

Organometallic Electrochemistry

RAYMOND E. DESSY* AND LEO A. BARES

Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Received November 1, 1971

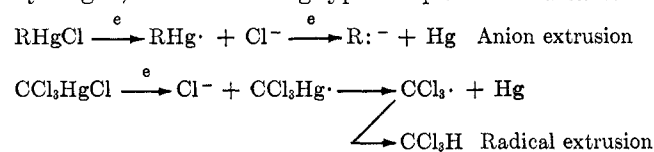
Although the areas of inorganic and organic electrochemistry have been explored rather intensively, only during the last 5 years has organometallic electrochemistry been probed in breadth and depth. Electrochemical techniques have been employed in organometallic syntheses,^{1,2} as an ancillary tool in electronic structural studies,²⁻¹¹ and in a miscellany of kinetic/mechanistic studies.¹²⁻¹⁹ This Account, which is not intended as a review of the field, will be directed primarily to work previously performed or in progress in this laboratory. It is aimed at a broad survey of organometallic electrochemistry. Special attention will be given to (a) the available pathways in organometallic electrochemical reductions, and (b) the physical consequences of the addition (or abstraction) of an electron from an organometallic molecule.

Pathways for Reduction

A systematic study²⁰ indicates that the types of electrochemical behavior shown in Scheme I are to be found in organometallic species; R is a σ - or π -bonded organic residue, M is a metal, and Q is another ligand such as R, MR, or halogen.

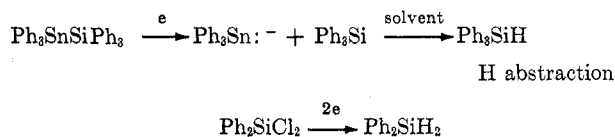
The exploration has involved electrochemical examination of the parent under three-electrode conditions in dimethoxyethane with tetrabutylammonium perchlorate as supporting electrolyte and with all potentials referenced to $10^{-3} M Ag^+ | Ag$. Electrochemical reversibility has been studied by triangular voltammetry at a hanging Hg drop. The n values (number of electrons/step) have been determined by exhaustive controlled-potential electrolyses, and chemical reversibility has been evaluated by reoxidation, followed by ir and uv spectroscopic examination of the solutions. (A very readable discussion of these techniques, used as tools by the experimental inorganic chemist, may be found in ref 2.)

Organometallic derivatives of main-group elements tend to extrude carbanions or radicals, or to abstract hydrogen, as the following typical equations indicate.²¹



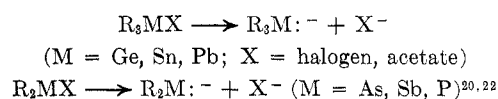
Raymond E. Dessy has been at Virginia Polytechnic Institute and State University since 1968, as Professor of Chemistry. He came there from the University of Cincinnati and before that he was a postdoctoral fellow with M. S. Newman and instructor at The Ohio State University. He received his B.S. in pharmacy in 1953 and a Ph.D. in chemistry in 1956 from the University of Pittsburgh. He was an Alfred P. Sloan Fellow, 1962-1964. His research interests revolve around study of fast organometallic reaction mechanisms.

Leo A. Bares is presently completing Ph.D. requirements under R. E. Dessy at Virginia Polytechnic Institute and State University.

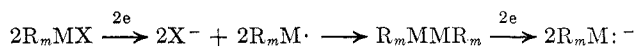


Homodimetallic Species (R_mMMR_m) and Their Anions ($R_mM:^-$)

Derivatives of groups IV and V give rise to some interesting metalloid anion species which are synthetically useful; e.g.



These species result from the reactions



and parallel classical metal and metal/amalgam reductions. All of the systems show a one-electron reduction near $-1 V$, typical of $R_mMX \rightarrow R_mM\cdot + X^-$, with a second wave at more cathodic potentials that can be identified with R_mMMR_m .

- (1) B. L. Laube and C. D. Schmulbach, *Progr. Inorg. Chem.*, **14**, 65 (1971), and references therein.
- (2) J. B. Headridge, "Electrochemical Techniques for Inorganic Chemists," Academic Press, New York, N. Y., 1969, and references therein.
- (3) C. Eilschenbroich and M. Cais, *J. Organometal. Chem.*, **18**, 135 (1959).
- (4) L. F. Warren and M. F. Hawthorne, "The Chemistry of Bis- $[\pi$ -(3)-1,2-dicarbonyl]metallates of Nickel and Palladium," *U. S. Clearinghouse Fed. Sci. Tech. Inform.*, AD-698136, AD 1969, and references therein.
- (5) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49, (1968), and references therein.
- (6) (a) S. P. Gubin, *Pure Applied Chem.*, **23**, 463 (1970), and references therein; (b) S. P. Gubin, S. A. Smirnova, and R. I. Denisovich, *J. Organometal. Chem.*, **30**, 257 (1971).
- (7) S. P. Gubin, S. A. Smirnova, and R. I. Denisovich, *ibid.*, **20**, 229 (1969).
- (8) A. N. Nesmeyanov, *et al.*, *ibid.*, **20**, 169 (1969).
- (9) T. J. Meyer and J. A. Ferguson, *J. Chem. Soc. D*, 623 (1971).
- (10) R. Pribil, Jr., J. Masek, and A. A. Viecek, *Inorg. Chim. Acta*, **5**, 57 (1971).
- (11) J. Masek, *Inorg. Chim. Acta Rev.*, 99 (1969).
- (12) T. J. Meyer and J. A. Ferguson, *Inorg. Chem.*, **10**, 1025 (1971).
- (13) R. L. Middaugh and F. Farha, Jr., *J. Amer. Chem. Soc.*, **88**, 4147 (1966).
- (14) R. J. Wiersema and R. L. Middaugh, *ibid.*, **89**, 5078 (1967); **91**, 2074 (1969).
- (15) J. A. McCleverty, *et al.*, *J. Organometal. Chem.*, **80**, C75 (1971).
- (16) T. Matsumoto, M. Sato, and A. Schmiru, *Bull. Chem. Soc. Jap.*, **44**, 1720 (1971).
- (17) G. Paliani, S. M. Murgia, and G. Cardaci, *J. Organometal. Chem.*, **30**, 221 (1971).
- (18) G. Piazza and G. Paliani, *Z. Phys. Chem. (Frankfurt am Main)*, **71**, 91 (1970).
- (19) R. F. Broman and R. W. Murray, *Anal. Chem.*, **37**, 1408 (1965).
- (20) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5112 (1966).
- (21) R. E. Dessy, W. Kitching, and T. Chivers, *ibid.*, **88**, 453 (1966).
- (22) R. E. Dessy, W. Kitching, and T. Chivers, *ibid.*, **88**, 467 (1966).

Scheme I

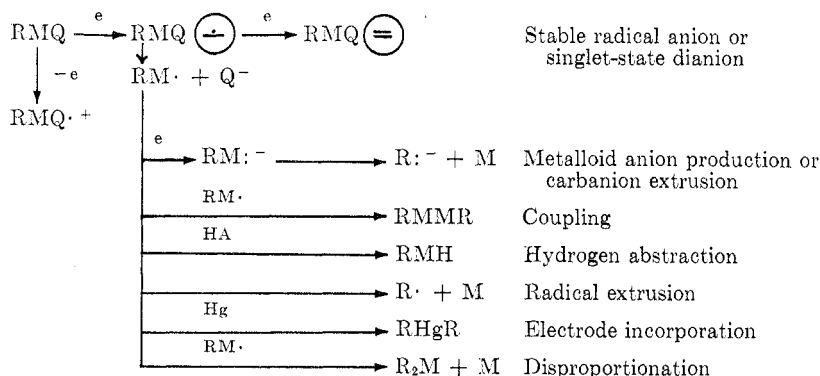


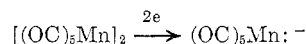
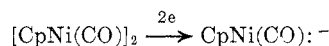
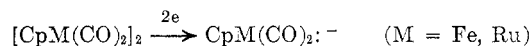
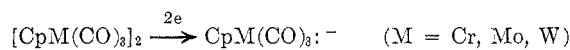
Table I

Catenated bond ^a	$E_{1/2}$	D_{m-m} , kcal/mole
si-si	No red	42
ge-ge	-3.5 ^b	37
sn-sn	-2.9 ^b	34
pb-pb	-2.0 ^b	
sb-sb	-2.5 ^b	30
bi-bi	-2.3 ^b	25

^a Lower case element symbols refer to the atom and one valence.

^b Ph derivatives.

These metalloid anions are related to the series of metallic anions derived from the transition series by electrochemical reduction of the corresponding metal-metal bonded dimers,²³⁻²⁵ *e.g.*



Each M-M bond system has a characteristic half-wave potential and there appears to be a primitive correlation between half-wave potential and bond strength; see Table I for examples.

Metal and Metalloid Anion Nucleophilicities. Figure 1 shows the good correlation between the rate of nucleophilic displacement of halide ion from an organic halide and the oxidation potential of the anion at a platinum electrode. This linear free energy relationship is of the type of Edwards' four-parameter equation

$$\log k/k_0 = aE_N + bH_N$$

In this expression, *a* and *b* are empirically determined coefficients, E_N is the standard electrode potential for the nucleophile involved, H_N is defined by the equation $H_N = \text{p}K_a + 1.74$, and k_0 refers to the corresponding process in water. Normally, E_N dominates the right-hand side of the equation. Oxidation is a fair model for nucleophilicity, since the latter does involve formal loss of electrons by the attacking nucleophile. This corre-

(23) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Amer. Chem. Soc.*, **88**, 5117 (1966).

(24) R. E. Dessy and P. M. Weissman, *ibid.*, **88**, 5124, 5129 (1966).

(25) R. E. Dessy, R. L. Pohl, and R. B. King, *ibid.*, **88**, 5121 (1966).

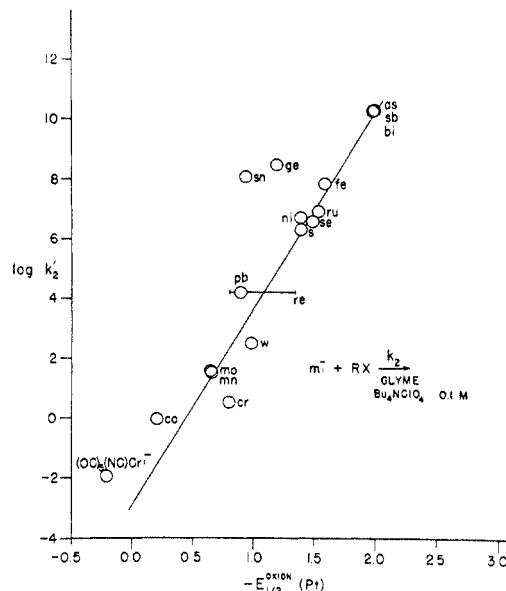
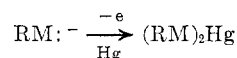


Figure 1. Rates of nucleophilic substitution processes for organometallic anions *vs.* oxidation potential.

lation should have considerable synthetic use, and its extension to new anions is easily implemented. It should be noted that correlations involving Hg microelectrodes fail because of the process

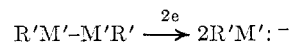
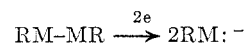


particularly when M is a transition metal.

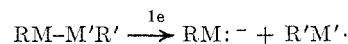
Heterodimetallic Species ($\text{R}_m\text{MM}'\text{R}_m$). The electrochemical characterization of heterodimetallic compounds resulting from the reaction



is very easy. Considering the half-wave potentials of the processes

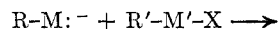


when the reduction potential for the electrochemical scission of $\text{RM-M}'\text{R}'$ lies between the two homodimetallic parents or is more anodic, the reduction will proceed as

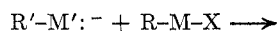


where $R'M'$ is associated with the parent reducing most cathodically. In a few cases (all containing Ph_3M moieties) $n = 2$, and the reduction proceeds to give both $RM:^-$ and $R'M:^-$.

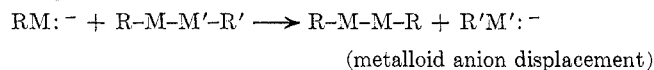
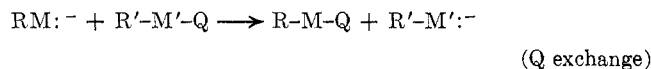
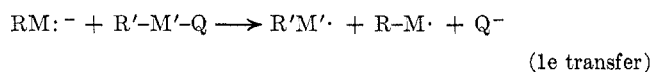
It has been possible, utilizing the reduction potentials for homo- and heterodimetallic species as identifying criteria, to examine whether the reactions



and

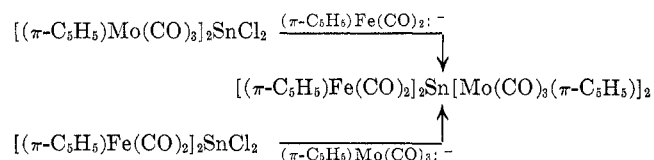


commute; *i.e.*, do two apparently equal pathways to the same product actually yield a unique compound? Figure 2 indicates that commutation is not always observed. (In the figure, lower case element symbols will be used to refer to the atom involved and one valence.) Further studies indicate that this is because of the following processes.



A more detailed study²⁶ indicates that the nucleophilicity of the metallic or metalloidal anions is a key to predicting whether the displacement reaction shown above will occur.

These facts should be useful in predicting which reactions would be most successful in an attempt to create species having a polymeric backbone, for example



As might be expected from available data, the bottom reaction has been reported to yield the desired compound. The top reaction fails because $CpFe(CO)_2:^-$ displaces $CpMo(CO)_3:^-$ anion from any intermediate $fe-mo$ compound.

Structural Reorganization. Many cases studied, particularly those involving acetylene-iron carbonyl complexes, the bipyridyliron dinitrosyls, and corresponding isoelectronic cobalt carbonyl nitrosyls mentioned later, show electrochemical reversibility *via* cyclic voltammetry; however, exhaustive controlled-potential reduction yields a solution whose oxidation potential is anodic with respect to the previously determined reduction potential. Yet, controlled-potential oxidation regenerates starting material. This appears to be akin to some of the reorganization or structural changes reported by Busch in his study of the electrochemistry of macrocyclic complexes²⁷ and to the geometric changes occurring on change in charge state

	$CpFe(CO)_2^-$	Ph_3Sn^-	Ph_3Pb^-	$(OC)_5Mn^-$	$CpMo(CO)_3^-$
$CpFe(CO)_2I$	1 fe-fe	7 sn-fe	9 pb-fe	11 N.R.	13 N.R.
Ph_3SnCl	6 fe-sn	2 sn-sn	15 ?	17 mn-mn sn-sn mn-sn	19 mo-sn
Ph_3PbOAc	8 fe-pb	14 sn-sn pb-pb Ph_4Pb	3 pb-pb Ph_4Pb	21 mn-pb	23 not mo-pb
$(OC)_5MnCl$	10 ?	16 ?	20 not mn-pb	4 N.R.	25 N.R.
$CpMo(CO)_3Cl$	12 N.R.	18 sn-sn mo^- mo^-Cl	22 pb-pb mo^- mo^-Cl	24 mn-mn mo^- mo^-Cl	5 N.R.

Figure 2. Organometallic anion-organometallic halide reaction products.

reported for classical coordination compounds by Gray and Dahl.⁵ The organic counterparts are the change in structure of cyclooctatetraene upon reduction (tub to planar geometry) and the bond angle-length changes reported for the tetracyanoquinonedimethide radical anion-neutral system. It is known in coordination chemistry that extensive structural changes lead to slow electron-exchange rates. This Franck-Condon-like limitation of electron-transfer rate is also seen in the cyclooctatetraene (COT) area. COT and $COT:^-$ exchange slowly (different geometry), but COT^{2-} and $COT:^-$ exchange rapidly (both planar).

Figure 3 indicates the extent of one-electron transfer between a large number of organometallic species. Complete transfer (CT) and no transfer (NT) are found in accord with Latimer redox concepts, where homoexchange ($A + A:^- \rightleftharpoons A:^- + A$) is involved. It is obvious that some exchange rates are slow compared to the diffusion limit, and that these slow rates occur where the above-mentioned electrochemical reversibility anomaly is seen. Equilibrium constants determined on opposite sides of the tieline are also not consistent for these species. Unfortunately, single-crystal X-ray work in the organometallic area has been hampered by crystallization problems and air sensitivity. At present the nature of the distortions involved is not known. However, the question of charge and spin delocalization has been carefully examined in those compounds formed from the group VI metals (Cr, Mo, and W) and from Fe and Ru. Both groups form a well-defined series of mononuclear and dinuclear species.

Physical Consequences of Organometallic Redox Processes

A meticulous study has been made of the following series of charged species involving mononuclear compounds by employing the indicated techniques to probe the nature of (1) the location of spin density in the radical species (esr);^{28,29} (2) the locus of charge distribution (nmr);^{30,31} (3) the nature of the electric field gradient at

(26) R. E. Dessy and R. L. Pohl, *J. Amer. Chem. Soc.*, **90**, 2005 (1968).

(27) D. H. Busch, *et al.*, *ibid.*, **92**, 400 (1970).

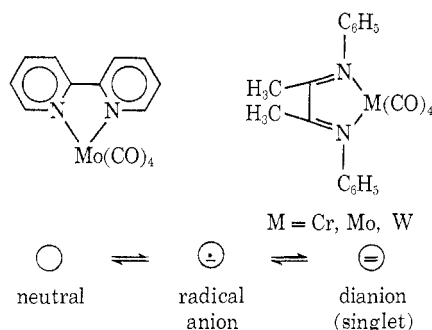
(28) R. E. Dessy and L. Wiczorek, *ibid.*, **91**, 4963 (1969).

(29) R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *ibid.*, **92**, 3947 (1970).

$$A \cdot + B \xrightleftharpoons{K} B \cdot + A; \quad A \cdot + A \xrightarrow{k} A + A \cdot$$

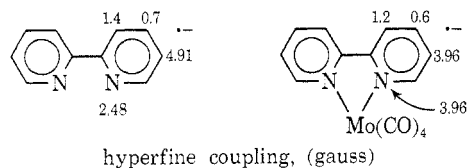
A \cdot (-E _{1/2})	B						
Fe ₂ (CO) ₉ (Cl-C ₆ H ₄) ₂ (1.2)	$k < 10^7$	$K = 0.3$	NT	NT	NT	NT	NT
Fe ₂ (CO) ₉ (C ₆ H ₄) ₂ (1.3)	$K = 30$	$k < 10^7$	$K = 0.1$	NT	NT	NT	NT
Fe ₂ (CO) ₉ (PhC ₂ Me) ₂ (1.5)	CT	$K = 1$	$k < 10^7$	SOME T	NT	NT	NT
Fe ₂ B-(PhCO) ₂ CH (1.6)	CT	CT	CT	$k \approx 10^7$...	NT	NT
Ph ₂ B-(PhCO) ₂ CH (1.7)	CT	CT	CT	...	$k \approx 10^7$	NT	NT
COT-Fe-(CO) ₂ (2.0)	CT	CT	CT	CT	CT	...	NT
(bipy)Mo-(CO) ₂ (2.2)	CT	CT	CT	CT	CT	...	$k \approx 1.8 \times 10^7$

Figure 3. Electron-transfer processes in organometallic systems.



the core metal atom (Mössbauer);²⁹ (4) the method of transmission of charge density (ir).^{28,29}

Octahedral Cases. The typical radical anion formed from a neutral precursor complex shows an esr hyperfine splitting pattern which greatly resembles that of the radical anion of the ligand itself. Hyperfine coupling constants derived from spectral simulation studies indicate that relatively small changes in hyperfine coupling constants are observed. This is exemplified in the case of 2,2'-bipyridyl and 2,2'-bipyridylmolybdenum tetracarbonyl radical anions shown. The



conclusion is that spin density in the coordinated ligand radical ion is not appreciably different from the uncoordinated ligand radical ion ($a = \rho Q$, where a = hyperfine coupling in gauss, ρ is the spin density at an aromatic carbon center, and Q is an empirical parameter, ~ 25 G for aromatic protons). Nmr studies on the dianion species,³¹ however, indicate that only a small amount of charge density resides in the organic ligand. Relative to the neutral precursors, incremental upfield

(30) R. E. Dessy, A. L. Rheingold, and G. D. Howard, *J. Amer. Chem. Soc.*, **94**, 746 (1972).

(31) R. E. Dessy, J. C. Charkoudian, and A. L. Rheingold, *ibid.*, **94**, 738 (1972).

shifts of approximately 0.2 ppm for aromatic protons are observed in the dianion species of the diacetylanil metal complexes ($\Delta\delta = qK$,³² where $\Delta\delta$ is the change in chemical shift, q is the excess charge at an aromatic carbon center, and K is a constant, approximately 10 ppm for aromatic protons). Roughly 10% of the charge density is retained in the organic ligand moiety of the complex. Although this is in marked contrast to the findings in aromatic organic radical ion-neutral systems, where a good correlation exists between spin and charge density, it is not, perhaps, very surprising when one views the pronounced ability of metal atom systems to serve as charge sinks and distributors, in comparison to organic systems.

Electronic absorption spectral studies tend to support the concept of charge and spin separation in these radical systems.³³ Aromatic diimine intraligand bands and metal to ligand (here, ligand refers only to the diimine) and metal to carbonyl charge-transfer bands have been identified. Shifts in these bands upon electrochemical reduction of diimine group VIb tetracarbonyls suggest that the electron reversibly added in forming the radical anion enters a π^* orbital predominantly ligand in character, but that much of the resultant charge is transmitted to the carbonyls.

The pertinent charge transfer bands for 1,10-phenanthrolinechromium tetracarbonyl are

	M \rightarrow π_{CO}^*	M \rightarrow π_L^*
\bigcirc	30,700 cm ⁻¹	20,400 cm ⁻¹
\ominus	$\sim 35,800$ cm ⁻¹	$\sim 23,800$ cm ⁻¹

The band assignments for the neutral complex were tentatively reported previously³⁴ and further sub-

(32) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *ibid.*, **82**, 5846 (1960).

(33) An extensive study of the electronic absorption spectra and electronic structures on neutral compounds, radical anions, radical cations, and singlet-state dianions of diimine derivatives of group VIb hexacarbonyls, Fe(NO)₂(CO)₂, and Co(CO)₂(NO) and on (olefin)-iron tetracarbonyls is near completion.

(34) H. Saito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **41**, 359 (1968).

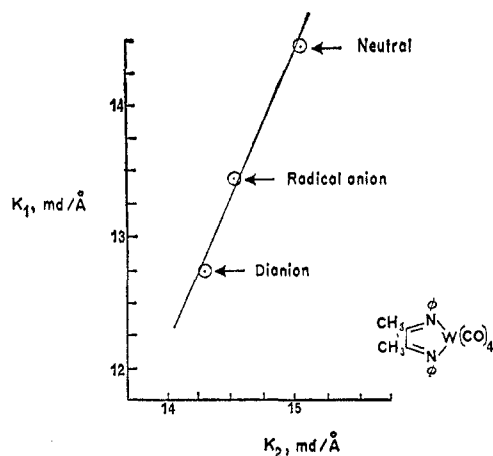
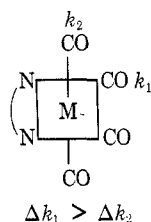


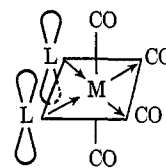
Figure 4. Carbonyl stretch force constants vs. charge.

stantiated in this laboratory by extensive ligand substitutional perturbations. Band assignments for the radical anion have been made by comparing the spectrum of the complex radical anion to that of the ligand radical anion. The same types of band structures, attributable to ligand $\pi \rightarrow \pi^*$ transitions, are clearly discernible in both spectra, although they do not occur at precisely the same energies. By subtracting out the $\pi \rightarrow \pi^*$ bands, it is possible to locate, with confidence, the charge-transfer bands. The $20,400\text{-cm}^{-1}$ band, assigned as $M \rightarrow \pi_L^*$, is the lowest energy band in the spectrum of the neutral complex. Consequently, the electron added during reduction enters a lowest unoccupied molecular orbital predominantly ligand in character. If the charge of this electron is localized on the ligand of the complex radical anion, one would predict, on the basis of gross electrostatic effects, that the $M \rightarrow \pi_L^*$ band would experience a more dramatic hypsochromic shift than would the $M \rightarrow \pi_{CO}^*$ band. This is not observed to be the case. The $M \rightarrow \pi_{CO}^*$ band shifts to higher energy by roughly 5100 cm^{-1} compared to a blue shift of about 3400 cm^{-1} for the $M \rightarrow \pi_L^*$ band. This observation suggests that much of the charge due to the reduction electron is transmitted *via* the metal to the carbonyls.

Charge distribution can be further studied by observing changes in the CO infrared stretching vibrations. Infrared studies, using the Cotton-Kraihanzel force field approximation method,^{28,29,31} indicate that as electrons are added to these molecules the CO stretching force constant decreases for all of the attached CO molecules. One finds experimentally that k_1 is affected more than k_2 (Figure 4) for all group VI derivatives, in contrast to the prediction based on a π -only mechanism of charge transmission to and through the metal atom.³⁵

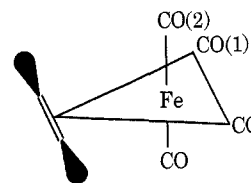


This has led to the suggestion that an anisotropic σ mechanism of transfer is involved. Unfortunately, the



study of the electric field gradient and charge distribution at the central core metal atom has not been possible in this series due to the lack of a nucleus appropriate for Mössbauer studies.

Trigonal-Bipyramidal Cases. However, in the (olefin)iron tetracarbonyl molecules (exemplified by the



structure) it has been possible to employ Mössbauer spectroscopy to study the transfer mechanism.²⁹ ESR studies indicate that spin density in the radical anion is largely confined to the olefin ligand (see Table II). In

Table II

Ligand	Olefin ^a radical anion a_H, G	$\ddagger\text{Fe}(\text{CO})_4$ radical anion a_H, G
Methyl fumarate	6.7	5.1
Methyl cinnamate	5.5	5.0

^a M. Baizar, Monsanto Central Research, unpublished observations.

studies show shifts of the CO stretch force constant, upon reduction of these complexes, to lower values as expected. The corresponding Mössbauer data reveal clearly the mode of charge transmission. The isomer shift is positive upon reduction, indicating a lower s-electron density at the core metal atom resulting from increased s-electron shielding due to ligand \rightarrow metal π donation (Table III).

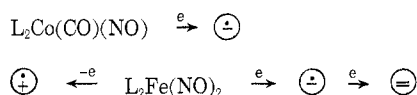
Table III
Mössbauer Parameters^a

Compound	—IS, ^{a,b} mm/sec—		—QS, ^b mm/sec—	
	Neutral molecule	Radical anion	Neutral molecule	Radical anion
$\text{Fe}(\text{CO})_5^c$	0.201		2.60	
Maleic anhydride- $\text{Fe}(\text{CO})_4$	0.266	0.28	1.359	0.87
<i>N</i> -Phenylmaleimide- $\text{Fe}(\text{CO})_4$	0.248	0.37	1.540	0.73
<i>N,N</i> -Dimethylacryl- amide- $\text{Fe}(\text{CO})_4$	0.260	0.30	1.654	1.26
Dimethyl fumarate- $\text{Fe}(\text{CO})_4$	0.263	0.39	1.563	0.79

^a All measurements made at -196° , relative to sodium nitroprusside. ^b Neutral compounds ± 0.005 ; radical anions ± 0.02 . ^c R. L. Collins and R. Petit, *J. Amer. Chem. Soc.*, **85**, 2332 (1963).

(35) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references therein.

Tetrahedral Cases. The tetrahedral species $L_2Fe(NO)_2$ and $L_2Co(CO)NO$ are of interest since a good "spin label" is present in the form of the nitrosyl *nitrogens* that can test spin density in this area.³¹ The systems form the charge states



Hyperfine coupling constants are indicated in Table IV.

Table IV

	a_M , G	a_N , G (no. of nuclei)	a_H , G (no. of nuclei)
Bipyridylcobalt carbonyl nitrosyl radical anion	6.9	3.4 (2)	6.9 (2)
(Di-2-pyridyl ketone)iron dinitrosyl radical anion		2.4 (2)	4.8 (2) 0.6 (2)

No *NO* hyperfine coupling is observable. The similarity between hyperfine coupling in the ligand radical anion and coordinated radical anion again suggests spin localization in the ligand π system. Mössbauer data indicate that charge transmission again is σ in nature, negative isomer shifts indicating increased electron density around iron (Table V).

Table V
Mössbauer Parameters^a

(Di-2-pyridyl ketone)- iron dinitrosyl	IS, mm/sec	QS, mm/sec
Radical cation	0.64	0.66
Neutral	0.52	0.72
Radical anion	0.43	0.97

^a All measurements made at -196° , relative to sodium nitroprusside.

Studies on the organic carbonyl stretching frequency in the (di-2-pyridyl ketone)iron and -cobalt complexes³¹ indicate that the radical-cation, neutral, and radical-anion species all have the same organic carbonyl group absorbing at 1661 cm^{-1} , although the *NO* frequencies shift by 40 cm^{-1} per unit charge. Since this carbonyl should be extremely sensitive to charge density, one has further proof that in $L-M-CO$ systems the coordinated ligand is a good spin sink, but a poor charge sink.

Effect of Charge on Fluxional Behavior and Geometry. Some geometric and energetic information is available for charge states of compounds from the group VI metals and Fe and Ru which involve *dimetallic* bridged species involving $M-M$ bonds. The accepted structures for these compounds are shown in Figure 5.³⁰

In all cases, we are dealing with systems that show electro-reversible two-electron reduction to singlet-state dianions, where neutral species and dianion are in equilibrium with radical anion.



Compounds of structure I constitute $X_3AA'X_3$ spin systems where $J_{XX'} = 0$, and compounds of structure II constitute $X_3X'_3AA'X'_3X''_3$ systems factorable into

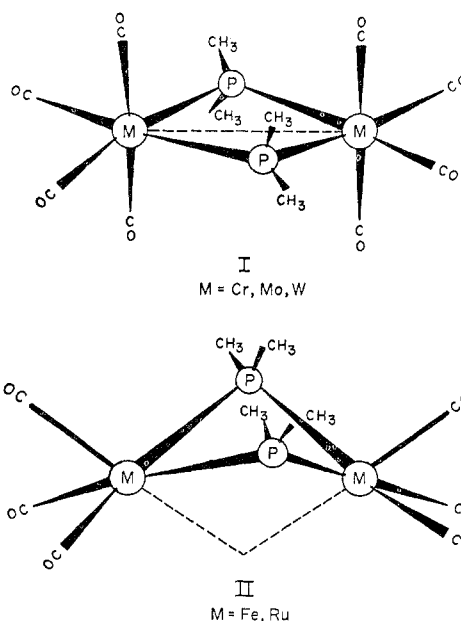
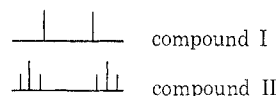


Figure 5.

two $X_3AA'X_3$ systems if $^4J_{HH'}$ is taken to be immeasurably small. Two parameters are important in analyzing these systems: $L = |J_{XA} - J_{XA'}|$; $N = |J_{XA} + J_{XA'}|$. Usually $^4J_{HP} < ^2J_{HP}$, and it is assumed that $L = N$.

The X part of the $X_nAA'X'_n$ system has a deceptively simple appearance when L and N are of similar magnitude. When $J_{AA'} \ll L$ the spectrum is a doublet. When $J_{AA'} \gg L$ it is a triplet.

Compounds of type I show doublet spectra, characteristic of a low $J_{PP'}$. Compounds of type II show a triplet nmr spectrum, characteristic of a high $J_{PP'}$, and division of the methyl hydrogens into two sets; one is exo to the dihedral angle, the other endo.



Upon electrochemical reduction to the radical anion, compounds of type I exhibit an esr spectrum which is characteristic of a high phosphorus coupling (1:2:1 triplet). Compounds of type II show an esr spectrum in which the exo hydrogens are still distinguished from the endo hydrogens, indicating that during the esr time scale of observation the dihedral angle is maintained.

Further reduction to the dianion species gives rise to solutions of I and II which exhibit strong P-P coupling. In the case of compounds of structure II, however, the nmr spectra are strongly temperature dependent (Figure 6). In retrospect, it seems obvious that the molecules are undergoing inversion and belong to a new class of fluxional molecules. The activation parameters for the inversion process are given in Table VI. Cotton has recently reported another member of this series, $(R_2GeCo(CO)_3)_2$.³⁵

The mechanism of the fluxional motion is still under

(36) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **92**, 5003 (1970).

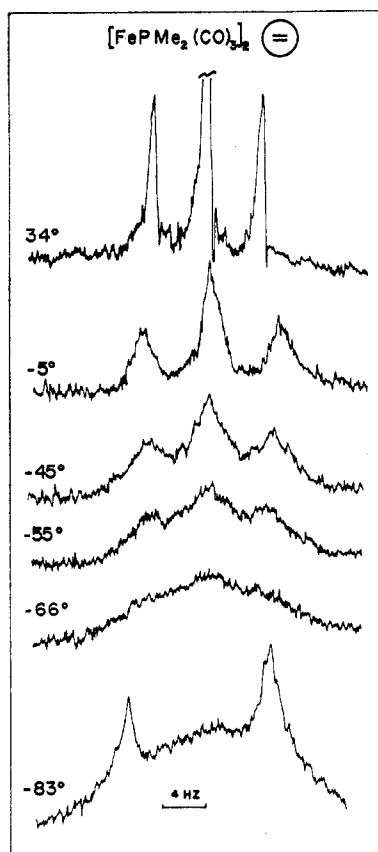


Figure 6. Nmr spectra of $[\text{FePMe}_2(\text{CO})_3]_2^{2-}$ as a function of temperature.

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.

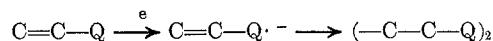
Consequently, one reaches the conclusion that the addition of electrons to a previously unoccupied molecular orbital results in a change in molecular geometry.

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.

This work has been supported by the Air Force Office of Scientific Research and the National Science Foundation.

Additions and Corrections

Volume 5, 1972

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."