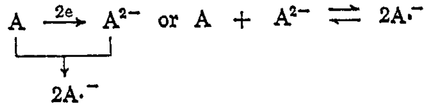
providing for only one electron per molecule, the resulting solution shows a single sharp electron spin resonance line due to the radical anion. One is dealing with a system type that is more adequately documented in the next paper in this series, but which may be represented as



$$A \xrightarrow{2e} A^{2-} \text{ or } A + A^{2-} \rightleftharpoons 2A\cdot^{-} \quad\quad (5)$$

$$\underbrace{A \longrightarrow A^{2-}}_{\downarrow \atop 2A\cdot^{-}}$$

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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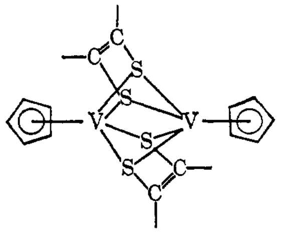
Table I. Electrochemistry of Bridged Bimetallic Species

No.	Compound	$-E^1{}_{1/2}$	$-E^2{}_{1/2}$	n^1 (n_{found})	$-E_{p,c/2}$[a,b]	$-E_{p,a/2}$	Chem[c] rev	Esr observations[e] ΔH, G	g	Comment[d]
1	$[(\pi\text{-}C_5H_5)V(SMe)_2]_2$	0.2	2.6	−1 (−0.8)	0.3	0.1	No			
2	$[(\pi\text{-}C_5H_5)VS_2C_4F_6]_2$	1.3	2.3	1 (1)	1.35	1.25	Yes	>52 hfl, 10-G sepn	1.990	
3	$[Cr(CO)_4PMe_2]_2$	1.85		2 (1.9)	1.9	1.7	Yes	1:2:1 triplet, ΔH_P = 13 G, each further split into 13 lines, ΔH_H = 1.2 G	1.993	(0) yel (·⁻) grn (2⁻) red
4	$[W(CO)_4PMe_2]_2$	1.9		2 (1.8)	1.9	1.6	Yes	3 hfl, ΔH_p = 15 G	1.994	(0) yel (·⁻) dk yel (2⁻) yel
5	$[W(CO)_4AsMe_2]_2$	1.8		2 (1.8)	1.9	1.4	Yes	No esr signal obsd at high gain		
6	$[Cr_2(CO)_{10}As_2Me_4]_n$	2.1		2 (1.75)	2.1	1.4	Yes	No esr signal obsd		
7	$[C_5H_5MoS_2Me_2]_2$	0.6	3.1	−1 (−0.8)	0.65	0.55	Yes	35 G	2.027	
8	$[(C_5H_5)MoPPh_2(CO)]_3$	Ill-def	Ill-def							
9	$(OC)_4MnS_2CNEt_2$	2.0		1	2.2	1.8	Slight	6 hfl, 6 G wide, 40-G sepn		
10a	$[Mn(CO)_4PPh_2]_2$	2.2			Irrev					
10b	$[Mn(CO)_3SPh]_2$	1.6	2.5	2 (1.8)	1.75	1.5	Yes	11 hfl, 7 G wide 14-G sepn		
11	$[(\pi\text{-}C_5H_5)Fe(CO)PPh_2]_2$	0.2(Pt)		−1 (0.9)	0.1	0.2	Yes			(0) yel
			0.5	−1 (0.9)	0.7	0.5	Yes	12.5 G	1.977	(·⁺) blue (2⁺) deep blue
12	$[(OC)_3FePMe_2]_2$	2.1		2 (1.8)	2.2	1.9	Yes	7 G (unres hfl)	1.999	
13	$[(OC)_3FeAsMe_2]_2$	0.2		−1 (1.1)	0.2	0.1	. . .	Weak esr signal		
			1.9	1 (1.1)	2.0	1.8	Yes	50 G	2.064	
14	$[(ON)_2FePPh_2]_2$	1.7		1 (1.0)	1.75	1.65	Yes	1:2:1 triplet, ΔH_P = 20 G	1.937	
			2.1	1	2.15	2.05	Yes			
15	$[(\pi\text{-}C_5H_5)Fe(CO)SCH_3]_2$	0.6		−1 (−1)	0.7	0.5	Yes	7 G	1.998	
16	$(\pi\text{-}C_5H_5)Fe(CO)_2SCH_3$	0.4		−1 (−1)	0.6	0.3	Yes	9 G	1.998	
17	$(\pi\text{-}C_5H_5)FeS_2C_4F_6$	2.1		2 (1.6)	2.2	1.8	No			
18	$SbFe_2(CO)_8$	2.3			Irrev					
19	$[(\pi\text{-}C_5H_5)CoPPh_2]_2$	0.3			Irrev		No		2.003	
			2.6	1 (0.9)	2.65	2.55	Yes	1:2:1 triplet, ΔH_P = 9 G, unres hfl		
20	$[(\pi\text{-}C_5H_5)CoSMe]_2$	0.5		−1 (−1.0)	0.5	0.4	Yes	75 G	2.120	
			2.4	1 (0.8)	2.45	2.35	Yes	250 G	2.105	
21	$(\pi\text{-}C_5H_5)CoS_2C_4F_6$	1.1		1 (1.1)	1.2	0.9	Yes	8 hfl, ΔH_{Co} = 41 G	2.454	
22	$(\pi\text{-}C_5H_5)RhS_2C_4F_6$	1.4		1 (1.2)	1.5	1.2	Yes	25 G		
23	$[(OC)_3Ni{\leftarrow}PPh_2\text{-}]_2$	2.4			Irrev					
24	$[(OC)_2NiPPh_2]_2$	1.7		1 (1.1)	1.75	1.65	Yes	6 G	1.979	(·⁻) purple
			2.3	1	2.35	2.25	Yes			(2⁻) red-brn
25	$[(\pi\text{-}C_5H_5)NiPPh_2]_2$	2.3		1 (1.25)	2.35	2.25	Yes	10 G	2.060	
26	$[(\pi\text{-}C_5H_5)NiSCH_3]_2$	0.5		−1 (−0.9)	0.6	0.4	Yes	25 G	2.007	
			1.8	(1.2)	2.0	1.7	Slight			

[a] *Vs.* 10^{-3} *M* $AgClO_4|Ag$ electrodes. [b] Potentials at half peak height observed by triangular voltammetry at a Hg microelectrode at sweep rates of 1 v/sec. [c] By controlled-potential electrolysis at a Hg pool. [d] (0) = uncharged species, (·⁻) = radical anion, (2−) = dianion, (·⁺) = radical cation, (2+) = dication. [e] Hfl = hyperfine lines.

(3) involves octahedral configuration about each chromium, the two octahedra sharing an edge which is occupied by the PMe_2 bridges. A metal–metal bond has been suggested to explain the diamagnetism of the neutral material. The compound (3) shows one well-defined polarographic wave, which remains unsplit on observation by triangular voltammetry at 1-v/sec sweep speeds. The reduction involves two electrons, yielding



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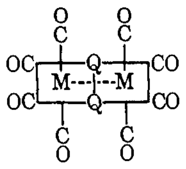
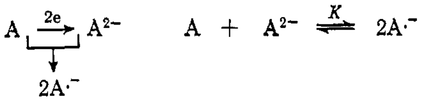


3-5

M = Cr, W
Q = PPh_2, $AsPh_2$

a singlet-state dianion. However, careful observation of the reduction under controlled-potential-electrolysis conditions indicates that as one reduces the original material which is yellow, to the dianion, which is red, a transient green color develops in midelectrolysis, at a point equivalent to the addition of one electron per molecule. Deliberate addition of dianion to neutral material gives a green solution instantaneously, which has a well-characterized esr signal. Apparently one is dealing with the system type



$$\underset{\displaystyle 2\mathrm{A}^{\cdot-}}{\mathrm{A}\xrightarrow{2e}\mathrm{A}^{2-}} \qquad \mathrm{A} + \mathrm{A}^{2-} \overset{K}{\rightleftharpoons} 2\mathrm{A}^{\cdot-} \qquad (1)$$

The esr spectrum for the radical anion consists of three main lines in the intensity ratio of 1:2:1 due to interaction of the electron with both phosphorus nuclei. The hyperfine splitting constant, ΔH_{P}, is 13 G. Each of these is further split into a 13-fold multiplet, ΔH_{H} = 1.2 G. Preliminary infrared spectra on the neutral material and the radical anion indicate that the CO stretching frequencies move to longer wavelengths by ~100 cm^{-1} upon reduction (ν_{CO} (neutral) 2015, 1950 cm^{-1}, ν_{CO} (radical anion) 1900, 1870 cm^{-1}, ν_{CO} (dianion) 1858, 1775 cm^{-1}). The decrease observed in the carbonyl stretching frequencies upon decreasing the metal oxidation state by increased negative charge can be rationalized on the basis of increased interaction between the metal dπ orbitals and the carbonyl antibonding 2π orbitals.

If the metal atom bridged is changed to tungsten, and the bridging unit is then subsequently altered to arsenic (compounds **4** and **5**), rather remarkable differences are seen. The reduction potential remains constant (~ −1.8 v), but the equilibrium constant, K, for process 1 alters such that in the W–P compound (**4**) the radical-anion spectrum is weak even under stressing of the equilibrium by addition of excess neutral compound. Hyperfine splitting constants are about the same as for the Cr–P system. The problem of exchange broadening limits the ability to judge equilibrium constants accurately, but it appears as if the Cr–P system favors radical anion strongly (K = 10), while the W–P system favors dianion ($K < 1$). In the W-As analog no esr signal could be seen under highest gain suggesting $K \ll 1$. In bridge systems of this symmetry then, increased polarizability of the bridged metal or the bridging group leads to changes in the equilibrium constant to values favoring dianion.

As might be expected, the two-electron reduction (assuming n = 1) of the polymer $[\mathrm{Cr_2(CO)_{10}As_2Me_4}]_n$ (**6**) gives a solution which shows no esr signal. The As–As bond is being ruptured, producing metalloid anion fragments.

Attempts at preparing radical species from the cluster system $[\mathrm{C_5H_5Mo(CO)PPh_2}]_3$ (**8**) failed, the polarographic waves being very irreversible and triangular voltammetry very ill defined. However, the bridged species $[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Mo(SMe)_2}]_2$ (similar to **1** in structure) yields a stable radical cation (**7**).

The one-electron reduction of $\mathrm{(OC)_4MnS_2CNEt_2}$ gives a rather unstable radical anion, which demonstrates a rapidly disappearing signal of six lines each 6 G wide and separated by 40 G, typical of spin interaction with the I = $^5/_2$ Mn nucleus (compound **9**).

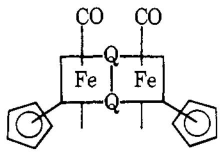
The dimeric species $[\mathrm{(OC)_4MnPPh_2}]_2$ (**10a**) proved to be electrochemically and chemically irreversible. This compound does not contain a metal–metal bond. However, the analogous $[\mathrm{(OC)_3MnSPh}]_2$ (**10b**) with a metal–metal bond shows clean reduction to a dianion, with electrochemical behavior characteristic of eq 1; *i.e.*, partial reduction gives a radical anion showing 11 lines, ΔH_{Mn} = 14 G, typical of interaction of the lone electron with both manganese nuclei.

As in the acetylene–metal complexes, the iron derivatives again provide a most rewarding field. Compound **11**, $[(\pi\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)PPh_2}]_2$, involves essentially octahedral configuration around the metal, with the octahedra sharing an edge, no metal–metal bond being present. The material *oxidizes* to a deep blue *radical cation*, which shows a featureless electron spin resonance signal 12.5 G wide, even at temperatures near the freezing point of solvent, −60°. The extensive delocalization observed in the Cr–P derivative (**4**) is apparently not present. At more anodic potentials the radical cation can be oxidized further to a dication, which shows no esr signal. Admixture of dication and neutral material produces radical cation

$$\mathrm{A} + \mathrm{A}^{2+} \rightleftharpoons 2\mathrm{A}^{\cdot+} \qquad (2)$$

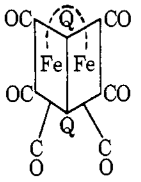
Although the oxidative wave generating dication appears well behaved at micromercury electrodes, a Pt electrode is necessary to generate stable dication.

The corresponding compound $[\mathrm{(OC)_3FePMe_2}]_2$ (**12**) involves a structure which is essentially octahedral around each iron, the octahedra sharing a *face*, a metal–metal bond occupying one of the ligand positions. This material reduces in one two-electron wave, unsplit on investigation by triangular voltammetry. Admixture of the dianion, which shows no esr signal, with neutral material gives a solution of radical anion, exhibiting a signal 7.5 G wide with some unresolved hyperfine structure. This compound will not oxidize at a Hg or Pt electrode, but the analogous As derivative, $[\mathrm{(OC)_3FeAsMe_2}]_2$ (**13**), shows an electrochemically reversible oxidation at a Hg microelectrode. Unfortunately it does not yield cation radical under controlled-potential-electrolysis conditions at a Hg pool and will not oxidize at a Pt electrode. As in the iron derivative above, working potentials near that of Hg ⇌ Hg^{2+} apparently lead to undesirable processes. The compound does, however, reduce by a one-electron step to a radical anion. It is apparent that the question of stability and ability to produce radical anion or cation, or dianion and dication, is extremely sensitive to the bridging group, the metal, and the remaining organic ligands.



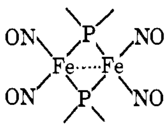
11, 16

Q = PMe$_2$, SCH$_3$



12, 13

Q = PMe$_2$, AsMe$_2$



14

Compound **14**, $[\mathrm{(ON)_2FePPh_2}]_2$, in which NO has replaced CO, reduces in two successive one-electron steps to give a radical anion and dianion, respectively. One is dealing with a system

$$A \xrightarrow{e} A\cdot^- \xrightarrow{e} A^{2-}$$

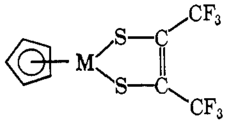
The radical anion exhibits a triplet 1:2:1 spectrum, with $\Delta H_P = 20$ G. The geometry of the molecules is presumably an approximate tetrahedral configuration about the metal, with the sharing of a tetrahedron edge. A metal–metal bond is present in the neutral material.

Although one compound does not make a series, the lack of N-induced hyperfine structure, coupled with large infrared shifts to longer wavelengths upon reduction, leads one to suspect that occupation of an orbital largely NO in character is not the cause of the infrared shifts. Back-bonding is again an important factor.

Compounds **15** and **16**, reported in the preliminary publication, represent the sulfur analog of this series. Both oxidize to give stable green radical cations with uncharacterized esr spectra.

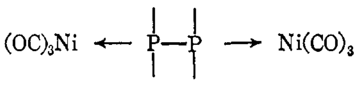
The two cobalt-bridged species investigated (**19** and **20**) probably have a structure similar to $[(OC)_3FeQR_2]_2$, octahedra sharing a face, with a bent metal–metal bond. Reduction of $[(\pi\text{-}C_5H_5)CoPPh_2]_2$ gives a radical anion which exhibits an esr spectrum exhibiting a triplet 1:2:1 signal with $\Delta H_P = 9$ G. Each member of the triplet exhibits further more complex splitting with $\Delta H = 2$ G. The sulfur-bridged species on the other hand both reduces to give a radical anion and oxidizes to give a radical cation. The esr signals from these species are rather broad but are uncharacterized. Attempts at eliciting electrochemiluminescence from the annihilation reaction between radical anion and cation failed.

Compounds **21** and **22**, the Co and Rh species containing $(\pi\text{-}C_5H_5)MS_2C_4F_6$, are included to demonstrate the difficulties encountered in interpreting esr spectra on derivatives of metals beyond the first long row. As Table I indicates, $(\pi\text{-}C_5H_5)CoS_2C_4F_6\cdot^-$ exhibits the expected eightfold multiplet, $\Delta H_{Co} = 41$ G; the Rh analog shows only one line, 25 G wide ($I_{Rh} = {}^1/_2$).

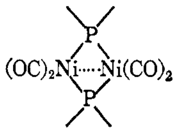


21, 22

The remaining four compounds are derivatives of Ni. Compound **23**, which lacks a metal–metal bond, is irreversible in its reduction. Compound **24**, which is derived from **23** by loss of two CO molecules, and which possesses a metal–metal linkage, undergoes two one-electron reductions, yielding a radical anion and a singlet-state dianion. The radical anion exhibits an esr spectrum consisting of a single line 6 G wide. Compound **25**, $[(\pi\text{-}C_5H_5)NiPPh_2]_2$, reduces to yield a stable radical anion, whose esr spectrum involves a single line 10 G wide.



23



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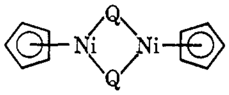

25, 26

Q = PPh$_2$, SMe

However, $[(\pi\text{-}C_5H_5)NiSCH_3]_2$ (**26**), which is analogous to the Co-containing **20**, oxidizes to yield a radical cation and reduces to a radical anion. The latter is fairly labile; no esr spectrum could be obtained, the rapidly growing ferromagnetic signal due to nickel metal growing to domain size, obscuring any narrow signal from the radical anion.

As the structural formulas imply, there appears to be no correlation between geometry and the nature of the electrochemistry of the system. In general, the presence of metal–metal bonds appears to correlate well with the ability to yield a stable radical anion (and possibly dianion), while the lack of metal–metal bonding correlates, albeit poorly, with ability to yield radical cations. At the moment, with predictability low, it is perhaps best to empirically explore the chemistry of these species, and this route is being pursued.

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