

Figure 6. Nmr spectra of $[\text{FePMe}_2(\text{CO})_3]_2^{2-}$ as a function of temperature.

Table VI
Kinetic and Thermodynamic Parameters^a

Compd II	T_c^a	E^\ddagger , kcal/mole	ΔS^\ddagger , eu	$k_1, 0^\circ$, l./sec	$J_{pp'}$, cps
Fe \bigcirc	338 ± 2	2.1 ± 0.2	-45 ± 1	15.3	85
Fe \ominus	207 ± 2	2.2 ± 0.3	-39 ± 2	352	>500

^a Coalescence temperature, °K.

study. The observations suggest the following explanation for the large change in kinetic parameters for inversion upon addition of the two electrons: occupation of an MO largely σ^* in character involving metal orbitals leading to an increased M-M distance and an increased charge on the metal. The nmr chemical shift data and the Mössbauer spectra are in agreement with occupation of an orbital with high σ character.

The methyl protons show a strong shift to higher field upon reduction, and the isomer shift of the iron is in the direction of increasing s-electron density at the nucleus. The consequence of σ^* occupation and addition of charge to the core metal atom would be a repulsion between the atoms and a lengthening of the Fe-Fe distance. The only way this can be achieved is to shorten the P-P distance and increase phosphorus coupling, as observed.

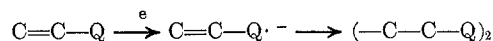
Consequently, one reaches the conclusion that the addition of electrons to a previously unoccupied molecular orbital results in a change in molecular geometry.

The Future

Thus far, the chemical reactivity and catalytic behavior of electrochemically generated organometallic species have not been fully exploited. Some of the avenues that need exploration hinge on the following observations.

Several of the species can induce polymerization of olefins. Bispyridinemolybdenum tetracarbonyl reduces in a multielectron process to give the radical anion of 2,2'-bipyridylmolybdenum tetracarbonyl. Since chemical reduction of pyridine yields the 4,4'-bipyridyl, a stereospecificity has been achieved by the template action of the core metal.

Although the precoupling lifetime of the radical anions derived from negatively substituted olefins



is of the order of milliseconds, the lifetime of the species coordinated to $\text{Fe}(\text{CO})_4$ is measured in months. The source of this stability must lie in the spin-charge distribution examined above.

It would thus seem that organometallic electrochemistry is a multifaceted area. The electrochemical results can be used to predict the pathways to new compounds. The large number of charge states existing for many species permits the study of spin and charge delocalization in a molecular species with minimal perturbation of the coordination sphere. Electrochemical template syntheses and tailoring of catalytic activity remain to be explored.

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Additions and Corrections

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Apostolos G. Anastassiou: The Heteronins.

Page 283. The last reference of footnote 19 should read: "... (R. T. Seidner and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 149 (1972)) as well."