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Communication

Ab Initio Quantum Calculation of the Diabatic Coupling Matrix Elements for the Self-Exchange Redox Couples $M(Cp)_2^{0/+}$ (M = Fe, Co; Cp = C_5H_5)

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The diabatic couplings between the metal centers in $M(Cp)_2^{0/+}$ (M = Fe, Co; Cp = C_5H_5) were evaluated using ab initio methods at the Hartree–Fock level of theory. Excellent agreement with the experimental estimate is found for the $Fe(Cp)_2^{0/+}$ couple. For $Co(Cp)_2^{0/+}$, the calculated numbers are substantially higher than the experimental estimates, suggesting that the latter may represent a considerable underestimate (a possibility mentioned in the experimental publication).

Understanding electron transfer (ET) processes on a molecular level and elucidating how electronic structure properties control ET behavior are challenging.[1−3] In principle, models for ET processes must include dynamic effects of both electrons and nuclei,[4−6] rendering ab initio studies on transition-metal-containing redox systems of realistic size practically impossible with currently available resources. However, the purely electronic, thus diabatic, coupling matrix element H_{if} (eq 1)[1,7] computed at a reasonable static donor−acceptor geometry, might be often sufficient to provide semiquantitative insight into the electron-transfer process for a particular problem of interest.

$$H_{\text{if}} = \frac{\int \Psi_{\text{i}}^{*} H \Psi_{\text{f}} - (\int \Psi_{\text{i}}^{*} \Psi_{\text{f}})(\int \Psi_{\text{i}}^{*} H \Psi_{\text{i}})}{1 - (\int \Psi_{\text{i}}^{*} \Psi_{\text{f}})^2} \qquad (1)$$

Several years ago,[8] we implemented a method for efficiently evaluating the matrix elements from ab initio calculations, and we have shown that systems containing as many as 150 atoms can be treated routinely using Hartree−Fock level of theory. In this communication, we report on ab initio calculations of H_{if} for the classical organometallic self-exchange couple $Fe(Cp)_2^{0/+}$, preparatory for future studies involving large organometallic and other metal-containing systems, such as molecular wires or electron reservoirs[10,11] based on organometallic materials. We also investigate the $Co(Cp)_2^{0/+}$ redox couple.

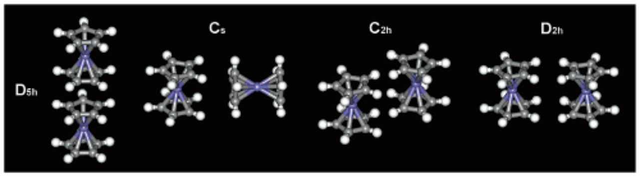

Figure 1. Idealized possible orientations of the donor−acceptor pair.

The self-exchange reaction of the $Fe(Cp)_2^{0/+}$ couple has previously been studied in an elegant experimental work by Weaver et al.[12] affording 35 cm^{-1} as an estimate for H_{if} at closest contact. Newton et al.[13] used a semiempirical method to obtain a computed value of 135 cm^{-1}. However, owing to the limitations of the semiempirical method, a few interesting details, such as the energy profiles of different possible geometries of the $Fe(Cp)_2^{0/+}$ couple, summarized in Figure 1, could not be quantified consistently. Ab initio calculations allow such systematic sampling of the potential energy surface.[14] Figure 2 summarizes the matrix elements and binding energies as functions of the Fe−Fe distance at each orientation, respectively. In disagreement with the estimates of the previous study,[13] only the D_{5h} orientation, where Cp rings from each fragment adopt a face-to-face arrangement, gives an energetically favorable interaction. All other geometries do not show an energy minimum and give negligible matrix elements at distances where the interactions are not repulsive. Thus, these arrangements are likely not relevant for the ET process. The closest contact in D_{5h}

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[7] Ψ_{i} = electronic state before ET.; Ψ_{f} = electronic state after ET. H = total electronic Hamiltonian

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[14] See Supporting Information for computational details.

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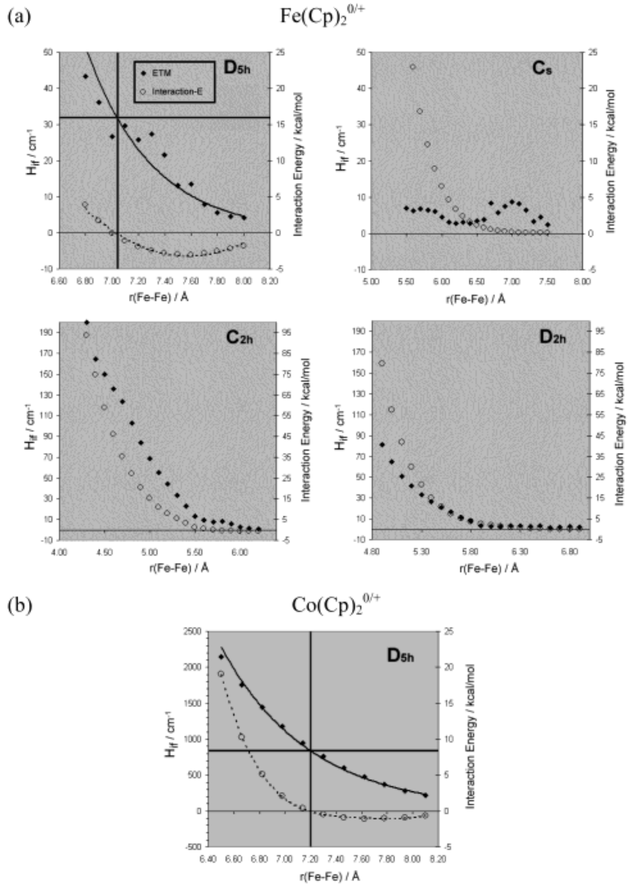

Figure 2. H_{if} and interaction energies of the (a) $Fe(Cp)_2^{0/+}$ couple at different orientations and (b) $Co(Cp)_2^{0/+}$ couple at D_{5h} geometry as functions of metal−metal distance.

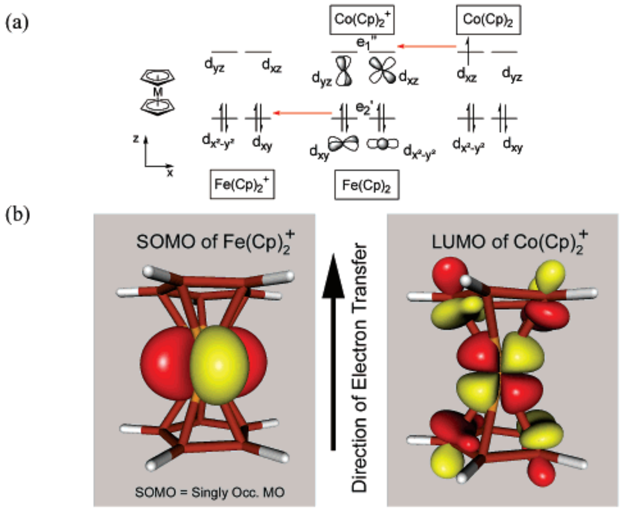

Figure 3. (a) Qualitative MO diagrams of $Fe(Cp)_2^{0/+}$ and $Co(Cp)_2^{0/+}$ showing only redox active, metal-based frontier orbitals. (b) Isosurface plots (isodensity value = 0.025 au) of the redox active orbitals.

geometry is approximately located at the Fe−Fe distance of 7.0 Å, where 32 cm^{-1} is computed for the matrix element. Beyond this distance, the repulsive part of the potential (for which Hartree−Fock calculations provide a reasonable estimation) begins to rise rapidly. This is in excellent agreement with the experimental estimate.

The coupling in the $Co(Cp)_2^{0/+}$ couple has been estimated to be roughly 175 cm^{-1} experimentally,[12] although for this case the authors state that “estimates may well be considerably smaller than the actual values”. A few fundamental differences between two sandwich systems are noteworthy. Figure 3a shows schematically the highest four metal-based frontier molecular orbitals. The donors, $Fe(Cp)_2$ and $Co(Cp)_2$, are formally d^6-Fe(II)/18-electron and d^7-Co(II)/19-electron complexes, respectively. As illustrated in Figure 3a, the redox active MOs transform as e_2', dominated by the metal d_{xy} orbital, and as e_1'' that contains mainly the metal d_{xz} orbital, respectively.[15] Isosurface plots of these MOs are shown in Figure 3b. As recognized previously,[16] substantial mixing of ring orbitals can be seen in the $Co(Cp)_2^+$ LUMO resulting in a significantly larger delocalization of the redox active electron. Thus, at the D_{5h} arrangement, a substantially larger coupling is expected for the $Co(Cp)_2^{0/+}$ couple, and the Cp rings serve as ET mediators, whereas such a delocalization pathway does not exist in the $Fe(Cp)_2^{0/+}$ case. Structural distortion upon electron removal from the neutral metallocene is expected to be more pronounced in $Co(Cp)_2$ because the redox active MO is highly metal−ring antibonding, as illustrated in Figure 3b. Indeed, computed changes of the metal−Cp distance are 0.20 Å for Co and 0.08 Å for Fe systems, respectively. Neglect of this inner sphere reorganization, as is done here, is therefore expected to be a more serious problem in the $Co(Cp)_2^{0/+}$ couple. At closest contact, our calculations predict a coupling of roughly 830 cm^{-1} (Figure 2b), which is essentially identical to the previously reported semiempirical value,[13] 920 cm^{-1}.

We draw several significant conclusions from these results. First, for ferrocene, we obtain considerably better agreement with experiment than that which resulted from semiempirical calculations.[17] This suggests that a systematic comparison of semiempirical and ab initio matrix elements should be carried out for transition-metal-containing species, to see whether the ab initio approach is consistently preferable if one is interested in quantitative or semiquantitative accuracy. Second, the source of the discrepancy for cobaltocene may lie in either the analysis of the experimental data (which required a substantial number of assumptions) or in our ab initio methodology (e.g., neglect of electron correlation, although such a large dependence of the coupling matrix element on correlation effects would be extremely unusual, or in geometrical effects as mentioned previously).

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Supporting Information Available: Computational details, coordinates of the structures and energies and electron transfer matrix elements of all structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Naturally, Jahn−Teller effects distort the geometry and break the symmetry. The D_{5h} labels are used only for simplicity and do not imply symmetry constraints in actual calculations.

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(17) See Supporting Information for more details (Table S3).