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 $[CpFe(CO)]_4$ system appears to cycle electrons ($n > 5$ with little diminution in polarographic wave height), the other systems are one-electron reductions. The $[CpCoCO]_3$ 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 crystallization 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.

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[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.

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

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

Abstract: The nucleophilicites 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 $\Delta F°$ (strength of the m–m′ bond), (b) a low $\Delta F^{\pm}_{\mathrm{m-m'}}$ (reasonable rate), and (c) $\Delta F^{\pm}_{\mathrm{m-m'}}$ lower than the activation free energy of any other process that $\mathrm{m}:^-$ 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

$$\underset{10^{-3}\,M}{\mathrm{m{-}m}} \xrightarrow[\mathrm{Bu_4NClO_4},\ 0.1\,M]{\mathrm{Hg,\ 2e,\ (CH_3OCH_2-)_2}} 2\mathrm{m}:^- \qquad (1)$$

provided a convenient source of metal and metalloidal metallic compounds[2] at known, low concentrations. 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.

$$\mathrm{m}:^- + \mathrm{m'{-}X} \begin{cases} \rightarrow \mathrm{m{-}m'} + \mathrm{X}^- \\ \rightarrow \mathrm{m}\cdot + \mathrm{m'}\cdot + \mathrm{X}^- \end{cases} \qquad (2)$$

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 ($\mathrm{m}:^- + \mathrm{RX}$ and R′X, $\mathrm{m'}:^- + \mathrm{R'X}$ and R″X), the

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(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 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.

relative nucleophilicities of the series may be estimated semiquantitatively.

Experimental Section

The basic equipment has been described previously.[1] The present study employed an H-cell, having a capacity of 25 ml in each arm. The arms were separated by a medium frit, 25 mm in diameter. One arm was inletted by a standard taper joint, allowing filling with supporting electrolyte and addition of mercury, which served as the counter electrode (3-cm diameter pool). The other compartment (cathode) was inletted by three standard taper joints, allowing entrance of a microtest electrode, reference electrode, and degassing tube. A Pt wire was pinch-sealed through the base, allowing contact to be made with another mercury pool (3-cm diameter) which could be used for exhaustive controlled-potential electrolysis work. A stopcock at the bottom provided for rapid draining and cleaning.

In a typical run, the parent homodimetallic compound was dissolved in the supporting electrolyte at millimolar concentrations. This solution was added to the cathode compartment and degassed. A dropping mercury electrode could be immersed in this solution, and a polarographic record made, using a Metrohm polarograph equipped with a Sargent IR compensator. Choosing a voltage well up on the diffusion plateau, controlled-potential electrolysis was effected, using the large pool electrode in the cathode compartment. The potentiostat was a pair of Kepco CK-60-0.5 power supplies in a master-slave configuration, the master unit modified for potentiostatic control and high-input impedance. A Heath voltage reference source was used to offset the summing point, thus setting the controlled potential.[3] After electrolysis, a rotating Pt electrode (600 rpm, Sargent synchronous motor) was immersed into the sample. Numerous bearing assemblies were tried, so as to prevent destruction of the anions by atmospheric water or oxygen. A mercury seal, or a simple punctured aluminum foil cap, with positive argon pressure proved most effective. The i/E plots using 0.025 v/sec triangular sweeps were very reproducible, provided that a preliminary sweep well beyond -2.0 v was made. Well-defined limiting oxidative currents for each anion were observed and $E_{1/2}$ values determined. By setting $E_{\mathrm{test}} - E_{\mathrm{ref}}$ well up on the limiting current plateau, a continual readout of a current proportional to concentration of anion could be obtained. Checks with $\mathrm{CpFe(CO)_2}:^-$, $\mathrm{CpMo(CO)_3}:^-$, and $\mathrm{Mn(CO)_5}:^-$ showed that over the range 5×10^{-3} to 0.5×10^{-3} M, current was linear with concentration.

For the kinetic experiments a magnetic stirrer in the cathode compartment was started and the limiting current set at full-scale travel on the Y axis of a Mosley 2D-2 X-Y recorder. The desired substrate was injected rapidly through a serum capped port, and simultaneously the time base on the X axis of the recorder was activated. A plot of concentration of anion *vs.* time was obtained. The fastest sweep used was 1 sec/in. (half-lives as short as 3 sec could be reproduced to within 10%). In almost all cases, the recorded currents fell smoothly to zero. Calculations, using the appropriate rate equation, showed adherence to second-order kinetics, both within a run and between runs, for those reactions involving near-equal initial concentrations of both reactants. Under psuedo-first-order conditions (excess halide) plots within a run showed good first-order fit and a constant k_2 calculated between runs.

Since the span of rates was so large, no single substrate could encompass the series. Table I shows the data which were used to evaluate the relative rate constants shown in Table II, where all systems are normalized to $\mathrm{(OC)_4Co}:^-$ being unit rate.

The anions of systems 4–11, 13, and 14 were generated by reduction of the homodimetallic. Anions for systems 15 and 16 were generated from the m–Hg–m compound. System 19 anion was derived from one-electron reduction of $\mathrm{CpW(CO)_3H}$. $\mathrm{Ph_2BiCl}$, $\mathrm{Ph_2SbOAc}$, and $\mathrm{Ph_2AsBr}$ served as precursors for the anions of systems 1–3. The anions of systems 17–19 were obtained as the sodium salts from R. B. King.

Of some importance is the observation made while testing the systems 5 and 6 for water sensitivity. The solvent (glyme) was dried by distillation, under argon, from $\mathrm{LiAlH_4}$ after $\mathrm{CaH_2}$ predrying and contained less than 1 ppm water. Deliberate addition of water sufficient to raise the concentration to the millimolar range

Table I

$$\mathrm{m}:^- + \mathrm{RX} \xrightarrow[\mathrm{Bu_4NClO_4},\ 0.1\ M]{\mathrm{(CH_3OCH_2-)_2},\ 25°} \mathrm{m{-}R} + \mathrm{X}^-$$

System	m:$^-$	RX	Concn	k_2,[e] M^{-1} sec^{-1}
1	$\mathrm{Ph_2Bi}:^-$	$\mathrm{(CH_3)_2CHBr}$	*a*	>100[g]
2	$\mathrm{Ph_2Sb}:^-$	$\mathrm{(CH_3)_2CHBr}$	*a*	140
3	$\mathrm{Ph_2As}:^-$	$\mathrm{(CH_3)_2CHBr}$	*a*	85
4	$\mathrm{Ph_3Ge}:^-$	$\mathrm{(CH_3)_2CHBr}$	*a*	1.34
5	$\mathrm{Ph_3Sn}:^-$	$\mathrm{C_2H_5Br}$	*a*	22
6a	$\mathrm{CpFe(CO)_2}:^-$	$\mathrm{C_2H_5Br}$	*a*	139
	$\mathrm{CpFe(CO)_2}:^-$	$\mathrm{(CH_3)_2CHBr}$	*b*	0.17
b	$\mathrm{CpRu(CO)_2}:^-$	$\mathrm{C_2H_5Br}$	*a*	15
7	$\mathrm{CpNi(CO)}:^-$	$\mathrm{C_2H_5Br}$	*a*	10.9
8	$\mathrm{PhSe}:^-$	$\mathrm{(CH_3)_2CHBr}$	*b*	0.01
9	$\mathrm{PhS}:^-$	$\mathrm{C_2H_5I}$	*a*	260
	$\mathrm{PhS}:^-$	$\mathrm{(CH_3)_2CHBr}$	*b*	0.06
10	$\mathrm{Ph_3Pb}:^-$	$\mathrm{CH_3I}$	*a*	490
	$\mathrm{Ph_3Pb}:^-$	$\mathrm{C_2H_5I}$	*b*	2.64
	$\mathrm{Ph_3Pb}:^-$	$\mathrm{C_2H_5Br}$	*b*	0.06
11	$\mathrm{(CO)_5Re}:^-$	$\mathrm{CH_3I}$	*b*	254
12	$\mathrm{CpW(CO)_3}:^-$	$\mathrm{CH_3I}$	*b*	[5][h]
13	$\mathrm{(CO)_5Mn}:^-$	$\mathrm{CH_3I}$	*b*	0.77
14	$\mathrm{CpMo(CO)_3}:^-$	$\mathrm{CH_3I}$	*b*	0.67
15	$\mathrm{CpCr(CO)_3}:^-$	$\mathrm{CH_3I}$	*d*	0.04
16	$\mathrm{(CO)_4Co}:^-$	$\mathrm{CH_3I}$	*c*	0.01
17	$\mathrm{Cr(CO)_5CN}:^-$	$\mathrm{CH_3I}$	*d*	*f*
18	$\mathrm{Mo(CO)_5CN}:^-$	$\mathrm{CH_3I}$	*d*	*f*
19	$\mathrm{W(CO)_5CN}:^-$	$\mathrm{CH_3I}$	*d*	*f*

[a] Anion and halide concn = 2.0×10^{-3} M. [b] Anion concn = 2.0×10^{-3} M, halide concn = 2.0×10^{-3} M. [c] Anion concn = 5.0×10^{-3} M, halide concn = 5.0×10^{-1} M. [d] Anion concn = 4.0×10^{-3} M, halide concn = 4.0×10^{-1} M. [e] Values represent averages for three or more runs usually differing by 10% or less. [f] Too slow to measure. [g] Owing to poor solubility of $\mathrm{Ph_2BiCl}$ in glyme and the instability of $\mathrm{Ph_2Bi}:^-$, an accurate value could not be determined. [h] Because of the overlap of two oxidative polarographic waves of $\mathrm{CpW(CO)_3}:^-$, an accurate value could not be determined.

Table II

$$\underset{\sim 10^{-3}\ M}{\mathrm{m}:^-} + \mathrm{RX} \xrightarrow[\mathrm{Bu_4NClO_4},\ 0.1\ M]{\mathrm{(CH_3OCH_2-)_2},\ 25°} \mathrm{m{-}R} + \mathrm{X}^-$$

System	m:$^-$	k_2'	$-E_{1/2}^{\mathrm{m-m}}$ (redn, Hg)	$-E_{1/2}^{\mathrm{m-m}}$ (oxidn, Pt)
1	$\mathrm{Ph_2Bi}:^-$	7×10^{10}	2.3	2.1
2	$\mathrm{Ph_2Sb}:^-$	7×10^{10}	2.5	2.0
3	$\mathrm{Ph_2As}:^-$	4×10^{10}	2.7	2.0
4	$\mathrm{Ph_3Ge}:^-$	6.5×10^{8}	3.5	1.2
5	$\mathrm{Ph_3Sn}:^-$	1.1×10^{8}	2.9	0.95
6a	$\mathrm{CpFe(CO)_2}:^-$	7.0×10^{7}	2.2	1.6
b	$\mathrm{CpRu(CO)_2}:^-$	7.5×10^{6}	2.6	1.5
7	$\mathrm{CpNi(CO)}:^-$	5.5×10^{6}	2.4	1.4
8	$\mathrm{PhSe}:^-$	5.0×10^{6}	~0.9 (n = 1) ~1.5 (n = 1)	1.5
9	$\mathrm{PhS}:^-$	2.6×10^{6}	1.7	1.4
10	$\mathrm{Ph_3Pb}:^-$	2.6×10^{4}	2.0	0.90
11	$\mathrm{(OC)_5Re}:^-$	2.5×10^{4}	2.3	Several pauses in step 0.8–1.4
12	$\mathrm{CpW(CO)_3}:^-$	~500	. . .	1.0
13	$\mathrm{(CO)_5Mn}:^-$	77	1.7	0.55
14	$\mathrm{CpMo(CO)_3}:^-$	67	1.4	0.55
15	$\mathrm{CpCr(CO)_3}:^-$	4	1.3	0.80
16	$\mathrm{(OC)_4Co}:^-$	1	1.0	0.20
17	$\mathrm{(OC)_5(NC)Cr}:^-$	≪0.01, too slow to measure accurately	. . .	~-0.2
18	$\mathrm{(OC)_5(NC)Mo}:^-$		. . .	~-0.2
19	$\mathrm{(OC)_5(NC)W}:^-$		. . .	~-0.2

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(3) These circuits were constructed with the aid of Paul Birman, Kepco Inc., New York, N. Y.

did not lead to destruction of the anions within the time range of reaction with halide substrates.

Results and Discussion

The current method of approach to establishment of a quantitative series of metal and metalloidal anion nucleophilicities utilizes, as has been mentioned previously, the electrochemical preparation, at $\sim 2 \times 10^{-3}$ M concentrations, of the anion by reduction of the parent homodimetallic compound. The resulting anions show well-defined polarographic waves, the majority apparently undergoing the electrochemical oxidation process

$$\mathrm{m}:^- \xrightarrow[\mathrm{Hg}]{-e} \mathrm{m{-}Hg} \longrightarrow {}^1/_2\mathrm{m_2Hg} \qquad (3)$$

If a rotating platinum electrode is substituted, well-defined steps are still observed, the electrode being very stable and reproducible, provided care in initial manipulations is taken. The rotating platinum electrode (600 rpm) with adequate magnetic stirring assures complete and rapid mixing of solution as a substrate alkyl halide is added to the solution.

$$\mathrm{m}:^-,\mathrm{Bu_4N^+} + \mathrm{RX} \longrightarrow \mathrm{m{-}R} + \mathrm{Bu_4N^+,X^-} \qquad (4)$$

The current-concentration curves utilizing a monitoring potential, $E_{\text{test}} - E_{\text{ref}}$, well up on the limiting current region for anion alone, indicate that over the range 5×10^{-3} to 0.5×10^{-3} M the response is linear, so that it is a simple matter to plot during a kinetic run limiting current *vs.* time and derive kinetic information. The processes reported in this paper are all second order within a run and show good behavior between runs.

Table I shows the observed k_2 values (millimolar concentration of anion, 0.1 M $\mathrm{Bu_4NClO_4}$ in $\mathrm{(CH_3OCH_2-)_2}$, 25°) for the anions studied. Table II shows a series of relative second-order rate constants, k_2', normalized to the $\mathrm{(OC)_4Co}:^-$ system, using paired triad sets, with the following rate ratios for calculation of k_2' values from the observed k_2 values: Br:I = 1:50 and Me:Et:*i*-Pr = 100:1:0.001.

Also shown in Table II are the half-wave potentials for the polarographic reduction of the parent homodimetallic compound and the half-wave potential for the oxidation of the anion at a rotating platinum electrode. The latter was chosen in preference to polarographic potentials because of the incursion of large, uncontrollable maxima in many anion solutions and the fear of variable contributions from metal-Hg bonding in the oxidative step. Figure 1 shows a plot of $\log k_2'$ *vs.* $-E_{1/2}^{\text{ox}}(\mathrm{Pt})$.

Although product isolation was not attempted in these microstudies, gas chromatographic analysis of the solutions after t_{inf} showed no evidence of starting halide when equal initial concentrations of reactants were used and no evidence of products from R· due to abstraction, disproportionation, or coupling. Polarographic scans showed no evidence of m-m or m-H from m. The rate data therefore are measurements of the nucleophilicity of the anions. The ultilization of the $\mathrm{Bu_4N^+}$ gegenion assures that electrophilic assistance by the gegenion is minimized, a factor that would be an important variable if a lithium counterion was employed.

The span of relative rates exceeds 10^{12}, with $\mathrm{(OC)_4Co}:^-$ near one extreme and the group V derivatives at the other. For comparison to the sequence of nucleophilicities accumulated by research in the physical organic area, the PhS:⁻ anion, which lies in the exact center of the scale, is a good reference point.

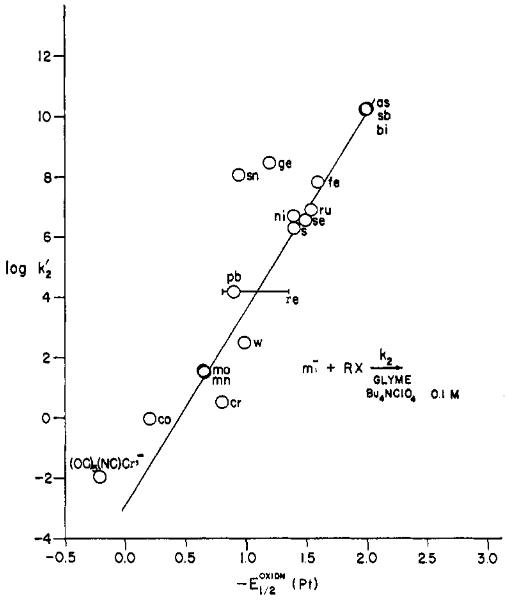

Figure 1.

The following generalities can be made from the observed data. (a) In groups VI and VII in the transition series, as one descends the table, nucleophilicity of the anion increases (systems 11, 13; 12, 14, 15). (b) In the limited samples from group VIII (Fe, Ru), as one descends the table nucleophilicity decreases (systems 6a,b). (c) In groups Va and VIa in the main group, as one descends the table, the nucleophilicity of the anion increases (systems 2, 3; 8, 9) (although the $\mathrm{Ph_2Bi}:^-$ was too unstable to get reliable data, its k_2' is approximately 7×10^{10}). Since some decomposition had taken place at the time of the kinetic run, and during it, this is a lower limit. (d) In group IVa in the main group (Ge, Sn, Pb), as one descends the table, the nucleophilicity of the anion decreases (systems 4, 5, and 10).

It seems wise at this point to compare the observed sequences with available literature data. Parshall[4] has attempted to establish a qualitative sequence of nucleophilicities among a similar series employing the equilibrium constant of the process

$$\mathrm{m}:^- + \mathrm{BH_3} \overset{K}{\rightleftarrows} \mathrm{m{\longrightarrow}BH_3^-} \qquad (5)$$

and concluded that $\mathrm{(OC)_5Re}:^- > \mathrm{(OC)_5Mn}:^- \gg \mathrm{(OC)_4Co}:^-$. No quantitative measure of K could be made, however. Stone[5] has empirically assigned two other anions to this series by observations on the ability of the anions in question to displace fluorine in perfluoroalkyl and aromatic compounds. The available data suggested that $\mathrm{CpFe(CO)_2}:^-$ was more nucleophilic than $\mathrm{(OC)_5Re}:^-$. Attempts by Shriver[6] to measure nucleophilicities for $\mathrm{CpMO(CO)_3}:^-$ and $\mathrm{CpW(CO)_3}:^-$ by coordination with $\mathrm{BF_3}$ lead to their respective dimers rather than complexes (*cf.* paper VIII, this series). Although little data are available in the

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(4) G. Parshall, *J. Am. Chem. Soc.* **86**, 361 (1964).

(5) F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

(6) M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966).

main group, Gilman[7] has reported that the acidities in the group IV Ph_3MH sequence are $Ph_3SiH < Ph_3GeH < Ph_3SnH$, which would suggest an opposite set of anion nucleophilicities. Finally, data[8] in aryl halide displacements suggest $PhSe^-$ to be a better nucleophile than PhS^-.

The correspondence of these available pieces of information with the present data suggests that the varied observations are not isolated pieces of information and that the quantitative data contained herein will have general application.

At the present it is somewhat more difficult to probe the area very far in a theoretical manner. The most hopeful observation is that a plot of log k_2' *vs.* $-E_{1/2}^{ox}$ (Pt) is linear (with the Sn and Ge anions lying off the line). Such a relationship is not unexpected, as Edwards[9] has pointed out. In viewing a possible source of constants for the four-parameter Edwards' equation

$$\log k_N/k_0 = aE_N + bH_N \qquad (6)$$

he chose E_N, the nucleophilicity of a group with reference to a general electrophile, as equal to $E° + 2.60$, where $E°$ is the couple potential for the process $2N^- \leftrightarrows N_2 + 2e$. The use of the oxidation half-cell potential as a model for nucleophilic reactivity was justified on the basis that the nucleophile is formally oxidized in a displacement reaction. The success of the equation in correlating data is excellent. It should be pointed out that the term E_N can be separated into a polarizability term and a basicity (toward proton) term, *i.e.*, $E_N = 3.60P_N + 0.0624H_N$. It is interesting that of the two terms in eq 6, since $b < 0.01a$ and $H_N < 10E_N$, it is usually the first term on the right-hand side which is the major contributor to log k_N/k_0. a values for alkyl halides are near 2.5–3, giving log $k_N/k_0 \cong 2.5E_N$. In the present study, log $k_{2N}{}^{m:-} \cong 6.6E_{1/2}^{ox} - 3$. There appears to be good reason to suggest that an Edwards' type correlation will exist for these types of anions. Attempts are being made to obtain basicity data for the anions to check this postulate. However, at least within the transition group derivatives, it would appear reasonable to assess the nucleophilicities of anions by assessment of their oxidation potential and comparison with the series reported herein.

Acknowledgments. The authors wish to thank the National Science Foundation for its support in the form of Grant GP1984.

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[7] H. Gilman in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960.

[8] *Cf.* J. Hine, "Physical Organic Chemistry, "McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[9] J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956).

Organometallic Electrochemistry. VIII.
The Formation of Metal–Metal Bonds

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Received May 23, 1966

Abstract: A detailed study has been made of the products from the interaction of $m:^- + m'$–x in comparison to those from $m':^- +$ m–x. In some instances the reactions commute (Chart I). In other instances, they do not, either because of a rate factor or the incursion of paths alternate to the expected SN displacement giving a metal–metal linkage, m–m′. These alternate pathways encompass a one-electron-transfer process, ligand displacement other than x, redistribution processes between m–m′ and $m:^-$, and/or charge–x interchange. It can be concluded that the success of a synthesis of a metal–metal bond will be determined by the care with which one of the pair of commuting reactions is chosen, the gegenion of the anion employed, and the order in which reactants are mixed.

The previous two papers in this series[1] have presented data surrounding the synthesis of a m–m′ bond from $m:^-$ and m′–x. The first subject dealt with was the stability of the m–m′ linkage to be formed. 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 observed and bond strength. The second area explored was the nucleophilicity of $m:^-$, and a study of 19 anions indicated that the relative nucleophilicities of anions derived from elements from group IV to group VIII have a span in excess of 10^{12}. A good correlation exists between the potential for oxidation of the anion to radical at a Pt electrode, $E_{1/2}^{ox}$(Pt) and log k_2'. Such a correlation is suggested by the Edwards equation.

This paper deals with the actual experiment of allowing $m:^-$ and m′–x to interact. The electrochemical reduction–scission (eq 1) of a homodimetallic material

$$\text{m–m} \xrightarrow[\text{2e, } Bu_4NClO_4]{(CH_3OCH_2-)_2,\ \text{Hg}} 2\text{m}:^- \qquad (1)$$

in dimethoxyethane using tetrabutylammonium perchlorate as a supporting electrolyte permits generation of metal and metalloidal anions,[2] with a Bu_4N^+ gegen-

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[1] For previous papers in this series, see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121 (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 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.