

A New Synthetic Route to Transition Metal Complexes of Unsymmetrically Substituted Dithiolenes: Evidence for a Metalladithiolenene Ring Current

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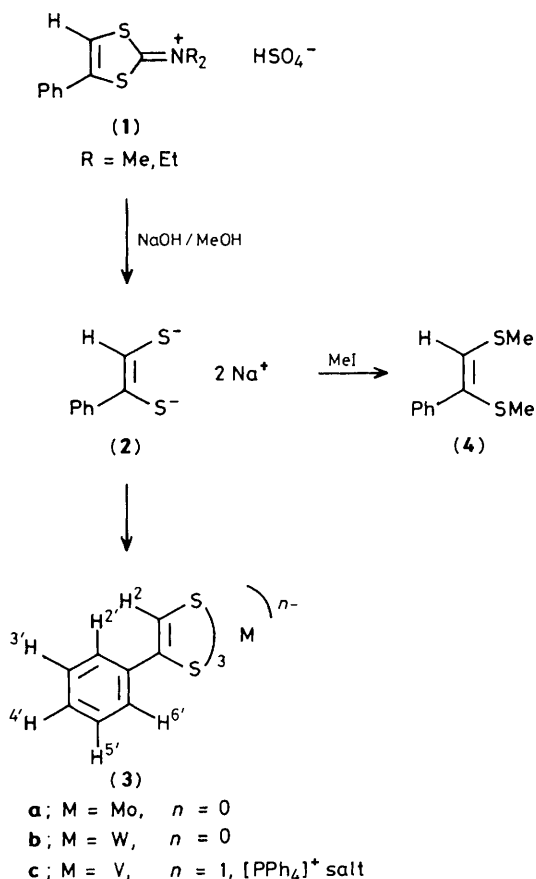
Alkaline hydrolysis of 2-*N,N*-diethylamino-4-phenyl-1,3-dithiolium hydrogen sulphate $\{[S(\text{PhC}=\text{C}(\text{H})\text{SC}=\text{NEt}_2)][\text{HSO}_4]\}$ in the presence of a metal complex has been used to prepare $[M\{S(\text{Ph})C=C(\text{H})S\}]^{n-}$ ($M = \text{Mo}, \text{W}$; $n = 0$; $M = \text{V}$, $n = 1$) complexes; ^1H n.m.r. studies of these systems have shown that the metalladithiolenene ring sustains a diamagnetic ring current.

Transition metal complexes of unsaturated 1,2-dithiolates (metal dithiolenes) have attracted much attention over the past twenty years owing to their interesting structural and electrochemical properties.^{1,2} This interest has been revived by the suggestion^{3,4} that the molybdenum-containing cofactor of the oxomolybdenum enzymes incorporates a molybdenum complex of an unsymmetrically substituted alkene-1,2-dithiolate. Few such unsymmetrically substituted dithiolenene complexes have been reported⁵⁻⁷ and we wished to develop a general synthetic method to allow the preparation of complexes of such ligands with early transition metals, to serve as chemical models of the proposed enzymic molybdenum site. Recently, we have devised a method of generating the alkene-1,2-dithiolate function by hydrolysis of dialkylamino-1,3-dithiolium salts (1);⁸ these salts are obtained in high yields and the method allows control over R^1 and R^2 , *i.e.* unsymmetrically substituted compounds may be prepared. Despite

failures to isolate the free ligands, we have succeeded in preparing metal dithiolenes from ene-1,2-dithiolates generated in this manner. Herein we report the synthesis, and selected electrochemical and spectroscopic characteristics of three compounds (3), containing 1-phenylethene-1,2-dithiolate (styrene-1,2-dithiolate, sdt), $[\text{Mo}(\text{sdt})_3]$, $[\text{W}(\text{sdt})_3]$, and $[\text{PPh}_4][\text{V}(\text{sdt})_3]$.

The reactions shown in Scheme 1 were accomplished under a dinitrogen atmosphere using standard Schlenk tube techniques. Addition of $[\text{MoO}_2(\text{pentane-2,4-dionate})_2]$ to a MeOH solution of Na_2sdt (2), generated by alkaline hydrolysis of the corresponding dithiolium salt,⁸ followed by acidification with HCl, gave a tarry precipitate of $[\text{Mo}(\text{sdt})_3]$ (3a) which was purified by flash chromatography on a silica column using hexane- CH_2Cl_2 (4:1) as eluant. An identical procedure, using WCl_6 in place of $[\text{MoO}_2(\text{pentane-2,4-dionate})_2]$, gave $[\text{W}(\text{sdt})_3]$ (3b); the corresponding use of $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ produced a solution of $[\text{V}(\text{sdt})_3]^-$ which was precipitated as $[\text{PPh}_4][\text{V}(\text{sdt})_3]$ (3c) by addition of $[\text{PPh}_4]\text{Br}$ and recrystallised from CH_2Cl_2 -MeOH. Analytically pure materials were obtained in 10–20% yield. Though these yields are not high, they are better than those obtained using the general method for the synthesis of complexes of substituted alkene-1,2-dithiolates, *i.e.* with reaction of a α -hydroxy- or α -halogenoketone with P_4S_{10} followed by treatment with a suitable compound of the metal.^{6,9} Furthermore, since dithiolium salts can be obtained in high yield and with control over substituents,⁸ the method is of much greater synthetic utility.

The u.v.-visible spectrum of each of these sdt complexes[†] is qualitatively very similar to that of the corresponding ethene-1,2-dithiolate (edt) or 1,2-diphenylethene-1,2-dithiolate (pdt) complex,^{1,2} especially in the visible region, implying that the sdt complexes possess the trigonal prismatic geometry of their symmetrically substituted analogues.¹



Scheme 1. Reagents: a; i, $[\text{MoO}_2(\text{pentane-2,4-dionate})_2]$; ii, HCl. b; i, WCl_6 ; ii, HCl. c; i, $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$; ii, HCl; iii, $[\text{PPh}_4]\text{Br}$.

Table 1. Potentials^a (E_V/mV vs. saturated calomel electrode) for reversible redox reactions of styrene-1,2-dithiolate complexes.

Complex	Process	
	$n = 0/n = 1$	$n = 1/n = 2$
$[\text{Mo}(\text{sdt})_3]^{n-}$	+10	-365
$[\text{W}(\text{sdt})_3]^{n-}$	-35	-420
$[\text{V}(\text{sdt})_3]^{n-}$	+260	-665

^a Potentials determined at a glass carbon working electrode by cyclic voltammetry for solutions of the complexes in CH_2Cl_2 at ca. 20°C containing 0.2 M $[\text{NBu}_4][\text{BF}_4]$. For all processes $i_{pa}/i_{pc} = 1.0 \pm 0.05$ and $\Delta E = 60 \text{ mV}$, independent of scan rate. Controlled potential electrolysis confirmed the one-electron stoichiometry.

[†] $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): $[\text{Mo}(\text{sdt})_3]$ 666 (17 000), 522sh (3 400), 443 (12 400), 330sh (7 700), 285sh (20 100), 242 (41 600); $[\text{W}(\text{sdt})_3]$, 631 (216 500), 503 (4 700), 407 (14 000), 310 (10 300), 272 (37 200), 240sh (57 500); $[\text{PPh}_4][\text{V}(\text{sdt})_3]$ 695sh (8 200), 605 (10 400), 550sh (8 500), 380sh (2 300) (sh = shoulder)

Table 2. ^1H N.m.r. data for styrene-1,2-dithiolate complexes.

Species	2-H	2'-,6'-H	3',4',5'-H ^a
$\text{Me}_2\text{sdt}(\mathbf{4})^b$	6.43	7.40	7.40
$[\text{Mo}(\text{sdt})_3](\mathbf{3a})^b$	9.52	7.80	7.40
$[\text{W}(\text{sdt})_3](\mathbf{3b})^b$	9.77	7.78	7.42
$[\text{V}(\text{sdt})_3](\mathbf{3c})^c$	8.83	7.78	7.31

^a For the phenyl ring carbons the value corresponds to the centre of the multiplet. ^b In CDCl_3 . ^c In $(\text{CD}_3)_2\text{SO}$.

The electrochemical behaviour of the sdt complexes has been investigated by cyclic voltammetry in CH_2Cl_2 . The data obtained (Table 1) show that each complex is part of a three-membered redox series; $[\text{M}(\text{sdt})_3]^{n-}$ ($n = 0, 1, 2$). Analogous behaviour has previously been reported for the corresponding edt and pdt complexes.¹ Cyclic voltammograms were also recorded in the hydrocarbon electrolyte $[\text{NBu}_4][\text{BF}_4] \cdot 3$ toluene¹⁰ but, despite the wider electrochemical window of this medium, no further reversible redox processes were detected.¹¹

The ^1H n.m.r. spectra of the sdt complexes are especially interesting. In each case, a low field singlet is observed for 2-H, with the *ortho* protons (2'-, 6'-H) of the phenyl substituent appearing as a doublet (J ca. 7 Hz), well separated from the multiplet for 3'-, 4'-, 5'-H. The chemical shift values, together with those for the bis-sulphide (**4**), are given in Table 2. In each case it is observed that, relative to the acyclic sulphide, the proton on the metalladithiolene (MS_2C_2) ring (2-H) is subject to a large (ca. 3 p.p.m.) downfield shift, the *ortho* protons to a smaller downfield shift, with the more distant protons little affected. This pattern is consistent with the presence of an induced diamagnetic ring current in the metalladithiolene ring, the resultant deshielding effect decreasing rapidly (as r^{-3}) with increasing distance from the centre of the ring current.¹² A downfield shift for the olefinic protons of ethene-1,2-dithiolate, $\text{S}_2\text{C}_2\text{H}_2$, on complexation to transition metals, has been noted previously and attributed to 'aromaticity' in the metalladithiolene ring.^{1,13} However, the

data reported here represent the first direct evidence for the presence of a metalladithiolene ring current, consistent with such an aromatic system, the observations being facilitated by the presence of protons both on the MS_2C_2 ring and on the substituent group. It is of considerable interest to note that in $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{sdt})_2]^7$ the olefinic proton of the styrene-1,2-dithiolate group resonates at δ 6.69, indicating that a diamagnetic ring current does not operate in this $\text{Mo}_2(\text{S}_2\text{C}_2)_2$ network.

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