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Intervalence charge transfer across noncovalent interactions on vinyl silyl bridged biferrocenyl compounds

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ABSTRACT

A series of vinyl-silyl-functionalized biferrocenyl compounds were very recently synthesized and studied by our group through cyclic (CV) and square-wave (SWV) voltammetric techniques, showing two well-resolved one-electron transfer oxidation processes. This fact might reflect a certain degree of electronic communication between ferrocenyl centers, but solvent or electrolyte effects could have an influence in the splitting. Gas-phase theoretical studies were carried out in order to determine the degree of iron-iron communication in absence of undesired environmental effects, revealing through the analysis of the topology of the electron density with different methods that organosilicon bridges between ferrocenyl units have mainly a steric but not an electronic-linking role, which is however of crucial importance, as they allow non-covalent paths for electronic communication between iron centers.

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1. Introduction

A very attractive research area in constant development is that of large molecular systems containing two or more metallocene moieties, which are susceptible to be used in different kinds of electronic devices due to electronic communication between metal atoms [1–3]. Among all metallocenes, ferrocene (Fc) is one of the most commonly used as building block, as its redox behavior is very well described in literature. It is because of this well-behaved redox chemistry of ferrocene that it constitutes an ideal test molecule to study the possibilities of new molecular bridges that link several metallocene units [4–10].

Since the pioneer works of Taube on inner sphere electron transfer (ISET) processes and the description of the Creutz-Taube ion [11,12], theoretical and conceptual elaborations on electron communication between metallic centers grow day by day [4,13–17]. The opposite of ISET processes, in which redox chemistry of the system is mainly due to the covalent linkage between redox-active sites, are OSET (outer sphere electron transfer) processes. In that case, electron transfer between metallic atoms occurs even if those atoms are separated, as described formally by Marcus Theory [18]. Regarding the formal oxidation state of each metallic atom after a one electron oxidation reaction in the system, usually different

degrees of mixed valence are defined depending on the localization or delocalization of the charge. Considering two active metallic centers, if only one metallic center is oxidized, charge remains completely localized and the system is defined as Class I, according to Robin-Day classification [19]. If both centers assume oxidation equally, each metallic center loses half an electron, the most delocalized scenario (Class III). Class II is then for those compounds in which oxidation occurs in an asymmetrical way, in which one of the centers becomes more oxidized than the other, revealing a certain communication between them. Electrochemical techniques, such as cyclic voltammetry (CV), have been among the most widely used tools to investigate metal-metal electronic interactions between two redox-active sites of a molecule [20]. The potential difference (ΔE) between two reversible waves (${}^1E_{1/2}$ and ${}^2E_{1/2}$) is representative of the thermodynamic stability of the corresponding mixed-valence state relative to the other redox states, under the conditions of solvent and electrolyte used. In a symmetrical homobimetallic complex, ΔE value ($\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$) is an indicator of the interactions between the two metal centers (assuming that both waves are reversible). If the value of ΔE is close to zero, the metals are noninteracting (either because of the great distance between them or because the ligand does not provide an electronic coupling pathway), and the compound belongs to Class I. A small ΔE separation represents a weak interaction between the metals, and the system is commonly assigned to a mixed-valence state involving trapped-valence systems

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(Class II). A large value of ΔE corresponds to a totally delocalized system assigned to Class III. Consequently, ΔE is a useful electrochemical magnitude for evaluating the possibility for isolating the mixed-valence species. ESR (Electron Spin Resonance) provides information about the electronic state of the metals. Also, spectroscopic studies in the near-Infrared region are one of the experimental techniques used to describe and quantify these phenomena. Near-IR region in mixed valence compounds can present a characteristic broad band, used by Hush in its model [21], called IVCT band (Inter Valence Charge Transfer band) with its associated α mixing coefficient [1].

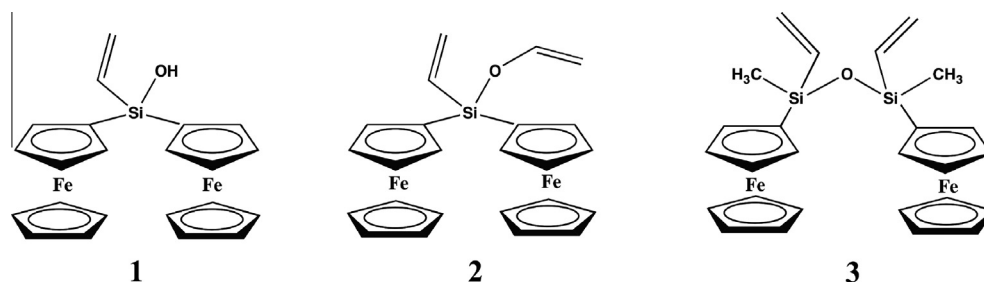
Very recently, several vinyl-functionalized silanes and disiloxanes containing two or more ferrocenyl units have been synthesized and characterized by our group [22]. The nature of the molecular bridge between two given redox centers is of crucial importance for the electronic coupling between them in ISET processes. Several factors play a role in the connectivity between centers: atom composition of the bridge, its longitude (i.e., the distance that impose between redox centers and conformational possibilities), its unsaturated (aromatic or not) or saturated nature, planarity, or even its redox chemistry [23]. In the case of our polyferrocenyl systems, it is of a Si–CH=CH₂ bridging moiety that we are talking about, and from them we selected for this work three case-studies shown in Scheme 1.

In all three cases, ferrocenyl units are linked through a saturated bridge: a single silicon atom (**1**, **2**) or a Si–O–Si siloxane chain (**3**). All of them have also vinyl substituents and oxygen atoms. A progressive modification in the linker from **1** to **3** is accompanied by small changes in the degree of electronic communication between iron atoms. The electrochemical behavior of these biferrrocenyl molecules has been thoroughly examined by cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments, in a low-polarity solvent (dichloromethane), using tetra-*n*-butylammonium hexafluorophosphate ([*n*-Bu₄N][PF₆]), and tetra-*n*-butylammonium tetrakis(pentafluorophenyl)borate ([*n*-Bu₄N][B(C₆F₅)₄]) as supporting electrolytes of different coordinating ability. We observed that using either [PF₆][−] (coordinating) or [B(C₆F₅)₄][−] (noncoordinating) electrolyte anions, all vinylsilanes **1**, **2** and **3** show two clearly defined reversible oxidation processes, which correspond to the sequential oxidation of two ferrocenyl groups. Experimentally observed differences between the first and second oxidation waves ($\Delta E_{1/2} = {}^2E_{1/2} - {}^1E_{1/2}$) are 264, 280 and 184 mV, respectively (in CH₂Cl₂/[*n*-Bu₄N][B(C₆F₅)₄]). The occurrence of two oxidation waves, instead of a single two-electron oxidation, indicates a stabilization of the mixed valence cations **1**⁺, **2**⁺ and **3**⁺ and suggests the possibility of their characterization. The separation between the half-wave potentials ($\Delta E_{1/2}$) of two redox sites in the cyclic voltammograms can be taken as a measure of the electronic interactions between them, although environmental effects cannot be neglected, as the solvent or the electrolyte may alter the measure. In addition, stepwise chemical and electrochemical oxidation of neutral compounds

1–3 allowed to generate the mixed-valence cations **1**⁺, **2**⁺ and **3**⁺, which show an IVCT band of low intensity in the near-IR spectra [24]. Taking into account these evidences and the very simple nature of the linkers between the two ferrocenyl moieties, we found very interesting to investigate the degree of communication between iron atoms in this series of compounds, as in principle it is not trivial how this connection can occur. Iron centers are quite separated and the bridges are not ideal covalent linker conductors, in which vinyl groups are not a part of the main connecting chain between ferrocenyls. It is important to understand the reasons behind electronic communication in systems as **1–3**; the more we understand this fact, the better we can control future design of new compounds with similar properties. Electronic structure calculations in the gas-phase can provided valuable information about these systems in which no environmental effects are considered, just looking at the isolated molecular system by itself. In particular, covalent and noncovalent phenomena can be well investigated by means of different computational tools based on the topology of the electron density, in order to give new light about the way these ferrocenyl units are communicated. Quantum Theory of Atoms In Molecules (QTAIM), Electron Localization Function (ELF) and Non Covalent Interaction (NCI) analysis, that will be immediately described in the Methodology section, are used in this work [25–29]. Comparison between experiment and theory will provide some ideas about the question, revealing the importance of noncovalent interactions. Few areas of knowledge can provide so much qualitative and quantitative information about weak interactions as computational chemistry can do.

2. Methodology

Structures of all compounds were fully optimized and their corresponding harmonic vibrational frequencies obtained with Gaussian 09 software [30]. BPW91 functional along with triple zeta 6-311 + G(d,p) Pople basis set was used for valence electrons, as it was shown to provide an excellent agreement with experimental results in analogous compounds, along with SDD Stuttgart–Dresden ECP (effective core potential) for core electrons (only for iron) [31–33]. Atoms In Molecules (AIM) Quantum Theory, Electron Localization Function and Non-Covalent Interaction Plot program (NCIPLOT) are different electron density topology-based tools that help to elucidate the complex nature of chemical bonding [25–29]. QTAIM calculations were carried out with AIMALL software to obtain the corresponding molecular graphs. Each molecular graph is formed by a collection of bond paths linking the nuclei, and each bond path contains a BCP (bond critical point), a (3, −1) saddle point in the topological analysis of the density, traditionally related to the existence of a bond and its strength. RCPs (ring critical point) and CCP (cage critical points) are other topological distinguished points of chemical interest. Not only covalent but also weak interactions, such as hydrogen bonds or van der Waals interactions, can



Scheme 1. Compounds **1** (diferrrocenyl(vinyl)silanol), **2** (diferrrocenyl(vinylether)vinylsilane) and **3** (1,3-divinyl-1,3-dimethyl-1,3-diferrrocenyl-disiloxane) were selected as case-studies.

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