Journal of Organometallic Chemistry 637–639 (2001) 820–822

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Control of the symmetry of binuclear ferrocene derivative by using chiral substituent and its mixed-valence state

Takashi Oda [a], Satoru Nakashima [b,*], Tsutomu Okuda [a]

[a] *Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan*

[b] *Radioisotope Center, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan*

Received 30 January 2001; received in revised form 12 June 2001; accepted 18 June 2001

Abstract

The mixed-valence 1′,1‴-bis((*R*)-2-phenylbutyl)-, 1′,1‴-bis((*S*)-2-phenylbutyl)- and 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium salts were investigated to reveal the importance of cation symmetry on the mixed-valence states. (*R*,*R*) and (*S*,*S*) samples never showed the perfect valence detrapping, while (*R*,*S*) sample showed the detrapped-valence state at room temperature. © 2001 Published by Elsevier Science B.V.

Keywords: Mixed-valence state; Binuclear ferrocene derivatives; ^{57}Fe Mössbauer spectroscopy; Cation symmetry

---

1. Introduction

The nature of electron transfer between well-separated metal sites has been discussed in superconductive materials and biological systems [1,2]. The study of mixed-valencey was advanced by the discovery of mixed-valence binuclear ferrocenes [3]. Binuclear ferrocenes have an advantage because of the ease of synthetic design and of various selectivities for counter anions. From investigations for many mixed-valence biferrocenium derivatives, it was shown that the effects of cation symmetry and its packing play an important role on the mixed-valence state [2,4–8]. To discuss the two effects separately, we started to study the mixed-valence state of binuclear ferrocenes having an asymmetric carbon in the substituent. Because the (*R*,*S*) sample has an inversion center, while (*R*,*R*) and (*S*,*S*) samples cannot. And we can control the intermolecular interaction by the construction of crystal using (*R*,*R*), (*S*,*S*) and (*R*,*S*) isomers as a building block.

In the present study, we synthesized 1′,1‴-bis((*R*)-2-phenylbutyl)-, 1′,1‴-bis((*S*)-2-phenylbutyl)- and 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium salts and investigated the mixed-valence state by means of ^{57}Fe Mössbauer spectroscopy in order to reveal the role of cation symmetry.

2. Experimental

2.1. Syntheses

1′,1‴-bis((*R*)-2-phenylbutyl)- and 1′,1‴-bis((*S*)-2-phenylbutyl)-1,1″-biferrocenes were synthesized according to the method reported for a series of ferrocene derivatives with alkyl substituents [9]. In the acylation, (*S*)-(+)- and (*R*)-(−)-2-phenylbutyryl chlorides were used. The products were isolated by column chromatography on alumina.

1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocene was synthesized by using the equimolar mixture of 1′-(*R*)-2-phenylbutyl-1-bromoferrocene and 1′-(*R*)-2-phenylbutyryl-1-bromoferrocene in the Ullman coupling reaction [10], which is shown in Scheme 1. After extraction by dichloromethane, the mixture was

---

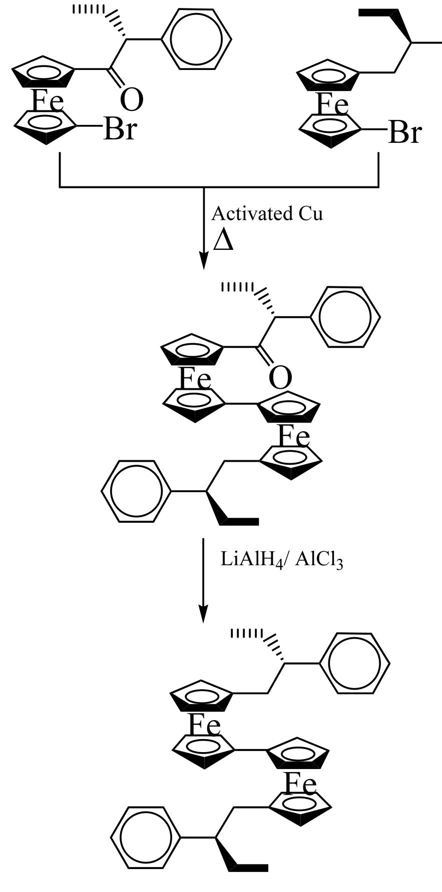
* Corresponding author. Tel.: +81-824-24-6291; fax: +81-824-24-0700.

E-mail address: snaka@hiroshima-u.ac.jp (S. Nakashima).

0022-328X/01/$ - see front matter © 2001 Published by Elsevier Science B.V.
PII: S0022-328X(01)01134-2

isolated by column chromatography on alumina. The first and second bands were (*R*)-2-phenylbutylferrocene and 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocene eluted with hexane, respectively. The third band was (*R*)-2-phenylbutyrylferrocene eluted with hexane/benzene (7:3). The forth band was 1′-((*R*)-2-phenylbutyl)-1‴-((*R*)-2-phenylbutyryl)-1,1″-biferrocene eluted with benzene. The fifth band was 1′,1‴-bis((*R*)-2-phenylbutyryl)-1,1″-biferrocene eluted with dichloromethane. Then, 1′-((*R*)-2-phenylbutyl)-1‴-((*R*)-2-phenylbutyryl)-1,1″-biferrocene was reduced by lithium aluminum hydride with aluminum chloride.

These 1′,1‴-bis(2-phenylbutyl)-1,1″-biferrocenes were oxidized by adding I_2 dissolved in hexane to a hexane solution of neutral complex. But, the triiodide salts were not obtained in these biferrocene derivatives although a stoichiometric amount (3/2 times) of I_2 was added. Moreover, by adding 5/2 times amount of I_2, the perfect pentaiodide salt was never obtained. About one-half of each sample was recrystallized from a dichloromethane solution under a hexane atmosphere at 0 °C.



Scheme 1. Synthesis of 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocene.

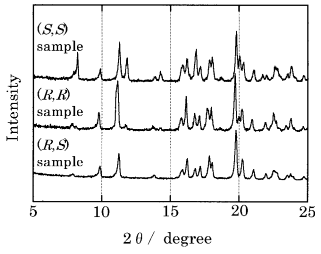


Fig. 1. Powder X-ray diffraction patterns at room temperature.

2.2. X-ray crystallography

All powder X-ray diffraction patterns were measured at room temperature by a Rigaku Rad-B system, using graphite-monochromated Cu–K_α radiation.

2.3. ^{57}Fe Mössbauer spectroscopic measurements

A ^{57}Co(Rh) source moving in a constant-acceleration mode was used for ^{57}Fe Mössbauer spectroscopic measurements. Variable-temperature ^{57}Fe Mössbauer spectra were obtained by using a Toyo-Research spectrometer and a continuous-flow cryostat. The ^{57}Fe Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to metallic iron.

3. Results and discussion

3.1. Powder X-ray diffraction patterns

1′,1‴-bis((*R*)-2-phenylbutyl)-, 1′,1‴-bis((*S*)-2-phenylbutyl)- and 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium salts are abbreviated to the (*R*,*R*), (*S*,*S*) and (*R*,*S*) samples, respectively. Fig. 1 shows the powder X-ray diffraction patterns of the (*R*,*R*), (*S*,*S*) and (*R*,*S*) samples from dichloromethane at room temperature. Diffraction patterns of all samples show no remarkable change by the recrystallization. The (*R*,*R*) and (*S*,*S*) samples show the same diffraction peak positions. There is no critical difference between them as is expected for both enantiomers. They may show the same mixed-valence state.

On the other hand, the powder X-ray diffraction pattern of the (*R*,*S*) sample is similar to those of (*R*,*R*) and (*S*,*S*) samples although some diffraction peaks are vanished. This suggests that each sample has the same crystal structure basically, but crystal symmetry is raised by the effect of cation symmetry. Moreover, the diffraction pattern is similar to that of the DL sample.

3.2. ^{57}Fe Mössbauer spectra

Fig. 2 shows the variable-temperature ^{57}Fe Mössbauer spectra of (*R*,*R*) sample from hexane. The observed spectra consist of outer and inner doublets at all

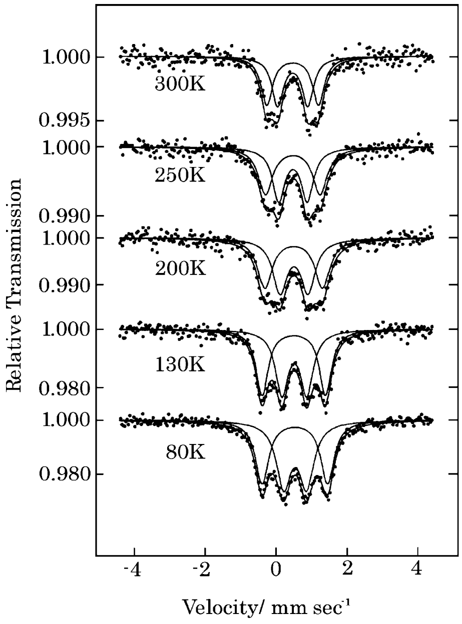


Fig. 2. Variable-temperature ^{57}Fe Mössbauer spectra of 1′,1‴-bis((*R*)-2-phenylbutyl)-1,1″-biferrocenium salt from hexane.

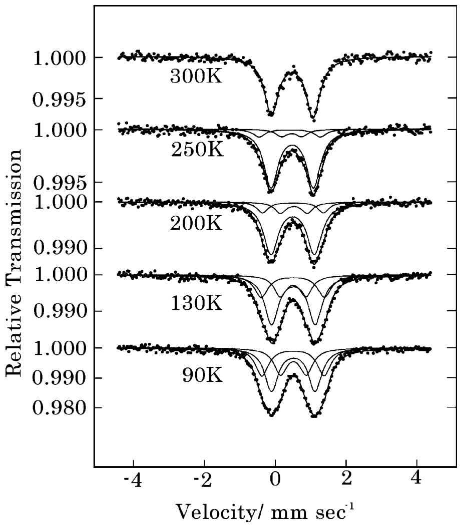


Fig. 3. Variable-temperature ^{57}Fe Mössbauer spectra of 1′-((*R*)-2-phenylbutyl)-1‴-((*S*)-2-phenylbutyl)-1,1″-biferrocenium salt from hexane.

temperatures. They have typical trapped-valence quadrupole splitting values ($\Delta E_Q = 1.84(2)$, 0.65(2) mm s^{-1} in the sample from hexane) at 80 K. Although they approach to each other with increasing temperature, they never fuse into one doublet even at 300 K. This temperature dependence of quadrupole splitting is similar to that of 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide from hexane [11], suggesting that the (*R*,*R*) sample will be kept in a close trapped-valence state above 300 K.

The (*R*,*R*) sample shows no significant difference in temperature dependence of ^{57}Fe Mössbauer spectra between samples from hexane and dichloromethane. This finding is different from that of 1′,1‴-bis(2-methylbutyl)-1,1″-biferrocenium triiodide. We believe that phenyl rings prevent to produce rotational isomers, because it is huge and solid. The temperature dependence of quadrupole splitting of the (*S*,*S*) sample was similar to that of the (*R*,*R*) sample as we expected for both enantiomers.

Fig. 3 shows the ^{57}Fe Mössbauer spectra of the (*R*,*S*) sample. Three quadrupole splitting doublets are observed at 90 K, which are assigned to the trapped-valence ($\Delta E_Q = 1.75(3)$ and 0.73(3) mm s^{-1}) and detrapped-valence state doublets ($\Delta E_Q = 1.23(3)$ mm s^{-1}). The relative area ratio for the detrapped-valence state is increased with increasing temperature, thus a perfect detrapped-valence state is observed at room temperature.

It was shown that we can control the symmetry of binuclear ferrocene and then the mixed-valence state by using chiral substituent. We revealed the role of cation symmetry for mixed-valence state in the present study. We continue the study to know whether the packing effect overcome the effect of cation symmetry or not.

4. Supplementary material

The table of ^{57}Fe Mössbauer spectral fitting parameters is available from the corresponding author.

References

[1] D.B. Brown, J.T. Wrobleskii, in: D.B. Brown (Ed.), Mixed-Valence Compounds: Theory and Applications in Chemistry, Physics, Geology, and Biology, D. Reidel, Dordrecht, 1980, pp. 243–270.
[2] D.N. Hendrickson, in: K. Prassides (Ed.), Mixed Valency Systems: Applications in Chemistry, Physics, and Biology, Kluwer, Dordrecht, 1991, pp. 67–90.
[3] D.O. Cowan, F. Kaufman, J. Am. Chem. Soc. 92 (1970) 219.
[4] H. Sano, Hyperfine Interact. 53 (1990) 97.
[5] S. Nakashima, in: S.G. Pandarai (Ed.), Recent Research Developments in Pure and Applied Chemistry, vol. 2, Transworld Research Network, Trivandrum, 1998, pp. 247–273.
[6] R.J. Webb, S.J. Geib, D.L. Staley, A.L. Rheingold, D.N. Hendrickson, J. Am. Chem. Soc. 112 (1990) 5031.
[7] M. Kai, M. Katada, H. Sano, Chem. Lett. (1988) 1523.
[8] S. Nakashima, A. Nishimori, Y. Masuda, H. Sano, M. Sorai, J. Phys. Chem. Solids 52 (1991) 1169.
[9] S. Nakashima, Y. Masuda, I. Motoyama, H. Sano, Bull. Chem. Soc. Jpn. 60 (1987) 1673.
[10] T.-Y. Dong, P.-J. Lin, K.-J. Lin, Inorg. Chem. 35 (1996) 6037.
[11] S. Nakashima, T. Oda, T. Okuda, M. Watanabe, Inorg. Chem. 38 (1999) 4005.