A Novel Iodine-bridged Piano-stool Iron Complex: Crystal Structure and Electronic State

Naoji Masuhara, Satoru Nakashima,*[†] and Koji Yamada
Department of Chemistry, Graduate School of Science, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8526
[†]*Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University,*
Kagamiyama, Higashi-Hiroshima 739-8526

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The iodine-bridged iodo(pentamethylcyclopentadienyl)iron dicarbonyl complex, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2I\text{–}I]_2$ (**1**) has been synthesized and characterized by single crystal X-ray diffraction method, IR spectroscopy, and ^{57}Fe Mössbauer spectroscopy.

Currently, there is much interest in the synthesis of materials possessing desired crystalline architectures as well as physical and electrochemical properties.[1] Chalcogen–chalcogen and halogen–halogen interactions as well as coordination bonds and hydrogen bonds can be used to control the organization of molecule in the solid state and have been used in crystal engineering and supramolecular design.[2] Especially, halogen atoms such as iodine, bromine, and chlorine have ability for assemblies by intermolecular interaction.[3] Our group has reported various biferrocenium polyiodide salts.[4] We have found interesting, various crystal structures and electronic states. Namely, redox-active supramolecules will be able to generate a novel redox system. Herein, we report the novel crystal structure of iodine-bridged piano-stool iron complex, $[Cp^*Fe(CO)_2I\text{–}I]_2$ (**1**), where Cp* stands for $\eta^5\text{-}C_5Me_5$, and its electronic state compared with $Cp^*Fe(CO)_2I$ by using IR and ^{57}Fe Mössbauer spectroscopy.

1 was synthesized by mixing iodine into dichloromethane solution of $Cp^*Fe(CO)_2I$[5] in a ratio of 1:1. The solution was left under hexane atmosphere at room temperature for several days and single crystals were obtained.[6] The single crystal of $Cp^*Fe(CO)_2I$ was obtained by the same method. All measurements were performed by using single crystal samples.

Figure 1 shows ORTEP drawing for **1** at room temperature.[7] It can easily be seen that iodine atoms of the two $Cp^*Fe(CO)_2I$ are bridged by iodine molecule and this structure is symmetrical at the center of bridged iodine. The I–I distance between linking iodine atom in $Cp^*Fe(CO)_2I$ unit and that in bridging iodine molecule is 3.392(1) Å. This distance is shorter than the sum of van der Waals radii of two iodine atoms. The Fe–C(CO) distances in **1** are 1.77(1) and 1.80(1) Å and the C–O distances of carbonyl groups are 1.15(2) and 1.08(1) Å, respectively. The average Fe–C(CO) distance in **1** is slightly longer by 0.02 Å than that of $Cp^*Fe(CO)_2I$, on the other hand the average C–O bond in **1** is shorter by 0.02 Å.[8] While, the average of Fe–C(Cp*) distance in **1** is 2.116(4) Å, which is slightly longer than that in $Cp^*Fe(CO)_2I$ (2.103(2) Å). Although each iron–carbon distance is different from $Cp^*Fe(CO)_2I$, the Fe–I distances are almost the same ($Cp^*Fe(CO)_2I$: 2.6050(9), **1**: 2.602(2) Å).

IR spectra for **1** and $Cp^*Fe(CO)_2I$ revealed almost the same features except for carbonyl stretching bands. Accordingly, we pay attention to the range of 1800–2200 cm^{-1}, which is shown in Figure 2. The carbonyl stretchings for **1** are larger by ≈7 cm^{-1} ($Cp^*Fe(CO)_2I$: $\nu_{CO} = 1957$, 2007 cm^{-1} **1**: $\nu_{CO} =$ 1965, 2014 cm^{-1}). The result is in consistent with the result of X-ray analysis, i.e., the C–O bonds of **1** are shorter than those of $Cp^*Fe(CO)_2I$.

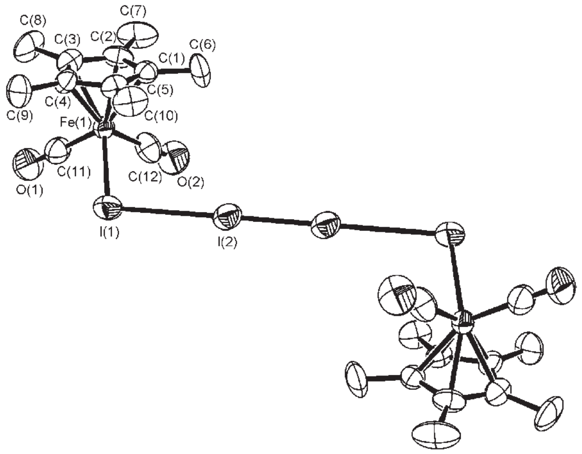

Figure 1. ORTEP drawing for **1**, showing 50% probability displacement ellipsoid. Hydrogen atoms are omitted for clarity.

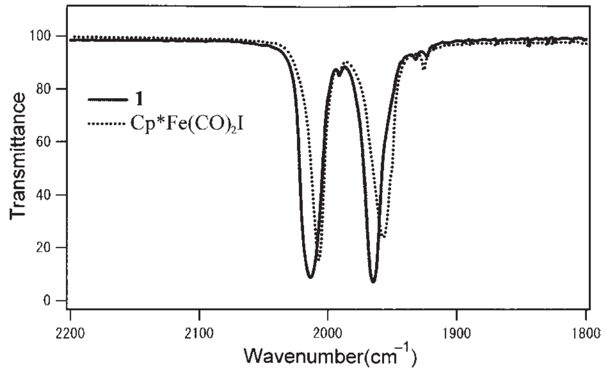

Figure 2. IR spectra for **1** and $Cp^*Fe(CO)_2I$ in the range of 1800–2200 cm^{-1}.

Figure 3 shows ^{57}Fe Mössbauer spectra for **1** and $Cp^*Fe(CO)_2I$ at room temperature. Only one doublet is detected in ^{57}Fe Mössbauer spectra in both samples. The isomer shift (I.S.) values of **1** and $Cp^*Fe(CO)_2I$ are 0.126 and 0.124 mm s^{-1} (relative to α-Fe) and the quadrupole splitting (Q.S.) values are 1.958 and 1.954 mm s^{-1}, respectively. It is well known that the I.S. value reflects metal s-electron density and the Q.S. value re-

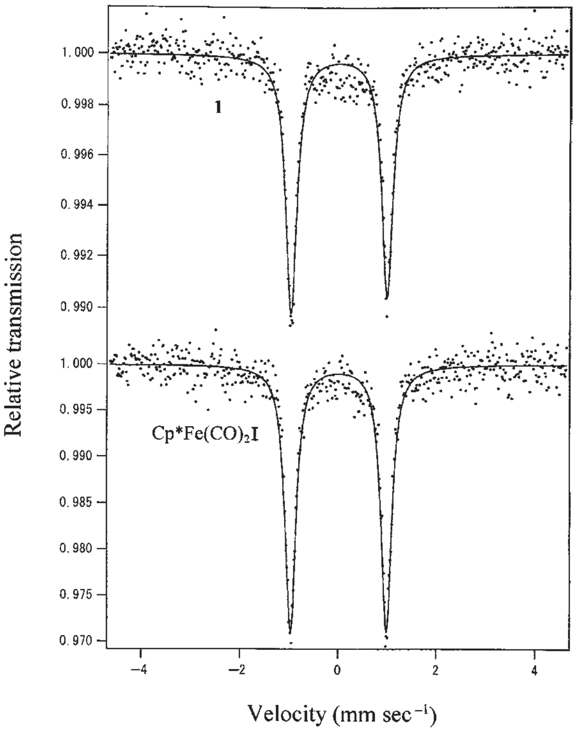

Figure 3. ^{57}Fe Mössbauer spectra for **1** and Cp*Fe(CO)$_2$I at room temperature.

flects symmetry around iron atom. In the piano-stool iron dicarbonyl complexes, the decreasing I.S. values reflect an increasing s-electron density at the iron nucleus and the Q.S. values are almost invariant.[9] The I.S. and Q.S. values for **1** and Cp*Fe(CO)$_2$I are almost the same to each other and are similar to those of Cp*Fe(CO)$_2$Cl.[9c] The Q.S. values for **1** and Cp*Fe(CO)$_2$I are slightly smaller than that of {Cp*Fe(CO)$_2$}$_2$ (I.S. $= 0.123$, Q.S. $= 2.109\,\mathrm{mm\,s^{-1}}$), suggesting an effect of iodine introduction. Systematic study of Fe–P(E)YZ (E = O or S; Y, Z = alkoxy, amino, or phenyl) revealed that a certain ratio of the electron density afforded by π donation from P(O)(OMe)$_2$ to Fe is equally donated to two CO ligands and the invariance of the Q.S. values has been attributed to the role of iron atom as the transit of the effect of donor or acceptor character from one ligand to the CO ligand.[9c] In the present case also, the effects of the introduced iodine molecule in **1** is transferred to CO ligands via iron atom. It is well known that the π-back donation from a filled d orbital of a transition metal to an empty π^* orbital of a CO ligand causes a decrease in ν_{CO}. It is considered that the decrease in this π-back donation in **1** is due to the introduction of iodine molecule.

In conclusion, we synthesized novel iodine-bridged piano-stool complex and determined the crystal structure. The bridged iodine affected the CO bond via iron atom, while the iron atom itself was not affected.

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References and Notes

1 a) F. A. Cotton, C. Lin, and C. A. Murillo, *Acc. Chem. Res.*, **34**, 759 (2001). b) O. R. Evans and W. Lin, *Acc. Chem. Res.*, **35**, 511 (2002). c) S.-S. Sun and A. J. Lees, *Coord. Chem. Rev.*, **230**, 171 (2002).

2 a) "Comprehensive Supramolecular Chemistry," ed. by J.-M. Lehn, J. L. Atwood, J. E. D. David, D. D. MacNicol, and F. Vögtle, Pergamon Press, Oxford (1990–1996), Vol. 1–11. b) J.-M. Lehn, "Supramolecular Chemistry, Concepts and Perspectives," VCH, Weinheim (1995). c) P. Metrangolo, G. Resnati, *Chem.—Eur. J.*, **7**, 2511 (2001). d) P. Metrangolo, H. Neukirich, T. Pilati, and G. Resnati, *Acc. Chem. Res.*, **38**, 386 (2005). e) P. Metrangolo, T. Pilati, G. Resnati, and A. Stevenazzi, *Chem. Commun.*, **2004**, 1492.

3 a) C. J. Horn, A. J. Blake, N. R. Champness, V. Lippolis, and M. Schröder, *Chem. Commun.*, **2003**, 1488. b) D. W. Alley, R. Berrige, N. Bricklebank, S. D. Forder, F. Palacio, S. J. Coles, M. B. Hursthouse, and P. J. Skabara, *Inorg. Chem.*, **42**, 3975 (2003).

4 a) S. Nakashima, A. Hori, H. Sakai, M. Watanabe, and I. Motoyama, *J. Organomet. Chem.*, **542**, 271 (1997). b) T. Oda, S. Nakashima, and T. Okuda, *J. Organomet. Chem.*, **637–639**, 820 (2001). c) T. Oda, S. Nakashima, and T. Okuda, *Inorg. Chem.*, **42**, 5376 (2003).

5 R. B. King, W. M. Douglas, and A. Efraty, *J. Organomet. Chem.*, **69**, 131 (1974).

6 Found: C, 29.00; H, 3.29%. Calcd for $C_{24}H_{30}O_4I_4Fe_2$: C, 28.77; H, 3.02%.

7 Crystal data: for Cp*Fe(CO)$_2$I; $C_{12}H_{15}O_2IFe$ (374.00), monoclinic, $P2_1/n$ (No. 14), $a = 7.293(4)$ Å, $b = 14.417(7)$ Å, $c = 13.095(6)$ Å, $\beta = 92.553(9)^\circ$, $V = 1375.5(12)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.806\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 33.24\,\mathrm{cm^{-1}}$, 5824 unique reflections measured, $R1 = 0.036$, $wR2 = 0.106$ ($I > 2.00\sigma(I)$). For **1**; $C_{12}H_{15}O_2I_2Fe$ (500.91), triclinic, $P\bar{1}$ (No. 2), $a = 7.749(3)$ Å, $b = 8.223(3)$ Å, $c = 13.781(5)$ Å, $\alpha = 79.859(6)^\circ$, $\beta = 92.553(9)^\circ$, $\gamma = 67.087(7)^\circ$, $V = 796.2(5)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 2.089\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 48.14\,\mathrm{cm^{-1}}$, 2253 unique reflections measured, $R1 = 0.053$, $wR2 = 0.139$ ($I > 2.00\sigma(I)$). Data were collected with a Bruker SMART-APEX three-circle diffractometer, equipped with a CCD area detector (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scan mode (0.3° steps), semiempirical absorption correction on Laue equivalents). The structures were solved by direct method and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.

8 M. Akita, M. Terada, M. Tanaka, and Y. Morooka, *J. Organomet. Chem.*, **510**, 255 (1996). For the comparison with **1** our data for Cp*Fe(CO)$_2$I were used. See Supporting Information.

9 a) G. M. Bancroft, K. D. Butler, L. E. Manzer, A. Shaver, and J. E. H. Ward, *Can. J. Chem.*, **52**, 782 (1974). b) G. J. Long, D. G. Always, and K. W. Barnett, *Inorg. Chem.*, **17**, 486 (1978). c) H. Nakazawa, S. Ichimura, Y. Nishihara, K. Miyoshi, S. Nakashima, and H. Sakai, *Organometallics*, **17**, 5061 (1998).

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