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^{57}Fe-Moessbauer Spectroscopic Studies of the Reaction Products of Binuclear Metallocenes with Iodine

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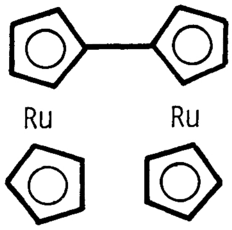
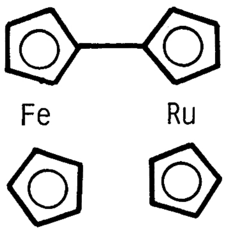
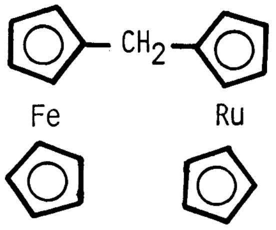
A dark red colored stable diamagnetic adduct of biruthenocene with iodine can be prepared by treating biruthenocene with iodine in a dry benzene-hexane mixture. A less stable diamagnetic adduct of ferrocenylruthenocene with iodine can also be obtained. ^{1}H-NMR and ^{57}Fe-Moessbauer spectroscopic studies of the adducts suggest the presence of a direct interaction between Ru and I atoms in the adducts. Ferrocenylruthenocenylmethane gave iodoruthenocenylmethyleneferrocenium triiodide.

It is well-known that ferrocene is oxidized by appropriate oxidizing agents, such as iodine and bromine, to give paramagnetic ferrocenium salts. A broad singlet peak is found in the ^{57}Fe-Moessbauer spectra of a number of ferrocenium salts. On the other hand, ruthenocene gives diamagnetic dark red precipitates which analyze as $[Ru(C_5H_5)_2X]X_3$ (X: I or Br), as the result of the treatment of ruthenocene with iodine or bromine, respectively. The products are known to have a chemical bond between the ruthenium and one halogen atom, based on the results of a X-ray diffraction study of $[Ru(C_5H_5)_2X]X_3$ by Sohn et al.$^{1)}$ On the other hand, it has also been reported that ferrocenylruthenocene reacts with $HgCl_2$ and $SnCl_4$ to give adducts with a chemical bond between the central metal atoms in the metallocenes and the Hg and Sn atoms of the metal halides.$^{2,3)}$ The question remains whether the iron atoms of the ferrocene moiety could be ligated to I^+ ions as in the case of $[Ru(Cp)_2X]X_3$, when ferrocenylruthenocene is used as a chelating agent. In order to try to answer this question, the present study was started to obtain information about the electronic structure in some ferrocene derivatives containing ferrocene and ruthenocene moieties, such as ferrocenylruthenocene and ferrocenylruthenocenylmethane.

Ferrocenylruthenocene and biruthenocene were prepared by the Ullmann coupling of bromoruthenocene and bromoferrocene at 120 °C for 12 h instead of iodoferrocene and iodoruthenocene.$^{4)}$ Ferrocenylruthenocenylmethane was prepared by the previous report.$^{5)}$ The reaction products of iodine with these metallocenes were prepared by mixing iodine and the metallocenes in dry benzene-hexane mixture. The purities of the reaction products were confirmed by elemental analyses. Found: C, 26.00; H, 1.91%. Calcd for ferrocenylruthenocene-I_4, $C_{20}H_{18}FeRuI_4$: C, 26.03; H, 1.97%. Found: C, 19.09; H, 1.45%. Calcd for ferrocenylruthenocenylmethane-I_7, $C_{21}H_{20}$FeRu-


Biruthenocene


Ferrocenylruthenocene


Ferrocenylruthenocenylmethane

I_7: C, 19.14; H, 1.50 %. Found: C, 24.88; H, 1.98%. Calcd for biruthenocene-I_4, $C_{20}H_{18}Ru_2I_4$: C, 24.81; H, 1.87%. ^{1}H-NMR spectra were taken on a JEOL JNM-FX20 Fourier Transform NMR Spectrometer in CD_3CN solution at 200 MHz using TMS as a standard. ^{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 ^{57}Fe-Moessbauer spectra are given relative to metallic iron and the experimental errors of the I. S. and quadrupole splitting (Q. S.) values are estimated to be within ±0.02 mm s^{-1}.

^{1}H-NMR spectra of ruthenocene and its iodine product in CD_3CN consist of a sharp singlet, as shown in Fig. 1. The chemical shift value of ruthenocene is found to be 5.371 ppm, while the value of the iodine adduct (6.871 ppm) is quite different, which reflects the decreased electronic density in the cyclopentadienyl-ring protons of the iodine adduct. It may be reasonable to assume that the anomalously large shift to a low field region is caused by the direct Ru-I bond formation in the iodine adduct as already verified by Sohn et al.$^{1)}$; i.e., an enhanced ligand-to-metal(Ru) donation of the electrons of two cyclopentadienyl-rings caused by the Ru-I bond formation may result in the decreased electronic density in the cyclopentadienyl-ring protons in the iodine adduct, giving an anomalously large chemical shift observed for the adduct.

Biruthenocene also reacts with iodine in benzene mixed with hexane, giving a stable diamagnetic dark-red adduct analyzed as biruthenocene-I_4 based on the elemental analysis. The chemical shifts of biruthenocene are found to be 5.532(t), 5.322(s) and 5.298(t) ppm, which are similar to the value of ruthenocene (5.371 ppm). Anomalously large shifts to a low field region are also observed for the iodine adduct (6.900(t), 6.650(s) 6.541(t) ppm), which values are nearly close to that of ruthenocene-I_4 adduct, as shown in Fig. 1, but still larger than those of original biruthenocene. The results also indicate that the biruthenocene-I_4 adduct should have a Ru-I bond, as already verified in the $SnCl_4$ adduct of biruthenocene.$^{3)}$ Moreover, the fact there is only an equivalent value of chemical shift for the two ruthenocene moieties of biruthenocene-I_4 adduct in acetonitrile suggests that biruthenocene may react with I_2 as a chelating agent $[(C_5H_5)(C_5H_4)Ru\text{-}I\text{-}Ru\text{-}(C_5H_4)(C_5H_5)]^+I_3^-$ in a similar manner to biruthenocene-3.5$SnCl_4$ adduct.$^{3)}$

Ferrocenylruthenocene reacts with I_2 giving a black diamagnetic precipitate which analyzes as ferrocenylruthenocene-I_4. The color of the precipitate is similar to that of biferrocenium triiodide. ^{57}Fe-Moessbauer spectra of the precipitate and the related compounds are shown in Fig. 2. The Q. S. value of ferrocenylruthenocene-I_4 was found to be 2.16 mm s^{-1} both at 78 and 300 K. This value is slightly smaller than the Q. S. value of original ferrocenylruthenocene (2.36 mm s^{-1} at 78 K) and is very similar to that of the ferrocenylruthenocene-2.5$SnCl_4$ adduct (2.25 mm s^{-1} at 78 K) and of biferrocenium triiodide salt (2.119 mm s^{-1} at 4.2 K).6)

The absence of either a broad ferrocenium-like singlet line or anomalously large quadrupole-split line such as found for [2]ferrocenophane-I_4 adduct7) (3.49 mm s^{-1} at 78 K) shows that the iron atom in ferrocenylruthenocene-I_4 is neither oxidized by iodine nor bonded with an iodine atom as in the [2]ferrocenophane-I_4 adduct. Therefore, only the ruthenium atom in ferrocenylruthenocene is expected to be ligated to an iodine atom, because the ruthenium atom in ferrocenylruthenocene has softer e_{2g} electrons without steric hindrance of Cp-rings compared with the iron atom. The adduct can be expressed as $[(C_5H_5)(C_5H_4)Fe(C_5H_4)(C_5H_5)Ru\text{-}I]^+I_3^-$ in accord with the elemental analysis data. However, the adduct is found to be not very stable. When the adduct is dissolved in acetonitrile its color changes into green and an electronic absorption peak characteristic of a ferrocenium ($_{max.}$ = 640 nm) increases very rapidly, suggesting that the ferrocene moiety is rapidly oxidized giving ferrocenium-type cations. The fact that all attempts to obtain an evidence for Ru-I bond formation in acetonitrile solution of a ferrocenylruthenocene-iodine adduct by means of ^{1}H-NMR have been unsucessful agrees with magnetic data which show the adduct becomes paramagnetic in acetonitrile.

The explanation for the slightly decreased Q. S. value observed in the ^{57}Fe-Moessbauer spectrum of ferrocenylruthenocene-I_4 adduct compared with the original ferrocenylruthenocene is given by assuming that the chemical bond of Ru-I may cause a decease in e_{2g} electrons in the ferrocene moiety through the fulvenide π-system (C_5H_4-C_5H_4).

Ferrocenylruthenocenylmethane reacts with iodine in dry hexane to give a

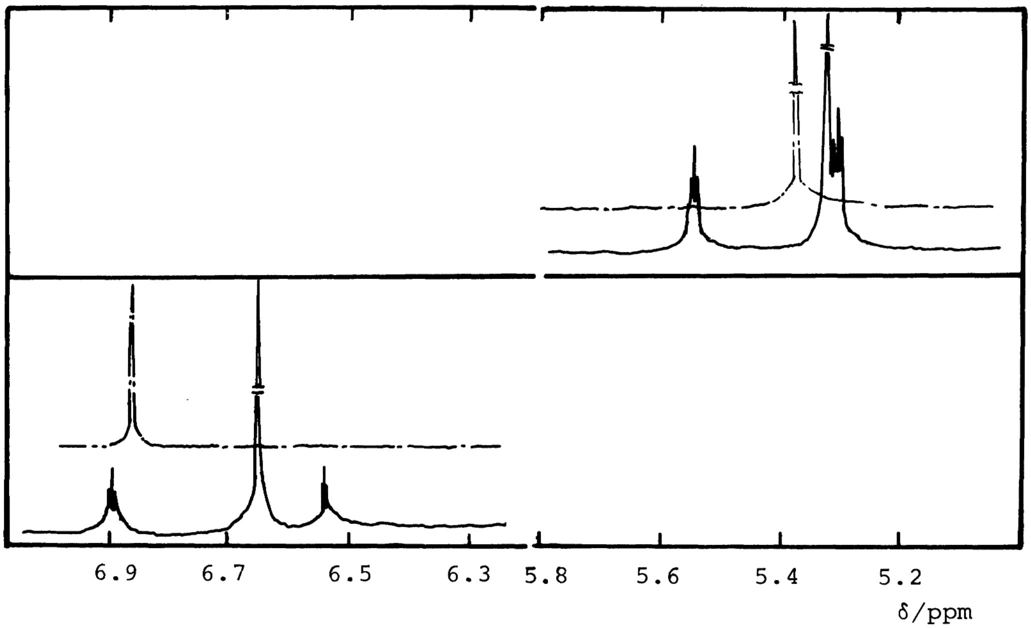


Fig. 1. ^{1}H-NMR spectra in acetonitrile solution. Upper (——) for biruthenocene and (---) ruthenocene. Lower (——) for biruthenocene-I_4 and (----) ruthenocene-I_4 adduct.

paramagnetic black precipitate of the composition ferrocenylruthenocenylmethane-I_7 based on the elemental analysis.

^{57}Fe-Moessbauer spectroscopic studies of this product show a broad singlet line from 78 K to 300 K. This fact suggests that iron atoms in the products are oxidized by iodine as in the case of most ferrocene derivatives except for the [2]ferrocenophanes.$^{7)}$

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 and this value is very similar to that observed for most ferrocenium salts.

This result is in good accordance with that of ^{57}Fe-Moessbauer spectroscopic study of this product, indicating that the ferrocene and ruthenocene moieties in ferrocenylruthenocenylmethane react with iodine independently, because the ferrocene and ruthenocene moieties are connected with a methylene bridge. The reaction product can be expressed as $[Fe(C_5H_5)(C_5H_4)CH_2(C_5H_4)(C_5H_5)Ru\text{-}I]^{2+}(I_3^-)_2$.

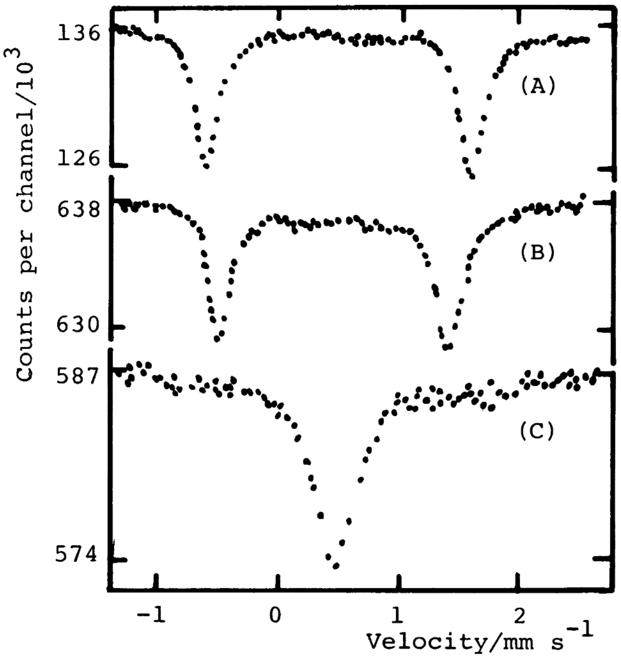


Fig. 2. ^{57}Fe-Moessbauer spectra of ferrocenylruthenocene (A), and reaction products of ferrocenylruthenocene (B) and ferrocenylruthenocenylmethane (C) with iodine, all at 78 K.

All the results in the present study lead us to the conclusion that biruthenocene and ferrocenylruthenocene give iodine adducts containing a chemical bond between Ru and I. The stability of the Ru-I bond is ascribed to the expanded d-electrons of the ruthenocene atoms in ruthenocene moieties with a larger distance between the two Cp-rings than in ferrocene moieties. A chelation such as $[(C_5H_5)\text{-}(\overline{C_5H_4)Ru\text{-}I\text{-}Ru(C}_5H_4)(C_5H_5)]$ is suggested in the case of biruthenocene adduct with iodine in an acetonitrile solution based on the ^{1}H-NMR spectroscopy.

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