Organometallic Electrochemistry. IV. The Transition Series

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Abstract: Sixty-four organometallic compounds derived from the transition metals have been surveyed electrochemically at mercury electrodes. Twenty-seven of the cases appear to involve chemically reversible electron addition–removal, with reasonable lifetimes for the new species generated.

The organometallic electrochemistry of σ-bonded derivatives of groups II-B, IV-A, and V-A has been previously described.[4] 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 preliminary findings in the transition metal derived materials, involving σ- or π-complexed derivatives.

Experimental Section

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

The compounds used were obtained from various projects currently active at the Mellon Institute, the Ethyl Corp., courtesy of Dr. Dubeck, Professor Roland Pettit, Dr. Richard Cramer, 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 4×10^{-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.

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,[5] (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 to compare with the initial solution. Omissions that occur in Table I, which show that portion of the work which is extensive enough at present to be systematically discussed, 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 4, 9, 23, 31, 49, 55b, 57a, and 61. In cases 30, 32–35, 47b, 48b, and 50, 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 1, 2, 12, 24, 36, 37, 47a, 48a, 53, 54, 58, 59, 62, and 63a are *electrochemically reversible* with stable products using as criteria either the identity of $E_{1/2}{}^{\mathrm{redn}}$ for the oxidized form and $E_{1/2}{}^{\mathrm{oxidn}}$ of the reduced species, or the 0.059/mv separation of the $E_{p/2}{}^{\mathrm{anodic}}$ and $E_{p/2}{}^{\mathrm{cathodic}}$ derived from the slow-sweep voltammograms. Therefore polarographic evidence of recovery was deemed completely adequate. System 1 is a classic, well-published example and indicates the approximate separation of $E_{p,c}$ and $E_{p,a}$

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[4] R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, 87, 453, 460, 467 (1965).

[5] Triangular sweep data are reported as $E_{p,c}$, the potential at maximum peak height on a cathodic going ramp, or the corresponding anodic value, $E_{p,a}$. $E_{p/2}$ represents the potential at one-half peak height.

Table I.[a] Electrochemistry of Transition Metal Organometallics

System	Compound	$-E^1{}_{1/2}$[a]	$-E^2{}_{1/2}$[a]	n^1 (n found)[b]	$(-E_{p.c},$	$-E_{p.a})$[c]	% oxidn.–redn. recovery[d]	Comment after oxidn.–redn. cycle
	Group VIb: Cr, Mo, W							
1.	$(\pi\text{-}C_6H_6)_2Cr^+B(C_6H_5)_4^-$	1.3	...	1 (1.0)	1.4	1.1	100	
2.	$(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)Cr^+PF_6^-$	1.2	...	1 (1.0)	1.4	1.1	100	
3.	$Cr(CO)_6$	2.7	...	? (1–2)	3.3	2.0	0	
4.	$(\pi\text{-}C_6H_6)Cr(CO)_3$	3.0	...	2 (2.2)	Ill behaved		100	
5.	$(\pi\text{-}C_7H_8)Cr(CO)_3$ (cycloheptatriene)	2.4	...	1 (1.0)	2.8	Ill defined $\sim$0.7	0	Two new unidentified species $-E_{1/2}$ = 2.3, 1.1; the latter elect. rev.
6.	$(\pi\text{-}C_7H_8)Cr(CO)_4$ (bicyclo[2.2.1]heptadiene)	2.8	...	2 (1.8)	3.2	0.8	0	
7.	$((CH_3)_2N)_3PCr(CO)_5$	2.9	...	2 (2.1)	...	...	0	
8.	$[((CH_3)_2N)_3P]Cr(CO)_4$	>3.6	...	...	...	...	...	
9.	$Mo(CO)_6$	2.7	...	1 (0.9)	3.2	2.0	50	
10.	$(\pi\text{-}C_7H_8)Mo(CO)_3$ (cycloheptatriene)	2.3	...	1 (0.9)	2.5	1.0	0	
11.	$(\pi\text{-}C_7H_8)Mo(CO)_4$ (bicyclo[2.2.1]heptadiene)	2.3	...	Decomposes in solvent			...	
12.	Bipyridyl·$Mo(CO)_4$	2.2	2.8	1 (1.05)	2.3	1.9	80	
13.	$(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_3H_5)$	2.9	...	(1.5)	Complex	1.0	0	
14.	$(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}CH_2{=}SCH_3)$	0.2 (oxidn)	2.7	1 (1.0) (redn)	3.0	1.5	0 0	
15.	$(\pi\text{-}C_5H_5)Mo(CO)_2[\pi\text{-}C_6H_5CH_2\text{-}]$	2.3	...	(2.4)	Complex		0	
16.	$(\pi\text{-}C_5H_5)Mo(CO)_2(\pi\text{-}C_7H_7)$	Ill defined	...	1 (1.1)	Ill behaved		0	Polarographic pattern identical, but ultraviolet shows compound regenerated is not initial material
17.	$(\pi\text{-}C_5H_5)Mo(CO)_3[\sigma\text{-}C_6H_5CH_2\text{-}]$	2.1	...	1 (1.1)	2.5	1.0	0	New wave, $-E_{1/2}$ = 1.3
18.	$(\pi\text{-}C_5H_5)Mo(CO)_3(CH_2CO_2CH_3)$	2.0	...	1 (1.0)	2.2	1.0	0	New wave, $-E_{1/2}$ = 1.3
19.	$(\pi\text{-}C_5H_5)Mo(CO)_3CF_3$	2.1	...	(1.6)	2.5	Wide multi peak envelope near 1.0	0	New wave, $-E_{1/2}$ = 1.3
20.	$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$	1.4	...	2 (1.8)	1.5	1.0	...	$[(\pi\text{-}C_5H_5)Mo(CO)_3]Hg$ recovered
21.	$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$	1.3	...	2 (2.0)	1.4	1.0	...	
22.	$(\pi\text{-}C_5H_5)Mo(CO)_3Fe(CO)_2(\pi\text{-}C_5H_5)$	1.4	...	1 (1.0)	1.7	1.0	...	
23.	$W(CO)_6$	2.6	...	1 (1.3)	3.0	2.0	20	
	Group VIIb: Mn, Re							
24.	$(\pi\text{-}1,3,5\text{-}(CH_3)_2C_6H_3)Mn(CO)_3^+I^-$ (mesitylene)	0.9	...	1 (1.1)	1.0	0.8	50	
25.	$(\pi\text{-}C_5H_5)Mn(CO)_3$	3.0	...		3.5	Poorly defined	0	Polarographic pattern ident, but ultraviolet shows compound regenerated is not initial material
26.	$(\pi\text{-}C_5H_5)Mn(CO_2)NO^+PF_6^-$	0.8	...	1 (0.75)	1.0	0	0	
27.	$[\pi\text{-}C_5H_5Mn(CO)NO]_2$	2.0	...	2 (2.0)	...	...	0	
28.	$(\pi\text{-}C_5H_5)_3Mn_2(NO)_3$	1.5	2.5	1 (1.0)	1.7	1.4	0	
29.	$[Mn(CO)_5]_2$	1.8	...	2 (1.9)	1.9	1.1	0	$[(OC)_5Mn]_2Hg$ recovered
	$[Re(CO)_5]_2$	2.3	...	2 (1.9)	2.6	1.4	0	$[(OC)_5Re]_2Hg$ recovered
	Group VIII: Fe							
30.	$Fe(CO)_5$	2.4	...	1 (0.95)	2.8	1.8	5	
31.	$(\pi\text{-}C_8H_8)Fe(CO)_3$	2.0	2.5	1 (0.85)	2.2	1.7	30	
32.	$(\pi\text{-}C_6H_8)Fe(CO)_3$	2.7	...	1 (1.1)	3.2	1.2	70	
33.	$(\pi\text{-}C_4H_6)Fe(CO)_3$	2.6	...	1 (1.3)	2.7	Poorly defined	0	
34.	$\pi\text{-}n\text{-}C_6H_9Fe(CO)_3^+(C_6H_5)_4^-$	2.6	...	? > 2	...	...	30	
35.	$(n\text{-cyclo-}C_7H_9)Fe(CO)_3^+BF_4^-$	0.7	...	? > 2	0.8	0.3	20	
36.	$(\pi\text{-}1,3,5\text{-}(CH_3)_3C_6H_3)Fe(\pi\text{-}C_5H_5)^+I^-$ (mesitylene)	2.0	...	...	2.1	1.9	...	
37.	$(\pi\text{-}C_6H_6)Fe(\pi\text{-}C_5H_5)^+PF_6^-$	1.9	2.9	1 (0.96)	2.0	1.8	40	
38a.	$(\pi\text{-}C_9H_7)_2Fe$ (indenyl)	0.4	...	−1 (1.1)	0.5	0.2	...	Ferricinum ion well known, stable species
38b.			2.7	2 (1.8)	3.0	1.1	0	
39.	$(\pi\text{-}C_5H_5)Fe(CO)_2SCOC_6H_5$	1.8	2.2	1 (1.1)	$\sim$2.0	Complex $\sim$1.0		New wave $-E_{1/2}$ = 1.2 elect. rev.
40.	$(\pi\text{-}C_5H_5)Fe(CO)_2COCH_3$	2.5	...	1 (1.1)	3.0	2.3	0	
41.	$(\pi\text{-}C_5H_5)Fe(CO)_2CH_2C_6H_5$	2.5	...	2 (2.0)	...	...	0	

Table I[a] (*Continued*)

System	Compound	$-E^1_{1/2}$[a]	$-E^2_{1/2}$[a]	n^1 (n found)[b]	($-E_{p.c}$,	$-E_{p.a}$)[c]	% oxidn.–redn. recovery[d]	Comment after oxidn.–redn. cycle
42.	$(\pi\text{-}C_5H_5)Fe(CO)_2(C_6F_5)$	2.3	3.0	(1.5)	Complex		0	
43.	$(\pi\text{-}C_5H_5)Fe(CO)_2COCH{=}CHC_6H_5$	2.4–2.7	ill defined	2 (2.0)	∼3.0	1.5	0	
44.	$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	2.2	...	2 (2.2)	2.4	1.9		$[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg$ 100% recovered
45.	$[(\pi C_5H_5)Fe(CO)_2]_2Hg$	2.0	2.4 (ill defined)	...	2.0, 2.4	1.9	...	
46.	$(\pi\text{-}C_5H_5)Fe(CO)_2I$	1.2	...	1 (1.0)	1.4	0.8	...	Product upon reduction *only* is $[(\pi\text{-}C_5H_5)\text{-}Fe(CO)_2]_2Hg$
47a.	$(\pi\text{-}C_5H_5)Fe(CO)_2SMe$	0.4	...	−1 (1)	0.6	0.3	50	Radical cation is green
47b.		...	2.1	2 (1.8)	2.5	1.8	50	
48a.	$[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2$	0.6	...	−1 (0.9–1.1)	0.7	0.4	100	Radical cation is green
48b.		...	2.4	2 (2.2)	Ill behaved		30	
49.	$[CH_3SFe(CO)_3]_2$	1.9	2.5 (ill defined)	1 (1.1)	Ill behaved		100	
50.	$Fe_2(CO)_9$	2.4	...	2 (1.8)	Ill behaved		50	
51.	$(\pi\text{-}C_{10}H_8)Fe_2(CO)_5$	2.2	...	Ill behaved	2.3	2.1	Nil	
			Group VIII: Co, Ni					
52.	$(\pi\text{-}C_5H_5)Co(CO)_2$	2.5	3.2 (ill defined)	1 (0.8)	2.9	2.1	0	Co metal detectable upon reoxidation
53.	$(\pi\text{-}C_5H_5)CoS_2C_4F_6$ (red)	1.1	2.9	1 (1.1)	1.2	0.9	100	Radical is colorless
54.	$Co(S_2C_4F_6)_2{}^{2-}2Et_4N^+$	0.84	∼3.0	−1 (1.0)	...	...	...	Yields green soln. on oxidation, system elect. rev.
55.	$Co(acac)_3$[e]	1.2	2.6	1 (0.85–1.1)	1.5	0.7	0	Redn. gives $Co(acac)_2$
	$Co(acac)_2$[e]	2.6	...	1 (1.2)	2.8	2.6	30	Radical is purple, yields Co on decompn.
56a.	$[(\pi\text{-}C_5H_5)Ni(CO)]_2$	0.55	...	−2 (1.9)	0.7	0.4	Nil	New elect. rev. couple $-E_{1/2} = 1.5$
56b.		...	2.4	2 (2.1)	2.7	2.2	0	
57a.	$[(\pi\text{-}C_5H_5)NiSCH_3]_2$	0.5	...	−1 (0.9)	0.6	0.3	100	
57b.		...	1.8	1 (1.2)	2.0	1.7	Nil	
58.	$(\pi\text{-}C_5H_5)NiS_2C_4F_6$ (green)	0.96	2.4	1 (1.0)	1.1	0.8	100	Reduction product is colorless
59.	$Ni(S_2C_4F_6)_2{}^{2-}2Et_4N^+$	0.84 (oxidn)	...	...	...	...	...	Yields green soln. on oxidation, system elect. rev.
60.	$Ni(acac)_2$[e]	2.2	...	1 (0.8)	2.5	2.0	0	Radical is deep blue yields Ni on decompn.
61.	$[\pi\text{-}C_5H_5)Ni]_2\cdot HC{\equiv}CH$	2.2	...	2 (2.15)	2.5	1.9	25	
			Group VIII: Rh					
62.	$Ni(CO)_4$	2.9	...	1 (0.8)	3.2	1.5	0	Radical is purple
63.	$(\pi\text{-}C_5H_5)RhS_2C_4F_6$	1.4	...	1 (1.2)	1.5	1.2	100	
64a.	$(\pi\text{-}C_5H_5)Rh(\pi\text{-}CH_2{=}CH_2)_2$	0.25	...	−1 (1.0)	...	...	100	System is nearly elect. rev.
64b.			3.2	Cycles (+n)	...	...		
65.	$(\pi\text{-}CH_2{=}CH_2)_2Rh(O_2C_5H_7)$	2.8	...	1 (0.9)	...	...	0	

[a] All data from three electrode potentiostatic geometry, 2×10^{-3} M in substrate, 1×10^{-1} M Bu_4NClO_4, in $CH_3OCH_2CH_2OCH_3$ with reference to 1×10^{-3} $AgClO_4|Ag$ suspended in 1×10^{-1} M Bu_4NClO_4 in $CH_3OCH_2CH_2OCH_3$ at 22°. [b] Exhaustive controlled potential electrolysis. (Positive values represent reductions, negative values oxidations.) Values are for the first wave except where oxidative waves are present. Both values are shown then. [c] Peak currents, cathodic (reductive) and anodic (oxidative), respectively, at 1 v/sec triangular sweeps on a hanging Hg drop employing the starting material. [d] Percentage of starting material recovered after exhaustive controlled potential reduction followed by oxidation (or *vice versa*) as determined by diffusion wave height or ultraviolet spectra or both. [e] Molecular weight data on $Co(acac)_2$ by osmometry indicated some association at 0.5 M concentrations; mol wt: calcd, 257; found, 312. For Ni $(acac)_2$, mol wt: calcd, 256; found, 420. acac = acetylacetonate.

for an electrochemically reversible system under the sweep conditions, *ca.* 300 mv.

Systems 4, 9, 48b, 49, 50, and 63a were investigated *via* esr techniques with *negative* results. Systems 4, 48b, and 50 might be expected to be diamagnetic, while heavy metals in systems 9 and 63 are prone to be difficult at low concentrations. Only system 49 is puzzling. Systems 31, 32, 37, 47a, 48a, 53, 55b, 58, and 60 gave *positive* results, and the findings are listed in Table II. Except for system 53 which showed the expected eightfold multiplet (I_{Co} = 7/2) all other radical species showed a single sharp line. The delocalization does not in these cases extend to the π-complexed organic function. The extent of delocalization into the other ligands is being probed by C^{13} labeling. Barring then a little reserve concerning the

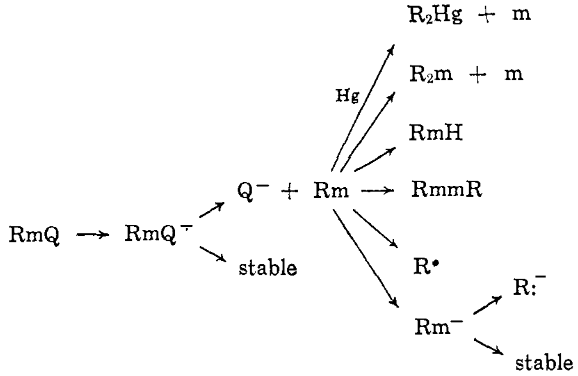
Table II. E.s.r. Results

System	Compound	ΔH, gauss	g	Comment
30	$Fe(CO)_5^{\overline{\cdot}}$	20.8	2.038	Signal grows with time–paramagnetic decomposition product
31	$(\pi\text{-}C_8H_8)Fe(CO)_3^{\overline{\cdot}}$	5.40[a]	2.0073	
32	$(\pi\text{-}C_6H_8)Fe(CO)_3^{\overline{\cdot}}$	11.4[a]	2.053	
37	$(\pi\text{-}C_6H_6)Fe(\pi\text{-}C_5H_5)$	. . .	~2.1	Broad signal due to ferromagnetic ppt (Fe) on reduction
47a	$(\pi\text{-}C_5H_5)Fe(CO)_2SCH_3^{\dot{+}}$	9.36[a]	1.9978	
48a	$[\pi\text{-}C_5H_5Fe(CO)SCH_3]_2^{\dot{+}}$	7.12[a]	1.9982	
54	$(\pi\text{-}C_5H_5)CoS_2C_4F_6^{\overline{\cdot}}$	288.1[b]	2.454	Eight lines, 41-gauss separation ($I_{Co} = 7/2$)
55b	$Co(acac)_2$	. . .	~2.5	Broad signal due to ferromagnetic ppt (Co) on reduction
58	$\pi\text{-}C_5H_5NiS_2C_4F_6$	9.88[a]	2.0479	Reduction destroys signal
60	$Ni(acac)_2$	. . .	~2.2	Broad signal due to ferromagnetic ppt (Ni) on reduction

[a] Signals are sharp, single-line presentations. [b] Signal consists of eight hyperfine lines, monotonically decreasing in intensity toward lower field.

six species (systems 30, 34, 35, 47b, 48b, and 50) which involve electrochemical irreversibility and which cannot be characterized well by spectral data, 42 of the 64 cases cited can be analyzed. Retaining the reserve mentioned above, 27 of the cases appear to involve *chemically reversible* electron donation or abstraction from the organometallic assembly involved. The synthetic applications of these new species are being explored. It is the purpose of the present paper to present a survey of the original findings, thus setting a stage for further work in this area. Findings on 60 other transition metal derivatives, and 50 compounds containing metal–metal bonds will be reported in future publications.

Discussion. Earlier publications in this series have indicated that when an electron is added to an assembly RmQ, there are nine possible fates for the $RmQ^{\overline{\cdot}}$ species produced. Examples of the upper routes have been presented from this laboratory.[4] 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 shown 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, and the correlations are probably qualitatively quite correct.

Group VI-B. Among the group VI-B derived materials, three rather distinct subunits may be observed: (1) formally M(I) derivatives with $-E_{1/2}$ near 1.3 ± 0.1 v (systems 1, 2, 20, 21, and 22); (2) a rather limited set (systems 17, 18, and 19) formally derivatives of Mo(II) involving σ-bonded organic functions $[(\pi\text{-}C_5H_5)Mo(CO)_2R]$ with $-E_{1/2} = 2.0 \pm 0.1$ v; and finally a heterogeneous set (3) made up of derivatives of M^0 ligated to neutral organic species capable of σ and $d\pi\text{-}p\pi$ bonding gathered together with π-complexed derivatives of M^0 and π-allyl type derivatives of $(\pi\text{-}C_5H_5)Mo(CO)_2^-$, with $-E_{1/2} = 2.3\text{-}3.0$.

In set 1 the electron addition essentially completes the inert gas configuration of a cation or dimerized radical. It is the later cases which are new (systems 20–22). They resemble the corresponding derivatives in the Fe series (systems 44–46), and deserve discussion together. $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$, $[(\pi\text{-}C_5H_5)Fe(CO)_2]$, and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2Hg$ undergo two electron reductions to the known anions $(\pi\text{-}C_5H_5)Mo(CO)_3{:}^-$ and $(\pi\text{-}C_5H_5)Fe(CO)_2{:}^-$, respectively. The existence or nonexistence of transient dianion diradicals or monoanion radicals enroute is not revealed by 1 v/sec voltammograms. Reoxidation of these anions, or reduction of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ ($n = 1$)[6] give the transient radicals $(\pi\text{-}C_5H_5)Mo(CO)\cdot$ and $(\pi\text{-}C_5H_5)Fe(CO)_2\cdot$ whose fate is to immediately react with the Hg electrode to yield $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]Hg$. The exceedingly rapid nature of this process is revealed by the identity of *cathodic* traces for the known $[(\pi\text{-}C_5H_5)M(CO)_x]_2Hg$ and anodic/*cathodic* voltammograms on the respective anions. The existence of RHg species may be postulated and the chemistry of these radicals generated at other electrodes is being explored.

In the coupled species $(\pi\text{-}C_5H_5)Mo(CO)_3Fe(CO)_2(\pi\text{-}C_5H_5)$ it is the discharge potential of the Mo fragment which is $E_{1/2}$ determining, the respective $-E_{1/2}$ (M–M) being, 1.4 v (Mo–Mo); 2.2 v (Fe–Fe); 1.4 v (Mo–Fe). Set 2, which extends this series to Mo–C< shows higher potentials ($-E_{1/2} = 2.0 \pm 0.1$ v), but the product of reduction in each case of $(\pi\text{-}C_5H_5)Mo(CO)_3R$ [$R = \sigma\text{-}PhCH_2, CH_2CO_2CH_3, CF_3$] is $(\pi\text{-}C_5H_5)Mo(CO)_3{:}^-$ and R·, the fate of the latter being unknown. Reoxidation of the solution gives $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$ identified *via* its characteristic ultraviolet spectra and polarographic behavior.

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[6] The $E_{p,a}$ at −0.8 v on voltammograms of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ is oxidation of I^-.

In set 3 one notices that in $M(CO)_6$ the nature of M (Cr, Mo, W) does not affect $E_{1/2}$. $(\pi\text{-}C_6H_6)Cr(CO)_3$ gives a stable yellow solution on reduction ($n = 2$) which upon electrochemical or chemical ($HgCl_2$) oxidation regenerates the initial compound. $Mo(CO)_6$ and $W(CO)_6$ gave radical anions on electrochemical reduction, the solutions assuming a deep orange color. Electrochemical or chemical oxidation led to recovery of some of the initial materials in each case, but a slow alternate pathway for destruction of the anion radical exists. This pathway is now being studied. Attempts at finding similar or more stable anions *via* substitution of CO in $M(CO)_6$ by π-complexed olefins or $\gg$P ligands failed, but bipyridyl·$Mo(CO)_4$ showed a well-behaved, long-lived anion radical (systems 7, 8, 10–12).

Group VII-B. The electrochemical reversibility of the $(\pi\text{-mesitylene})Mn(CO)_3^+$ is of interest, as is the neutral radical that is the other member of the couple. Unfortunately alteration of the ligands did not lead to a stable series of radical anions from initially neutral material.

The data on $[M(CO)_5]_2$ (M = Mn, Re) suggest formation of $M(CO)_5{:}^-$ which upon reoxidation gives $M(CO)_5\cdot$ which in turn attacked the electrode to give $[(OC)_5M]_2Hg$. The $E_{1/2}$ value of -1.8 v for $[(OC)_5Mn]_2$ agrees closely with the couple potential reported by Hieber[7] after reference electrode corrections. Exhaustive controlled potential electrolytic reduction, then oxidation did not regenerate starting material but instead gave an orange solid similar in appearance to the known mercurials, and with the same polarographic behaviors (system 29).

Group VIII. The most rewarding group thus far has been group VIII. Although the parent $Fe(CO)_5$ (system 30) yields an extremely unstable radical anion, the species $(\pi\text{-}C_8H_8)Fe(CO)_3^{\dot{-}}$ (system 31) was quite well behaved, esr, spectral, and electrochemical data being well correlated. Similar data occur in the π-cyclohexadiene derivative. $(\pi\text{-}C_4H_6)Fe(CO)_3$ (system 33) was destroyed upon reduction, but π-hexadienyltricarbonyliron (system 34) did show some regeneration on oxidation–reduction cycling, although the n value was very untoward. The reduction potentials for this series of Fe^0, and Fe(II) derivatives are not widespread. Systems 36 and 37, representing $(\pi\text{-ArH})Fe(\pi\text{-}C_5H_5)^+ \rightarrow (\pi\text{-ArH})Fe(\pi\text{-}C_5H_5)$, are comparable to the $(\pi\text{-ArH})Mn(CO)_3^+ \rightarrow (\pi\text{-ArH})Mn(CO)_3$ case described earlier, but unfortunately broad paramagnetic resonance absorption in the sample due to atomic iron growing in domain size to eventual ferromagnetic aggregates precludes establishment of the location of the spin density.

Although ferrocene itself does not reduce before supporting electrolyte (-3.7 v), the indene analog does, but does not yield a stable product. Various substituted $(\pi\text{-}C_5H_5)Fe(CO)_2R$ compounds also reduce. Unlike the Mo analogs, where R = CH_2Ph, $COCH_3$, C_6F_5, or COCH=CHPh (systems 39–43), the product is not $(\pi\text{-}C_5H_5)Fe(CO)_2{:}^-$. Reoxidation of the reduced solution gives only a polarogram of slightly positive slope in the voltage region 0.0–3.6 v, typical of all cases where 0% oxidation–reduction recovery is indicated.

Sulfur-containing ligands cause quite different behavior. System 47, where R = SCH_3 shows that oxidation gives a radical cation $(\pi\text{-}C_5H_5)Fe(CO)_2SCH_3^{\dot{+}}$ while reduction apparently gives a dianion. A similar pattern is shown by the dimer $[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2$ where both a *radical cation* and a *dianion* are capable of being electrochemically generated and then returned to starting material. The esr spectrum of this green radical cation is identical with that of the compound prepared *via* $[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2 + AgSbF_6$ (system 48). Further oxidation can be achieved at a Pt electrode to give $[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2^{2+}$ (or monomer cation) which like the neutral parent is yellow. Admixture of the two species immediately yields the green cation radical. An analogous cation $[(\pi\text{-}C_5H_5)NiSCH_3]_2^+$ is formed from the neutral parent in an electrochemically reversible process (system 57a). Finally a radical anion $[CH_3SFe(CO)_3]_2^{\dot{-}}$ can be generated from the parent dimer (system 49).

As might be expected, the compound $Fe_2(CO)_9$, with CO bridges, and an Fe–Fe link yields a dianion. This is similar to the behavior of $[(\pi\text{-}C_5H_5)Ni]_2\cdot HC{\equiv}CH$ which gives a dianion, and in which a Ni–Ni bond is formulated (systems 50 and 61).

In the Co, Ni series sulfur ligands are again the origin of well-behaved electrochemical behavior. $(\pi\text{-}C_5H_5)MS_2C_4F_6$ (M = Co and Ni) both form anions, the former paramagnetic, the latter diamagnetic. No hyperfine splitting due to ring protons is observable in the paramagnetic species. There is little doubt that the basic structure remains intact since comparison in each case to the $M(S_2C_4F_6)_2^{2-}$ compounds shows both spectral and electrochemical differences.[8] Chemical reductions have led to these species, so caution should be taken in extrapolating from electrochemical reduction to chemical reduction and, of course, *vice versa*, (systems 53, 54, 58, 59). The corresponding $(\pi\text{-}C_5H_5)Rh(S_2C_4F_6)^{\dot{-}}$ has been prepared (system 63). An unusual cation $(\pi\text{-}C_5H_5)Rh(\pi\text{-}CH_2{=}CH_2)^+$ has been prepared (system 64) and characterized. Also of interest is the intensely colored product (purple, λ_{max} 550, 378 mμ) which is obtained from the one-electron reduction of $Ni(CO)_4$. This does not reoxidize to the parent, as evidenced by gas chromatographic analyses, although the resulting solution does show a polarographic wave identical with that of the original carbonyl. The product of this, as well as other carbonyl reductions, may be the polynuclear carbonyl anions of which so little is known systematically. This is being explored.

In the discussion thus far scant attention has been paid to the subtleties associated with the concepts of electrochemical reversibility–irreversibility and what is of interest to the synthetic chemist, chemical reversibility–irreversibility. The former is a condition associated with the activation free energy, $\Delta F_e{}^*$, for electron transfer. When this is small the rate constant for electron transfer is fast enough to maintain surface concentrations of reactants and products near their equilibrium value, and the process is classified as electrochemically reversible. When $\Delta F_e{}^*$ is high, the system is electrochemically irreversible. Electrochemical reversibility in the above systems has been assigned on the basis of $E_{1/2}$ or $E_{p/2}$ congruences for reductive–oxidative processes. In the cases cited chemical reversibility has been observed. Other systems have shown electrochemical irreversibility but chemical reversibility with

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[7] W. Hieber and D. Wagner, *Z. Naturforsch.*, **13b**, 339 (1955).

[8] A series of $M(S_2C_4F_6)_x^{n-}$ compounds has been reported on by Holm: *cf.* A. L. Balch, T. Rohrscherd, and R. A. Holm, *J. Am. Chem. Soc.*, **87**, 2301 (1965).

varying degrees of lability of the new species as indicated by the reduction–oxidation cycling recovery of starting material, but incongruous E_p values. A third combination of these, electrochemical reversibility, but "chemical irreversibility" can be found in systems 51 and 57b, the reduction of $(\pi\text{-}C_{10}H_8)Fe_2(CO)_5$ and $[(\pi\text{-}C_5H_5)Ni\text{-}SCH_3]_2$ ($n = 1$) to anions. Both of these systems show small (50 mv) separations of $E_{p/2}^{\text{anodic}}$ and $E_{p/2}^{\text{cathodic}}$. Polarograms immediately after partial reduction show reductive–oxidative wave contributions at the $E_{1/2}$ value noted. The oxidative component rapidly disappears augmenting a new oxidative wave at more anodic potentials. The electrochemically reversible reduction ($n = 1$) of $(\pi\text{-}C_5H_5)_3Mn_2(NO)_3$ gives an even more unstable anion, no oxidative component being observable after electrolysis. Similar data have been accumulated for the oxidation of $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ (system 56a), a well-defined but unstable reductive component being observable after oxidation. Oscillographic sweeps on single drops in the vicinity of 50 v/sec show that even at this short time some decomposition is occurring. Apparently here we are encountering the problem of the time scale to judge events by. Over the long run these new species are unstable while over short time periods we may conceive of them as useful entities and even characterize them. The question then arises concerning the entries in Table I for which no oxidation–reduction recovery is listed, but which exhibit related reductive–oxidative peak currents which are formally electrochemically irreversible on triangular voltammetry. These may represent labile materials belonging in a chemically reversible set whose time scale is short. Unfortunately, the difficulty in assigning peaks to definite species, except where models may be predicted and examined, is a distinct barrier. However, it is to this interesting area of short-lived species that the present work is extending.

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Addition and Metalation Reactions of Organolithium Compounds. I. Products

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Abstract: Reactions of organolithium compounds and diphenylacetylene have been shown to give products arising from addition and/or metalation depending upon the choice of lithium reagent, solvent, and temperature.

This project[3] was prompted by a consideration of the unusual ability of organolithium compounds to polymerize isoprene in hydrocarbon solution to the all-*cis* polymer, natural rubber.[4] Other organoalkali compounds produce a considerably more random structure. The stereospecificity is related to the covalent character of the organolithium bond, and the polymerization must proceed by a series of concerted *cis* additions of growing organometallic chain to monomer. The intimate nature of this addition process is drastically affected by a change to more basic solvents which leads to a random polymer.[4] Stereospecific isoprene polymerization presumably occurs by a series of six-center transition states.[5] It was of interest to determine whether a similar *cis* stereospecific addition to acetylenes might occur, perhaps by a process involving a four-center addition. Acetylenes and organolithium compounds might react to produce vinylic lithium derivatives, and it is known that under the proper conditions, *i.e.*, low temperature and solvents of low basicity, such compounds retain their configuration.[6] The adduct could then be trapped by carbonation, a process known to proceed with retention of configuration.[6,7]

The literature contains little information concerning the reactions of noncarbonyl conjugated acetylenes with organoalkali metal compounds. In contrast Grignard reagents under the usual conditions do not react with nonterminal alkynes.[8] However, in refluxing xylene–tetrahydrofuran, diphenylacetylene and phenylmagnesium bromide react to form hexaphenylbenzene and octaphenylcyclooctatetraene.[9,10] This is a process which does not involve Grignard addition to the triple bond but rather coordination of the

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[1] From the Ph.D. Thesis of Z. G. Gardlund.

[2] From the M.S. Thesis of S. L. Gardlund.

[3] A preliminary report describing a portion of this work has appeared: J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963).

[4] H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 2451 (1957).

[5] H. Sinn and F. Patat, *Angew. Chem. Intern. Ed. Engl.*, **3**, 93 (1964).

[6] D. Y. Curtin and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **84**, 1967 (1962), and references cited therein to earlier Curtin papers.

[7] D. Seyferth and L. G. Vaughan, *ibid.*, **86**, 883 (1964).

[8] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954.

[9] H.-P. Throndsen and H. Zeiss, *J. Organometal. Chem.*, **1**, 301 (1964); M. Tsutsui, *Chem. Ind.* (London), 780 (1962).

[10] The latter compound was originally identified by Tsutsui[9] as a tricyclooctatetraene derivative. It appeared, however, to be identical with a compound tentatively suggested to be octaphenylcubane (H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, 84, 2837 (1962)), but more recently shown to be the cyclooctatetraene derivative (G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *ibid.*, **86**, 4725 (1964)).