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Tunable electronic coupling in iron–chromium mixed-valence ions of methylated Cp-indene ligands

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Dedicated to Professor Christopher Elschenbroich on the occasion of his 70th birthday

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ABSTRACT

A series of heterobimetallic η^6-[(ferrocenyl)indene]-Cr(CO)$_3$ complexes differing for the position of the ferrocenyl group, 1-(ferrocenyl)indene and 2-(ferrocenyl)indene, and the degree of indene methylation (tetramethyl- and hexamethyl-) have been prepared and studied with the aim to stabilise the mono- and dications generated by chemical and electrochemical oxidation, and at same time to tune the metal–metal electronic coupling in the mixed-valence cations. The magnitude of electronic delocalisation and spin density in the cations have been monitored by means of optical techniques (UV–Vis, near-IR, mid-IR) and EPR spectroscopy. The results have been rationalised in the framework of Marcus-Hush theory and at quantum chemistry level by DFT and TD-DFT methods, establishing that a metal-to-metal electronic coupling occurs the magnitude of which depends on the degree of indene methylation.

1. Introduction

Electronic communication in polynuclear complexes has received, and currently receives, a great interest with special regard to bimetallic complexes in which the two metals are linked by a π-electron conjugated system [1]. In particular, much attention has been paid to those systems in which two transition metal groups, ML$_n$, are bound to a fulvalenyl bridge [2]. Depending on the flexibility of the bridge and the nature of the metal groups the degree of coupling may vary to a large extent. In this regard, while complexes featuring two equivalent redox centres as ferrocene ($M_1 = M_2$; symmetric complexes) represent the most investigated class, complexes with two different metals ($M_1 \neq M_2$; unsymmetrical complexes) have received much less attention likely because of their synthetic difficulty.

Despite some important results on the communication in heterobimetallic complexes that have been obtained in recent years [3], the effect of the “metal asymmetry factor” in determining the extent of the communication is still little known.

In a preliminary communication [4], we have reported on the structures and the electrochemical behaviour of two heterobimetallic isomers, η^6-(3-ferrocenyl)indene]-Cr(CO)$_3$ (**1**) and η^6-(2-ferrocenyl)indene]-Cr(CO)$_3$ (**2**). By combining these results with the IR and near-IR data on the mixed-valence ions **1**$^+$ and **2**$^+$ obtained at −80 °C by chemical oxidation with ferrocenium-BF$_4$ in CH$_2$Cl$_2$, it was shown that electronic coupling is principally in **2**$^+$ and much less in **1**$^+$. The stronger electronic coupling in **2**$^+$ was attributed to the almost planarity of the bridging ligand and to the *cisoid* conformation of the two metal groups. The planarity of the two cyclopentadienyl-indene (Cp-indene) moieties favours the π-electron resonance in the corresponding conjugated atom grouping of the bridge. In contrast, in isomer **1** the metals exhibit a *transoid* arrangement and the bridge shows a torsion angle about the σ-bond of around 30°.

Described in this contribution is a complete study of the electronic interaction occurring between the iron and chromium centres in the (ferrocenyl)indenyl complexes shown in Scheme 1.

The information gathered by EPR, near-IR spectroscopy, and DFT calculations indicate that the cations of the parent complexes **1** and **2** and of the methylated complexes η^6-[(3-ferrocenyl) 1,2,4,5,6,7-hexamethylindene]-Cr(CO)$_3$ (**3**), η^6-[(2-ferrocenyl) 4,5,6,7-tetramethylindene]-Cr(CO)$_3$ (**4**), and η^6-[(2-ferrocenyl) 1,3,4,5,6,7-hexamethylindene]-Cr(CO)$_3$ (**5**) (Scheme 1) belong to the mixed-valence Class II according to the classification of Robin and Day and that the extent of the metal-metal electronic interaction can be modulated by the degree of methylation and cyclopentadienyl-indene planarity. Accordingly, the results of the

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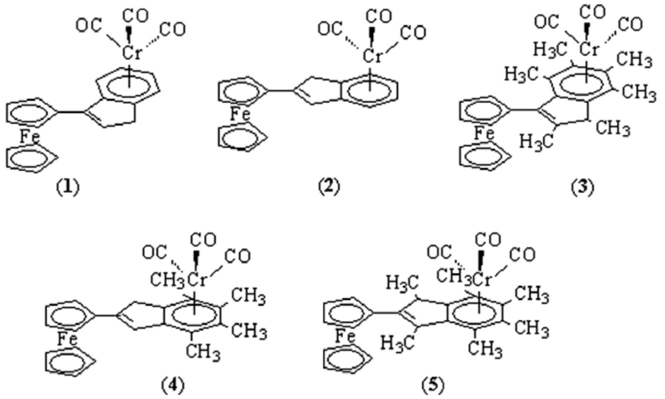

Scheme 1.

CO-substitution-P(OEt$_3$)-addition reaction of 1^+ and 2^+ are in favour of an activation of chromium mediated by an oxidative process at the iron atom.

The methylation of the indenyl skeleton, as expected, stabilises both mono and dications due to the electronic and steric effects of the methyl groups and modifies the planarity of the bridge to some extent.

2. Results and discussion

2.1. Synthesis and structures

The synthetic procedure of heterobimetallic complexes **1** and **2** [4] was successfully applied to **3**–**5** starting from the corresponding monometallic (ferrocenyl)indenes [5]. The crystal structures of **3** and **5** have been obtained and compared with those of **1** and **2** previously reported [4] (Fig. 1, Tables 1 and 2). In this regard, we could justify the *transoid* conformation of **1** (Fig. 1a) and the *cisoid* conformation of **2** (Fig. 1b) in terms of co-existence of balanced weak intramolecular π-hydrogen bond interactions and competitive van der Waals repulsive interactions, suggesting that *transoid* or *cisoid* conformations are expected to be almost isoenergetic for both **1** and **2**. The molecular structure of **3** (Fig. 1c, Table 1) supports this hypothesis at least for the case of complex **1**. In Table 2 some geometrical parameters are reported.

Actually, in **3** the ferrocenyl group is bonded in a *cisoid* orientation, in contrast with the *transoid* conformation of **1**, giving rise to a π-hydrogen bond interaction between H12 and the carbonyl C1=O1 at the distance H12…O1 of 2.84 Å. The Cr(CO)$_3$ group assumes a staggered *endo*-conformation. The observed molecular conformation is tolerated in spite of the presence of the bulky methyl groups which produce quite short and strongly repulsive intramolecular non-bonded carbon–carbon contact distances in the range of 3.00 Å (see C28…C5 = 3.04 Å), typical of an overcrowded molecular structure.

It is to be noted that in the case of **1** an analogous *cisoid* conformation would produce the same π-hydrogen bond interaction and a very short contact between H5 and H19 at a distance of ca. 2.00 Å, as it can be verified by exchanging the methyl group C28 with a H atom in **3**.

The torsion angle about the bond C4–C14 joining the ferrocenyl group to the indene ligand is here around 45° similar to that in **1,** so excluding any relevant resonance effect in the Cp-indene. These results lead to surmise that for **1** a similar *cisoid* conformation would be reasonably predictable, although probably a little less stable. A *cisoid* orientation of Cr(CO)$_3$ with respect to the methyl group C24 is clearly disfavoured for steric reasons; this fact is not present in the case of the corresponding non-methylated complex in the absence of the stereoisomeric centre on C16.

Interestingly, in the reaction conditions complex **3** undergoes a 1–3 (H16–H14) *protonic shift* giving rise to the isomeric molecular structure **3′** (Fig. 1e) in which very short intramolecular C…C contact interactions are absent, thus favouring a decreasing of its internal conformational energy. We think that this *protonic shift* is promoted by the necessity to relieve the molecular constraints present in the isomeric complex **3**. We note that in the case of the complex **1**, where similar constraints are absent, this *protonic shift* has not been observed. All the carbon-carbon non-bonded distances are larger than 3.20–3.25 Å. The ferrocenyl group is *transoid* with respect to Cr(CO)$_3$, which assumes here too a staggered *endo*-conformation. The less common *endo-staggered* [5] conformations of the Cr(CO)$_3$ groups, observed both in **3** and in **3′** in contrast with the *exo-staggered* [5] conformation of **1,** are likely someway influenced by the vicinal methyl groups which form a number of probable weak π-hydrogen bond interactions in the range of ca. 2.8–2.9 Å. Here too, the configuration having the Cr(CO)$_3$ group *cisoid* with respect to the ferrocenyl group appears to be more disfavoured for steric reasons.

The molecular structure of **5** is shown in Fig. 1f and its geometrical parameters are reported in Table 2. The conformation of the (2-Cp)-hexamethylindene skeleton is almost the same as that of the monometallic (2-ferrocenyl)hexamethylindene [6]. The torsion angle C1–C2–C11–C12 is around 23°, as compared with 24–25° there observed, proving that the conformation is still controlled by the repulsive interactions between H3…H15 and H1…C24 at distances of 2.31 and 2.88 Å, respectively. The Cr(CO)$_3$ group assumes an eclipsed conformation which allows probable π-hydrogen bonding interactions between O3…H10 and O3…H15 at distances of 2.85 and 2.79 Å, respectively.

2.2. Electrochemistry

The electrochemical oxidation within cyclic voltammetry (CV) experiments of the bimetallic complexes **1**–**5** ($Fe^{II}–Cr^0$) into their cationic and dicationic forms displays two fully reversible waves (Fig. 2) occurring at E_p in the range of 0.51–0.59 ($Fe^{III}–Cr^0$) and 0.72–0.89 ($Fe^{III}–Cr^I$) V versus SCE in CH_2Cl_2/0.1 M n-Bu_4NPF_6 (Table 3).

The $\Delta E_{1/2}$ values which are indicative of thermodynamic stability of the cationic species with respect to disproportionation [7] and the related values of the equilibrium constant (Table 3) for the comproportionation, K_c (Eq. (1)), suggest that is possible to characterise the mixed-valence cations 1^+–5^+ in solution.

$$[Fe^{II} - Cr^0] + [Fe^{III} - Cr^I] = 2[Fe^{III} - Cr^0] \qquad (1)$$

Interestingly, the peak separation of the two waves in **1**–**5** in the range of 210–300 mV is almost the same found between the monometallic compounds, i.e. ferrocene and (indene)Cr(CO)$_3$ (**6**) or (heptamethylindene)Cr(CO)$_3$ (**7**) (Table 3). As the CVs of the bimetallic complexes are approximately the sum of the CVs of monometallic compounds, it might appear that communication at the level of 1^+–5^+ is almost absent. In contrast, chemical and optical data will show that electronic communication between iron and chromium exists (*vide infra*).

2.3. The addition-substitution reaction of 1^+ and 2^+ with P(OEt)$_3$

It was determined [8] that the oxidation of benzene-Cr(CO)$_3$ in the presence of P(OEt)$_3$ leads to rapid substitution of one CO according to Scheme 2

$$(Ar)Cr(CO)_3 \underset{}{\overset{-e^-}{\rightleftharpoons}} (Ar)Cr(CO)_3^+ \xrightarrow[-CO]{P(OEt)_3} (Ar)Cr(CO)_2P(OEt)_3^+ \overset{+e^-}{\rightleftharpoons} (Ar)Cr(CO)_2P(OEt)_3$$

Scheme 2.