Electrochemical Oxidation of Thio-bridged Binuclear π-Cyclopentadienyl Complexes of Molybdenum, Iron, Cobalt, and Nickel

By **P. Douglas Frisch, Malcolm K. Lloyd, Jon A. McCleverty,*** and **Duncan Seddon,** Chemistry Department, The University, Sheffield S3 7HF

The species $[(cp)M(L)(SR)]_2$ (R = alkyl or aryl, cp = π-cyclopentadienyl; M = Mo, L = NO; M = Fe, L = CO; M = Co or Ni, L = nothing) have been oxidised voltammetrically and monocationic (all M) and dicationic (M = Fe or Ni) species detected. The $E_{\frac{1}{2}}$ values of the oxidation processes are dependent on M and R. Monocationic iron and nickel complexes, prepared chemically and by electrolysis, have been characterised spectroscopically. Comparison is made with the isoelectronic complexes $[(cp)Mn(NO)(SR)]_2$, and the possible effects of oxidation on the structures of these molecules are discussed.

In a previous paper [1] we described the redox behaviour of a series of complexes $[(cp)Mn(NO)(SR)]_2$ (cp = π-cyclopentadienyl, R = alkyl group), which underwent, voltammetrically, two one-electron oxidations. Although we were unable to isolate dicationic species, we obtained stable paramagnetic monocationic complexes, and illustrated the similarity between these manganese dimers and their isoelectrionc iron analogues, $[(cp)Fe(CO)(SR)]_2$. In fact, the redox behaviour of species containing the $[(cp)Fe(CO)]$ group is well established. Thus, polarographic data have been obtained for the complex $[(cp)Fe(CO)(SMe)]_2$,[2] and the isolation of related mono-[3,4] and di-cationic complexes [5] has been reported. Furthermore, electrochemical oxidations of the complexes $[(cp)Fe(CO)_2]_2$, $[\{(cp)Fe(CO)\}_2(Ph_2PCH_2CH_2PPh_2)]$, and $[(cp)Fe(CO)]_4$ have been described.[6]

The fact that these isoelectronic manganese and iron complexes exhibited redox behaviour prompted us to look for similar properties in other closely related species. We have described [7] zinc reduction of the complexes $[(cp)Mo(NO)(SR)X]_2$ (X = halide) to $[(cp)Mo(NO)(SR)]_2$, and, although we were unable to effect reoxidation using X_2, we felt that, in principle, the related dications $[(cp)Mo(NO)(SR)]_2^{2+}$ should exist. It has been demonstrated polarographically [2] that $[(cp)M(SMe)]_2$ (M = Co or Ni) can be oxidised or reduced affording, respectively, monocations or anions. The molybdenum, cobalt, and nickel complexes are very similar to the iron and manganese species discussed above, and in this paper we describe a systematic examination of the oxidative electrochemistry of these complexes.

RESULTS

The complexes were investigated voltammetrically using a rotating Pt electrode for conventional voltammetry and a stationary Pt electrode for cyclic experiments. All species examined underwent at least one one-electron oxidation process, and the voltammograms of many complexes exhibited a second anodic wave.

Voltammetric Studies. Iron complexes, $[(cp)Fe(CO)SR]_2$. The iron complexes underwent two one-electron oxidations (Table 1). The first wave was reversible, by cyclic voltammetry, while the second wave was accompanied by anodic peaking. The potential for the first wave occurred at *ca.* 0·0 V and the $E_{\frac{1}{2}}$ value increased according to the order R = Et < Me < Bu^t < p-MeC_6H_4 < p-ClC_6H_4; $E_{\frac{1}{2}}$ values for the alkyl-substituted species occurred below 0·0 V, those for the aryl-species at *ca.* +0·1 V. Chemical oxidation (see below) of the neutral species afforded the corresponding monocations, $[(cp)Fe(CO)SR]_2^+$, and the $E_{\frac{1}{2}}$ values obtained for reduction of these corresponded very closely to oxidation potentials obtained for the neutral species.

The second waves occurred at *ca.* +0·50 V and had a

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[1] P. Hydes, J. A. McCleverty, and D. G. Orchard, *J. Chem. Soc.* (*A*), 1971, 3660.

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[6] J. Ferguson and T. J. Meyer, *Inorg. Chem.*, 1971, **10**, 1025; *Chem. Comm.*, 1971, 1544; T. J. Meyer and J. Ferguson, *Inorg. Chem.*, 1972, **11**, 631.

[7] J. A. McCleverty and D. Seddon, *J.C.S. Dalton*, 1972, 2588.

dependence of $E_{\frac{1}{2}}$ on the group R similar to that observed for the first wave. Although this wave was not cyclically reversible, it presumably corresponded to formation of the ions $[(cp)Fe(CO)SR]_2^{2+}$. A linear correlation may be established between the value of the first oxidation potential and ν(CO) obtained for the complexes $[(cp)Fe(CO)SR]_2$ (Table 1).

TABLE 1

Voltammetric and i.r. spectral data obtained for the iron and manganese complexes $[(cp)Fe(CO)(SR)]_2^z$ and $[(cp)Mn(NO)(SR)]_2^z$

M	R	z [a]	$E_{\frac{1}{2}}$ [b]	$(E_{\frac{3}{4}} - E_{\frac{1}{4}})$ [c]	D [d]	$(E_{pa} - E_{pc})$ [e]	Comment [f]	ν(CO), ν(NO) [g]
Fe	Me	0	−0·11	65	4·7	165	R	1 950
			+0·48	80	7·8	230	QR	
	Et	0	−0·13	70	5·1	200	R	1 946
			+0·54	55	4·2	370	QR	
	Et	+1	−0·14	70	4·3	170	R	
			+0·53	60	4·4		QR (0·62)	
	Bu^t	0	−0·01	56	5·0	185	R	1 956
			+0·58	65	5·3		QR (0·66)	
	Bu^t	+1	−0·01	75	5·1	180	R	1 990
			+0·57	55	4·4		QR (0·69)	
	p-MeC$_6$H$_4$	0	+0·10	60	4·5	180	R	1 968
			+0·68	60	5·0	155	QR	
	p-MeC$_6$H$_4$	+1	+0·10	65	5·4	170	R	1 980
			+0·69	50	5·2	180	QR	
	p-ClC$_6$H$_4$	0	+0·16	55	5·0	155	R	1 972
			+0·64	65	5·6	145	QR	
Mn [h]	Pr^i	0	−0·33					1 722
			+0·43					
		+1						1 779, 1 742
	Bu^s	0	−0·18					1 722
			+0·54					
		+1						1 780, 1 748
	Bu^t	0	−0·18					1 720
			+0·55					1 771, 1 736
		+1						

[a] Change on complex; when $z = +1$, salt is PF_6^-. [b] In volts at a rotating Pt electrode in CH_2Cl_2 at 20 ± 2 °C. [c] Reversibility criterion in mV; for a reversible one-electron process, $(E_{\frac{3}{4}} - E_{\frac{1}{4}}) = 59$ mV. [d] $D = i_d/c$ in μA mmol^{-1} (calc. for $n = 1$); for the one-electron process $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^- + e^-$, $D = 5{\cdot}1$ at the electrode used in this work. [e] $(E_{pa} - E_{pc})$ in mV in cyclic voltammogram; for a reversible process $(E_{pa} - E_{pc}) \simeq 200$ mV. [f] Data reversible (R), quasi-reversible (QR) (coupled chemical reaction or anodic peaking), or irreversible (IR); numbers refer to anodic peak if no cathodic peak detected. [g] In CH_2Cl_2 in cm^{-1}. [h] Data from ref. 1.

Molybdenum complexes, $[(cp)Mo(NO)(SR)]_2$. Voltammograms of the molybdenum complexes exhibited one generally reversible oxidation wave, corresponding to generation of the ions $[(cp)Mo(NO)(SR)]_2^+$ (Table 2). A number of voltammograms contained a second anodic and probably catalytic wave, but unequivocal evidence for the existence of a dication could not be obtained. The neutral species could not be reduced at potentials down to −1·6 V.

TABLE 2

Voltammetric and i.r. spectral data obtained for the molybdenum complexes $[(cp)Mo(NO)(SR)]_2$

R	$E_{\frac{1}{2}}$ [a]	$(E_{\frac{3}{4}} - E_{\frac{1}{4}})$ [b]	D [c]	$(E_{pa} - E_{pc})$ [d]	Comment [e]	ν(NO) [f]
Me	+0·71	107	9·9		QR (0·76)	1 618, 1 579
Et	+0·71	100	10·2	170	R	1 600, 1 578
Pr^i	+0·72	102	13·1	130	R	1 612, 1 573
Pr^n	+0·71	100	11·1	160	R	1 612, 1 574
Bu^i	+0·69	90	9·9	140	R	1 612, 1 576
CH$_2$Ph	+0·79	95	8·4		QR (0·84)	1 616, 1 578

[a] In volts, in CH_2Cl_2 at 20 ± 2 °C. [b] Reversibility criterion in mV; for reversible couple $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^- + e^-$, $(E_{\frac{3}{4}} - E_{\frac{1}{4}}) = 80$ mV. [c] i_d/c; for the test couple, $D = 10{\cdot}1$. [d] $(E_{pa} - E_{pc})$ in mV; in cyclic voltammogram for the reversible test couple, $(E_{pa} - E_{pc}) \simeq 115$ mV. [e] Data reversible (R) or quasi-reversible (QR; anodic peaks quoted where no cathodic peak detected). [f] Data obtained from ref. 7 in CH_2Cl_2, in cm^{-1}.

With the exception of the benzyl derivative, the molybdenum complexes were all reduced at approximately the same potential, *ca.* +0·71 V. That the oxidation potential of the complex $[(cp)Mo(NO)(SCH_2Ph)]_2$ was 80 mV more anodic is consistent with data obtained for the nickel complexes (*vide infra*) and with the electron-withdrawing properties of the phenyl group. The correlation between ν(NO) and $E_{\frac{1}{2}}$ (oxidation) is not especially good; ν(NO) is essentially invariant when R = Me to Bu^i and occurs at only slightly higher frequencies when R = CH$_2$Ph.

Nickel and cobalt species. The nickel complexes underwent two oxidation reactions (Table 3), the first occurring at potentials of *ca.* 0·0 V and the second at *ca.* +1·0 V. $E_{\frac{1}{2}}$ Values of both waves were dependent on the nature of the substituent R, those of the alkyl-substituted species being some 100 mV more cathodic than those of their aryl analogues. While no regular substituent effect could be discerned in the potential data obtained from the former, it may be noted that oxidation of the t-butyl and benzyl species was significantly easier than oxidation of the other alkylthio-species. When R = aryl, the order of oxidation potentials was R = Ph < *o*-, *m*-, or p-MeC$_6$H$_4$ < p-ClC$_6$H$_4$ < 2-naphthyl. The second wave was also dependent on R, but the order was somewhat different.

The three cobalt complexes $[(cp)CoSR]_2$ (R = Me, p-MeC$_6$H$_4$, or p-ClC$_6$H$_4$) underwent only one oxidation reaction (Table 3), the $E_{\frac{1}{2}}$ value becoming more anodic in the order R = Me < p-MeC$_6$H$_4$ < p-ClC$_6$H$_4$. It has been reported [2] that, in dimethoxyethane at a dropping mercury electrode, $E_{\frac{1}{2}}$ values for generation of the ions $[(cp)M(SR)]_2^+$ (M = Co or Ni) are identical. However, our data show that, in dichloromethane using Pt, the oxidation potential for the complex $[(cp)Co(SMe)]_2$ is 200 mV more negative than that of its nickel analogue. This presumably reflects differences in electronic and molecular structure (*vide infra*). However the complex $[(cp)Co\{S(p\text{-}MeC_6H_4)\}]_2$ is oxidised at a potential 70 mV more *positive* than its nickel analogue.

TABLE 3

Voltammetric data obtained for the complexes $[(cp)NiSR]_2$ and $[(cp)CoSR]_2$

M	R	$E_{\frac{1}{2}}$ [a]	$(E_{\frac{3}{4}} - E_{\frac{1}{4}})$ [b]	D [c]	$(E_{pa} - E_{pc})$ [d]	Comment [e]
Ni	Me	−0·06	70	4·1	230	R
		0·79	70	5·7		0·90
	Et	−0·05	57	5·3	220	R
		0·85	60	4·8		0·97
	Pr^i	−0·04	75	8·5	220	R
		0·91	56	5·1		1·02
	Pr^n	−0·08	60	7·5	200	R
		0·93	60	5·6		1·02
	Bu^t	0·00	56	4·6	190	R
		0·88	58	5·8		1·02
	CH_2Ph	−0·02	57	6·9	190	R
		0·95	90	6·5		1·01
	Ph	0·09	60	4·4	190	R
		1·04	90	6·4		1·10
	$o\text{-}MeC_6H_4$	0·08	65	6·6	195	R
		1·08	75	5·8	400	IR
	$m\text{-}MeC_6H_4$	0·06	60	5·6	210	R
		1·05	80	6·0		1·19
	$p\text{-}MeC_6H_4$	0·08	60	5·4	185	R
		0·93	55	5·8	390	IR
	2-Naphthyl	−0·02	85	5·3	200	R
		0·90	60	5·4	360	IR
	$p\text{-}ClC_6H_4$	0·07	57	6·1	210	R
		0·80	65	5·9	300	IR
Co	Me	−0·22	70	4·3	180	R
	$p\text{-}MeC_6H_4$	0·15	100	5·0		QR
	$p\text{-}ClC_6H_4$	0·21	60	4·3	185	R

[a] In volts at a rotating Pt electrode in dichloromethane. [b] Reversibility criterion in mV; for a reversible one-electron process, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 59$ mV. [c] $D = i_d/c$ in µA mmol⁻¹ (calculated for $n = 1$); for the one-electron process $[Ni\{S_2C_2(CN)_2\}_2]^{2-} \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^- + e^-$, $D = 5{\cdot}1$ at the electrode used in this work. [d] $(E_{pa} - E_{pc})$ in mV, in cyclic voltammogram; for a reversible process $(E_{pa} - E_{pc}) \simeq 200$ mV. [e] Data reversible (R) or irreversible (IR); numbers correspond to E_{pa} (in volts) when no E_{pc} detected.

TABLE 4

Analytical (%), conductivity, and m.p. data for the new iron complexes

Complex	C Found (calc.)	H Found (calc.)	S Found (calc.)	Cl Found (calc.)	Δ [a]	M.p. (t/°C)
$[(cp)Fe(CO)SBu^t]_2PF_6$	38·85 (38·65)	4·70 (4·50)	10·5 (10·3)		73	204 (decomp.)
$[(cp)Fe(CO)\{S(p\text{-}MeC_6H_4)\}]_2$	57·0 (57·35)	4·70 (4·40)	11·7 (11·75)			180 (decomp.)
$[(cp)Fe(CO)\{S(p\text{-}MeC_6H_4)\}]_2PF_6$	45·15 (45·3)	4·00 (3·50)	9·15 (9·30)		85	250
$[(cp)Fe(CO)\{S(p\text{-}Cl_6C_6H_4)\}]_2$	49·1 (49·25)	2·35 (2·55)	10·7 (10·95)	11·85 (12·15)		200 (decomp.)

[a] Conductivity in Ω cm⁻¹ mol⁻¹ (nitromethane); for a 1 : 1 electrolyte, Δ *ca.* 80 Ω cm⁻¹ mol⁻¹.

Synthetic and Associated Spectral Studies.—Oxidation potentials for all the complexes, except those containing Mo, occur at values sufficiently low that chemical oxidation of the neutral species to the monocations should be achieved using air (with or without acid), I_2, or Ag^+. This expectation has already been realised when L = CO or NO and M = Fe or Mn. However, with the iron complexes it is, in fact, unnecessary to use either I_2 or Ag^+,[3,4] since aerial oxidation in the presence of HPF_6 affords the desired ions $[(cp)Fe(CO)SR]_2^+$ (Table 4).* These monocations are paramagnetic ($S = \frac{1}{2}$) and afford singlet e.s.r. spectra ($\langle g \rangle$ 1·98) in dichloromethane at room temperature (Table 5). In acetone glasses at *ca.* 103 K, three-fold anisotropy of the *g* tensor was resolved which was consistent with data described elsewhere [8] for the ion $[(cp)Fe(CO)(SMe)]_2^+$. We were unable to isolate the species $[(cp)Fe(CO)(SR)]_2^{2+}$ by oxidation of the neutral species with either Ag^+ or HNO_3, but these species have been prepared [5] using Br_2; these observations are not inconsistent with our voltammetric data.

Oxidation potentials of the molybdenum complexes are substantially more anodic than any of their electronically equivalent analogues. Thus attempts to prepare these species would require powerful oxidising agents, such as Br_2 or Cl_2, and, as we have described,[7] this was largely unsuccessful. However, controlled-potential electrolysis of the complex $[(cp)Mo(NO)(SCH_2Ph)]_2$ in dichloromethane afforded orange-red solutions which exhibited weak e.s.r. signals [$\langle g \rangle$ *ca.* 2·00; one central strong line with six weak satellites symmetrically displaced about the central signal ($\langle a \rangle$ 69 G); additional very weak signals were also observed]. This spectrum is consistent with association of one unpaired electron with two molybdenum atoms (^{95}Mo and ^{97}Mo, $I = 5/2$). We also observed that, in dichloromethane, the complex $[(cp)Mo(NO)(SR)Br]_2$ (R = n-propyl) exhibited an identical e.s.r. spectrum and we believe that this is consistent with our suggestion [7] that the bromothiolato-complex dissociates in solution giving $[(cp)Mo(NO)(SR)]_2$ and Br_2; the bromine presumably reoxidises the dimer giving, perhaps, some $[(cp)Mo(SR)]_2^+$ which may be responsible for the e.s.r. signals.† Continued electrolysis of the dimer afforded a green-brown solution from which a neutral red solid, the nature of which will be discussed elsewhere, was obtained. There was no evidence for formation of the salt $[(cp)Mo(NO)(SCH_2Ph)]_2PF_6$.

Chemical or electrochemical oxidation of the complexes $[(cp)Ni(SR)]_2$ clearly afforded the monocations, although isolation proved impossible. At room temperature these species exhibited a single e.s.r. signal ($\langle g \rangle$ 2·039 at 103 K in

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* Use of acetic acid or HCl in the presence of BF_4^- is also effective (ref. 5).

† The same e.s.r. signals may be obtained from solutions containing the complexes $[(cp)Mo(NO)(SR)]_2$ and Br_2.

[8] H. A. O. Hill, M. Clare, C. E. Johnson, and R. Richards, *Chem. Comm.*, 1970, 1376.

acetone glasses, $\langle g_1 \rangle$ 2·0842, $\langle g_{11} \rangle$ 1·995), whose parameters were consistent with that previously reported [2] for the ion $[(cp)NiSMe]_2^+$. That oxidation of these species was particularly easy was reflected in the broadness of ^1H n.m.r. spectral lines obtained from neutral species whose solutions had been made up in air. Attempts to oxidise the complexes $[(cp)CoSR]_2$ may have been successful (metallic Ag was precipitated) but we were unable to detect e.s.r. spectral signals from electrochemically or chemically oxidised samples in solution.

TABLE 5

E.s.r. data for $[(cp)Fe(CO)SR]_2^+$ complexes

R	$\langle g_z \rangle$	$\langle g_x \rangle$	$\langle g_y \rangle$	$\langle g_{xy} \rangle$	$\langle g_{av} \rangle$
Me	1·9256	2·0167	1·9978	2·0072	1·9800
Et	1·9247	2·0269	1·9991	2·0100	1·9815
Bu^t	1·9245			1·9912	1·9689
p-MeC_6H_4	1·9101			2·0195	1·9830

Measured in frozen acetone at *ca.* 103 K; *X*-band spectrum on a Varian Endor spectrophotometer (1,1-diphenyl-2-picrylhydrazyl, $\langle g \rangle$ 2·0036).

We note that a comparison of $E_{\frac{1}{2}}$ values obtained from the oxidations of analogous μ-thio- and μ-phosphino-complexes [2,9] reveals that the latter are always oxidised at potentials more cathodic than the former. This may account for the easier formation of the ions $[(cp)Fe(CO)(PPh_2)]_2^{0,1+,2+}$ relative to the corresponding thio-species. We may predict that the series $[(cp)Mn(NO)PR_2]_2^{0,1+,2+}$ and $[(cp)Mo(NO)(PR_2)_2]_2^{0,1+,2+}$ will be obtained, and that the related complexes $[(cp)M(PR_2)]_2$ (M = Co or Ni) may be oxidised in two one-electron processes, the first of which will have an $E_{\frac{1}{2}}$ value substantially below 0·0 V.

DISCUSSION

It can be seen from the $E_{\frac{1}{2}}$ data in Tables 1—3 that values of the oxidation potentials for the complexes $[(cp)M(L)(SR)]_2$ are dependent on the nature of the group R. It is entirely reasonable that when R = aryl in $[(cp)M(L)(SR)]_2$ oxidation is harder than when R = alkyl, reflecting, simply, the superior electron-withdrawing (or π-acceptor) capabilities of aryl relative to alkyl groups. Within the alkyl series we expected that oxidation of the species where R = Bu^t would be easier than that where R = Me. However, the reverse is true, although the relative differences in $E_{\frac{1}{2}}$ values are small, and we are presently unable to explain this in simple MO terms. These effects could arise from relative electronic properties of the Me and Bu^t groups (*i.e.* SMe is a better σ-donor–poorer π-acceptor ligand than SBu^t [*]) or as a result of steric effects derived from the size of the Bu^t group. The latter could cause severe distortion of the $Fe_2(SR)_2$ framework [†] which would have a substantial influence on the nature of the redox orbital. Support for this view is lent by the observation that $E_{\frac{1}{2}}$ for oxidation of the complex $[(cp)NiSR]_2$ (R = 2-naphthyl) is substantially more *cathodic* than those for R = *p*-MeC_6H_4, *p*-ClC_6H_4, or Ph, and even R = alkyl. It would have been expected on electronic grounds that $E_{\frac{1}{2}}$ would be fairly anodic,[‡] but models of the Ni complex indicate that the Ni–Ni distance may well be lengthened thereby significantly altering the molecular geometry and nature of the redox orbital.

The molecular structures of the complexes $[(cp)Fe(CO)SPh]_2$ [10] and $[(cp)Fe(CO)SMe]_2^+$ [4] have been determined. In both species, the Fe_2S_2 group is non-planar, being bent about a line joining the two S atoms. In the neutral species the dihedral angle between the two FeS_2 planes is 161°, with an Fe–Fe distance of 3·39 Å (regarded as non-bonding) and an Fe–S–Fe bond angle of 98°. In the cationic species the respective bond angles and lengths are 153°, 2·93 Å, and 82°. The general 'tightening up' of the dimensions on oxidation is regarded as evidence for formation of a one-electron Fe–Fe bond in the ion $[(cp)Fe(CO)SMe]_2^+$, since the electron removed may be regarded as having originated from a σ* orbital associated with the $Fe_2(SR)_2$ group.[11-13] It might be expected that a second oxidation, giving $[(cp)Fe(CO)SR]_2^{2+}$, would lead to further contraction of the molecular dimensions, commensurate with formation of a two-electron Fe–Fe bond. Indeed, just such an effect has been observed in the closely related species *cis*-$[(cp)Fe(CO)PPh_2]_2^{0,1+,2+}$ (Fe–Fe distances 3·49, 3·12, and 2·78 Å respectively).[13] Similar behaviour presumably occurs in the isoelectronic manganese species $[(cp)Mn(NO)SR]_2^{0,1+,2+}$.[1]

The structure of the complexes $[(cp)Ni(SR)]_2$ is probably similar to that of the corresponding μ-phosphino-complex $[(cp)Ni(PPh_2)]_2$,[14] the $Ni(SR)_2Ni$ group being essentially planar, with no formal Ni–Ni bond. As in the iron complex, the uppermost filled molecular orbital is probably a σ* level associated with the metal–sulphide framework and so stepwise removal of electrons from the σ* level should lead to formation of a one- and two-electron metal–metal bond. This would occur with shortening of the internuclear distance; it may be noted that the ions $[(cp)Ni(SR)]_2^{2+}$ are isoelectronic with the complexes $[(cp)Co(SR)]_2$. Thus, oxidation may be accompanied by bending of the $Ni(SR)_2Ni$ framework.

The cobalt complexes $[(cp)Co(SR)]_2$ are presumably

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[*] Such effects have been noted in the oxidation potential of the complexes $[Co(CNR)_3(PR_3')_2]^+$ and $[Cr(NO)(CNR)_5]^+$, where steric problems are minimal (J. W. Dart, M. K. Lloyd, J. A. McCleverty, R. Mason, and J. Williams, *J.C.S. Dalton*, 1973, 1747).

[†] Molecular models indicate that the *trans*- and, especially, the *cis*-isomers of $[(cp)Fe(CO)Bu^t]_2$ are extremely sterically crowded.

[‡] Fused benzene rings act as an electron sink and generally cause an anodic shift of $E_{\frac{1}{2}}$ values relative to those species without the fused ring.

[9] P. D. Frisch, D. G. Orchard, and J. A. McCleverty, unpublished work.

[10] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Comm.*, 1968, 1165.

[11] L. F. Dahl, personal communication.

[12] R. Mason and D. M. P. Mingos, personal communication; *J. Organometallic Chem.*, 1973, **50**, 53.

[13] N. G. Connelly, L. F. Dahl, and J. D. Sinclair, personal communication.

[14] J. Coleman and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 542.

structurally analogous to $[(cp)Co(PPh_2)]_2$,[14] so that the $Co(SR)_2Co$ group is bent about the thio ' hinges ' (*ca.* 105°) and a Co–Co bond is formally required to account for the diamagnetism of the complexes and the short intermetallic distance. Similarly, in the molybdenum complexes $[(cp)Mo(NO)(SR)]_2$, which are probably isostructural with their Cr analogues,[15] a metal–metal bond is also necessary and the $Mo(SR)_2Mo$ framework is probably planar. A symmetry-based molecular-orbital description of the bonding in binuclear complexes of this type[12] suggests that the uppermost orbitals are antibonding with respect to the metal–metal bonds and non-bonding with respect to the metal–(bridging ligand) bonds. It would predict unit bond order for the neutral dimers and bond order 1·5 for the corresponding monocations; therefore, significant contractions of the metal–metal bonds would be expected on oxidation with no concomitant change in the metal–sulphur bond. While there is presently no structural information, our electrochemical observation that there is a significant substituent effect on the oxidation potentials of all species studied suggests that the redox orbital (presumably the highest-occupied molecular orbital) does contain considerable thio-ligand character.

We emphasise that these electrochemical data can give no insight whatsoever into geometrical changes which may accompany electron transfer. It is our opinion, however, that the nature of the redox orbital, and hence the value of the oxidation potential, is strongly influenced by both electronic and structural effects.

EXPERIMENTAL

The complexes $[(cp)NiSR]_2$, $[(cp)CoSR]_2$, $[(cp)Fe(CO)SR]_2^{0,1+}$, and $[(cp)Mo(NO)(SR)]_2$ (cp = π-cyclopentadienyl) were prepared by published procedures.[3,4,7,16]

Electrochemical studies were made with a Beckman Electroscan 30 polarograph, using dichloromethane as solvent (complex 10^{-3}M) and $(Et_4N)ClO_4$ as base electrolyte (0·05M). The data are quoted against the s.c.e. (1M in aqueous LiCl), recorded at 20 ± 2 °C, and are accurate to ±10 mV. Where necessary results were corrected for *iR* drop. Voltammetric and cyclic voltammetric data (scan speeds 0·05 V s^{-1}) were obtained using a Pt electrode. Controlled-potential electrolyses were carried out using a Chemical Electronics Potentiostat TR70/2A, using acetonitrile as solvent and $(Et_4N)PF_6$ as base electrolyte (0·1M). The complexes were 10^{-2}M in solution, the working electrode was Pt gauze, the auxiliary electrode Pt foil, and the reference cell Ag–AgI made up in MeCN. Electrolyses were carried out at potentials at least 50 mV more anodic than the recorded oxidation wave.

Conductivities were measured in nitromethane at 20 ± 2 °C using a Phillips conductivity meter. E.s.r. and ^1H n.m.r. spectra were obtained with Varian Endor (*X*-band) and HA100 spectrometers respectively. I.r. spectra were measured using a PE180 spectrophotometer.

$[(cp)Fe(CO)SR]_2PF_6$ (R = Bu^t *or* p-MeC_6H_4).—The complexes $[(cp)Fe(CO)SR]_2$ (0·5 g) were dissolved in acetone (20 cm^3) and treated with HPF_6 (60%; 2·0 cm^3). On shaking in air the brown solution became dark green. The solvent was removed *in vacuo* affording a green solid which was recrystallised from dichloromethane–n-heptane (yield 89%).

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