

The redox behavior of 9-nickelafluorenyl sandwich complexes

Fulvio Rossi · Fabrizia Fabrizi de Biani · Piero Zanello · Piotr Buchalski

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Abstract A collection of nickelocene and cobaltocene analogs with one or two nickelafluorenyl rings has been recently synthesized starting from 9-nickelafluorenyllithium complex. The redox ability of the whole series of derivatives has been investigated by electrochemical techniques, and the nature of the frontier orbitals responsible for the electron transfer activity of this class of compounds has been supported by extended Hückel calculations.

Keywords Electrochemistry · Metallametallo-cyclic sandwich complexes · Extended Hückel calculations

Introduction

In metallametalloenes, one or two cyclopentadienyl rings of metallocenes are replaced by five-membered metallacyclic rings [1–13] (Scheme 1).

We have recently reported on the synthesis of nickela-metalloenes possessing one nickelaindenyl or nickelafluorenyl ring [14–16] and their electrochemical properties [17].

Although the synthesis of heterofluorenyl–alkali metal complexes containing main group elements [18–23] and transition metals (zirconium) [24] has been reported, they were not employed in the formation of the compounds in which the metal atom is bonded to the heterocyclic ring.

Recently, we have found that reaction of nickelocene and 2,2'-dilithiobiphenyl in different solvents affords novel 9-nickelafluorenyllithium [25] complexes that contain a transition metal in the five-membered metallacyclic ring, which can be used to prepare new nickelacyclic complexes [26]. For example, in the reaction between nickel or cobalt ions (as bromide or acetylacetonate derivatives) and 9-nickelafluorenyllithium, the anions are displaced as lithium salts to form the complexes **2** and **3** illustrated in Chart 1, in which the nickel or cobalt atoms are sandwiched between two 9-nickelafluorenyl fragments [26]. On the other hand, 9-nickelafluorenyllithium can also form metallametalloenes with only one metallacyclic ring, as what happens for example for the cobalt–cyclopentadienyl–9-nickelafluorenyl complex **1**.

In the present paper, we present the electrochemical characterization of the complexes illustrated in Chart 1.

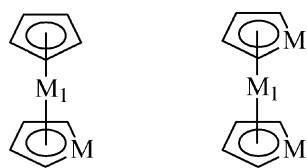
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F. Rossi · F. F. de Biani · P. Zanello (✉)
Dipartimento di Chimica, Università di Siena,
Via A. De Gasperi, 2
53100 Siena, Italy
e-mail: zanello@unisi.it

P. Buchalski
Faculty of Chemistry, Warsaw University of Technology,
Koszykowa 75,
00-662 Warsaw, Poland
e-mail: pjb@ch.pw.edu.pl

Experimental section

Synthesis of 1 9-Nickelafluorenyllithium (DME) complex 0.371 g (0.96 mmol) and 40 cm³ of diethyl ether were placed in Schlenk flask and cooled to –30°C. The solution of pentamethylcyclopentadienylcobaltacetylacetonate (0.250 g, 0.97 mmol) in 20 cm³ of diethyl ether was slowly added. The reaction was stirred for 1 h at –30°C and then at room temperature overnight. After the reaction was completed, the white precipitate was allowed to settle. The clear solution was transferred to another Schlenk flask and



Scheme 1

evaporated to dryness. The black solid was dissolved in 10 cm³ of toluene, filtered and put in the refrigerator. After 24 h, the solution was removed and dark solid of **1** was dried under vacuum (0.255 g, 0.53 mmol, 55%).

EIMS of **1** (70 eV) *m/e* (rel. int.) (⁵⁸Ni): 483 (36%, M⁺), 273 (73%, C₁₆H₂₂Co⁺), 193 (46%, C₁₀H₁₄Co⁺), 154 (100%, C₁₂H₁₀⁺), 134 (50%, C₁₀H₁₄⁺), 119 (30%, C₉H₁₁⁺). Magnetic moment in toluene solution at 294 K is 1.68 μ_B. EI HR MS: observed 483.10199, calculated for C₂₈H₃₀Co⁵⁸Ni 483.10330.

Complexes **2** and **3** were prepared according to literature [26].

Magnetic susceptibility was determined by NMR measurements at 298 K by Evans method [27–29] from the differences in the chemical shift of methyl group protons of toluene used as solvent and as external standard.

Electrochemical measurements were performed in deaerated, freshly distilled THF solutions containing [NBu₄][PF₆] (0.2 mol dm⁻³) as supporting electrolyte (Fluka, electrochemical grade). Cyclic voltammetry was performed in a three-electrode cell containing the working electrode surrounded by a platinum-spiral counter electrode and the reference electrode mounted with a Luggin capillary [30]. Platinum or gold electrodes were used as working electrodes. A BAS 100W electrochemical analyzer was used as a polarizing unit. All the potential values are referred to the silver/silver chloride electrode (Ag/AgCl) filled with the working THF solution. Controlled potential coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered/glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. Under the

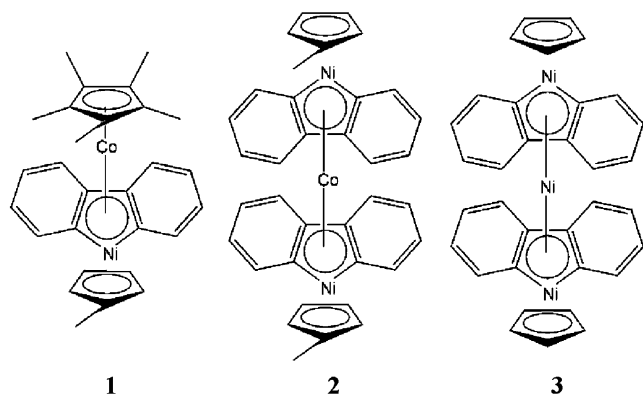


Chart 1

present experimental conditions, the one-electron oxidation of ferrocene occurs at +0.54 V (vs. Ag/AgCl). All the measurements were carried out at 253 K in order to slow down the eventual chemical complications following the electron transfer processes.

Extended Hückel (EH) calculations were performed using the CACAO98 for windows programs package [31]. The basis set for the metal atom consisted of *ns*, *np* and (*n*-1)*d*-orbitals. The *s* and *p* were described by single Slater-type wavefunctions, and *d*-orbitals were taken as linear combinations of two Slater-type wavefunctions. Standard parameters, predefined in this software, were used for all atoms. Bond distances and angles of the model molecule were taken as the average of the experimental values. While the MOs energy reported in this work are those obtained using CACAO98, the MOs drawings have been obtained by repeating the EH calculation with the software Hyperchem, which allows an enhanced graphical representation of the orbitals [32]. In fact, the relative energy of the orbitals obtained with the two softwares was basically the same.

Results and discussion

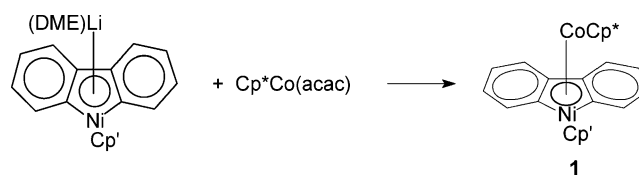
Synthesis

Complex **1** was prepared by reaction of compound 9-nickelafluorenyllithium (DME) with pentamethylcyclopentadienylcobaltacetylacetonate, according to Scheme 2, which will be discussed in more detail in a further paper (Buchalski et al., manuscript in preparation).

The parent ion was at *m/e* 483 (⁵⁸Ni calc.). Even if the magnetic moment in toluene solution at 294 K is 1.68 μ_B, which indicates a one unpaired electron paramagnetism, no signals in the electron paramagnetic resonance (EPR) spectrum could be detected either at room temperature or at 77 K, either in solid state or in benzene solution. In reality, this is not surprising in that we have proved that such class of compounds is EPR active at liquid helium temperature [17].

Electrochemistry

As illustrated in Fig. 1, the dinuclear complex **1** undergoes in the THF solution one oxidation and one reduction, only



Scheme 2

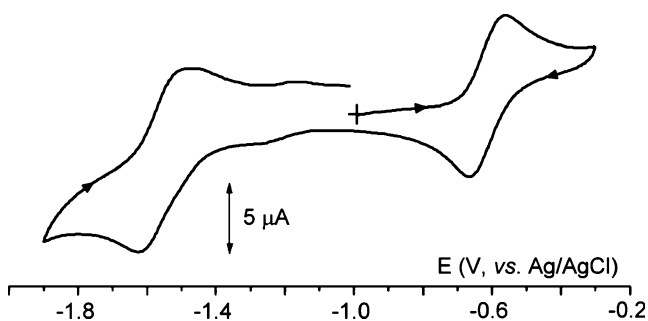


Fig. 1 Cyclic voltammogram recorded at a platinum electrode in THF solution of **1** ($1.6 \cdot 10^{-3} \text{ mol dm}^{-3}$). $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1} , $T=253 \text{ K}$

the anodic process having features of complete chemical reversibility in the cyclic voltammetric time scale. Controlled potential coulometry in correspondence of such anodic process ($E_w = -0.2 \text{ V}$) consumed one electron/molecule. As a matter of fact, analysis of the pertinent cyclic voltammetric response with scan rates progressively increasing from 0.02 to 2.0 V s^{-1} confirms the nature of a simple one-electron removal [30], in that the current ratio i_{pc}/i_{pa} is constantly equal to 1, the current function $i_{pa} \times v^{-1/2}$ maintains substantially constant, and the peak-to-peak separation does not appreciably depart from the theoretical value of 57 mV expected for a one-electron process.

In spite of the lack of any color change consequent to the exhaustive one-electron removal, the final solution displays a cyclic voltammetric profile quite complementary to the original one, thus confirming the chemical reversibility of the passage $1/1^+$ also in the long times of macroelectrolysis.

A reliable support to the chemical stability of the monocation 1^+ comes from the chemically and structurally characterized analog with a basal unmethylated cyclopentadienyl ring, which has been obtained upon oxidation of the neutral parent by $[\text{Cp}_2\text{Fe}]^+\text{PF}_6^-$ (Buchalski et al., manuscript in preparation).

As far as the reduction process is concerned, analysis of the response with scan rate shows that i_{pa}/i_{pc} ratio progressively increases from 0.1 at 0.05 V s^{-1} to 0.5 at 50 V s^{-1} , thus indicating that a fast chemical complication follows the generation of the monoanion 1^- . In fact, the exhaustive reduction ($E_w = -1.8 \text{ V}$) consumes 1.2 electrons *per* molecule and the resulting solution no more exhibits well resolved redox processes. Even if we cannot rule out that the fractional excess of electrons might be due traces of air which cause slight reoxidation of the reduced species (a drawback usually occurring in macroelectrolysis of processes occurring at rather negative potentials), we assume that in the present case the generation of unstable, redox active byproducts is more likely (which contrasts with the stability of the monoanion of the above mentioned analog with a basal unmethylated cyclopentadienyl ring; Buchalski et al., manuscript in preparation).

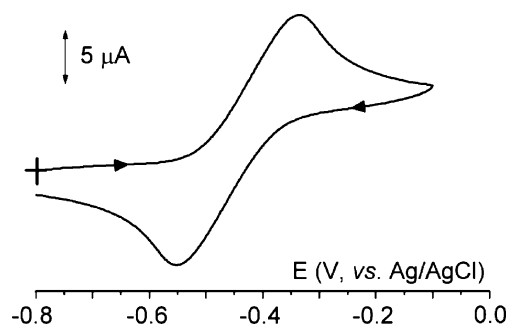


Fig. 2 Cyclic voltammogram recorded at a platinum electrode in THF solution of **2** ($1.1 \cdot 10^{-3} \text{ mol dm}^{-3}$). $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1} , $T=253 \text{ K}$

Let us now pass to the trinuclear complexes **2** and **3**, in which the pentamethylcyclopentadienyl group of the dinuclear complex (Ni/Co or Ni/Ni) is replaced by a nickelaflorenyl-cyclopentadienyl fragment.

As illustrated in Fig. 2, complex **2** only exhibits an oxidation process with features of chemical reversibility and electrochemical quasireversibility.

Controlled potential coulometry ($E_w = -0.1 \text{ V}$) proved the one-electron nature of the electron removal. No appreciable color change with respect to the original deep green solution occurred upon exhaustive electrolysis.

Also in this case, analysis of the cyclic voltammetric response with scan rates progressively increasing from 0.02 to 2.0 V s^{-1} confirms the nature of a simple one-electron process.

The redox activity of **3** appeared more extended. In fact, as illustrated in Fig. 3, it exhibits two consecutive oxidations and two consecutive reductions.

As far as the oxidation processes are concerned, the first anodic process exhibits features of chemical and electrochemical reversibility in the cyclic voltammetric time scale, and once again, in the long times of exhaustive one-electron oxidation, the solution maintains its original red color.

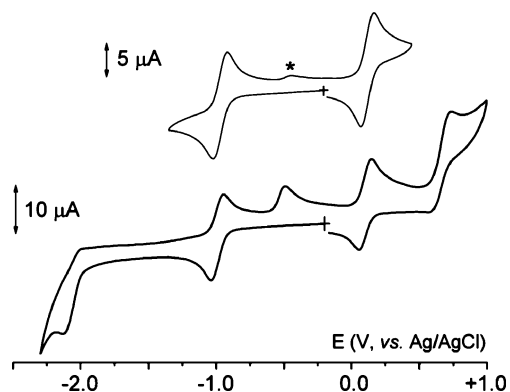
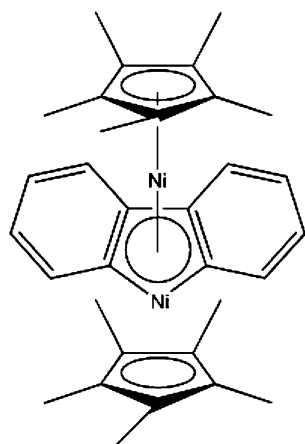


Fig. 3 Cyclic voltammogram recorded at a platinum electrode in THF solution of **3** ($1.7 \cdot 10^{-3} \text{ mol dm}^{-3}$). $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1} , $T=253 \text{ K}$



Scheme 3

Concerned with the second anodic step, the results were accompanied by chemical complications, in that it exhibits a current ratio i_{pc}/i_{pa} lower than unity at scan rates up to 1 V s^{-1} (at higher scan rates the forward peak substantially merges with the solvent oxidation, we did not try to determine coulometrically the number of electrons involved, but we confidently assign it as a one-electron process by comparison with the peak height of the first oxidation).

Passing to the reduction processes, the first step clearly exhibits chemical reversibility in the cyclic voltammetric time scale (the i_{pa}/i_{pc} ratio maintains about 1 even at the slowest scan rates). Nevertheless, it is useful to note the appearance of the asterisked spurious peak in the backscan, in that, the cyclic voltammetric response recorded after exhaustive one-electron reduction ($E_w = -1.1 \text{ V}$) shows the significant increase of such system (see Fig. S1 in the Supplementary material), thus indicating the presence of a chemical complication which affords a new, unidentified species, able to undergo a partial reversible oxidation at $E^{\circ} = -0.45 \text{ V}$.

In spite of the different nuclearities of complex **3** with respect to the nickelanickelocene analog illustrated in Scheme 3, we note that they apparently afford a qualitatively similar electrochemical behavior [17].

The electrode potentials of the different redox changes are compiled in Table 1.

Extended Hückel calculations

An extended Hückel study has been carried out to better understand the interactions between the metal centers in the present compounds.

In a previous work, a similar approach was undertaken to figure out the redox behavior of a family of related nickelanickelocene compounds [17]. The results indicated that, given the asymmetry of the system, the pertinent frontier molecular orbitals were sequentially localized or delocalized. As a consequence, the description of such complexes through fractional oxidation states appeared more suitable to describe their electronic structure. In fact, the complexes were better represented as containing two differently charged nickel ions: $\text{Ni}_{\text{apical}}(2.5+)$ and $\text{Ni}_{\text{basal}}(1.5+)$, where “apical” indicates the sandwiched ion and “basal” indicates the nickel ion in the nickelafluorenyl ring.

A similar picture is obtained in this case. To begin with, we may assign a 2+ “formal” oxidation state to both the nickel and cobalt ions in these compounds, so that a $\{\text{CoNi}\}^{4+}$ couple may be envisaged. The three frontier orbitals (HOMO, SOMO, and LUMO) of complex **1** required for the present discussion are shown in Fig. 4.

In brief, the interaction between the two metal centers is, in sequence, nonbonding/antibonding/nonbonding so that in the SOMO (antibonding orbital) there is a strong mixing between the d_{yz} orbitals of the two metal centers, while the HOMO and the LUMO (nonbonding orbitals) are mainly localized on the basal nickel ion and on the apical (sandwiched) cobalt ion, respectively.

Also in this case, because of the localized/delocalized nature of the occupied frontier orbital, formally the metal ions in the group $\{\text{CoNi}\}^{4+}$ bears a fractional oxidation state. In fact, to assign the oxidation state 2+ to the nickel ion, there should be two electrons localized on this atom, while in this case, because of the delocalized nature of the SOMO, these are 2.5. Similarly, only 0.5 electron lies on the cobalt center, instead of 1 (Ni^{2+} has a d^8 configuration,

Table 1 Formal electrode potentials (V, vs. Ag/AgCl), peak-to-peak separations (mV), and current ratios for the redox changes of **1–3** in THF solution, $T=253 \text{ K}$

Complex	E_c^{θ} , 2nd oxidation	ΔE_p^a	$\left(\frac{i_p(\text{reverse})}{i_p(\text{direct})}\right)^a$	E_c^{θ} , 1st oxidation	ΔE_p^a	$\left(\frac{i_p(\text{reverse})}{i_p(\text{direct})}\right)^a$	E_c^{θ} , 1st reduction	ΔE_p^a	$\left(\frac{i_p(\text{reverse})}{i_p(\text{direct})}\right)^a$	E_p^a , 2nd reduction
1	–	–	–	–0.61	99	1.0	–1.56	84	0.3	–
2	–	–	–	–0.44	190	1.0	–	–	–	–
3	+0.71	134	0.5 ^a	+0.14	79	1.0	–0.96	88	0.9	–2.06

^a Measured at 0.2 V s^{-1}

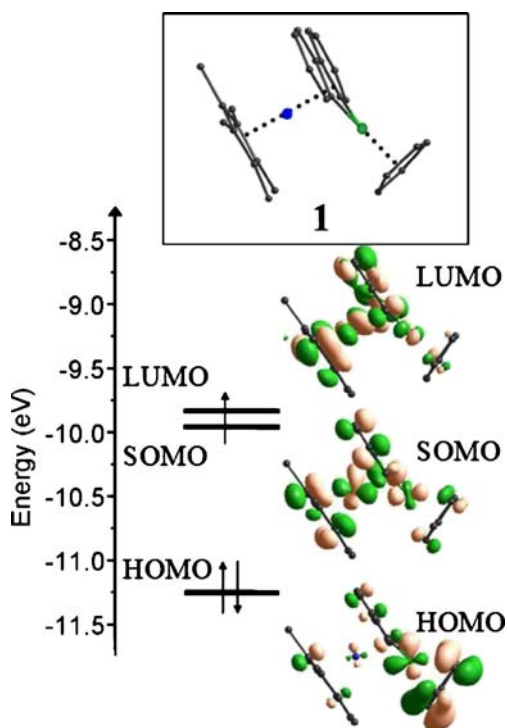


Fig. 4 Frontier orbitals of complex 1

but six electrons are coupled in the lower lying orbitals, so only two electrons occupy the frontier orbitals. Likewise for Co^{2+} with a d^7 configuration, only one electron occupies the frontier orbitals). So the system is better represented as $\text{Co}_{\text{apical}}^{2.5+}\text{Ni}_{\text{basal}}^{1.5+}$. Apparently, the removal of one electron from the SOMO of complex 1 involves both the metal ions and would formally correspond to the redox change $\text{Co}_{\text{apical}}^{2.5+}\text{Ni}_{\text{basal}}^{1.5+} \rightarrow \text{Co}_{\text{apical}}^{3+}\text{Ni}_{\text{basal}}^{2+}$. On the other hand, the proximity of SOMO and LUMO suggests that, on reduction, the extra electron should be added to the LUMO, which is mainly localized on the apical cobalt ion. The reduction would then correspond to the redox change $\text{Co}_{\text{apical}}^{2.5+}\text{Ni}_{\text{basal}}^{1.5+} \rightarrow \text{Co}_{\text{apical}}^{1.5+}\text{Ni}_{\text{basal}}^{1.5+}$.

By sandwiching the cobalt with another nickelacyclic group instead of the cyclopentadienyl ring, both the SOMO and the LUMO are slightly stabilized (Fig. 5).

In fact, now, the strong antibonding interaction of cobalt with the cyclopentadienyl ligand (as in 1) is substituted by a weak bonding interaction with the organic region of the nickelafuorenyl ring. This is coherent with the electrochemical data. In fact, the oxidation process is easier for complex 1 than for complex 2 (-0.61 vs. -0.44 V). On the other hand, the reduction process, expected at a potential more anodic than that measured for 1, was not observed. This may be due to the spin pairing energy, which possibly plays here a key role.

As it is evident from Fig. 5, the LUMO is localized mainly on the central cobalt ion, the SOMO is a mixing of

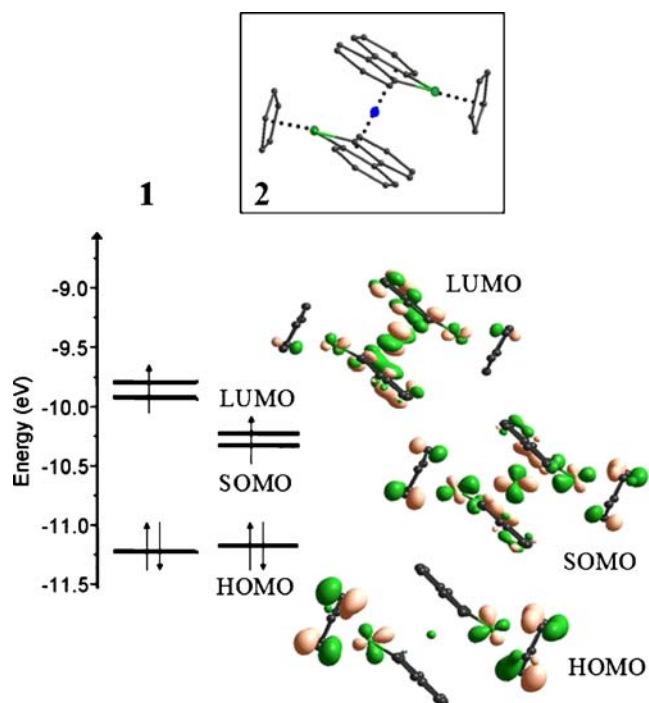
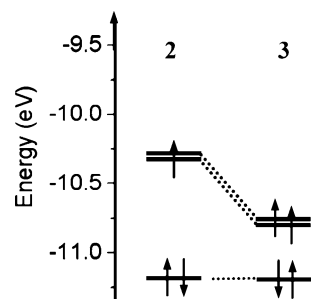


Fig. 5 Frontier orbitals of complex 2 with respect to complex 1

the d_{yz} orbitals of the three metal ions, while the HOMO is a combination of d_{yz} orbitals of the two basal nickel ions. In fact, as soon as the central cobalt ion is replaced by a nickel atom as in complex 3, there is a further stabilization of higher energy frontier orbitals, which follows the energetic trend of the d orbitals of the apical ion, while the energy of the HOMO remains unaltered (Fig. 6).

Complex 3 possesses one more electron with respect to complex 2 and, in agreement with the value of the magnetic moment ($2.34 \mu_B$, at 294 K), there are two unpaired electrons (Buchalski et al., manuscript in preparation). As discussed, complex 3 undergoes two one-electron oxidations: the first process is thus centered mainly on the central nickel ion, whereas the second process involves all the three metals. Also, in this case, the results of the EH calculations are coherent with the electrochemical data, in fact, the oxidation process is easier for complex 2 than for the isoelectronic cation 3^+ ($+0.73$ vs. -0.44 V).

Fig. 6 Energy of the frontier orbitals of complex 3 with respect to complex 2



Conclusions

In this paper, the ability of some 9-nickelafluorenyl sandwich complexes to exchange electrons has been determined.

On the basis of joint electrochemical and theoretical studies, the molecular frontier orbitals could be localized or delocalized depending on their interaction with the π -system of the 9-nickelafluorenyl ring(s). These orbitals are perturbed by the presence of one or two metallacyclic rings and by the nature of the central metal ion. Such an electronic situation accounts for a theoretical difference of the redox activity of the different complexes, in accord with the experimental data collected by electrochemistry.

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