic studies; i.e., the Q. S. value of ferrocenylruthenocene-5HgCl₂ (2.99 mm s⁻¹) is slightly smaller than that of ferrocene-7HgCl₂ adduct (3.09 mm s⁻¹).⁶ Based on the results obtained in the present studies it can be summarized that there are two kinds of metal-metal chemical bonds (Fe-Hg, Ru-Hg) in the ferrocenylruthenocene-5HgCl₂ adduct.

On the other hand, the absence of the large Q. S. values in the SnCl₄ and I₂ adducts suggests that the Fe atom in the metallocene is ligated neither to the Sn nor I atom in the adducts. The ¹³C-chemical shift values of ferrocenylruthenocene-2I₂ adduct are found to be 93.6 ppm for ruthenocene and 76.5 ppm for ferrocene moieties. Although a small low-field shift in ferrocene moiety (5.2 ppm) is found, a relatively large shift (20.7 ppm) is found for the ruthenocene moiety, which is very similar to the trend found in ruthenocene-2I₂ adduct (20.2 ppm).⁵ The facts show that only the Ru atom is ligated to the I atom as in the case of ruthenocene-2I₂ adduct and the adduct may be expressed as [(C₅H₅)(C₅H₄)-Fe(C₅H₄)(C₅H₅)Ru-I]⁺I₃⁻.

The SnCl₄ adduct is so hygroscopic that all attempts to obtain the ¹³C-CP-MAS NMR spectrum have been unsuccessful but the ¹¹⁹Sn-Moessbauer study was carried out. ¹¹⁹Sn-Moessbauer spectroscopic study shows the presence of an organotin(IV)-type species (l. S. = 2.14 mm s⁻¹ at 78 K) in the SnCl₄ adduct as in the case of ruthe-

nocene- 1.5SnCl_4 adduct (I. S. = 2.08 mm s^{-1} at 78 K).⁷ The fact shows that ferrocenylruthenocene reacts with SnCl_4 giving an adduct containing a chemical bond between the Ru and Sn atoms. The results show that the ferrocenylruthenocene- 5HgCl_2 adduct has two kinds of chemical bonds (Ru-Hg and Fe-Hg), while the I_2 and SnCl_4 adducts have only Ru-I and Ru-Sn bonds.

Ferrocenylruthenocenylmethane reacts with HgCl_2 in ether giving a diamagnetic orange-yellow unstable product which is analyzed as ferrocenylruthenocenylmethane- 2.5HgCl_2 . Figure 1 shows the ^{57}Fe -Mössbauer spectrum of ferrocenylruthenocenylmethane(II) (e) and reaction products of II with HgCl_2 (f) and I_2 (g). The Q. S. value found in the HgCl_2 adduct (2.84 mm s^{-1} at 78 K) is much smaller than the values of the HgCl_2 adducts with ferrocene (3.09 mm s^{-1} at 80 K)⁶ and ferrocenylruthenocene (2.99 mm s^{-1} at 78 K)¹, but still larger than that of the original ferrocenylruthenocenylmethane (2.44 mm s^{-1} at 78 K).

The ^{13}C -chemical shift values are found to be 93.6 (C_1), 71.9 (C_5H_5) ppm for ruthenocene and 91.0 (C_1) and 70.3 (C_5H_5) ppm for ferrocene moieties for the ferrocenylruthenocenylmethane and 80.6 (C_5H_5) for ruthenocene and 70.7 ppm for ferrocene moieties in the HgCl_2 adduct from the results of ^{13}C -CP-MAS NMR spectroscopic studies. The low-field shift value of the ruthenocene (8.7 ppm) is in good agreement with the ferrocenylruthenocene- 5HgCl_2 adduct (8.5 ppm) but the value of ferrocene moiety (0.4 ppm) is much smaller than the value of ferrocenylruthenocene- 5HgCl_2 (7.8 ppm).

The facts indicate that the ferrocenylruthenocenylmethane- 2.5HgCl_2 adduct has two kinds of chemical bond formation, that is, one is strong Ru-Hg bond formation and the other is much weaker Fe-Hg bond formation than that of ferrocenylruthenocene- 5HgCl_2 adduct. Actually, the HgCl_2 adduct of ferrocenylruthenocenylmethane is not as stable as the HgCl_2 adduct of ferrocenylruthenocene; after being allowed to stand in air for few days after preparation, the color of the HgCl_2 adduct gradually changes into blue-green, while the

color of the ferrocenylruthenocene-5HgCl₂ adduct remains upon standing under the same conditions.

Ferrocenylruthenocenylmethane reacts with I₂ in hexane to give paramagnetic precipitates with the composition of ferrocenylruthenocenylmethane-3.5I₂. ⁵⁷Fe-Moessbauer spectroscopic studies of the product show a broad singlet line from 78 K to 300 K, as shown in Fig. 1-g. This fact suggests that the Fe atoms in the products are oxidized by I₂ as in the case of most ferrocene derivatives. Magnetic susceptibility measurements show that the reaction products are paramagnetic. The effective magnetic moment is estimated to be 2.63 BM in the temperature range from 78 K to 300 K. Although no significant ¹³C-CP-MAS NMR data have been available owing to the paramagnetism of the reaction products, the results indicate that the ferrocene and ruthenocene moieties in ferrocenylruthenocenylmethane react with I₂ independently, because the ferrocene and ruthenocene moieties are connected with a methylene bridge. The reaction product can be expressed as [Fe(C₅H₅)(C₅H₄)CH₂(C₅H₄)(C₅H₅)Ru-I]⁺(I₃⁻)₂, based on the results of the elemental analysis data.

Biruthenocene reacts with HgCl₂, SnCl₄ and I₂, giving stable adducts, analyzed as biruthenocene-3.5HgCl₂, -3.5SnCl₄(H₂O) and -2I₂, respectively. ¹³C-CP-MAS NMR spectra of the metallocene (e) and its adducts with 3.5HgCl₂ (f), 3.5SnCl₄(H₂O) (g), and 2I₂ (h) are shown in Fig. 2. The ¹³C chemical shift values of the metallocene are found to be 87.5(C₁), 72.3(C₅H₅) and 69.1(C_{3,4}) ppm. The other signal of C_{2,5} is hidden in the main signal of C₅H₅ ring. A broad signal is found for the HgCl₂ adduct with the chemical shift value of 81.2 ppm assigned to C₅H₅ ring. This value corresponds to that of ruthenocene-3HgCl₂ adduct (81.2 ppm) and a relatively large low-field shift (8.9 ppm) shows the chemical bond formation between the Ru and Hg atoms. The facts indicate that the two Ru atoms in the HgCl₂ adduct are bound equivalently to the Hg atoms.

Similar results are also found for the SnCl_4 adduct; i.e., the chemical shift value of the Cp-ring carbon atoms in the SnCl_4 adduct is found to be 88.4 ppm. The low-field shift value (16.1 ppm) well corresponds to that of the ruthenocene-1.5 SnCl_4 adduct (15.9 ppm). Moreover, ^{119}Sn -Moessbauer spectroscopic studies show the presence of an organotin(IV) species (I. S., 2.12 mm s $^{-1}$ at 78 K) as in the case of ferrocenylruthenocene-2.5 $\text{SnCl}_4(\text{H}_2\text{O})$ adduct. The results indicate that two Ru atoms in a SnCl_4 adduct are bound equivalently to the Sn atom.

On the other hand, two kinds of broad ^{13}C -CP-MAS NMR signals are found for the I_2 adduct, as shown in Fig. 1-h. The chemical shift values of the peaks are found to be 92.9 and 77.4 ppm. The former value corresponds to that of the I_2 adduct of ruthenocene (93.4 ppm) and the latter to that of biruthenocene itself (72.3 ppm). The fact that two kinds of low-field shift values (20.6 and 5.1 ppm) are found, indicates that one of the two Ru atoms in biruthenocene is bound with the I^+ atom and that the adduct may be expressed as $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{Ru}(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)\text{Ru}-\text{I}]^+\text{I}_3^-$ in the solid state.

All the results obtained in the present studies lead us to the conclusion that ruthenocene moiety in the hetero-binuclear metallocenes gives a coordination bond easier than ferrocene moiety, presumably because the ruthenocene moiety has less steric hindrance than the ferrocene moiety.

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