Termetallocenes

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Abstract

Selected properties of seven termetallocenes with the metal sequences Fe–Co–Fe, Co–Ru–Co, Co–Os–Co, Co–Fe–Co, Rh–Fe–Rh, Ni–Fe–Ni and Rh–Fe–Co, synthesized by different published routes are described and compared with the parent compound terferrocene. The crystal structure of the hexafluorophosphate of the 1,1'-dicobaltocenyl-ruthenocene dication was determined by X-ray diffraction: crystals are monoclinic, space group $C2/c$, $a = 10.378(2)$, $b = 14.070(2)$, $c = 24.841(2)$ Å, $\beta = 92.02(1)°$, $V = 3625$ Å^3, $Z = 8/2$. This is the first structure determination of a termetallocene and the molecular alignment is unprecedented. The electrochemical behaviour of all bi-heterometallic systems was supplemented by unpublished CV measurements and compared with 1,1'-ferrocenediyl-bis(fulvalene)diiron, a formal quinquemetallocene. In addition, the elusive ^{1}H NMR of rhc-fec-coc^{++} is presented.

Key words: Transition metals general; Cluster; Metal–metal interactions; Structure; Metallocenes; Electrochemistry

1. Introduction

Oligonuclear transition metal complexes attract considerable attention since they allow the study of interactions between redox-active linked moieties. Such interactions result in properties which are not derivable from the molecular behaviour of the parent substances, which applies to homonuclear and particularly to heteronuclear compounds [1]. Fulvalene bridged complexes serve as favourable models as they are of high thermodynamic stability and allow electronic communication between the metal nuclei through the delocalized system of π-electrons [2].

Since three linked metallocene units represent the simplest oligometallocenes, we explored systematic routes to homo- and heteronuclear termetallocenes with heteroannular arrangement (Scheme 1). These compounds allow direct comparison of the influence of different electrophores as substituents on a bridging metallocene, which is of special interest for extreme donor-acceptor aromatic compounds like neutral metallocenes linked to valence trapped metallocene cations [3].
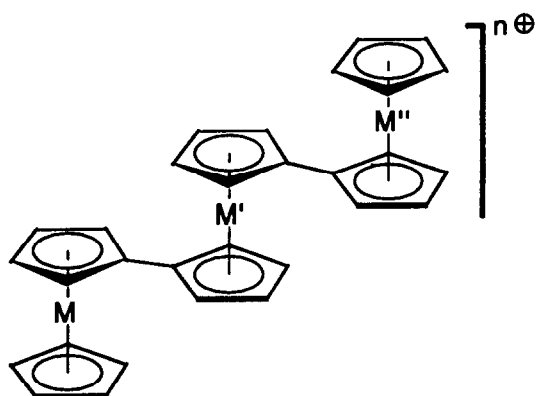
2. Directed syntheses

Systematic routes to heteronuclear fulvalene compounds normally involve site specific reactions [4]. As an alternative to specific routes, statistical reactions offer the great advantage of requiring only a few syn-


Scheme 1. Termetallocenes with heteroannular structure.

thetic steps with common starting materials. The remaining problem is to separate the target compounds from the reaction matrix in acceptable yields. New termetallocenes were separated from undesired metallocenes, starting metallocenes and by-products by means of preparative HPLC. A reversed phase system was established, which is sufficiently selective for separating the different cationic species [5] (Scheme 2).

Most of the synthetic approaches to directly linked cyclopentadienyl complexes, require metallocenylcyclopentadienides as one of the basic precursors. Established routes start from cyclopentenones as a formal Cp$^+$ synthon, which react with lithiated metallocenes or other aromatics to cyclopentenols. Final water elimi-
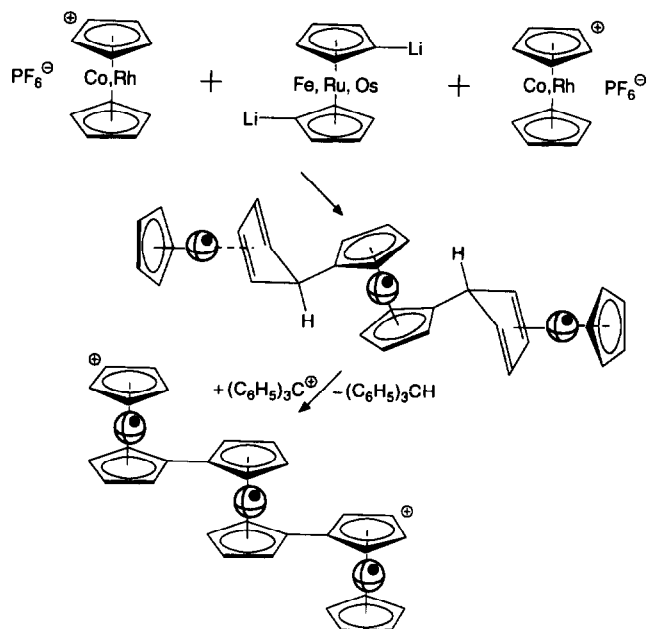
Scheme 2. General synthesis for linking complete metallocene units.

nation yields the corresponding cyclopentadienes. However, this concept involves major disadvantages such as low yields due to competitive 1,4 additions or Diels Alder dimerizations of the protonated target intermediates [6–8]. Therefore, syntheses which allow a direct, spontaneous generation of the stable anionic
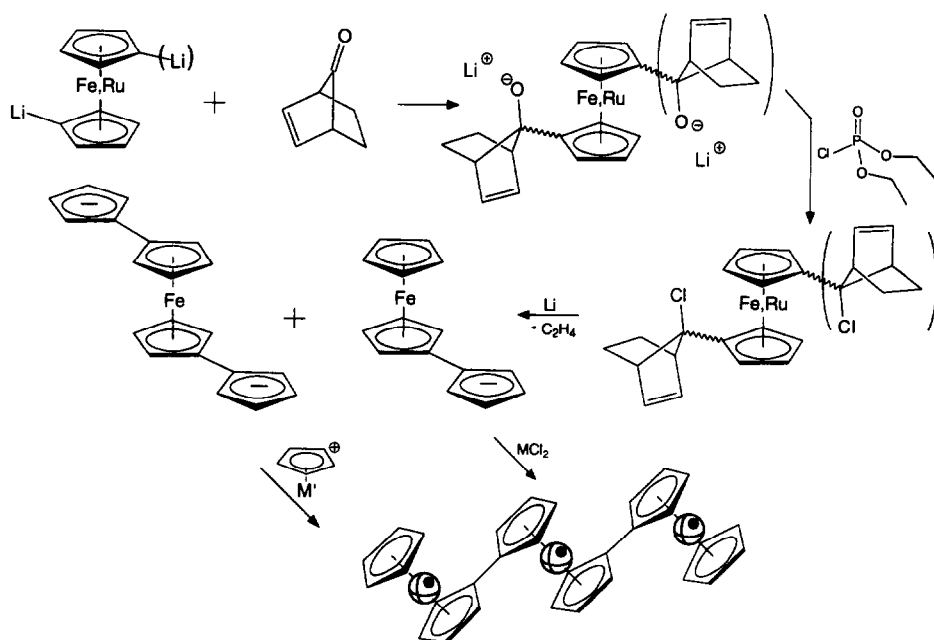
Scheme 3. Formation of termetallocenes via metallocenylcyclopentadienides.

intermediate, i.e. by retro Diels Alder sequences *via* substituted norbornenyl anions are desirable [9]. The required key intermediate, norborn-2-en-7-one is accessible by an optimized procedure [10] (Scheme 3.) It is noteworthy that Negishi's reagent, usually used for phosphonylations of enolates, acts in the case of sterically congested metallocenyl-norbornenolates as a chlorinating agent.
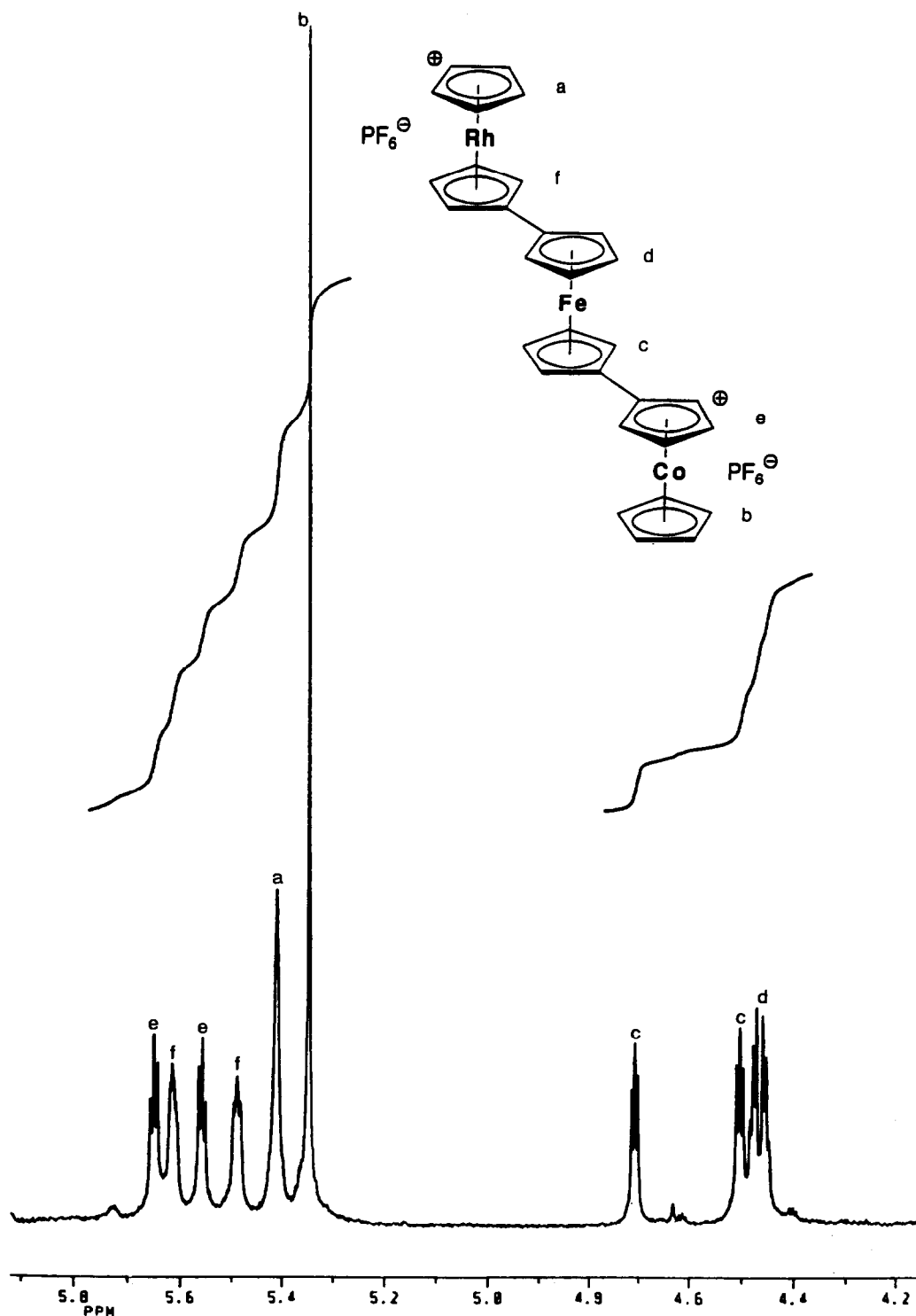

Fig. 1. ^{1}H NMR spectrum of the 1-rhodocenyl-1'-cobaltocenylferrocene dication.

Fig. 2. The eclipsed double *transoid* information of a termetallocene.

3. Characterization methods

3.1. Spectroscopy

For the diamagnetic members of the termetallocene family, ^{1}H NMR characterization is the method of choice since one can easily distinguish the different deshielded cyclopentadienyls and fulvalene parts of the respective metal. As an elusive example, the spectrum of 1-rhodocenyl-1′-cobaltocenylferrocene dication, prepared by a statistical variant and isolated by preparative HPLC [5] is shown in Fig. 1.

The nearby isochronic shifts of the corresponding protons in the related bimetallocene fec-rhc$^+$, the termetallocenes coc-fec-coc^{2+}, rhc-fec-rhc^{2+} and rhc-fec-coc^{2+} [11,5] reveal almost no electronic interaction between the terminating cationic moieties by the mediating ferrocene bridge.

3.2. Crystallographic studies

C–C bond distances in fulvalene bridging units are informative parameters indicating perimeter dependent interactivity by observing structural deviations from a ferrocene-like or a biferrocene-like geometry, as has been found e.g. in bis(fulvalene)dinickel [12]. In this paper the first molecular structure of a termetallocene is reported. In solution, it is likely to assume a stair-like conformation caused by electrostatic repulsion of the cationic ends of the termetallocene. Inter-
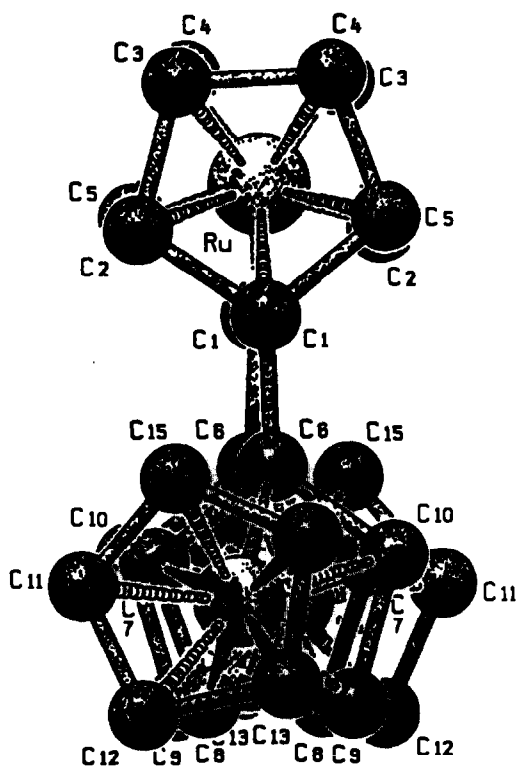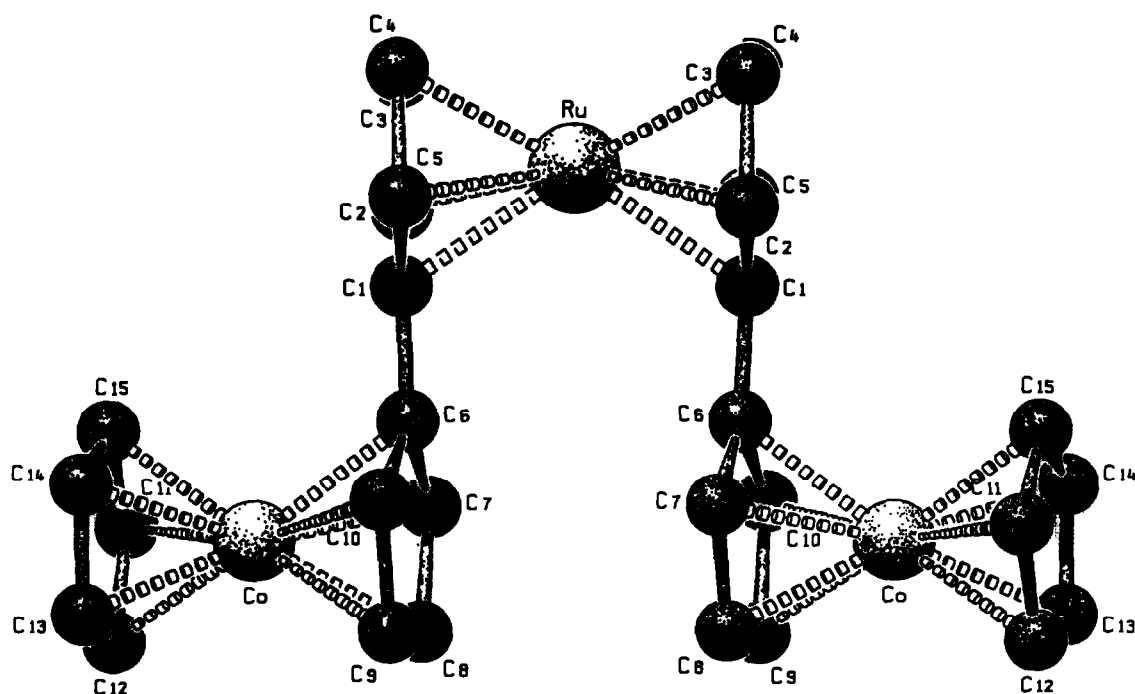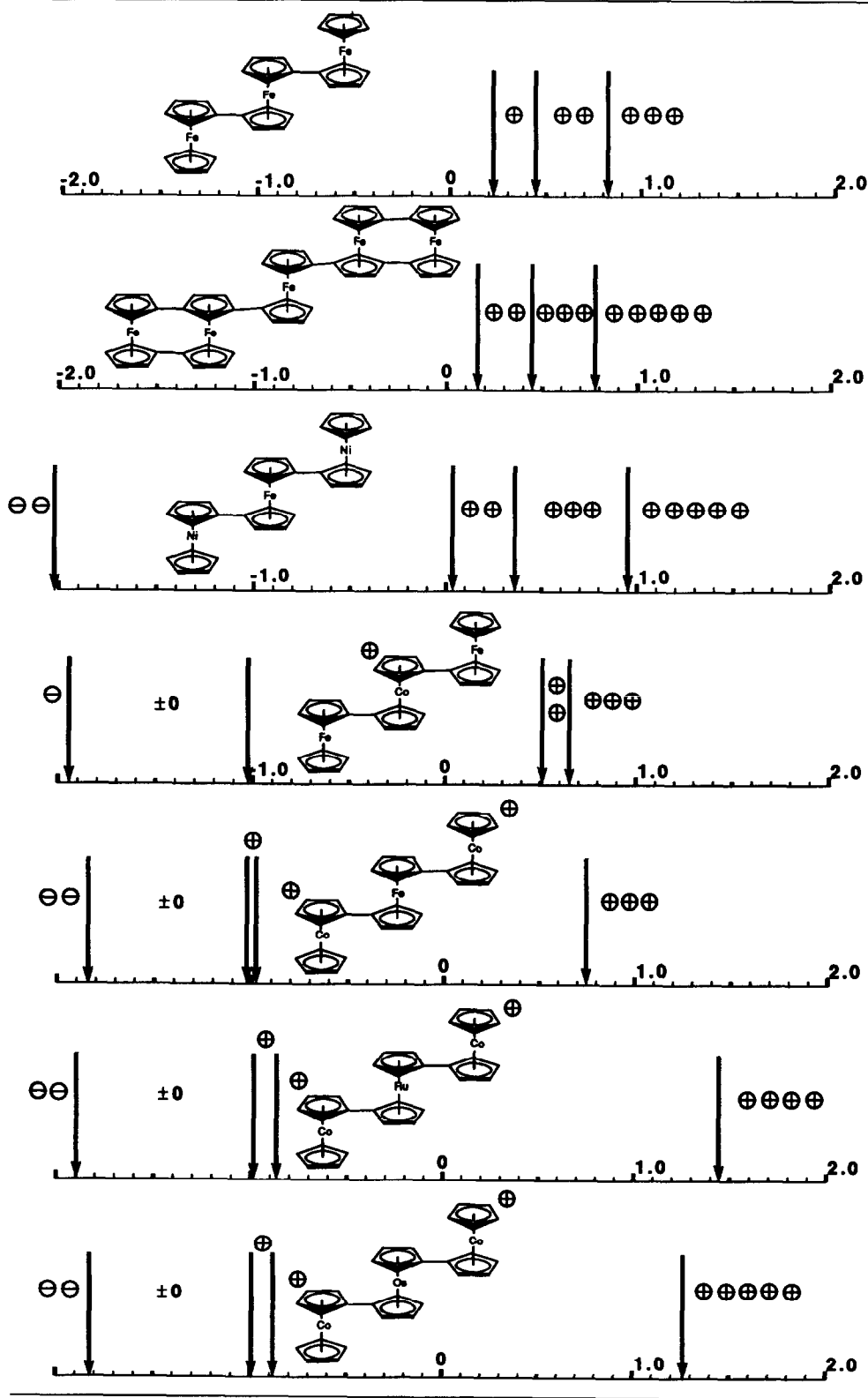

Fig. 3. A side view showing the "crankshaft" arrangement.

TABLE 1. Half wave potentials of selected termetallocenes

estingly, the packing requirements in the crystal lattice afford an eclipsed double *transoid* conformation (Fig. 2).

One part of the molecule is rotated in such a manner that the two cobaltocenium cations are nearly stacked over each other. A sideview of the molecule is shown in Fig. 3 illustrating a "crankshaft" alignment. The deviation of the two cobaltocenium units from a fully eclipsed conformation is too small to consider it as a helical orientation. The disordered PF_6 anions and a solvent molecule (CH_3CN) are omitted in the SCHAKAL plots [13].

3.3. Cyclovoltammetry

Since CV studies allow direct observation of the mutual influence of the oxidation potentials on adjacent redox centres, the moderately interacting oligometallocenes represent valuable models for the interpretation and prediction of analogous or related oligomers and polymers [14,15]. Half wave potentials of selected termetallocenes are summarized in Table 1.

3.4. Terferrocene

The oxidation properties of terferrocene in solution were reported 1975 by Meyer et al. [16] and are presented at the top of Table 1. It shows three waves at 0.24, 0.48 and 0.84 V vs. Ag/AgCl. The first two oxidations of 1,1'-terferrocene, corresponding to the outer ferrocene units are electrochemically reversible, but the third oxidation step (of the bridging ferrocene), which exhibits a notably higher half wave separation also indicates a slight decomposition of the trication.

3.5. Ferrocenediyl-[bis(fulvalene)-diiron]₂

This formal quinquemetallocene is described for the first time. The compound has been obtained as a deep green dication by reaction of dilithioferrocene with the bis(fulvalene)Fe_2 monocation and subsequent hydride abstraction in analogy to previously published termetallocene syntheses. The cyclic voltammogram of fec-$(BFFe_2)_2^+$, a formal quinquemetallocene is included for comparison (Fig. 4). It shows three waves between 0 and 1.5 V. At negative potential up to -2.0 V, no signal was detected. The peak separations of the three waves account for 60 mV, indicating reversibility of all steps. When comparing the potentials with those of the parent compounds, ferrocene and $BFFe_2$ and the value of the peak height, one can assign the potentials to following redox processes: peak 1 at 0.16 V and peak 3 at 0.78 V correspond to the oxidation of two Fe-atoms, one of each $BFFe_2$ unit. The interaction between the two Fe atoms in the $BFFe_2$ unit is obvious (620 mV separation of the redox-potentials), however, an additional contribution of the intermittently oxidized bridg-
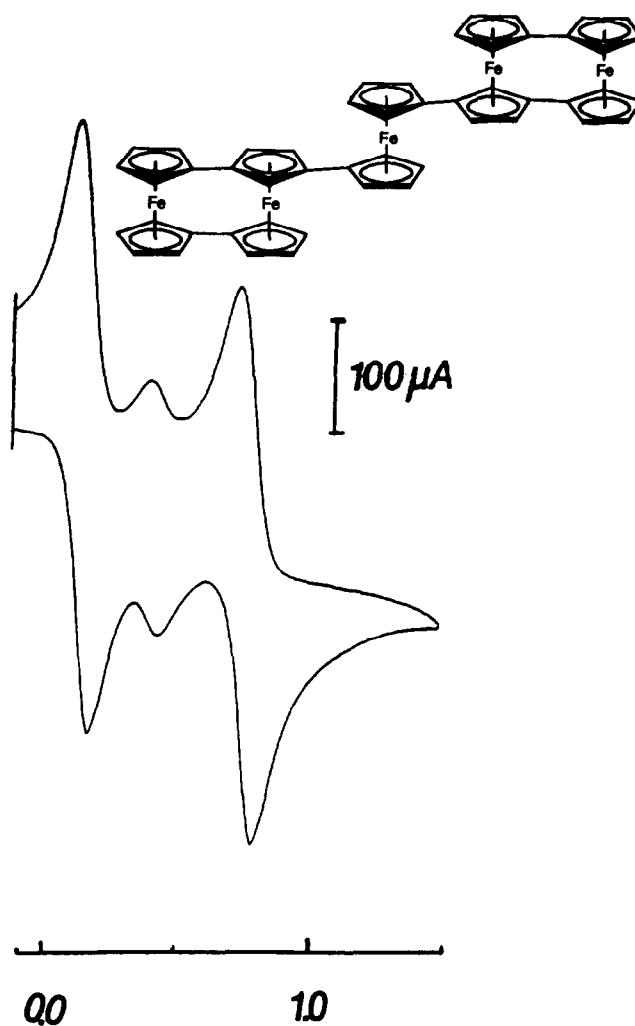

Fig. 4. Cyclic voltammogram of fec-$(BFFe_2)^+{}_2$.

ing ferrocene has to be considered (for comparison $BFFe_2$ 590 mV). Peak 2 at 0.44 V is assigned to this oxidation of the central ferrocene. The half wave potential of ferrocene has a value of 0.42 V indicating that the $BFFe_2$ substituents have a negligible influence on the oxidation of the bridging ferrocene (in contrast to this biferrocene, $E_{1/2}(1) = 0.35$ V, $E_{1/2}(2) = 0.67$ V; terferrocene, $E_{1/2}(1) = 0.24$ V, $E_{1/2}(2) = 0.48$ V, $E_{1/2}(3) = 0.84$ V; literature values [16] shifted versus sat. Ag/AgCl [17]). Virtually no interaction between the two different $BFFe_2$ substituents seems to take place, since peaks 1 and 3 are higher than peak 2, but show no additional separation. In such cases, redox processes occur in a statistical manner with all signs of reversible electron transfers. The chronoamperometric measurements correspond to multiples of single electron transfers. In the present case, the $BFFe_2$ peaks are slightly above the expected double height. This is

attributed to contamination with a by-product from the synthesis, bis(fulvalene) diiron, which could not be separated due to similar insolubility.

3.6. Nic-fec-nic (Fig. 5)

The oxidation of dinickelocenylferrocene occurs in three discrete steps, with peak separations of 80 mV, indicating quasi-reversibility. The waves at 0.02 V and 0.96 V are attributed to the oxidation of the two nickelocene moieties and represent formal two-electron oxidations where the two successive single electron steps are not resolved. The wave at 0.36 V is attributed to the one-electron oxidation of the bridging ferrocene. The formal potentials for all three waves lie very close to those of the parent metallocenes. This is surprising as normally in the case of homo- and heteronuclear bi- and termetallocenes, a shift of the redox potentials to more positive or negative values is observed, reflecting the nature and strength of interaction between the two linked metal centres. This remarkable electrochemical behaviour seems to be a special feature of the nickelocene moiety, since it has already been observed in the case of other metallocene substituted nickelocenes, e.g. binickelocene [18] and ferrocenylnickelocene [10]. Reduction of nic-fec-nic at 1.99 V is irreversible with formation of a dianion and subsequent decomposition.

3.7. Fec-coc-fec

The compound is obtained as a neutral complex by reacting ferrocenyl-cyclopentadienylide with anhydrous $CoCl_2$ [6] showing three waves at 0.67, 0.55 and -1.05 V which represent reversible one-electron steps. The fourth wave at -1.93 V indicates reduction to the termetallocene anion and is nearly reversible [19].

3.8. Coc-fec-coc (Fig. 6)

The quasi reversible two-electron reduction at 1.83 V for the dianion formation has not been reported previously. Since the potential difference between the one-electron transfers at each linking cobaltocene is too low, the two half waves are not resolved. In contrast to the very active cobaltocene anion, which undergoes rapid subsequent degradation in acetonitrile, the dicobaltocenylferrocene dianion is almost reversible and stable on the electrochemical time scale. With the dication as starting compound, higher scan rates are required to observe it; as a consequence, the two neighbouring cationic waves are not resolved (see Figs. 6a,b).
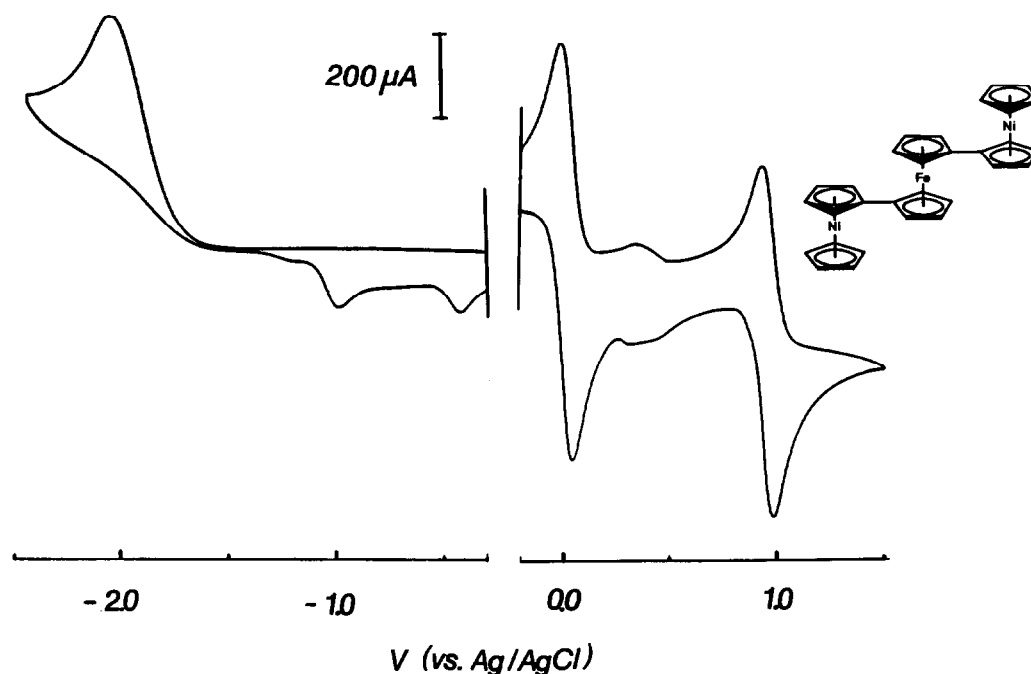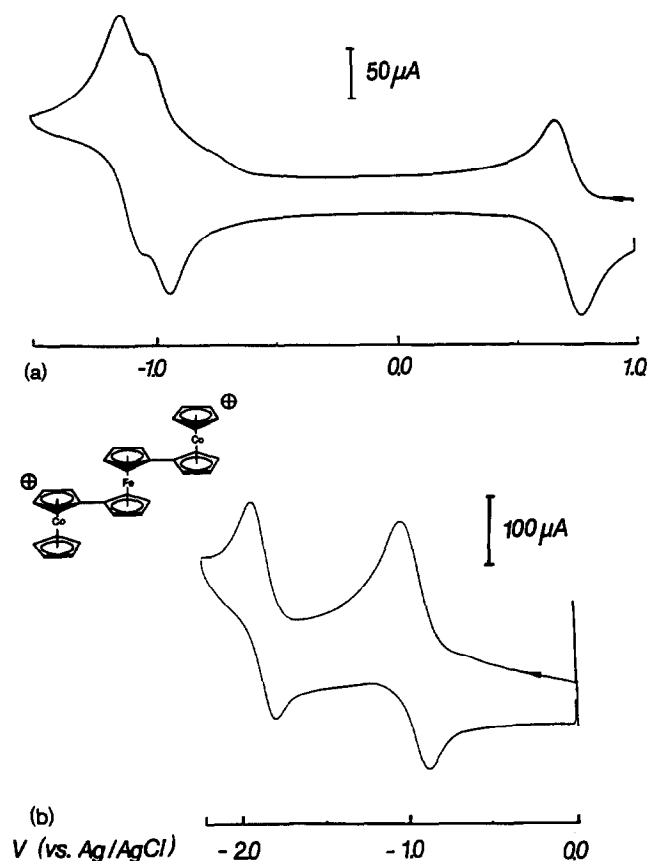

Fig. 5. Cyclic voltammogram of nic-fec-nic.

Fig. 6. Cyclic voltammogram of coc-fec-coc.

3.9. Coc-osc-coc^{2+} and coc-ruc-coc^{2+}

The cyclic voltammograms of coc-osc-coc^{2+} and coc-ruc-coc^{2+} are very similar. In the case of coc-osc-coc^{2+} the irreversible peak at 1.27 V is assigned to a two-electron oxidation of the osmocene unit and the waves at −0.89 and −0.98 to successive oxidations reductions of the two cobaltocene moieties. The last wave at −1.82 V indicates a two-electron transfer of the neutral compound to a dianion. The redox behaviour of coc-ruc-coc^{2+} is almost identical to that of coc-osc-coc^{2+}, as indicated from slightly shifted values (1.44 V, −0.87 V, −0.99 V and −1.89 V) [19].

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