complexes under discussion seems to indicate the presence of some strong ion-dipole interaction between halide ions and urea molecules. Halide ion size should influence not only the strength of the ion-dipole interaction but also the spatial arrangement of the lattice which determines the crystal stability. Similar statements can be made about complexes $Pr_4NX \cdot 2CO(NH_2)_2$ (where X represents Cl or Br but not I) which do not contain water. Pure salts of Pr_4NBr and Pr_4NI are not hygroscopic but they can form complexes with urea which contain water, $Pr_4NX \cdot 3CO(NH_2)_2 \cdot H_2O$ (where X represents Br or I but not Cl). When these complexes are dried, the anhydrous 1:3 complexes remain which can reabsorb moisture and transform back to the original 1:3:1 complexes.

For the understanding of the crystal structure of these complexes one has to wait a detailed X-ray structural analysis. We may, however, say a few words about the structure of these crystalline complexes. The crystal structure of R_4NX-urea binary complexes is certainly not that of urea-*n*-paraffin hydrocarbon complexes in which urea molecules form a channel to accommodate the planar zigzag hydrocarbon molecule. The binary complexes are most likely to have cage structures in which a host component forms a cage-like network imprisoning a guest component. The host cages may be formed by urea molecules and halide ions, while R_4N^+ ions are the guest locating inside the appropriate cages. This kind of arrangement may be considered to be somewhat analogous to the clathrate hydrates formed by some tetra-*n*-butylammonium salts in which water molecules and anions form the mixed host and Bu_4N^+ ions the guest.[11] The structure will be more complicated for the ternary complexes of R_4NX-urea-water. Our speculation will place water molecules as part of the mixed host, hydrogen bonded to urea molecules and halide ions. R_4N^+ ions probably remain as the only guest in the clathrate structures.

Acknowledgments. This research was supported by the Public Health Service (Grant No. GM-11684) and the United States Department of the Interior, Office of Saline Water (Grant No. 14-01-0001-456).

(11) R. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, 31, 1231 (1959); D. Feil and G. A. Jeffrey, *ibid.*, 35, 1863 (1961); R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *ibid.*, 39, 3295 (1963).

Organometallic Electrochemistry. V. The Transition Series

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Abstract: In a continuation of the report made in paper IV[4] of this series, 65 additional transition metal derived organometallics have been studied electrochemically in dimethoxyethane.

The organometallic electrochemistry of σ-bonded derivatives of groups IIb and IVa has been previously described.[5] The basic technique involves polarographic, cyclic triangular voltammetric, and controlled potential electrolytic studies on organometallic species dissolved in dimethoxyethane with Bu_4NClO_4 as supporting electrolyte. Coupled with ultraviolet spectroscopy considerable information can be obtained concerning the fate of the organometallic assembly RmQ, when an electron is added or removed. The symbol m represents a metal, M, and a less than normal number of valence positions. The present paper presents further findings in the transition metal derived materials, involving σ- or π-complexed derivatives. For convenience of discussion the compounds in the present study are numbered consecutively from paper IV of this series which discusses 65 other compounds.[4]

Experimental Section

The experimental details have been described previously.[4] All solutions for electrochemical studies were $2 \times 10^{-3}\ M$.

The compounds used were obtained largely from various projects currently active at the Mellon Institute, or from commercial sources when available. Where necessary, further purification was accomplished by standard methods, until a polarographically "clean" material was obtained.

Electron spin resonance spectra were obtained using a classical cell designed around a Pt counter electrode and a Hg test electrode, the two being separated by a large medium-fritted disk. The reference electrode ($10^{-3}\ M$ $AgClO_4|Ag$) was placed as near the pool as possible. Transfer of the electrolyzed solutions to the 3-mm i.d. quartz esr cells was accomplished *via* and through appropriate arrangement of three Delmar O-ring valves, the normal Viton seat being replaced by Teflon and the barrel rings by low-temperature silicon rings. Evacuation of the esr cell and leads to the electrolysis cell, followed by isolation from the vacuum pump, allowed rapid transfer of the electrochemically generated species. The esr cell was attached to the electrolytic cell by an O-ringed (Viton) ball and socket joint. All solutions were $4 \times 10^{-3}\ M$. Where it appeared that hyperfine structure might be contained in a single absorption envelope, the esr spectra were measured at temperatures down to the freezing point of the solvent (−70°). The measurements were made with standard Varian equipment in the chemical laboratory, Phillips Petroleum Co.

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(4) R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 471 (1966).

(5) R. E. Dessy, *et al.*, *ibid.*, **88**, 453, 460, 467 (1966).

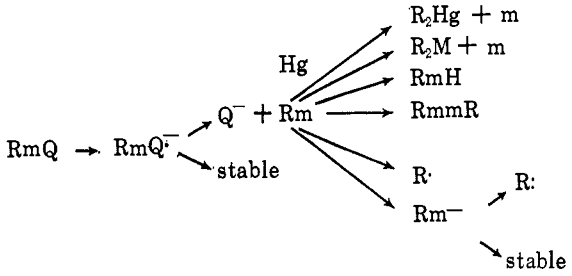
Results and Discussion

Results. The normal survey of any particular compound involved (1) polarographic examination, (2) multiple triangular sweep studies to establish chemical or electrochemical reversibility in the system, (3) exhaustive controlled-potential electrolyses at the appropriate potential and determination of n, the number of electrons involved in the polarographic step, (4) polarographic study of the resulting solution, (5) esr studies at this point if warranted, (6) attempted reoxidation (or reduction) of the electrochemically generated species to the initial compound, and (7) polarographic and spectroscopic studies of this final solution. Omissions that occur in Table I indicate that circumstances did not warrant or would not allow the surveying of that particular point for one or more of many reasons, *e.g.*, poor behavior, solubility problems, inherent instability, or logistic problems. Since the polarograms of solutions after initial reduction (or oxidation) often exhibited maxima or other irregularities, rendering evaluation of $E_{1/2}$ values difficult, triangular sweep data are provided instead. The oxidative polarographic waves produced upon reduction (or *vice versa*) were usually in the vicinity of the E_p values listed for the reversal on triangular sweep, but the two do not necessarily reflect the same species. Thus no interpretations based upon questionable $E_{1/2}$ values being compared to E_p or $E_{p/2}$ values, which for many electrochemical processes are a function of experimental parameters, are made in this manuscript.

The recovery of starting material upon subsequent reoxidation (or rereduction) was established by concurrent polarographic and ultraviolet spectral data in cases 68, 74, 76, 80, 104, and 122. In cases 99, 102, 116, 118, 123, and 130 the uncharacterized ultraviolet spectra of the initial compound forbid this route, and the sole criterion of recoverability was identity of $E_{1/2}$. The cases listed under numbers 66, 69, 71, 76, 84, 90, 97, 106, 107, 116, 123, 125, 128, and 130 are electrochemically reversible, although systems 66, 69, 90, 106, 107, 125, and 128 are chemically irreversible, the lifetime of the reduced species being short.

Systems 66, 68, 69, 70, 71, 99, 102, 116, 118, 122, 123, and 130 (from the present paper), and systems 12, 57a, and 64a (from paper IV of this series) were investigated by esr techniques. Systems 69, 99, 102, and 122 gave no signal either before or after reduction. System 130 was paramagnetic before reduction[6a] with $g_{\|} = 2.1050$, $g_{\perp} = 2.0225$, in agreement with earlier results. The reduced system showed a markedly reduced signal, suggesting a diamagnetic product. All other systems showed well-defined signals upon reduction or oxidation. The findings are reported in Table II. It is the purpose of this paper to correlate the findings concerning the 130 compounds thus far studied in this program.

Discussion. Earlier publication in this series have indicated that when an electron is added to an assembly RmQ, there are nine possible fates for the RmQ species produced. Examples of the upper routes have been presented from this laboratory.[5] Although these routes are utilized in a few of the cases in the transition series described herein, the majority that are interpretable follow the lower pathway to stable or metastable products.

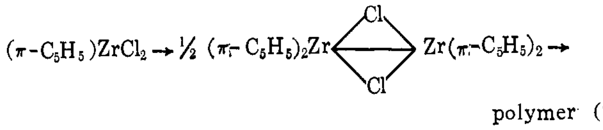


It should be realized in the following discussion that the majority of cases are diffusion controlled and in some $E_{3/4} - E_{1/4}$, for $n = 1$ processes, often approached the ~60-mv value required for electrochemical reversibility. Except where noted, however, the data of the present survey do not always allow electrochemical classification and unless such reversibility is demonstrated by data shown in the tables no simple relationship should be assumed to exist between $E_{1/2}$ and thermodynamic energy levels. However, in most cases comparisons can be made between compounds of very similar structure, where transfer coefficients are likely to be nearly identical, and the correlations will probably be qualitatively quite correct.

Group IVb. Electrochemical reduction of the cherry-red solution of $(\pi\text{-}C_5H_5)_2TiCl_2$ at the first wave yielded a paramagnetic substance, pale green in color (system 66). The esr signal showed one main line, with the satellites expected from the Ti($I = {}^5/_2$) and Ti($I = {}^7/_2$) isotopes present to the extent of 13%. The hyperfine coupling constant was 13.14 gauss, with $g = 1.9789$. Reduction at the second wave gave a dark blue solution with a paramagnetic signal identical with the above, but diminished greatly in strength. Titanocene has been recently reported to be diamagnetic,[6b] and we are therefore dealing with the sequence

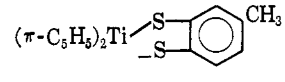
$$(\pi\text{-}C_5H_5)_2TiCl_2 \longrightarrow (\pi\text{-}C_5H_5)_2TiCl \longrightarrow (\pi\text{-}C_5H_5)_2Ti \qquad (1)$$

Surprisingly, reduction of zirconocene dichloride at either wave showed no paramagnetic signal, and it is suggested that one is observing



(2)

since the product at the second wave is a highly insoluble white powder (system 69). Reduction of the two sulfur analogs of titanocene dichloride (systems 67 and 68) show that the former is electrochemically and chemically irreversible, while the latter, in which a ring system involving the sulfur ligands is present, is electrochemically and chemically reversible. Esr data on the reduced species ($n = 1$) show the same satellite types as titanocene chloride, with a hyperfine coupling constant of 9.58 gauss and $g = 1.9857$, suggesting



If the ring had remained intact it seems likely that proton coupling with the odd electron would have been observed.

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[6] (a) H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, 5, 417 (1962); (b) G. W. Watt, L. J. Baye, and F. O. Drummond, *J. Am. Chem. Soc.*, 88, 1138 (1966).

Table I. Electrochemistry of Transition Metal Organometallics

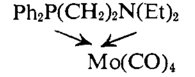
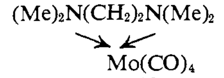
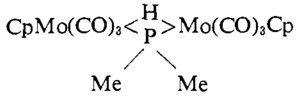
System no.	Compound	$-E^{1}{}_{1/2}$	$-E^{2}{}_{1/2}$	$n^{1\prime}$ (n^1 found)	$-E_{p,c}$	$-E_{p,a}$	% oxidn–redn	Comment after oxidn–redn cycle
				Group IVb: Ti, Zr				
66	$(\pi\text{-}C_5H_5)_2TiCl_2$	1.4	2.7	1 (0.8)	1.5	1.3	. . .	
67	$(\pi\text{-}C_5H_5)_2Ti(SPh)_2$	1.9	Ill-def	1 (1.0)	2.1	1.6	0	
68	$(\pi\text{-}C_5H_5)_2Ti(S_2C_6H_3CH_3)$	1.7	3.4	1 (1.0)	1.9	1.4	30	
69	$(\pi\text{-}C_5H_5)_2ZrCl_2$	2.3	2.7	1 (1.0)	2.4	2.2	. . .	White solid ppt at E_2
				Group Vb: V				
70	$(\pi\text{-}C_5H_5)_2VCl_2$	1.0	2.3	1 (1.0)	. . .	. . .	. . .	
71	$[(\pi\text{-}C_5H_5)VS_2C_4F_6]_2$	1.4	Complex	2 (2.0)	1.6	0.14	. . .	Electrochem and chem rev
72	$(\pi\text{-}C_5H_5)V(CO)_4$	2.4		1 (1.1)	2.7	Ill def.	0	
				Group VIb: Cr, M, W				
73	$(\pi\text{-}C_4H_4S)Cr(CO)_3$	2.5		1 (1.4)	2.7	1.2	Nil	
74	$[(\pi\text{-}C_5H_5)Cr(CO)_3]_2Hg$	1.2		2 (1.6)	. . .	. . .	100	Redn gives 2cr:$^-$
75	$(\pi\text{-}C_6H_5C_6H_5)Cr(C_6H_6)^+,Ph_4B^-$	1.3	3.3	1 (1.0)	. . .	. . .	100	Biphenyl redn at −3.3 v
76	$(\pi\text{-}C_{14}H_{10})_2Cr^+,PH_4B^-$ (anthracene)	1.4	None	1 (1.0)	1.6	1.3	100	$C_{14}H_{10}$ redn at −2.6–3.1 v
77	$Cr(CO)_5CN^-,Na^+$	0.2	2.6 (Na^+)	−1 (1.0)	0.5	0.1	0	
78	$Ph_3PMo(CO)_5$	2.7	3.7	2 (1.8)	3.2	2.1	Nil	
79	$[(CH_3)_2N]_3PMo(CO)_5$	2.9		1 (1.0)	3.1	0.7	0	
80	 $Ph_2P(CH_2)_2N(Et)_2 \rightarrow Mo(CO)_4$	2.9		2 (1.8)	3.2	2.2	100	Ultraviolet shows peak at 390 mμ as does original sample
81	 $(Me)_2N(CH_2)_2N(Me)_2 \rightarrow Mo(CO)_4$	3.0		1 (0.8)	3.2	None	Nil	
82	$(C_5H_5N)_3Mo(CO)_3$	2.8	Ill-def	. . .	3.0	None	0	
83	$(\pi\text{-}C_5H_5)Mo(CO)_3Cl$	1.4		2 (2.0)	1.9	1.1, 0.9	. . .	R_2Hg recovered on oxidn–redn cycle
84	$[(\pi\text{-}C_5H_5)MoS_2C_4F_6]_2$	1.7	2.3	2 (2.3)	1.9	1.7	0	Chem irr
85	$[(\pi\text{-}C_5H_5)MoNO(S_2C_4F_6)]_2$	1.3	1.9	2 (2.4)	1.5	0.8	0	
86	$(\pi\text{-}C_{10}H_8)(Mo(CO)_3)_2$ (azulene)	1.5	 2.3 ($-E^{3}{}_{1/2}$ = 2.7)		1.6 2.3	None 2.2	0	Azulene redn at −2.3, −3.0 v
87	$(\pi\text{-}C_5H_5)(\pi\text{-}C_3H_5)Mo(CO)_2$	2.9		(1.4)	3.1	1.0	0	
88	$p\text{-}CH_3C_6H_4N_2Mo(CO)_2(\pi\text{-}C_5H_5)$	2.3		1 (1.0)	2.7	1.1	0	Redn gives mo:$^-$
89	$(\pi\text{-}C_5H_5)MoCO(\pi\text{-}C_6H_6)^+,$ Ph_4B^-	1.4			1.7	None	0	
90	$[\pi\text{-}C_5H_5)Mo(P(Me)_2)CO]_3$	2.0	2.4	. . .	2.1	1.9	100	
91	$(\pi\text{-}C_5H_5)W(CO)_3Cl$	1.5		2 (1.8)	1.7	Complex	. . .	Redn gives w:$^-$
92	$(\pi\text{-}C_5H_5)W(CO)_3H$	2.5		1 (0.8)	2.9	0.8	. . .	Redn gives w:$^-$
93	$(\pi\text{-}C_7H_8)W(CO)_4$ (bicyclo[2.2.1]heptadiene)	2.8		1 (1.0)	3.1	Ill-def	0	
94	$(\pi\text{-}C_6H_{12})W(CO)_4$ (cyclooctadiene)	2.9		1 (1.3)	3.2	Ill-def	0	
95	$(CH_3COCH{=}CH_2)_3W$	3.0		2 (2.0)	3.5	2.0	Nil	
96	$(C_2H_5C{\equiv}CC_2H_5)_3WCO$	2.7			3.0	None	0	
97	$(\pi\text{-}C_5H_5)W(CO)_2NO$	2.4		1 (1.0)	2.7	2.3	0	Short-lived anion
98	 $CpMo(CO)_3<\overset{H}{P}>Mo(CO)_3Cp$, P(Me)(Me)	2.4		1 (1.0)	3.2	1.5	0	
99	$W_2(CO)_{10}H^-,Et_4N^+$	2.7		1 (1.2)	2.9	1.8	75	Ultraviolet unchar.
				Group VIIb: Mn, Re				
100a	$(OC)_5MnBr$	1.4		1 (1.2)	. . .	. . .	. . .	Wave at −2.4 v on redn
100b	$(OC)_5MnCl$	2.2	2.4 (small)	(1.5)	. . .	. . .	. . .	Wave at −2.4 v on redn
101	$(OC)_5MnH$	No wave to supp elect						
102	$(OC)_4MnPPh_3$ (may be dimer)	2.0	3.5	1 (0.8)	2.4	1.1	25	
103	$CH_3SCH_2CH_2COMn(CO)_4$	2.2		(1.4$^+$)	2.8	1.7	0	
104	$(CH_3)_2NCH_2CH_2COMn(CO)_4$	2.3		2 (2.2)	2.1	1.7	25	Ultraviolet shoulder at 344 mμ
105	$(\pi\text{-}C_3H_5)[Mn(CO)_5]_2$	1.8		1 (1.2)	2.1	Complex	0	
106	$(\pi\text{-}C_5H_5)_2Mn_2(NO)_3$	1.6		1 (1.0)	1.8	1.5	0	
107	$(\pi\text{-}C_5H_5)_6Mn_6(NO)_8$	1.9		Cycles	2.0	1.6	. . .	
108	$(\pi\text{-}C_5H_5)Re(CO)_3$	3.3			3.5	1.5	0	

Table I (*Continued*)

System no.	Compound	$-E^1{}_{1/2}$	$-E^2{}_{1/2}$	$n^{1\prime}$ (n^1 found)	$-E_{p,c}$	$-E_{p,a}$	% oxidn–redn	Comment after oxidn–redn cycle
	Group VIII: Fe^-							
109a	$(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)^+$, PF_6^-	0.8		1 (0.7)	1.2	0.2		$[CpFe(CO)_2]_2$
			2.2	cal	2.4	1.9		
109b	$(\pi\text{-}C_5H_5)Fe(CO)_2PPh_3^+,PF_6^-$	1.4		1 (0.7)	1.6	0.2		$[CpFe(CO)_2]_2$
			2.2					
110	$(\pi\text{-}C_5H_5)Fe(CO)_3^+,PF_6^-$	1.4	2.2	1 (0.7)	1.6	0.2		$[CpFe(CO)_2]_2$
111	$(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)_2^+,PF_6$	1.4	. . .	1 (1.0)	1.7	None		
112	$Fe_3(CO)_{12}$	1.6	2.4	1 (0.7)	1.7	1.3	0	Not $HFe_3(CO)_{11}^-$
113	$HFe_3(CO)_{11}^-,Et_3NH^+$	0.2			0.3	0.1		
			1.9		2.2	None		
114	$CpFeS_2C_4F_6$	2.0		2 (1.7)	2.5	1.8		Perhaps short-lived species, $-E^{ox}{}_{1/2}$ = = 1.1 v
115	$CpFe(CO)S_2CN(CH_3)_2$	2.3	2.9	1 (1.1)	2.6	2.1	0	
116	$(\pi\text{-}C_8H_8O)Fe(CO)_3$ (cyclooctatrienone)	1.7	2.2	1 (0.9)	1.9	1.5	60	Ultraviolet unchar.
117	$(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_6H_7)$	0.6		−1 (1.0)	None	0.3	0	
118	$C_6H_{10}COFe(CO)_3$	2.1		(1.5)	2.3	1.8	40	Ultraviolet unchar.
119	$(\pi\text{-}C_8H_{10})Fe_2(CO)_6$	1.8		. . .	2.6	None	0	
120	$((OC)_3FeNH)_2$	2.2		1 (1.0)	2.5	Complex	0	
121	$(\pi\text{-}C_{12}H_8)Fe_2(CO)_6$ (acenaphthylene)	1.8			2.1	Ill-def	0	
			2.4	1 (1.1)	2.6	2.2		
			($-E^3{}_{1/2}$ = 3.5)					
122	Biferrocenyl	0		−1 (1.1)	0	−0.3	100	
			0.2	−1 (0.9)	0.4	0	100	
	Group VIII: Co, Rh, Ir							
123	$[(\pi\text{-}C_5H_5)Co(CO)]_3$	1.6		1 (1.0)	1.8	1.6	50	
		Complex			1.6	1.4		
124	$Co_2(CO)_6 \cdot PhC{\equiv}CPh$	1.6	Ill-def	1 (1.0)	2.1	Complex		$PhC{\equiv}CPh$ generated on redn
125	$ClC(Co(CO)_3)_3$	1.1	2.0	1 (1.0)	1.2	0.9	0	
126	$Co_2(CO)_7(C_4HO_2)$	1.2		1 (0.8)	1.6	Complex	0	
127	$(\pi\text{-}C_2H_4)(\pi\text{-}C_2F_4)Rh(O_2C_5H_7)$	1.9	Ill-def	. . .	2.2	Ill-def	0	
128	$(\pi\text{-}C_5H_5)IrS_2C_4F_6$	1.7		1 (0.8)	2.1	1.7	0	
	Group VIII: Ni, Pt							
129	$(Ph_3P)_2Pt \cdot PhC{\equiv}CPh$	3.4	. . .	. . .	. . .	. . .	. . .	
		Ill-def						
130	$(\pi\text{-}C_5H_5)_3Ni_3(CO)_2$	1.5	2.7	1 (0.7)	1.7	1.4	100	

Hydrocarbon ligands used in this study	$E^1{}_{1/2}$	$E^2{}_{1/2}$
Anthracene	2.6	3.1
Acenaphthylene	2.3	3.0
Azulene	2.3	3.0
Cyclopheptatriene	3.2	
Cyclooctadiene	No wave	
Cyclooctatetraene	2.5	
Biphenyl	3.3	
Bipyridyl	2.9	3.2
Bicyclo[2.2.1]heptadiene	3.1	
$PhC{\equiv}CPh$	3.0	
$C_4H_9C{\equiv}CH$	No wave	

Group Vb. $(\pi\text{-}C_5H_5)_2VCl_2$ is paramagnetic in solution, giving an eight-line spectrum with a hyperfine splitting constant of 70–80 gauss (V, $I = {}^7/_2$) and g = 1.99. On reduction the green solution turns pale, giving a new esr signal, consisting of eight lines, ΔH. = 82–96 gauss, g = 1.98. Further reduction, at the second wave, gives an extremely air-sensitive blue solution that could not be handled well enough to obtain a good signal. Vanadocene, which is blue, is reported to have ΔH = 27.4 gauss.[7] The pathway of reduction therefore parallels eq 1.

The dithietene complex $[(\pi\text{-}C_5H_5)VS_2C_4F_6]_2$ shows, upon two-electron reduction, a complex esr signal which is still being analyzed. The system is electrochemically and chemically reversible.

Group VIb. Considering first zerovalent metal species, $M(CO)_xL_3$, systems 3, 4, 6, 7, 9, 23, 78, 82, 93, and 94 illustrate that the reduction potential of such species is largely independent of ligand and is close to the same value for all three metals ($-E_{1/2}$ = 2.85 ± 0.15 v).

In the area of M(I), two sets of species are encountered: first, the uncharged species of the type $(\pi\text{-}C_5H_5)M(CO)_3X$. Systems 17–22, 74, 83, 91, and 92 suggest that the reduction potential of $(\pi\text{-}C_5H_5)M(CO)_3X$,

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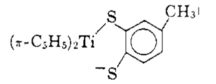
(7) B. McConnell, *J. Chem. Phys.*, **24**, 764 (1959); **30**, 442 (1959).

Table II. Esr Results

System	Compound	g	ΔH, gauss	Comment
12	Bipyridyl · $Mo(CO)_4 \cdot^-$	2.0031	. . .	Signal consisted of 45 lines, made up of what appears to be five main groups, in intensity ratio 1:2:3:2:1, each 5.4 gauss wide. The spacing of the 45 lines is *ca.* 0.6 gauss ($I_N = 1$)
57a	$[(\pi\text{-}C_5H_5)NiSCH_3]_2 \cdot^+$	2.0267	15	Very small signal with hyperfine structure also observed
64a	$(\pi\text{-}C_5H_5)Rh(\pi\text{-}C_2H_4)_2 \cdot^+$	1.9855	14	Hyperfine structure unresolved owing to low concentration of sample and poor signal: noise ratio
66	$(\pi\text{-}C_5H_5)TiCl$	1.9789	2.0	Satellite signals due to Ti^{47} ($I = ^5/_2$) and Ti^{49} ($I = ^7/_2$), total abundance 13.2%, are evident, with hyperfine coupling constant of 13.14 gauss
68		1.9857	2.0	Satellite signals due to Ti^{47} and Ti^{49} are evident, with hyperfine coupling constant of 9.58 gauss
69	$(\pi\text{-}C_5H_5)_2ZrCl_2$	No esr signal at either wave		
70	$(\pi\text{-}C_5H_5)_2VCl_2$	1.99[a]	493	Eight-line spectrum of approximately equal intensity with an average hyperfine coupling constant of 75 gauss ($I_V = ^7/_2$)
	$(\pi\text{-}C_5H_5)_2VCl$	1.98[a]	578	Eight-line spectrum of approximately equal intensity with an average hyperfine coupling constant of 89 gauss ($I_V = ^7/_2$)
71	$[(\pi\text{-}C_5H_5)VS_2C_4F_6]_2 \xrightarrow{2e}$		578	~64 lines, intensity pattern complex, but suggestive of eight major signals, each further split ($I_V = ^7/_2$)
116	$(\pi\text{-}C_8H_8O)Fe(CO)_3 \cdot^-$	2.0403	12.8	Signal gradually decreased with time
118	$C_6H_{10}COFe(CO)_3 \cdot^-$	2.0572	8 (very weak)	
		2.0341	8[b] (strong)	
123	$[(\pi\text{-}C_5H_5)Co(CO)]_3 \cdot^-$	. . .	~700	>18 observable lines of variable, but approximately equal intensity ($I_{Co} = ^7/_2$)

[a] Midpoint of two center lines. [b] Modulation broadened.

either by a one-electron step (to yield $CpMo(CO)_3:^-$) or a two-electron step (to yield $CpMo(CO)_3:^- + X^-$) is a function of the bond strength of m–X. Although these latter values are not available, comparison of reduction potentials with $\geqslant$C–X bond strengths[8] show X, $-E_{1/2}$ (E_{C-X} in kcal/mole): Cl, 1.35 ± 0.15 (80); C, 2.05 ± 0.15 (80); C, 2.05 ± 0.05 (83); H, 2.5 (90).

The second series deals with the π-arenechromium compounds involving Cr(I), but where the molecular species is positively charged. Systems 1, 2, 75, and 76 have reduction potentials of the order of -1.2 ± 0.1 v, despite the fact that the reduction potentials of the arene ligands alone vary from -2.6 v to beyond supporting electrolyte. In the latter two cases it is interesting that although anthracene reduces at -2.6 v, bisanthracenechromium cation shows just one wave at -1.4 v. On the other hand, biphenylphenylchromium cation shows a reduction wave at -3.3 v, identical with that of biphenyl, in addition to the more anodic reduction at -1.3 v.

System 86, in which a mo–mo bond exists, follows the pattern to be discussed in paper VI of this series,[9] where it is shown that m–m bonds in vastly different molecules often have similar reduction potentials (*cf.* system 20).

Group VIIb. Once again an empirical correlation appears to exist between the reduction potential, and a good estimate of m–X bond strengths in $(OC)_5Mn\text{–}X$ reductions (systems 100a,b and 101), with H > Cl > Br. Also, in those systems showing a mn–mn bond (systems 27–29 and 105–107) either in simple bimetallic species or in cluster systems (*cf.* paper VI of this series[9]) the reduction potential appears to have a common value near -1.8 v, despite rather large changes in ligands in the moiety.

Finally, the trend observed earlier (*cf.* system 29, $[M(CO)_5]_2$) of increasing reduction potentials of analogs as one descends the table holds true for the $(\pi\text{-}C_5H_5)$-$M(CO)_3$ case (M = Mn and Re).

Group VIII. In the iron triad, the most noticeable feature occurs in the reduction of $(\pi\text{-}C_5H_5)Fe(CO)_xL^+$ (systems 109a,b and 110) in which reduction by an $n = 1$ step gives $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Only when $x < 2$ does this fail (system 111).

Again, in the compounds having relatively simple fe–fe bonds (systems 49, 51, 119, 121) the reduction potentials group closely together at -2.0 ± 0.2 v.

The hopes that electrochemical reduction of $Fe_3(CO)_{12}$ would give $HF_3(CO)_{11}^-$ were not fulfilled (systems 112, 113) as comparison ultraviolet spectra indicated.

Finally, at a Pt working electrode it was possible to see biferrocenyl oxidize by, first, an $n = 1$ step to give a species in which two different valence states of Fe exist (*cf.* system 48a) followed by further oxidation to the biferrocenyl dication, which could be rereduced to the initial material.[10]

General Discussion. Of the 130 compounds screened thus far in this survey, 28 proved electrochemically reversible. Of these, 11 involved such short-lived reduction products that the system was chemically

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(8) F. G. Cottrell, "The Strengths of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954.

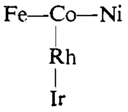
(9) R. E. Dessy, M. Weissman, and R. L. Pohl, *J. Am. Chem. Soc.*, **88**, 5117 (1966).

(10) E. G. Perevalova, S. P. Gubin, S. A. Smirnova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **147**, 384 (1962), have reported on chemical oxidation to the monocation.

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



$$\begin{array}{ccc} \mathrm{Fe} - & \mathrm{Co} & - \mathrm{Ni} \\ & | & \\ & \mathrm{Rh} & \\ & | & \\ & \mathrm{Ir} & \end{array}$$

reduction potentials of the neutral chelate $(\pi\text{-}C_5H_5)MS_2C_4F_6$ 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 $(\pi\text{-alkene})Fe(CO)_3$ complexes, yield radical anions with no evidence of spin density on the organic ligand. Similar findings are observed for the $(\pi\text{-}C_5H_5)MS_2C_4F_6$ 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.

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(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

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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′ liason from $m:^- + m'\text{-}x$ (or $m': + m\text{-}x$) (1) is the ΔF° favorable (strength of the m–m′ bond), (2) is $\Delta F^{\pm}{}_{m-m'}$ favorable (reasonable rate), (3) is $\Delta F^{\pm}{}_{m-m'}$ lower than the activation free

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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 (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.