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Priority Communication

N-Substituted 2-aza-[3]-ferrocenophanes. New synthesis using $RuCl_2(PPh_3)_3$ catalyzed condensation, structure, and electrochemical behavior

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Abstract

The reactions of 1,1′-ferrocenedimethanol with arylamine and with alkylamine in the presence of $RuCl_2(PPh_3)_3$ catalyst led to condensation of CH_2OH and NH groups to afford N-alkyl-(or N-aryl-)2-aza-[3]-ferrocenophanes. The ^{1}H- and ^{13}C-NMR spectra and crystallography of N-(4-butylphenyl)-2-aza-[3]-ferrocenophane showed the proposed structure. Electrochemical oxidation of the N-aryl- and N-alkyl-2-aza-[3]-ferrocenophane was studied. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ferrocene and its derivatives are of various kinds of use in synthetic organic chemistry and material science, owing to stable coordination of the cyclopentadienyl (Cp) ligands, possible induction of chirality in the molecules, and reversible redox behavior of the metal center [1]. Introduction of functional groups onto Cp ligands of ferrocene leads to the synthesis of a number of new reagents, ligands for transition metal complexes, and polymers containing ferrocene derivative in the repeating unit. Ferrocenophanes with bivalve-like structures are expected to show unique chemical properties owing to functionality of the side arm. There has been a lesser number of studies carried out on structure and properties of aza-[n]-ferrocenophanes than on other ferrocenophanes in spite of the rich functionality of the side arm. 2-Aza-[4]-ferrocenophanes were prepared by several reactions, starting from oxoferrocenophane and were revealed to be unstable at room temperature (r.t.) [2]. Reaction of 1,1′-ferrocenedimethanol with aryl isocyanate gave N-aryl-2-aza-[3]-ferrocenophane but often in very low yields (7% for phenyl isocyanate) [3]. N-Methyl-2-aza-[3]-ferrocenophane was recently prepared by Plenio et al. in 35% yield from condensation of methylamine with [1,1′-ferrocenediylbis(methylene)]-bis(pyridinium) tosylate [4]. The above preparation methods, however, often suffer from insufficient yields and lack in the generality of product structures.

Recent progress in synthetic organic reactions using Groups 8–10 metal complexes as catalysts have enabled condensation of primary alcohols with amines to form C–N bonds under relatively mild conditions [5,6]. Extension of this reaction to primary amine and 1,1′-ferrocenedimethanol would provide a general preparation method for N-alkyl-(or N-aryl)-2-aza-[3]-ferrocenophanes. In this paper we reported results of the reaction using aliphatic and aromatic amines to afford N-substituted-2-aza-[3]-ferrocenophanes as well as their structures and properties.

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Table 1
Preparation of *N*-alkyl (or aryl)-2-aza-[3]-ferrocenophanes [a]

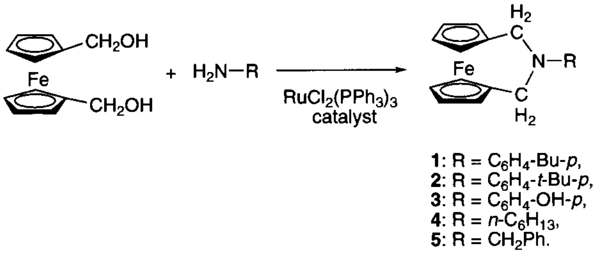
Amine	Product	Yield (%)	Analysis (%) [b]		
			C	H	N
4-Butylaniline	**1**	63	73.87	6.73	3.89
			(73.54)	(7.01)	(3.90)
4-*t*-Butylaniline	**2**	58	72.89	6.85	3.85
			(73.54)	(7.01)	(3.90)
4-Hydroxyaniline	**3**	56	67.73	5.37	3.39
			(67.72)	(5.36)	(4.42)
Hexylamine	**4**	40	69.46	8.10	4.50
			(69.36)	(7.95)	(4.25)
Benzylamine	**5**	70	72.66	5.68	4.02
			(71.94)	(6.04)	(4.42)

[a] The reactions were carried out by heating of the NMP solution for 24 h at 180°C under a nitrogen or argon atmosphere.

[b] Required values are in parentheses.

2. Results and discussion

Heating of an NMP solution of 1,1′-ferrocenedimethanol and 4-butylaniline in the presence of $RuCl_2(PPh_3)_3$ catalyst gave *N*-(4-butylphenyl)-2-aza-[3]-ferrocenophane in 63% yield (Eq. 1).



(1)

Similar reactions with 4-*t*-butylaniline, 4-hydroxyaniline, hexylamine, and benzylamine afforded the corresponding *N*-substituted 2-aza-[3]-ferrocenophanes as summarized in Table 1. Yields of the isolated products are moderate to high, and not lowered by the presence of the OH-*p* group in preparation of **3**. The complexes were characterized by NMR spectroscopy and elemental analyses. The ^1H- and $^{13}C\{^1H\}$-NMR spectra of **1**–**5** show the signals at δ 2.8–3.9 (^1H) and δ 46–48 (^{13}C) due to the CH_2 group attached to the nitrogen atom and to the Cp rings. Fig. 1 depicts the molecular structure of **1** determined by X-ray crystallography. The unit cell contains two crystallographically independent molecules which have similar structures to each other. The two Cp rings are at almost staggered positions, similar to the previously reported structures of [3]-ferrocenophanes [7,8]. N–C(aryl) bond distances (1.400(6) and 1.396(6) Å) are significantly shorter than those of N–CH_2 bonds (1.467(6), 1.464(6), 1.464(6), and 1.462(6) Å), suggesting conjugation of the phenyl rings and the nitrogen atom.

The obtained ferrocenophanes are air and thermally stable, but electrochemically easily oxidized. Fig. 2 depicts cyclic voltammograms of **1** and **4** in MeCN solutions. Two reversible peaks (I and II) are observed at $E_{1/2} = 0.10$ and 0.72 V, respectively, for **1**, whereas **4** exhibits the peaks (III and IV) at $E_{1/2} = 0.03$ and 0.35 V. The first oxidation and reduction are close to that of ferrocene and assigned to redox between the ferrocene and ferricenium cation. The second peaks are assigned to oxidation of the ammonium salt formed via protonation of the nitrogen atom. Scheme 1 summarizes a plausible mechanism for the oxidation of the *N*-substituted-2-aza-[3]-ferrocenophanes. The intermediate (**A′**), formed via initial oxidation of the Fe^{II} center of ferrocenophane and intramolecular electron transfer (i), undergoes further oxidation of the Fe^{II} center

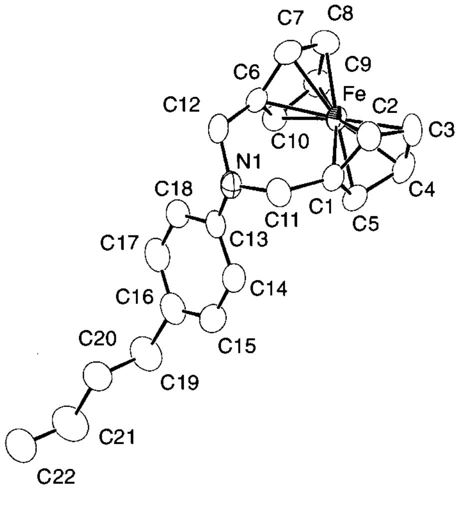


Fig. 1. ORTEP drawing of *N*-(4-butylphenyl)-2-aza-[3]-ferrocenophane (**1**) with 50% thermal ellipsoidal level. One of the two crystallographically independent molecules is shown. Selected bond distances (Å) and angles (°): Fe–C1 2.010(4), Fe–C2 2.042(4), Fe–C3 2.062(5), Fe–C4 2.051(5), Fe–C5 2.036(5), Fe–C6 2.009(4), Fe–C7 2.032(4), Fe–C8 2.065(5), Fe–C9 2.053(4), Fe–C10 2.036(4), C1–C11 1.519(6), C6–C12 1.514(6), N1–C11 1.467(6), N1–C12 1.464(6), N1–C13 1.400(6), C11–N1–C12 113.8(4), C11–N1–C13 120.7(4), C12–N1–C13 119.6(4), N1–C11–C1 115.4(4), N1–C12–C6 115.1(3).

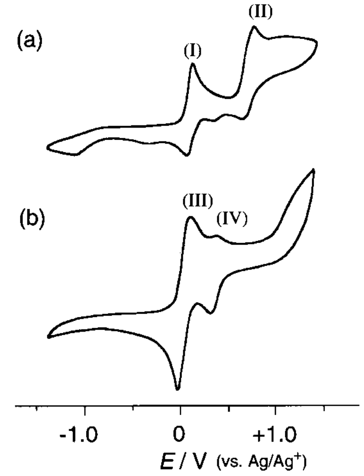
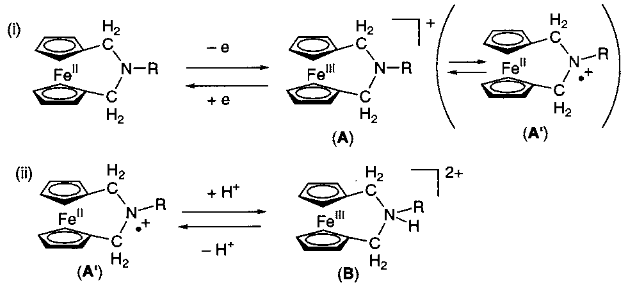


Fig. 2. Cyclic voltammograms for the oxidation of 2.5×10^{-3} M solutions of (a) **1** and (b) **4** in acetonitrile containing 0.10 M NEt_4BF_4 at 0.05 V s^{-1} and 25°C.

accompanied by reduction and protonation at the nitrogen with a radical cation character (ii) to afford the two electron oxidation product (**B**). Similar two-step electrochemical oxidation of cationic *N*,*N*-dimethyl-2-aza-[3]-ferrocenophane was reported to occur at a higher potential than *N*-methyl-2-aza-[3]-ferrocenophane [4,9]. The proton in (ii) may come from water impurities contained in the solvent or the ammonium salt.

The difference in the first and second oxidation potentials of **1** is larger than that of **4**. Plenio et al. found a wide range of oxidation potentials for various ferrocene derivatives containing ammonium groups and assigned the Fe–N nonbonding distances as a primary factor [4]. However, the above results indicate that the kind of *N*-substituent is also to be considered and that the second oxidation potential can be controlled by change of the substituent.

In summary we have demonstrated a new preparation method of *N*-substituted-2-aza-[3]-ferrocenophanes. The reaction is applied to syntheses of various kinds of *N*-alkyl and *N*-aryl-2-aza-[3]-ferrocenophanes including that containing the reactive OH group. The rigid structure and unique electrochemical properties suggest their potential utility as a new material.



Scheme 1.

3. Experimental

3.1. Preparation of N-substituted-2-aza-[3]-ferrocenophanes.

To an NMP (3 cm^3) solution of $RuCl_2(PPh_3)_3$ (67 mg, 0.070 mmol) was added 4-butylaniline (298 mg, 2.0 mmol) and then 1,1′-ferrocenedimethanol (492 mg, 2.0 mmol) at r.t. under a nitrogen atmosphere. The solution was heated for 24 h at 180°C and then kept at r.t. overnight. The product was purified by column chromatography (silica gel, hexane: ethyl acetate, 1:1) and recrystallized from a chloroform–methanol mixture to afford **1** as orange crystals (226 mg, 63%). $\delta_H(CDCl_3)$ 0.93 (3H, t, CH_3, $J = 8$ Hz), 1.38 (2H, tq, CH_2, $J = 7–8$ Hz), 1.59 (2H, tt, CH_2, $J = 8$ Hz), 2.54 (2H, t, $CH_2–C_6H_4$, $J = 8$ Hz), 3.80 (4H, s, CH_2N), 4.06 and 4.18 (4H, s, C_5H_4), 6.93 and 7.07 (4H, d, C_6H_4, $J = 8$ Hz); $\delta_C(CDCl_3)$ 14.0 (CH_3), 22.4 (CH_2CH_3), 33.9 and 34.6 (CH_2), 46.9 (CH_2N), 69.1 and 70.0 (CH in C_5H_4), 84.6 ($C–CH_2N$), 114.7, 129.2, 132.3 and 147.9.

Compounds **2**–**5** were prepared analogously. **2** was purified by recrystallization from $CHCl_3$–MeOH. NMR data for **2**: $\delta_H(CDCl_3)$ 1.32 (9H, s, CH_3), 3.81 (4H, s, CH_2N), 4.07 and 4.19 (4H, s, C_5H_4), 6.93 and 7.23 (4H, d, C_6H_4, $J = 9$ Hz); $\delta_C(CDCl_3)$ 31.5 (CH_3), 33.8 (CCH_3), 47.0 (CH_2N), 69.1 and 70.0 (CH in C_5H_4 group), 84.7 ($C–CH_2N$), 114.4, 126.1, 140.6 and 147.7. NMR data for **3**: $\delta_H(CDCl_3)$ 3.69 (4H, s, CH_2N), 4.08 and 4.18 (4H, s, C_5H_4), 4.38 (1H, s, OH), 6.80 and 6.93 (4H, d, C_6H_4, $J = 5$ Hz). NMR data for **4**: $\delta_H(CDCl_3)$ 0.92 (3H, t, CH_3, $J = 7$ Hz), 1.36 (6H, br, $CH_2CH_2CH_2CH_3$), 1.59 (2H, $CH_2(CH_2)_3CH_3$, quintet, $J = 10$ Hz), 2.68 (2H, t, $CH_2(CH_2)_4CH_3$, $J = 7$ Hz), 2.88 (4H, s, CH_2N), 4.07 and 4.08 (4H, s, C_5H_4); $\delta_C(CDCl_3)$ 14.1 (CH_3), 22.7 (CH_2CH_3), 27.2 ($CH_2CH_2CH_3$), 27.6 ($CH_2(CH_2)_2$-CH_3), 31.8 ($CH_2(CH_2)_3CH_3$), 52.2 (Cp–CH_2N), 57.8 ($CH_2(CH_2)_4CH_3$), 69.0 and 69.8 (CH in Cp group), 83.9 (C–CH_2N). NMR data for **5**: $\delta_H(CDCl_3)$ 2.91 (2H, s, NCH_2Ph), 3.86 (4H, s, $CpCH_2N$), 4.07 and 4.12 (4H, s, C_5H_4), 7.27 (2H, d, ortho-, $J = 6$ Hz), 7.36 (2H, t, meta-, $J = 6$ and 7 Hz), 7.44 (1H, t, para-, $J = 7$ Hz).

*3.2. X-ray structure determination of **1***

Data were collected at 23°C on a Rigaku AFC-5R automated diffractometer and monochromatic Mo–K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by a direct method. All nonhydrogen atoms were refined anisotropically. For the hydrogen atoms the riding model was used. Crystal data for **1**: $C_{22}H_{25}NFe$, $M_r = 359.29$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.803(4)$, $b = 13.020(4)$, $c = 12.764(4)$ Å, $\alpha = 113.51(3)$, $\beta = 99.48(3)$, $\gamma = 63.37(2)°$, $V = 1743(1)$ Å^3, $Z = 4$, $D_{calc.} = 1.368$ g cm^{-3}, $\mu = 8.66$ cm^{-1}, 8375 reflections collected of which 8023 were unique ($R_{int} = 0.026$); 5127 data with $I > 3\sigma(I)$ used for the refinement of 433 parameters, $R = 0.042$ and $R_w = 0.053$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 115661 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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