

**Redox-Triggered Molecular Switches.  
Electronic Communication in Heterobimetallic  
Indacenyl Mixed Valence Complexes.**

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Since the synthesis of the Creutz-Taube<sup>1</sup> mixed valence ion, continuing investigations on the way in which two or more metals linked by a bridging ligand interact have been directed in the building-up of bimetallic complexes which can be regarded as models for molecular-sized electronic devices.

The goal is to tune the electronic and chemical interactions<sup>2</sup> between ligand-bridged metal groups among which at least one undergoes reversible reduction or oxidation and may behave as a molecular switch that can be turned on and off by electron transfer.<sup>3,4</sup>

Among the physical properties which afford information on the mixed valence ions, two of these, the  $\Delta E_{1/2}$  values relative to the redox potential of the two metal centers, and the optical intervalence transfer (IT) band in the near-IR,<sup>5,6</sup> are widely used to classify the extent of interaction between the metals.

The *s*- (a) and *as*- (b) indacene-diide ligands (Fig. 1), owing to the high delocalizability of their 14  $\pi$ -electron system, have been identified as suitable bridging ligands in view of strong electronic interactions between two coordinated metal centers which may result in interesting chemical and physical properties.<sup>7</sup>

In comparison to the numerous reports on homobimetallic complexes of indacene, to the best of our knowledge no mixed valence heterobimetallic ions of this bridging ligand have been described up to now.

Here we will present the electrochemical and optical properties of *syn* and *anti* [ $\text{CpFe}(\mu\text{-}\eta^5\text{:}\eta^5\text{-as-indacene-diide})\text{-RhL}_2$ ]<sup>+</sup> ( $\text{L}_2$  = cyclooctadiene, norbornadiene,  $\text{L} = \text{CO}$ ) mixed valence ions (Fig. 2) generated by chemical and electrochemical oxidation of the corresponding neutral complexes.

The huge enhancement of the reactivity in the substitution of COD and NBD with carbon monoxide induced by electron transfer will be discussed.

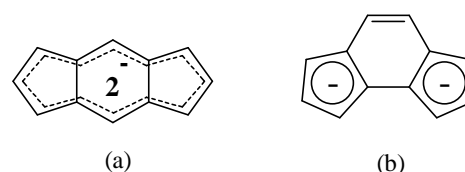


Fig. 1

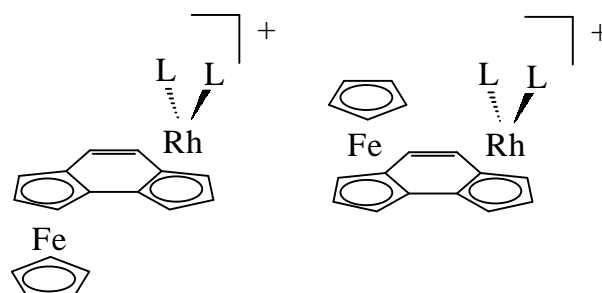


Fig. 2

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