

New studies on the chemical oxidation of bis(η^5 -cyclopentadienyl)dithiolatemolybdenum(IV) complexes. Crystal structures of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)][\text{BF}_4]$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$

Alberto R. Dias ^a, M. Helena Garcia ^{a,b,*}, M. Fátima Minas da Piedade ^{a,b},
M.A.A.F. de C.T. Carrondo ^{c,*}

^a Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon codex, Portugal

^b Faculdade de Ciências da Universidade de Lisboa, C1, R. Ernesto de Vasconcelos, 1700 Lisbon, Portugal

^c Instituto de Tecnologia Química e Biológica, R. da Quinta Grande 6, 2780 Oeiras, Portugal

Received 21 February 2001; accepted 30 April 2001

Dedicated to Professor A.R. Dias on the occasion of his 60th birthday

Abstract

A new pattern on the reactivity of bis(η^5 -cyclopentadienyl)dithiolatemolybdenum(IV) metalloligands was found upon study of several chemical reactions involving the redox behaviour of these compounds. Chemical oxidants, such as Ag^+ and NO^+ , led to very different monochelate and binuclear final products. The molecular structure of the new compound which contains the metalloring cation $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]^+$ was characterised by single-crystal X-ray diffraction, and for comparison, also the molecular structure of the parent compound $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SPh})_2]$ is also presented and discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenocenes; Thiolates; Oxidation reactions; Cyclic voltammetry; Crystal structures

1. Introduction

The chemistry of bent metallocene derivatives of the general formula $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$ ($\text{M} = \text{Mo(IV)}$, W(IV) , Ti(IV) ; $\text{R} = \text{alkyl or aryl}$) was for many years related exclusively with their use as chelating ligands in the synthesis of different polynuclear complexes through thiolate bridges [1].

Our studies on the electrochemistry of these metalloligands by means of cyclic voltammetry showed that they could be easily oxidised, with formation of new stabilised species [2]. These studies suggested to us a new approach on the reactivity of these bithiolates, besides their use as bidentate ligands. In fact, the

exploitation of their redox chemistry using a mild chemical oxidant such as a ferrocenium salt led to the synthesis of a new family of cationic monothiolate-related compounds with the general formula $[\text{M(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})\text{L}][\text{PF}_6]$, where L is a nucleophile such as NCCH_3 , PPh_3 , NH_3 , CO , etc. [3]. Moreover, our further studies in this field revealed that $\text{M(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2$ also could be involved in more complicated redox reactions, and we were able to characterise by X-ray diffraction a new bimetallic Mo^{III} structure, containing one fulvalene and one $-\text{SC}_6\text{H}_5^-$ group both acting as bridging ligands, obtained upon the reaction of $[\text{M(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$ with $[\text{Re}_2(\text{CO})_{10}]$ [4]. Surprisingly, the analogous reaction with $[\text{Mn}_2(\text{CO})_{10}]$, led to an unusual manganese(I) cubane-type with an empty corner structure, formed by $\text{Mn(I)}(\text{CO})_3$ metal fragments bridged by $-\text{SC}_6\text{H}_5^-$ thiolate ligands, which was also characterised by X-ray diffraction studies [5].

* Corresponding authors. Tel.: +351-21-8419317; fax: +351-21-8464455/7.

E-mail address: lena.garcia@ist.utl.pt (M. Helena Garcia).

These unexpected results led us to pursue the study of new redox reactions in order to get a better understanding on the reactivity of these bithiolate metalloligands; and we present in this paper, reactions involving oxidants stronger than ferrocenium cations, namely Ag^+ and NO^+ . In the cases studied, new unexpected structures were found.

2. Results and discussion

2.1. Chemical studies

2.1.1. Chemical oxidation of

$[\text{Mo(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$ with AgBF_4

The reaction was carried out in a non-coordinative solvent (CH_2Cl_2), by addition of the molar equivalent of AgBF_4 to a stirred suspension of $[\text{Mo(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$, at room temperature. A deep orange–brown solution was formed almost instantaneously producing, after work up, a very stable orange crystalline compound. Slow diffusion of diethyl ether on this filtered solution, afforded red single crystals suitable for X-ray diffraction studies.

2.1.2. Spectroscopic characterisation of

$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)][\text{BF}_4]$

The $^1\text{H-NMR}$ spectrum of the studied compound in CD_3CN solutions displayed multiplet signals in the aromatic region, characteristic of *ortho*-disubstituted phenyl rings at 7.01, 7.19, 7.34 and 7.65 ppm (relative integrals, 1:1:1:1), together with two multiplets attributed to the thiolate ligand at 7.42 and 7.54 ppm (relative integrals, 2 and 3, respectively). To this new compound was attributed the formulation $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)][\text{BF}_4]$, which was also in good agreement with the 1:1 electrolyte behaviour of a 10^{-3} M solution of the pure compound in nitromethane (molar conductivity = $76 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

2.1.3. Chemical oxidation of $[\text{Mo(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$ ($\text{R} = \text{C}_6\text{H}_5$ and $t\text{Bu}$) with NOBF_4

To a suspension of NOBF_4 in dichloromethane, was added one equivalent of the corresponding bithiolate. The reaction was found to occur almost instantaneously with the formation of an orange precipitate, in the case of $[\text{Mo(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$, and a deep-red solution in the case of $[\text{Mo(IV)}(\eta^5\text{-C}_5\text{H}_5)_2(\text{S}^t\text{Bu})_2]$. To both new compounds, was attributed the binuclear $[\text{Mo(IV)}\text{Cp}_2(\mu\text{-SR})_2\text{Mo(III)Cp(NO)}][\text{BF}_4]_2$ structure, on the basis of the IR and $^1\text{H-NMR}$ spectroscopic data, molar conductivities ($\sim 165 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, as expected for 2:1 electrolytes) and elemental analysis.

2.1.4. Spectroscopic characterisation of

$[\text{Mo(IV)Cp}_2(\mu\text{-(SC}_6\text{H}_5)_2\text{Mo(III)Cp(NO)}][\text{BF}_4]_2$

The NO (three-electron donor) ligand was identified as a linear end-group on the basis of the IR spectrum, which showed $\nu(\text{NO}) = 1660 \text{ cm}^{-1}$, in good agreement with the studies of Lewis and Wilkinson [6,7]. The $^1\text{H-NMR}$ spectrum at room temperature, in a CD_3CN solution, displayed three typical sharp Cp singlets, with chemical shifts of 6.397, 6.194 and 5.284 ppm, and two additional multiplets centered at 7.610 and 7.690 ppm, corresponding to phenyl proton rings, with the relative intensities of 5:5:5:3:2, respectively. The existence of two different Cp signals attributed to the fragment $\text{MoCp}_2(\text{IV})(\mu\text{-SC}_6\text{H}_5)_2$ suggests a *cis*-structure for this bimetallic complex. Variable temperature $^1\text{H-NMR}$ studies showed some broadening on the phenyl multiplets at -30°C , that can be explained by a *cis-trans* isomerisation equilibrium, involving pyramidal inversion at the sulfur centres, which was also found for other sulfur derivatives [8]. The stability observed for this new compound might be explained by a metal–metal interaction, providing the 18-electron configuration, to both metals. Our electrochemical studies by means of cyclic voltammetry, in 10^{-3} M CH_3CN solutions, showed a quasi-reversible wave at $E_{\text{p}1/2} = 0.99 \text{ V}$ ($\Delta E = 90 \text{ mV}$), which was assigned to $\text{Mo}^{\text{IV}} \rightarrow \text{Mo}^{\text{V}}$ oxidation on the $\text{Mo(IV)Cp}_2(\mu\text{-SC}_6\text{H}_5)_2$ moiety, according to our knowledge of this family of compounds [1,2]. Moreover, a second quasi-reversible redox process at $E_{\text{p}1/2} = 0.05 \text{ V}$ ($\Delta E = 90 \text{ mV}$), was found compatible with the $\text{Mo}^{\text{III}} \rightarrow \text{Mo}^{\text{IV}}$ oxidation occurring at the Mo(III)Cp(NO) moiety.

Unfortunately, the slow decomposition in acetonitrile solutions (the only solvent found to dissolve the compound) did not allow to grow adequate crystals for X-ray diffraction studies to confirm this structure.

2.1.5. Spectroscopic characterisation of

$[\text{Mo(IV)Cp}_2(\mu\text{-(S}^t\text{Bu})_2\text{Mo(III)Cp(NO)}][\text{BF}_4]_2$

The stretching vibration band attributed to the NO group was found at 1585 cm^{-1} , a value in the frontier between the linear NO and NO bent structures. The bent structure could be explained, in this case, by the existence of $\text{Mo} \rightarrow \text{NO} \pi$ backdonation as was found for $\text{MoCp(NO)}(\text{Me}_2\text{CHCHMe}_2)$ [9] and $\text{MoCp(NO)}\text{-(CH}_2\text{C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$ [10], due to the better donor properties of $t\text{Bu}$, compared with the phenyl group. However, our experimental data supports the existence of NO as a three-electron donor ligand, slightly bent as a result of the bulky S^tBu bridging ligands, lowering the NO stretching vibration energy. The influence of the bulky S^tBu ligands on the structure of the new bimetallic species is also present in the $^1\text{H-NMR}$ data spectrum obtained at room temperature in a CD_2Cl_2 solution, which presented only one sharp singlet at 6.197 ppm attributed to the $\text{MoCp}_2(\mu\text{-S}^t\text{Bu})_2$ moiety and the ex-

pected singlet for Mo(III)Cp(NO) fragment at 6.092 ppm (relative intensities 2:1). Therefore, the existence of two equivalent Cp rings in MoCp₂(μ-S'Bu)₂ can be explained by the adopted *trans*-structure, converse to the analogous SPh-bridged compound.

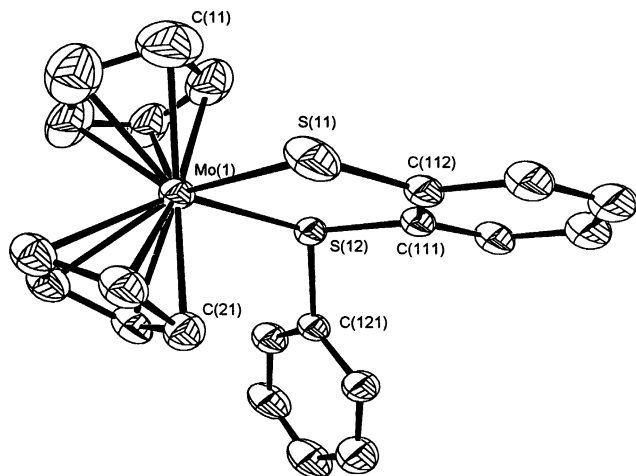


Fig. 1. An ORTEP view of cation $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-SC}_6\text{H}_5)]^+[\text{BF}_4]^-$, with the labelling scheme used. The ellipsoids were drawn with 40% probability level. The hydrogens are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]^+[\text{BF}_4]^-$

<i>Bond lengths</i>	
Mo(1)–S(11)	2.447(2)
Mo(1)–S(12)	2.496(2)
Mo(1)–Cp(11)	1.984(8)
Mo(1)–Cp(2)	1.944(5)
S(11)–C(112)	1.757(7)
S(12)–C(111)	1.788(6)
S(12)–C(121)	1.793(6)
<i>Bond angles</i>	
S(11)–Mo(1)–S(12)	82.93(7)
C(112)–S(11)–Mo(1)	106.0(2)
C(111)–S(12)–C(121)	102.1(3)
C(111)–S(12)–Mo(1)	106.7(2)
C(121)–S(12)–Mo(1)	116.1(2)
C(112)–C(111)–S(12)	118.7(5)
C(111)–C(112)–S(11)	125.5(5)
C(113)–C(112)–S(11)	117.0(6)
Cp(1)–Mo(1)–Cp(2)	135.4(6)

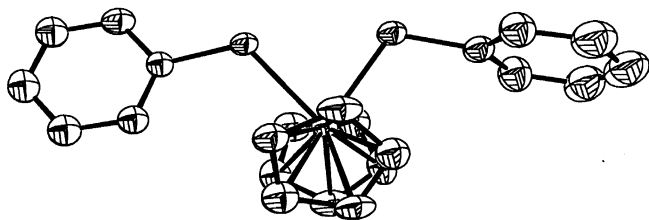


Fig. 2. Molecular diagram of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$ along the plane defined by S–Mo–S atoms.

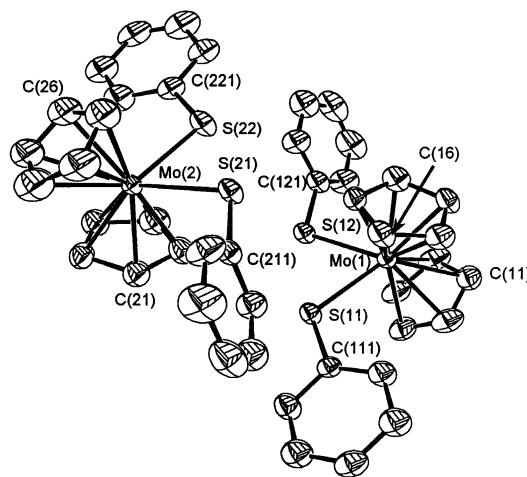


Fig. 3. ORTEP drawings of the two independent molecules in the asymmetric unit in the crystal structure of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$ with the labelling scheme used (ellipsoids with 40% probability level). The hydrogens are omitted for clarity.

2.2. Crystallographic studies

2.2.1. Structures of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]^+[\text{BF}_4]^-$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$

X-ray diffraction studies, carried out on a single crystal obtained by slow diffusion of diethyl ether in a dilute dichloromethane solution of the pure compound, confirm the structure suggested by our spectroscopic data, and the presence of a dithioaryl fragment unevenly chelated to the metal centre, forming a five-member metalloring, as shown in Fig. 1. This five-member metalloring is clearly on the same plane as the disubstituted phenyl group (showing a dihedral angle between the plane S–Mo–S and the phenyl group of 2.2(3)°). The structural study confirmed the presence of a BF_4^- anion. The values of selected bond lengths and bond angles for the complex are given in Table 1.

For comparison, Fig. 2 represents the molecular diagram of the bisthiolate starting material $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2$ along the plane defined by S–Mo–S, showing also one of the phenyl groups in the equatorial plane almost bisecting the angle defined by the $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2$ fragment. The molecular structure of $\text{MoCp}_2(\text{SC}_6\text{H}_5)_2$ is shown in Fig. 3 which has two independent molecules per asymmetric unit. The structural parameters of each individual $\text{MoCp}_2(\text{SPh})_2$ molecule are essentially the same (Table 2). The crystal packing diagram of this compound indicates a relatively close interaction (within 2.80(1) Å) of a hydrogen on a Cp ring with a sulfur of an adjacent molecule, similar to that found in the structure of the $\text{NbCp}_2(\text{SPh})_2$ [11].

In both complexes, $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]^+[\text{BF}_4]^-$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$, the metal is coordi-

Table 2

Bond lengths (Å), bond angles (°) and torsion angles (°) for $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{SC}_6\text{H}_5)_2][\text{BF}_4]$

Molecule 1		Molecule 2	
<i>Bond lengths</i>			
Mo(1)–S(11)	2.470(2)	Mo(2)–S(21)	2.494(2)
Mo(1)–S(12)	2.505(2)	Mo(2)–S(22)	2.463(2)
Mo(1)–Cp(C11–C15))	1.988(6)	Mo(2)–Cp(C21–C25)	1.984(6)
Mo(1)–Cp(C16–C20)	1.989(6)	Mo(2)–Cp(C26–C30)	2.002(8)
S(11)–C(111)	1.769(8)	S(21)–C(211)	1.786(8)
S(12)–C(121)	1.760(9)	S(22)–C(221)	1.776(8)
<i>Bond angles</i>			
S(11)–Mo(1)–S(12)	73.17(7)	S(22)–Mo(2)–S(21)	73.56(7)
Cp–Mo(1)–Cp	132.3(4)	Cp–Mo(2)–Cp	134.6(4)
C(111)–S(11)–Mo(1)	115.9(3)	C(211)–S(21)–Mo(2)	110.2(2)
C(121)–S(12)–Mo(1)	108.9(3)	C(221)–S(22)–Mo(2)	113.8(3)
<i>Torsion angles</i>			
S(12)–Mo(1)–S(11)–C(111)	174.4(3)	S(22)–Mo(2)–S(21)–C(211)	–170.9(3)
S(11)–Mo(1)–S(12)–C(121)	168.1(3)	S(21)–Mo(2)–S(22)–C(221)	–173.1 (4)

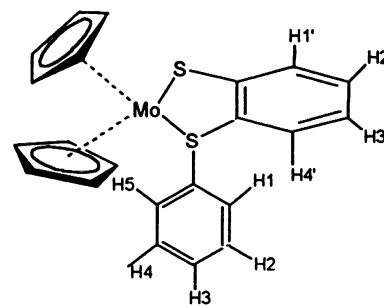
nated to two η^5 -cyclopentadienyl rings and two sulfur atoms of the thiolate ligands, showing the typical structures of metallocene complexes in a tetrahedral distorted geometry. The structural parameters are similar to molybdenocenes with thiolate ligands found in the Cambridge Structural Database [12], as can be seen in Table 3.

Each one of the independent molecules of $\text{MoCp}_2(\text{SPh})_2$ displays a torsion angle R–S–Mo–S close to

Table 3

Structural data for molybdenocenes with bisthiolate ligands

	Mo–S	S–Mo–L	Cp–Mo	Cp–Mo–Cp	S–Mo–S–C	ref. code
$\text{MoCp}_2(\text{S}^t\text{Bu})_2$	2.501 2.491	71.06	2.014/1.999	130.4	173.3/173.5	BIGPAI10
$\text{MoCp}_2(\text{SPh})(\text{NH}_3)[\text{PF}_6]\cdot\text{CH}_3\text{COCH}_3$	2.467	76.7	1.988/1.989	134.8	–178.7	JAFNIN
$\text{MoCp}_2(\text{SPh})(p\text{-NC}(\text{C}_6\text{H}_4)\text{NMe}_2)[\text{PF}_6]$	2.473	79.8	1.986/1.989	137.0	–171.4	JILHAN
$\text{MoCp}_2(\text{SPh})(\sigma\text{-CH}(\text{CN})\text{CH}_3)$	2.500	77.4	1.982/1.987	132.9	–156.1	DIGKIN
$\text{MoCp}_2(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$	2.435/2.430	82.4	1.992/1.999	132.5	–	CPDTMO10
$\text{MoCp}_2(\text{S}_4)$	2.450 2.456	88.2	2.002 1.997	134.2	–	CPMOTS
$\text{MoCp}_2(\text{S}_2\text{C}_2(2\text{-quinoxalina})(\text{C}(\text{O})\text{Me}))$	2.436 2.438	81.94	1.998 1.990	135.1	–	KOLRAE
$[\text{MoCp}_2(\text{S}(\text{CH}_2)_2\text{NH}_2)[\text{I}]]$	2.439	78.4	1.977 2.001	130.9	–	CPMOAE
$[\text{MoCp}_2(2,3\text{-S,S-C}_4\text{H}_3\text{CONEt}_2)]$	2.431 2.424	81.98	1.997 1.998	132.6	–	LEHQUK
$[\text{MoCp}_2(o\text{-S,S-C}_4\text{S}_2\text{H}_2)]$	2.436/2.440	81.91	1.970 2.018	131.9	–	ZOLLAN
$\text{MoCp}_2(\text{SPh})_2$	2.470(2) 2.505(2) 2.494(2) 2.463(2)	73.17(7) 73.56(7)	1.988(6) 1.989(6) 1.984(6) 2.002(8)	132.3(4) 134.6(4)	174.4(3) 168.1(3) –170.9(3) –173.1(4)	This work
$[\text{MoCp}_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)][\text{BF}_4]$	2.447(2) 2.496(2)	73.17(7)	1.984(8) 1.944(5)	135.4(6)	–	This work

Fig. 4. Numbering scheme for $^1\text{H-NMR}$ of cation $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4)\text{SC}_6\text{H}_5]^+$.

180° , (see Table 2) confirming the *exo* configuration expected by electronic factors at the molybdenum atom and predicted by theoretical calculations [13].

It might be suggested, by comparison of both crystal structures shown in Figs. 1 and 2, that the *exo* structure adopted by the bithiolate starting material might contribute to the stabilisation of any possible reactional intermediate species leading to the formation of the second co-planar sulfur metalloring.

The formation of the new $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_4\text{-}o\text{-S-C}_6\text{H}_5)]^+$ cationic species by oxidation of the parent bithiolate shows a new pattern for the reactivity of these compounds involving the coordinate thiolate groups, where the sulfur atom plays an active role towards the final product. In fact, this is the very first case, in all our studies concerning redox reactions on $[\text{M}(\text{IV})(\eta^5\text{-C}_5\text{H}_5)_2(\text{SR})_2]$ compounds, where the reaction

proceeds without de-coordination of the thiolate ligands, being the final product apparently formed through an intramolecular reaction.

In addition to the well-known oxidation of $\text{MCp}_2(\text{SR})_2$ with the mild ferrocenium oxidant, this work shows two different patterns of reactivity with strong oxidising reagents.

Indeed, the stronger oxidant Ag^+ gave a mononuclear biscyclopentadienyl structure, where a dithioaryl chelate ligand was formed, while the stronger and coordinative oxidant, NO^+ , gave dimolybdenum thiolate-bridged compounds, where a Cp ring in one of the fragments MoCp_2 is substituted by NO.

3. Experimental

3.1. General procedures

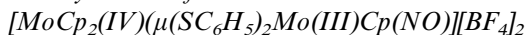
All experiments were carried out under nitrogen by the use of standard Schlenk-tube techniques. Solvents were purified according to the usual methods [14]. Solid-state IR spectra were measured on a Perkin–Elmer 457 spectrophotometer, with KBr pellets; only significant bands are cited in the text.

$^1\text{H-NMR}$ spectra were recorded on a Bruker CXP 300 spectrometer, at probe temperature. Microanalyses were performed, in our laboratories, using a Fisons Instruments EA1108 system. Data acquisitions, integration and handling were performed using a PC with the software package Eager-200 (Carlo Erba Instruments). The $^1\text{H-NMR}$ ($\text{MeCN-}d_3$ and $\text{CHCl}_3\text{-}d$) chemical shifts are reported in parts per million downfield from internal Me_4Si .

3.2. Synthesis of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$

To a solution of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$ (0.4 g, 0.9 mmol), in CH_2Cl_2 , was added AgBF_4 (0.175 g, 0.9 mmol). The solution became immediately dark-red. After a 30 min period stirring, the light-brown solution was filtered, leaving a precipitate and a thin glass mirror in the Schlenk tube. Slow diffusion of Et_2O in this solution produces orange-reddish crystals suitable for X-ray diffraction studies. $^1\text{H-NMR}$ ($\text{MeCN-}d_3$): δ 5.44 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$), 7.01 (m, 1H, H3'), 7.19 (m, 1H, H2'), 7.34 (dd, 1H, H4', $J_{\text{HH}} = 7.9, 1.2$ Hz), 7.42 (m, 2H, H1, H5), 7.54 (m, 3H, H2, H3, H4), 7.65 (dd, 1H, H1', $J_{\text{HH}} = 7.9, 1.2$ Hz) Fig. 4.

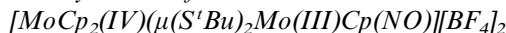
3.3. Synthesis of



To a solution of NOBF_4 (0.105 g, 0.9 mmol) in 20 ml of CH_2Cl_2 , was added $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_5)_2]$ (0.4 g, 0.9 mmol), at room temperature (r.t.). The suspension was stirred for 2 h, and the orange solid precipitated

was filtered, washed with Et_2O , and dried in vacuo. The compound was insoluble in acetone, CH_2Cl_2 , Et_2O , EtOH , THF, hexane, pentane and toluene, but it was moderately soluble in MeCN. Yield, 45%. Anal. Found: C, 40.47; H, 3.31; N, 1.87; Mo, 24.56. Calc. for $\text{C}_{27}\text{H}_{25}\text{NOS}_2\text{B}_2\text{F}_8\text{Mo}_2$: C, 40.08; H, 3.31; N, 1.73; Mo, 23.71%. IR (KBr, cm^{-1}): $\nu(\text{C}_5\text{H}_5)$ 3100; $\nu(\text{C}_6\text{H}_5)$ 3040; $\nu(\text{NO})$ 1660; $\nu(\text{BF}_4)$ 1100. $^1\text{H-NMR}$ ($\text{MeCN-}d_3$): δ 5.24 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 6.19 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 6.39 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 7.61 (m, 6H, $2 \times \text{SC}_6\text{H}_5\text{-meta, para}$), 7.69 (m, 4H, $2 \times \text{SC}_6\text{H}_5\text{-ortho}$).

3.4. Synthesis of



To a solution of $[\text{MoCp}_2(\text{S}^t\text{Bu})]$ (0.3 g, 0.74 mmol) in CH_2Cl_2 , was added NOBF_4 (0.098 g, 0.84 mmol). A change of colour from red to grenat was observed immediately. The mixture was stirred at r.t. for 2 h. After filtration, Et_2O was added yielding a precipitate which was filtered, washed with ether and dried in vacuo. Yield, 45%. Anal. Found: C, 40.50; H, 4.51; N, 1.63; S, 9.47. Calc. for $\text{C}_{23}\text{H}_{33}\text{NOS}_2\text{BF}_4\text{Mo}_2$: C, 40.49; H, 4.87; N, 2.05; S, 9.40%. IR (KBr, cm^{-1}): $\nu(\text{C}_5\text{H}_5)$ 3110; $\nu(\text{CH}_3)$ 2950–2880; $\nu(\text{NO})$ 1585; $\nu(\text{BF}_4)$ 1100. $^1\text{H-NMR}$ ($\text{CH}_2\text{Cl}_2\text{-}d_2$): δ 1.47 (s, 18H, $\text{S}(\text{CH}_3)_3$), 6.09 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 6.19 (s, 10H, $\eta^5\text{-C}_5\text{H}_5$).

3.5. X-ray analysis of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$

Diffraction data for both the complexes, $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$, were obtained at 298 K on an Enraf–Nonius TURBOCAD4 diffractometer with graphite monochromatised Mo– K_α radiation using a ω – 2θ scan technique. Unit cell dimensions and the orientation matrix were obtained by least-squares refinement of 25 centred reflections with $8.1 < \theta < 15.4^\circ$ for $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ and with $14.0 < \theta < 16.8^\circ$ for $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$. Using the MOLEN software [15], data were corrected for Lorentz and polarization effects and for absorption using experimental ψ -scans.

The structures were solved by a combination of direct methods and Fourier synthesis and then refined by full-matrix least-squares on F^2 .

Non-hydrogen atoms were anisotropically refined and all hydrogen atoms were inserted in calculated positions and refined isotropically with a thermal parameter equal to 1.2 times that of the carbon atoms to which they are bonded. In both the structures, the thermal parameters of the carbon atoms of one of the

Table 4

Crystal data and structure refinement parameters for $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$

	$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$	$[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$
Empirical formula	$\text{C}_{22}\text{H}_{19}\text{BF}_4\text{MoS}_2$	$\text{C}_{44}\text{H}_{40}\text{Mo}_2\text{S}_4$
Formula weight	530.24	888.88
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	10.977(2)	13.828(2)
<i>b</i> (Å)	8.603(5)	21.766(2)
<i>c</i> (Å)	22.094(5)	24.830(2)
β (°)	91.24(2)	—
<i>V</i> (Å ³)	2086.0(14)	7473.3(14)
<i>Z</i>	4	8
<i>D</i> _{calc} (g m ^{−3})	1.688	1.580
Absorption coefficient (mm ^{−1})	0.871	0.927
<i>F</i> (000)	1064	3616
Theta range for data collection (°)	1.84–25.49	2.04–27.96
Index ranges	$-13 \leq h \leq 13, 0 \leq k \leq 10, 0 \leq l \leq 26$	$0 \leq h \leq 18, 0 \leq k \leq 28, 0 \leq l \leq 32$
Reflections collected	3386	8983
Reflections observed [$I > 2\sigma(I)$]	2660	5571
Independent reflections	3386	8983
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3386/54/271	8983/30/452
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0589$	$R_1 = 0.0588$
<i>R</i> indices (all data)	$R_1 = 0.0824$	$R_1 = 0.1187$
Goodness-of-fit on F^2	1.170	1.083
Largest difference peak and hole (e Å ^{−3})	1.581 and −0.904	1.465 and −1.088

Cp ligands were restrained (E.S.D. of 0.005). The thermal parameters of the fluorine atoms of the anion in the complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ were also refined with ISOR (E.S.D. of 0.01). All calculations to solve and refine the structures were carried out with SHELXS-86 [16] and SHELX-93 [17] from OSCAIL8 package [18]. The illustrations were drawn with the program ORTEP-III [19], also included in the same package. Other details of data collection and refinement are given in Table 4.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 157905 and 157906, for the compounds $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{S}(\text{C}_6\text{H}_4\text{-}o\text{-SC}_6\text{H}_5)]\text{[BF}_4\text{]}$ and $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SPh})_2]$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This research was financially supported by Junta Nacional de Investigação Científica e Tecnológica.

References

- [1] (a) A.R. Dias, M.L.H. Green, J. Chem. Soc. A (1971) 1951; (b) A.R. Dias, M.L.H. Green, J. Chem. Soc. A (1971) 2807; (c) M.A.A.F. de C.T. Carrondo, A.R. Dias, M.H. Garcia, P. Matias, M.F.M. Piedade, M.J. Villa de Brito, J. Organomet. Chem. 466 (1994) 159.
- [2] J.C. Kotz, W. Vining, W. Cocco, R. Rosen, A.R. Dias, M.H. Garcia, Organometallics 2 (1983) 68.
- [3] M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T. Domingos, M.T.L.S. Duarte, M.H. Garcia, C.C. Romão, J. Organomet. Chem. 320 (1987) 63.
- [4] M.J. Calhorda, M.A.A.F. de C.T. Carrondo, A.R. Dias, V. Félix, A.M. Galvão, M.H. Garcia, P.M. Matias, M.J. Villa de Brito, J. Organomet. Chem. 453 (1993) 231.
- [5] M.J. Villa de Brito, PhD thesis, Faculdade de Ciências da Universidade de Lisboa, 1995.
- [6] J. Lewis, R.J. Irving, G. Wilkinson, J. Inorg. Nucl. Chem. 7 (1958) 32.
- [7] W.P. Griffith, J. Lewis, G. Wilkinson, J. Inorg. Nucl. Chem. 7 (1958) 38.
- [8] J.R. Ascenso, M.D. Carvalho, A.R. Dias, C.C. Romão, M.J. Calhorda, L.F. Veiros, J. Organomet. Chem. 478 (1994) 147.
- [9] A.D. Hunter, P. Legzdins, C.R. Nurse, F.W.B. Einstein, A.C. Willis, J. Am. Chem. Soc. 107 (1985) 1791.
- [10] P. Legzdins, R.H. Jones, E.C. Phillips, V.C. Yee, J. Trotter, F.W.B. Einstein, Organometallics 10 (1991) 986.
- [11] M.Y. Darensbourg, R. Silva, J. Reibenspies, C.K. Prout, Organometallics 8 (1989) 1315.
- [12] F.H. Allen, O. Kennard, R. Taylor, Acc. Chem. Res. 16 (1983) 146.
- [13] M.J. Calhorda, A.M. Galvão, Bonding and conformations in biscyclopentadienyl-thiolate derivatives of early transition metals, in: M. Gielen (Ed.), Topics in Physical Organometallic Chemistry, Freud Publishing House, Tel-Aviv, 1991, pp. 93–138.
- [14] D.D. Perrin, W.L.F. Amarego, D.R. Perrin, Purification of Laboratory Chemicals, 2nd ed., Pergamon, New York, 1980.
- [15] Enraf–Nonius, CAD-4 Software, Version 5.0, Enraf–Nonius, Delft, The Netherlands, 1989.
- [16] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
- [17] G.M. Sheldrick, SHELXL-97: A Program for Refining Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [18] P. McArdle, J. Appl. Crystallogr. 28 (1995) 65 (PC Windows Version).
- [19] C.K. Johnson, M.N. Burnett, ORTEP-III, Report ORNL-6895, Oak Ridge National Laboratory, TN, USA, 1996.