CHEMISTRY LETTERS, pp. 1981-1984, 1987.

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

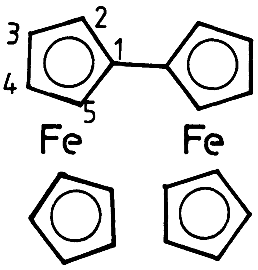
Masanobu WATANABE, Yuichi MASUDA, Izumi MOTOYAMA, and Hirotoshi SANO*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan
University, Fukasawa, Setagaya-ku, Tokyo 158

Adducts of ferrocene, biferrocene, and [2]ferrocenophane with HgX_2 (X = Cl, Br, I) were studied by means of high resolution solid state ^{13}C-NMR and ^{57}Fe-Moessbauer spectroscopies. Large low-field shifts found in the ^{13}C-CP-MAS NMR and large quadrupole splitting (Q. S.) values in the ^{57}Fe-Moessbauer spectroscopies suggest the presence of a direct chemical bonding between the Fe and Hg atoms.

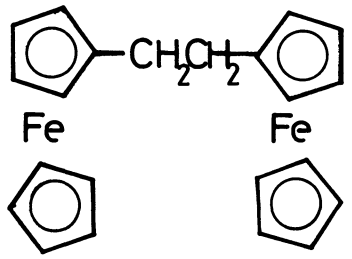
It has recently been shown in our previous reports that [2]ferrocenophane derivatives react with some Lewis acids, such as $SnCl_4$, $HgCl_2$, $CdCl_2$, and I_2, giving stable adducts containing a chemical bond between the Fe and Lewis acid atoms (Hg^{2+}, Sn^{4+}, Cd^{2+}, and I^+).1-4) Although all the adducts are less soluble in organic solvents, 1,1,2,2-tetramethyl[2]ferrocenophane-$2I_2$ is well soluble in some organic solvents, such as acetonitrile and dichloromethane, and gives a single crystal. X-Ray diffraction study of the I_2 adduct shows that the Fe atoms squeezed out of the tilted cyclopentadienyl (Cp) structure have I atoms at a short distance (2.675 Å),4) which is much smaller than the sum of the van der Waals radii of the Fe and I atoms. All attempts to obtain single crystals of the other adducts have so far been unsuccessful.

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.5-8) The present study was planned to clarify the structure of some ferrocene derivatives' adducts with $HgCl_2$, by obtaining information about the chemical state of carbon atoms by means of high-resolution ^{13}C-CP-MAS NMR spectroscopy.

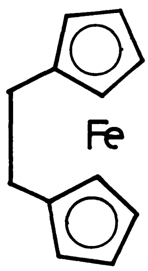
The reaction products of ferrocene,9) binuclear ferrocenes,10) and [2]ferrocenophane1) with $HgCl_2$ were prepared by the methods reported previously. ^{13}C-NMR spectra were obtained under the same conditions as in the case of a previous



Biferrocene



Diferrocenylethane



[2]Ferrocenophane

report.[11] Chemical shifts were measured with respect to external adamantane and were converted to the shifts from TMS. ^1H- and ^{13}C-NMR spectra in solution were measured by using a JEOL FX-200 spectrometer at 200.0 and 50.1 MHz, respectively.

Although ferrocene gives only an unstable $HgCl_2$ adduct in the reaction with $HgCl_2$ in ether, biferrocene and [2]ferrocenophane give stable $HgCl_2$ adducts. Based on the results of ^{57}Fe-Moessbauer spectroscopic studies, the Q. S. values of the starting metallocenes are found to be 2.41, 2.33, and 2.41 mm s^{-1} for ferrocene, biferrocene, and [2]ferrocenophane, respectively, whereas large Q. S. values are found for the $HgCl_2$ adducts (3.09, 2.93, and 3.29 mm s^{-1}, for ferrocene-$7HgCl_2$,[12] biferrocene-$2HgCl_2$[10], and [2]ferrocenophane-$3HgCl_2$[2], respectively, all at 78 K).

The ^{13}C-CP-MAS spectra of ferrocene (a) and its -$7HgCl_2$ adduct (b) consist of a singlet, as shown in Fig. 1. The chemical shift value of the Cp-ring carbon signals in ferrocene is found to be 69.79 ppm, while the value of the $HgCl_2$ adduct (79.71 ppm) is quite different. Similar observation is also obtained for ruthenocene (73.20 ppm) and its -$3HgCl_2$ adduct (81.20 ppm),[11] in which chemical bond formation (Ru-Hg) was found by means of X-ray diffraction study.[13] The facts that a relatively large low-field shift (9.92 ppm) and a large Q. S. value are found for the $HgCl_2$ adduct, indicate the direct Hg-Fe bond formation in the adduct.

Similar low-field shifts are also observed for the $HgCl_2$ adduct of biferrocene. The ^{13}C-CP-MAS spectra of biferrocene (c) and its -$2HgCl_2$ adduct (d) are shown in Fig. 1 together with the high resolution ^{13}C-NMR spectrum of biferrocene in $CDCl_3$ solution (e). The ^{13}C chemical shift values of the biferrocene in $CDCl_3$ solution are found to be 83.9(C_1), 69.2(C_5H_5), 67.6($C_{3,4}$), and 66.4($C_{2,5}$) ppm. The assignment of the carbon signals was carried out by using the selective protone decoupling experiment. The ^{13}C chemical shift values of the biferrocene in solid are found to be 84.77(C_1), 70.66(C_5H_5), 67.06($C_{3,4}$ and $C_{2,5}$) ppm. The broader ^{13}C-CP-MAS NMR spectrum of the $HgCl_2$ adduct, however, cannot be resolved into each carbon signal. The ^{13}C chemical shift values of the $HgCl_2$ adduct are found to be 79.71(C_5H_5), 71.35($C_{3,4}$ and $C_{2,5}$) ppm. The peak of C_1 is not well resolved, being superimposed in the main C_5H_5-ring signal. The large low-field shift of the main C_5H_5-ring signal (9.05 ppm) is similar to that of ferrocene-$7HgCl_2$ (9.92 ppm). This

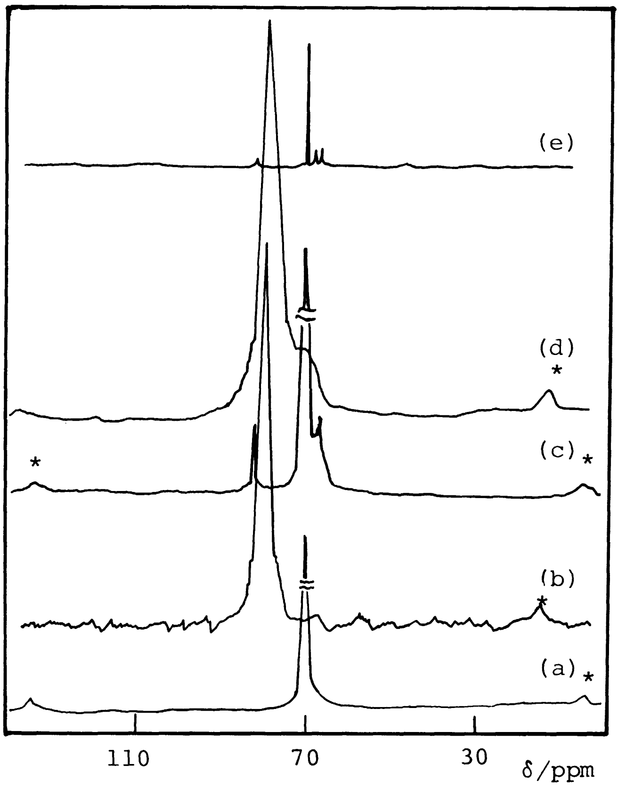


Fig. 1. ^{13}C-CP-MAS NMR spectra of ferrocene (a), its -$7HgCl_2$ adduct (b), biferrocene (c), and its -$2HgCl_2$ adduct (d) together with ^{13}C-NMR spectrum of biferrocene in $CDCl_3$ solution (e).
* Stands for spinning side bands.

shows that there is also direct bond formation between the Fe and Hg atoms in the biferrocene-$2HgCl_2$ adduct. The result of ^{13}C-CP-MAS NMR spectroscopy corresponds to that of the ^{57}Fe-Moessbauer study.

[2]Ferrocenophane reacts with HgX_2 (X = Cl, Br, I) in ether or ethanol giving stable adducts. Figure 2 shows the ^{13}C-CP-MAS NMR spectra of the [2]ferrocenophane (a), its -$3HgCl_2$ (b), -$2.5HgBr_2$ (c), and -$2.2HgI_2$ (d) adducts together with high resolution ^{13}C-NMR spectrum of the [2]ferrocenophane in $CDCl_3$ solution (e). The ^{13}C chemical shift values of [2]ferrocenophane in $CDCl_3$ are found to be 91.2(C_1), 72.2($C_{2,5}$), 67.9($C_{3,4}$), and 33.7(CH_2CH_2) ppm. The assignment of the carbon signals was carried out by using the same method as in the case of biferrocene based on the results of [n]ferrocenophane (n = 1,2) derivatives.[14] Although relatively sharp signals are found for the [2]ferrocenophane, broader signals are found for the HgX_2 adducts in solid. The ^{13}C chemical shift values of [2]ferrocenophane and its -$3HgCl_2$ adduct in solid are found to be 92.56(C_1), 74.95($C_{2,5}$), 70.76($C_{3,4}$), 35.25(CH_2CH_2) ppm and 114.16 (C_1), 78.55($C_{2,5}$ and $C_{3,4}$), 35.05(CH_2CH_2) ppm, respectively. The low-field shift values of $C_{2,5}$ and $C_{3,4}$ for the $HgCl_2$ adduct are almost the same as that of $HgCl_2$ adducts with ferrocene and biferrocene. The most striking feature is the low-field shift value of the C_1 signal in the adduct, which is found in a lower field by about 21.60 ppm compared with the C_1 signal of the original metallocene. The same large low-field shift of C_1 signal is also observed for other [2]ferrocenophane-$2.5HgBr_2$ and -$2.2HgI_2$ adducts.

The Q. S. values of the adducts (3.08 for the $HgBr_2$ and 3.12 mm s^{-1} for the HgI_2 adducts, both at 78 K) are a little smaller than that of the $HgCl_2$ adduct but much larger than that of the [2]ferrocenophane. The ^{13}C chemical shift values of the adducts are found to be 119.61(C_1), 83.02($C_{2,5}$), 77.18 ($C_{3,4}$), 35.58(CH_2CH_2) ppm for the $HgBr_2$ and 116.69(C_1), 81.75($C_{2,5}$ and $C_{3,4}$), and 36.29 (CH_2CH_2) ppm, for the HgI_2 adduct.

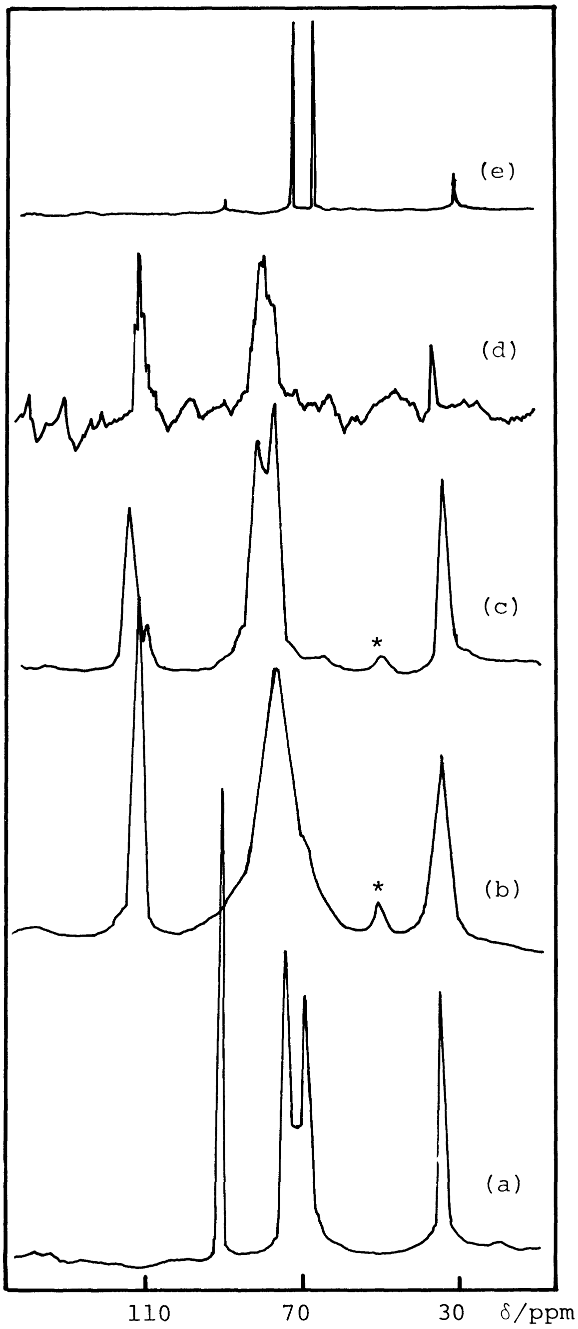


Fig. 2. ^{13}C-CP-MAS spectra of [2]ferrocenophane (a) and its -$3HgCl_2$ (b), -$2.5HgBr_2$ (c), -$2.2HgI_2$ (d) adducts together with ^{13}C-NMR spectrum of [2]-ferrocenophane in $CDCl_3$ solution (e).

For the sake of comparison of these data, we have treated diferrocenylethane with $HgCl_2$ in the same conditions as in the case of ferrocene-$7HgCl_2$. An unstable orange-yellow adduct was obtained and analyzed as diferrocenylethane-$6HgCl_2$. The Q. S. values of the $HgCl_2$ adduct is found to be 3.00 mm s^{-1} at 78 K, indicating direct chemical bond formation between the Fe and Hg atoms. ^{13}C chemical shift values of diferrocenylethane and its -$6HgCl_2$ adduct are found to be 90.12(C_1), 70.00(C_5H_5, $C_{2,5}$, and $C_{3,4}$), 36.61(CH_2CH_2) ppm, and 91.88(C_1), 78.35 (C_5H_5), and 31.74(CH_2CH_2) ppm, respectively, as shown in Fig. 3. The other signals of the $C_{2,5}$ and $C_{3,4}$ for the diferrocenylethane-$6HgCl_2$ are hidden in the main C_5H_5-ring signal. Although the low-field shift value (8.35 ppm) of C_5H_5-ring carbon of the diferrocenylethane-$6HgCl_2$ adduct is similar to that of the $HgCl_2$ adducts of ferrocene and biferrocene, the value of C_1 (1.76 ppm) is much smaller than that of the [2]ferrocenophane-$3HgCl_2$ adduct (21.60 ppm).

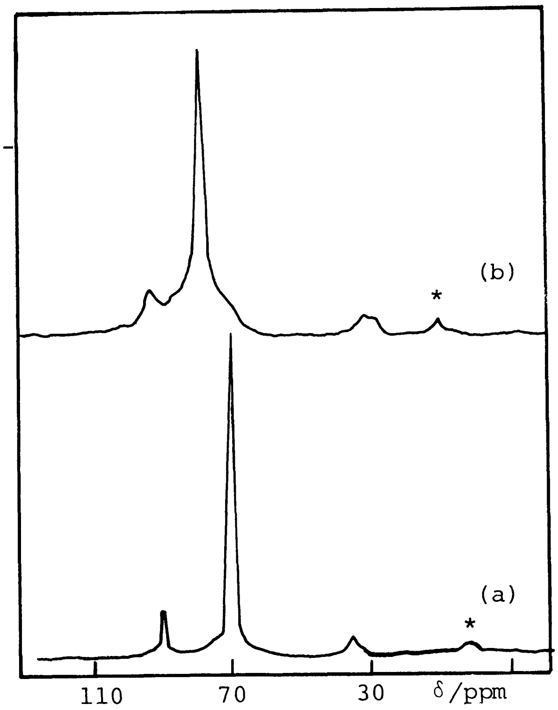


Fig. 3. ^{13}C-CP-MAS spectra of diferrocenylethane (a) and its -$6HgCl_2$ adduct (b).

From the results obtained in the present study, it is concluded that anomalously large low-field shifts of the C_1 atoms for the [2]ferrocenophane-HgX_2 adducts suggest the structural distortion at the C_1 atoms caused by the stable Fe-Hg bond formation.

References

1) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, Chem. Lett., 1983, 1009.
2) M. Watanabe, H. Ichikawa, I. Motoyama, and H. Sano, Bull. Chem. Soc. Jpn., 56, 3291(1983).
3) H. Sano, M. Watanabe, and I. Motoyama, Hyperfine Interactions, 28, 833(1986).
4) M. Watanabe, K. Sato, I. Motoyama, and H. Sano, Chem. Lett., 1983, 1775.
5) S. R. Hartman and E. L. Hahn, Phys. Rev., 128, 2042(1962).
6) A. Pines, M. G. Gibby, and J. S. Waugh, J. Chem. Phys., 59, 569(1973).
7) J. Schaefer, S. H. Chin, and S. I. Weissman, Macromolecules, 5, 798(1972).
8) J. Schaefer, E. O. Stejskal, and R. Buckdahl, Macromolecules, 10, 384(1977).
9) W. H. Morrison, Jr. and D. N. Hendrickson, Inorg. Chem., 11, 2912(1972).
10) M. Watanabe, K. Suto, I. Motoyama, and H. Sano, Chem. Lett., 1984, 1317.
11) M. Watanabe. Y. Masuda, I. Motoyama, and H. Sano, Chem. Lett., in press.
12) R. M. G. Roberts, J. Silver, and I. E. G. Morrison, Organomet. Chem., 209, 385 (1981).
13) A. I. Gusev and U. T. Struchkov, Zh. Struckt. Kim., 6, 1121(1972).
14) A. G. Osborne, R. H. Whitely, and Meads, Organomet. Chem., 193, 345(1980); T. H. Barr and W. E. Watts, Tetrahedron, 24, 6111(1968).

(Received August 3, 1987)