A Comment on the Chemistry and the Electrochemistry of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{0/2+}$

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Recently, the authors of the present paper investigated independently the electrochemical behaviour of the $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ complexes (R = Me, t-Bu, Ph) and reported conflicting results [1, 2]. Whereas one report provided evidence in support to the assertion that the title species undergo an oxidatively-induced isomerisation [1], the conclusion of the other one was quite different [2] since it suggested that, in the solvent MeCN or even CH_2Cl_2, carbon monoxide is displaced by solvent and that this accounts for the occurrence of the two peaks in the cyclic voltammetry (c.v.), Scheme 1.

In this Scheme, according to Jaitner and Winder's previous paper, process I is responsible for the peaks labelled a_1/c_1 and process II for the peaks labelled a_2/c_2 in their published figure [2]§. We now report further results which contradict the latter interpretation and confirm that isomerisation, Scheme 2, is actually responsible for the two peaks, Fig. 1.

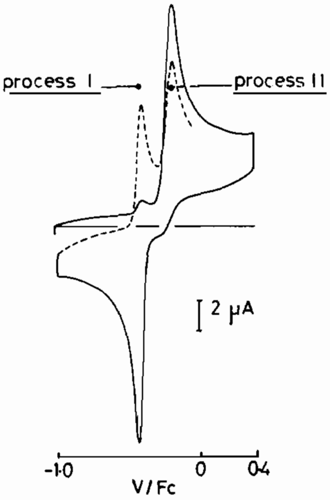

Fig. 1. Cyclic voltammetry of *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ in MeCN–0.1 M Bu_4NPF_6. Dotted line: second anodic scan (vitreous carbon electrode; scan rate: 0.2 V s^{-1}).

$$\begin{tikzcd}
{[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]} \arrow[r, "-2CO", "\text{solvent}"'] \arrow[d, "-2e"', "a_2/c_2"] & {[Mo_2Cp_2(CO)_2(\text{solvent})_2(\mu\text{-}SR)_2]} \arrow[d, shift left, "a_1/c_1"] \\
{[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}} & {[Mo_2Cp_2(CO)_2(\text{solvent})_2(\mu\text{-}SR)_2]^{2+}} \arrow[u, shift left, "\pm 2e"] \\
\text{process II} & \text{process I}
\end{tikzcd}$$

Scheme 1.

$$\begin{tikzcd}
trans\text{-}[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2] \arrow[d, "-2e"'] & cis\text{-}[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2] \arrow[d, shift left] \\
trans\text{-}[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+} \arrow[r, "\text{fast}"] & cis\text{-}[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+} \arrow[u, shift left, "\pm 2e"] \\
\text{process II} & \text{process I}
\end{tikzcd}$$

Scheme 2.

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§The cyclic voltammogram of the tellurolato derivative presented by Jaitner and Winder [2] looks different from that of the –SPh analogue shown in Fig. 1 of the present paper since for the latter species, the first oxidation (process I) is almost absent on the first anodic scan. This is in agreement with the fact that only one isomer of $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ is observed in solution [3]. However, the slight increase of the first oxidation peak on standing indicates the equilibration of both isomers in MeCN solutions.

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As we reported previously [1], controlled-potential oxidations of $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]$ at the first peak (R = Me) or at the second one (R = Me, Ph, t-Bu) in THF or MeCN (see below) electrolytes produce a species which analyses for $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2][A]_2$ (A = PF_6 or BF_4). The X-ray crystal structure determination carried out with the SBu^t derivative demonstrated that the isolated dication adopts a *cis* geometry, which confirmed the results of a variable ^1H NMR study [1]. Therefore, the species giving rise to the reversible reduction process is, in the solid, $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]\ [A]_2$.

Several facts indicate that such is also the formula of the complex in solution. The fact that the reversible reduction occurs at a potential which is essentially solvent-independent (see $E^{1/2}$ for the *cis*-isomer, Table III in ref. 1) suggests that the solvent does not replace CO ligands. If MeCN displaces CO extensively in solution, we must observe a difference in solution infrared spectra recorded in MeCN and solid state spectra recorded in KBr. We find that, for the neutral and dicationic species, the ν(CO) bands of the solution IR spectra recorded in MeCN do not show the shift toward low frequencies which should be observed in the case of the substitution of MeCN for CO (Table I) [4–6].

It might be argued that Scheme 1 would be valid if the displacement ot CO were inextensive but the equilibrium fast enough to maintain Nernstian behaviour at the electrode. If this were the case, then purging a MeCN solution of the complex with argon should drive the equilibrium over towards the substituted product(s). We have purged a *ca.* 6 mM acetonitrile solution of the phenyl thiolate neutral and dicationic complexes with Ar for 2 h and we did not detect any difference in the IR spectra (KBr pellets) recorded before and after this experiment. On the other hand, the oxidative part of the c.v. of the neutral complex recorded under CO is identical to the curves obtained under N_2 or Ar apart from the presence of a small peak due to $[MoCp(CO)_3SPh]$ in the presence of CO. This is consistent with the results reported by Watkins and George [7].

The infrared experiments reported above confirm that $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]^z$ ($z = 0$, +2) do not undergo facile CO loss in MeCN solutions. Accordingly, the redox processes of these complexes must be assigned as shown in Scheme 2.

Ligand substitution reactions may be induced by electron-transfer processes, and it is indeed the case for the $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]^z$ species ($z = 0$, +2). As we mentioned previously (see ref. 26 in ref. 1), controlled-potential oxidations of the neutral dimers in a MeCN electrolyte produce a substituted complex in addition to the expected *cis*-dication. Additional work [4] showed that the same product, e.g. a monosubstituted dication *cis*-$[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SR})_2]^{2+}$,[†] is also obtained on electrochemical reduction of *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]^{2+}$ (R = Me, Ph) in a MeCN electrolyte, according to an electron-transfer chain catalyzed process [4]. In Fig. 2 are depicted both the reversible couple associated with *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]^{0/2+}$ and the irreversible reduction of *cis*-$[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SR})_2]^{2+}$. The mono-acetonitrile species is by about 0.3 V harder to reduce than the tetracarbonyl dication. This potential shift is paralleled by the shift of the

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[†] An X-ray analysis of a crystal of *cis*-$[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SPh})_2][BF_4]_2$ confirms the coordination of a single acetonitrile to one molybdenum atom. In this complex, the coordinated CH_3CN molecule is linear (Mo–N = 2.11 Å). M. Guéguen, F. Y. Pétillon, J. Talarmin, and R. Mercier, manuscript in preparation.

TABLE I. Infrared Data for the $[Mo_2Cp_2(CO)_3L(\mu\text{-SR})_2]^z$ Complexes

Z	L	R	ν(CO) cm^{-1}		
			MeCN	CH_2Cl_2	KBr
0	CO	Me	1945, 1930sh, 1850, 1820sh	1955, 1940, 1860	1930, 1910, 1840, 1820
0	CO	Ph	1955sh, 1940, 1855	1960sh, 1945, 1865	1950, 1930 1860, 1840
+2	CO	Me	2085, 2050		2080, 2040
+2	CO	Ph	2095, 2060		2090, 2050
+2	CO	t-Bu	2080, 2050		2085sh, 2075, 2050sh, 2030
+2	MeCN	Me	2060, 2025		2060, 2010, 1980sh [2310, 280:ν(CN)]
+2	MeCN	Ph	2070, 2030		2060, 2035 [2310sh, 2280:ν(CN)]

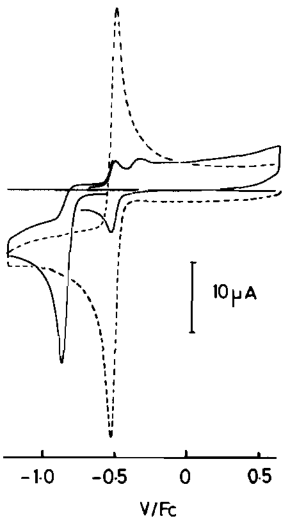

Fig. 2. Cyclic voltammetry of *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{2+}$ before (dotted line) and after (solid line) electrolysis at −0.57V, showing the formation of the mono-substituted dication *cis*-$[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$. ($T = 40$ °C; $n = 0.44$ F/mol of *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{2+}$).

ν(CO) bands (Table I) both of which are consistent with the substitution of a comparatively good donor ligand for CO.

We believe that the results of the electrochemical and spectral studies are quite consistent with an oxidatively-induced isomerisation process [1], as shown in Scheme 2.

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