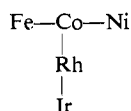


irreversible. Eleven other systems were chemically reversible, although electrochemically irreversible. Thus 39 systems gave long-lived stable reduction products. A general trend in generation of stable anion products can begin to be seen. The greatest success has been met with (a) $L_2Fe(CO)_3$ species, (b) $L_2Mo(CO)_4$, (c) S and P (see paper VI) bridged bimetallic systems, and (d) metal cluster systems (see paper VI). It is in these areas that intensive efforts are being made.

With the availability of these data within a closely defined series, and with the completion of the investigation of a series of 50 further samples provided by Professor R. B. King and Dr. Walter Hubel, a detailed discussion would seem possible. The availability of transition group derived organometallics with added electrons (as ion radicals) suggests that a fruitful area of study would be a comparison of the spectral and dimensional characteristics of the original neutral species and the ion radical. It would be expected that with the occupation of a low-lying orbital, these factors would be considerably altered. These possibilities are also being explored with suitable samples from the above list. At the moment the following observations are possible, however.

Dithietene Complexes. Systems 53, 58, 63, 114, and 128 indicate that for the T-shaped segment of Table I composed of



reduction potentials of the neutral chelate ($\pi-C_5H_5$)- $MS_2C_4F_6$ tend to become more cathodic as one traverses the table from right to left, or descends the table. Like the analogous $M(S_2C_4F_6)_2^{m-}$ compounds investigated by Davidson,¹¹ the processes involved are electrochemically reversible. There appears to be no observable correlation between this reduction potential sequence and those reported by Davidson, *et al.*

π -Complexed Cycloolefins. Systems 31–33 and 116, which involve (π -alkene) $Fe(CO)_3$ complexes, yield radical anions with no evidence of spin density on the organic ligand. Similar findings are observed for the ($\pi-C_5H_5$) $MS_2C_4F_6$ species (*cf.* system 53). Bipyridyl- $Mo(CO)_4$ radical anion, on the other hand, exhibits well-defined spin density on the ligand. The hyperfine coupling is markedly different from that reported for the bipyridyl anion radical.¹²

(π -Arene) Complexes. Systems 51, 76, 86, 121, and 129 indicate, in comparison to the reduction characteristics of the organic ligand itself, that complexation does lead to an alteration of this physical parameter, as might be expected. ESR spectra of polynuclear π -arene complex radical anions are being studied.

Acknowledgment. The authors wish to thank the Army Research Office, Durham, for its support and encouragement in the form of Grant USDA-ARO(D) 31-124-G681.

(11) See A. Davidson, N. Edelstein, R. H. Holm, and A. D. Maki, *Inorg. Chem.*, **3**, 814 (1964), and previous publications.

(12) J. Veiga, W. L. Reynolds, and J. R. Bolton, *J. Chem. Phys.*, **44**, 2214 (1966).

Organometallic Electrochemistry. VI.¹ Electrochemical Scission of Metal–Metal Bonds

Raymond E. Dessy, Paul M. Weissman, and Rudolph L. Pohl

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. Received May 23, 1966

Abstract: The electrochemical scission of over 50 compounds containing metal–metal bonds has been studied, and $E_{1/2}$ and n values have been obtained. For dimetallic compounds two modes of decomposition exist. The first involves acceptance by the assembly of two electrons and the production of two inorganoidal anions. The second route involves acceptance of only one electron and the production of an anion and a radical. In homodimetallic compounds only the first route is utilized; in heterodimetallic compounds either may be followed. When only one electron is accepted the anionic fragment may be predicted from a knowledge of the reduction potentials of the parent homodimetallic materials. The relationship between the reduction potentials, n values, and the nature of the metal–metal bond is discussed. Results with a few bridge and cluster systems are also reported.

Recently great interest has centered upon the formation of bonds between the metallic elements. Although limited catenation was considered to be a relatively rare type of bonding at one stage of development, it has now been claimed in some valence state for some, if not most, of the members of each family in the periodic table, except groups VIII and IIa.^{2–4} Of

the basic problems confronting the synthetic chemist in this area, three factors seem to be paramount: in the formation of a $m-m'$ liaison from $m:- + m'-x$ (or $m': + m-x$) (1) is the ΔF° favorable (strength of the $m-m'$ bond), (2) is $\Delta F_{m-m'}^\pm$ favorable (reasonable rate), (3) is $\Delta F_{m-m'}^\pm$ lower than the activation free

(1) For previous papers in this series, see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112 (1966).

(2) J. Lewis and R. S. Nyholm, *Chemistry*, 557 (1963).

(3) The symbol m is used to represent a metal, M , and one of its coordination or valence positions.

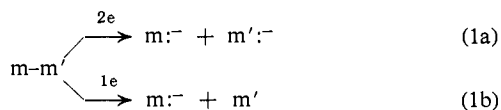
(4) W. E. Dasent, "Nonexistent Compounds," Marcel Dekker, Inc., New York, N. Y., 1965.

energy for any other process that $m:^-$ and $m-x$ may utilize in their interaction which leads to a different product than $m-m'$? This paper and the following two (papers VII and VIII) approach these problems in succession.

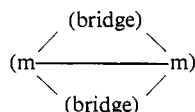
Results

In the dimetallic species, Lewis and Nyholm² found it convenient to define the oxidation state of each metal partner as the formal charge left on the atom in question after all ligands are removed with closed-shell configuration and all element-element bonds are ruptured homolytically. It is also convenient to assign a formal electron configuration to the atom in this state, *e.g.*, d^0 through d^{10} . Finally, it is of value to describe systems as homodimetallic (two alike elements joined together) or heterodimetallic (two unlike elements joined together).

A rather extensive series of compounds containing metal-metal bonds has been reduced at a mercury electrode in dimethoxyethane, employing tetrabutylammonium perchlorate as a supporting electrolyte (0.1 *M*). The reference electrode, employed in three-electrode geometry cells, was a 10^{-3} *M* $Ag^+|Ag$ couple. The apparatus and techniques have been previously described.¹ In conjunction with exhaustive controlled potential electrolysis data, these findings lead to the discovery of two common, and exclusive, routes for the electrochemical reduction of homo- and heterodimetallic assemblies³



These involve two-electron addition to the assembly leading to two metallic anions *via* scission of the parent metal-metal bond, or a one-electron reduction leading to one anion and a radical species. Employing the notations mentioned in the initial paragraph, the present findings are shown in Table I. The compounds are listed in order of complexity: (a) simple homo- and heterodimetallic compounds, (b) polymetallic substances, (c) bridged dimetallic species



and (d) cluster systems (*i.e.*, those in which at least three center molecular orbitals are involved).

Discussion

Homodimetallics. Data are available (systems 1, 2, 10, 11, 17, 18, 26-33, and 34-36) on analogs within six families. In groups VIb (Cr, Mo), VIIb (Mn, Re), and VIII (Fe, Ru) as one descends the table the reduction-scission of the metal-metal link requires more cathodic potentials. In groups IVa (Si, Ge, Sn, Pb), Va (As, Sb, Bi), and VIa (S, Se), reduction requires less cathodic potentials as one descends the table. These reductions are electrochemically irreversible processes, both on mercury and Pt microelectrodes, and therefore the potentials cannot be correlated directly to a thermodynamic function. However, one interesting partial correlation exists. The bond strengths in the catenated

main group elements are fairly well established, $m-m$ (D_{m-m} (kcal/mol)): si-si (42.2), ge-ge (37.6), sn-sn (34.2), as-as (32.1), sb-sb (30.2), bi-bi (25), s-s (50.9), se-se (44).⁴ Although the actual bond strengths among the transition series are not known, workers in the field tend to feel that stability *increases* as one descends the table.⁵ The parallel with reduction potentials is obvious.

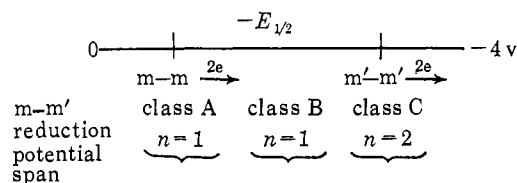
McDaniel⁶ has pointed out a derivation for the thermodynamic relationship between the pK_a of an acid, LH, the couple potential, E° , for the process $2L^- \rightleftharpoons L-L + 2e$, and the bond energy, D_{L-L}

$$1.36pK_a - 23.06E^\circ = D_{HL} - \frac{1}{2}(D_{H_2} + D_{L_2}) \quad (2)$$

In comparable two-electron irreversible reductions, such as C_2H_5-X , the empirical parallel between reduction potentials and bond strength is obvious [X , $-E_{1/2}$ (D_{C-X} in kcal/mole): Cl, no step (80); Br, 2.08 (67); I, 1.67 (51)]. As more data become available it is possible that a firm correlation will be found between metal-metal bond strengths and reduction potentials within a closely related series.

For those interested in large-scale chemical reduction syntheses of the anions described above, starting with the parent homodimetallic compound, a comparison of the present findings with King's reported reductions using tetrakis(dimethylamino)ethylene (TDAE) is essential.⁷ The oxidation potential ($n = 2$) of the latter is -1.2 v with respect to the present reference. King has reported that it will reduce $[(OC)_4Co]_2$ (-1.0 v) and $[CpMo(CO)_2]_2$ (-1.4 v) but not $[CH_3SFe(CO)_3]_2$ (-1.9 v) or $[CpNiCO]_2$ (-2.0 v). The reason for failure in the last two cases is now obvious. Although the electrochemical processes are not electrochemically reversible, precluding exact predictions, it appears safe to state that TDAE will reduce any homodimetallic with an $E_{1/2}^{redn}$ more anodic than -1.5 v but will fail if this potential is more cathodic than -1.5 v.

Heterodimetallics. Three classes of heterodimetallic reductions are observed



Class A comprises those heterodimetallic species which reduce at potentials more *anodic* than either of the homodimetallic parents (systems 6 and 12). Only one electron is required for reduction, the anion extruded being that whose homodimetallic parent has the most anodic reduction potential. The residual radical in the case of $(OC)_3Mn-Fe(CO)_2Cp$, $CpFe(CO)_2\cdot$, couples rapidly to yield $[CpFe(CO)_2]_2$, as evidenced by polarographic data before and after controlled potential electrolysis. A well-defined wave at $-E_{1/2} = 2.2$ appears in the polarogram of the original heterodimetallic compound and remains there after controlled-potential electrolysis at the first wave. The question of the radical fate with the $CpMo(CO)_3-$

(5) J. Lewis and R. B. King, Abstracts, 151st National Meeting of the American Chemical Society, March 22-31, 1966, Pittsburgh, Pa., Papers H-19 and H-45, respectively.

(6) D. McDaniel and A. Yingst, *J. Am. Chem. Soc.*, **86**, 1334 (1964).

(7) R. B. King, *Inorg. Chem.*, **4**, 1518 (1965).

Table I. Electrochemical Data for m-m' Systems

			$m-m' \xrightarrow[\text{Bu}_4\text{NClO}_4, 0.1 M]{e, \text{Hg}, (\text{CH}_3\text{OCH}_2)_2} \text{products}$			
System no.	Electronic config (m-m')	Oxidn state (m-m')	Compound (m-m')	$-E_{1/2}^a$	n	Product(s)
Homo- and Heterodimetallics						
1	d ⁵ -d ⁵	I-I	[CpCr(CO) ₃] ₂	1.3	2	2cr: ⁻
2			[CpMo(CO) ₃] ₂	1.4	2	2mo: ⁻
3	d ⁵ -d ⁰	I-III	CpMo(CO) ₃ -CH ₂ Ph	2.1	1	mo: ⁻ + R·
4			CpMo(CO) ₃ -CH ₂ COCH ₃	2.0	1	mo: ⁻ + R·
5			CpMo(CO) ₃ -CF ₃	2.1	1	mo: ⁻ + R·
6	d ⁵ -d ⁷	I-II	CpMo(CO) ₃ -Fe(CO) ₂ Cp	1.4	1	mo: ⁻ + ?
7	d ⁵ -d ¹⁰	I-III	CpMo(CO) ₂ -SnMe ₃	1.9	1	mo: ⁻ + sn·
8			CpMo(CO) ₃ -SnPh ₃	2.4	1	mo: ⁻ + sn·
9			CpMo(CO) ₃ -PbPh ₃	2.2	2	mo: ⁻ + pb: ⁻
10	d ⁷ -d ⁷	0-0	[(OC) ₅ Mn] ₂	1.7	2	2mn: ⁻
11		0-0	[(OC) ₅ Re] ₂	2.3	2	2re: ⁻
12	d ⁷ -d ⁷	0-I	(OC) ₃ Mn-Fe(CO) ₂ Cp	1.6	1	mn: ⁻ + fe·
13	d ⁷ -d ¹⁰	0-III	(OC) ₃ Mn-SnMe ₃	1.9	1	mn: ⁻ + sn·
14a			(OC) ₃ Mn-SnPh ₃	2.5	1	mn: ⁻ + sn·
b			(OC) ₃ Re-SnPh ₃	2.5	1	Unknown
15			(OC) ₃ Mn-PbEt ₃	1.8	1	mn: ⁻ + pb·
16a			(OC) ₃ Mn-PbPh ₃	2.1	2	mn: ⁻ + pb: ⁻
b			(OC) ₃ Re-PbPh ₃	2.4	1	Unknown
17	d ⁷ -d ⁷	I-I	[CpFe(CO) ₂] ₂	2.2	2	2fe: ⁻
18			[CpRu(CO) ₂] ₂	2.6	2	2ru: ⁻
19	d ⁷ -d ⁷	I-III	CpFe(CO) ₂ -C ≡	2.3-2.5	1-2	Not fe: ⁻
20			CpFe(CO) ₂ -SnPh ₃	2.6	1	fe: ⁻ + sn
21			CpFe(CO) ₂ PbPh ₃	2.1	2	fe: ⁻ + pb: ⁻
22	d ⁹ -d ⁹	0-0	[(OC) ₄ Co] ₂ ^b	0.9	2	2co: ⁻
23	d ⁹ -d ¹⁰	0-III	(OC) ₄ Co-SnMe ₃	1.6	1	co: ⁻ + sn·
24			(OC) ₄ Co-SnPh ₃	1.6	1	co: ⁻ + sn·
25	d ⁹ -d ⁹	I-I	[CpNi(CO)] ₂	2.4	2	2ni: ⁻
26	d ⁰ -d ⁰	I-I	PhS-SPh	1.6	2	2s: ⁻
27	d ¹⁰ -d ¹⁰	I-I	PhSe-SePh	0.9	1	se: ⁻ + se-hg
28	d ⁰ -d ⁰	III-III	Ph ₃ Si-SiPh ₃	No wave		
29	d ⁰ -d ¹⁰		Ph ₃ Si-GePh ₃	No wave		
30	d ⁰ -d ¹⁰		Ph ₃ Si-SnPh ₃	3.1	1	sn: ⁻ + si-H
31	d ¹⁰ -d ¹⁰	III-III	Ph ₃ Ge-GePh ₃	3.5	2	2ge: ⁻
32	d ¹⁰ -d ¹⁰		Ph ₃ Sn-SnPh ₃	2.9	2	2sn: ⁻
33	d ¹⁰ -d ¹⁰		Ph ₃ Pb-PbPh ₃	2.0	2	pb: ⁻
34	d ¹⁰ -d ¹⁰	II-II	Ph ₂ As-AsPh ₂	2.7	2	2as: ⁻
35			Ph ₂ Sb-SbPh ₂	2.5	2	2sb: ⁻
36			Ph ₂ Bi-BiPh ₂	2.3	2	2bi: ⁻
Polymetallics						
37	d ⁵ -d ¹⁰ -d ⁵	I-II-I	CpMo(CO) ₂ -Sn(Me) ₂ -Mo(CO) ₃ Cp	1.8	2	2mo: + Me ₂ Sn
38	d ⁷ -d ¹⁰ -d ⁷	I-II-I	CpFe(CO) ₂ -Sn(Me) ₂ -Fe(CO) ₂ Cp	2.7	2	2fe: ⁻ + Me ₂ Sn
39			[CpMo(CO) ₃] ₂ Sn[Fe(CO) ₂ Cp] ₂	1.8 2.0 2.5		
40	d ⁶ -d ¹⁰ -d ⁵	I-0-I	[CpCr(CO) ₃]Hg	1.3	2	2cr: ⁻ + Hg
41	d ⁶ -d ¹⁰ -d ⁵	I-0-I	[CpMo(CO) ₃] ₂ Hg	1.3	2	2mo: ⁻ + Hg
42	d ⁷ -d ¹⁰ -d ¹⁰	0-0-0	[(OC) ₅ Mn] ₂ Hg	1.1	2	2mn: ⁻ + Hg
43	d ⁷ -d ¹⁰ -d ⁷	I-0-I	[CpFe(CO) ₂] ₂ Hg	2.0	2	2fe: ⁻ + Hg
44	d ¹⁰ -d ¹⁰ -d ¹⁰	III-0-III	Ph ₃ Sn-Se-SnPh ₃	2.4	1	Ph ₃ SnSe: ⁻ + sn ⁻
45			Ph ₃ Sn-Se-GePh ₃	2.4	1	Ph ₃ SnSe: ⁻ + geH
Bridged Species						
46	d ⁴ -d ⁴	II-II	[CpMo(CO)PPh ₂] ₃	2.0	...	Stable redn species
47	d ⁸ -d ⁸	I-I	[(OC) ₄ CrPMe ₂] ₂	1.8	2	Stable dianion
48			[(OC) ₃ WAsMe ₂] ₂	1.8	2	Stable dianion
49	d ⁷ -d ⁷	I-I	[(OC) ₃ FePMe ₂] ₂	2.0	2	Stable dianion
50			[(OC) ₃ FeAsMe ₂] ₂	1.9	2	Stable dianion
51	d ⁸ -d ⁸	0-0	Fe ₂ (CO) ₉	2.4	2	Stable dianion
	d ⁹ -d ⁹	I-I	[CpNi] ₂ ·HC≡CH	2.2	2	Stable dianion
Cluster Systems						
52			[CpMo(CO)P(Ph) ₂] ₃	2.0	...	Stable redn species
53			[CpFe(CO)] ₄	1.9	Cycles	...
54			[CpCo(CO)] ₃	1.6	1	Stable anion
55			Cp ₃ Ni ₃ (CO) ₂	1.5	1	Stable anion

^a V_s . 10⁻³ M Ag⁺|Ag electrode. ^b Done in CH₂Cl₂; pilot ion studies show negligible voltage correction needed. Co₂(CO)₈ is unstable in glyme.

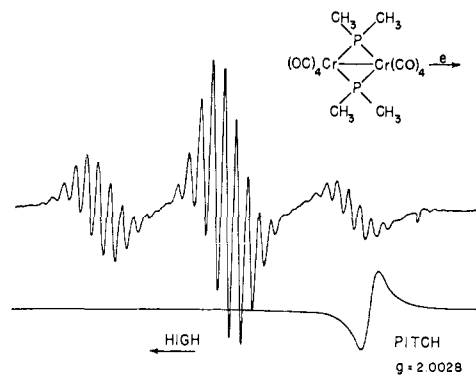


Figure 1.

$\text{Fe}(\text{CO})_2\text{Cp}$ is less certain. No second wave is apparent, nor is there any esr signal in the solution after controlled-potential electrolysis, precluding radical anion formation.

Class C comprises those species which reduce at potentials *more cathodic* than either homodimetallic parent (systems 9 and 16). Two electrons are required for reduction, both fragments being extruded as an anion, the latter being identified by comparison with the oxidative polarograms shown by reduced solutions of the parent homodimetallic, where it is known that anions are produced.

The vast majority of compounds lie in class B where the reduction potential of the heterodimetallic material lies between that of the two parent homodimetallic materials. In all of these, barring $\text{CpFe}(\text{CO})_2\text{-PbPh}_3$ (system 21), $n = 1$. The anion extruded is again that whose parent homodimetallic has the most anodic reduction potential. The radical extruded couples to give its parent homodimetallic in solution as evidenced again by polarographic data both before and after controlled-potential electrolysis at the first wave. All cases involving Ph_3Sn , Ph_3Pb , and Et_3Pb as half of the heterodimetallic showed a second wave in addition to that reported in Table I at $-E_{1/2} = 2.9, 2.0,$ and 2.9 , respectively. This wave remained after the first had been removed by the exhaustive electrolysis. ($\text{R}_3\text{Sn-SnR}_3$, where R is alkyl, does not reduce before supporting electrolyte.) In the $\text{CpFe}(\text{CO})_2\text{-PbPh}_3$ case, the reduction potentials of the parent homodimetallic materials are separated by only 0.2 v, and $n = 2$. As reported previously, the $\text{CpFe}(\text{CO})_2\text{-C}\llcorner$ series shows variable n values, as R is modified, and the products do not include $\text{CpFe}(\text{CO})_2\text{:}^-$. The exact nature of the products is unknown, as are the products in the re-sn and re-pb systems (14b and 16b).

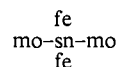
Of peculiar interest is the observation that in both the $\text{CpMo}(\text{CO})_2\text{-}$ and $(\text{OC})_5\text{Mn-}$ series the Me_3Sn derivatives reduced at potentials more anodic than Ph_3Sn , and in the latter case a similar story is true for Et_3Pb vs. Ph_3Pb . It is possible that this represents an extension of the concepts of Lewis and Nyholm,² who have pointed out that in heterodimetallic compounds where nonbonding d-electron interaction can lead to instability, electron-withdrawing ligands will reduce such interaction and increase stability. If this is so, the use of perfluoroalkyl and aryl groups could lead to a series of extremely stable metal-metal bond compounds.

Polymetallics. The polymetallic compounds investigated can be conveniently divided into three categories.

The first considers linear, symmetrical trimetallic species of the type m-Hg-m. Systems 40-43 show that the two-electron reduction to yield Hg and two anions occurs at potentials from 0.2 to 0.4 v more anodic than the corresponding m-m compound.

In linear trimetallics of the form m-Se-m', one-electron reductions occur to give m-Se:⁻ and m':[·] (which couples or abstracts) as systems 44 and 45 indicate.

Systems 37-39 suggest a potential synthetic and analytical application of this method. In the family shown, the two-electron reduction of a mo-sn-mo system (-1.8 v) occurs where one might expect ($\text{CpMo}(\text{CO})_3\text{SnMe}_3$, $-E_{1/2} = 1.9$ v) as does the reduction of the fe-sn-fe system (compare systems 20 and 38). The crossed system

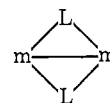


shows polarographic steps at $-E_{1/2} = 1.8, 2.0$ (ill-defined), and 2.5 (ill-defined), and it is suggested that one is observing the electrochemical amputation of organometallic side chains at each step. $\text{CpFe}(\text{CO})_2\text{-SnCl}_2$ shows three polarographic steps at $-E_{1/2} = 1.8, 2.0,$ and 2.7. Controlled-potential electrolysis at the third wave shows $n = 4-5$, while electrolysis at the first wave shows $n = 1$. In analogy with previous work on R_2SnCl_2 this could involve the intermediate production of an fe-sn-sn-fe system. This is under study.

Bridged Species. Although only a few examples of bridged complexes have been probed, it appears as if a very fruitful area has been opened.

Systems 50 and 51, $\text{Fe}_2(\text{CO})_9$ and $(\text{CpNi})_2\cdot\text{HC}\equiv\text{CH}$, have been reported previously, and their two-electron reduction, at potentials in close agreement with those found for unbridged homodimetallic species (systems 17, 24), suggested simple rupture of the metal-metal linkage and dianion formation. Reduced solutions of $\text{Fe}_2(\text{CO})_9$ showed no esr signal.

In systems of the type



where L is a member of group V (systems 46-49), a well-defined two-electron reduction is observed, systems 46 and 49 being electrochemically reversible. System 48 is nearly so, and system 47 is electrochemically irreversible. All systems showed chemical reversibility. System 46 ($[(\text{OC})_4\text{CrPMe}_2]_2$) was examined by esr spectrometry. The initial sample showed no signal, but upon reduction a clearly defined spectrum (Figure 1) due to a pale green species was observed. The main triplet, due to phosphorus ($I = 1/2$), gave $\Delta H_P = 12.87$ gauss; the fine structure on each, consisting of 13 lines due to the four equivalent CH_3 groups, gave $\Delta H_{\text{CH}_3} = 1.19$ g. The g value was 1.9936.

Either one is observing a rather interesting biradical species, the hyperfine splitting being remarkably well developed and characterized for such a configuration, or one is observing a signal due to a monoanion radical

formed by equilibrium of the original dianion with unreduced species in the environment. This, as well as similar systems, is being explored.⁸

Cluster Systems. The reductions of the four cluster systems studied (systems 52–55) are electrochemically reversible. Although the $[\text{CpFe}(\text{CO})_4]$ system appears to cycle electrons ($n > 5$ with little diminution in polarographic wave height), the other systems are one-electron reductions. The $[\text{CpCoCO}]_3$ shows an ill-defined wave at -1.6 v; triangular voltammetry at 1 v/sec sweep speeds shows two electrochemically reversible steps in this voltage region. King has reported that there are two forms of this compound; preferential crystalliza-

(8) NOTE ADDED IN PROOF. Subsequent studies indicate that the latter is the correct interpretation. Admixture of the yellow dianion and the red parent give the green radical anion.

tion of one form over another can be accomplished from solutions of either by careful choice of solvent. In systems 52, 54, and 55 reoxidation of the anions gave back starting material.

Acknowledgments. The authors wish to thank the Petroleum Research Foundation for its encouragement in the form of Grant 1086 A3,4. R. E. D. wishes to thank the Sloan Foundation for a fellowship during the years spent building the equipment which made the present study possible, and to thank M. A. Waldrop of Phillips Petroleum Co. for running the esr spectra. Finally, they wish to thank Professors R. B. King, M. Orchin, H. C. Clark, W. P. Neumann, and E. O. Fisher, and Drs. M. Dubeck and R. G. Hayter for some of the samples which made the project possible.

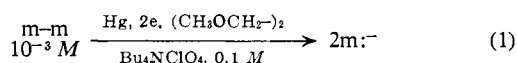
Organometallic Electrochemistry. VII.¹ The Nucleophilicities of Metallic and Metalloidal Anions Derived from Metals of Groups IV, V, VI, VII, and VIII

Raymond E. Dessy, Rudolph L. Pohl, and R. Bruce King

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Abstract: The nucleophilicities of 19 transition element and main group derived anions have been established by comparison of relative rates of reactivity with alkyl halides. Within groups VIb, VIIb, Va, and VIa, nucleophilicities increase as one descends the table. In group VIII (Fe, Ru) and IVa derived species, nucleophilicities decrease as one descends the table. The over-all span observed in relative rates exceeds 10^{12} . There is linear correlation between the $\log k_2'$ and the potential required to oxidize the anion to radical at a Pt electrode, in agreement with the postulate of Edwards for inorganic nucleophiles. The correlation should be useful in establishing the nucleophilicities of anions not studied in this investigation.

The previous papers in this series dissected the problems faced in the synthesis of a given metal-metal bond from $m:-$ and $m'-x$ into three categories, based on the thermodynamic or kinetic parameters that must be met in order to achieve a successful preparation. These were (a) a favorable ΔF° (strength of the $m-m'$ bond), (b) a low $\Delta F_{m-m'}^\ddagger$ (reasonable rate), and (c) $\Delta F_{m-m'}^\ddagger$ lower than the activation free energy of any other process that $m:-$ and $m'-x$ may utilize in their interaction which leads to a different product than $m-m'$. An extended study of the electrochemical reduction-scission of 55 compounds containing metal-metal bonds indicated that a possible parallel exists between the reduction potential and bond strength. In addition, reduction of the homodimetallic species by a process involving two electrons



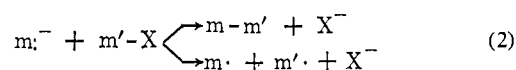
provided a convenient source of metal and metalloidal metallic compounds² at known, low concentrations.

(1) For previous papers in this series, see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, (1966).

(2) This nomenclature is due to the development of Professor J. Eisch. The term organometallic is reserved for species containing carbon-metal bonds; organometalloids cover the area of species containing

Thus controlled-potential electrolysis of the homodimetallic species reported in the previous paper in dimethoxyethane, with tetrabutylammonium perchlorate as a supporting electrolyte, gave stable solutions of the respective anion, with Bu_4N^+ gegenion.

Point b above refers to the nucleophilic activity of such anions, a parameter that could be evaluated by measurement of reaction rates with an electrophilic substrate. However, care must be observed in choosing a substrate to probe such nucleophilicity since the third paper in this series suggests strongly that electron-transfer processes are prevalent in anion-substrate interactions.



Since such processes appear to be more prevalent with highly active halogen compounds, and those possessing low-lying open orbitals, the present study reports on the rates of reaction of anions with simple aliphatic R-X compounds. By means of paired-triad sets ($m:- + \text{RX}$ and $\text{R}'\text{X}$, $m':- + \text{R}'\text{X}$ and $\text{R}''\text{X}$), the

carbon-metalloid bonds. Materials such as Ph_3SiLi are organoidal metallic species. The symbol m is used to represent a metal, M, and one of its coordination or valence positions.