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.

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

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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

$$\text{m–m} \xrightarrow[\text{2e, Bu}_4\text{NClO}_4]{(\text{CH}_3\text{OCH}_2\text{–})_2\text{, Hg}} 2\text{m}:^- \qquad (1)$$

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.

ion in low, known concentrations. Addition of m′–x, equally at low concentrations, permits one to evaluate the product, if a reaction does occur. Some possibilities are

$$\underset{10^{-3}\,M}{\mathrm{m}:^-} + \underset{10^{-3}\,M}{\mathrm{m'{-}x}} \longrightarrow \begin{cases} \mathrm{m{-}m'} + \mathrm{x}^- & \mathrm{S_N}\text{ substitution (x displacement)} \\ \mathrm{m}\cdot + \mathrm{m'}\cdot + \mathrm{x}^- & \text{electron transfer} \\ \mathrm{m{-}x} + \mathrm{m'}:^- & \text{charge–x interchange} \\ \mathrm{m{-}m'{-}x} & \mathrm{S_N}\text{ substitution (L displacement)} \end{cases} \quad (2)$$

The identity of the heterodimetallic products from direct displacement of x could be identified at millimolar concentrations from the polarographic data reported in paper VI in this series and by ultraviolet spectroscopy. The products from electron transfer may be the desired heterodimetallic compound, provided a caged process occurs (eq 3) or a mixture of hetero- and homodimetallic

$$\begin{tikzcd} \left.\begin{matrix}\mathrm{m{-}m'}\\ \mathrm{m{-}m}\\ \mathrm{m'{-}m'}\end{matrix}\right\}\\ \text{and/or}\\ \text{m–H products} & & \mathrm{m}:^- + \mathrm{m'{-}x} \arrow[ll, "\text{noncage}"'] \arrow[d] \\ & & \mathrm{m}\cdot + \mathrm{m'}\cdot + \mathrm{x}^- \xrightarrow{\text{cage}} \mathrm{m{-}m'} \end{tikzcd} \quad (3)$$

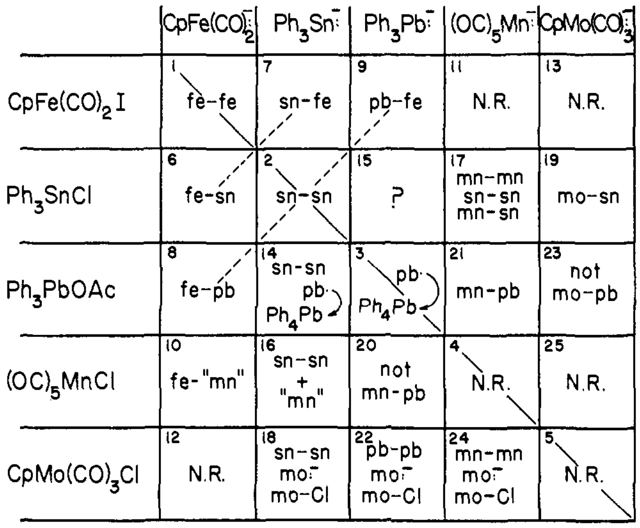
products if the radicals are cold (long-lived) species. The exact ratios would be determined by the relative reactivities of the radical species. Alternatively hydrogen abstraction could result in organometallic hydrides, or a combination of these last two might present themselves. In any of these cases, comparison of polarographic data from the experiment and from known samples reported earlier should allow establishment of the products. Charge–x (*cf.* metal–halogen) interchange might occur or, finally, a displacement of a ligand other than x might yield a new anionic species. The data on anionic oxidation potentials reported in paper VII[1] would aid in product identification for the former. It is only in the latter case that identification difficulties would arise. Finally, it is possible that redistribution reactions might occur after a metal–metal bond had been formed (eq 4). Considerable data have

$$\mathrm{m}:^- + \mathrm{m'{-}x} \longrightarrow \mathrm{m{-}m'} \xrightarrow{\mathrm{m}:^-} \mathrm{m{-}m} + \mathrm{m'}: \quad (4)$$

been accumulated on this process in this laboratory, and unfortunately it is a quite common reaction. Fortunately it is also quite easy to detect and investigate. These findings appear in the following paper.

The premise of this work then has been to generate electrochemically a series of anions, at millimolar concentrations and in the presence of 0.1 *M* tetrabutylammonium perchlorate, and permit these to react independently, and successively, with the series of related halides. The concept is illustrated by Chart I.

Chart I



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

Basically the question asked is: does the interaction $\mathrm{m}:^- + \mathrm{m'{-}x} \rightarrow$ lead to the same product as the interaction $\mathrm{m'}:^- + \mathrm{m{-}x} \rightarrow$?; and, do either, or both, lead to the hoped-for m–m′ species. The former question involves the concepts of commutation, the mathematical term suggesting that $A \cdot B = B \cdot A$, and noncommutation, where $A \cdot B \neq B \cdot A$. The answer to the latter question is one of utmost importance to the transition metal chemist who is attempting to join one or more metals to another. It has been suggested that, given enough time, energy, and funds, a compound containing all the elements from the first long row could be prepared. The present data would be of interest to the chemist who has the courage to attempt this.

Experimental Section

Equipment. The polarographic and controlled potential electrolysis apparatus has been described in a previous publication.[1]

Chemicals. Dimethoxyethane (Ansul 121) was purified by distillation from $LiAlH_4$ under an argon atmosphere. The liquid is always degassed with an argon bubbler immediately prior to use. Tetrabutylammonium perchlorate (TBAP) was purchased from Matheson Coleman and Bell and dried with P_2O_5 *in vacuo* before use. The starting materials were obtained commercially or prepared in this laboratory. The compounds were purified before use, when necessary, and examined polarographically for trace impurities.

Small-Scale Reactions in the Polarographic Cell. The preparation of $CpFe(CO)_2Sn(C_6H_5)_3$ *via* the electrochemical generation of triphenyltin anion is representative of the reactions performed in the polarographic cell and the techniques used to identify products. In the cathode compartment of the polarographic cell described previously, 14.5 mg of hexaphenylditin (25×10^{-3} mmole) dissolved in 25 ml of degassed electrolyte solution (0.1 *M* tetrabutylammonium perchlorate in dimethoxyethane) is added along with mercury and a magnetic stirring bar. Into the anode compartment mercury and a portion of the same electrolyte solution is added. The cell is then placed under the cell cover which is fitted with the dropping mercury electrode, reference electrode, glass-sealed platinum wire, rubber syringe inlet, and argon bubbling tube. After degassing the solution a second time, a polarograph of the solution is taken, indicating $E_{1/2} = -2.90$ v for hexaphenylditin. The controlled-potential electrolysis unit is then connected to the sitrred mercury pool cathode *via* the platinum wire and a potential of -3.1 v is applied to the pool *vs.* the reference. The current passed is measured as a function of time, and the reduction is continued until virtually no current is observed. Calculation of the number of coulombs required by graphical integration indicates that 2.0 electrons/molecule was added. A polarogram at this time shows a large anodic wave for $Ph_3Sn:^-$, but no cathodic wave for $Ph_3SnSnPh_3$. $CpFe(CO)_2I$, 50×10^{-3} mmole in 5.0 ml of electrolyte solution, is then added by means of a hypodermic syringe.

A polarographic wave immediately appeared ($E_{1/2} = -2.61$ v) whose size and shape did not change upon standing. This wave was shown to be caused by the nearly quantitative formation of $CpFe(CO)_2SnPh_3$ by comparison with authentic material which showed the same polarographic characteristics as well as ultraviolet spectra (λ_{max} 298 mμ). Three relatively small waves at -1.14, -2.16, and -2.95 v had also appeared after addition of the reactant. The first two are due to unreacted $CpFe(CO)_2I$. The latter wave, which was also observed on the polarogram of authentic $CpFe(CO)_2SnPh_3$, is due to the liberation of triphenyltin radicals on the drop surface by heterolytic cleavage of the metal–metal bond. These may then couple to give hexaphenylditin which reduces at the potential observed for the third wave. Data for the other reactions appear in Tables I and II.

$CpFe(CO)_2Pb(C_6H_5)_3$ (Electrochemical Preparation). Hexaphenyldilead, 0.877 g (1.00 mmole), and 40.0 mmoles of tetrabutylammonium perchlorate (TBAP) were dissolved in 200 ml of glyme and placed in the large preparative cell. After adding the mercury pool and a magnetic stirrer bar, the solution was degassed

Table I. Authentic Sample Physical Constant Data

Compd no.	Compound	$-E_{1/2}$,[a] v	n_1[b]	Ultraviolet λ_{max}, mμ	Ultraviolet ε
1	$[CpFe(CO)_2]_2$	2.2	2	344	
2	$Ph_3SnSnPh_3$	2.9	2	247	
3	$Ph_3PbPbPh_3$	2.0	2	End abs	
4	$[Mn(CO)_5]_2$	1.7	2	342 276	15,000 160,000
5	$[CpMo(CO)_3]_2$	1.4	2	386	
6	$CpFe(CO)_2I$	1.2, 2.2	1	350	
7	Ph_3SnCl	1.6	1	. . .	
8	Ph_3PbOAc	1.4, 2.2	1	End abs	
9	$Mn(CO)_5Cl$	2.1 (2.4)	2	280	
10	$CpMo(CO)_3Cl$	1.3	2	234 324	17,000 2,200
11	$CpFe(CO)_2SnPh_3$	2.6	2	298	
12	$CpFe_2(CO)_2PbPh_3$	2.1	2	327	
13	$CpFe(CO)_2Mn(CO)_5$	1.5, 2.1	1	384	3,000
14	$CpFe(CO)_2Mo(CO)_3Cp$	1.4	1	382 286 252	Weak 8,000 8,000
15	$CpMo(CO)_3SnPh_3$	2.4	1	282	12,200
16	$CpMo(CO)_3PbPh_3$	2.2	2	End abs	
17	$(OC)_5MnSnPh_3$	2.5	1	End abs	
18	$(OC)_5MnPbPh_3$	2.1	2	295	22,000
19	Ph_3SnH	3.1	1	. . .	
20	$Mn(CO)_5H$	No wave	. . .	. . .	
21	Ph_4Pb	3.2	. . .	. . .	

[a] *Vs.* 10^{-3} *M* $Ag^+|Ag$. [b] Number of electrons accepted per molecule at $E_{1/2}$, as determined by exhaustive controlled-potential electrolysis.

with argon and a portion of it was drawn up into the anode compartment (about 30 ml). The hexaphenyldilead was exhaustively electrolyzed at −2.1 v, and 0.608 g, 2.00 mmoles, of $CpFe(CO)_2I$ in 50 ml of previously degassed electrolyte solution was added by means of a hypodermic syringe. After stirring for about 30 min the mercury was decanted and the solution was poured into a 1-l. flask. Ether was then added until the precipitation of TBAP could no longer be observed. The solid TBAP was removed by filtration. The solvent in the filtrate was then removed completely by low-pressure evaporation and the solid residue recrystallized from 95% ethanol giving pale orange needles, mp 134–137°.

Anal. Calcd for $C_{25}H_{20}FeO_2Pb$: C, 48.79; H, 3.27. Found: C, 49.05; H, 3.48.

The pure material showed an ultraviolet maximum at 327 mμ (glyme) and a polarographic wave at $E_{1/2} = -2.12$ v ($n = 2.0$).

$CpFe(CO)_2Sn(C_6H_5)_3$ (Electrochemical Preparation). Using the same techniques as described above, 0.708 g (2.00 mmoles) of $[CpFe(CO)_2]_2$ in 200 ml of 0.2 *M* electrolyte solution was reduced to the monomer anion at a potential of −2.4 v. After the electrolysis was virtually complete, 1.540 g (4.00 mmoles) of $(C_6H_5)_3SnCl$ in 50 ml of electrolyte solution was added. Precipitation of TBAP by addition of ether, filtration, and evaporation of the solvent gave a viscous residue which was frozen to an orange-brown solid with Dry Ice. The solid was extracted with refluxing *n*-heptane. A brown gum remained which was insoluble in *n*-heptane but very soluble in methylene chloride. Analysis showed this material to be largely $[CpFe(CO)_2]_2$. Chilling of the *n*-heptane solution gave a precipitate of pale yellow needles, mp 141–143° (lit.[3] mp 139–141°), $E_{1/2} = -2.60$ v ($n = 2.0$), with λ_{max} 298 mμ (glyme).

$CpMo(CO)_3Sn(C_6H_5)_3$. In a 300-ml three-necked flask, fitted with a mechanical stirrer, dry nitrogen inlet, and stopcock, 0.30 g of sodium metal was added in portions to 6 ml of mercury. While keeping the flask under a nitrogen atmosphere, 75 ml of dry glyme and 2.45 g (5.00 mmoles) of $[CpMo(CO)_3]_2$ were added. The solution was stirred vigorously for about 30 min, the excess amalgam removed through the stopcock, and the solvent removed under vacuum. To the residue, 250 ml of petroleum ether (bp 30–60°), 40 ml of 95% ethanol, and 3.85 g (10.0 mmoles) of triphenyltin chloride were added. After vigorous stirring for 2 hr the solvent was evaporated, and the residue was extracted with benzene, filtered, and concentrated. Recrystallization from a mixture of benzene and petroleum ether gave a white solid, mp 207°, λ_{max} 282 mμ (ε 12,200), $E_{1/2} = -2.38$ v ($n = 1.0$).

Anal. Calcd for $C_{26}H_{20}MoO_3Sn$: C, 52.51; H, 3.39. Found: C, 52.36; H, 3.33.

$CpMo(CO)_3Pb(C_6H_5)_3$. $CpMo(CO)_3Na$, 10.0 mmoles, was prepared as described above. Using the same procedure 4.74 g (10.0 mmoles) of $(C_6H_5)_3PbCl$ was added, and the product isolated from a benzene–petroleum ether mixture appeared as pale yellow needles which decomposed at about 201°, $E_{1/2} = -2.1$ v. The ultraviolet spectra had no characteristic peaks.

Anal. Calcd for $C_{26}H_{20}MoO_3Pb$: C, 45.68; H, 2.96. Found: C, 45.45; H, 3.13.

$(CO)_5MnPb(C_6H_5)_3$. Using the techniques described above, 2.00 g (5.13 mmoles) of manganese carbonyl was converted to $NaMn(CO)_5$ in tetrahydrofuran solution. After removing the excess amalgam, 4.86 g of $(C_6H_5)_3PbCl$ was added and the solution stirred for 30 min. About half of the solvent was then evaporated, the solution poured onto ice-water, and the solid filtered, dried, and recrystallized from *n*-hexane. The pale yellow solid appeared to decompose at 133° (lit.[3] mp 146–148°) and had a λ_{max} 295 mμ (ε 22,000) in glyme, $E_{1/2} = -2.14$ v ($n = 2$).

Anal. Calcd for $C_{23}H_{15}MnO_5Pb$: C, 43.60; H, 2.39. Found: C, 43.38; H, 2.57.

$(CO)_5MnSn(C_6H_5)_3$. This compound was prepared in a similar manner, giving a white solid upon recrystallization from *n*-hexane, mp 140–142° (lit.[3] mp 148–150°), $E_{1/2} = -2.52$ v ($n = 1.0$).

Results and Discussion

Chart I presents the conclusions of the present findings concerning the products from the interaction of m:⁻ and m′–x. The supporting data for product identification are to be found in Tables I and II. The three factors which have been the theme of this series exhibit themselves strikingly in this simple study.

Symmetrical Sets. First, considering the symmetrical diagonal in Chart I, where reactions of the type $m{:}^- + m{-}x$ are shown, it is evident that the drop in nucleophilic character in the sequence $fe{:}^- \cong sn{:}^- > pb{:}^- > mn{:}^- > mo{:}^-$ is responsible largely for the failure of systems 4 and 5 to react. In each case observations were made during a 2-hr period after mixing indicating a k_2 of less than 0.01 M^{-1} sec^{-1}. In systems 1 and 2 product formation was complete within the time required to make the first measurements, indicating that k_2 is greater than 10, and pilot runs using the technique described in paper VII of this series indicate that they are greater than 500 M^{-1} sec^{-1}. Only in the interaction of pb:⁻ and pb–OAc was an observable reaction rate encountered. Here, addition of the Ph_3PbOAc to the electrochemically generated $Ph_3Pb{:}^-Bu_4N^+$ caused immediate disappearance of the oxidative waves typical of $Ph_3Pb{:}^-$ and the appearance of a new reductive wave at −2.2 v (*cf.* $Ph_3PbPbPh_3$, $-E_{1/2} = 2.0$ v); this gradually diminished in diffusion height, being replaced by a wave at 3.2 v. These observations paralleled the appearance and subsequent disappearance of an intense yellow color in the solution. Ph_4Pb reduces at −3.2 v, and it appears that we are seeing the results of an electron-transfer process which can yield ultimately Ph_4Pb (eq 5). The potential for the intermediate, −2.2 v, is

$$\begin{tikzcd} \mathrm{Ph_3Pb{:}^-} + \mathrm{Ph_3PbOAc} \arrow[r] & 2\,\mathrm{Ph_3Pb\cdot} + \mathrm{OAc^-} \arrow[d] \arrow[dr, "\text{direct}"] & \\ & \mathrm{Ph_3PbH} \arrow[r] & \mathrm{Ph_4Pb} \end{tikzcd} \qquad (5)$$

where one might expect the unstable Ph_3PbH to be (*cf.* Ph_3SnH, −3.2 v; $Ph_3SnSnPh_3$, −2.9 v). Ph_3PbH is reported to decompose to Ph_4Pb.[4]

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(3) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

(4) F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

Table II. Commutation Experiments Product Identification Data

System no.	Interaction	$-E_{1/2}$,[a] v	Ultraviolet[b] λ_{max}, mμ	Other observations	Conclusion[c]
1	fe:$^-$ + fe–I	1.2			
		(small)			fe–I (unreacted)
		2.2	344		fe–fe
2	sn:$^-$ + sn–Cl	2.9	247		sn–sn
3	pb:$^-$ + pb–OAc	2.2		Initial wave at −2.2 v slowly (10 min) disappears as wave at −3.2 v appears; transient yellow color observed	
		3.2			Ph_4Pb
4	mn:$^-$ + mn–Cl	2.1		mn:$^-$ wave undisturbed	No reaction
5	mo:$^-$ + mo–Cl	1.3		mo:$^-$ wave undisturbed	No reaction
6	fe:$^-$ + sn–Cl	2.6	298		fe–sn
7	sn:$^-$ + fe–I	2.6	298	fe–sn isolated in large-scale run	fe–sn
8	fe:$^-$ + pb–OAc	2.1	327		fe–pb
9	pb:$^-$ + fe–I	2.1	327	fe–pb isolated in large-scale run	fe–pb
10	fe:$^-$ + mn–Cl	2.1	290		?
			310		?
			340		fe–fe
			(weak)		
11	mn:$^-$ + fe–I	1.2	350	mn:$^-$ wave undisturbed	No reaction
		2.2			
12	fe:$^-$ + mo–Cl	1.3		fe:$^-$ wave undisturbed	No reaction
13	mo:$^-$ + fe–I	1.2	350	mo:$^-$ wave undisturbed	No reaction
14	sn:$^-$ + pb–OAc	2.2		Initial wave at −2.2 v slowly (30 min) disappears as wave at −2.9 and −3.2 v appears transient. Yellow color observed	
		2.9			sn–sn
		3.2			Ph_4Pb
15	pb:$^-$ + sn–Cl	. . .		Irreproducible, waves ill-defined. Only modest step at −2.9 v	?
16	sn:$^-$ + mn–Cl	2.4			?
		2.9	244	Authentic mn–sn shows only small wave in this region (see above)	sn–sn
17	mn:$^-$ + sn–Cl	1.7	340 sh		mn–mn
		2.5			mn–sn
		2.9			sn–sn
		(strong)			
18	sn:$^-$ + mo–Cl	1.3		Only $^1/_2$ halide (m–x) required to produce all mn–mn	mo–Cl
		2.9	244		sn–sn
19	mo:$^-$ + sn–Cl	2.4			sn–mo
20	pb:$^-$ + mn–Cl	2.2	268		Not pb–mn
21	mn:$^-$ + pb–OAc	2.1	296		pb–mn
22	pb:$^-$ + mo–Cl	1.3	308	Only $^1/_2$ halide (m–x) required to produce all pb–pb	
		2.0			pb–pb
23	mo:$^-$ + pb–OAc	1.6	312		Not mo–pb
		2.0			
		(small)			
24	mn:$^-$ + mo–Cl	1.3		Only $^1/_2$ halide (m–x) required to produce all mn–mn	mo–Cl
		1.7	276		mn–mn
25	mo:$^-$ + mn–Cl	2.0		mo:$^-$ wave undisturbed	No reaction
		2.4			

[a] *Vs.* 10^{-3} *M* $Ag^+|Ag$. [b] In $(CH_3COH_2-)_2$, 10^{-1} *M* in Bu_4NClO_4. [c] In this column all metal–metal bond compounds, m–m′, refer to those derived from m:$^-$ + m′–x by formal displacement of halide ion, not another ligand.

Commutation Sets. Systems 6, 7 (fe, sn) and 8, 9 (fe, pb) commute nicely, the heterodimetallic being produced by either an SN displacement or a caged process involving electron-transfer pathways. These two alternatives cannot be distinguished. The Experimental Section describes the large-scale preparation of $Ph_3PbFe(CO)_2Cp$ from electrochemically generated Ph_3Pb:$^-$. This route is rather clean and offers much promise for other applications involving organolead anions.

Noncommutation Sets (Rates). Lack of commutation under the conditions of these experiments (millimolar concentrations, highly polar, basic environment) may be due to a low specific reaction rate constant for one of the members of the set. This is true for systems 10 (fe:$^-$ + mn–Cl) and 11 (mn:$^-$ + fe–I). The latter has $k_2 < 0.01$. Unfortunately, the former does not yield the anticipated heterodimetallic fe–mn, a compound which has been previously reported.[3] The data in Tables I and II exclude a one-electron transfer to give significant amounts of $Mn_2(CO)_{10}$ and $[CpFe(CO)_2]_2$, since a reductive half-wave potential for the former was not observed, and only a weak ultraviolet absorption in the area characteristic of the iron dimer was observed. The species produced by the reaction, reducing at −2.2 v, is most probably an anionic species derived from displacement by the iron anion of CO, rather than halide ion. The ease of displacement of CO in compounds of the type $Mn(CO)_5X$ to give $Mn(CO)_4XL$ (L = N, P, As ligands) has been studied.[5] For the purposes of the present study, the establishment of the exact structure of the species produced was not pertinent, but studies are underway in this area. Another example of noncommutation due to rate differences is found in systems 24 (mn:$^-$ + mo–Cl) and 25 (mo:$^-$ + mn–Cl). The latter system has $k_2 < 0.01$. The former system, upon mixing of the reagents in a 2:1 ratio, shows the appearance of a wave at −1.7 v, characteristic of $Mn_2(CO)_{10}$, which can be identified by its ultraviolet absorption at 276 mμ. Further addition of the halide gives no augmentation of this wave, adding to the polarographic display only a wave at more anodic potentials characteristic of $CpMo(CO)_3Cl$. This cannot be an example of charge–x interchange

$$\text{mn:}^- + \text{mo–Cl} \rightleftarrows \text{mn–Cl} + \text{mo:}^-,\quad \text{mn–Cl} + \text{mm:}^- \not\longrightarrow \qquad (6)$$

since the latter reaction has been shown to be too slow. One possibility is

$$\text{mn:}^- + \text{mo–Cl} \longrightarrow \text{mn–mo} \xrightarrow{\text{mn:}^-} \text{mn–mn} + \text{mo:}^- \qquad (7)$$

This hypothesis cannot be checked, since the necessary $CpMo(CO)_3Mn(CO)_5$ compound has never been prepared, although numerous attempts by our group and that of King[6] have been made. However, the following sequence has been established polarographically in millimolar concentrations, with $k_2 > 10\ M^{-1}\ \text{sec}^{-1}$

$$2Ph_3Sn:^- + [CpMo(CO)_3]_2 \longrightarrow Ph_3SnSnPh_3 + 2CpMo(CO)_3:^- \qquad (8a)$$

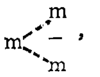
and

$$Ph_3Sn:^- + CpMo(CO)_3SnPh_3 \longrightarrow Ph_3SnSnPh_3 + CpMo(CO)_3:^- \qquad (8b)$$

thus suggesting that (8b) is involved in (8a) and that these redistribution reactions, which have been heretofore unreported, involve anion–anion displacement and not electron transfer and free radicals. The question of whether a linear (i), or angular (ii), or triangular (iii) transition state is involved is being explored.

m---m---m^-

i



ii

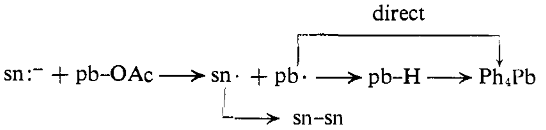
iii

These findings strongly suggest that (7) is a reasonable source of the present observations. They indicate also that inverse addition of anions to metal halide substrates (with halide always in large excess) may lead to quite different products than normal addition, where redistributions such as those indicated above may occur readily (anion is always in excess).

Finally, it should be pointed out that systems 12 and 13, involving fe:$^-$ + mo–Cl and mo:$^-$ + fe–I, both have $k_2 < 0.01$. This would appear to be due to the difficulty of the already seven-coordinate molybdenum species to enter into a reaction pathway in which its coordination was increased.

At higher concentrations or temperatures or with different counterions, these segregations in the noncommutation sets may disappear. Indeed, several literature reports exist on the preparation of heterodimetallics using similar reactions.[7]

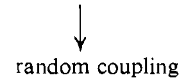
Noncommutation Sets (Product). Five sets in the matrix belong to the class in which the products of the two pathways are different. Systems 14 (sn:$^-$ + pb–OAc) and 15 (pb:$^-$ + sn–Cl) differ in the sense that the former yields $Ph_3SnSnPh_3$ and Ph_4Pb *via* one-electron transfer



(9)

$$\text{sn:}^- + \text{pb–OAc} \longrightarrow \text{sn}\cdot + \text{pb}\cdot \longrightarrow \text{pb–H} \longrightarrow Ph_4Pb;\quad \text{pb}\cdot \xrightarrow{\text{direct}} Ph_4Pb;\quad \text{sn}\cdot \longrightarrow \text{sn–sn} \qquad (9)$$

while the latter certainly does not. Unfortunately, the latter reaction is also irreproducible, and no reportable product data are felt worthy of presentation. Systems 16 (sn:$^-$ + mn–Cl) and 17 (mn:$^-$ + sn–Cl) also do not commute. The latter gives a mixture of mn–mn, mn–sn, and sn–sn compounds in roughly equal proportions. It is probable that one is dealing with a noncage process subsequent to a one-electron transfer process

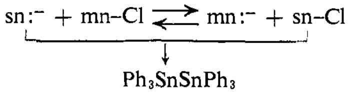


$$\text{mn:}^- + \text{sn–Cl} \longrightarrow \text{Cl}^- + \underbrace{\text{mm}\cdot + \text{sn}\cdot}_{\text{random coupling}}$$

It is not the result of processes like those of eq 8.[8]

System 16 results in a compound reducing at −2.4 v, which is neither $Ph_3SnMn(CO)_5$, $Mn_2(CO)_{10}$, nor $HMn(CO)_5$. It is probably significant that the one-electron electrochemical reduction of $BrMn(CO)_5$, which has a reductive wave at −1.4 v, produces a solution showing a new well-defined wave at −2.4 v also. System 16 also shows a well-defined wave at −2.9 v. The data are consistent with a one-electron transfer reaction yielding $Ph_3Sn\cdot$ and a Mn moiety, the former coupling to $Ph_3SnSnPh_3$, the latter being identical with the product from the electrochemical reduction of $BrMn(CO)_5$.

System 18 (sn:$^-$ + mo–Cl) behaves in a manner similar to system 24, and a process identical with eq 7 or a true charge–halogen interchange is occurring. The latter is possible here since it has been shown that $Ph_3Sn:^-$ reacts with Ph_3SnCl rapidly to give $Ph_3SnSnPh_3$ (eq 10), but $(OC)_5Mn:^-$ does not react rapidly



(10)

$$\text{sn:}^- + \text{mn–Cl} \rightleftarrows \text{mn:}^- + \text{sn–Cl};\quad \text{sn:}^- + \text{sn–Cl} \longrightarrow Ph_3SnSnPh_3 \qquad (10)$$

with $ClMn(CO)_5$. However, $Ph_3Sn:^-$ also reacts with $Ph_3SnMn(CO)_5$ to give $Ph_3SnSnPh_3$ + $(OC)_5Mn:^-$.[8] The pathways are indistinguished.

System 19 (mo:$^-$ + sn–Cl) gives the expected heterodimetallic compound, $CpMo(CO)_3SnPh_3$.

System 20 (pb:$^-$ + mn–Cl) yields a compound whose polarographic behavior and ultraviolet spectrometric behavior are inconsistent with the expected heterodimetallic. The similarity to system 10 is obvious. The commutation experiment, system 21, gives the $(OC)_5MnPbPh_3$ cleanly.

Finally, systems 22 and 23 (mo, pb) do not commute, and neither gives the desired $CpMo(CO)_3PbPh_3$ compound. System 23 gives an unidentifiable material. System 22 behaves the same as the $CpMo(CO)_3Cl$, $Ph_3Sn:^-$, and $(OC)_5Mn:^-$ systems. It has been shown

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[5] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).

[6] R. B. King, private communication.

[7] R. B. King, *Advan. Organometal. Chem.*, **2**, 157 (1964).

[8] R. E. Dessy, unpublished results, and R. E. Dessy and P. M. Weissman, *J. Am. Chem. Soc.*, **88**, 5129 (1966).

that $CpMo(CO)_3PbPh_3$ reacts with $Ph_3Pb:^-$ with $k_2 > 10$ to give $Ph_3PbPbPh_3$ and $CpMo(CO)_3:^-$.[8] Since $Ph_3Pb:^-$ does not react with Ph_3PbCl to give $Ph_3PbPbPh_3$, the source of the latter in this experiment is not charge–halogen interchange but intermediate formation of the heterodimetallic, mo–pb.

Before summing up these observations it is important to note that it appears that gegenion effects are extremely important in these reactions. For example, if system 17 (mn:$^-$ + sn–Cl) is attempted with Na^+ gegenion, the reported product,[3] in 81% yield, is $(OC)_5MnSnPh_3$. The present study, with Bu_4N^+ gegenion, gives only 30–40%, the remainder being symmetrical products.[5] Attempts to probe gegenion effects have been blocked by the fact that reduction of both the $[CpFe(CO)_2]_2$ and $Ph_3PbPbPh_3$ precursors fails to give stable anion solutions, the latter showing large traces of Pb metal. It is most likely that in the reductions of homodimetallics, a transient dianionic species is produced whose fate is determined by the gegenion. In the present case, with Bu_4N^+, that fate is to give $Ph_3Pb:^-$, for example. With Li^+, the fate is perhaps to yield PhLi and Ph_2Pb, the latter redistributing rapidly. In any case, the current observations hold for only the gegenion employed, Bu_4N^+.

In summary then it appears that interactions of m:$^-$ and m–x can lead to at least five possible results, as indicated in eq 2–4. Considerable care must be observed in choosing a reaction to synthesize a metal–metal bond. It is hoped that this work will aid the synthetic chemist choose such a path with logic and certainty.

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Organometallic Electrochemistry. IX.[1] Redistribution Reactions in Homo- and Heterodimetallic Compounds

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

Abstract: Approximately 50 redistribution reactions of the type m:$^-$ + m′–m″ $\leftrightarrows$ m–m′ + m″:$^-$ have been studied, involving anions derived from the transition and main group elements acting on metal–metal bonds of similar constitution. For $(\pi\text{-}C_5H_5)Fe(CO)_2:^-$, $Ph_3Sn:^-$, and $Ph_3Pb:^-$, the reactions are extremely rapid, with $k_2 > 10\ M^{-1}\ sec^{-1}$ and $K > 100$. The anion extruded from the heterodimetallic compound is always the least nucleophilic (most stable anion). The data have much practical advantage, in that they can aid in predicting, along with facts from previous papers in this series,[1] the proper approach to be used in the synthesis of polymetallic compounds.

Previous papers in this series reported interactions of transition and main group derived anions, m:$^-$, with analogous halides m–x. The discovery of a redistributon reaction of the following type was encountered.

$$\text{m:}^- + \text{m–m}' \longrightarrow \text{m–m} + \text{m}':^- \qquad (1)$$

The purpose of this paper is to present the scope of this reaction and discuss the conclusions which may be drawn from Chart I, where the available data are presented. This redistribution reaction, along with the conclusions reached in paper VIII of this series, sets strict boundary conditions on the proper route to heterodimetallic compounds, and thence to polymetallic compounds.

Experimental Section

The basic equipment has been previously described. The necessary compounds and their identification criteria were available from the work described earlier.[1]

In the present study, a homodimetallic compound was dissolved in dry dimethoxyethane containing 0.1 M Bu_4NClO_4. The solution, 2×10^{-3} M in homodimetallic compound, under argon, was placed in the cathode compartment of an H cell. The anode compartment contained supporting electrolyte and a large Hg pool. The cathode compartment was inletted by standard taper joints to accommodate a reference electrode (10^{-3} M Ag^+ Ag), a degassing tube, and a dropping mercury electrode. A polarogram (three-electrode geometry) was taken immediately, using the dme, reference electrode, and Hg pool in the anode compartment. A Metrohm Polarecord, modified to accept a Sargent IR compensator, was used. The connections were then made for controlled-potential electrolysis to two Kepco CK 60-0.5 power supplies wired in master–slave configuration and boot-strapped for high-input impedence. A Heath voltage reference source was used to offset the summing point of the master unit, thus setting the controlled potential, $E_{ref} - E_{test}$, for electrolysis at the large mercury pool in the cathode compartment. Current passed during the electrolysis was monitored by a small dropping resistor in series with the working electrodes, the IR drop being fed into a Yellowsprings instrument recorder. After the current had fallen to the residual level, a polarogram was made to assure that all the parent homodimetallic had been consumed. Then a degassed solution of the desired substrate (to give a 2×10^{-3} M solution) was injected rapidly, and a polarogram was taken immediately. From the potentials available[1] it was an easy matter to make the assignments shown in Chart I for the resulting products.

Results and Discussion

Chart I presents the products(s) obtained from the interaction of $(\pi\text{-}C_5H_5)Fe(CO)_2:^-$, $Ph_3Sn:^-$, $Ph_3Pb:^-$,

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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, 5124 (1966).