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Preliminary communication

THE ELECTROCHEMISTRY OF [1.1]METALLOCENOPHANES: A CYCLIC VOLTAMMETRY STUDY OF HOMO-BINUCLEAR AND HETERO-BINUCLEAR SYSTEMS

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Summary

The redox chemistry of ferrocene is well known: oxidation to the ferrocenium ion is a highly reversible one-electron step. Several studies on ruthenocene have led to conflicting results, but it is now clear that an electrochemically irreversible two-electron oxidation at comparatively high potential is involved. For [1.1]ferrocenophane, two reversible one-electron oxidations are known to exist, which indicate the absence of significant cooperative interactions between the two ferrocene units of this homo-binuclear compound. For the analogous hetero-binuclear iron/ruthenium system we find a ferrocene-centered reversible one-electron oxidation and a ruthenocene-centered irreversible two-electron oxidation, showing the independence of the two different metallocenes in this system. In contrast to this finding, the two ruthenocenes in [1.1]ruthenocenophane appear to interact strongly: this compound shows a quasi-reversible two-electron oxidation at an unusually low potential. The electronic structure of the dication of [1.1]ruthenocenophane is uncertain, but independent evidence indicates a mixed valence species with one ruthenocene and one ruthenocene dication.

In the preceding communication [1], we have described the synthesis of two novel [1.1]metallocenophanes. One reason for investigating these compounds lies in our interest in materials which are similar in structure to [1.1]-ferrocenophane (**1**), but which have different redox properties. This interest is motivated by an earlier report [2] that **1** reacts with acids to produce dihydrogen and the dication of **1**. The mechanism of this protonation-elimination reaction is unclear, but a number of intermediates can be envisaged. Certainly, the proximity of the two metal atoms in **1**, its conformational flexibility [3] and the stability of its mono- and di-cation must be important factors.

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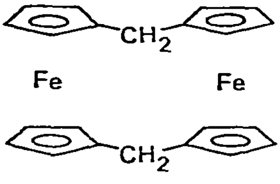
Protonation at both iron atoms, through which two hydrogens are brought into close contact, followed by their elimination as dihydrogen, will lead to the dication of 1. In search of similar materials, we have investigated the heterometallic iron/ruthenium [1.1]metallocenophane 2 and the homometallic [1:1]-ruthenocenophane 3. We here report their electrochemical properties as evidenced by cyclic voltammetry.



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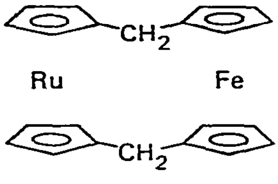

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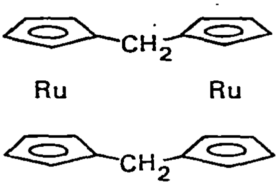

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The cyclic voltammograms of 1—3 and of ferrocene and ruthenocene were recorded at room temperature using benzonitrile as solvent (to combine polarity and solubility), a sodium chloride calomel (NaSCE) reference electrode and tetrabutylammonium tetrafluoroborate as electrolyte. In Table 1, the results obtained at 50 mV/sec scan rates are given as standard potentials $E°$ in mV versus NaSCE for electrochemically reversible systems and as peak potentials E_{pa} for the oxidation steps of irreversible oxidations. For the comparison of reversible and irreversible redox processes, the peak separation ΔE in mV as a measure of reversibility is given as well. The peak heights scaled linearly with the square root of the sweep rate in every case, as is expected for a diffusion controlled process. The coulometrically determined number of electrons (n) involved in the respective oxidation step is given in the last column.

Whereas ferrocene shows a perfectly reversible redox chemistry, there has been some confusion about the nature of the oxidation product of ruthenocene. Early reports about a one-electron oxidation [4] have been shown [5] to be in error. It is now firmly established by studies in widely varying media [6] that ruthenocene undergoes a two-electron oxidation at a much higher potential than the one-electron oxidation of ferrocene. Our results confirm the electrochemical irreversibility of this oxidation, which, however, is chemically reversible (no change in the cyclic voltammogram during repeated scans).

TABLE 1

CYCLIC VOLTAMMETRY DATA FOR FERROCENE, RUTHENOCENE AND THE FERROCENE AND RUTHENOCENE CONTAINING [1.1]METALLOCENOPHANES 1—3

	$E°$ (mV)	E_{pa} (mV)	ΔE (mV)	n
Ferrocene	500		60	1
Ruthenocene		920	[a]	2
1	410		80	1
	610		80	1
2	400		80	1
		940	[a]	2
3	380		80	2

[a] The corresponding reduction peak appears at approximately +400 mV, depending on solvent and scan rate.

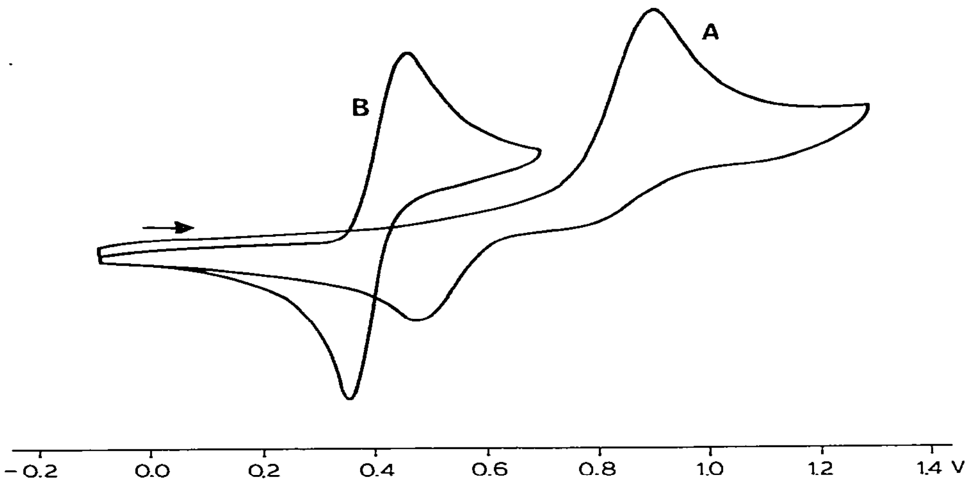

Fig. 1. Cyclic voltammograms of ruthenocene (Curve A) and [1.1]ruthenocenophane (Curve B) in benzonitrile solution containing Bu_4NBF_4 as the electrolyte. The scan rate was 50 mV/sec. Potentials are given relative to a SCE reference electrode.

One might speculate that the ruthenocene dication relaxes to a ruthenium(II) structure with neutral cyclopentadiene ligands, which reduces to neutral ruthenocene at a much lower potential than the oxidation step.

[1.1]Ferrocenophane (**1**) shows two quasi-reversible one-electron oxidations [3]. Knowing that ferrocene shows one and only one fully reversible one-electron oxidation [4], it would appear most probable that the first one-electron oxidation in **1** is centered on one of its ferrocenes, and the second one on the other. Although there has been some indication of a more extensive metal—metal interaction in the cations of [1.1]ferrocenophanes [6], it is still more probable that the dioxidized form of **1** exists as two independent ferrocenium ions.

The mixed iron-ruthenium system **2** also shows the presence of two independent metallocenes, with a quasi-reversible, ferrocene based one-electron oxidation and an electrochemically clearly irreversible two-electron oxidation centered on the ruthenocene part of the molecule.

A quite different situation is encountered in the case of [1.1]ruthenocenophane (**3**). Here we observe a quasi-reversible two-electron oxidation at the surprisingly low potential of 380 mV. Evidently, **3** has a dicationic state available which differs considerably from that of its iron analog **1**. The speculation about what the nature of the [1.1]ruthenocenophane dication might be is narrowed down by the observation that **3** can be oxidized chemically (e.g. by benzoquinone and borontrifluoride etherate in methylene chloride/ether) to a material which in its ^1H NMR spectrum shows four metallocene resonances (sharp multiplets at 6.1, 5.9, 5.6 and 5.5 ppm, considerably downfield from the position of the corresponding signals in neutral **3**) and a sharp four-proton singlet for the methylene bridges at 3.6 ppm. Neutral [1.1]ruthenocenophane, like **1** and **2**, undergoes rapid exchange between degenerate *syn* conformations, through which its NMR spectrum becomes very simple: the ruthenocene protons average out to give two multiplets, the methylene protons appear as a singlet [1]. Since in the NMR spectrum of the dioxidized 3 the methylene bridges also appear as a sharp singlet, the *syn-syn* exchange must still be rapid, so that the inequivalence of the ruthenocene protons must be based on different levels of oxidation in the two halves of the dication. Based on the knowledge that ruthenocene undergoes a two-electron oxidation and because the NMR spectrum proves the dication to be diamagnetic, we propose that this dication of 3 contains one neutral and one dioxidized ruthenocene. However, even the NMR spectrum itself already presents a problem with this interpretation: all ring protons are shifted downfield by 1.0 to 1.5 ppm. The UV-VIS spectrum of 3 in CH_3CN shows a weak, broad transition at 510 nm, which may be associated with a two-electron intervalence transfer transition. This certainly is a case meriting further study.

Ferrocene and ruthenocene can be protonated by strong acids, the products having a metal—hydrogen bond [9]. From the earlier NMR results, it was concluded that ruthenocene was considerably less basic than ferrocene, because the integral ratio of the ten ring protons to the proton at the metal was higher in ruthenocene. We have now reinvestigated the room temperature NMR spectra of ferrocene and ruthenocene in HBF_3OH at 90 and 360 MHz and found that for both compounds the integral ratio is exactly 10:1, so that the difference in basicity cannot be as large as previously assumed. For this reason and because the cation of 3 is much more stable than that of 1, we are currently studying the protonation of the [1.1]ruthenocenophane system.

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