

INTERACTION OF BETWEEN TWO IRON METALS WITH A π -CONJUGATED BRIDGES AS A MOLECULAR WIRES

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Introduction

Electronic equipments are gone by inclination of minia-
turization although it sees a computer, cellular phone,
and digital camera etc. However to slenderize wiring in
electronic device is limited by lithographical method.
Recent, many researcher were interested in unimolecular
wire to apply for the miniaturization of the electronic
circuit in molecular electronic device such as molecular
rectifier, molecular transistor, molecular switch, and
molecular diode. In this report, we present the materials
for electronic communication between dimetallic
complexes with electron transfer chain-bridged (Figure
1). One-dimensional molecular wire is possible
information communication between two metals when
stimulus (redox, photon, pH) gives the one electron
transfer to the other via conjugated chain-bridged. We
report the synthesis and characterization of conjugated
dirion complexes, $[\text{Cp}^*(\text{dppe})\text{Fe}]_2(\mu\text{-C}\equiv\text{C-CH=CH-C}\equiv\text{C})$
and $[\text{Cp}^*(\text{CO})(\text{PPh}_3)\text{Fe}]_2(\mu\text{-CH=CH-CH=CH})$.

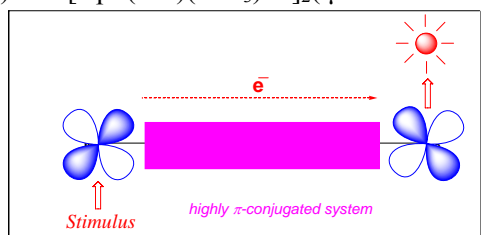


Figure 1. One-dimensional molecular wire

Experimental

All reactions and manipulations were carried out under
an inert atmosphere (N_2 or Ar gas) using the Schlenk
technique. Solvents were freshly distilled under Ar using
the standard procedures (Na/K/benzophenone or CaH_2).
Electrochemical measurements obtained with a BAS
100B/W potentiostat. CV samples were prepared in $n\text{-Bu}_4\text{NPF}_6$
electrolyte solution (0.1 M) in THF. Working
electrode was a platinum disk, the auxiliary electrode

was a platinum wire, and the pseudoreference electrode
was an Ag/AgCl. Potentials were internally referenced to
the $\text{Cp}_2\text{Fe}^{0/+}$ couple by adding Cp_2Fe at the end of the
experiment.

1. Synthesis of the $[\text{Cp}^*(\text{CO})(\text{PPh}_3)_2\text{Fe}]_2(\mu\text{-CH=CH-CH=CH})$ (1)

A mixture of compound, $[\text{Cp}^*(\text{CO})_2\text{Fe}]_2(\mu\text{-CH=CH-CH=CH})$ (104.7 mg, 0.1917 mmol), 3 eq. of the PPh_3 (163mg), and 20 ml of THF was photolyzed for 1 hr in 25ml Pyrex vessel at 0 °C, using the 450 W Hanovia broad-band UV Lamp. The vessel was flushed with N_2 gas and shaken three times during the photolysis. The THF solution was filtered, solvent was removed under vacuum, and the residue was re-dissolved in minimum amount of pentane. The solution was placed in -25°C freezer without disturbance. After 2 days, mother liquor and crystal was separated. The crystal part is *meso*-isomer (**1-meso**, 60 mg, 30% in yield), and mother liquor part is *dl*-isomer (**1-dl**, 67 mg, 33% in yield).

meso-form: $^1\text{H-NMR}$ (C_6D_6): δ_{H} , 7.73(t, $J=9.6$ Hz, 12H, Ph) 7.02 ~ 7.12(m, 18H, Ph), 6.60(s, 4H, Fe-CH=CH), 1.39(s, 30H, C_5Me_5). $^{13}\text{C-NMR}$ (C_6D_6): δ_{C} , 224.7(d, $J=29.7$ Hz, Fe-CO), 151.9 (d, $J=2.8$ Hz, Fe-CH=CH), 146.8(d, $J=31.8$, Fe-CH=CH), 137.8, 137.6, 134.3, 129.4, 128.1, 128.0(Ph), 92.9(s, C_5Me_5), 10.1 (s, C_5Me_5). $^{31}\text{P-NMR}$ (C_6D_6): δ_{P} , 79.6 ppm. IR(KBr, cm^{-1}): 1989 (CO), Anal. Calcd for $\text{C}_{62}\text{H}_{64}\text{P}_2\text{O}_2\text{F} + \text{C}_5\text{H}_{12}$: C,74.03; H,7.05. Found: C,74.18; H,7.46.

dl-form: $^1\text{H-NMR}$ (C_6D_6): δ_{H} , 7.67(t, $J=9.6$ Hz, 12H, Ph) 6.98(m, 18H, Ph), 6.59(d, 4.5 Hz, 2H, Fe-CH=CH), 6.57(d, $j=3.3$ Hz, 2H, Fe-CH=CH), 1.43(s, 30H, Cp^*). $^{13}\text{C-NMR}$ (C_6D_6): δ_{C} , 225.1(d, $J=29.7\text{Hz}$, Fe-CO), 152.6 (d, $J=2.8$ Hz, Fe-CH=CH), 146.7(d, $J=31.8$, Fe-CH=CH), 137.1, 137.3, 134.8, 134.7, 129.4, 128.1, 128.0, 92.9(s, C_5Me_5), 10.1 (s, C_5Me_5). $^{31}\text{P-NMR}$ (C_6D_6): δ_{P} , 78.2 ppm. IR(KBr, cm^{-1}): 1900 (CO).

2. Synthesis of *cis*-(dppe) $\text{Cp}^*\text{Fe-C}\equiv\text{C-CH=CH-C}\equiv\text{C-FeCp}^*(\text{dppe})$ (2)

The 1 eq. of KOBu^t (185 mg, 1.648 mmol) was added to

a solution of complex 1 in THF (50 ml). The reaction mixture was stirred for 1 hr at room temperature, filtered with alumina. The complex 2 (yield 97%) was collected by dried under vacuum.

$^1\text{H-NMR}(\text{C}_6\text{D}_6)$, δ_{H} , 1.20 (s, Cp*, 15H), 1.33, 2.30(m, dppe, 8H), 5.45 ($-\underline{\text{C}}\underline{\text{H}}=\underline{\text{C}}\underline{\text{H}}-$, 2H), 6.76~7.02, 7.68~7.72(m, Ph, 40H)

Results and Discussion

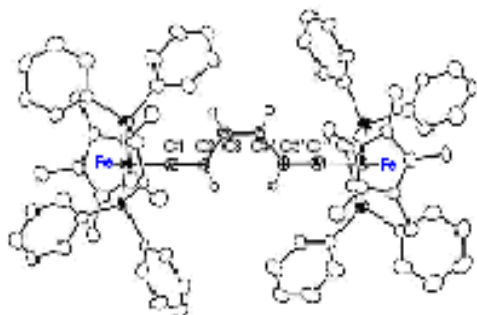


Figure 2. Molecular Structure of 2

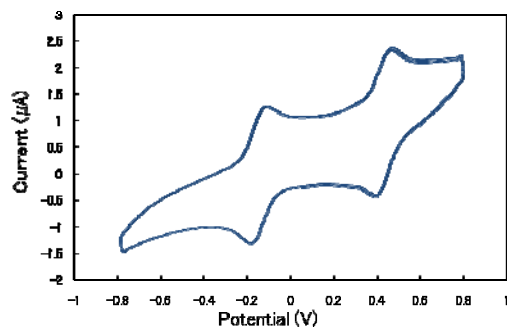


Figure 3. The cyclic voltammogram of complex **1-meso**. (5×10^{-5} M in 0.1 M n- Bu₄NPF₆ electrolyte solution (0.1 M) in CH₂Cl₂, referenced to the Cp₂Fe^{0/+} at 0.0 V, room temp., 100 mV/s

Molecular structure of the dication complex 1 is shown in Figure 1. As shown in Figure 1, the compound contains two iron centers linked by a C=C-CH=CH-C=C bridge, and the isomer is (Z)-form. The bond distance of Fe(1)-C(1), C(1)-C(2), C(2)-C(3), C(3)-C(3'), are 1.740(4), 1.329(5), 1.412(9), 1.36(1) Å, respectively. Complex **1-meso** show two well resolved, single electron, reversible oxidation waves by CV, and a representative voltammogram is shown in Figure 3. Comproportionation constant, **Kc**, calculated from the CV data for complexes. The **Kc** value is very high, above 10^7 . The Mixed-valence (MV) radical cation **2⁺** show strong absorptions in the near IR, 1586 nm, and this band is more readily assigned as MV π - π band of delocalized complex (Robin and Day Class III).

Conclusions

Table 1. Dimetallic Complexes
($(\text{C}_5\text{R}_5)_2\text{L}_2\text{Fe-Bridge-FeL}_2(\text{C}_5\text{R}_5)$)

R	L ₂	Bridge	Kc
H	dppe	$\mu\text{-C}_4\text{H}_4$	9.2×10^7
Me	dppe	$\mu\text{-C}_4\text{H}_4$	1.5×10^{10}
Me	dppe	$\mu\text{-C}_4$	1.1×10^{12}
Me	dppe	$\mu\text{-C}_6\text{H}_2$	1.9×10^7
Me	<i>meso</i> -(CO)(PPh ₃)	$\mu\text{-C}_4\text{H}_4$	3.0×10^9
Me	<i>dl</i> -(CO)(PPh ₃)	$\mu\text{-C}_4\text{H}_4$	1.0×10^9

In conclusion, The C₆H₂ and C₄H₄-bridged complexes have fully conjugated structure, as indicated by the NMR, CV, UV/VIS-near IR. From the CV data, it appears that The C₆H₂ and C₄H₄-bridges can mediate electronic communication between metal centers.

Acknowledgment

This work was supported by the GT-FAM Regional Innovation Center Program (RIC) of Sunchon National University.

References

- (a) Lapinte, C.; Paul, F. *Coord. Chem. Rev.*, 1998, **178**, 431(1998), (b) Weyland, T.; Costuas, K.; Halet, J.; Lapinte, C., *Organometallics*, **19**, 4228 (2000), (c) N.L. Narvor; L. Toupet; C. Lapinte, *J. Am. Chem. Soc.*, **117**, 7129 (1995)
- (a) Sakurai, A.; Akita, M.; Moro-oka, Y.; *Organometallics*, **18**, 3241(1999). (b) Akita, M.; Chung, M.; Sakurai, A.; Sugimoto, S.; Terada, M.; Tanaka, M.; Moro-oka, Y.; *Organometallics*, **16**, 4882(1997), (c) Akita, M.; Sakurai, A.; Chung, M.; Moro-oka, Y., *J. Organomet. Chem.*, **670**, 2(2003)
- Etzenhouser, B.A.; Chen, Q.; Sponsler, M. *Organometallics*, 1994, **13**, 4176(1994)