Reviews

Organometallic Electrochemistry: Origins, Development, and Future

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The evolution of organotransition metal electrochemistry from its origin with ferrocene to its promise in future applications is presented. Examples are given of key findings on the relationships of electron transfer to molecular structures and to the reactions of organotransition metal complexes.

I. Introduction and Goals

Just as modern organotransition metal chemistry is traced to the discovery of ferrocene, so too may the broader topic of the electrochemical behavior of organometallic compounds. Examination of the 1952 paper “The Structure of Iron-*bis*-Cyclopentadienyl” by Wilkinson, Rosenblum, Whiting, and Woodward[1] reveals that almost half of that pivotal communication was devoted to the ferrocenium ion, even to the degree of reporting a polarographic potential for the ferrocene/ferrocenium couple. Although electrochemical studies lagged far behind those involving the synthetic and structural characterizations of organotransition metal complexes over the next decade, electron-transfer (e.t.) processes are now well known to constitute an important subset of reactions that have broadened the understanding and applications of these compounds.

There can be little dispute that efficacious development of organometallic e.t. processes relies primarily on the craft of electrochemistry, both in its traditional, independent, sense and as a methodology that interfaces easily with ancillary approaches such as spectroscopy and redox synthesis. There is a plethora of resources, some of which are included in Section XIV.D, available to those interested in either an introduction to electrochemical methods or reviews of specific organometallic redox systems. The most comprehensive fairly recent treatment of organometallic electrochemistry is found in Part II of Astruc’s book,[2] which organizes redox processes by the types of reactions and mechanisms undergone, covering the literature until approximately 1995. Bringing this topic to currency, while desirable, is not the purpose of the present review. Rather, its intention is to track the origin and development of organometallic electrochemistry and to offer one person’s thoughts on some of the major questions answered to date, as well as the prospects for future advances.

A major theme that emerges from analysis of the early work is one that is well known to scientists, namely, that progress in one area is often a product of the interplay between emerging disciplines. In the present case these include progress in redox studies of organic compounds, main-group organometallic compounds, and transition metal chelate complexes, as well as technological and theoretical advances in the broad area of electroanalytical chemistry.

II. Pre-ferrocene Studies

Pre-ferrocene electrochemical studies of main-goup organometallics have been reviewed.[3] These efforts, which were largely focused on compounds of Mg and Hg, had a decidedly cathodic (reductive) nature. Because dc polarography[4] was the dominant electroanalytical method in the pre-1960s era, most electrochemical experiments were performed at mercury electrodes. The fact that mercury itself undergoes a thermodynamically facile oxidation to Hg(I) makes it poorly suited to function as a benign electrode material for oxidation processes. Anodic reactions of compounds were therefore not well studied in this period, and, except for a few very facile oxidation processes, systematic studies of electrochemical oxidations awaited the development of solid electrodes having reproducible surfaces.[5] The emphasis on cathodic processes carried forth to the pioneering work of Dessy and co-workers, which will be detailed below.

III. Modern Organometallic Electrochemistry: Ferrocene

The first electrochemical characterization of ferrocene (FcH), while lacking the drama[6] surrounding the discovery and structural characterization of that molecule, nevertheless has

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(1) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

(2) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH Publishers: New York, 1995.

(3) (a) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; pp 403−418. (b) Morris, M. D. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1974; Vol. 7, pp 80−121.

(4) Comprehensive treatments of direct current polarography prior to 1965 may be found in: (a) Kolthoff, I. M.; Lingane, J. J. *Polarography*, 2nd ed.; Interscience Publishers: New York, 1952 (in two volumes). (b) Heyrovský, J.; Kůta, J. *Principles of Polarography*; Academic Press: New York, 1965. (c) Meites, L. *Polarographic Techniques*, 2nd ed.; Interscience Publishers: New York, 1965.

(5) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969.

(6) See the collection of papers by Pauson, P. L; Fischer, E. O.; Jira, R.; Rosenblum, M.; Whiting, M. C.; and Cotton, F. A. In *J. Organomet. Chem.* **2001**, *637*−*639*, pp 3 ff, Adams, R. D., Ed.

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Figure 1. John Page (with tie) teaching in quantitative analysis lab, ca. 1953, at Harvard University. Photo courtesy of J. Page.

interesting aspects over and above the measurements themselves. As noted above, much of the original note[1] proposing the sandwich structure for ferrocene was devoted, in fact, to the ferrocenium ion. The Harvard authors noted that "oxidation may be effected *anodically*" (my emphasis), by air, or by oxidants, giving the now well-known deep blue color. Cotton recalled[7] that the oxidation of ferrocene became a target for study when it was noticed that its solution tended to turn blue (also noted by Kealy and Pauson)[8] and that blue edges were frequently seen for solid samples that had been left out in the air. The ferrocenium ion was subsequently isolated as a number of different salts (including $[GaCl_4]^-$ and $[ClO_4]^-$ as counterions) after oxidation of FcH by mild oxidants such as *p*-benzoquinone. Curiously, the polarographic potential first reported for the ferrocene/ferrocenium couple[1] was apparently given the wrong sign.[9]

Within 2 months of the appearance of this article, a series of three communications was submitted to *Journal of American Chemical Society* by Geoffrey Wilkinson (1921−1996) and published as consecutive papers in the Dec 5, 1952, copy of the *Journal*.[10] Two of these papers were devoted to the preparation of other metallocenes, specifically ruthenocene and the cobaltocenium ion. The third, the only one having a coauthor, was devoted to the electrochemistry of all three of the metallocenes MCp_2, M = Fe, Ru, Co^+.[10c]

John A. Page (Figure 1) was just beginning graduate studies at Harvard after obtaining an M.S. degree from McMaster University. He joined the analytical chemistry group of James J. Lingane (1909−1994), who was an expert in electrochemistry.[11,12] When Page was asked by Wilkinson to try to obtain a polarogram of ferrocene, he did so using a 0.01 M solution of perchloric acid in 90% EtOH that contained 0.1 M $Na[ClO_4]$ as a supporting electrolyte. An $E_{1/2}$ of 0.31 V vs SCE was obtained, and a "polarographic constant" was reported, which can be used to calculate a diffusion coefficient of 3.2×10^{-6} $cm^2\ s^{-1}$ for ferrocene in this medium. The one-electron nature of the oxidation was confirmed by the measured 0.91 F/equiv released during bulk anodic electrolysis at a mercury electrode using a Lingane-designed potentiostat. After completion of the electrolysis, a polarogram of the ferrocenium cathodic process was obtained, establishing the chemical reversibility of the reaction. Polarographic experiments also established that the ferrocenium ion spontaneously re-formed ferrocene in neutral aqueous solutions. It is rather remarkable that such a sophisticated understanding of the basic redox chemistry of ferrocene was obtained so soon after its synthesis and characterization.

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(7) Cotton, F. A. (1930−2007), personal communication to W.E.G., November 2005.

(8) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.

(9) In a discussion of the ferrocenium cation, ref 1 states "Polarographic studies indicate an oxidation-reduction potential of −0.59 V". It is very likely that the authors were meaning to specify a half-cell potential for the reduction of ferrocenium ion to ferrocene, rather than the experimentally measured $E_{1/2}$ for the $FeCp_2^{0/+}$ process. Anyone who has taught electrochemistry to undergraduates previously exposed to the thermodynamics of redox processes will appreciate how common this error is, which mixes up the thermodynamic convention (changing sign when the half-cell reaction is reversed) with the experimental measurable ($E_{1/2}$ independent of direction of reaction for a Nernstian system). For a discussion of this conceptual problem see: Anson, F. *J. Chem. Educ.* **1959**, *36*, 394.

(10) (a) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146. (b) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6148. (c) Page, J. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6149.

(11) Lingane, J. J. *Electroanalytical Chemistry*; Interscience Publishers: New York, 1958. Although Lingane received an acknowledgement in ref 10(c), he apparently was not involved significantly, if at all, in the metallocene work. The original polarograms were measured by Page using a simple "Sargeant" polarograph owing to the fact that the more sophisticated instruments were not available to a beginning graduate student. Page went on to an academic career and, at the time of this writing, was Professor Emeritus at Queen's University in Ontario.

(12) Ironically, one of the outstanding electrochemists of our time, Allen J. Bard, started his graduate studies in the Wilkinson group in September 1955. When Wilkinson, later honored for his work with the 1973 Nobel Prize in chemisitry, failed to get tenure and left Harvard in January, 1956, Bard joined the Lingane group.

The first measurements of ferrocene in nonaqueous solutions appear to have been done in 1959 by Theodore (Ted) Kuwana, then a graduate student at the University of Kansas. Ted was working in the laboratory of Ralph Adams (1924−2002), who was the first to systematically use solid electrodes in nonaqueous media. By circumventing the problem of the facile oxidation of mercury, the use of solid (usually Pt) electrodes elevated the study of anodic processes. The Adams group was working exclusively on organic systems at the time.[13] Coincidentally, two other Kansas graduate students, Donald Bublitz and George Hoh, were making iron-group metallocene derivatives in the organic synthesis groups of William McEwen and Jacob Kleinberg, respectively. At some point the three students decided to make electrochemical measurements on the series of Fe, Ru, and Os compounds. They worked intensely (Kuwana: "day and night") over an Easter holiday to complete the work, with Bublitz and Hoh preparing the compounds and solutions and Kuwana doing the electrochemistry, using the then-popular technique of chronopotentiometry.[14,15] The products[16] of this brief graduate student collaboration were significant. The ferrocene oxidation was shown to be well-behaved and reversible in acetonitrile/0.2 M Li[ClO_4] at a Pt electrode ($E_{1/2} = 0.31$ V vs SCE). The oxidations of ruthenocene and osmocene were shown to lack the simple one-electron character of their lighter congener (in fact, the medium-dependent nature of the ruthenocene oxidation continues to produce surprises to this day).[17] The $E_{1/2}$ of ferrocene was shown to be sensitive to substituent effects when H was replaced by an alkyl, alcohol, acid, or ketone group, and the $E_{1/2}$ shifts were shown to follow Taft σ^* values, showing that the more easily oxidized compounds were also those that were more susceptible to electrophilic substitution reactions.

After viewing the manuscript drafts, Adams opined that the research had been done so independently of the three research directors that the students should coauthor the papers themselves. A preliminary account soon appeared in a British journal,[16a] followed later by a full paper.[16b] It is a fascinating coincidence that all of the students (Page, Kuwana, Bublitz, and Hoh) whose names appear on the first important papers describing the electrochemical oxidation of ferrocene and ruthenocene authored the work independent of their faculty mentors. Taken together, references 10c and 16 constitute the seminal contributions to the concept of molecular electrochemistry of organotransition metal systems.[18] It should also be mentioned that Myron Rosenblum, who had been involved in the original identification of ferrocene while doing graduate work in Woodward's group,[1] was using potentiometric titrations at roughly this time to measure changes in the oxidation potentials of arylferrocenes and, along with J. A. Mason, published these results later in 1960.[19] A number of papers quickly followed, detailing additional substituent effects on the $E_{1/2}$ values of ferrocene derivatives.[20,21] By 1970, Mann and Barnes were already able to make a table of these values for over 100 ferrocene derivatives.[3a]

IV. Additional Metallocenes

In their historic paper,[10c] Page and Wilkinson also reported on the oxidation of ruthenocene and the one-electron reduction of cobaltocenium ion. Whereas these experiments established that one-electron redox chemistry was common to metallocenes, more complex results were obtained for the Ru and Co systems, due in large part to the use of the aqueous electrolytes that were employed in that era. One significant error in this paper was the claim of isolation of a yellow ruthenocenium ion, $[RuCp_2]^+$ as the perchlorate salt, after bulk anodic oxidation of ruthenocene at a Hg pool electrode. The product in question was later shown to be the Hg(II) adduct $[(RuCp_2)_2Hg][ClO_4]_2$.[22]

Of the other metallocenes, only nickelocene attracted significant redox attention in the early years. This 20-electron system was an obvious candidate for removal of electrons, and Cotton et al. reported its anodic oxidation ($E_{1/2} = -0.08$ V vs SCE) in "alcoholic supporting electrolyte" in 1954.[23] In that work, polarography was employed to follow the one-electron oxidation of $NiCp_2$ to $[NiCp_2]^+$ by ceric ion. An attempt to generate the corresponding nickelocenium *di*cation, which would be isoelectronic with ferrocene, resulted in decomposition. In fact, 18-electron $[NiCp_2]^{2+}$ is quite reactive toward nucleophiles, and the first reports of reversible formation of the dication came much later, based on experiments under dry nonaqueous conditions.[24] The Cotton paper[23] also reported the one-electron reduction of the bent sandwich compound $TiCp_2Br_2$.

There was a lapse of some 25 years between the preparation of the early first-row metallocenes, namely, vanadocene and chromocene, and the reporting of their redox potentials. This was particularly surprising for the case of $CrCp_2$, from which

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[13] Among the systems studied by Ralph (Buzz) Adams was dopamine, which was becoming known to be involved in neurological functions. Adams' goal of *in vivo* electrochemical studies of neurotransmitters has been realized by him and his students. For leading references to the important and rapidly developing area of analytical neuroelectrochemistry see: Venton, B. J.; Michael, D. J.; Wightman, R. M. *J. Neurochem.* **2003**, *84*, 373.

[14] Chronopotentiometry is a constant *current* technique that measures changes in working electrode potential as a function of time. The resulting potential versus time plot gives information about the redox mechanism, and reversal chronopotentiometry may be used to probe the chemical reversibility of a redox couple. Difficulties in determining precise transition times in reversal chronopotentiometry limited the development of this method, and it never achieved the popularity of cyclic voltammetry. For a description of chronopotentiometry see: (a) Davis, D. G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker Inc.: New York, 1966; Vol. 1, pp 157 ff. (b) Ref 15, chapter 8.

[15] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley and Sons: New York, 2001.

[16] (a) Kuwana, T.; Bublitz, D. E.; Hoh, G. *Chem. Ind. (London)* **1959**, 635 (b) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811.

[17] For leading references to papers dealing with the oxidation of ruthenocene, see: Trupia, S.; Nafady, A.; Geiger, W. E. *Inorg. Chem.* **2003**, *42*, 5480.

[18] Kuwana also tried to measure the standard heterogeneous e.t. rate of ferrocene under nonaqueous conditions while postdocing in Fred Anson's lab at Cal Tech. Although his results were never published, he was able to estimate a k_s value of between 0.5 and 2 cm s^{-1} through galvanostatic experiments recorded on an oscilloscope. Although the values of k_s (also called k^0) are now known to differ significantly depending on the type and quality of the electrode surface (see Geiger, W. E. In *Organometallic Redox Processes*, Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; pp 150−151), the Kuwana/Anson estimate is consistent with the most reliable measurements made on ferrocene (see (a) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787; (b) Wipf, D. O.; Kristensen, E. W.; Deakin, M. R.; Wightman, M. *Anal. Chem.* **1988**, *60*, 306; (c) Fawcett, W. R.; Opallo, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2131). Note that somewhat higher k_s values have recently been reported using Pt nanoelectrodes (Sun, P.; Mirkin, M. V. *Anal. Chem.* **2006**, *78*, 6526).

[19] Mason, J. G.; Rosenblum, M. *J. Am. Chem. Soc.* **1960**, *82*, 4206.

[20] (a) Hoh, G. L. K.; McEwen, W. E.; Kleinberg, J. *J. Am. Chem. Soc.* **1961**, *83*, 3949. (b) Little, W. F.; Reilley, C. N.; Johnson, J. D.; Lynn, K. N.; Sanders, A. P. *J. Am. Chem. Soc.* **1964**, *86*, 1376.

[21] Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 1551.

[22] Hendrickson, D. N.; Sohn, Y. S.; Morrison, W. H., Jr.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 808.

[23] Wilkinson, G.; Pauson, P. L.; Cotton, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1970.

[24] A reversible CV was observed for $[NiCp_2]^{+/2+}$ at low temperatures in: Wilson, R. J.; Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 758. This oxidation was chemically reversible at room temperature if the experiment was carried out under moisture-free conditions: Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 158.

the chromocenium ion had been isolated.[25] These very air-sensitive systems required the use of much more stringent conditions than the quasi-Schlenk methods being used by most electrochemists at the time. Two students in my research group, Fred Sentleber and John Holloway, designed vacuum electrochemical cells, which, although cumbersome, allowed reliable redox measurements to be made on these systems.[26a] With them, the standard methods of voltammetry (including dc polarography) and electrolysis were carried out under rigorous conditions, providing the desired information on the oxidations and reductions of VCp_2 and $CrCp_2$.[26]

A comprehensive listing of the redox states detected electrochemically for metallocenes has been provided by Strelets.[27]

V. Other Early Reports

Another important group of sandwich compounds receiving electrochemical attention in the early years was that of bis(arene)chromium systems, which were known to form isolable monocations when oxidized. $Cr(benzene)_2$, for example, was shown in 1957 to undergo a polarographic one-electron oxidation in methanol/benzene solution,[28] and more measurements were reported on this class of molecules in the years immediately following.[29]

Before leaving the pre-1960s work, a report on the polarography of $Fe(CO)_5$ should be mentioned. A contribution by the outstanding Czech electrochemist A. A.Vlček showed that this compound was reduced in ethanol in a two-electron process with loss of CO to form $[Fe(CO)_4]^{2-}$.[30] Vlček also described the polarographic reduction of $Fe_3(CO)_{12}$ in a conference paper.[31] The instrumentation employed in this era did not permit use of the lower-conductivity, aprotic, electrolyte media that became known for offering the optimum conditions for producing uncomplicated, chemically reversible, redox processes.

[**Parenthetic Aside A.** Antonín (Tony) Vlček (1927−1999) authored what might be considered to be the first broad treatment of inorganic molecular electrochemistry with a review in *Prog. Inorg. Chem*. **1963**, *5*, 211. It contained a modern treatment of electrode mechanisms, including aspects of electron-transfer rates and coupled chemical reactions, within a context of molecular structures. Vlček, who studied under 1959 Nobel laureate Jaroslav Heyrovský (1890−1967), was honored in a special volume of *Collect. Czech. Chem. Commun.* **2001**, *66*, 1−396. His son, A. A. Vlček, Jr., has made important contributions to the photochemistry of metal complexes and authored an informative treatment comparing the photochemical and electrochemical activations of organometallic complexes. See: Vlček, A. A., Jr. *Chemtracts-Inorg. Chem.* **1993**, *5*, 1.]

VI. Systematic Studies by the Dessy Group

The first systematic work on organotransition metal electrochemistry was done by Raymond E. Dessy (Figure 2) and his colleagues, whose strategic objective was to probe the possibly large family of reversible organometallic redox processes. Conducting their research first at the University of Cincinnati and then at Virginia Polytechnic Institute (now Virginia Tech), this group produced a remarkable set of 10 numbered papers on organometallic electrochemistry that appeared in *J. Am. Chem. Soc.* in 1966,[32−42] nearly half of them involving organotransition metal compounds provided largely by R. Bruce King. Because Dessy's training was in physical organic chemistry rather than electrochemistry, he spent his sabbatical leave in the 1963−1964 academic year acquainting himself with the latter. His sojourn took him to several different universities, where he interacted with experts in electroanalytical chemistry and instrument construction.[43] One must keep in mind that commercial availability of fast, high-powered, potentiostats was still a few years away. The three-electrode, operational-amplifier-based, potentiostat constructed by Dessy allowed experiments to be conducted in more resistive nonaqueous electrolyte solutions, thereby minimizing the Brønsted-acid-dominated coupled reactions so common to redox reactions in protonic media. A strong power supply, interfaced with the potentiostat, allowed bulk electrolyses to be performed, and

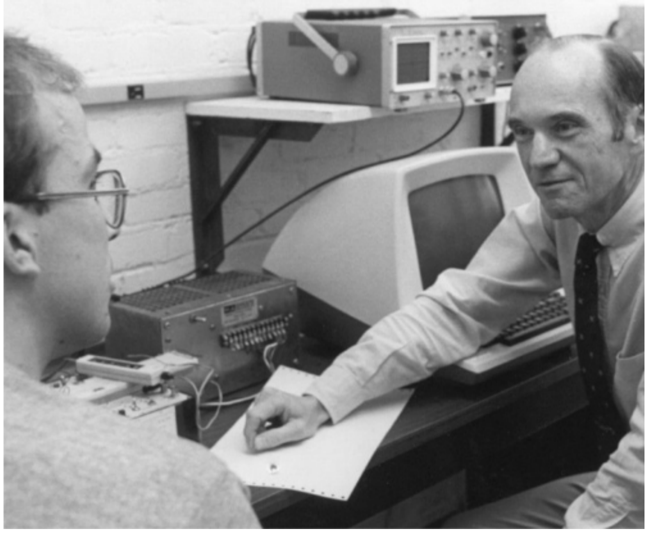

Figure 2. Ray Dessy at Virginia Tech, ca. 1970. Photo courtesy of R. Dessy.

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[25] Fischer, E. O.; Ulm, K. *Chem. Ber.* **1962**, *95*, 692.

[26] (a) Holloway, J. D. L.; Senftleber, F. C.; Geiger, W. E., Jr. *Anal. Chem.* **1978**, *50*, 1010. (b) Holloway, J. D. L.; Bowden, W. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 7089. (c) Holloway, J. D. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2038.

[27] Strelets, V. V. *Coord. Chem. Rev.* **1992**, *114*, 1.

[28] Furlani, C.; Fischer, E. O. *Z. Elektrochem.* **1957**, *61*, 481. The discovery and development of bis(arene)chromium chemistry has been the subject of earlier reviews in this *Journal*. See: Seyferth, D. *Organometallics* **2002**, *21*, 2800.

[29] (a) Furlani, C.; Sartori, G. *Ric. Sci.* **1958**, *28*, 973. (b) Vlček, A. A. *Z. Anorg. Chem.* **1960,** *304*, 109. (c) Korshunov, I. A.; Vertylina, L. N. *Prog. Acad. Sci. USSR, Chem. Sec.* **1958,** *122*, 729.

[30] Vlček, A. A. *Nature* **1956**, *177*, 1043.

[31] Vlček, A. A. In *Proceedings of the 5th International Conference on Coordination Chemistry*; The Chemical Society: London, 1959; p 121 (quoted in ref 3b, p 132).

[32] Dessy, R. E.; Kitching, W.; Chivers, T. *J. Am. Chem. Soc.* **1966**, *88*, 453.

[33] Dessy, R. E.; Kitching, W.; Psarras, T.; Salinger, R.; Chen, A.; Chivers, T. *J. Am. Chem. Soc.* **1966**, *88*, 460.

[34] Dessy, R. E.; Chivers, T.; Kitching, *J. Am. Chem. Soc.* **1966**, *88*, 467.

[35] Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471.

[36] Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

[37] Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117.

[38] Dessy, R. E.; Pohl, P. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

[39] Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5124.

[40] Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5129.

[41] Psarras, T.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 5132.

[42] The potentials given in the Dessy papers are given versus an uncommon reference electrode (silver wire in 10^{-3} M $Ag[ClO_4]$ in dimethoxyethane) for which the potential of ferrocene has not, to our knowledge, been reported. By inspection of several potentials reported in refs 35 and 36 compared to those measured in our own laboratory, I estimate that addition of approximately +0.2 V converts the reported potentials to the ferrocene/ferrocenium reference potential.

[43] Dessy's contacts included Howard Malmstadt (University of Illinois), Chris Enke (Princeton University), and Fred Anson and Bob Osteryoung (Cal Tech).

most, if not all, of the work was carried out at mercury electrodes. Owing to the fact that cathodic processes were the main target of the studies, they were carried out in 1,2-dimethoxyethane (glyme, dielectric constant 7.2), which, along with THF, was well known in organic ESR circles as an excellent solvent for radical anions. The great majority of charged species reported in these papers were, in fact, monoanions or dianions.

In two successive papers,[35,36] a total of 130 transition metal complexes, mostly metal π-complexes, were discussed. The experimental routine consisted of polarography and cyclic voltammetry of the compound, followed by bulk cathodic electrolysis, monitoring of the solution by voltammetry, and finally an attempt at anodic "back-electrolysis" to see if the original compound would be regenerated. The primary goal is therefore seen to be the detection of chemically reversible redox systems. When a "reversible" system was encountered, a sample of the reduced solution was removed for spectral monitoring, especially by ESR spectroscopy in these papers. The massive tables of results in these two papers still make interesting reading, and although they had a "survey" quality to them, they showed unequivocally that one-electron reductions are an expected property of 18-electron organotransition metal compounds. More in-depth studies of the thermodynamic, structural, and electronic aspects of the reductions and the reduction products appeared in other papers in this series. Among them was the finding[37] that reductions of metal−metal bonded systems are often accompanied by cleavage of the M−M bond, giving 18 e^- anionic monomers (eq 1), which may be reoxidized to give back the starting dimer.

$$[FeCp(CO)_2]_2 + 2\, e^- \rightleftharpoons 2\, [FeCp(CO)_2]^- \qquad (1)$$

These monomer/dimer processes were early examples of organotransition metal systems that undergo chemically reversible redox processes consisting of a pair of electrochemically irreversible couples.

[**Parenthetic Aside B.** Description of the "reversibility" of a redox process has to deal with the unfortunate similar designations of couples exhibiting charge transfer that is fast on the experimental time scale as *electrochemically* reversible, and reactions going smoothly back and forth between oxidized and reduced redox products as *chemically* reversible, no matter how fast the individual charge-transfer reactions. It is less confusing when fast charge-transfer reactions are termed Nernstian or quasi-Nernstian processes.

A common misconception is that observation of a fully reversible CV wave, in which the redox process seems to be both Nernstian and chemically reversible, shows that there are no chemical reactions coupled to the electron-transfer process. In fact, what is being demonstrated is that any coupled reaction is, on the voltammetric time scale, either too slow to be observed or *fast and reversible*. Examples of the latter are the rapid loss and gain of protons in organic systems (e.g., quinone/hydroquinone) or ligands in metal complexes. Although fewer organometallic examples are known, we have observed several redox systems that exhibit this phenomenon. Interested readers may refer to: (a) Richards, T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494 (monomer/dimer equilibria), (b) Robben, M. P.; Rieger, P. H.; Geiger, W. E. *J. Am. Chem. Soc.* **1999**, *121*, 367 (terminal-to-bridging carbonyls), and (c) Geiger, W. E.; Camire Ohrneberg, N.; Yeomans, B.; Connelly, N. G.; Emslie, D. J. H. *J. Am. Chem. Soc.* **2003**, *125*, 8680.]

The 1968 and 1969 contributions to this series are also relevant to the early development of organometallic electrochemistry.[44−47] Here Dessy and co-workers examined spectroscopically the reduction products of mono- and dinuclear complexes as well as some metal clusters. Particularly noteworthy is the in-depth treatment of changes in energies and force constants of carbonyl stretching frequencies for different oxidation states of dimetallic complexes.[47] This series concluded with three exceptional papers in the early 1970s, in which the charge and spin distributions of organometallic π-complexes were delineated as a function of redox state. A powerful group of spectral techniques, including NMR, ESR, IR, optical, and Mössbauer spectroscopies, were employed.[48] An overview account of this and previous work appeared in 1972.[48d]

The intense activity of the Dessy group should not obscure the less regular pre-1970 contributions of other groups emanating, for the most part, from central and eastern Europe. This work has been well covered by Morris[3b] and is represented in part by references 49−53.

By ca. 1970, there was a significant rise in activity in this area. For example, Ferguson and Meyer published several papers on the redox processes of iron dimers and iron clusters with a view to delineating the alterations in structure that might be coupled to changes in the redox state.[54] This work generally focused on anodic processes, in contrast to the cathodic emphasis of Dessy's studies. The current/potential curve shown in Figure 3 was one of the first published cyclic voltammograms of an organometallic redox system. Other papers that appeared in the 1960s have been covered by Morris.[3b]

[**Parenthetic Aside C.** Little if any mention of cyclic voltammetry can be found in the European electrochemistry published prior to about 1970. The chemical reversibility of a redox couple was sometimes probed using the Kalousek method, in which a square wave of ca. 25 Hz was superimposed on the polarographic scan (Kalousek, M. *Collect. Czech. Chem. Commun*. **1948**, *13*, 105; Kalousek, M.; Rálek, M. *Collect. Czech. Chem. Commun*. **1954**, *19*, 1099). For a discussion of the Kalousek commutator switch see: Galus, Z. *Fundamentals of Electrochemical Analysis*; Ellis Horwood Limited: Chichester, 1976; pp 425−427. This method was used to great advantage by the Czechs and the Russians.]

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(44) Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 1995.

(45) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001.

(46) Dessy, R. E.; Pohl, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 2005.

(47) Dessy, R. E.; Wieczorek, L. *J. Am. Chem. Soc.* **1969**, *91*, 4963.

(48) (a) Dessy, R. E.; Charkoudian, J. C.; Abeles, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 3947. (b) Dessy, R. E.; Charkoudian, J. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 738. (c) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746. (d) Dessy, R. E.; Bares, L. *Acc. Chem. Res.* **1972**, *5*, 415. One anecdote of this period involves the work of Arnold Rheingold, who was beginning a postdoc with Dessy after receiving his Ph.D. from the University of Maryland in 1970. He was assigned the task of obtaining NMR spectra of diamagnetic charged species being generated electrochemically. Expanding and being strapped for space, the Dessy group appropriated a room that was being used only periodically and moved its 100 MHz NMR spectrometer into it. Arnie Rheingold recorded his spectra in this converted men's room.

(49) Gutmann, V.; Schöber, G. *Monatsh. Chem.* **1957**, *88*, 206.

(50) Vlček, A. A. *Collect. Czech. Chem. Commun.* **1965**, *30*, 952.

(51) Mǎsek, J. *Collect. Czech. Chem. Commun.* **1965**, *30*, 4117.

(52) Denisovich, L. I.; Gubin, S. P.; Chapovski Yu, A.; Ustynok, N. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1968**, 891.

(53) Piazza, G.; Paliani, G. *Z. Phys. Chem. (Frankfurt/Main)* **1970**, *71*, 91.

(54) (a) Ferguson, J. A.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1971**, 623. (b) Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025. (c) Ferguson, J. A.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1971**, 1544. (d) Ferguson, J. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 3409. (e) Meyer, T. J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Interscience: New York, 1975; Vol. 19, pp 1−50.

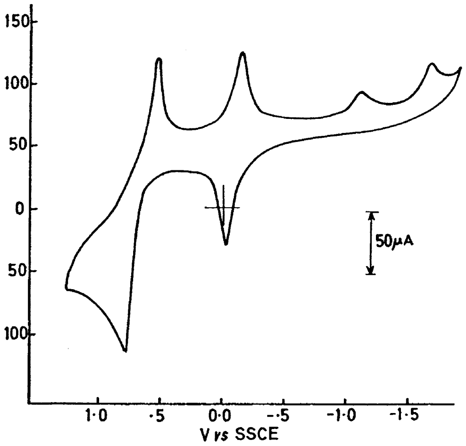

Figure 3. An early publication of a CV scan of an organometallic system, $Fe_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}dppp)$ (dppp = diphenylphosphinopropane) at Pt electrode in $[NBu_4][PF_6]/CH_3CN$. Reprinted with permission from ref 54c.

VII. Parallel Developments

VII.A. Advances in Instrumentation. Fundamental advances in the theory, methodology, and instrumentation of electroanalytical chemistry occurred as a consequence of intense activity starting in the late 1950s, aspects of which is summarized elsewhere.[55−58] Two factors relevant to the organometallic theme combined to allow the more widespread probing of redox processes under the nonaqueous conditions that are more amenable to the chemical properties of organometallic compounds. These were the development of operational-amplifier-based three-electrode potentiostats[56,59] and advances in the application of solid electrodes.[5] The former minimized the resistive errors invariably encountered when working in lower to medium polarity solvents, and the latter took the focus away from the dropping mercury electrode, thereby expanding the positive potential "window" and facilitating the study of anodic reactions.

Accompanying these experimental improvements was the development of new numerical approaches to cyclic voltammetry (CV), which lifted this method from a qualitative (or "visual", see Figure 3) to a quantitative technique. Owing to the complex time-dependent effects of mass transfer and heterogeneous electron transfer on the relative concentrations of Ox and Red in the electrochemical reaction layer, the current/voltage relationship of fast linear scan voltammetry cannot be expressed in an easily solved mathematical equation. Hence, there is no generalized equation for a CV curve as there might be for a spectroscopic absorption peak or even for the plots obtained in other electrochemical techniques such as polarography or chronoamperometry. However, approximate computational methods may be employed, with very acceptable accuracy, to calculate the shapes of CV curves for even complex electron-transfer mechanisms. The ground-breaking paper of Nicholson and Shain,[60] which applied a numerical integration approach to common redox mechanisms (E, EC, ECE, etc.),[61] was greatly instrumental in advancing the quantitative use of fast linear scan and cyclic voltammetry, leading ultimately to the latter becoming the linchpin of modern molecular electrochemistry. The accuracies of present-day finite-difference computational methods (i.e., digital simulations (*vide infra*)) are evaluated on the basis of their level of agreement with the Nicholson−Shain numerical results.

The fact that these advances were taken advantage of outside the school of electrochemical aficionados was due to introduction of commercially available high-performance potentiostats. The archetypes of these multipurpose instruments were marketed by the Princeton Applied Research (PAR) company and provided advanced voltammetric methods such as ac voltammetry and differential pulse voltammetry in addition to CV and bulk electrolysis.[57,62,63]

VII.B. Discovery of Inorganic and Organometallic Electron-Transfer Series. In the early to mid-1960s, a flurry of activity on the characterization of metal dithiolate complexes resulted in the unearthing of transition metal complexes having "noninnocent" ligands, which obscured the true oxidation state of the metal.

Polarography and cyclic voltammetry played an important role in detailing the "electron-transfer series" represented by Figure 4, from which the metal dithiolate complexes, $[MS_4]^{n-}$,[64] might be isolated in two or three different redox states.

The chemical, physical, and spectroscopic investigations that went into classification of these ligands as noninnocent are fascinating in their own right[65] and form the basis of our understanding of the still expanding area of delocalized metal−chelate systems.[66] Relevant to the present review is the

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(55) Bond, A. M. *Modern Polarographic Methods in Analytical Chemistry*; Marcel Dekker, Inc.: New York, 1980; pp 1−5.

(56) Smith, D. E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker Inc.: New York, 1966; Vol. 1, pp 102−110.

(57) Flato, J. B. *Anal. Chem.* **1972**, *44*(11), 75A.

(58) Kissinger, P. T. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; Chapter 6.

(59) (a) Booman, G. L. *Anal. Chem.* **1957**, *29*, 213. (b) DeFord, D. D. American Chemical Society 133rd Meeting, San Francisco, April 1958. (c) Smith, D. E. *Anal. Chem.* **1963**, *35*, 1811. (d) Schwarz, W. M.; Shain, I. *Anal. Chem.* **1963**, *35*, 1770.

(60) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(61) The now widely used lettering system E and C refers to an electron-transfer process as E and a chemical reaction as C. Structural changes that are not concomitant with electron transfer are included in the latter.

(62) Gunasingham, H. In *Electrochemistry, Past and Present*; Stock, J. T., Orna, M. V., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1989; Vol. 390, Chapter 17.

(63) The first commercial potentiostat used in my lab was the PAR 173, to which a waveform generator was interfaced to scan potentials. This unit, purchased in early 1971, is still used in our lab for spectroelectrochemical experiments, having required only the replacement of two switches during its lifetime.

(64) Here the MS_4 drawing is used to symbolize a square-planar complex having two dithiolate ligands. Other stoichiometries were also observed.

(65) Reviews of the early metal dithiolene work may be found in: (a) McCleverty, J. A. In *Progress in Inorganic Chemistry*; Cotton, F. A., Ed.; John Wiley and Sons: New York, 1968; Vol. 10, p 49. (b) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 595. (c) Clemenson, P. I. *Coord. Chem. Rev.* **1990**, *106*, 171. For a more recent paper, including DFT calculations, see: Lim, B. S.; Fomitchev, D. V.; Holm, R. H. *Inorg. Chem.* **2001**, *40*, 4257. See also: Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275. For a review of hybrid organometallic dithiolates (e.g., cyclopentadienyl metal dithiolates) see: Fourmigué, M. *Acc. Chem. Res.* **2004**, *37*, 179.

(66) (a) Lange, C. W.; Pierpont, C. G. *J. Am. Chem. Soc.* **1992**, *114*, 6582. (b) Pierpont, C. G.; Lange, C. W. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; 1994; Vol. 41, p 331. (c) Pierpont, C. G.; Attia, A. S. *Collect. Czech. Chem. Comm.* **2001**, *66*, 33. (d) Andrea, R. R.; de Lange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1988**, *7*, 1100. (e) Hirao, T. *Coord. Chem. Rev.* **2002**, *226*, 81. (f) Ray, K.; Weyhermüller, T.; Goossens, A.; Crajé, M. W. J.; Wieghardt, K. *Inorg. Chem.* **2003**, *42*, 4082. (g) Kaim, W. *J. Chem. Soc., Dalton Trans.* **2003**, 761 (h) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. *Acc. Chem. Res.* **2004**, *37*, 827. (i) Chlopek, K.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2005**, *44*, 7087. (j) Berry, J. F.; Bill, E.; Bothe, E.; Weyermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2005**, *127*, 11550.

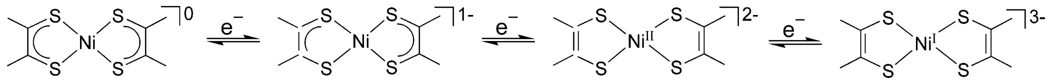

Figure 4. Electron-transfer series for nickel dithiolenes.

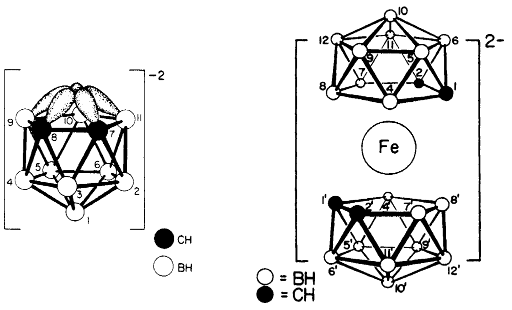

Figure 5. Schematic representation of bonding orbitals in $[C_2B_9H_{11}]^{2-}$ (left) and structure of first reported metallacarborane, the ferrocene-like $[Fe(C_2B_9H_{11})_2]^{2-}$ (right). Reprinted with permission from ref 68.

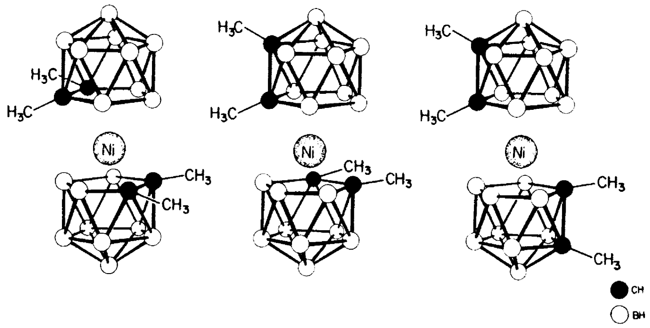

Figure 6. Three observed positional isomers of the monoanion $[Ni(Me_2C_2B_9H_9)_2]^-$. Reprinted with permission from ref 68.

integration of electrochemistry with synthetic transition metal chemistry both by the Gray group at Columbia and by the Harvard group consisting of Davison, Holm, Maki, and Edelstein. The latter used the measured $E_{1/2}$ potentials as guides to redox-based synthesis of metal dithiolates in adjacent oxidation states and developed the useful one-electron oxidant $Ni(S_2C_2(CF_3)_2)_2$ based on their findings.[67]

Very soon after the initial reports of the dithiolene work, Fred Hawthorne's group at the University of California at Riverside reported the preparation of a large number of redox-active metal carborane complexes.[68] Although these compounds, and the ligands used to generate them, may be viewed as modified inorganic borane clusters,[69] the fact that they possess metal–carbon bonds clearly places them in the category of organometallic systems. The fact that coordination occurred between the metal and five (three boron and two carbon) atoms of the open face of the dicarbollide dianion supported a parallel between $[B_9C_2H_{11}]^{2-}$ and $[C_5H_5]^-$ ligands (Figure 5), which was supported by the preparation of analogous sandwich- and half-sandwich-type complexes.[68] The first report[70] of a metal–dicarbollide compound in 1965 included, perhaps not surprisingly, the Fe(II) analogue of ferrocene, $[Fe(1,2\text{-}B_9C_2H_{11})_2]^{2-}$ (Figure 5). Its one-electron oxidation potential of −0.42 V vs SCE in acetone/H_2O/Li[ClO_4] gave the first indication of the now well-established fact that the dicarbollide ligand stabilizes metals in higher oxidation states. This communication was followed by systematic electrochemical characterization of comprehensive sets of transition metal dicarbollides in the late 1960s and early 1970s,[68,71] with $E_{1/2}$ shifts of −0.4 to −0.5 V being generally observed for a metal dicarbollide analogue of a metallocene.[71] It is interesting to note that Hawthorne's group employed a potentiostat of quite modern design, based on the DeFord operational amplifier model.[59b] This must have been one of the first applications of DeFord-type potentiostats (see Section VII.A) by groups not specializing in electrochemistry.

The metallocarborane sandwich complexes generally underwent reversible redox reactions. The most extensive electron-transfer series was observed for Ni derivatives, eq 2, with some of these derivatives being isolated in three different redox

$$Ni(C_2B_9H_{10}R)_2 \underset{}{\overset{+e^-}{\rightleftharpoons}} [Ni(C_2B_9H_{10}R)_2]^- \overset{+e^-}{\rightleftharpoons} [Ni(C_2B_9H_{10}R)_2]^{2-} \overset{+e^-}{\rightleftharpoons} [Ni(C_2B_9H_{10}R)_2]^{3-} \quad (2)$$

states, comprising nominally 18 e⁻ to 20 e⁻ metal centers, the latter, of course, being the dianionic analogue of nickelocene. The further one-electron reduction to the corresponding (not isolated) trianion shown in eq 2 was observed in later CV scans[72] conducted at more negative potentials, therein confirming a four-membered electron-transfer series equivalent to that observed for nickel dithiolene systems (Figure 4).

I wish to mention one specific Hawthorne group paper that was particularly impressive in its degree of electrochemical sophistication. Graduate student Les Warren had observed thermal isomerizations for several nickel and palladium complexes in which one or two CMe groups exchanged position with the same number of BH groups in the more distant pentagonal face (see Figure 6).[73] By investigating the CV behavior of these compounds, the rates of these isomerization processes were shown to depend on the metal oxidation state. Consider Figure 7, which shows the CV curves of *pure* samples of neutral isomer **B** (top) and the monoanion **A**⁻ (bottom) in acetonitrile/[NEt_4][ClO_4].[74]

Note that the "benign" potential, i.e., the potential of zero current, is in between the two reversible waves for isomer **A**, so that the positive-going scan from about −0.1 V records the oxidation of **A**⁻ to **A**. Only after that oxidation occurs at ca. +0.6 V does the wave for isomer **B** appear at ca. +0.3 V. This demonstrates that the oxidation of **A**⁻ obeys an EC mechanism

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(67) Davison, A.; Holm, R. H. in Meutterties, E. L., Ed.; *Inorganic Synthesis*; McGraw-Hill: New York, 1967; Vol. 10, pp 8–26.

(68) For a review of this early metal carborane work see: Callahan, K. P.; Hawthorne, M. F. *Adv. Organomet. Chem.* **1976**, *14*, 145.

(69) O'Neill, M. E.; Wade, K. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 1.

(70) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818.

(71) A 1982 review of the electrochemistry of metalloboranes and -carboranes contained exhaustive coverage of the Hawthorne group results to that date. See: Geiger, W. E. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982; Chapter 6.

(72) Geiger, W. E.; Smith, D. E. *J. Chem. Soc., Chem. Commun.* **1971**, 8. Hawthorne's group supplied the metal dicarbollides studied in this work. For a report of their electron-transfer kinetics see: Geiger, W. E.; Smith, D. E. *J. Electroanal. Chem.* **1974**, *50*, 31.

(73) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 1157.

(74) Paxson, T. E.; Kaloustian, M. K.; Tom, G. M.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 4882. Note that the systems studied in this paper were a modification of the parent system in that the two CMe groups shown in Figure 6 are replaced by a bridging trimethylene group.

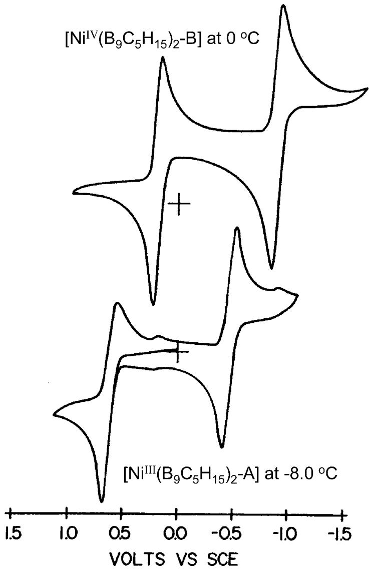

Figure 7. CV curves of neutral isomer B (top) and anion of isomer A (bottom) of nickel dicarbollides in $CH_3CN/[NEt_4[ClO_4]$(top), scan rate 0.1 V s^{-1}, See text for details. Reprinted with permission from ref 74.

in which electron transfer is followed by an isomerization process (eqs 3a and 3b):

$$[\mathbf{A}\text{-Ni(dicarbollide)}_2]^- - e^- \rightleftharpoons \mathbf{A}\text{-Ni(dicarbollide)}_2 \qquad \text{E} \quad (3a)$$

$$\mathbf{A}\text{- Ni(dicarbollide)}_2 \rightleftharpoons \mathbf{B}\text{-Ni(dicarbollide)}_2 \qquad \text{C} \quad (3b)$$

The fact that the isomerization process is detected so easily by cyclic voltammetry supports the notion of CV being the "spectroscopy of electrochemistry". There are obvious limitations to this concept, but in this case one obtains a rapid and semiquantitative analysis of the oxidation products. Curve fitting through digital simulations would probably be used nowadays to obtain the isomerization rate constant, but Paxson et al. employed reversal chronopotentiometry for this purpose, finding a half-life of 2.7 s at 288 K for isomer **A** of the neutral Ni(dicarbollide)$_2$.[74] This is one of the earliest examples, perhaps the first electrochemically quantified example, of an electron-transfer-induced organometallic "square scheme" (see Section X).

[**Parenthetic Aside D.** It is important to keep in mind that voltammetric methods alter the composition of the analyte solution (close to the electrode, in the reaction layer) during the scan. Cyclic voltammetry is therefore detecting both the electroactive compounds diffusing in from the bulk of solution *and* the electron-transfer products before they are "lost" by diffusion away from the reaction layer. Such chemical perturbations of analytes are less commonly encountered in spectroscopic analytical techniques.]

VII.C. Combining Electrochemistry with Targeted Chemical Redox Agents. We turn now to one of the most powerful strategies for exploiting organometallic redox chemistry for synthetic purposes, namely, the combination of electrochemical methods with chemical redox agents. To be sure, there are many examples in which the two different synthetic approaches are used independently. A strictly electrochemical approach would involve general characterization of the analyte couple by voltammetry, followed by bulk electrolysis at a larger electrode, as employed by Page and Wilkinson[10c] as well as by the Dessy group.[32−41,44−48] In those cases, however, it was *in situ*, rather than isolated, electrode products that were characterized by electrochemistry and spectroscopy. A number of issues arise when using a strictly electrochemical approach for the *isolation* of electrode products, including the length of the electrolysis time (typically 15−30 min)[75] and the removal of product from an excess of supporting electrolyte. These and other factors have been discussed in detail elsewhere,[76] the net effect of which is that actual isolation of electrolysis products is not widely encountered in the organometallic literature.[77]

An integrated electrochemical/chemical approach combines the analytical strengths of electrochemistry with the synthetic utility of chemical redox agents. Typically, voltammetry is first employed to quantify the potentials of oxidations or reductions of a test compound and to estimate the lifetime(s) of its primary redox product(s). Isolation of the desired product is then achieved through a chemical redox reaction involving the test compound and an appropriate oxidant or reductant, in the absence of supporting electrolyte [for Nernstian systems, 99% completion of a one-electron oxidation process requires that the $E_{1/2}$ of the oxidant (at room temperature) be 0.118 V positive of that of the test compound; 0.118 V negative for a reduction].

As alluded to in Section VII.B, an integrated redox approach was used effectively for the preparation of metal dithiolenes in different redox states,[64] and Davison and Holm summarized the most easily accessible oxidation states of redox pairs based on their polarographic potentials.[67] For example, complexes with $E_{1/2}$ values less than about 0 V vs FcH [78] could be oxidized by iodine, but those with potentials negative of about −0.4 V vs FcH were readily oxidized in solution by air. The oxidizing powers of a family of metal dithiolene complexes were ranked, and the strongest oxidants, either $Ni(S_2C_2(CF_3)_2)_2$ among square-planar complexes or trigonal-prismatic $Mo(S_2C_2(CF_3)_2)_3$ among six-coordinate complexes, were subsequently used as one-electron oxidants of other members in the series. The Ni complex, which is reduced to its monoanion at $E_{1/2} = 0.33$ V, has proven to be a useful oxidant for a number of organometallic systems.[76] Although the options for electron-transfer reagents were limited when the Harvard group summarized their findings, their work established the utility of the combined approach to synthetic redox chemistry.

The more systematic development of the electrochemical/chemical blend began with Neil Connelly's postdoctoral work. After finishing his Ph.D. in 1969 at Sheffield University, where he studied the synthesis and voltammetry of metal dithiolenes

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(75) The time required for virtually complete (>99%) bulk electrolysis is a function of diffusion coefficient of the analyte at a given temperature, physical aspects of the electrolysis cell (especially the ratio of working electrode area to solution volume), and mechanical aspects of mass transfer such as stirring efficiency. For an excellent treatment of these and other experimental factors see: Bard, A. J.; Santhanam, K. S. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1970; Vol. 4, pp 215 ff.

(76) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(77) The same cannot be said for the organic literature, which has a long history of using bulk electrolysis for synthetic-level preparations. Whereas the discrepancy in development of these two subdisciplines is due to a number of factors, it is worth noting that a high percentage of isolated organic electrolysis products are uncharged, making them easy to separate from the supporting electrolyte. For comprehensive treatments of organic electrochemistry see: (a) Steckhan, E., ed. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1987; Vol. 142. (b) Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed.; Wiley: New York, 1989. (c) Lund, H.; Hammerich, O. *Organic Electrochemistry*, 4th ed.; Marcel Dekker: New York, 2001. (d) Shono, T. *Electroorganic Synthesis*; Academic Press: London, 1991. (e) Schäfer, H. J. In *Encyclopedia of Electrochemistry*; Bard, A. J., Stratmann, M., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 8.

(78) To convert to the ferrocene reference potential, 0.4 V has been subtracted from the potentials vs SCE reported in ref 67.

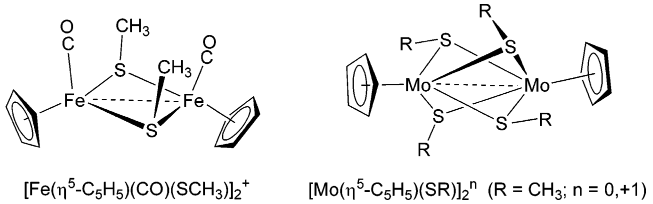

Figure 8. Dinuclear species characterized structurally by Connelly and Dahl as both neutral species and monocations. Adapted from ref 79.

under Jon McCleverty, Connelly took a position in Lawrence Dahl's group at the University of Wisconsin. Dahl, who was in the midst of his fascinating work on dimetallic and cluster organometallic compounds, was particularly interested in the relationship between molecular structure and the number of valence electrons in these systems. On the basis of Dessy's publications, he had every reason to expect that a number of his compounds and clusters would form one- or two-electron redox pairs that would be at least persistent in solution. He and Connelly set out to extend the idea of stable redox pairs to synthetic and structural studies, and they made several attempts to isolate crystallographic quality crystals of cations derived from the one-electron oxidation of sulfido-bridged dimers. They were able to achieve this with $[Mo_2Cp_2(\mu\text{-SMe})_4]^+$ and $[Fe_2Cp_2(\mu\text{-SMe})_2(\mu\text{-CO})_2]^+$ by oxidation of the neutral compounds with Ag[X] (X = PF_6 or BF_4).[79] X-ray crystal analysis showed that the diiron redox pair experienced a decrease of over 0.47 Å in the Fe−Fe distance on going from the neutral compound to the monocation, whereas the Mo−Mo distance was essentially unaffected by the charge of the dimolybdenum redox pair (Figure 8).

Perhaps ironically, $E_{1/2}$ data were not obtained on these compounds, and the redox agents (including $Na[BH_4]$ for the back reduction of the cation) were chosen the old-fashioned, semiempirical, way. That point aside, besides being an important early contribution to the question of how metal complexes adjust structurally to changes in electron count, these studies were central in focusing Connelly's interest in melding the electrochemical approach of Dessy with the chemical redox synthetic approach of Dahl. Others, including Tom Meyer, were also seeing these benefits, and in a 1972 paper he and Ferguson described[54d] their approach as "combining electrochemical methods with chemical studies".

Over the next decade, however, Connelly (Figure 9) became the principal developer of the combined electrochemical/chemical approach to organometallic redox chemistry that has become standard practice. Here we make mention of two early contributions. In one, cyclic voltammetry was combined with magnetic resonance to show that the reaction of $Cr(\eta^6\text{-}C_6Me_6)(CO)_2(alkyne)$ with $[NO]^+$ gave the simple 17-electron cation $[Cr(\eta^6\text{-}C_6Me_6)(CO)_2(alkyne)]^+$ rather than the expected nitrosyl complex (Figure 10).[80,81] Connelly later noted one somewhat disappointing aspect involving the early examples of isolated 17-electron cations, namely, that they did not show the expected increase in reactivity toward nucleophiles or radicals.[81] The first significant increases in reactivity encountered in Connelly's studies were for 17-electron cations of the five-coordinate iron carbonyl complexes $[Fe(CO)_3(PPh_3)_2]^+$ with halides.[82] As shown in Section XI, however, dramatic increases in the reactivity of radical cations compared to their 18-electron counterparts were eventually to become a general theme in organometallic anodic chemistry.

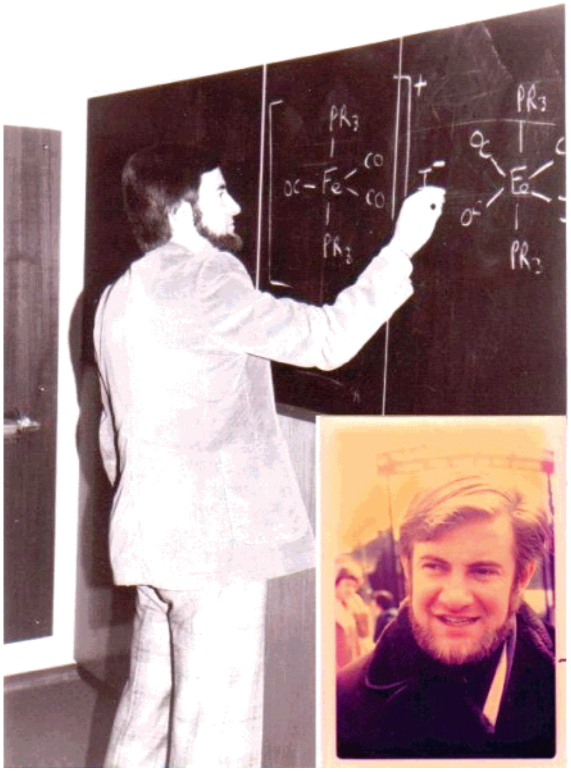

Figure 9. Neil Connelly in early 1970s. Photos courtesy of A. Connelly.

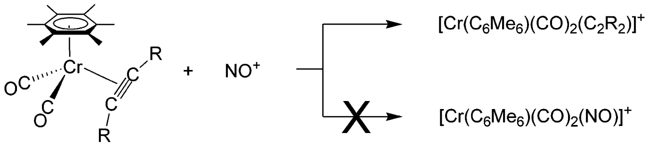

Figure 10. Surprising result obtained for reaction of $Cr(C_6Me_6)(CO)_2(\eta^2\text{-alkyne})$ with $[NO]^+$, as reported in ref 80.

[**Parenthetic Aside E.** Schrock and co-workers have made excellent use of organometallic redox agents in their impressive recent studies on the reduction of dinitrogen using molybdenum catalysts. Several steps in the overall, closely spaced, six-electron, six-proton process were induced by finely tuned reducing agents such as $Co(C_5R_5)_2$ (R = H, $E_{1/2} = -1.33$ V; R = Me, $E_{1/2} = -1.84$ V) and $Cr(C_5Me_5)_2$ ($E_{1/2} = -1.47$ V). See: (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76; (b) Ritleng, V.; Yandulov, D. V.; Weare, W. W.; Schrock, R. R.; Hock, A. S.; Davis, W. M. *J. Am. Chem. Soc.* **2004**, *126*, 6150; (c) Schrock, R. R. *Acc. Chem. Res.* **2005**, *38*, 955.]

VIII. Personal Evolution

My own interests in organometallic electrochemistry arose rather indirectly from my academic experiences. After doing organic polarography under Raymond Annino during my B.S.

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[79] (a) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7470. (b) Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7472.

[80] Connelly, N. G.; Johnson, G. A. *J. Organomet. Chem.* **1974**, *77*, 341.

[81] Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153.

[82] (a) Baker, P. K.; Connelly, N. G.; Jones, B. M. R.; Maher, J. P.; Somers, K. R. *J. Chem. Soc., Dalton Trans.* **1980**, 579. (b) Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1982**, 471.

degree at Canisius College in Buffalo, NY, I joined the group of David Geske (1931−1967) at Cornell University for Ph.D. studies in 1965. Although Geske's Ph.D. training had been in electrochemistry, his group was then almost exclusively engaged in ESR studies of organic radical ions. Although the projects assigned to me, involving ^{17}O-labeling of nitrobenzene and semiquinone anion radicals, yielded worthwhile results,[83] I was becoming interested in transition metal complexes and had noted the papers coming out of the Dessy group. Geske gave me permission to introduce projects in organometallic electrochemistry and ESR spectroscopy into my graduate research, but the tragic death of this talented and generous young scientist in December 1967 necessitated a change of plans. The final year of my graduate studies was spent at the University of California (Riverside) working with August (Gus) Maki, who had been both friend and collaborator with Geske and who graciously offered to have me in his group while I was finishing up my degree requirements from Cornell. Maki's group was involved in its last ESR studies of metal dithiolene systems, and Hawthorne's group, which was soon to move to UCLA, was doing its seminal work on metal dicarbollide electron-transfer series (Section VII.B). Interactions with these two groups furthered my interest in metal-based redox chemistry, and I sought a postdoctoral position specifically to investigate organometallic systems. One of the electrochemists recommended to me by Donald Sawyer, then Chair of the Chemistry Department at Riverside, was Donald Smith at Northwestern University. Smith had developed the area of ac polarography[56] and, in collaboration with Donald DeFord (see Section VII.A), was responsible for the design of state-of-the-art potentiostats. It turned out that Smith and A. Louis Allred, an organometallic chemist at Northwestern, had been talking about a joint project, but had not been able to get a student interested in it. Together, they supported my postdoctoral position through the troubling[84] 1969−1970 academic year.

Ac polarography was the optimum method for the measurement of fast heterogeneous electron-transfer processes. One of Smith's students, Barry Huebert, was measuring such rate constants for the reduction of cyclooctatetraene (COT), a system that has intrigued chemists on the basis that this molecule changes its structure from tub-like to planar when reduced to the dianion.[85] Heubert's determination of charge-transfer rates for the COT$^{0/1-}$ and COT$^{1-/2-}$ processes confirmed that the major structural change occurred in the first redox step, leading to the model shown in Figure 11. I was intrigued by the fact that, at least in this case, electrochemistry could be used to gain information about molecular structural changes, and it is no accident that my first results in organometallic redox-induced structural changes involved metal−COT complexes. In retrospect, it was a bit naïve to think about expanding this approach, particularly the kinetic aspects, to a large number of systems. However, the basic theme of the relationship between organometallic structures and redox states became a central factor in my research interests for a considerable period after the mid-1970s.

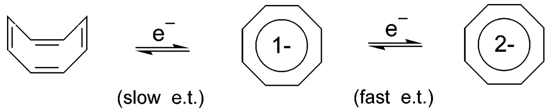

Figure 11. Idealized structures of cyclooctatetraene and its anions.

[**Parenthetic Aside F.** I met Neil Connelly at a meeting of the "Organic Electrochemistry" section of the Electrochemical Society in Philadelphia (1977), which was organized by James White and Manuel Baizer of the Monsanto Company. We began a collaboration aided, in subsequent years, by each of us being able to spend a sabbatical leave period in the other's laboratory in Vermont or Bristol. Our review of chemical redox agents (*Chem. Rev.* **1996**, *96*, 877) had its origin in notes taken over the years by Connelly.]

IX. Second-Generation Electrochemistry of Metallocenes

The graduate students joining my group at the time of my first faculty appointment[86] chose to work on extensions of metal dithiolene redox chemistry. My own experimental time was largely devoted to building fast-scan instrumentation and vacuum electrochemical cells, but some progress was made on our first organometallic studies. It was surprising to find an essentially Nernstian one-electron *reduction* of cobaltocene to the corresponding anion, [CoCp$_2$]$^-$. Although this anion is isoelectronic with nickelocene, metallocene anions were unknown at the time.[87−89] We and others[89−91] went on to show that anions could, in fact, be observed by voltammetry for a number of metallocenes, although their very negative potentials and high degree of air sensitivity have kept them from being of synthetic importance.

We also noted that reliable one-electron potentials had not been measured for a number of other metallocenes that had been synthesized over two decades earlier and that were known to undergo facile chemical oxidations. Chromocene and vana-

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(83) (a) Gulick, W. M., Jr.; Geiger, W. E.; Geske, D. H. *J. Am. Chem. Soc.* **1968**, *90*, 4218. (b) Geiger, W. E.; Gulick, W. M., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 4657.

(84) In the spring of this tumultuous academic year, protests against the Vietnam war reached their apex at American colleges and universities. Owing to campus and political pressures, support of fundamental academic research by defense agencies, which included Allred's grant funding my work on organogermanium radical ions, disappeared almost overnight. As I recall, the chemistry building at Northwestern was closed for some days in response to those same pressures. The chemistry students and faculty expressed themselves through speeches and arguments on the steps of the building regarding less the war than the ethics of militarily funded fundamental academic research. Northwestern was just one of many universities that were severely affected. The Kent State shootings occurred on May 4, 1970.

(85) Huebert, B. J.; Smith, D. E. *J. Electroanal. Chem.* **1971**, *31*, 333. For later work on the reduction of cyclooctatetraene see: Petersen, R. A.; Evans, D. H. *J. Electroanal. Chem.* **1987**, *222*, 129.

(86) Before moving to the University of Vermont in 1974, I held an Assistant Professor position at Southern Illinois University at Carbondale. The *tri*anions shown in Figure 4 were based on our metal dithiolene work. See: (a) Mines, T. E.; Geiger, W. E. *Inorg. Chem.* **1973**, *12*, 1189. (b) Senftleber, F. C.; Geiger, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 5018. Harry Gray once mentioned to me that after seeing the Mines paper he pulled out old voltammograms of [Ni(S$_4$C$_4$(CN)$_4$]$^{2-}$ recorded at Columbia and noted that, indeed, there was a one-electron reduction wave close to cathodic electrolyte breakdown that had not been reported in their papers. Besides simply extending the metal dithiolene electron-transfer series, the Mines and Senftleber results established that more traditional *metal-localized* redox processes were also possible in these systems once the ligand orbitals that had given rise to their noninnocence had been filled. These papers described genuine Ni(I) complexes.

(87) Geiger, W. E. *J. Am. Chem. Soc.* **1974**, *96*, 2632.

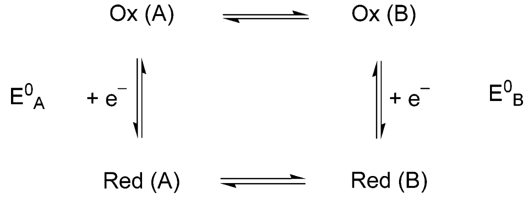
(88) Although we presented work on the kinetics and mechanism of the reduction of CoCp$_2$ at an international symposium in 1973 (see *VI International Conference in Organometallic Chemistry, Proceedings*; 1973; p 250), a manuscript was not submitted for reviewers' comments until after we had identified the conditions (vacuum electrolysis, weak acceptor solvent) under which the very nucleophilic and air-sensitive anion [CoCp$_2$]$^-$ was persistent. The first publication of a reversible CV for [CoCp$_2$]$^{0/1-}$ in a refereed journal was authored by El Murr et al.[89]

(89) El Murr, N.; Dabard, R.; Laviron, E. *J. Organomet. Chem.* **1973**, *47*, C13.

(90) Holloway, J. D. L.; Bowden, W. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 7089.

(91) For a review of activity in this area see: Strelets, V. V. *Coord. Chem. Rev.* **1992**, *114*, 1.

Scheme 1



docene, which were commercially available, became our targets. Owing to the pyrophoric nature of these compounds, we constructed rather elaborate vacuum electrochemical cells for their study.[92] Although these cells permitted the use of all the standard electrochemical methods, even including dc polarography, under technically rigorous conditions, the vacuum approach was eventually abandoned in our lab in favor of more practical drybox methods.

X. Redox-Induced Structural Changes

An important contribution of organometallic electrochemistry has been to deepen our understanding of the specific ways in which electron-transfer processes affect the structures (and often, thereby, the reactivities) of these compounds. Structural change is intrinsic to molecular charge-transfer processes owing to the effects of altering the occupancies of the molecular orbitals. Most of these structural changes are quite modest. The ferrocene/ferrocenium redox pair, for example, undergoes only a slight enlargement of the sandwich profile as the iron-to-center-Cp distance increases in the oxidized form.[93] Systems like this, in which the structural change is concerted with electron transfer, are designated as obeying a simple E mechanism, and their charge-transfer kinetic properties are largely accounted for by Marcus theory.[94,95] By the mid-1970s, knowledge about the precise structures of organometallic redox pairs was growing thanks to the efforts already discussed, and many of the results of this period were summarized in a later review.[81] For the most part, the observed structural changes, even those involving significant shortening and elongation of metal−metal bonds, did not require large inner-sphere reorganizational energies,[95] so that these systems usually had the Nernstian or quasi-Nernstian voltammetric behavior associated with fast charge-transfer processes. The fact that metallocenes generally exhibit such behavior[96] is at the heart of many applications involving their redox chemistry (*vide infra*).

A fundamentally different type of charge-transfer mechanism is that in which the structural change *follows* electron transfer (the so-called two-step EC process). Chemically reversible EC processes require two steps in each direction, so that the overall process is described as a square scheme (Scheme 1). The one-step E mechanism, having a concerted e.t. and structural change, essentially follows the diagonal of the square scheme. Square schemes had received theoretical attention and were becoming known for organic systems by the mid-1970s.[97,98] We thought it likely that most of the structural changes we were seeking to explore, in which redox pairs would be intuitively recognized as separate geometric or electronic *isomers*, would follow square-scheme behavior. That this proved to be the case will be shown in some of the following examples, but it is informative to first make note of the bis(hexamethylbenzene)-ruthenium system, which helped focus our attention on metal−polyolefin complexes.

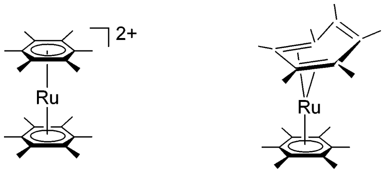


Figure 12. Different arene hapticities in the two redox states of bis(hexamethybenzene)ruthenium isolated by Elschenbroich and Fischer (ref 99).

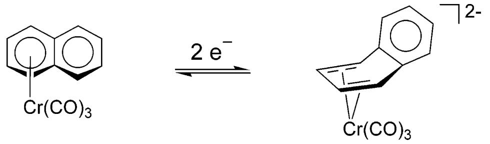


Figure 13. Change in naphthalene hapticity in the two-electron reduction of Cr(naphthalene)$(CO)_3$ (ref 100).

Fischer and Elschenbroich had isolated a neutral compound following the chemical reduction of $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$.[99a] On the basis of its fluxional ^{1}H NMR behavior, the authors boldly proposed the 18-electron structure $Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)$ (Figure 12), which was later confirmed by X-ray crystallography.[99b] The net two-electron process was therefore shown to involve an η^6/η^4 change in arene hapticity, achieved by bending of one pair of arene carbons away from the metal center. This was the first example of a structurally characterized organometallic redox pair differing in ligand hapticity. Shortly thereafter, Rieke et al. postulated that η^6 to η^4 slippage occurred in the two-electron electrochemical reduction of $Cr(CO)_3$-(naphthalene)[100] (Figure 13). Although these two important contributions affirmed the utility of the formal metal “electron count” being a predictor of metal−ligand hapticity, they only addressed processes involving the gain and loss of *two* electrons. The one-electron intermediate had not been characterized for either system, and in fact, there was no published evidence for structural interconversions in *one-electron* processes for any transition metal polyolefin complex. Owing to the more general and fundamentally important nature of one-electron transfers, we sought polyolefin complexes that would allow systematic studies along these lines. As it turned out, we were eventually able to show that the one-electron intermediate in the Ru system very likely retains its η^6-hapticity (*vide infra*, Section X.C), but that investigation was sometime in the future.

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(92) Holloway, J. D. L.; Senftleber, F. C.; Geiger, W. E. *Anal. Chem.* **1978**, *50*, 1010.

(93) Johnson, M. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, p 479.

(94) Marcus, R. A.; Eyring, H. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(95) Hale, J. M. In *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971; pp 229 ff.

(96) Reliable values for the heterogeneous charge-transfer rates of metallocenes were first obtained by ac polarography. The first broad study of heterogeneous e.t. rates of metal sandwich systems was done in the late Michael Weaver’s lab at Purdue. See: (a) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213. (b) Gennett, T.; Weaver, M. J. *J. Electroanal. Chem.* **1985**, *186*, 179.

(97) (a) Laviron, E.; Roullier, L. *J. Electroanal. Chem.* **1985**, *186*, 1, and references therein. (b) Evans, D. H.; O’Connell, K. M. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1988; Vol. 14, pp 113 ff, (c) Rieger, P. H. *Electrochemistry* 2nd ed.;, Chapman and Hall: New York, 1994; p 264.

(98) Geiger, W. E. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1985; Vol. 33, pp 275−352.

(99) (a) Fischer, E. O.; Elschenbroich, Ch. *Chem. Ber.* **1970**, *103*, 162. (b) Huttner, G.; Lange, S. *Acta Crystallogr.* **1972**, *B28*, 2049. A later NMR study determined the activation barrier of the fluxional process: Darensbourg, M. Y.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *100*, 7425.

(100) (a) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R., Jr.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951. (b) See also: Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420. In this work, the arene hapticity change was postulated to occur at the one-electron stage, but the experimental evidence was ambiguous.

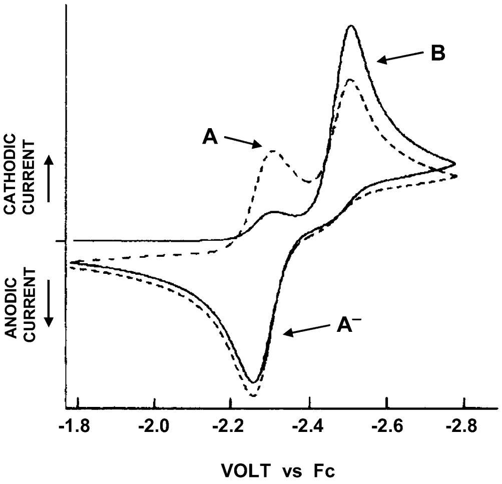


Figure 14. Two successive CV scans of an isomeric mixture of CoCp(η^4-1,3-COT) (minor isomer A) and CoCp(η^4-1,5-COT) (major isomer B) at $\nu = 100$ V s^{-1}. The dashed line is the second scan, recorded without pause. Reprinted from ref 113a.

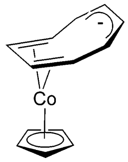
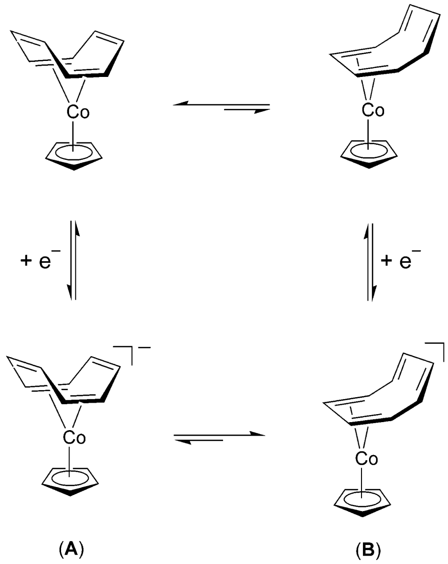


Figure 15. Idealized electronic structure of the anion of the "18 + δ" radical anion, [CoCp(η^4-1,3-COT)]$^-$, reprinted from ref 113a.

Scheme 2



X.A. Metal−Cyclooctatetraene Complexes. The ligand chosen to center our probe was cyclooctatetraene, which was known to exhibit a fascinating range of bonding modes to transition metals.[101] Electrochemical studies on metal−COT complexes were limited to reports on Fe(CO)$_3$(η^4-COT), which did not address the structure of the nominally 19-electron monoanion [Fe(CO)$_3$(η^4-COT)]$^-$.[35,102] We first looked at the more sandwich-like analogue CoCp(COT). The CV of this system had a dominant, chemically irreversible, cathodic wave ($E_{pc} = -2.63$ V in THF, peak B in Figure 14), which was preceded by the puzzling mini-"prewave" A ($E_{pc} = -2.34$ V). We first considered the possibility that the compound might be partially dissociated in solution and involved in an equilibrium with free COT, which has a reduction potential close to that of the prewave.[103] This was not supported, however, by the characteristics of this compound reported in three different synthetic papers,[104−106] all of which identified it as being stable in solution and having the structure CoCp(η^4-1,5-COT), **A** in Scheme 2). Careful investigation of the ^{1}H NMR spectrum[107] revealed the minor isomer CoCp(η^4-1,3-COT), **B** in Scheme 2. This isomer, in which the cyclooctatetraene ring is bonded to the metal in a butadiene-like manner, turned out to be responsible for the cathodic prewave. Owing to the fact that three of the four possible square-scheme members were detectable by voltammetry, namely, **A**, **B**, and **A**$^-$, the reduction of CoCp(COT) was shown[109] to follow Scheme 2, in which the thermodynamically favored isomers possess the tub-like 1,5-COT structure in the 18-electron complex and the lawnchair-like 1,3-COT structure in the 19-electron complex. The preference for the latter in the reduced complex was explained by EHMO calculations[110] and ESR data,[111] which showed that the SOMO of the anion was made up of about one-third Co d$_{xy}$ and two-thirds COT character, with the majority of the ligand contribution being from the four *uncomplexed* carbons of the eight-membered ring (Figure 15). In terms of a simple bonding model, the η^4-hapticity of the COT ring is unaltered by electron transfer, but the tub-to-chair isomerization essentially relieves the metal of its excess electron density. This was the first finding of the redox-controlled geometric isomerization of a metal−polyolefin bond and was the origin of a number of papers on the general subject of metal−COT reductions.[109−112]

[**Parenthetic Aside G.** Although 19-electron compounds and ions are very often subject to facile reoxidation processes and radical reactions, they are not predisposed to instability any more than organic radical anions might be said to be. Indeed, in terms

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[101] See: Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: London, 1979; Chapter II.

[102] El Murr, N.; Riveccié, M.; Laviron, E.; Deganello, G. *Tetrahedron Lett.* **1976**, 3339. This paper confirmed the earlier Dessy result that Fe(CO)$_3$(η^4-COT) undergoes two successive one-electron reductions. The authors also showed that addition of trimethylammonium ion resulted in rapid protonation of the dianion. The cyclooctra*triene* complex Fe(CO)$_3$(η^4-C$_8$H$_{10}$) was then synthesized by reduction of Fe(CO)$_3$(η^4-COT) with potassium, followed by addition of water. The CV curves for this system were not published in the original paper, but appeared later in ref 101, p 223.

[103] We also considered the possible presence of an impurity, especially because we were not very confident in our synthetic abilities at the time. Proper Schlenck techniques were not introduced into our lab until after my sabbatical leave in Richard Schrock's group at MIT in 1979.

[104] (a) Fritz, H. P.; Keller, H. *Z. Naturforch.* **1961**, *16B*, 348. (b) Fritz, H. P.; Keller, H. *Chem. Ber.* **1962**, *95*, 158.

[105] Nakamura, A.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 425.

[106] Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1966**, *5*, 2059.

[107] Although the singlets of the chair isomer at $\delta = 5.1$ (fluxional COT ring) and 4.7 (Cp) were easily visible even in the old 60 MHz instruments, their presence was not discussed in the literature. Even the temperature-dependent NMR study of ref 106 did not identify the 1,3-isomer. After the publication of our communication on this system, the author received several notes from individuals who had worked on CoCp(COT) and had wondered what the "persistent impurity" was. We had the advantage of seeing from CV scans that the minor (ca 20%) and major species in solution gave electrochemically identical monoanions.

[108] Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 3407.

[109] Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779.

[110] Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787.

[111] The definitive analysis of the ESR data was done by Phil Rieger and published as part of a larger paper on the reductions of cobalt and nickel-group-COT complexes: Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314.

[112] Geiger, W. E.; Gennett, T.; Grzeszczuk, M.; Lane, G. A.; Moraczewski, J.; Salzer, A.; Smith, D. E. *J. Am. Chem. Soc.* **1988**, *108*, 7454.

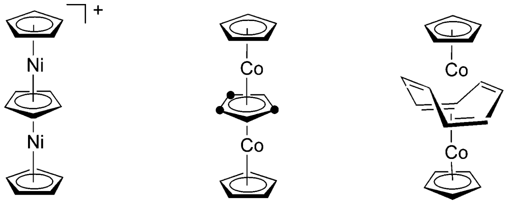

Figure 16. "Triple-decker"-type complexes having, left to right, 34 valence electrons (VE) $[Ni_2Cp_3]^+$ (Salzer, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 930), 30 VE $Co_2Cp_2(C_2B_3H_5)$ (• = BH) (Beer, D. C.; Miller, V. R.; Sneddon, L.; Miller, V. R.; Palenik, G. *J. Am. Chem. Soc.* **1973**, *95*, 3046), and 36 VE $Co_2Cp_2(C_8H_8)$ (see ref 104).

of sandwich compounds, the 19 e^- system of Astruc, $Fe(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6R_6)$, is to electron-rich organometallics what the 17 e^- ferrocenium ion is to electron-deficient organometallics (Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377). Electronic delocalization in 19-electron metal π-complexes plays an important role in lessening the need for gross structural changes in such relatively electron-rich systems.[113] For more on electron-rich systems, see Aside I.]

The geometric and electronic flexibility of COT was also a factor in encouraging an inquiry into the redox properties of *di*nuclear cyclooctatetraene complexes. During this period we were strongly influenced by the theoretical papers on metal−polyolefin bonding reported by Roald Hoffmann and his colleagues.[114] Inspection of a compound's HOMO and LUMO orbitals allowed conjecture on how loss or gain of electrons, respectively, might affect its structure. In a paper on "triple-decker" sandwich compounds, for instance, it was shown that the total valence electron count for triple deckers such as $[Ni_2Cp_3]^+$ and $Co_2Cp_2(\mu\text{-}C_2B_3H_5)$ (Figure 16) should not exceed 34.[114a] Since the bis(cobalt cyclopentadienyl)COT complex, $Co_2Cp_2(\mu^4;\mu^4\text{-}C_8H_8)$ (Figure 16), was called a "near-miss" 36 e^- triple decker, it seemed logical that its two-electron oxidation might yield a true triple decker having a flat C_8H_8 ring between the two metals. We were encouraged by observation of a chemically reversible *two*-electron anodic process for this system, which implied a significant structural change for the 34 e^- system.[115] However, this dication defied our attempts at its isolation. We were subsequently able to obtain NMR spectra of the more stable Cp* analogue $[Co_2Cp^*_2(\mu;\mu\text{-}C_8H_8)]^{2+}$ and eventually obtained crystals of the dirhodium congener $[Rh_2Cp_2(\mu;\mu\text{-}C_8H_8)]^{2+}$. These 34 e^- dications were thereby shown to be members of a "slipped" pseudo-triple-decker family in which the COT ring has two planar four-carbon fragments twisted with respect to each other (by 34.8° in the Rh system) (Figure 17), the two metals being connected through a three-center, two-electron, C−C bridge.[116] Structural information could not be confidently assigned to a one-electron intermediate detected by low-temperature voltammetry.

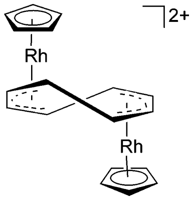

Figure 17. "Slipped" triple-decker structure of the 34 VE system $[Rh_2Cp_2(C_8H_8)]^{2+}$. The Co congener having C_5Me_5 ligands appears to have the same structure. See refs 115 and 116.

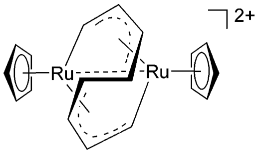

Figure 18. Structure of the "flyover" 32 VE dication $[Ru_2Cp_2(C_8H_8)]^{2+}$ obtained upon oxidation of $Ru_2Cp_2(C_8H_8)$. See ref 120.

Further investigations of pseudo-triple-decker redox processes followed the preparation of new dimetallic COT complexes, particularly those of Albrecht Salzer.[117] His group prepared the diruthenium complex $Ru_2Cp_2(\mu;\mu\text{-COT})$, which was both isoelectronic and isostructural with the just-discussed $[Rh_2Cp_2(\mu;\mu\text{-COT})]^{2+}$. Remarkably, Salzer's ruthenium compound also gave a chemically reversible two-electron oxidation, in this case giving an apparent 32 e^- dication. From the ^1H NMR spectrum of $[Ru_2Cp_2(\mu;\mu\text{-COT})]^{2+}$, postdoctoral associate Joseph Edwin argued for a "flyover" structure in which the eight-membered ring is *linear* rather than cyclic (Figure 18), strengthening his argument by pointing out that a similar structure was known for a 32 e^- chromium complex, $Cr_2Cp_2(C_8H_8)$.[118] I was quite skeptical that a tub-to-flyover structural change could be induced through a reversible electrochemical process, given the number of bond alterations that would have to accompany the charge-transfer reactions.[119] Nevertheless, this turned out to be the case, and more detailed voltammetric studies indicated that the major part of the structural change occurred in the *first* one-electron process, $[Rh_2Cp_2(C_8H_8)]^{0/+}$. The startling and complex nature of these redox systems slowed completion of the studies, but finally a pair of full papers was published in 1990 giving a detailed mechanistic description.[120] Scheme 3 shows how the structures of this family of compounds change as the pseudo-triple-decked 36 e^- complexes progressively lose electrons, culminating in the flyover structures of the 32 e^- systems.

[**Parenthetic Aside H.** It may be of instructive value to consider the specific role played by electrochemical methods in helping to detail Scheme 3. Obviously, one cannot simply look at CV scans and draw conclusions about the structures of the electrode products, for the measurables (current and

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[113] (a) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351. (b) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

[114] Representative examples are: (a) (triple-deckers) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (c) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (d) Schilling, B. E. R.; Hoffmann, R. *Acta Chem. Scand.* **1979**, *B33*, 231.

[115] Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 7429.

[116] Edwin, J.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 3052.

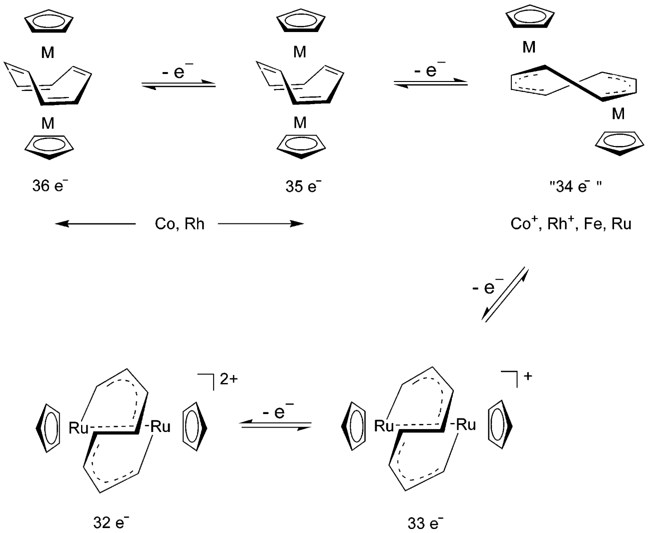
[117] For examples see: (a) Salzer, A.; Egolf, T.; Linowsky, L.; Petter, W. *J. Organomet. Chem.* **1981**, *221*, 339. (b) Salzer, A.; Egolf, T.; von Philipsborn, W. *J. Organomet. Chem.* **1981**, *221*, 351. (c) Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413.

[118] (a) Elschenbroich, Ch.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *Angew. Chem., Int. Ed.* **1983**, *22*, 330. (b) Heck, J.; Rist, G. *J. Organomet. Chem.* **1988**, *342*, 45.

[119] I was not the only skeptic. When I was giving a talk on this system at a meeting of organometallic chemists, I showed our CV results with the proposed structure of the dication. After hearing cries from the audience that might be politely translated as "no way", it was with admitted pleasure that I showed the next slide having Arnie Rheingold's X-ray results.

[120] (a) Edwin, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 7104. (b) Geiger, W. E.; Salzer, A.; Edwin, J.; von Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113. For a recent description of a redox-driven skeletal rearrangement of a triruthenium complex, see: Takao, T.; Moriya, M.; Suzuki, H. *Organometallics* **2007**, *26*, 1349.

Scheme 3



potential) have no intrinsic relationship to molecular structure (I often indicate this to students by pointing out that the $E_{1/2}$ value for the oxidation of ferrocene is virtually identical to that of the iodide ion). In the triple-decker case, voltammetry and electrolysis determined the free energies and e.t. stoichiometries (i.e., one or two electrons) of the reactions, as well as the lifetimes of the products. Time- and temperature-dependent CV scans offered indirect information on which redox step might involve a major structural change. Structural identification of the products, however, required NMR or X-ray characterization, no different than if the reactions were carried out by more traditional means. Modern computational methods, specifically DFT calculations, now add a powerful tool to molecular redox investigations in being able to calculate the structures of difficult-to-characterize products and intermediates.]

X.B. Isomerization of Octahedral Complexes. There were early indications that the preference for *cis* or *trans* isomers might be affected by the metal electron count for six-coordinate metal carbonyl systems.[121] Two papers appearing almost simultaneously used cyclic voltammetry to demonstrate that one-electron oxidation of the d^6 *cis* complexes $M(CO)_2(dppe)_2$ (dppe = diphenylphosphinoethane, M = Cr, Mo) gave the corresponding *trans* complex in the d^5 monocation (Figure 19).[122,123] Thus began a fruitful study by Bond, Colton, and co-workers on the redox-induced isomerizations of a large number of metal−carbonyl-containing octahedral complexes, which remain under study to the present as models of electron-transfer-induced structural changes.[124] The strong preferences for the *trans* structure in dicarbonyl compounds and *mer* structure in tricarbonyls were rationalized as arising from an electronic effect that outweighed the steric factors which are the structural determinant in the 18-electron compounds.[125]

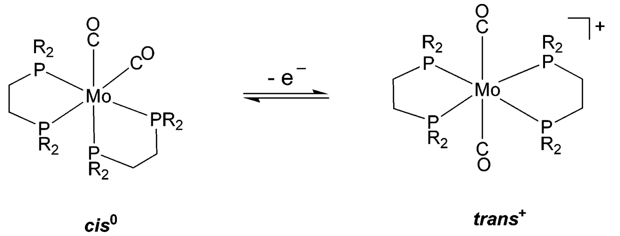


Figure 19. Prototypical one-electron redox process showing the favored isomers for $[Mo(dppe)_2(CO)_2]^{0,+}$ as exploited by Bond and co-workers. See ref 123.

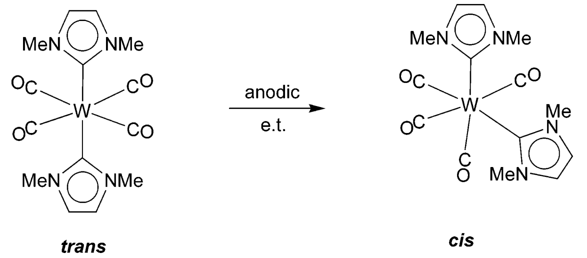


Figure 20. Structures of the molybdenum bis-carbene complexes for which anodic oxidation catalyzes a *trans* to *cis* isomerization. See ref 126.

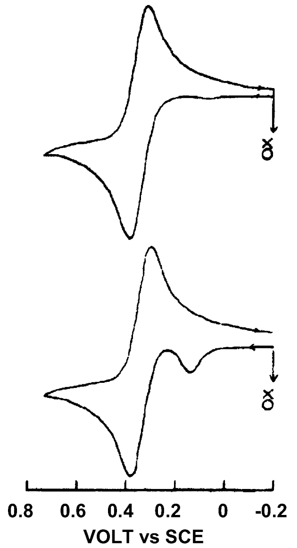


Figure 21. CV scans of a solution containing only the *trans* isomer of $W(C_3N_2Me_2)_2(CO)_4$. Top: slower scan at 295 K; bottom: faster scan at 271 K. The major wave arises from the *cis* isomer, formed by anodic catalysis of the *trans* isomer. The anodic wave of the latter is seen as the small feature, at ca. 0.1 V, when the voltammetric scan rate partially outruns the rate of the catalytic conversion process. Reprinted with permission from ref 126.

An anodically induced *cis*/*trans* isomerization with a catalytic twist was reported by Rieke and co-workers, who were able to isolate both isomers of 18 e$^-$ $M(CO)_4(imid)_2$ (imid = $(C_3H_2(NMe)_2)$, M = Mo, W)[126] (Figure 20). The CV curves observed separately for the two isomers were virtually the same at slow scan rates, but separate features were seen at faster sweep rates or at subambient temperatures. This behavior arises from the fact that the thermodynamically disfavored *trans* isomer ($E_{1/2} \approx 0.10$ V vs SCE, the small "prewave" seen in the lower CV of Figure 21) is electrocatalytically converted to the neutral *cis* isomer ($E_{1/2} = 0.30$ V, the larger wave) as the CV scan proceeds positive (eqs 4−6).[127]

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(121) (a) Snow, M. R.; Stiddard, M. H. B. *J. Chem. Soc. A* **1966**, 777. (b) Crossing, P. F.; Snow, M. R. *J. Chem. Soc. A* **1971**, 610. (c) Lewis, J.; Whyman, R. *J. Chem. Soc.* **1965**, 5486. (d) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1971**, *32*, C44.

(122) George, T. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2548.

(123) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(124) For review see: Bond, A. M.; Colton, R. *Coord. Chem. Rev.* **1997**, *166*, 161.

(125) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

(126) Rieke, R. D.; Kojima, H.; Öfele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735.

(127) A homogeneous reaction between the *cis* cation and the *trans* neutral also seems to play a role in this reaction. See the original paper as well as ref 98, pp 308−309.

$$\textit{trans}\text{-W(CO)}_4(\text{imid})_2 \rightleftharpoons [\textit{trans}\text{-W(CO)}_4(\text{imid})_2]^+ + e^- \qquad E_{1/2} \approx 0.10\text{ V} \quad (4)$$

$$[\textit{trans}\text{-W(CO)}_4(\text{imid})_2]^+ \rightarrow [\textit{cis}\text{-W(CO)}_4(\text{imid})_2]^+ \text{ fast} \quad (5)$$

$$[\textit{cis}\text{-W(CO)}_4(\text{imid})_2]^+ + e^- \rightleftharpoons \textit{cis}\text{-W(CO)}_4(\text{imid})_2 \qquad E_{1/2} = 0.30\text{ V} \quad (6)$$

A solution of the neutral *trans* complex was exhaustively electrolyzed to the neutral *cis* complex at $E_{\text{appl}} = 0.20$ V with only 0.1 F/equiv of charge, confirming the catalytic conversion. This is a vivid example of one way in which a voltammetric scan may alter the concentration of the analyte in the reaction layer, as mentioned in parenthetic aside D. We will come back to electron-transfer-catalyzed processes when discussing redox-induced substitution reactions in Section XI.A.

An interesting contrast to these anodically driven isomerizations of octahedral organometallic carbonyls was observed by Kochi and co-workers in the *cathodic* behavior of members of this family. The 18-electron cationic complex [*trans*-Mn(CO)$_2$-(η^2-dppe)$_2$]$^+$ undergoes a cathodic two-electron reduction to a monoanion, [Mn(CO)$_2$(η^2-dppe)(η^1-dppe)]$^-$, now made five-coordinate by the loss of a Mn−P bond as one dppe ligand becomes mono-hapto-coordinated, allowing the metal to regain the 18 e$^-$ count. Detailed voltammetric studies combined with ESR data provided evidence that the neutral radical intermediate was also five-coordinate, implying rapid Mn−P bond cleavage from the putative 19 e$^-$ system Mn(CO)$_2$(η^2-dppe)$_2$ in favor of Mn(CO)$_2$(η^2-dppe)(η^1-dppe) (Figure 22).[128]

A working model emerges for the structural consequences of redox reactions of octahedral 18 e$^-$ metal carbonyls: loss of electrons favors six-coordinate *trans* or *mer* structures in some, but not all, cases, and isomerizations of this type usually occur on a CV time scale (seconds to milliseconds); gain of electrons may lead to cleavage of a metal−ligand bond and very rapid formation of a five-coordinate system.

[**Parenthetic Aside I.** Cleavage of a Mn−P bond in the *anion* [Mn(CO)$_2$(dppe)$_2$]$^-$ is easily rationalized on the basis of avoidance of a 20-electron count at the metal. But must the putative Mn(CO)$_2$(η^2-dppe)$_2$ radical also become five-coordinate to avoid a 19 e$^-$ metal structure? Loss of an electron-pair bond occurs in this case and in some other “19 e$^-$” metal−chelate systems, such as FeCp*(S$_2$CNMe$_2$)$_2$ (see Delville-Desbois, M.-H.; Varret, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 249), but it is arguable whether or not organometallic radicals should generally prefer a 17 e$^-$ structure over its 19e$^-$ counterpart. I have argued elsewhere that the one-electron intermediates in overall 18 e$^-$ to “20 e$^-$” [129] processes are more likely to be structurally similar to the 18 e$^-$ system, owing to metal−ligand charge delocalization, an issue that is now receiving quantitative inquiry through DFT calculations on 19 e$^-$ systems.[130] For a somewhat different take on this question, using a model involving equilibrating 17 e$^-$ and 19 e$^-$ forms, see: Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36.]

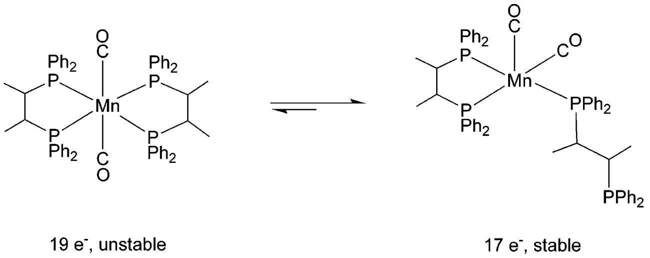

Figure 22. The two possible hapticity forms of the radical Mn-(CO)$_2$(dppe)$_2$, as discussed in ref 128.

X.C. Hapticity Changes: Intramolecular Making and Breaking of M−C Bonds. As mentioned in the beginning of Section X, the η^6/η^4-hapticity change associated with addition of two electrons to the bis(hexamethylbenzene)ruthenium dication (see Figure 13), involving the hefty 42° arene hinge angle, was intellectually satisfying on the basis of adherence to the 18-electron rule. One’s comfort level drops, however, when considering the possible structure of the one-electron putative intermediate [Ru(C$_6$Me$_6$)$_2$]$^+$. Is it a 19 e$^-$ system with η^6,η^6 arene bonding, a 17 e$^-$ system with η^6,η^4 bonding, or something in between? This question is of more than just intellectual interest, as hapticity changes have been shown, beginning with the work of Fred Basolo (1920−2007),[131] to be of fundamental importance in influencing the reactivities of organometallic π-complexes. Where electrochemistry makes its unique contribution to this question is its ability to probe the effects of one-electron change. Consequently, the electrochemistry of metal−arene and metal−cyclopentadienyl complexes has been regularly probed in the years since the report of Fischer and Elschenbroich.[99] A varietry of different arenes have been probed for their possible η^6/η^4-hapticity changes,[132−139] but definitive inquiries into analogous η^5/η^3 models have been largely limited to metal−indenyl systems.[140−145] We will address some of these findings, but let us first ask: what was eventually learned about [Ru(C$_6$-

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[128] Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 2574.

[129] Quotation marks are used for the 20 e$^-$ designation to bring attention to the fact that changes in ligand hapticity may, indeed, formally remove two electrons from the metal valence orbitals.

[130] (a) Braden, D. A.; Tyler, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 942. (b) Braden, D. A.; Tyler, D. R. *Organometallics* **2000**, *19*, 1175. (c) Braden, D. A.; Tyler, D. R. *Organometallics* **2000**, *19*, 3762. (d) Ogliaro, F.; Halet, J.-F.; Astruc, D.; Saillard, J.-Y. *New J. Chem.* **2000**, *24*, 257. (e) Srinivas, G. N.; Yu, L. W.; Schwartz, M. *J. Organomet. Chem.* **2003**, *677*, 96.

[131] Schuster-Wolden, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. For a review of early work on cyclopentadienyl hapticity effects see ref 147.

[132] (a) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *1*, 1415. (b) Finke, R. G.; Voegeli, R. H.; Langanis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.

[133] (a) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657. (b) Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084. (c) Bowyer, W. J.; Merkert, J.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191. (d) Bowyer, W. J.; Geiger, W. E. *J. Electroanal. Chem.* **1988**, *239*, 253.

[134] Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

[135] Elschenbroich, C.; Bilger, E.; Koch, J.; Weber, J. *J. Am. Chem. Soc.* **1984**, *106*, 4297.

[136] (a) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. (b) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36. (c) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (d) Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287.

[137] Brennessel, W. W.; Young, V. G.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2002**, *41*, 1211.

[138] (a) Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657. (b) Veauthier, J. M.; Chow, A.; Fraenkel, G.; Geib, S. J.; Cooper, N. J. *Organometallics* **2000**, *19*, 661.

[139] Reingold, J. A.; Virkaitis, K. L.; Carpenter, G. B.; Sun, S. H.; Sweigart, D. A.; Czech, P. T.; Overly, K. R. *J. Am. Chem. Soc.* **2005**, *127*, 11146.

[140] (a) Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460. (b) Miller, G. A.; Therien, M. J.; Trogler, W. C. *J. Organomet. Chem.* **1990**, *383*, 271.

[141] Pevear, K. A.; Holl, M. M. B.; Carpenter, G. B.; Rieger, A. L.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1995**, *14*, 512.

[142] Lee, S.; Lovelace, S. R.; Cooper, N. J. *Organometallics* **1995**, *14*, 1974.

[143] Amatore, C.; Ceccon, A.; Santi, S.; Verpeaux, J.-N. *Chem.−Eur. J.* **1997**, *3*, 279.

[144] Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777.

[145] Pierce, D. T. Ph.D. dissertation, University of Vermont, 1991, pp 57−67.

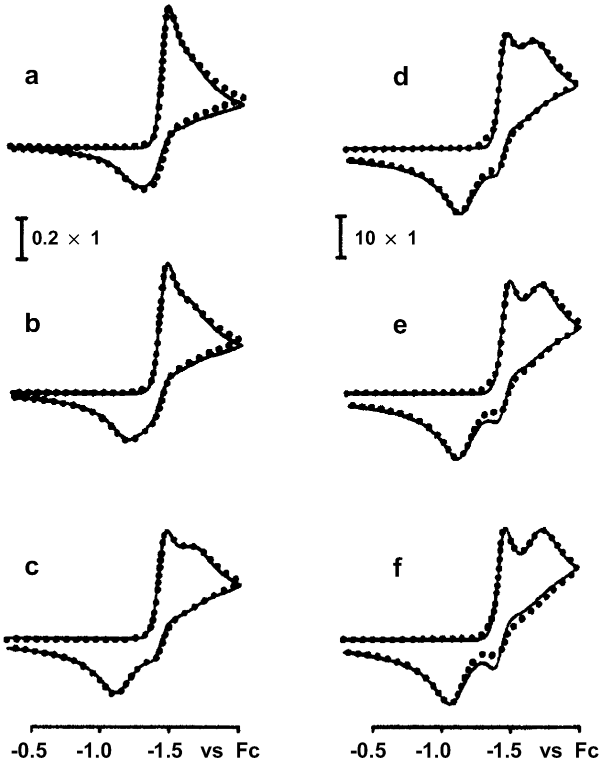

Figure 23. Set of CV scans at increasing scan rates (0.4 to 50 V s^{-1} from (a) to (f)) showing how the second oxidation of $[\mathrm{Ru(C_6Me_6)_2}]^{2+}$ becomes resolved from the first at shorter observation times. Reprinted with permission from ref 134.

$\mathrm{Me_6)_2}]^+$, the presumed middleman in the conversion of $[\mathrm{Ru(C_6Me_6)_2}]^{2+}$ to $\mathrm{Ru(C_6Me_6)_2}$? The first published electrochemical data were not encouraging in terms of either its thermodynamic or kinetic stability. As part of a study of cyclophane derivatives, Finke, Boekelheide, and co-workers recorded CV scans for the reduction of $[\mathrm{Ru(C_6Me_6)_2}][\mathrm{BF_4}]_2$ in acetonitrile and dichloromethane. A single two-electron wave was seen in the former,[132a] and barely resolved one-electron features were seen in the latter.[132b] The monocation $[\mathrm{Ru(C_6Me_6)_2}]^+$ was clearly unstable with respect to disproportionation (eq 7). More

$$2\,[\mathrm{Ru(C_6Me_6)_2}]^+ \rightleftharpoons \mathrm{Ru(C_6Me_6)_2} + [\mathrm{Ru(C_6Me_6)_2}]^{2+} \qquad K_{\mathrm{disp}} \quad (7)$$

perplexing was the fact that the cathodic reduction of $[\mathrm{Ru(C_6Me_6)_2}]^{2+}$ was *not* fully chemically reversible. The implication was that, in spite of the fact that the two outlying members of the two-electron process were kinetically stable, the one-electron intermediate was not. Hoping to better understand this e.t. process, David Pierce set out to look in detail at the voltammetry of $[\mathrm{Ru(C_6Me_6)_2}]^{2+}$ and eventually solved what is certainly one of the most challenging mechanistic problems that my group has encountered.

Pierce showed[134] that the disproportionation constant for the radical (eq 7, $K_{\mathrm{disp}} = C_{\mathrm{Ru(C6Me6)2}}C_{\mathrm{[Ru(C6Me6)2]2+}}/C^2_{\mathrm{[Ru(C6Me6)2]+}}$) increased from 4.3×10^{-3} $\mathrm{M^{-1}}$ in $\mathrm{CH_2Cl_2}$ to 2 $\mathrm{M^{-1}}$ in $\mathrm{CH_3CN}$ and that the monocation decomposed on the CV time scale. The truly unique aspect of this system was that the single two-electron CV wave in $\mathrm{CH_3CN}$ became a *resolved pair* of one-electron cathodic waves at high sweep rates (Figure 23). Scan rates up to 11 000 V s^{-1} were used to show that the second reduction, i.e., $[\mathrm{Ru(C_6Me_6)_2}]^{+/0}$, became time-resolved from the first owing to the fact that its heterogeneous charge-transfer rate is much slower (at least 3 orders of magnitude) than that of $[\mathrm{Ru(C_6Me_6)_2}]^{2+/+}$. The k_s value of 2 cm s^{-1} determined for $[\mathrm{Ru(C_6Me_6)_2}]^{2+/+}$ is ferrocene-like and argues for very minor structural changes in the one-electron reduction of the 18 e^- dication. The greatly increased inner-sphere reorganizational energy of the $[\mathrm{Ru(C_6Me_6)_2}]^{+/0}$ couple leads to the Marcus-based[94] conclusion that the η^6/η^4 structural change occurs in the *second* reduction of the dication. On this basis, the mysterious monocation $[\mathrm{Ru(C_6Me_6)_2}]^+$ was assigned a 19-electron structure having two planar arene rings, thereby completing characterization of the $[\mathrm{Ru(C_6Me_6)_2}]^{2+,+,0}$ triad (Figure 24).

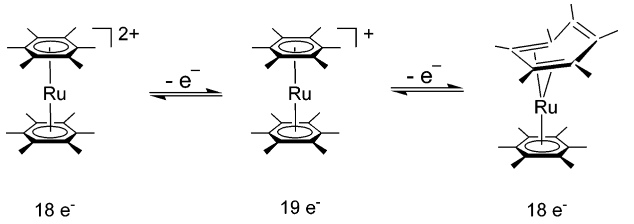

Figure 24. Three idealized structures of bis(hexamethylbenzene)ruthenium as it traverses its three-membered electron-transfer series. See ref 113a for discussion.

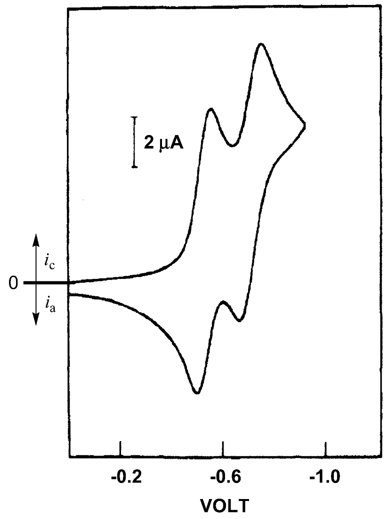

Figure 25. CV scan of the two successive one-electron reductions of $[\mathrm{RhCp^*(C_6Me_6)}]^{2+}$. In contrast to $[\mathrm{Ru(C_6Me_6)_2}]^{2+}$, the monocation is stable with respect to disproportionation, allowing direct voltammetric observation of the 19 e^- radical at a slow scan rate (0.1 V s^{-1}). Reprinted with permission from ref 133a.

An analogous sandwich system that yielded more directly to a combined electrochemical/spectroscopic inquiry was $[\mathrm{RhCp(\eta^6\text{-}arene)}]^{2+}$. In this case, the reductions were sufficiently separated (several hundred mV, see Figure 25) to allow direct electrochemical observation of the sequential one-electron products in the electron-transfer sequence of eq 8:[133]

$$[\mathrm{RhCp(\eta^6\text{-}arene)}]^{2+} \xrightleftharpoons{e^-} [\mathrm{RhCp(\eta^6\text{-}arene)}]^{+} \xrightleftharpoons{e^-} \mathrm{RhCp}(\eta^4\text{-arene}) \quad (8)$$

In this case the bent η^4-bound arene of the neutral compound was established by X-ray crystallography, but the 19-electron character of the Rh(II) monocation was concluded from paramagnetic NMR data on the hexamethylbenzene complex. Details of these studies have been given in a review.[113a]

[**Parenthetic Aside J.** The $\mathrm{Ru(arene)_2}$ system, as well as its mixed-sandwich RhCp(arene) counterpart, taught us an important lesson about the high reactivity of organometallic radicals and the enormous stability imparted to "20 e^-" species by a

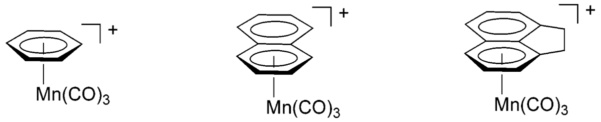

Figure 26. Some of the $[Mn(CO)_3(arene)]^+$ complexes undergoing cathodic reduction as discussed in ref 139.

change in ligand hapticity. Both of these systems underwent two successive one-electron reductions from an 18-electron dication to another isolable 18-electron neutral compound. In each case, the one-electron intermediates were quite reactive, befitting their radical character. Although we did not fully characterize the long-term reaction products of these 19-electron systems, in the case of the hexamethylbenzene derivatives, they appeared to involve loss of an H atom from a methyl group of the arene.[145] Astruc has demonstrated the occurrence of such H atom reactions for isoelectronic iron hexamethylbenzene complexes.[136b,c] This bimodal picture of stable/reactive/stable members of an electron-transfer series is less common in organic systems, for which successive oxidations or reductions usually give more harmonious trends in kinetic stability. The possibility of changes in metal−ligand hapticity opens organometallic systems to electron-transfer processes (including net two-electron reactions) that are less readily attained in organic or metal chelate systems.]

More recent work reported by Sweigart et al.[139] showed that the degree of arene ring slippage may depend significantly on the nature of the arene, particularly on whether it is polycyclic. Eighteen-electron $[Mn(\eta^6\text{-arene})(CO)_3]^+$ complexes of the type shown in Figure 26 may exhibit dramatically different voltammetric curves. Even though an anion of the benzene complex can be generated by low-temperature chemical reduction,[138] it shows only an irreversible one-electron reduction in CV scans at room temperature. The single two-electron wave of the naphthalene complex and the two barely separated waves of the acenaphthene complex were chemically reversible. DFT calculations on the three compounds in their three different redox states (cation/neutral/anion) gave a clear picture of how the degree of ring slippage tracks the metal oxidation state and the nature of the arene. The arene fold angle was calculated to be about 35−40° for each anion, but the degree of folding was significantly different in the neutral radicals, from only 10° for the benzene complex to about 15−17° for the naphthalene and acenaphthene complexes, sending the polycyclic systems almost halfway to their ultimate η^4 structures. The thermodynamics and kinetics of the individual e.t. reactions were consistent with the computed structural changes. One interesting finding in this study was that the SOMO of $Mn(CO)_3$(naphthalene) is of predominantly ligand character, whereas that of $Mn(CO)_3$(benzene) is predominantly metal based. There is little question that our understanding of the complexities of changes in radical structure and reactivity will profit enormously by modern computational methods.

Recent studies have also shown that the idea[140−145] that metal−indenyl radicals will have either η^5 or η^3 ligand hapticity (i.e., either a 19 e^- or 17 e^- structure) deserves more scrutiny. Electrochemical, spectroscopic, and calculational studies were again combined to show[146] that reduction of the 18-electron complex $[MoCp(\eta^5\text{-indenyl})(P(OMe)_3)_2]^{2+}$ results in progressive folding of the indenyl ligand to 11° in the monocation and finally to 22° in the neutral complex. The one-electron product is better characterized as having η^4 bonding of the indenyl ring (see Figure 27).

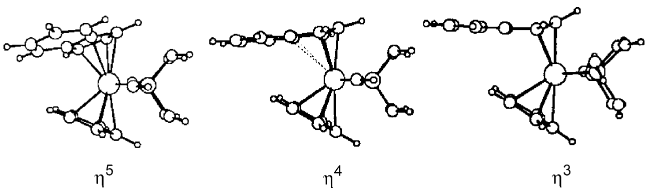

Figure 27. Edge-on pictures of the three different oxidation states of $[Mo(\eta^n\text{-indenyl})Cp(PR_3)_2]^{2+,+,0}$ (dication to neutral, left to right) showing the gradual change from η^5- to η^4- to η^3-hapticity of the indenyl ligand. Reprinted with permission from ref 146.

In summaries of the literature of redox-induced hapticity changes of metal−cyclic polyolefin complexes up to 2005,[139,146] the relatively sparse knowledge about fates of complexes of the cyclopentadienyl ligand itself stands out. Owing to the wide attribution of substitution and other important reactions of metal−cyclopentadienyl compounds to η^5/η^3 ring slip/folding,[131,147,148] as well as calculations predicting a variety of redox-induced hapticity changes for such compounds,[149] experimental work is needed in this area. There are other remaining electrochemical challenges on the subject of metal−polyolefin redox processes. For instance, it would be valuable to be able to compare calculated and measured inner-sphere reorganizational energies for reactions in which there is apparent concomitant electron transfer and cleavage of M−C or $M-C_2$ bonds. This could lead to a better understanding of the relationship between slow heterogeneous electron transfer and the possible loss and gain of metal−carbon bonds.

There are relatively few examples known of redox-driven *reversible* alterations of a *single* M−C bond in non-polyolefin complexes. One of these is the oxidatively induced isomerization of chromium-group vinylidene complexes to their alkyne counterparts (see Scheme 4).[150,151]

X.D. Intramolecular Making and Breaking of M−M Bonds. As exemplified by eq 1, the reduction of unbridged dimetallic systems is generally a two-electron process in which fast cleavage of the M−M bond gives 2 equiv of the 18-electron monomer. Well-studied examples of this chemically reversible process include those based on the monomers $[Mn(CO)_5]^-$, $[MoCp(CO)_3]^-$, and $[FeCp(CO)_2]^-$.[37,152,153] It is perhaps not surprising that an analogous *intra*molecular process has been shown for dimetallic systems having a single flexible ligand

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(146) (a) Stoll, M. E.; Belanzoni, P.; Calhorda, M. J.; Drew, M. G. B.; Félix, V.; Geiger, W. E.; Gamelas, C. A.; Gonçalves, I. S.; Romão, C. C.; Veiros, L. F. *J. Am. Chem. Soc.* **2001**, *123*, 10595. (b) Garg, A.; Nemer, D. M.; Choi, H. J.; Sheridan, J. B.; Geiger, W. E. *Organometallics* **2006**, *25*, 275.

(147) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(148) Lee, S.; Cooper, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 716.

(149) (a) Veiros, L. F. *Organometallics* **2000**, *19*, 5549. (b) Fan, H.-J.; Hall, M. B. *Organometallics* **2001**, *20*, 5724. These refs show computationally that the Cp ligand is known to be capable of a number of different hapticities in odd-electron species. Although the authors of ref 148 postulated an η^5/η^3-hapticity change to account for the chemically reductive activation of $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$ by the alkalide [K(18-crown-6)]K, no electrochemical data were reported. An η^1-bonded ring is calculated for the lowest energy structure of $[MnCp(CO)_3]^{2-}$ by Veiros (*vide ante*). In unpublished work, we have strong electrochemical evidence matching the DFT calculations of Dr. Michael Bühl (Max Plank Institute, Mülheim/Ruhr) for an equilibrium between η^2- and η^1-coordinated cyclopentadienyl rings in $[Mo(\eta\text{-}C_5Me_5)(CO)(C_2Ph_2)_2]^-$, which will be reported in due course.

(150) Bartlett, I. M.; Connelly, N. G.; Martín, A. J.; Orpen, A. G.; Paget, T. J.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1999**, 691.

(151) Connelly, N. G.; Lagunas, C.; Metz, B. Rieger, A. L.; Rieger, P. H.; Geiger, W. E.; Shaw, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 12202.

(152) (a) Lacombe, D. A.; Anderson, J. E.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 2074. (b) Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

(153) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087.

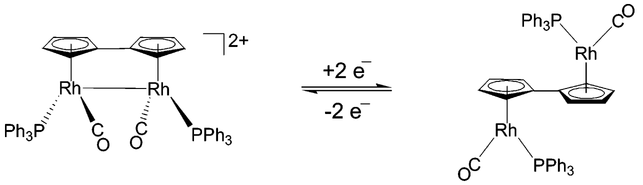
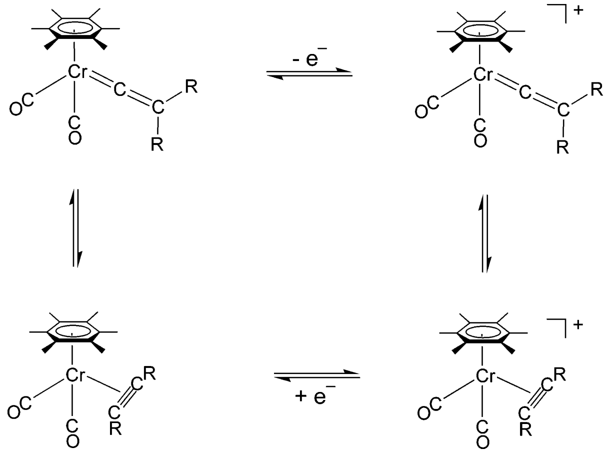


Figure 28. Chemically reversible two-electron redox process $[Rh_2Fv(CO)_2(PPh_3)_2]^{2+}$ (Fv = $C_{10}H_8$). See ref 155.

Scheme 4



bridge between the metals. Perhaps the earliest example of such a system involved the two-electron reduction of the fulvalenyl[154] dicationic complex $[Rh_2Fv(CO)_2(PPh_3)_2]^{2+}$ (Fv = $C_{10}H_8$) wherein cleavage of the Rh−Rh bond accompanied by *trans*-to-*cis* isomerization gave the neutral compound $Rh_2Fv(CO)_2(PPh_3)_2$, having two 18-electron metals (Figure 28).[155] This theme has played out for a number of fulvalenyl redox processes, including the oxidations of $[M_2Fv(CO_6)]^{2-}$ (M = Mo, W)[156] and the reductions of the heterobimetallic systems $WMFv(CO)_5$, M = Fe, Ru.[157] Taken as a whole, fulvalenyl complexes mimic the redox behavior of their cyclopentadienyl counterparts in that stong metal−metal bond formation is found predominantly for second- and third-row metals. The oxidation of $Mn_2Fv(CO)_4(PPh_3)_2$, for instance, gives a persistent radical cation that shows no evidence of direct Mn−Mn interactions.[158]

There appears to be no evidence to date that analogous making and breaking of M−M bonds occur in the redox chemistry of dimetallic systems linked only by a biphenyl group. The radical cation of $Cr_2(biphenyl)(CO)_4(PPh_3)_2$ (Figure 29) appears to retain its *transoid* metal centers.[159] Although it must be kept in mind that oxidation of the heavier metals in this group (more amenable to metal−metal bond formation) has not been reported, it is useful to note that a biphenyl ligand provides an alternate electronic option, namely, the formation of an exocyclic C═C double bond between aryl groups, which may obviate the need for M−M bond formation in the formal biradical. Consider the diiron system $[Fe_2(biphenyl)Cp^*{}_2]^{2+}$, which has two redox centers that might each be expected to undergo one-electron reduction to the 19-electron Fe(arene)Cp-type systems that have been so well characterized by Astruc and co-workers.[160] The once-reduced monocation of this system distorts only slightly compared to the 36 e⁻ precursor. However, in the twice-reduced neutral compound, significant aryl folding occurs, leaving two 18-electron metals bonded to a bicyclohexadienylidene bridge (Figure 29).[161] A similar structural change had been postulated earlier by Rieke et al. for the dianion of $Cr_2(biphenyl)(CO)_6$.[162] Although this conclusion was later supported by calculational results on $[Cr_2(biphenyl)(CO)_6]^{2-}$,[163] the structure of the *mono*anion $[Cr_2(biphenyl)(CO)_6]^{-}$ remains open to question.[164]

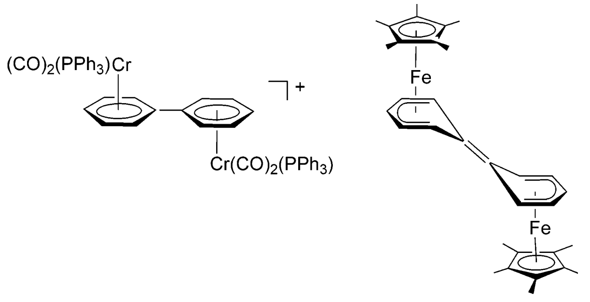


Figure 29. (Left) Retention of the *transoid* structure for the radical cation $[Cr_2(biphenyl)(CO)_4(PPh_3)_2]^{+}$ (see ref 159). (Right) Formation of an exocyclic C═C bond between aryl groups when $[Fe_2(biphenyl)Cp^*{}_2]^{2+}$ is reduced by two electrons (see ref 160).

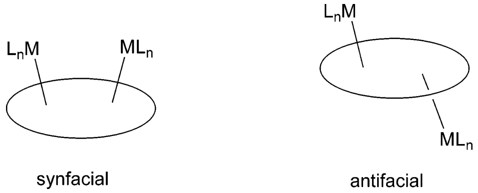


Figure 30. Schematic representation of *syn*-facial and *anti*-facial isomers linked by an unsaturated hydrocarbon, as depicted by Bögels, G.; Brussaard, H.C.; Hagenau, U.; Heck, J.; Kopf, J.; van der Linden, J.G.M.; Roelofsen, A. *Chem.−Eur. J.* **1999**, *3*, 1151.

Other compounds having either an *anti*-facial or *syn*-facial dimetallic structure (Figure 30) across a single cycloolefinic bridge have also been probed. *Syn*-facial analogues of the μ-COT complexes discussed in Section X.A may have dramatically different redox properties compared to their *anti*-facial analogues. Consider, for example, *syn*-$Ru_2Cp_2(\mu\text{-}C_8H_8$ (Figure 31), in which the neutral compound already has an appreciable Ru−Ru interaction (d_{M-M} = 2.956 Å). Upon two successive one-electron oxidations, the metal−metal distance decreases first to 2.822 Å in the monocation and then to 2.661 Å in the dication. The eight-membered bridging ring also increases its hapticity from $\eta^4;\eta^4$ to an unusual $\eta^5;\eta^5$ mode in the dication.[165] Another interesting *syn*-facial system is the indenyl Cr−Rh complex (Figure 31), in which the 34 e⁻ neutral complex is reduced in a single two-electron process to a dianion. The source of the

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(154) The proper nomenclature for this formally dinegative ligand is fulvalene*di*yl, but this usage is not often found in the literature.

(155) (a) McKinney, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 603. (b) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1983**, 121. (c) Freeman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2283.

(156) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. J. *Inorg. Chem.* **1986**, *25*, 1846.

(157) Brown, D.; Delville-Desbois, M.-H.; Vollhardt, K. P. C.; Astruc, D. *New J. Chem.* **1992**, *16*, 899, and references therein.

(158) Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **2000**, *122*, 5477.

(159) Pierce, D. T.; Geiger, W. E. *Inorg. Chem.* **1994**, *33*, 373.

(160) (a) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. (b) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

(161) Lacoste, M.; Rabaâ, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y.; Le Beuze, A. *J. Am. Chem. Soc.* **1990**, *112*, 9548.

(162) (a) Rieke, R. D.; Henry, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 6314. (b) Rieke, R. D.; Milligan, S. N. *Organometallics* **1983**, *2*, 171. (c) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699. (d) Rieke, R. D.; Daruwala, K. P.; Forkner, K. P. *Organometallics* **1991**, *10*, 2946.

(163) Rabaâ, H.; Saillard, J.-Y.; Le Beuze, A. *J. Organomet. Chem.* **1993**, *463*, 109.

(164) See ref 2, pp 151−154.

(165) Heck, J.; Lange, G.; Malessa, M.; Boese, R.; Bläser, D. *Chem.−Eur. J.* **1999**, *5*, 659.

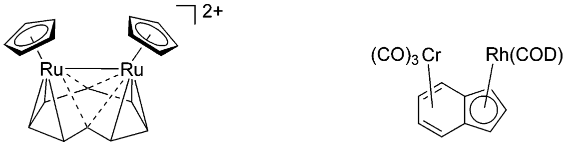

Figure 31. Structures of two *syn*-facial complexes. (Left) Oxidation product of *syn*-$Ru_2Cp_2(\mu\text{-}C_8H_8)$ (ref 165). (Right) Starting material for the reduction of *syn*-$Cr(CO)_3Rh(COD)(\mu$-indenyl) (ref 166).

thermodynamic stabilization of the dianion has been postulated to be changes in ligand hapticity and, possibly, a stronger interaction between the metal centers.[166]

X.E. Square Schemes and the Question of When a Structural Change Occurs. A key mechanistic question, mentioned in the beginning of Section X, is whether a structure change is concomitant with, or separate from, the electron transfer. Considering one direction of the redox process, these two possibilities are referred to, respectively, as a concerted (single-step, E) process or a two-step (EC) process. The chemically reversible extension of the latter produces the square scheme of Scheme 1.[167] The importance of this distinction cannot be overstated owing to its implications in the temporal aspects of the redox chemistry. The mechanistic factor is key, for example, to the question of whether or not a given redox reaction is a candidate for applications in particular types of electronic devices.

Among the excellent treatments of the theory and application of square-scheme models,[97] the most comprehensive is that of Evans and O'Connell, who also discussed the distinction between square schemes and concerted processes.[97b] At the risk of oversimplifying complex mechanistic issues, let us at least introduce the practical question of how the two different mechanisms might be experimentally distinguished. Consider a chemically reversible redox process in which the stable oxidized form has structure A and the stable reduced form has structure B (eq 9). For the purpose of discussion, consider A

$$\mathrm{Ox\,(A)} + e^- \rightleftharpoons \mathrm{Red\,(B)} \tag{9}$$

and B to be isomers. The simulations in Figure 32 show how the CV scans might appear for the *concerted* process having a slow charge transfer (left side) versus the *square scheme* (right side) at two different scan rates, the slower scans being responsible for the top set of CVs. The species responsible for the voltammetric peaks are labeled according to the listing in Scheme 1. At slow scan rates, although there are subtle differences in peak shapes for the two mechanisms,[97] the CVs are qualitatively similar. At faster scan rates, appearance of a new anodic peak demonstrates the chemical reversibility of Ox(A) $\rightleftharpoons$ Red(A), as the rate of conversion of Red (A) to Red (B) no longer outruns the time scale of the scan, thereby eliminating the possibility of a concerted mechanism. It must be kept in mind, however, that *absence* of a third peak does not disprove the square scheme, since the conditions for its observation might lie outside those employed in the experiment. It is, indeed, very difficult to "prove" a concerted mechanism for a chemically reversible redox process, owing to limitations of the voltammetric time scale and the fact that EC systems may also undergo significant (nonisomeric) structural changes in the electron-transfer step, prior to isomerization. Another way of stating this last point is that occurrence of a follow-up structural change *after* electron transfer does not dictate that the E step prior to it must be Nernstian.

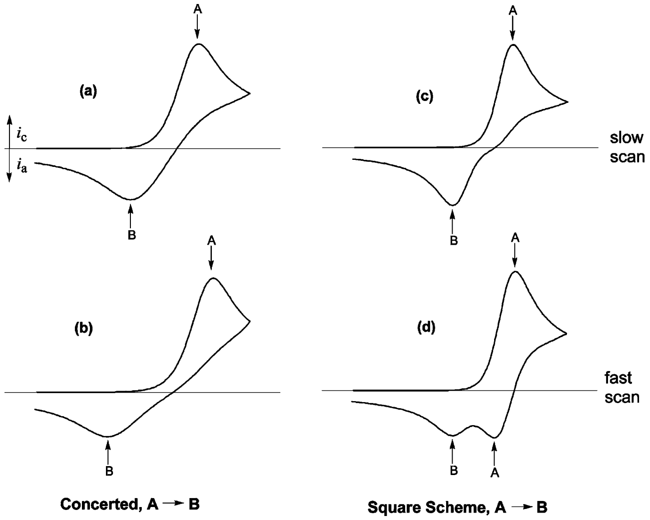

Figure 32. Digital simulations comparing two mechanisms for the electron-transfer-induced interconversions of structural forms A and B. In CVs (a) and (b), Ox(A) is reduced to Red(B) through a process in which the structural change is concerted with electron transfer (eq 9). In CVs (c) and (d), which are simulated for the square scheme of Scheme 1, the reduction of Ox(A) to Red(A) is followed by isomerization of Red(A) to Red(B). Faster scan rates (d) begin to outrun the rate of the isomerization, confirming the square scheme.

Fortunately, the mechanistic questions can often be clarified by precise analysis of the way in which the peak potentials and peak shapes are affected by scan rate changes, and the extensive literature on this subject should be consulted.[97,167,168] As pointed out by Savéant, determination of the charge-transfer coefficients α and β is a powerful mechanistic probe of the concerted versus the two-step mechanism.[168] Inspection of a recent paper may be helpful in seeing how voltammetric diagnostics are used to distinguish between the two mechanisms.[169]

[**Parenthetic Aside K.** There is a rather short list of transition metal electron-transfer reactions that are likely to retain widespread acceptance as having a concerted major structural change. Certainly, the electron-transfer-induced "breathing" of symmetrical octahedral metal complexes belongs in this category (see Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2795). While redox-induced metal−arene hapticity changes have been treated as concerted in refs 133 and 134 (but see Nielson, R. M.; Weaver, M. J. *Organometallics* **1989**, *8*, 1636), computational methods would be welcome in addressing this interpretation. A recent article by Macías-Ruvalcaba and Evans provides a very readable general treatment of the concerted versus square scheme question and describes the relatively small number of organic systems for which there is strong evidence for concerted processes (e.g., nitroalkanes). See: Macías-Ruvalcaba, N. A.; Evans, D. H. *Chem.−Eur. J.* **2007**, *13*, 4386.]

XI. Redox-Induced Changes in Reactivity

All of the "chemical" processes described in Section X were of an intramolecular nature, essentially structural in character, involving neither loss nor gain of an atom by the molecule. We now consider some aspects of the wider range of follow-

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(166) Amatore, C.; Ceccon, A.; Santi, S.; Verpeaux, J. N. *Chem.−Eur. J.* **1999**, *5*, 3357.

(167) Jacq, J. *J. Electroanal. Chem.* **1971**, *29*, 149.

(168) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455.

(169) Geiger, W. E.; Ohrenberg, N. C.; Yeomans, B.; Connelly, N. G.; Emslie, D. J. H. *J. Am. Chem. Soc.* **2003**, *125*, 8680.

up chemical reactions, essentially those of electrochemically generated organometallic radicals and radical ions. Different expectations are possible based on two divergent electronic views. One would assume significant metal−ligand delocalization in 17 e^- or 19 e^- systems, raising the possibility of organic radical-like reactions at the ligand. An alternative model is that of a metal-based process in which the redox reaction is viewed as causing a unit change in the metal oxidation state, suggesting reactivity changes akin to those known from traditional inorganic transition metal chemistry. These dual-natured reactivity models are essentially the basis of the question "Is the electron transfer metal or ligand based?" when a new molecular redox process is observed.

Astruc's systematic treatment of organometallic redox reactions[2] is the most in-depth coverage of this larger subject, an update of which is beyond the scope of the present review.[170] We will therefore restrict ourselves to a discussion of the dramatic way in which one-electron processes affect kinetic and thermodynamic factors in a few important reactions, emphasizing (i) carbonyl substitution processes, (ii) increases in metal hydride acidities, and (iii) migratory insertion reactions.

XI.A. Enhancement of Carbonyl Substitution Reactions. Substitution of carbonyls by other two-electron ligands is among the most valuable of organometallic reactions.[171] Until an unexpected observation by Philip Rieger (1931−2004) at Brown University in 1981, such reactions were known to proceed only through thermally or photochemically driven processes. The Rieger group was studying the reductions of certain metal carbonyl complexes, none of which showed any reactivity with phosphines in their neutral 18 e^- forms. They noted a number of cases in which addition of a phosphine to a solution containing a multimetallic test compound resulted in diminution, or even the virtual disappearance, of the cathodic wave of the compound.[172]

The observed voltammetry (Figure 33, modified here for consistency with the present text) is accounted for by eqs 10−12, in which $M_mL(CO)_n$ stands for a metal or multimetal complex containing *n* carbonyl groups.

$$M_mL(CO)_n + e^- \rightleftharpoons [M_mL(CO)_n]^- \qquad E^\circ_1 \qquad (10)$$

$$[M_mL(CO)_n]^- + L' \rightarrow [M_mL(CO)_{n-1}L']^- + CO \qquad k_{sub} \qquad (11)$$

$$[M_mL(CO)_{n-1}L']^- \rightleftharpoons M_mL(CO)_{n-1}L' + e^- \qquad E^\circ_2 \qquad (12)$$

The initial one-electron reduction at E°_1 gives the radical anion $[M_mL(CO)_n]^-$, which undergoes rapid exchange of carbonyl for the donor L′ (eq 11). Owing to the fact that L′ is a stronger donor than the carbonyl it replaced, E°_2 is more negative than E°_1 (i.e., $E^\circ_2 < E^\circ_1$), and the substitution product $[M_mL(CO)_{n-1}L']^-$ is oxidized as it is formed (eq 12).[173] There is no net transfer of electrons, resulting in the overall electron-transfer-catalyzed (e.t.c.) substitution reaction[174] of eq 13:

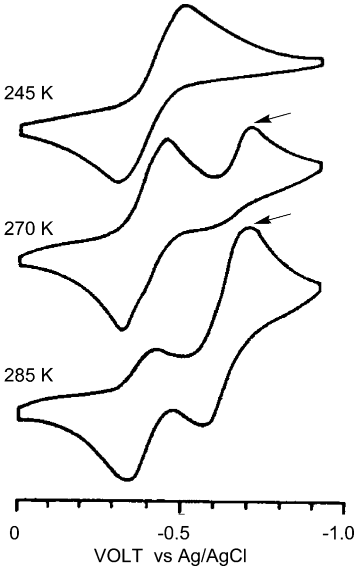

Figure 33. Cyclic voltammograms at three different temperatures for 1 mM $Co_3(CO)_9(\mu\text{-}CPh)$ in the presence of 1 mM PPh_3, adapted from ref 172. The more negative wave denoted by the arrow is that of the substitution product $Co_3(CO)_8(PPh_3)(\mu\text{-}CPh)$. Note that as the temperature increases, conversion to the substitution product becomes more prominent. Scan rate constant at 1.38 V s^{-1}.

$$M_mL(CO)_n + L' \xrightarrow{\text{e.t.c.}} M_mL(CO)_{n-1}L' \qquad (13)$$

Since this reaction requires a large k_{sub} value to proceed at a reasonable rate, it is reasonable to ask why substitution of the 19 e^- complex $[M_mL(CO)_n]^-$ should be so greatly accelerated over that of its 18 e^- precursor. Whereas some 19 e^- metal carbonyl complexes may lose a carbonyl ligand, their tendency toward CO lability is diminished by increased backbonding. The authors[172] therefore postulated an associative mechanism made possible by cleavage of a M−M bond in the primary anion radical $[M_mL(CO)_n]^-$, creating a 17 e^- metal center capable of accepting L′ in the transition state (see Figure 34, based on the dicobalt system $Co_2(CO)_6(\mu\text{-}C_2R_2)$). A number of papers on e.t.c. substitution processes of these complexes as well as the metal cluster compounds $Co_3(CO)_9(\mu_3\text{-}CR)$ followed rapidly, thanks to the efforts of Rieger and his occasional collaborators in New Zealand and Australia: Bruce, Downard, Robinson, and Simpson.[175] An important aspect of this work, some of which involved a mixture of electrochemistry and chemical redox reactions, was that the substitution reactions were taken beyond the voltammetric to the synthetic level.

Efficient reductive e.t.c. carbonyl substitution reactions of *mono*nuclear complexes were not reported until some time later,[176] and a convincing argument for a dissociative mechanism (CO loss from the 19 e^- intermediate) did not appear until

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[170] Reference 2 contains over 240 pages on the topic of reactions of redox-induced and radical reactions of transition metal complexes, most of which are organometallic.

[171] Basolo, F. *New J. Chem.* **1994**, *18*, 19.

[172] Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265.

[173] The oxidation of $[ML(CO)_{n-1}L']^-$ occurs through either a heterogeneous process (at the electrode) or a homogeneous reaction with $ML(CO)_n$.

[174] Mechanistically similar electrochemical examples were already known for organic and inorganic systems. See: Feldberg, S. W.; Jeftic, L. *J. Phys. Chem.* **1972**, *76*, 2439.

[175] (a) Bruce, M. I.; Kehoe, D. C.; Matisons, J. G.; Nicholson, B. K.; Rieger, P. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442. (b) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K.; Williams, M. L. *J. Organomet. Chem.* **1982**, *236*, C57. (c) Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (d) Arewgoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893. (e) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1122. (f) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1132 (g) Downard, A. J.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1140 (h) Bruce, M. I. *Coord. Chem. Rev.* **1987**, *76*, 1.

[176] (a) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130. (b) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471.

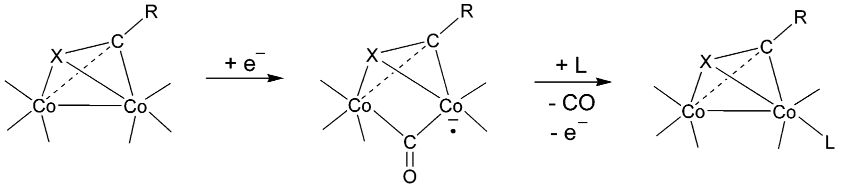

Figure 34. Mechanism postulated for substitution of CO by PPh_3 in ref 172, X = RC or $Co(CO)_3$, lines = CO, L = PPh_3.

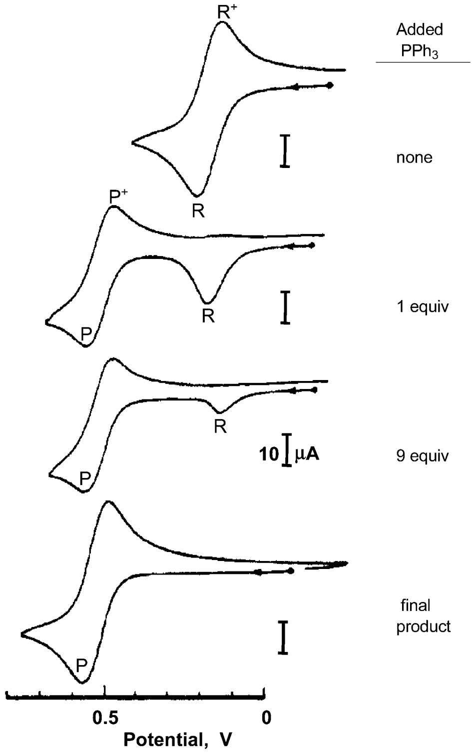

Figure 35. CV scans of 1 mM $Mn(C_5H_4Me)(CO)_2(NCMe)$ (R) in the presence of increasing amounts of PPh_3. The wave at $E_{1/2} = 0.55$ V arises from the phosphine-substituted product $Mn(C_5H_4Me)(CO)_2(PPh_3)$ (P), measured for the genuine compound in the lowest scan. The smaller, non-diffusional-shaped "prewave" (E_{pa} 0.2 V vs SCE) in the two mixed solutions is due to oxidation of R. No reverse wave is seen for R^+ at this scan rate (0.2 V s^{-1}) owing to its rapid substitution. Adapted from ref 178c.

1994.[177]Almost co-incident with the Rieger discoveries were those of Kochi et al., who were taking an *oxidative* approach to e.t.c. substitution chemistry. This allowed for the direct generation of a 17-electron system having a weakened M−CO bond and an electronic configuration favoring an associative substitution process. The oxidative approach has the important advantage of broadening the electrochemical substitution method to include monometallic systems. However, it suffers from the fact that the very strong accepting character of the carbonyl group makes the $E°$ potentials of M−CO complexes very high compared to their M−L′ counterparts, essentially eliminating the thermodynamic driving force for the catalytic production of M−L′. To counter this restriction, Kochi's group changed their "starting material" from $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$ to $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2L$, where L was a strong donor ligand, either pyridine or acetonitrile. E.t.c. substitution was then possible, and a series of complexes $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2L'$ was prepared having weaker donor groups, such as phosphines, phosphites, or isonitriles (e.g., eq 14).[178,179]

$$Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(NCMe) + L' \xrightarrow{\text{e.t.c.}} Mn(\eta^5\text{-}C_5H_4Me)(CO)_2L' + NCMe \quad (14)$$

Figure 35 shows the types of voltammograms observed in these processes, this set describing the changes when increasing amounts of PPh_3 are added to a solution containing $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(NCMe)$.[178c] With phosphine addition, the anodic wave of the acetonitrile complex ($E_{1/2} = 0.15$ V vs SCE) grows smaller and finally disappears as the cation $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(NCMe)]^+$, produced at the electrode, reacts rapidly to form the substitution product $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(PPh_3)]^+$, which is immediately reduced to its neutral form, providing the new reversible wave for $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(PPh_3)]0/^+$ at $E_{1/2} = 0.55$ V. At higher scan rates, the currents for the more positive wave decrease relative to those of the first as the reaction time becomes insufficient for completion of the substitution process, allowing determination of the substitution rate constants. From a well-designed series of measurements, Kochi et al. were able to differentiate the effects on the substitution rate constant, k_{sub}, of the Brønsted basicity of the entering ligand L, that of the leaving ligand L′, and the cone angle (θ) of the entering ligand (eq 15).

$$\log k_{sub} = 17 - 0.15\ pK_a^{\ L} + 0.28\ pK_a^{\ L'} - 0.12\ \theta \quad (15)$$

This definitive and quantitative voltammetric treatment was aided by the involvement of Christian Amatore, working at the University of Houston through a cooperative NSF-CNRS program.[178d] Although the substitution rates for these systems, exceeding 10^4 M^{-1} s^{-1}, are not as great as those seen for some photochemically generated 17 e$^-$ neutral radicals such as $Mn(CO)_5$,[180] they greatly exceed those of the thermal reactions of their 18 e$^-$ precursors, which are generally too slow to measure.

A later study by Trogler and co-workers of the substitution reactions of $[Fe(CO)_3(PR_3)_2]^+$ by pyridine showed that the substitution rates of the electrochemically generated 17 e$^-$ complexes were about 10^9 faster than their 18 e$^-$ counterparts.[181] An associative mechanism involving a 19 e$^-$ transition state structure is apparently often responsible for the greatly accelerated reactions of 17 e$^-$ systems with nucleophiles.[182]

Although anodically induced e.t.c. catalysis offers an efficient pathway to a number of substitution products from a single

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[177] Huang, Y.; Neto, C. C.; Pevear, K. A.; Holl, M. M. B.; Sweigart, D. A.; Chung, Y. K. *Inorg. Chim. Acta* **1994**, *226*, 53.

[178] (a) Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem Commun.* **1982**, 212. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3034. (c) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (d) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

[179] Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

[180] Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700.

[181] Therien, M. J.; Ni, C.-L.; Anson, F. C.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037.

[182] (a) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (b) Tyler, D. R. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1988; Vol. 36, pp 125 ff. (c) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 4942. (d) Song, L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 3355. (e) For acceleration of CO addition to a 17 e$^-$ complex see: Dixon, F. M.; Masar, M. S., III; Doan, P. E.; Farrell, J. R.; Arnold, F. P., Jr.; Mirkin, C. A.; Incarvito, C. D.; Zakharov, L. N.; Rheingold, A. L. *Inorg. Chem.* **2003**, *42*, 3245.

starting material, its synthetic utility suffers from the need to do the substitution on a compound having a strong donor ligand, which must usually be prepared from the beginning carbonyl complex. This extra step could be avoided through an electrochemical "switching" scheme[183] in which the parent metal carbonyl compound $ML(CO)_n$ is oxidized in the presence of the donor ligand L′ (eq 16), after which the substituted cation, $[ML'(CO)_{n-1}]^+$, is reduced back to the desired 18-electron neutral complex (eq 17). Although the literature is replete with

$$ML(CO)_n + L' - e^- \rightarrow [ML'(CO)_{n-1}]^+ + L \qquad (16)$$

$$[ML'(CO)_{n-1}]^+ + e^- \rightarrow ML'(CO)_{n-1} \qquad (17)$$

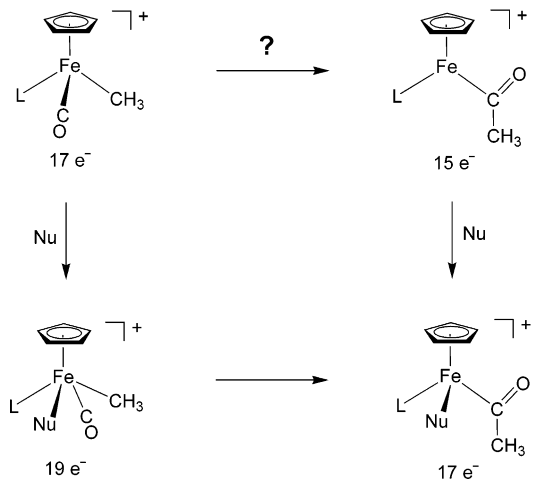
such examples observed by CV,[184] we are not aware of descriptions of synthetic-level switching-based substitution chemistry. The reasons for this are largely technical and could be overcome with modification of the experimental conditions, most importantly in the choice of the supporting electrolyte anion. We have, for example, obtained high yields of $Cr(\eta^6\text{-}C_6H_6)(CO)_2L$ (L = phosphine or phosphite) from $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ by electrochemical switching in gentle electrolytic media containing weakly coordinating anions.[185]

XI.B. Oxidatively Induced Migratory Insertion. Another reaction that is greatly accelerated in 17 e^- complexes is that of migratory insertion of CO into a metal−alkyl bond. Although chemical oxidants were known to catalyze this important reaction, it was not until the 1980 report of Magnuson, Giering, and co-workers that one-electron processes were shown to be involved.[186] Anodic oxidation of $FeCp(CO)_2(CH_3)$ is irreversible ($E_{pa} \approx 0.48$ V vs Fc), but in acetonitrile a product wave ($E_{1/2} = -0.22$ V) attributed to the relatively persistent solvent-coordinated iron *acyl* cation radical $[FeCp(MeCN)(CO)(COCH_3)]^+$ was observed (eq 18):

$$FeCp(CO)_2(CH_3) - e^- + MeCN \rightarrow [FeCp(MeCN)(CO)(COCH_3)]^+ \qquad (18)$$

Although the reversibility of eq 18 was not demonstrated, when it was assumed to be so for purposes of estimating the extent to which the reaction was favored for the 17 e^- radical $[FeCp(CO)_2(CH_3)]^+$ over its 18-electron precursor, an increase of 10^{12} in K_{eq} was calculated and an increase of 10^{13} in k_f was estimated.[187] Controversy about the mechanism of this process was subsequently introduced through an electrochemical study by Therien and Trogler,[188] which focused on the related phosphine derivative $FeCp(CO)(PPh_3)(CH_3)$. Since the one-electron oxidation of the phosphine compound is reversible in CH_2Cl_2 ($E_{1/2} = 0$ V vs Fc), the response of the 17 e^- cation to a systematic addition of MeCN or pyridine could be probed. A debate ensued over whether the migratory insertion occurred before or after uptake of the nucleophile, i.e., in the 17 e^- system (Scheme 5, top) or in the 19 e^- system (Scheme 5, bottom). Further studies favored the latter and brought attention to the involvement of solvent-coordinated radicals.[189] Perhaps relevant to the mechanistic question is Vlćek's earlier observation of migratory insertion in the 19 e^- anion $[FeCp(CO)_2(CH_3)]^-$.[190] Whatever the mechanistic details, the chief observation is that migratory insertion is greatly accelerated in organometallic radicals.[191]

Scheme 5



XI.C. Acidity of 17 e⁻ Metal Hydrides. Whereas the previous two sections refer to redox-driven kinetic enhancements, we turn now to the use of electrochemistry in deriving important thermodynamic data, specifically the pK_a values and homolytic M−H bond dissociation enthalpies (BDE) of metal hydrides.

One-electron oxidation greatly enhances the acidity of metal hydrides. In investigations of a number of such systems, Tilset et al. found almost no evidence for a reversible oxidation process, rapid deprotonation of the initially formed 17 e^- species accounting for the reaction products.[192] The follow-up reactions of the deprotonated radical can be complex. For example,[193] the 17 e^- complex $[RuCp(CO)(PMe_3)H]^+$ (**A**$^+$ in Figure 36) may transfer a proton to a weak (perhaps adventitious) base,

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[183] Here "switching" refers to turning a reaction on and off by cycling the system between two different redox states. For conceptual aspects forming the basis of this extensive literature see: (a) Feringa, B. L., Ed. *Molecular Switches*; Wiley-VCH Publishers: Weinheim, 2001. (b) Ratner, M. A.; Jortner, J. *Molecular Electronics*; Blackwell Science: Malden, 1997.

[184] A clever combination of redox switching and enhanced substitution rates is based on the oxidation of $Cr(\eta^6\text{-}C_6H_5Fc)(CO)_3$ (Fc = ferrocenyl) in the presence of phosphites. The cation generated by oxidation of the ferrocenyl group has sufficiently reduced electron density at Cr to undergo substitution reactions. This study was complicated by the tendency of oxidized $Cr(arene)(CO)_3$ complexes to undergo nucleophilic attack by electrolyte anions. See: Yeung, L. K.; Kim, J. E.; Chung, Y. K.; Rieger, P. H.; Sweigart, D. A. *Organometallics* **1996**, *15*, 3891.

[185] 50 mg quantities of pure $Cr(\eta^6\text{-}C_6H_6)(CO)_2(PPh_3)$ and $Cr(\eta^6\text{-}C_6H_6)(CO)_2(P(OPh)_3$ have been obtained through switching electrolyses in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ and extraction of the electrolyte by hexane (Nicole Camire Ohrenberg and Russell DeWitte, unpublished work, University of Vermont, paper in preparation).

[186] Magnuson, R. H.; Zulu, S. J.; T'sai, W-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6888.

[187] Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790.

[188] Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127.

[189] Fernandez, A. L.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 2784, and references therein.

[190] Micholová, D.; Vlek, A. A. *J. Organomet. Chem.* **1982**, *240*, 413.

[191] (a) Bly, R. S.; Silverman, G. S.; Bly, R. K. *Organometallics* **1985**, *4*, 374. (b) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. (c) Sheridan, J. B.; Han, S-H.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 8097. (d) Gipson, S. L.; Kneten, K. *Inorg. Chim. Acta* **1989**, *157*, 143. (e) (More recently) Pospíšil, L.; Hromadová, M.; Fiedler, J.; Amatore, C.; Verpeaux, J.-N. *J. Organomet. Chem.* **2003**, *668*, 9. For a review of nonredox approaches to migratory insertions, see: Ford, P. C.; Massick, S. *Coord. Chem. Rev.* **2002**, *226*, 39.

[192] Some metal hydrides having strong donor ligands, e.g., $RuCp(PR_3)_2H$, give 17 e^- cations that are more persistent. For such a system in which the radical cation in MeCN may protonate the starting material, see: (a) Ryan, O. B.; Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1991**, *421*, 315. Smith, K.-T.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681. See also: (b) Pilloni, G.; Schiavon, G.; Zotti, G.; Zecchin, S. *J. Organomet. Chem.* **1977**, *134*, 305. (c) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163. (d) Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808. (e) Pleune, B.; Poli, R.; Fettinger, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 3257.

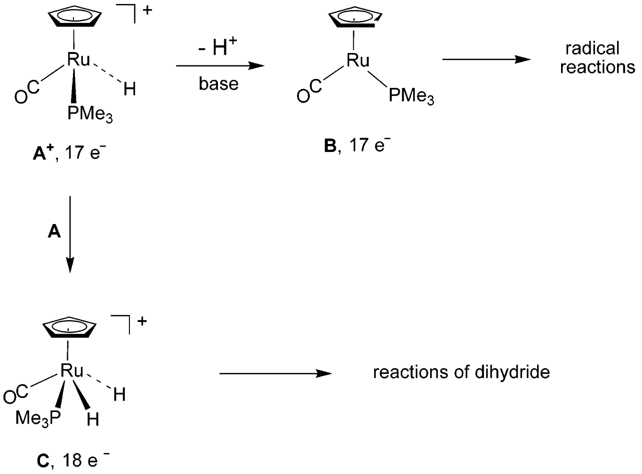
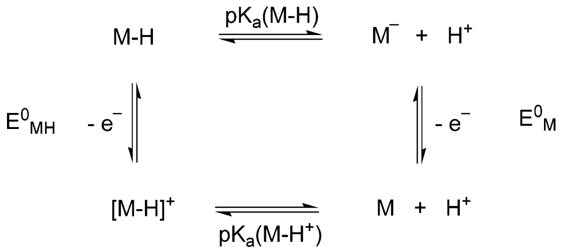


Figure 36. Partial description of reactions involving the 17 e− metal hydride complex $[RuCp(CO)(PMe_3)H]^+$. See ref 193 for more detailed account.

Scheme 6



forming the very reactive neutral radical **B**, or obtain one from another mole of the original 18 e− compound **A**, thereby forming the equally reactive dihydride (or dihydrogen) complex **C**.

The specific nature of the ultimate reaction products is of less importance to our discussion than the fact that oxidation greatly increased the acidity of the original 18 e− complex. Tilset explored this quantitatively for a number of important metal hydride complexes, providing reasonable estimates of how the pK_a and BDE values change with changes in redox state.

The thermodynamic cycles shown in Scheme 6, which had been employed earlier for pK_a measurements of organic systems,[194] comprised the heart of the analysis. If three of the thermodynamically significant quantitites are known, the fourth may be calculated.

One set of compounds for which values of pK_a(M−H) and $E°_M$ were already known was that of the half-sandwich hydrides $MCp(CO)_3H$ (M = Cr, Mo, W). Measurement of the missing $E°_{MH}$ values gave the desired pK_a units for $[M - H]^+$ through eq 19 (298 K, $E°$ values in volts):

$$\mathrm{p}K_a(\mathrm{M{-}H^+}) - \mathrm{p}K_a(\mathrm{M{-}H}) = [E°_{\mathrm{MH}} - E°_{\mathrm{M}}]/\,0.059 \qquad (19)$$

The pK_a values of the 17 e− complexes, which were as low as −9.5 for $[CrCp(CO)_3H]^+$, decreased by the startling amount of 20.6 ± 1.5 with loss of an electron from the 18 e− complex.[195] This was shown[196] to correspond to a decrease of about 10 kcal/mol in the M−H BDE in the radical cation. Quantitative insight into ways that alterations in (i) ligand type (e.g., PR_3 vs CO), (ii) ligand substituents (e.g., Cp vs Cp*), and (iii) the type of metal (especially, first-row versus second and third) affect metal-hydride acidity came from this work and from subsequent studies employing the thermo-electrochemical approach.[196,197]

An interesting extension of thermo-electrochemical cycle calculations was made to determine the acidities of methyl hydrogens in the π-ligands of metal−arene complexes.[198] Astruc and co-workers calculated that the 17 e− mixed-sandwich dications $[Fe(\eta^5\text{-}C_5R_5)(\eta^6\text{-}C_6Me_6)]^{2+}$ (R = H or Me) had pK_a values that were up to 40 units lower than their 18 e− counterparts. These authors also tracked acidities and enthalpies of homolytic C−H cleavage for the benzylic hydrogens, in several oxidation states, and compared them to those of the free arenes (e.g., hexamethylbenzene).[198]

[**Parenthetic Aside L.** The majority of the metal-hydride $E°_{MH}$ values were not directly measured owing to the chemical irreversibility of the couple $MH - e^- \rightarrow M + H^+$. Therefore most of the calculations used values of E_{pa} (when referring to an oxidation) as an approximation of $E_{1/2}$(MH), which is close to the value of $E°_{MH}$. Both the direction and amount of error introduced by this approximation depend on the cause of the irreversibility. In short, if an anodic reaction is electrochemically irreversible (an $E_{irrev}C$ process in which the electron-transfer step is slow), using E_{pa} in place of $E_{1/2}$ introduces a *positive* error, the amount of which is essentially the overpotential of the measurement, which in turn depends on the heterogeneous electron-transfer rate constant and the scan rate. If the EC process has rapid charge transfer followed by a fast follow-up reaction ($E_{rev}C$, which is likely in the present case), using E_{pa} introduces a *negative* error in $E_{1/2}$, the amount of which depends on the rate of the follow-up reaction.[199] There are standard voltammetric tools for diagnosis of the mechanism (and hence the sign of the error), but it is much harder to quantify the *amount* of the error. A partial discussion of the $E_{rev}C_{fast}$ case is available.[196]]

XII. Important Omissions

Owing to the limits of the present review, there are many important topics and areas of organometallic electrochemistry not discussed here. Among them are the following.

(1) *Mixed-Valence Chemistry*. This rich and still expanding area is the subject of ongoing papers and reviews[200] and is being

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[193] (a) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554. (b) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organmetallics* **1991**, *10*, 298. (c) Smith, K.-T.; Romming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681.

[194] (a) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741, and references therein. (b) Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175. (c) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905. (d) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979. (e) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1989**, *111*, 1792. (f) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

[195] (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (b) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740.

[196] The M−H BDE of the 18-electron system, for instance, was shown to obey the equation BDE = 1.37 pK_a + 23.06 $E°_M$ + 59.5 if the redox potential was measured versus ferrocene. See: Parker, V. D.; K. L. Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493.

[197] (a) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935. (b) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51.

[198] Astruc, D. *Acc. Chem. Res.* **2000**, *33*, 287.

[199] The value of E_{pa} shifts negative by approximately 30 mV for each 10-fold increase in the rate of the chemical follow-up reaction after a reversible electron transfer. Since a first-order follow-up reaction only begins to substantially affect the value of E_{pa} when its rate constant exceeds 10^2 s^{-1}, assuming a CV scan rate of 1 V s^{-1}, the error in $E°$ is approximately 8 × −30 mV (−240 mV) up to the diffusion-controlled limit of 10^{10} s^{-1}. A positive error in $E°$ occurs for a cathodic process.

[200] (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (b) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (c) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755. (d) Demadis, K. D.; Hartshorn, C. M.; Meyer, T. J. *Chem. Rev.* **2001**, *101*, 2655. (e) Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275.

developed in hope of applications to molecular electronics.[201] Early organometalllic papers in this area described biferrocene-type molecules.[202]

(2) *Multielectron Processes*. Here we are mainly referring to compounds that undergo net two-electron events within a single CV cathodic/anodic wave pair. The broadest and most interesting subset of these systems is that involving an electronic or structural effect, such as formation of a metal−metal bond, which thermodynamically facilitates the electrostatically more difficult second electron transfer. The molecular and environmental factors that favor two-electron processes, some of which have been mentioned above, are still being disclosed, and interested readers are referred to the literature.[203] A separate subcategory of multielectron processes is that of dendrimers having redox-active groups at either their edges or interiors.[204] The ways in which the fundamental electrochemical properties of dendrimers differ from those of the corresponding small molecule have begun to be studied.[205]

(3) *Metal Clusters*. Electrochemistry has proven to be a powerful tool aiding the investigation of how the structures of metal clusters are related to the number of valence electrons in the cluster. References through about the year 2000 are given in a chapter of Zanello's book,[206] and there are leading references in the journal literature.[207]

(4) *Redox Mediators*. The intensely studied electron-transfer mediation of ferrocene in sensor applications[208] is but one important example of this area of application.[209]

(5) *Electrocatalysis of Organic Reactions*. Prototypical examples in this area can be found in the investigations of Amatore and co-workers on the coupling reactions of aryl groups catalyzed by the cathodic reactions of Ni and Pd complexes.[210]

(6) *Parametrization of Electrochemical Ligand Effects*. A number of groups have addressed the effect of specific ligand changes on the $E_{1/2}$ potentials of their metal complexes, with the most comprehensive set of ligand electronic parameters being given in papers by Lever and co-workers.[211] A critique of the various models has recently appeared.[212]

(7) *Chemically Modified Electrodes*. For recent developments and leading references in this important area, including organometallic polymer-based electrodes, see recent reviews.[213−215] A very readable introduction to concepts and techniques in this area is available.[216]

(8) *Electrolyte Effects*. The role of solvent and supporting electrolyte in influencing the course of electrochemical reactions has been more intensely investigated for organic systems,[217] but the seminal paper[218] by Mann et al., using $[B(C_6H_3(CF_3)_2)]^-$ as the supporting electrolyte anion, has inspired systematic medium studies for anodic organometallic systems. Of critical importance is the low nucleophilicity of this and other so-called "weakly coordinating anions" (WCAs),[219] which has made possible the bulk anodic generation of a number of long-sought organometallic radical cations. Taking advantage of this change in supporting electrolytes, new chemistry has been described for the cation radicals of ruthenocene,[17] $CoCp(CO)_2$,[220,221] Cr-

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(201) For leading references to this very broad area see: (a) Reference 2, Chapter 4. (b) Launay, J.-P. *Chem. Soc. Rev.* **2001**, *30*, 386. (c) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175. (d) Ren, T. *Organometallics* **2005**, *24*, 4854. (e) A special issue of *Chem. Phys.* **2006**, *326*, pp 1−270.

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(9) *Methodology: The Contemporary Experimental Approach.* Naturally, there has been consistent growth in the techniques and approaches available to those utilizing electrochemistry in the study of organometallic redox processes. These now include fast-scan cyclic voltammetry; square-wave voltammetry; background-subtraction and minimization of resistance errors in voltammetry; computer simulations of voltammograms; ultramicroelectrodes; low-temperature electrochemistry; electrochemistry in dryboxes; spectroelectrochemistry; chemically modified electrodes; greater choices of solvents and supporting electrolytes; and DFT calculations for structural characterization of unstable products and intermediates.

XIII. Future Directions and Growth

Historically speaking, systematic organometallic electrochemistry can be said to have been initiated with the first set of papers[32−41] by the Dessy group in 1966. In the ensuing period of more than 40 years our understanding of how electron transfer affects the structures and reactions of organometallic compounds has become increasingly sophisticated, with electrochemistry acting as the linchpin for the physical, spectroscopic, synthetic, and computational efforts in these areas. Considering the breadth of this knowledge and the fact that redox reactions can effect dramatic changes in structure/reactivity relations, electrochemistry remains underutilized for organometallic applications, compared to its organic and inorganic counterparts (consider, for example, the widespread use of electrochemistry in organic synthesis).[224] The recent literature gives strong indications, however, that this situation is changing, as one easily notices organometallic redox processes applied to some of the currently most important problems facing chemistry, biochemistry, and nanotechnology. These include the production and release of dihydrogen,[225] the reduction of carbon dioxide,[226] advances in bioorganometallic chemistry,[227] development of new sensors[228] and nanostructured materials,[229] single-site catalysts,[230] surface-confined redox polymers,[231] opto- or magneto-electronic materials,[232] and molecular wires and other devices.[233] Further to this point, the general area of "redox switching", in which a physical or chemical property of a molecule or material is controlled by altering the redox state of a molecular redox tag,[234] is one rich with opportunities to go beyond the valued but simple and predictable behavior of attached ferrocenyl groups.

The fact that whatever predictions made in the present document about specific areas of growth will become rapidly out of date, as the next months of journal articles appear, speaks to the vibrancy of the field of organometallic electrochemistry. Putting aside nuclear reactions, there are only three sources of the energy required to run chemical reactions: heat, light, and electricity. Given the ubiquitous nature and intrinsic importance of electron-transfer reactions, applications and exploitations of the last of these energy options in organometallic systems promise to be limited only by the ingenuity of the chemical community.

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XIV. Appendixes

XIV.A. Ferrocene/Ferrocenium as a Standard Redox Potential. An abundance of different reference electrodes are used in electrochemical experiments (saturated calomel (SCE), Ag/AgCl, etc). The potentials of test compounds reported versus different reference electrodes can be compared, of course, by knowing the relative potentials of the electrodes. Owing to the fact that there may be alterations in the composition and function of reference electrodes from one laboratory to the next, a

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standard reference *couple* (as opposed to a reference *electrode*) was sought against which to compare the potentials of test compounds measured in different laboratories. Any redox couple serving as such a reference standard should have minimal, or ideally no, dependence of its $E°$ value on the solvent/supporting electrolyte medium in order to obviate errors introduced by the so-called liquid junction potential between the test solution and the reference electrode. These errors cause the measured potentials to vary by 100 mV or more in a largely unpredictable way as the medium is changed.[235] In a 1958 paper by Strehlow et al., [236] ferrocene was said to have the molecular and electrochemical properties to serve as a redox standard: an easily accessible one-electron Nernstian couple expected to have a medium-independent $E°$ owing to the oversimplified idea that its redox reaction involved a metal center ‘buried” by surrounding ligands. This working model of the ferrocene/ferrocenium redox standard was widely adopted, and in 1984 IUPAC recommended that it be used as a standard redox couple.[237] Most papers reporting organometallic electrochemistry now give potentials versus $FeCp_2^{0/+}$ or at least give the potential measured for ferrocene against the experimental reference electrode.

To what extent ferrocene fits the desired model of a medium-independent[238] redox couple has been the source of debate and experimental inquiry. One conceptual improvement is to add ring substituents that reduce the interaction of the compound with most solvents or with the electrolyte counteranion. To this end, decamethylferrocene has received considerable attention, with the most comprehensive study being that of Noviandri et al., who measured the difference between the $FeCp_2^{0/+}$ and $FeCp*_2^{0/+}$ couples in 28 nonaqueous solvents.[239] Changes in $\Delta E_{1/2}$ ($=E_{1/2}(FeCp_2^{0/+}) - E_{1/2}(FeCp*_2^{0/+})$) from a low of 427 mV in THF, increasing to 532 mV in CH_2Cl_2, to a high of 575 mV in trifluoroethanol, were interpreted as showing that the potential of the decamethylferrocene couple showed *less dependence* on solvent than did the ferrocene couple. Other studies have supported this finding and led to the conclusion that decamethylferrocene would make a superior standard redox couple.[240] Conversions between $FeCp_2^{0/+}$ and $FeCp*_2^{0/+}$ potentials are now available for many different media,[239,240] including mixed aqueous−organic solvents.[241] Surprisingly, studies integrating the effects of solvation versus ion-pairing are still lacking. Although the case for reporting of potentials versus $FeCp*_2^{0/+}$ is a strong one, the downside of such a change is the possible confusion that might arise owing to the fact that, for many years, literature potentials have been reported versus ferrocene.[242]

There are two experimental approaches to determination of the potential of a test compound versus the standard couple (ferrocene here, for the sake of discussion). One is to measure the test compound and ferrocene in two separate experiments, using the same reference electrode (e.g., Ag/AgCl). Subtraction of the ferrocene potential from that of the test compound gives the potential of the latter versus ferrocene. A second approach is the *in situ* method, in which both the test compound and ferrocene are present in the solution. This approach has the advantage of requiring a single measurement to determine the test potential, but suffers from the possibility that the presence of ferrocene in solution may alter the electrochemical behavior of the test compound.[243] The *in situ* method, to the best of our knowledge introduced in the literature by Gagne et al.,[244] works in most cases and has become widely employed.

One frequently finds papers in the literature wherein ferrocene was said to have been used as an internal standard, but the data are plotted and reported versus the normal hydrogen electrode (NHE). To the present author, doing so introduces unnecessary opportunities for error. The potential reported versus NHE for ferrocene, 0.40 V in water, [245] varies greatly with solvent. Lever and co-workers employed a value of 0.66 V for acetonitrile, based on more recent Russian work,[246] and noted that a value of 0.60 V is implied in the compilation of conversion tables for reference electrodes published by Bard and Faulkner.[247] A standard potential of 0.076 V versus NHE has been reported for ferrocene/ferrocenium in propylene carbonate.[248] The uncertainties about the medium effect on the ferrocene potential (*vide ante*) are certainly exacerbated when considering non-aqueous versus aqueous media. A safer practice, therefore, is to report electrochemistry in nonaqueous solvents against the ferrocene potential and that in aqueous solutions against a traditional reference electrode such as the SCE. At the very least, authors employing ferrocene as a reference standard but reporting potentials versus NHE must specify their method of converting the measured potentials to values versus NHE.

[**Parenthetic Aside M.** On the basis of the assumption that “burial” of the iron center beyond that in $FeCp*_2$ would further diminish medium-based alterations in the reference potential, Nicole Camire in my group measured the $E_{1/2}$ potentials of the highly sterically encumbered $Fe(1,2,4\text{-}(SiMe_3)_3C_5H_2)_2$, $FeCp^{Si3}_2$ (Okuda, J.; Herdtweck, E. *Chem. Ber.* **1988**, *121*, 1899) against $FeCp_2$ and $FeCp*_2$ in a representative group of solvents. Relevant to decamethylferrocene, we observed the following values for $E_{1/2}(FeCp^{Si3}_2) - E_{1/2}(FeCp*_2)$ with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte: 1,2 dimethoxyethane, 550 mV; THF, 526 mV; CH_3CN, 477 mV; CH_2Cl_2, 472 mV; 1,2 dichloroethane, 459 mV. The fact that the $E_{1/2}$ difference changes by 91 mV within this range of solvents suggests to us that medium effects are still exerting an influence on the $E_{1/2}$

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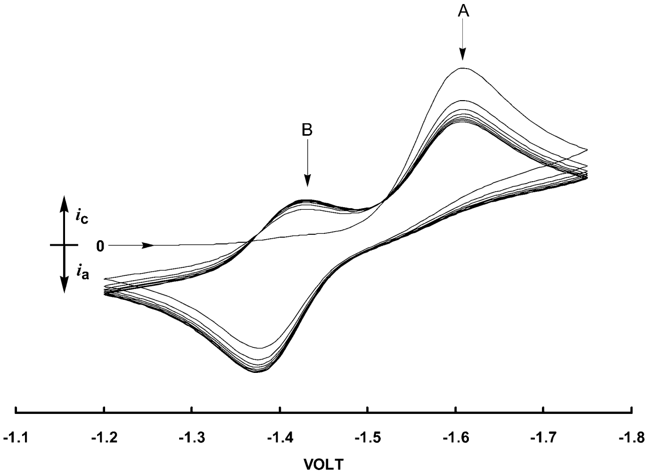

Figure 37. Simulated CV curves for a square scheme in which Ox(A) and Ox(B) are in equilibrium favoring Ox(A), whereas Red-(A) rapidly isomerizes to Red(B) as it is produced cathodically. The small cathodic feature for the reduction of Ox(B) in the initial scan (with arrow) increases upon cycling back and forth as the number of scans increases. The results of eight consecutive scans, taken without pause, are shown.

of decamethylferrocene. Electrolyte anion ion-pairing effects were not addressed.]

XIV.B. Recommendations for Publication of Cyclic Voltammograms. Here we do not intend to get into diagnostic aspects of cyclic voltammograms, which are treated in-depth in many other places. Rather, a few comments are in order with the goal of increasing the quality and clarity of published CV curves: (1) The community remains split on whether the first quadrant of a current/voltage plot should be used for positive potentials and anodic currents (the IUPAC convention) or negative potentials and cathodic currents (the traditional or "polarographic"[249] convention, which was used almost exclusively for many decades). As long as the *y*-axis contains proper labels for the directions of cathodic (i_c) and anodic (i_a) currents, these alternative approachs to plotting CVs need cause no serious problems, but the directions of i_c and i_a must always be shown. No CV curve should be published without designating the *y*-axis sensitivity (usually in μA), and the *point of zero current* should always be specified. (2) The CV shown should be that of the *first* scan from the rest potential at which it was initiated (see Figure 37 for a comparison of first and subsequent scans for a square-scheme process).[250] The direction of the initial scan should be shown by an arrow. (3) The *x*-axis may be labeled either versus the experimental reference electrode (e.g., SCE) or versus the reference couple (e.g., $FeCp_2^{0/+}$). If the former is used, the potential measured for the reference couple versus that reference electrode should be given in the experimental section, permitting the reader to make any desired potential conversions.

XIV.C. Note About Digital Simulations of CV Curves. Programs for the digital simulations of CV scans are now readily available. Although they can serve as powerful aides to mechanistic studies in electrochemistry, a few cautionary comments must be made. First, the experimental voltammogram must be of very high quality, ideally being obtained under conditions of charging current subtraction and *iR* compensation. Second, fits between theory and experiment must be tested at different scan rates. Finally, a successful fit proves only that the proposed mechanism and chemical parameters are *not inconsistent* with experiment, a logical conclusion know well to those who investigate chemical mechanisms in general. For more discussion of this point and sample voltammograms showing the need for fitting multiple scan rates, see: Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; pp 683 ff. For treatments of the theory and applications of digital simulations see: Feldberg, S. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1969; Vol. 3, pp 199 ff; Britz, D. *Digital Simulations in Electrochemistry*, 2nd ed.; Springer: Berlin, 1998; Rudolph, M. *J. Electroanal. Chem.* **2002**, *529*, 97.

XIV.D. A Potpourri of Useful Sources of Information

(1) An Introduction to Cyclic Voltammetry. Mabbott, G. A. *J. Chem. Educ.* **1983**, *60*, 697.

(2) Cyclic Voltammetry. Kissinger, P. T.; Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 702.

(3) Instructional Examples of Electrode Mechanisms of Transition Metal Complexes. Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; pp 683−718.

(4) Theory and practice of bulk electrolysis: Application of Controlled Potential Coulometry to the Study of Electrode Reaction. Bard, A. J.; Santhanam, K. S. V. In *Electroanalytical Chemistry*; Bard, A. J. Ed.; Marcel Dekker, Inc.: New York, 1970; Vol. 4, pp 215−315.

(5) Determination of electrode areas and diffusion coefficients: (a) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; pp 214−217. (b) Diffusion coefficients of ferrocene in CH_3CN/0.1 M $[NEt_4][ClO_4]$ at various temperatures: 2.40×10^{-5} cm^2 s^{-1} (294 K); 1.70×10^{-5} cm^2 s^{-1} (273 K); 1.27×10^{-5} cm^2 s^{-1} (262 K); 1.07×10^{-5} cm^2 s^{-1} (252 K); 0.86×10^{-5} cm^2 s^{-1} (241 K); 0.76×10^{-5} cm^2 s^{-1} (233 K), as measured by chronoamperometry. See: Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (c) As an alternative standard for measurement of electrode area, use $D_o = 2.07 \times 10^{-5}$ cm^2 s^{-1} (ambient temp) for 9,10-anthraquinone in CH_3CN/0.6 M $[NEt_4][ClO_4]$, reported in: Howell, J. O.; Wightman, R. M. *Anal. Chem.* **1984**, *56*, 524.

(6) *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Reichardt, C., Ed.; Verlag Chemie: Weinheim, 1988.

(7) Frank, S.N.; Park, S.-M. Electrochemistry in the Dry Box. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; pp 569−582.

(8) Evans, D. H.; Lerke, S. A. Electrochemical Studies at Reduced Temperature. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; pp 487−510.

(9) Guide for determination of "edge diffusion" effects at planar disc electrodes: Voltammetric Measurement of Ultraslow Diffusion Rates in Polymeric Media with Microdisk Electrodes. Longmire, M. L.; Watanabe, M.; Zhang, H.; Wooster, T. T.; Murray, R. W. *Anal. Chem.* **1990**, *62*, 747.

(10) Michael, A. C.; Wightman, R. M. Microelectrodes. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.;

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[249] The great majority of dc polarograms were recorded by scanning to more negative potentials using strip-chart recorders. This gave a plot in which cathodic currents were "up" and negative potentials increased left to right.

[250] Much less desirable is the CV recorded after the triangular sweep has been repeated one or more times without stopping at the rest potential. Under the scan rates often employed for routine CV scans, such scans have an approximately "steady state" behavior, which may be misleading.

Kissinger, P. T.; Heineman, W. R., Eds.; Marcel Dekker Inc.: New York, 1996; pp 367−402.

(11) Heterogeneous versus homogeneous electron-transfer reactions: Solution Electron-Transfer Reactions in Organic and Organometallic Electrochemistry. Evans, D. H. *Chem. Rev.* **1990**, *90*, 739.

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(13) Electrochemical Parametrization in Sandwich Complexes of the First Row Transition Metals. Lu, S.; Strelets, V. V.; Ryan, M. F.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1996**, *35*, 1013.

(14) Nineteen-Electron Complexes and Their Role in Organometallic Mechanisms. Astruc, D. *Chem. Rev.* **1988**, *88*, 1189.

(15) Seventeen-Electron Metal Centered Radicals. Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

(16) Organometallic Ions and Ion Pairs. Kochi, J. K.; Bockman, T. M *Adv. Organomet. Chem.* **1991**, *33*, 51

(17) Electron Transfer and Charge Transfer: Twin Themes in Unifying the Mechanisms of Organic and Organometallic Reactions. Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

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