gent) was purified by fractional crystallization.[22] Argon, used for deoxygenating test solutions, was passed through a column of Drierite and then through pyridine thermostated at the same temperature as that of the test solution. Triple-distilled mercury was used for the dropping mercury electrode (dme).

Apparatus. Polarograms were recorded with a Leeds and Northrup Electro-Chemograph Type E, used in conjunction with an IR compensator.[23]

Cyclic voltammograms, obtained with an operational amplifier control circuit,[24] were recorded on Moseley Model 135 and 7035A X-Y recorders. The hanging mercury drop electrode (hmde), used as the indicating electrode, consisted of a platinum wire sealed in the end of a piece of glass tubing, filed flush with the end of the tubing and then plated with mercury.

Capillary constants of the dme at a mercury height of 41.0 cm (uncorrected for back pressure) in deoxygenated 0.1 *M* Et_4NClO_4 in pyridine solution at 25° and at open circuit were m = 1.24 mg/sec and t = 5.70 sec; $m^{2/3}t^{1/6}$ = 1.54.

The jacketed three-compartment cell used has been described.[7] The temperature was regulated to 25 ± 0.2° except where indicated otherwise.

Potentials were measured *vs.* the Ag|$AgNO_3$ (1 *M* in pyridine) electrode, NAgE,[25] whose potential is +0.09 V *vs.* the aqueous saturated calomel electrode (liquid junction potentials included).

Procedures. Stock solutions of background electrolytes were prepared by dissolving weighed quantities and diluting to known volume. Stock solutions of benzophenone and 3,4-dimethylphenol were prepared by dissolving weighed quantities in and diluting to known volume with stock background solution. Tests solutions were prepared by pipetting appropriate amounts of stock solutions into 10-ml volumetric flasks and diluting to volume with background solution.

Argon was bubbled through the test solution for 10 min. The dme was then inserted and polarograms were recorded with argon passing over the solution.

For cyclic runs at the hmde, two drops of mercury were collected from the dme capillary, which was inserted in the test solution, and were hung on the hanging drop electrode assembly. Potentials were scanned in a negative direction to some preset potential and then back to the starting potential. Scan rates were 40 and 200 mV/sec.

Acknowledgment. The authors thank the Petroleum Research Fund of the American Chemical Society and the National Science Foundation, which helped support the work described.

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(22) D. A. Hall and P. J. Elving, *Anal. Chim. Acta*, **39**, 141 (1967).

(23) R. Annino and K. J. Hagler, *Anal. Chem.*, **35**, 1555 (1963).

(24) G. Dryhurst and P. J. Elving, *ibid.*, **39**, 606 (1967).

(25) A. Cizak and P. J. Elving, *J. Electrochem. Soc.*, **110**, 160 (1963)

Organometallic Electrochemistry. XI.[1] Stable Radical Anions Derived from Acetylene–Metal Carbonyl Complexes

Raymond E. Dessy and Rudolph L. Pohl

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia. *Received July 19, 1967*

Abstract: The electrochemical behavior of 35 metal–acetylene complexes have been explored. Evidence for stable anion radical and dianion formation has been found in many cases. Dianion production may result from two one-electron steps, or by one two-electron step. Several examples in which structural reorganization of the molecule occurs upon reduction are reported.

Two previous papers in this series have demonstrated that cyclic polyolefin π complexes of $Fe(CO)_3$ such as (π-C_8H_8)$Fe(CO)_3$ and (π-C_6H_8)$Fe(CO)_3$ are capable of yielding, upon reduction, stable radical anions. During the past decade a number of complexes derived from reactions of various acetylenes with one of the three iron carbonyl parent materials, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, have been reported. These contain a variety of π-complexed organic fragments ranging from cyclobutadiene derivatives to substituted tropones.

It has recently been found in our laboratory that in many cases these compounds reduce to give quite stable radical anions and dianions. The presence in the same molecule (both neutral parent and radical anion and dianion reduction products) of coordinated CO ligands, π-complexed organic unsaturated ring systems, and iron atoms permits the use of infrared spectroscopy, electron spin resonance spectroscopy, and Mössbauer spectroscopy to evaluate the location of unpaired electron density and symmetry in the radical anion. This paper reports on the new radical anion and dianions prepared for this study and presents their electrochemical and electron spin resonance characteristics. Experimental work in the remaining two areas is extremely slow and will be reported in a subsequent publication.

Preliminary concepts, derived from the work of Gray,[2] Holm,[3] and Dahl[4] and unpublished work from this laboratory,[5,6] suggest that, when a coordination complex of a transition metal is reduced (or oxidized), the locus of high-spin density in the radical anion (or cation) may range between two extremes. The first is occupation of an orbital which is predominantly metal in origin, giving rise to unusual oxidation states of the metal. The second is occupation of an orbital which is predominantly ligand in character, giving rise to a ligand radical anion (or cation) stabilized by coordina-

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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, 5129, 5132 (1966).

(2) H. B. Gray, personal communication.

(3) R. Holm, personal communication.

(4) L. Dahl, personal communication.

(5) Gordon Conference on Electrochemistry, Santa Barbara, Calif., Jan 1967.

(6) The first suggestions along these lines appear to have been proferred in a personal communication of Professor Larry Dahl to one of the present authors (R. E. D.) in Sept 1965.

tion to the metal ion.[7] In addition, many of these species appear to involve gross structural modifications upon reduction or oxidation, apparently to better support the gain or loss of the electron in question. The purpose of this paper is to focus on these concepts in the area of organometallic radicals.

Experimental Section

All of the electrochemical studies were done in dimethoxyethane employing tetrabutylammonium perchlorate as supporting electrolyte at 0.1 *M* concentrations. Substrate concentrations ran from 0.001 to 0.1 *M* depending upon whether the sample was to be employed for ultraviolet or esr spectroscopy (0.001 *M*), infrared spectroscopy (0.01 *M*), or Mössbauer spectroscopy (0.1 *M*).

The equipment employed was a Metrohm polarograph equipped with a Sargent IR compensator. Triangular voltammetry was performed using a triangular wave generator constructed on a Philbrick 6009 manifold feeding into a polarograph constructed from operational amplifiers also. Readout of current-voltage curves was done on a Moseley 11 × 17 in. X-Y plotter or a Tektronix Model 564 storage oscilloscope. Standard gating circuits were employed for single or multiple triangular voltammetry. Three-electrode geometry was used in all cases, employing a 0.001 *M* $AgClO_4|Ag$ reference couple. Oxidative studies anodic to 0 v were conducted at a button Pt electrode or using a conventional rotating platinum electrode. Controlled-potential electrolysis was performed using a unit also based on standard operational amplifier design for small-scale (10 mg) runs. For larger runs (1–2 g) two Kepco CK 60–0.5 power supplies, properly boot-strapped and master-slaved, were used in conjunction with a voltage reference source. For very large-scale runs an Anatrol potentiostat, with booster supply, was employed, or a Kepco KS 125-5 power unit, properly modified.

The cells used for very small-scale runs were standard two-compartment, three-electrode glass cells. The membrane material was a 30-mm medium frit. Hg working electrodes were used. Intermediate-scale runs were performed in a two-compartment, three-electrode cell with concentric compartments. A mercury test electrode and Pt disk counter electrode were employed. The large-scale runs were performed in a concentric two-compartment, three-electrode cell constructed of 316 stainless steel. The membrane material was a porous polyethylene sleeve. Each compartment was connected to a surge drum by polyethylene and/or stainless tubing *via* Swage-Lok fittings. Pumping was achieved by a RAC Corp. dual-bellows (stainless steel) pump.

Solvent and supporting electrolyte were prepared or purified as previously described.[1]

All small-scale runs and most intermediate scale runs were performed in a Vacuum Atmospheres Dry Lab-Dry Train using an argon atmosphere whose H_2O and O_2 content was below 1 ppm. A few intermediate scale runs were performed in cells attached to a vacuum line to achieve transfer of radical anion and dianion samples.

Ultraviolet and esr sample cells were standard cuvettes attached to Delmar Teflon needle valves. The infrared cell was a standard Beckman housing holding Irtran windows and machined needle valve seals of 316 stainless steel.

Ultraviolet spectra were recorded on a Beckman DK-2A. Infrared spectra were traced by a Perkin-Elmer 621 double-grating instrument. Esr spectra were obtained on a Varian E-3 unit with variable-temperature accessory.

Results and Conclusions

Tables I and II show the electrochemical and electron spin resonance data for the 36 compounds examined in this study. In addition to the main group composed of iron compounds, selected samples involving Mo, W, Mn, and Ni are included for comparison purposes.

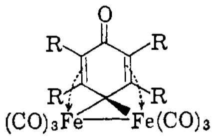
In the molybdenum series, $Ph_4C_4(PhC_2Ph)_2MoCO$ (**1**) reduces to a radical anion which has a predecomposition lifetime of about 1 sec. Its dinuclear analog, the blue $(Ph_4C_4)_2PhC_2PhMo_2(CO)_4$ (**2**), gives a green radical anion, whose esr spectrum consists of a single narrow line, 2.5 G wide. Cooling to near the freezing point of solvent (−60°) gave no evidence of hyperfine splitting. This same compound undergoes an electrochemically reversible reduction at more negative potentials to a dianion, but the predecomposition lifetime is somewhere between 10 sec and 5 min, and attempts to examine its properties by normal sampling methods failed. The compound is being examined by *in situ* generation techniques. The other Mn and W compounds studied gave polarographically irreversible reduction waves, and no further study was made (compounds **3** and **4**).

Similar results were obtained with a series of iron derivatives (**5–11**) containing fulvene, tetrakistrifluoromethylcyclopentadienone, ferracyclopentadiene, anthracene, and fulvalene ligands; no evidence of even a transiently stable radical anion was found.

On the other hand, similar ligands such as tetraphenylcyclopentadienone, diferracyclohexadienone (**12** and **13**), and vinylnaphthalene do give iron carbonyl complexes which show electrochemical reversibility upon triangular voltammetry, indicating at least transiently stable radical anions. Unfortunately, once again, their lifetimes are too short to permit observation by normal controlled-potential reductive generation and standard sampling.

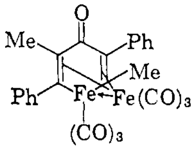
A large number of iron compounds studied gave stable radical anions whose inertness allowed them to be examined over a period of 2–3 hr (*e.g.*, **14** and **15**). The routine examination of a sample involved the following: (1) polarography, (2) triangular voltammetry, (3) controlled-potential reduction, (4) sampling for spectroscopy, (5) reoxidation to neutral species, (6) sampling for spectroscopy (ultraviolet and infrared), (7) controlled-potential reduction at second wave (if present), (8) step 7 followed by steps 4–6.

The reduction process for **14** is electrochemically reversible, on the basis of both *i–E* plots from the polarogram and triangular voltammetry. However, controlled-potential reduction of the solution gives a radical anion, ΔH = 13 G, g = 2.0619, which has an oxidation potential of −0.5 v, compared to the reduction potential of −1.2 v for the parent. Reoxidation of the solution at −0.4 v gives a neutral material whose polarographic and ultraviolet spectral properties[9] are identical with those of starting material.



$R = p\text{-}C_6H_4Cl$

14



15

The only way in which a reduction may be electrochemically reversible (based on *i–E* slope analysis and triangular voltammetry) and chemically reversible (based on recovery of starting compound on reduction–oxidation (R-O) cycling) and yet have $E_{1/2}^{ox} \neq E_{1/2}^{redn}$

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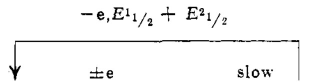
[7] The above concept is quite reminiscent of the reports of Kochi[8] on alkyl radical–metal ion coordination (which leads to eventual oxidation or reduction of the radical), a process which stabilizes the bound radical prior to charge transfer.

(8) J. K. Kochi and R. G. Gilliom, *J. Am. Chem. Soc.*, **86**, 5251 (1964).

(9) In previous reports it has been demonstrated that polarographic half-wave potentials alone cannot be used unambiguously for identification purposes in this type of study. They must be augmented by ultraviolet and/or infrared spectral studies to authenticate regeneration of the neutral species. Polarographic half-wave potentials are not sensitive to minor changes in structure or composition.

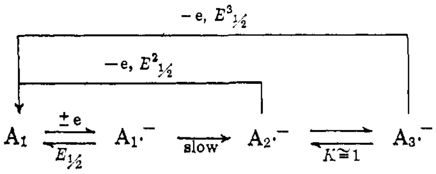
is to have some reorganizational process take place relatively slowly after reduction, *i.e.*



(1)

As indicated earlier, Gray has suggested similar occurrences in some of the classical thiol chelates of the transition metals based on preliminary X-ray data, and Dahl and coworkers have shown from structural investigations not only that metal–metal bonds can drastically influence the molecular geometries of organometallic ligand-bridged complexes[10] but also that the addition of an unpaired electron can significantly alter the molecular parameters of a metal cluster system.[11]

Compound **15**, $Fe_2(CO)_6(PhC_2Me)_2CO$, undergoes a similar electrochemically reversible reduction at −1.5 v. The resulting solution exhibits oxidative waves at −0.8 and −1.3 v. The esr spectrum shows two well-developed rather narrow signals separated by 104 G and centered around $g = 2.0322$. Controlled-potential oxidation at −0.7 v results in regeneration of the initial compound as evidenced by polarographic studies and ultraviolet and infrared spectra. Furthermore controlled-potential electrolysis at −1.2 v causes *both* oxidative waves to disappear and also leads to regeneration of the starting compound. The most rational explanation of these phenomena is a system



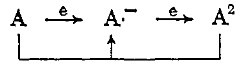
(2)

There is no evidence of further hyperfine structure in the electron spin resonance spectra, suggesting that spin density on hydrocarbon ligand is small. On the other hand, infrared stretching frequencies for the radical anion solution (2075, 2045, and 2010 cm^{-1}) have moved toward longer wavelengths compared to the neutral parent (1942, 1895, and 1853 cm^{-1}). This considerable decrease of frequencies with increasing negative charge also is found for the anionic metal carbonyls compared to their isoelectronic and isostructural neutral analogs (*e.g.*, $V(CO)_6^-$ *vs.* $Cr(CO)_6$; $Mn(CO)_5^-$ *vs.* $Fe(CO)_5$; $Co(CO)_4^-$ *vs.* $Ni(CO)_4$) and has been rationalized in terms of increased M–CO back-bonding with decreasing metal oxidation state. At present a correlation is being made between Mössbauer isomer shifts, quadrupole splitting factors, and the infrared spectral data. These may allow an interpretation of where the unpaired electron in the radical is.

Two basic questions have therefore been asked and partially answered in the reduction of a transition metal derived organometallic compound: what is the spin density distribution, and do structural modifications occur in the basic skeletal framework upon reduction? The preparative and catalytic chemistry of these species will be highly dependent upon these factors, and it is therefore important to evaluate them.

A further analysis of the data presented in Table I shows **16**, $Fe_2(CO)_5\{(EtC_2Et)_3CO\}$, to exhibit a behavior similar to **15**. The complex $(Ph_4C_4)Fe(CO)_2PPh_3$ (**18**) is electrochemically irreversible and exhibits two oxidative waves on reduction and one narrow esr signal. Reoxidation regenerates about 75% of the initial compound. Compounds **17** and **19**, structural isomers of formula $Fe_3(CO)_8(PhC_2Ph)_2$, show well-behaved radical anion formation, and the latter exhibits dianion production (singlet state). There is no evidence of structural reorganization upon reduction.

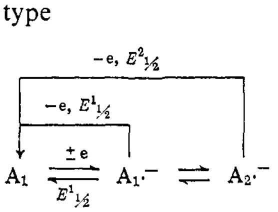
Three systems investigated in the iron derivatives showed electrochemical reduction to radical anions, combined with further reduction at more negative potentials to dianions (**19–21**). Electron spin resonance studies on the dianions indicates that they also are not in triplet states. As might be expected, in all three cases, admixture of the dianion and neutral material gives the radical anion.



(3)

Compounds **22–25**, although not acetylene–iron derived complexes, are included because of the close similarity of their behavior to the materials discussed above. Compound **22** is chemically irreversible, but electrochemically reversible. Compound **23** shows some chemical reversibility, indicating a rather long-lived radical anion. The extensive decomposition precludes, however, observation of the esr spectra of the radical.

Related derivatives, **24** and **25**, show excellent reversibility upon reduction, both electrochemical and chemical. The polarogram of the reduced solution shows another oxidative wave considerably shifted from the reduction potential of the parent, and the electron spin resonance spectra are characterized by two overlapping absorptions of about equal intensity. Reoxidation gives a solution whose infrared and ultraviolet spectra are identical with those of starting material and whose polarographic behavior is characteristic of starting solution, indicating regeneration of the compound. These are two cases then of reduction unquestionably leading to an equilibrium condition between two anion radicals of the type



(4)

In the cobalt-derived species (**26–28**) no examples of chemical reversibility were found. Compound **28** is electrochemically irreversible, by all criteria. Compound **26** shows electrochemical reversibility using triangular voltammetry with 20-v/sec sweep speeds, while compound **27** is electrochemically reversible using sweep speeds as low as 1 v/sec.

Two nickel compounds were investigated; (π-cyclooctatetraene)(π-duroquinone)nickel (**29**) is electrochemically irreversibly reduced in a one-electron step to yield the radical anion of duroquinone. On the other

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(10) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).

(11) L. F. Dahl, Abstracts of the 3rd International Symposium on Organometallic Chemistry, Munich, Aug 28–Sept 1, 1967, p 92.

Table I. Electrochemical Data

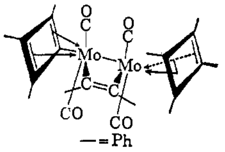
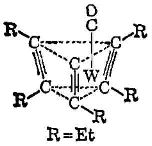
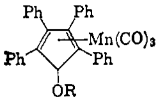
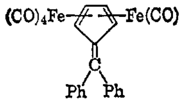
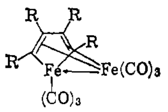
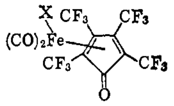
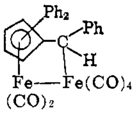
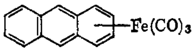
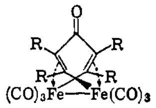
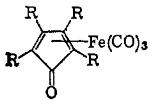
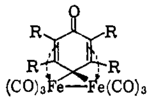
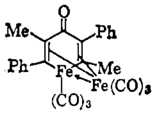
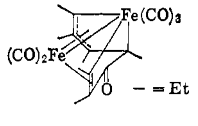
No.	Compound	$-E_{1/2}$, v (1)[a]	$-E_{1/2}$, v (2)[a]	n (n found)[b]	$-E_{p/2}^{\text{cath}}$ [c]	$-E^{\text{an}}$ [c]	Chem[d] rev	Comment
1	$(Ph_4C_4)(PhC_2Ph)_2$-[e] MoCO	2.24	2.58	2 (2.0)	2.4 Irrev	2.2	No	
2		1.70	2.40	1 (1.2)	1.7 2.4	1.6 2.2	Yes No	Radical anion green
3	 R=Et	2.70	. . .	. . .	Irrev[f]		No	
4a	 R=H	2.80	3.40	1 (1.1)	1.1 Irrev	2.8	No	
4b	R=Sn(Ph)$_3$	1.71	3.10	1 (1.1)	1.7 Irrev	1.2	No	
5		1.91	2.35	? (2.8)	Irrev[f] Irrev		No	
6	 R=C$_6$H$_4$Cl	1.87	. . .		Irrev[f]		No	
7	$(PhC_2H)_5Fe(CO)_4$[g]	1.72	. . .	1–2	Irrev[f]		No	
8	 X=CO	1.1	2.6	1 (0.9)	Irrev[f] Irrev		No	
9	X=PPh$_3$	1.2	. . .	1 (0.8)	Irrev[f]		No	
10		1.5	. . .	. . .	Irrev[f]		No	
11		1.8	2.4	. . .	Irrev[f] Irrev		No	
12	 R=Ph	1.27	2.01	1 (1.1)	1.3	1.2	No	
13	 R=Ph	1.93	2.28	1 (1.2)	2.0 2.3	1.8 2.1	No	
14	 R = p-C$_6$H$_4$Cl	1.24	1.87	1 (1.1) 1 (1.1)	1.25 1.4	1.2 1.7	Yes No	$-E_{1/2}^{\text{ox}}$ = 0.5 v; struct reorg on redn; radical anion yellow
15		1.50	2.12	1 (0.9) 1	1.5 2.2	1.4 2.1	Yes No	$-E_{1/2}^{\text{ox}}$ = −0.84, −1.32; struct reorg on redn; radical anion dark red-brown
16		1.66	2.62	1 (1.0)	1.6 Irrev	1.5	Yes	$-E_{1/2}^{\text{ox}}$ = 0.7, 1.6; struct reorg on redn; anion straw colored

Table I (*Continued*)

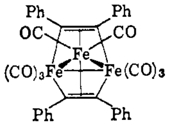
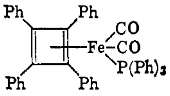
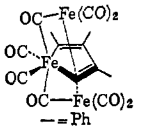
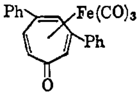
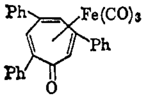
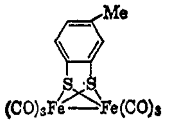
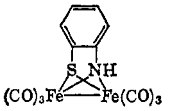
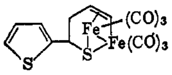
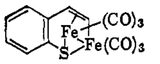
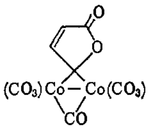
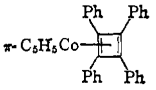
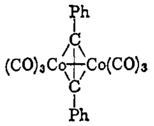
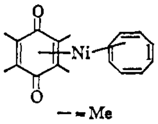
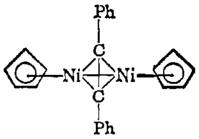
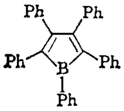
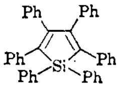
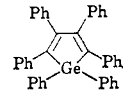
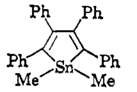
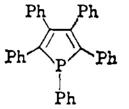
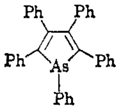
No.	Compound	$-E_{1/2}$, V (1)[a]	(2)[a]	n (n found)[b]	$-E_{p/2}^{cath\,c}$	$-E^{an\,c}$	Chem[d] rev	Comment
17		1.56	 2.32	1 (1.0) 1	1.6 Irrev	1.5	Yes	Radical anion deep burgundy
18		2.69	...	1 (1.0)	2.8	2.3	Yes 75%	$-E_{1/2}^{ox}$ = 0.7, 1.0; struct reorg on redn; radical anion brown
19		1.3	2.0	1 (0.9)	1.3	1.2	Yes	Radical anion dark green, dianion black
20		1.61	 1.92	1 (1.0) 1 (1.1)	1.6 2.0	1.5 1.8	Yes Yes	Radical anion brown
21		1.62	 1.98	1 (1.1) 1	1.6 1.9	1.5 1.8	Yes Yes	Radical anion brown-red, dianion red
22		1.60	...	2 (1.9)	1.7	1.4	No	
23		1.60	...	1 (1.1)	1.7	1.5	Slight or 20%	
24		1.4	 2.0	1 (1.0) 1	1.5 2.0	1.4 1.9	Yes	$-E_{1/2}^{ox}$ = 0.61, 1.4 (small); struct reorg on redn
25		1.64	 2.50	1 (1.1) 1	1.5 2.0	1.4 1.9	Yes	$-E_{1/2}^{ox}$ = 1.40, 1.56; struct reorg on redn
26		1.3	...	1 (1.1)	1.4	1.3	No	
27		2.9	...	1	2.9	2.8	No	
28		1.6	 2.1	1 (1.2)	Irrev[f]		No	
29		2.0	...	1 (1.1)	Irrev[f]		No	Duroquinone radical anion formed on redn
30		2.2	...	1 (0.9)	2.2	2.1	Yes	
31		2.8	...	2 (1.9)	Irrev[f]		Yes	Radical anion blue
32		2.5	 2.9	2 (2.0)	2.6	2.5	Slight	Radical anion blue

Table I (*Continued*)

No.	Compound	$-E_{1/2}$, v (1)[a]	$-E_{1/2}$, v (2)[a]	n (n found)[b]	$-E_{p/2}^{cath}$ [c]	$-E^{an}$ [c]	Chem[d] rev	Comment
33		3.2	. . .	2 (2.1)	Irrev[f]			Radical anion blue, half-life ~1 min
34		2.6	3.0	2 (2.1)	Irrev[f]		Yes	Stable blue radical anion formed if 1 e/molecule added
35		2.6	. . .	2 (1.8)	2.7	2.6	Yes	Same comment as above
36		2.6	3.0	Cycles	Irrev[f]		No	Blue radical anion, half-life 1 min; formed if 1 e/molecule added

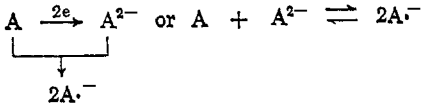
[a] Half-wave potentials at the first and second polarographic waves, respectively. All data from three-electrode potentiostatic geometry 2×10^{-3} *M* in substrate, 1×10^{-1} *M* Bu_4NClO_4 in 1,2-dimethoxyethane with reference to 1×10^{-3} *M* $AgClO_4|Ag$ in 1×10^{-1} *M* Bu_4NClO_4 in 1,2-dimethoxyethane at 22°. [b] Exhaustive controlled-potential electrolysis. [c] Potential at half-height, cathodic (reductive) and anodic (oxidative), respectively, at 1 v/sec triangular sweeps on a hanging Hg drop employing the starting material. [d] Chemical reversibility based on recovery of starting material after the reduction–oxidation cycle as determined by polarography and ultraviolet spectra. [e] Structure unknown. [f] Sweep data are very complex.

Table II. Esr Results

No.[b]	Compound	ΔH, G	g	Comment
2	$(Ph_4C_4)_2PhC_2PhMo_2(CO)_4$	2.5	1.9953	One-line spectrum
14	$Fe_2(CO)_6[(ClC_6H_4C)_4CO]$	13	2.0619	One-line spectrum
15	$Fe_2(CO)_8(PhC_2Me)_2CO$	11 4.5	2.0322[a]	Two lines separated by 104 G; line at lower field is the broader
16	$Fe_2(CO)_6(EtC_2Et)_3$	4	2.0415[a]	Two lines of equal intensity separated by 27 G
17	$Fe_3(CO)_8(PhC_2Ph)_2$ (violet isomer)	2	2.0031	One-line spectrum
19	$Fe_3(CO)_8(PhC_2Ph)_2$ (black isomer)	5	2.0106	One-line spectrum
20	(2,4-Diphenyltropone)$Fe(CO)_3$	5	2.0247	One-line spectrum
21	(2,4,6-Triphenyltropone)$Fe(CO)_3$	10.0	2.0251	One-line spectrum
24	(Dithienyl)$Fe_2(CO)_6$	2.5	2.0291[a]	Two overlapping lines of *ca.* equal intensity and width sep by 3.5 G
25	(Thianaphthene)$Fe_2(CO)_6$	5.2	2.0261[a]	Two overlapping lines of *ca.* equal intensity and width sep by 5.2 G
30	$(\pi\text{-}C_5H_5Ni)_2(PhC_2Ph)$	6.0	2.0526	One-line spectrum
31	$Ph_4C_4B(Ph)$	. . .	2.0016	Greater than 50 lines
32	$Ph_4C_4Si(Ph)_2$	4.5	2.0016	Five lines observed at 5×10^{-5} *M* sep by 0.9 G
33	$Ph_4C_4Ge(Ph)_2$	10	2.0037	Extreme modulation broadening
34	$Ph_4C_4Sn(CH_3)_2$	7	2.0020	One main line with two small satellites; $\Delta H_{Sn^{117,119}} = 35$ G
35	$Ph_4C_4P(Ph)$	2.5	2.0021[a]	Two lines; $\Delta H_P = 15$ G

[a] Value at half the distance between two signals. [b] Compound numbers correspond with those in Table I. Structures are given in Table I.

hand, bis(cyclopentadienylnickel)diphenylacetylene (**30**) undergoes a one-electron reduction at −2.2 v. The anion radical is quite stable. The analogous acetylene complex $(CpNi)_2HC{\equiv}CH$ shows a two-electron reduction process at −2.2 v. However, if controlled-potential reduction is limited to the passage of current providing for only one electron per molecule, the resulting solution shows a single sharp electron spin resonance line due to the radical anion. One is dealing with a system type that is more adequately documented in the next paper in this series, but which may be represented as



$$A \xrightarrow{2e} A^{2-} \text{ or } A + A^{2-} \rightleftharpoons 2A\cdot^{-} \qquad \downarrow 2A\cdot^{-} \tag{5}$$

Finally, it was hoped that electrochemical reduction of the metallocyclopentadienes derived from group III, IV, and V metals (**31–36**) might provide anion radicals in which the bonding in the ring system might be probed.

The metal-ole derivatives of Si, Ge and Sn, P and As, and B showed well-developed reduction waves near −2.6 v, irrespective of the metal. All of these involve two-electron steps. The behavior is typified by eq 5. Partial reduction in all cases gives a radical anion. Only in the phosphole case was a stable dianion formed. In all other cases decomposition followed electrolysis experiments exceeding 1 e/molecule. In the phosphole case dianion and neutral parent yields radical anion.

The esr spectra of the series is quite varied. Although yet to be analyzed the borole spectrum exhibits extensive spin delocalization into the substituent phenyl groups.

The silole derivative exhibits a single absorption line, with unresolved hyperfine structure, and the stannole radical anion shows satellite absorptions due to hyperfine interaction with $Sn^{117,119}$ species, $\Delta H_{Sn} = 35$ G. The phosphole shows the expected doublet, $\Delta H_P = 15$ G, but no further hyperfine splitting. Unfortunately the lifetimes of the arsenic- and germanium-containing cycles were too short to permit acquisition of good esr data; *in situ* generation is being studied.

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Organometallic Electrochemistry. XII.[1] Bridged Bimetallic Species

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Abstract: An exploration of the electrochemistry of bridged bimetallic species has revealed examples of systems that reduce or oxidize to give stable radical anions or cations, respectively. More complex systems are observed of the type $A \xrightarrow{2e} A^{2-}$, with $A + A^{2-} \rightleftharpoons 2A\cdot^{-}$, or $A \xrightarrow{e} A\cdot^{-} \xrightarrow{e} A^{2-}$, and $A \xrightarrow{-e} A^{+} \xrightarrow{-e} A^{2+}$. The electron spin resonance spectra and electrochemical properties of 27 compounds are presented.

In a previous paper in this series[1] the oxidation of a bridged bimetallic compound, $[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2$, to a radical cation and a dication was reported. The previous paper has discussed the possibility of structural reorganization of a molecule upon reduction (or oxidation) and the question of the nature of the orbital occupied by the unpaired electron in the radical. The bridged bimetallic species offer a particularly tempting area for further exploration of these concepts since they can involve group V bridge elements such as P and As, as well as S, and in several cases two species differing primarily by the presence and absence of a M–M linkage can be synthesized. The present paper reports the electrochemical properties and electron spin resonance spectra of a series of 27 such compounds (Table I). Mössbauer and infrared spectra for the series will be published in a succeeding paper, along with similar data for the acetylene–iron complexes reported in the preceding paper. The experimental techniques involved have been described previously.

Experimental Results

The dimer of cyclopentadienylvanadium bistrifluoromethylethylenedithiolate (**2**) yields a radical anion on reduction which shows a very complex esr spectrum. Eight major lines are present, each approximately 75 G wide. Each of these appears to be split further into eight lines, suggesting a structural reorganization upon reduction which removes the equivalency of the two vanadium atoms ($I = 7/2$).

The chromium triad gives rise to a number of group V bridged species whose electrochemistry is rather rewarding. The structure of the dimer $[(OC)_4CrPMe_2]_2$

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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, 5129, 5132 (1966); **90**, 1995 (1968).

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