

*Journal of Organometallic Chemistry*, 390 (1990) C39–C44  
 Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
 JOM 20979PC

**Preliminary communication**

**Electrogeneration of the molybdenum–molybdenum double bond from thiolate-bridged dinuclear precursors: carbon monoxide catalysed isomerisation about the Mo=Mo bond**

Christine Le Floch<sup>a</sup>, François Y. Pétilion<sup>a</sup>, Christopher J. Pickett<sup>b</sup>  
 and Jean Talarmin<sup>a\*</sup>

<sup>a</sup> URA CNRS 322 "Chimie, Electrochimie, et Photochimie Moléculaires"

Université de Bretagne Occidentale, 29287 Brest-Cedex (France)

<sup>b</sup> AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ (U.K.)

(Received March 28th, 1990)

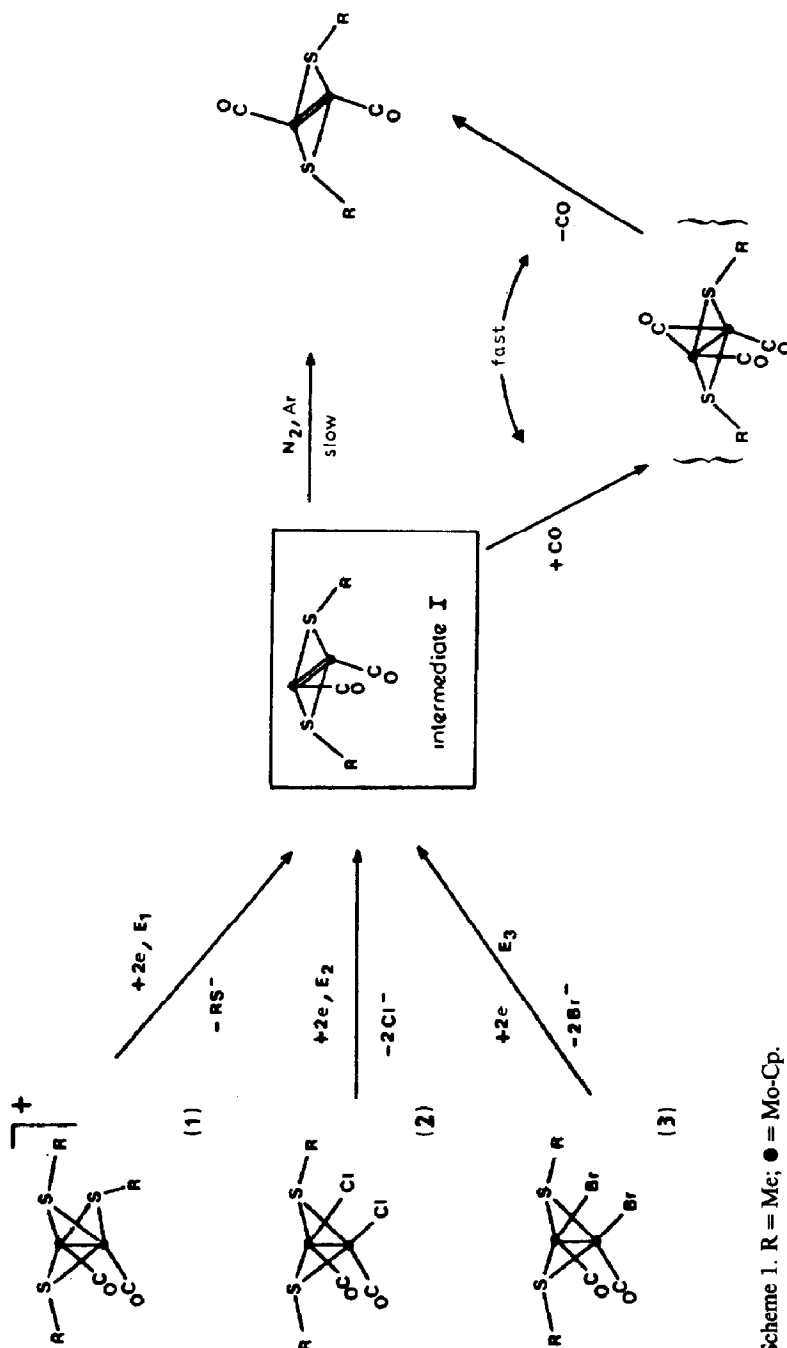
**Abstract**

The irreversible electroreduction of any of the three distinct dimolybdenum thiolate complexes  $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_3]^+$  and  $[\{\text{MoCp}(\text{CO})\text{X}\}_2(\mu\text{-SMe})_2]$  (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; X = Cl or Br) gives a common intermediate which we identify as *cis*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$  (I). This intermediate slowly isomerises to the isolable product *trans*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$ ; the isomerisation is catalysed by carbon monoxide, a process which we suggest takes place through CO binding across and elimination from the molybdenum–molybdenum double bond of (I).

We report the electrogeneration of the Mo=Mo double bond from various thiolate bridged precursors and the first example of a CO-catalysed rearrangement about this bond.

Each of the complexes  $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_3]^+$  (1),  $[\{\text{MoCp}(\text{CO})\text{X}\}_2(\mu\text{-SMe})_2]$  (X = Cl (2) or Br (3)) undergoes an irreversible two-electron reduction that yields a common product, *trans*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$ . This complex has been prepared by bulk electrolysis in essentially quantitative yield from 1, 2 and 3, isolated from the catholytes, and characterised spectroscopically (Scheme 1). The closely related complex *trans*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SBU}^t)_2]$  has been prepared by an independent route and its structure confirmed by X-ray crystallography [1].

Cyclic voltammetry shows that the primary irreversible reduction of either 1, 2 or 3 does not immediately give the product *trans*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$  but that a *common* intermediate (I) is first formed. This intermediate is characterised by its two successive reversible one-electron reduction steps (Fig. 1a, dashed line) and by



Scheme 1. R = Me; ● = Mo-Cp.

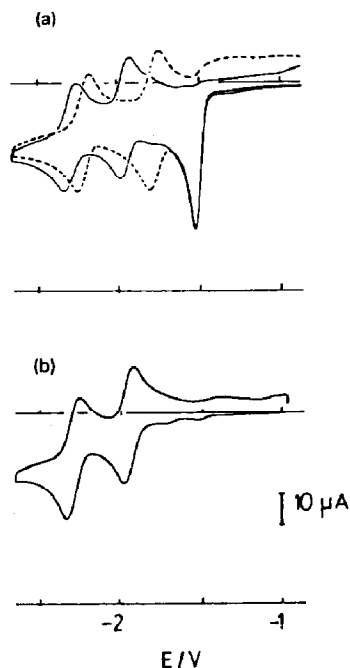


Fig. 1. Cyclic voltammetry of a 0.8 mM MeCN solution of  $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_3](\text{BF}_4)$ , **1**. (Vitreous carbon electrode; scan rate  $0.2 \text{ V s}^{-1}$ ; supporting electrolyte  $[\text{Bu}_4\text{N}][\text{PF}_6]$ .) (a) (-----) Under  $\text{N}_2$ ; (—) under  $\text{CO}$ . (b) After controlled potential electrolysis at  $-1.6 \text{ V}$  under  $\text{Ar}$ .

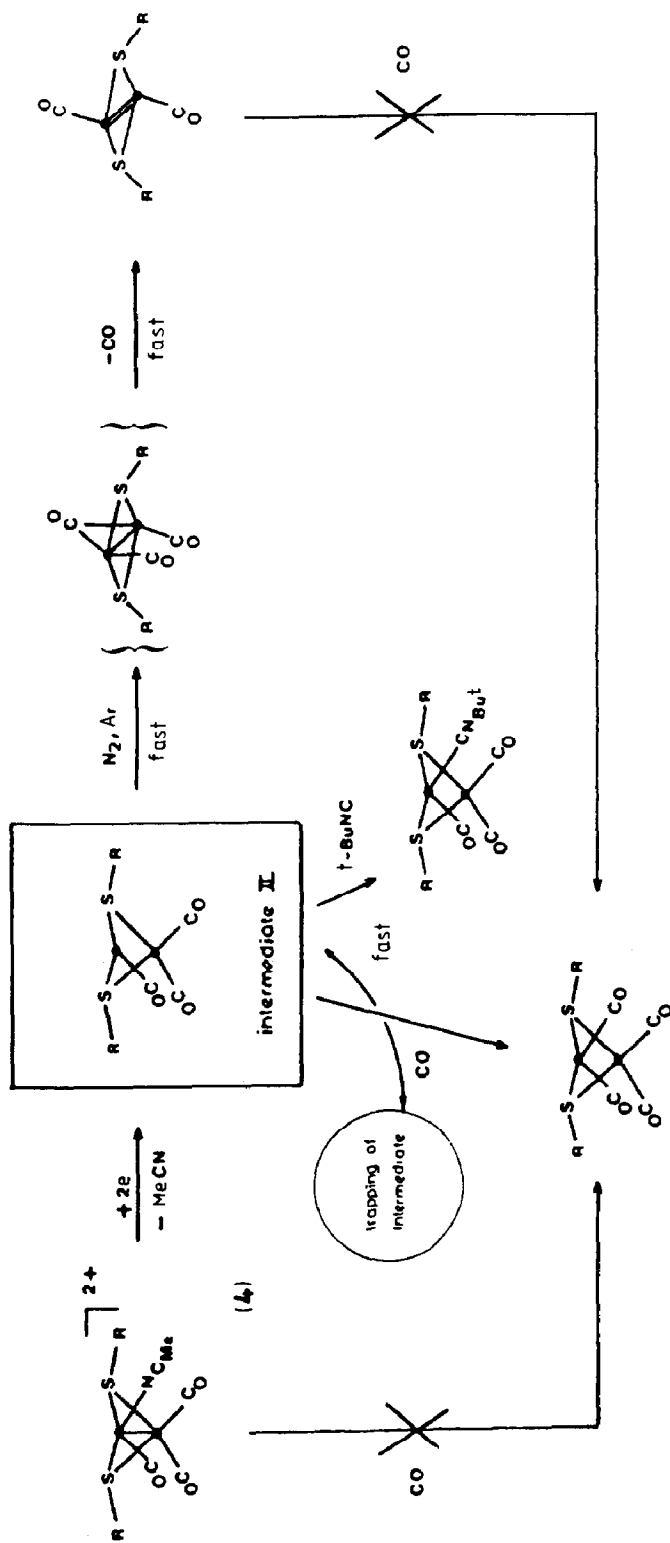
an irreversible oxidation. The three redox potentials associated with these processes unambiguously define (I) as a common intermediate, (Table 1).

The closely similar pattern of reduction of (I) and *trans*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$ , as illustrated by Figs. 1a and b, and the facts that (I) cannot possess halide ligands (nor three thiolate groups) and that it is quantitatively converted into the product on the longer time-scale of preparative electrolysis, lead us to conclude that (I) is *cis*- $[\{\text{MoCp}(\text{CO})\}_2(\mu\text{-SMe})_2]$ , a kinetically favoured isomer of the *trans*-product. The formation of the *cis*-isomer is entirely consistent with the established *cis* arrangement of the CO ligands in **1** [2] and in related dinuclear  $\text{Mo}^{\text{III}}$  complexes [3,4].

Table 1

Redox potentials of complexes **1**, **2** and **3** and of their primary reduction product (intermediate I); potentials in volts relative to  $\text{Fc}^+/\text{Fc}$

Complex	Solvent	$E_p^{\text{red}}$	Intermediate I		
			$E_{1/2}^{\text{red1}}$	$E_{1/2}^{\text{red2}}$	$E_p^{\text{ox}}$
<b>1</b>	THF	-1.57	-1.90	-2.47	-0.12
	MeCN	-1.47	-1.77	-2.19	-0.23
<b>2</b>	THF	-1.79	-1.89	-2.47	-0.12
	MeCN	-1.65	-1.78	-2.20	-0.22
<b>3</b>	THF	-1.70	-1.90	-2.47	-0.12
	MeCN	-1.59	-1.78	-2.20	-0.21



Scheme 2. R = Me; ● = Mo-Cp.

The thermal isomerisation of the *cis*-intermediate to the *trans*-product requires a 180° rotation of one {MoCp(CO)} fragment with respect to the other and, under an inert atmosphere, this substantial rearrangement is slow ( $t_{1/2} > 100$  s, ca. 20 °C). However, we observe an unprecedented catalysis of the isomerisation by carbon monoxide.

Figure 1a shows that under CO the peaks of the *cis*-intermediate are completely removed, and only those peaks associated with the stable *trans*-isomer are observed. Clearly, CO catalyses the transformation of the intermediate to the product. We explain this catalysis in the following way: CO adds rapidly across the Mo=Mo moiety at the "exposed" face [5\*] (Scheme 1). Subsequent loss of CO from the opposite face and reformation of the double bond [5\*] gives the *trans*-product.

To provide further support for this mechanism, we have studied a system in which CO is set up for intramolecular catalysis. The Mo<sup>III</sup> complex *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(MeCN)(μ-SMe)<sub>2</sub>]<sup>2+</sup>, **4**, reduces rapidly under N<sub>2</sub> or Ar to the *trans*-product [{MoCp(CO)}<sub>2</sub>(μ-SMe)<sub>2</sub>] (Mo=Mo) (Scheme 2), and no intermediate is detected by cyclic voltammetry [6]. Clearly, the presence of a third CO ligand favours the formation of *trans*-[{MoCp(CO)}<sub>2</sub>(μ-SMe)<sub>2</sub>]. Although the intermediate is too reactive in this system for detection by cyclic voltammetry, it can be trapped by CO to give the stable isolable product [{MoCp(CO)<sub>2</sub>}<sub>2</sub>(μ-SMe)<sub>2</sub>] (Scheme 2) [7\*]. Importantly, neither *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(MeCN)(μ-SMe)<sub>2</sub>]<sup>2+</sup> nor *trans*-[{MoCp(CO)}<sub>2</sub>(μ-SMe)<sub>2</sub>] reacts with CO to generate the tetracarbonyl complex (Scheme 2). The fact that the loss of a CO ligand from *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(MeCN)(μ-SMe)<sub>2</sub>]<sup>2+</sup>, **4**, is not concomitant with the electron-transfer step is further confirmed by the detection of *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>3</sub>(t-BuNC)(μ-SMe)<sub>2</sub>] when the cyclic voltammetry of **4** is carried out under N<sub>2</sub> or Ar in the presence of the isocyanide (Scheme 2).

These data demonstrate that the intermediate (II, Scheme 2) contains three carbonyl groups. The mechanism described in Scheme 2 is therefore the intramolecular counterpart of the CO-catalysed isomerisation shown in Scheme 1.

In conclusion, electroreduction of the cationic complex **1** and of the dihalides **2** and **3** (Scheme 1) proceeds via the generation of a common intermediate which slowly isomerises to a single *trans*-dicarbonyl product: this isomerisation is catalysed by CO binding to the intermediate.

Finally, we note that substrate binding to the *cis*-isomer is not confined to carbon monoxide but appears to extend to other π-acid ligands, e.g. PhCH<sub>2</sub>NC.

**Acknowledgement.** The CNRS is thanked for financial support of this work.

## References and notes

- 1 I.B. Benson, S.D. Killops, S.A.R. Knox and A.J. Welch, *J. Chem. Soc., Chem. Commun.*, (1980) 1137.
- 2 M.B. Gomes de Lima, J.E. Guerschais, R. Mercier and F.Y. Pétillon, *Organometallics* 5 (1986) 1952.
- 3 J. Courtot-Coupez, M. Guéguen, J.E. Guerschais, F.Y. Pétillon, J. Talarmin and R. Mercier, *J. Organomet. Chem.*, 312 (1986) 81.
- 4 M. El Khalifa, M. Guéguen, R. Mercier, F.Y. Pétillon, J.Y. Saillard and J. Talarmin, *Organometallics*, 8 (1989) 140.

\* Reference number with asterisk indicates a note in the list of references.

- 5 As suggested by the preliminary results of EHMO calculations on the *cis* isomer, its reactivity might arise from the presence of two 17e molybdenum centres. In this case, the intermediate (I) would contain a single metal–metal bond. (J.Y. Saillard, personal communication).
- 6 M. Guéguen, F.Y. Pétillon and J. Talarmin, *Organometallics*, 8 (1989) 148.
- 7 The *cis*-isomer of  $[\{\text{MoCp}(\text{CO})_2\}_2(\mu\text{-SMe})_2]$  is detected by cyclic voltammetry whereas electrolyses lead to a mixture of the *cis*- and *trans*-complexes.