Available online at www.sciencedirect.com

SCIENCE DIRECT

ELSEVIER

Coordination Chemistry Reviews 250 (2006) 1012–1022

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Functionalized ferrocenes
Unique properties based on electronic communication between amino group of the ligand and Fe center

Kohtaro Osakada*, Tatsuaki Sakano, Masaki Horie, Yuji Suzaki

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatduta, Midori-ku, Yokohama 226-8503, Japan

Received 25 August 2005; accepted 30 November 2005
Available online 30 January 2006

Contents

Abstract

Recent results of our studies on preparation and properties of the ferrocene derivatives with amine-containing ligands are reviewed. We established a route to 2-aza[3]ferrocenophanes with an *N*-aryl or *N*-alkyl substituent by using $RuCl_2(PPh_3)_3$ as catalyst for condensation of 1,1′-bis(hydroxymethyl)ferrocene with primary amines. The obtained ferrocenophanes show reversible redox of the Fe center. At higher potentials, quasi-reversible or irreversible electrochemical oxidation of amino groups of the ligand is observed for most of the 2-aza[3]ferrocenophanes. The initially formed one-electron-oxidized species undergo rapid and reversible intramolecular electron transfer between the Fe center and the nitrogen atom of the ligand. The 2-aza[3]ferrocenophanes with *N*-aryl group bonded to *trans*-aminoazobenzene group undergo photo-induced isomerization to its *cis* isomer, giving an equilibrated mixture under photostationary state. Electrochemical oxidation of the Fe(II) center shifts the equilibrium to formation of the *trans*-azobenzene even under photoirradiation. Thus, thermodynamics of the isomerization of azobenzene group is regulated by changing the oxidation state of the molecule. Protonation of ferrocene derivatives with aminomethyl group on the cyclopentadienyl ligand forms the dialkylammonium group which forms a complex with dibenzo[24]crown-8 (DB24C8) with interlocked structures. The pseudorotaxanes obtained were characterized by X-ray crystallography and mass spectrometry. Electrochemical oxidation of the ferrocene with aminomethyl group at a cyclopentadienyl ligand in the presence of 1-hydroxy-2,2,6,6-tetramethylpiperidine (TEMPOH) leads to formation of the dialkylammonium group which produces the pseudorotaxane instantly with added DB24C8.

Keywords: Ferrocene; Rotaxane; Azobenzene; Electrochemistry

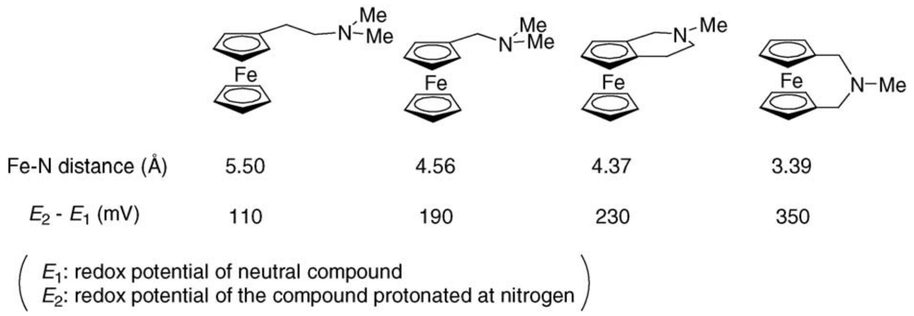
1. Introduction

A number of the ferrocene derivatives have been synthesized and used as electronic and optical materials because the cyclopentadienyl (Cp) ligand of ferrocene is readily functionalized by nucleophilic organic reagents and because electrochemical properties of the $Fe(II)Cp_2$ fragment can be tuned by selecting the substituents introduced to the Cp ligand [1]. The redox between the neutral Fe(II) state and cationic Fe(III) state, involving fast and reversible electron transfer, is the important property of the ferrocene derivatives. Introduction of electrochemically active organic groups in the ligand of ferrocene forms the molecules containing the inorganic and organic redox-active centers. The ferrocene derivatives with aminoalkyl substituents at a Cp ligand were reported by Plenio et al. to show two electrochemical oxidation reactions, redox of the Fe center and

---

* Corresponding author. Tel.: +81 45 924 5224; fax: +81 45 924 5224.
E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.11.022



Scheme 1.

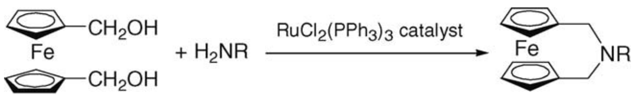
oxidation of the amino group of the ligand [2]. The compounds having a shorter Fe–N distance exhibit a higher potential for oxidation of the amino group due to interaction between the Fe(III) center and the amino group (Scheme 1).

2-Aza[3]ferrocenophanes were reported to contain a short Fe–N distance due to the methylene spacer and to the cyclic structure that fixes relative positions of these atoms. Electron transfer between the Fe and N atoms of the 2-aza[3]ferrocenophanes is expected to take place easily.

Reports of detailed studies on the ferrocene derivatives with amino group in the ligand were limited partly because of lack in general preparation methods of these compounds. We have recently succeeded to prepare a series of the 2-aza[3]ferrocenophanes by using coupling reactions catalyzed by transition metal complexes and investigated detailed properties of these compounds. In this review article, we summarizes preparation, structures, and properties of the aminomethylferrocene and 2-aza[3]ferrocenophanes which function as unique materials responding to electrochemical stimulus.

2. Preparation and properties of 2-aza[3]ferrocenophanes

Murahashi, Tsuji, and their respective co-workers reported that $RuCl_2(PPh_3)_3$ catalyzed coupling of the compounds having OH and NH groups via condensation of these polar groups to form the products with new C–N bonds [3]. This type of reaction was employed for preparation of not only the organic compounds but also the polymers having polar functional groups [4]. We conducted condensation of 1,1′-bis(hydroxymethyl)ferrocene with primary amines catalyzed by the Ru complex and obtained 2-aza[3]ferrocenophanes, as shown in the following equation [5]:

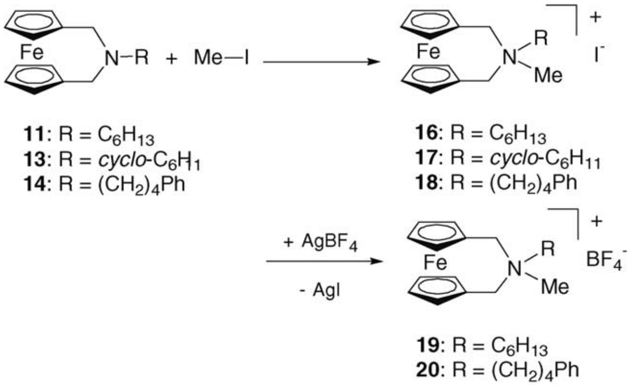


(1)

Chart 1 summarizes the ferrocenophanes prepared in this study. In spite of high temperature of the reaction (ca. 180 °C), cyclizative condensation of the diol with the aromatic and aliphatic amines produces the ferrocene derivatives whose cyclopentadienyl ligands are bridged by a CH_2–NR–CH_2 group in moderate and high yields.

Compounds **4**–**6**, **12**, and **15** having Br, OH, and ferrocenyl groups as the *N*-substituents are obtained selectively. Molecular structures of **1**–**3**, **8**, and **9** were determined by X-ray crystallography. The N–C bond distances are shown in Table 1. Compounds **1**–**3** have the N–C(aryl) bonds which are significantly shorter than the CH_2–N bond distance. It may be partly ascribed to an sp^2 character of the nitrogen atom bonded to the aromatic ring or possible canonical structures shown in Scheme 2.

The ferrocenophanes **11**, **13**, and **14** with *N*-alkyl substituent undergo addition of MeI to the nitrogen atom to form the ferrocenophane containing quaternary ammonium group and iodide as the counter anion **16**–**18**, as shown in Eq. (2). Exchange of the anion of **16** and **18** with BF_4^- leads to the formation of **19** and **20** smoothly:



(2)

N–C bond distances of these ionic compounds (1.49–1.57 Å, Table 1) are in the range of C–N single bonds, and are consistent with the sp^3 hybridization of the nitrogen atom.

Cyclic voltammogram of the ferrocenophanes **1**–**14** in MeCN shows reversible electrochemical oxidation and reduction of the Fe center at $E_{1/2} = -0.02$ to $+0.08$ V (versus Ag^+/Ag), which are at similar positions to redox of ferrocene. Ferrocenophane **6** with 4-hydroxyphenyl group at the nitrogen atom shows additional reversible electrochemical oxidation and reduction at $E_{1/2} = +0.41$ V. Scheme 3 depicts the plausible mechanism that accounts for reversible two-step oxidation. Initial oxidation of **6** occurs at the Fe(II) center to form a ferrocenium species. Electron transfer from the amino group of the ligand to the Fe(III) center partly forms a Fe(II) species with radical cation at the