Chemical Communication Induced by Intramolecular Electron Transfer in Heterobimetallic Ferrocenyl-Indenyl-$Cr(CO)_3$ Complexes

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It is commonly assumed that cooperative interaction between two metal centers might cause significant increase in the reaction rates,[1] lead to transformations which do not occur when monometallic complexes are involved, and finally set up unique physical properties such as, charge or energy transfer,[2] non linear optical properties, etc.

The main goal is the preparation of mixed valence complexes in order to estimate the chemical and electronic interaction among the metals through the bridging ligand, tuned by varying the distance and the reciprocal orientation of the donor-acceptor centers, and the nature of the solvent. If one of the two metal centers shows a redox reversible behavior, it might behave as a molecular switch causing an electronic transfer.[3]

Whereas homobimetallic complexes were widely studied, in spite of their intrinsic interest less attention has been paid to those complexes having two different metal units. These complexes offer the unique opportunity to explore the dependence of electronic co-operativity on redox asymmetry, and of chemical reactivity upon the presence of a second different redox center in the same molecule.

Recently, we prepared a series of heterobimetallic (1-ferrocenyl)-indenyl-RhL_2 [3b] and CpFe-(*as*-indacene-diide)-RhL_2 [4] compounds and studied the voltammetric and spectroscopic behavior, showing that a strong chemical and electronic interaction is active in the radical cations.

Here we present the results of chemical and electrochemical oxidation of heterobimetallic iron-chromium indenyl complexes in which the ferrocenyl group is connected in 2 or 3 position of indenyl and the coordination of $Cr(CO)_3$ can be easily varied from hexahapto (Figure 1) to pentahapto mode (Figure 2) upon deprotonation or reduction. In such a way the distance and the relative configuration between the two metal centers can be considerably changed. The reactivity in the substitution reaction of CO with a phosphite induced by electron transfer, and the influence of the solvent in the electrochemical process will be discussed.

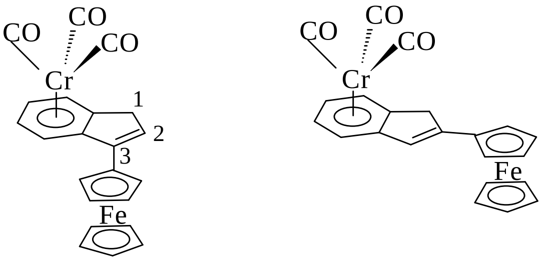

Figure 1

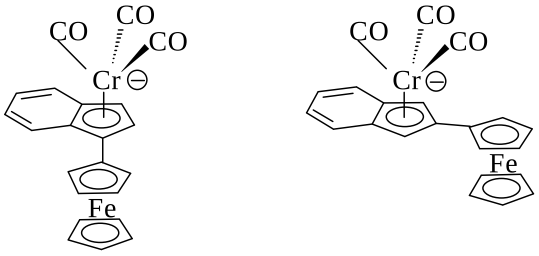

Figure 2

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3. (a) Jeung, L.K; Kim J. E; Chung, Y.K.; Rieger, P. H. Sweigart, D.A., *Organometallics* 1996, 15, 3891; (b) Santi; S, Ceccon, A.; Crociani, L.; Gambaro, A.; Ganis, P.; Tiso, M.; Venzo, A.; Bacchi, A. *Organometallics*, 2002, 21, 565.
4. Santi, S.; Ceccon, A.; Carli, F.; Crociani, L.; Bisello, A.; Tiso, M.; Venzo, A. Organometallics 2002, 21 2679.