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

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Adducts of ruthenocene derivatives with Lewis acids ($HgCl_2$, $SnCl_4$, and I_2) were studied by means of ^{13}C-CP-MAS NMR spectroscopy and other physicochemical techniques. Large low-field shifts found in the ^{13}C-CP-MAS NMR spectroscopy suggest the presence of a direct chemical bonding between the ruthenium and the Lewis acids.

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 protonic solvent, such as CH_3Cl, CX_3COOH (X = Cl, F), and H_2SO_4.[1-2] Especially, [2]ferrocenophanes react with an appropriate Lewis acid species giving diamagnetic stable adducts with a direct chemical bond between the iron atom and the Lewis acid atom.[3,4] Ruthenocene also reacts with the Lewis acids giving much more stable adducts than ferrocene because ruthenocene has a less steric hindrance than ferrocene.[5] Although [2]ferrocenophane and ruthenocene are well soluble in most organic solvents, these adducts are less soluble. All attempts to obtain a single crystal of [2]ferrocenophane-$3HgCl_2$ and -$1.5SnCl_4$ adducts have so far been unsuccessful, while a few adducts, such as ruthenocene-$nHgX_2$ (X = Cl, Br), were obtained as single crystals in which direct metal-metal chemical bonds (Ru-Hg) have been found based on the X-ray structural analysis of the adducts.[5]

Recently, improved sensitivity and resolution in cross-polarization (CP), dipolar decoupling and magic angle spinning (MAS) techniques have made it possible to obtain a high-resolution ^{13}C-CP-MAS NMR spectrum even in the solid state.[6-9] The present study was planned to clarify the structure of some ruthenocene derivatives' adducts with a Lewis acid by obtaining information about the chemical state of carbon atoms by means of ^{13}C-CP-MAS NMR spectroscopy.

The reaction products of ruthenocene and ferrocenylruthenocene with I_2, $HgCl_2$, and $SnCl_4$ were prepared by the methods reported previously.[4,5,10] ^{13}C-NMR spectra were obtained at a frequency of 45.28 MHz using a JEOL FX-200 spectrometer. Four thousands datum points at a sweep width set in 20 kHz were collected in a spin-locking cross-polarization sequence. ^{1}H- and ^{13}C-rf field strengths were 33 kHz. Sample spinning rates in the magic angle at 3 to 3.5 kHz were achieved using Kel-F rotors. Chemical shifts were measured with respect to external adamantane and were converted to the shifts from TMS.

Ruthenocene reacts with $HgCl_2$, $SnCl_4$, and I_2 giving adducts with a direct chemical bond (Ru-Hg, Ru-Sn, and Ru-I), as already verified by means of X-ray diffraction studies[5,10)] and ^{119}Sn-Moessbauer spectroscopy.[4)] 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 chemical shift value of the cyclopentadienyl (Cp) ring's carbon of ruthenocene is found to be 73.2 ppm, while quite higher values are found for those of the adducts (81.2 for $HgCl_2$, 89.1 for $SnCl_4$, and 93.4 ppm for I_2 adducts). These low-field shifts (8.0 for $HgCl_2$, 15.9 for $SnCl_4$, and 20.2 ppm for I_2 adducts) can be attributed to the Ru-Hg, Ru-Sn, and Ru-I bond formation in the adducts. The low-field shift values indicate the precence of interaction between Ru and the Lewis acids. As mentioned previously, [2]ferrocenophane-Lewis acid adducts give large quadrupole splitting (Q. S.) values (3.29, 3.49, and 3.65 mm s^{-1}, for $HgCl_2$, $SnCl_4$, and I_2 adducts, respectively) by means of ^{57}Fe-Moessbauer spectroscopy.[3-4,11)] The fact that the order of the increase of the low-field shift of ruthenocene-Lewis acids adducts is similar to that of the Q. S. values of [2]ferrocenophane-Lewis acids adducts, suggests that the effect of Lewis acids on the Ru atoms in ruthenocene is similar to that on the Fe atoms in [2]ferrocenophane.

Similar low-field shifts were also observed in the ^{1}H-NMR spectra of ruthenocene and its adducts in CD_3CN. The shift value of ruthenocene is found to be 5.37 ppm, while the values for the $HgCl_2$ and I_2 adducts are 6.21 and 6.87 ppm, respectively. Although the ruthenocene-$2I_2$ and -$3HgCl_2$ adducts are stable in CH_3CN the $SnCl_4$ adduct is unstable in solution; e.g., the $SnCl_4$ adduct is soluble in CH_3CN giving a yellow solution which changes into a colorless solution in a few minutes. The chemical shift value of the $SnCl_4$ adduct in the solution (5.35 ppm) is very similar to that of the ruthenocene itself (5.37 ppm). The facts indicate the dissociation of the $SnCl_4$ adduct in CH_3CN. Although all attempts to obtain a single crystal of ruthenocene-$1.5SnCl_4$ adduct are unsuccessful, it seems reasonable to conclude that the structure of the $SnCl_4$ adduct can be expressed as $[(C_5H_5)_2\text{-}Ru\text{-}SnCl_2\text{-}Ru(C_5H_5)_2]^{2+}(SnCl_5^-)_2$ based on the results of the ^{119}Sn-Moessbauer[4)] and ^{13}C-CP-MAS NMR data as Mann et al. have already proposed based on their infrared spectroscopic studies.[12)]

Ferrocenylruthenocene was found to react with $HgCl_2$ giving orange-yellow diamagnetic precipitates which were analyzed as ferrocenylruthenocene-$5HgCl_2$. As seen in Fig. 2, a large Q. S. value (2.99 mm s^{-1}

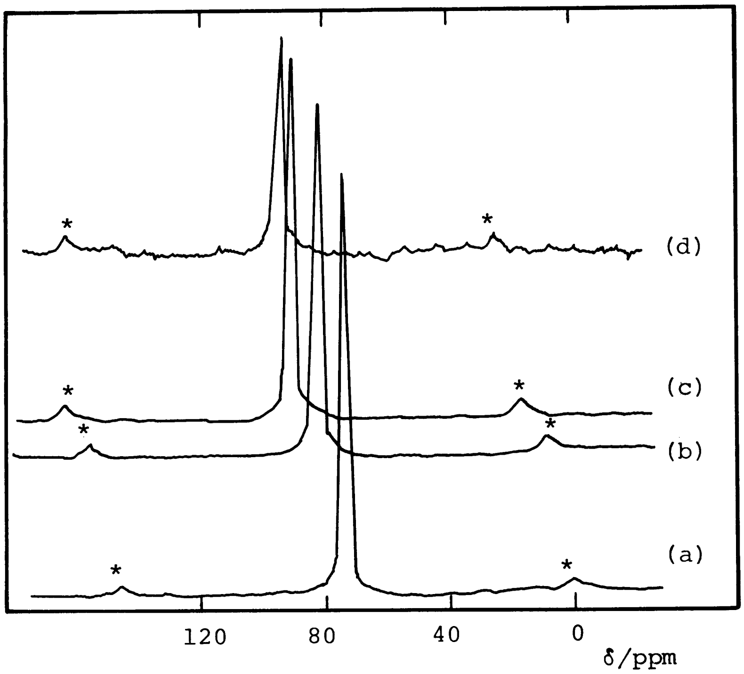
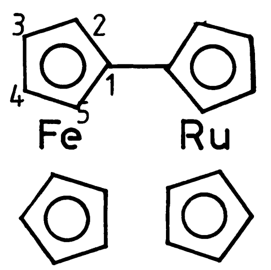


Fig. 1. ^{13}C-CP-MAS NMR spectra of ruthenocene (a) and its $HgCl_2$ (b), $SnCl_4$ (c), and I_2 (d) adduct. Star marks(*) indicate spinning side bands.

at 78 K) is found in the ^{57}Fe-Moessbauer spectrum of ferrocenylruthenocene-5$HgCl_2$, indicating a direct interaction between the Hg and Fe atoms as in the case of [2]-ferrocenophane-3$HgCl_2$ adduct.$^{3)}$ Figure 3 shows ^{13}C-CP-MAS NMR spectra of the ferrocenylruthenocene (a) and its -2I_2 (b), and -5$HgCl_2$ (c) adducts. The peaks can be assigned based on the results of ^{13}C-NMR spectroscopy on the starting material in $CDCl_3$. The chemical shift values of the carbon atoms in the Cp-ring of ferrocenylruthenocene in solid state are found to be 72.9 ppm for ruthenocene and 71.3 ppm for ferrocene moieties giving two main peaks. The values of C_1 are found to be 88.5 and 84.6 ppm for ruthenocene and ferrocene, respectively. Although the values of $C_{2,5}$ and $C_{3,4}$ are found to be 69.9 and 69.6 ppm for ruthenocene and 67.2 and 67.4 ppm for ferrocene moiety in $CDCl_3$, respectively, these peaks are hidden in the Cp-ring's main peaks in the solid state, as shown in Fig. 3. Therefore, only the low-field shift values of Cp-ring carbon will be discussed.

The Cp-ring's chemical shift values of the ferrocenylruthenocene-5$HgCl_2$ 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, respectively, compared with the values in ferrocenylruthenocene. The decrease is in a good agreement with the difference in the values between ruthenocene and ruthenocene-3$HgCl_2$ adduct (8.0 ppm). Based on the results of ^{57}Fe-Moessbauer and ^{13}C-CP-MAS NMR spectroscopic data, it is concluded that there are two kinds of metal-metal chemical bonds (Fe-Hg, Ru-Hg) in the ferrocenylruthenocene-5$HgCl_2$ adduct.



Ferrocenylruthenocene

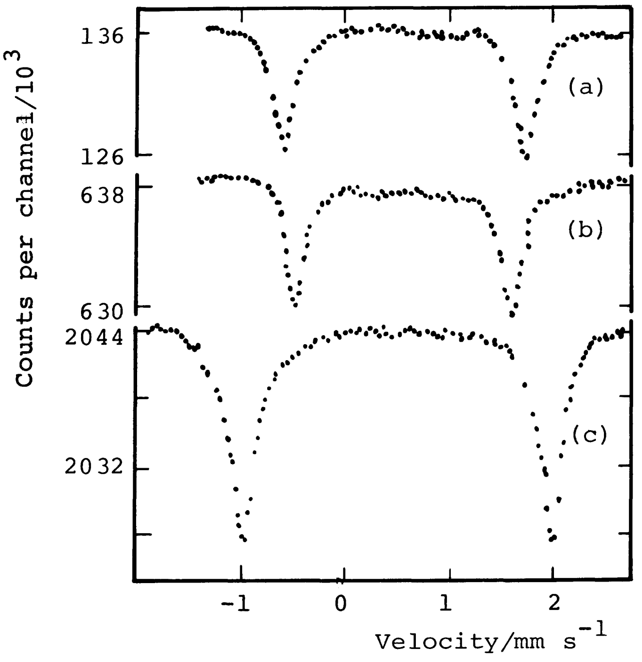


Fig. 2. ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene (a) and its I_2 (b), $HgCl_2$ (c) adducts, all at 78 K.

On the other hand, ferrocenylruthenocene reacts with I_2 giving black diamagnetic precipitates which are analyzed as ferrocenylruthenocene-2I_2. The Q. S. value of ferrocenylruthenocene-2I_2 is found to be 2.16 mm s^{-1}, which is slightly smaller than the value of original ferrocenylruthenocene (2.36 mm s^{-1} at 78 K). The absence of large Q. S. line shows that the Fe atom is not ligated to the I atom in the ferrocenylruthenocene-2I_2 adduct. The ^{13}C-chemical shift values of ferrocenylruthenocene-2I_2 adduct are found to be 93.6 ppm for ruthenocene and 76.5 ppm for ferrocene moiety. 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--2I_2 adduct (20.2 ppm). The facts show that the ruthenium atom is ligated to the iodine atom as in the case of ruthenocene-2I_2 adduct and the adduct may be expressed as $[(C_5H_5)(C_5H_4)Fe(C_5H_4)(C_5H_5)Ru\text{-}I]^+I_3^-$.[13)]

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

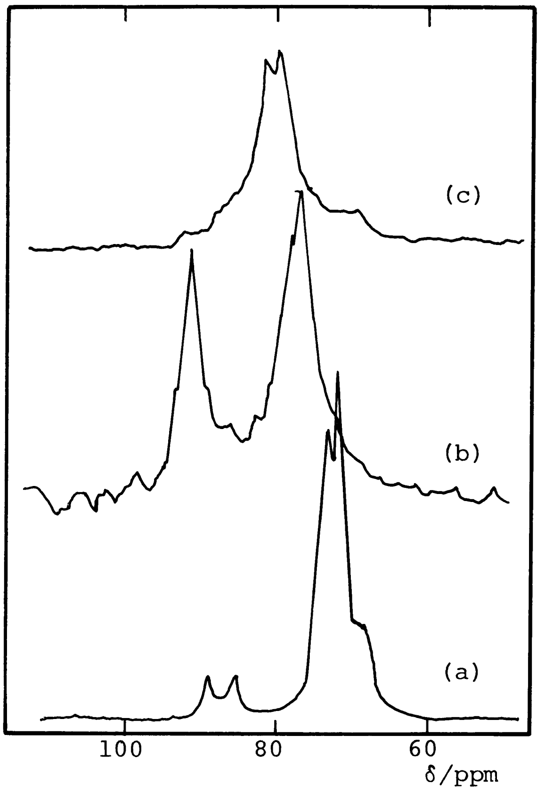


Fig. 3. ^{13}C-CP-MAS NMR spectra of ferrocenylruthenocene (a) and its I_2 (b), $HgCl_2$ (c) adducts.

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