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# THEORETICAL ANALYSIS OF THE *CIS*/*TRANS* ELECTROCHEMICALLY-INDUCED AND CO-CATALYSED ISOMERISATION REACTION OF $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$ AND ITS REACTIVITY TOWARD ISOCYANIDE LIGANDS

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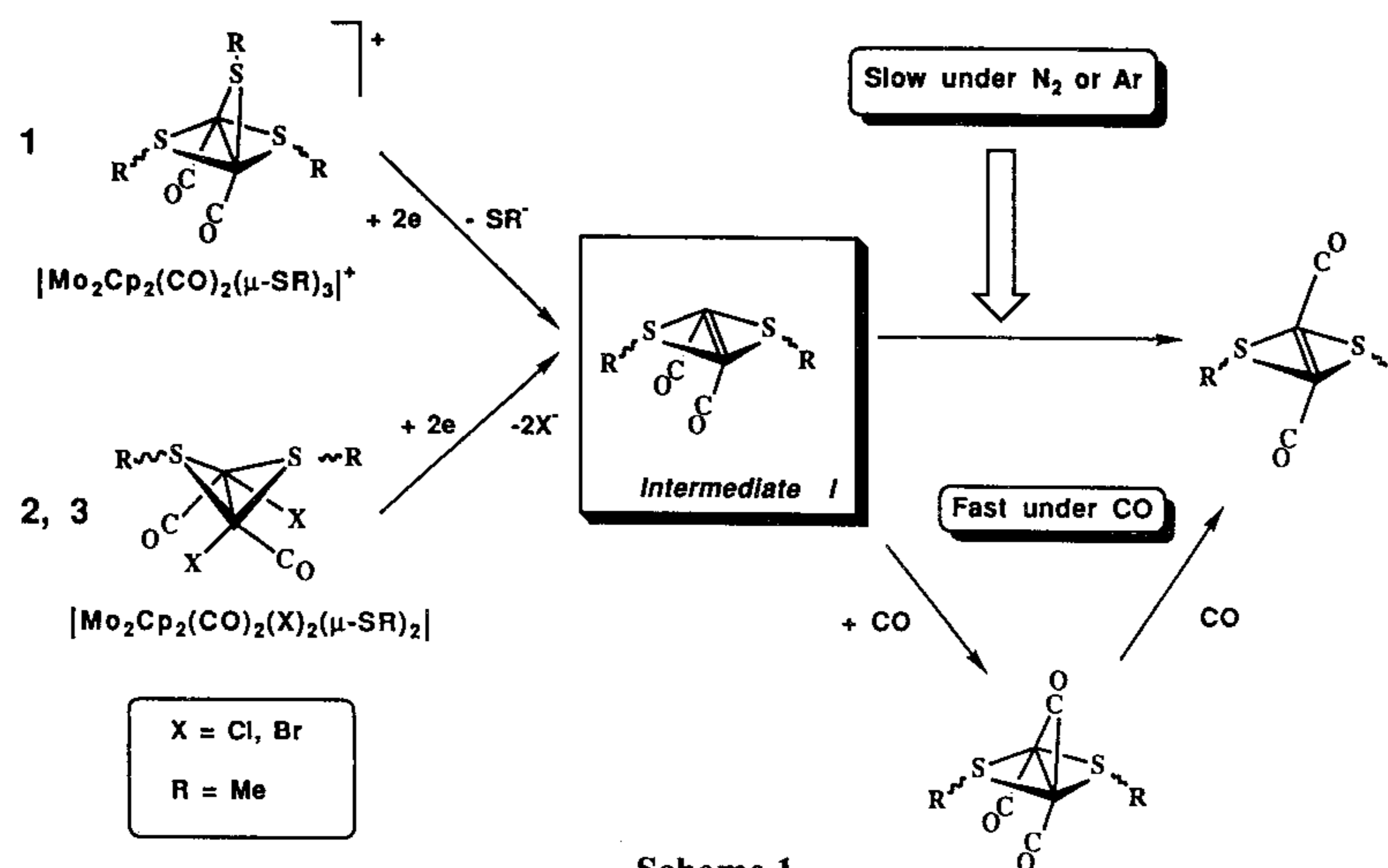
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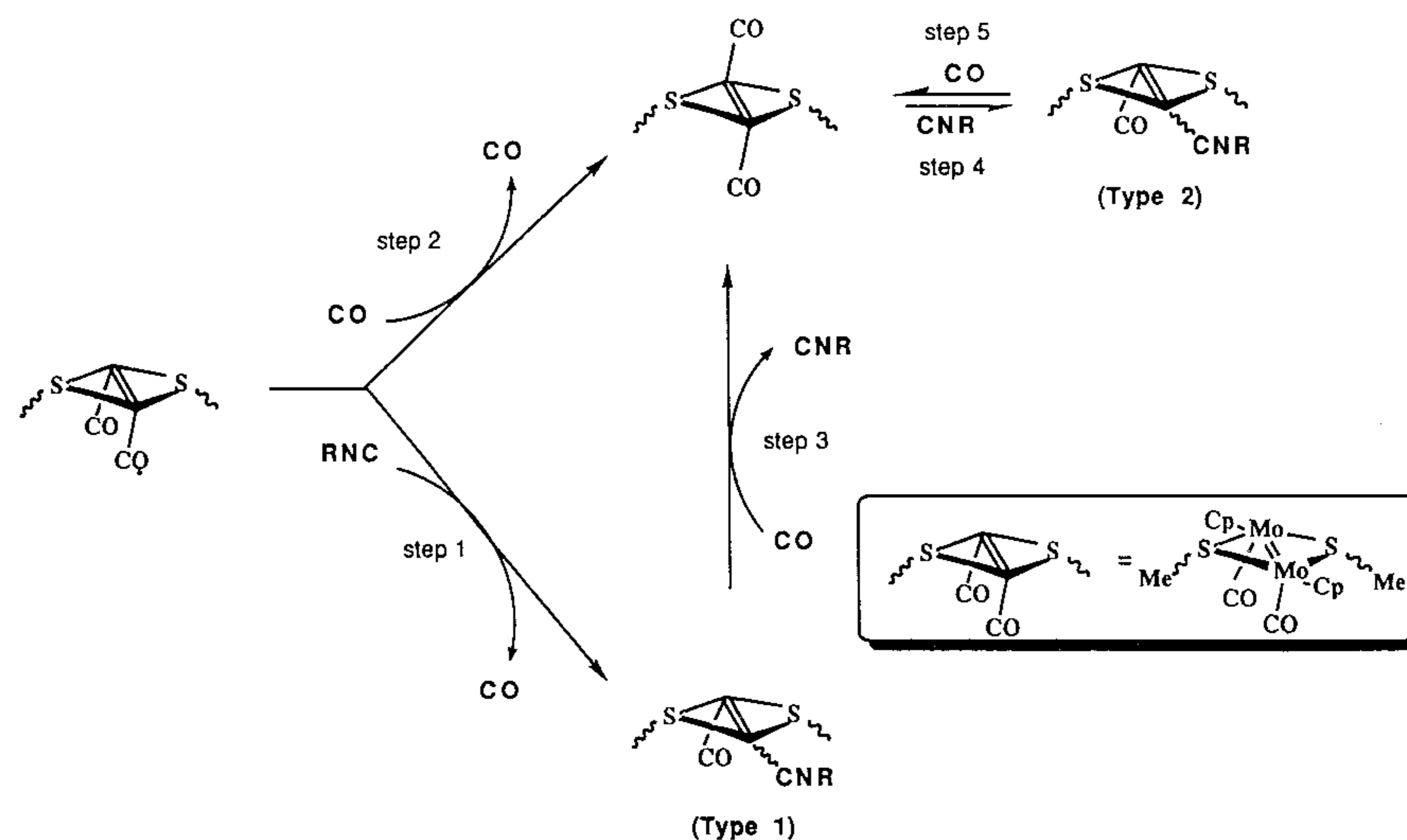
**ABSTRACT.** — Extended Hückel MO calculations have been performed on the reactants, products and possible intermediates or transition states of electrochemically-induced *cis-trans* isomerisation and ligand exchange reactions involving *cis*- and *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . It is shown that the *cis* isomer is very reactive toward CO attack and that the *cis/trans* isomerisation reaction, which is observed under the presence of CO, involves the intermediate  $[\text{Mo}_2\text{Cp}_2(\text{CO})_3(\mu\text{-SMe})_2]$ , which is also the intermediate of a similar *trans* → *trans* ligand exchange reaction. Ligand exchange reactions under the presence of isocyanide can be interpreted in the same way. Taken as a whole, the experimental and theoretical results allow a full understanding of the mechanisms of the studied reactions.

## Introduction

In a recent publication<sup>1</sup> we described electrochemical experiments on the thiolato dinuclear  $\text{Mo}^{\text{III}}$  complexes  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$  (**1**) and  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\text{X})_2(\mu\text{-SMe})_2]$  [ $\text{X}=\text{Cl}$  (**2**);  $\text{X}=\text{Br}$  (**3**)]. The reduction, in various solvents and under inert atmosphere, of **1**, **2** and **3** leads, after cleavage of two Mo-S or Mo-X bonds, to the formation of the final product *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . In the three reduction reactions a common intermediate was detected, but could not

be isolated. All the experimental data concurred to suggest that this intermediate, namely *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (**I**), is a kinetic isomer of the final product<sup>1</sup>. The conversion of **I** into *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  was found to be a slow step. However, when the experiments were made under an atmosphere of carbon monoxide, this conversion was found to be fast, indicating that this process is catalysed by CO, possibly via the formation of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_3(\mu\text{-SMe})_2]$  as an intermediate or transition state. From all these experiments we proposed the mechanism shown in Scheme 1.





Scheme 2

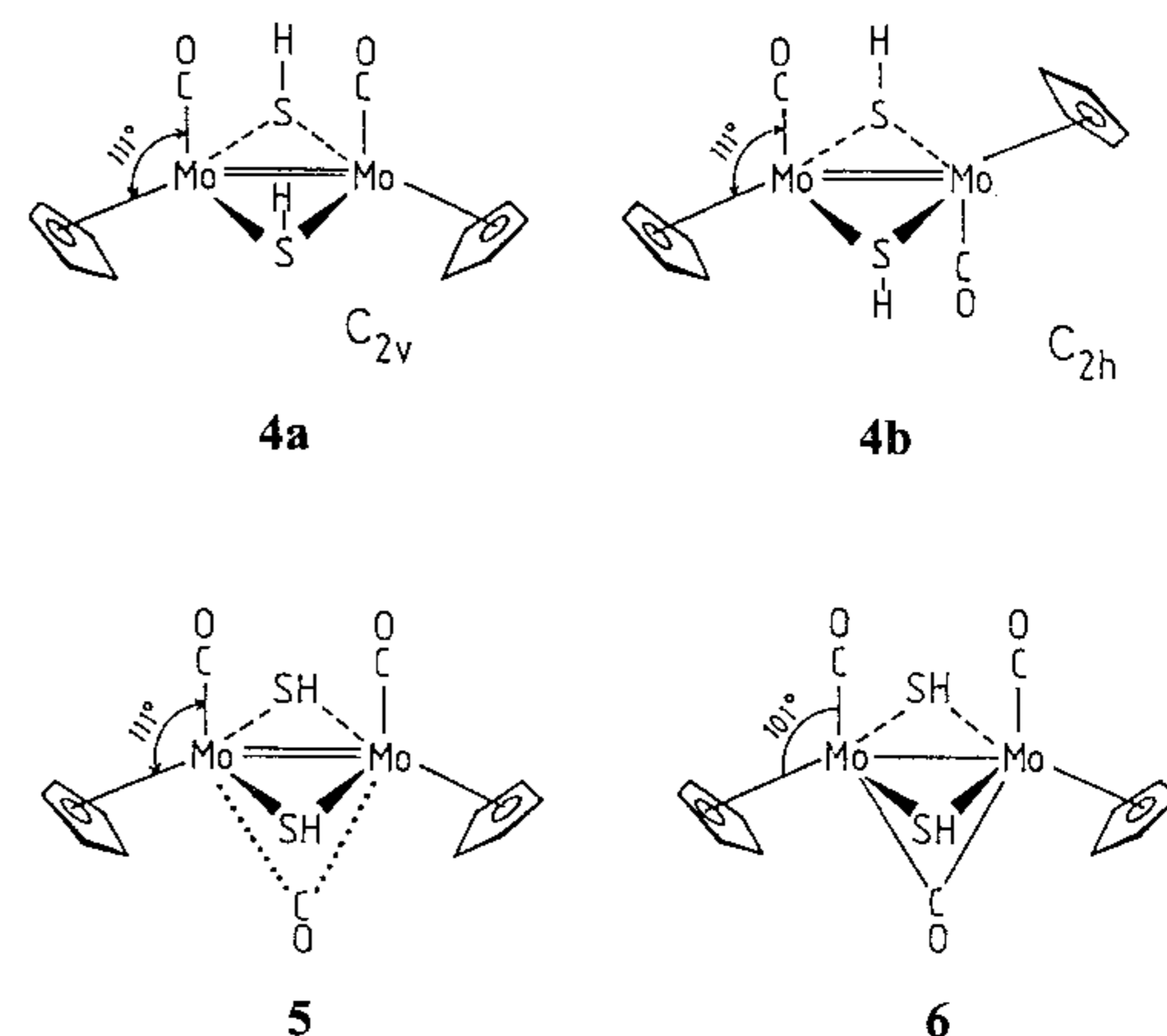
The electrochemical reduction of **1**, **2** and **3** were also performed in the presence of different alkyl and aryl isocyanides in each case. Two final compounds were detected. From the voltammetric experiments and from NMR and IR data on the products extracted from the catholyte, it was possible to identify these compounds as two isomers (named Type 1 and Type 2) of formula  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$ . The isomer Type 2 was formed more slowly on the electrolysis time scale. Therefore, on the basis of the experimental results, we propose, for these reactions in the presence of isocyanides, the mechanism shown in Scheme 2. Assuming that the reactive intermediate **I** is *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (*vide supra*), a ligand exchange reaction produces the isomer Type 1 (step 1). The carbonyl released during this step can react with **I**, and with isomer Type 1, to produce *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (steps 2 and 3). This latter compound reacts with CNR giving rise to the ligand exchange equilibrium with the type 2 isomer (steps 4 and 5).

The aim of this paper is, with the help of extended Hückel calculations, to shed some light on the electronic factors governing the mechanisms of Scheme 1 and Scheme 2, in particular to explore the structure, the stability and the reactivity of the major intermediates involved in the ligand exchange steps. We have recently reported<sup>1</sup> some preliminary results of our theoretical study of these reactions. We are now able to present a full orbital analysis on these electrochemical processes. From the voltammetric experiments on the reduction of **1**, **2** and **3**, we were able to determine unambiguously the elementary steps leading to the formation of the intermediate **I**<sup>1</sup>. Therefore, we will focus our study on this key intermediate and the subsequent steps in which it is involved (Sch. 1 and Sch. 2).

#### MO analysis of *cis*- and *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$

We start our analysis with the key intermediate **I** detected by the voltammetric experiments. From these data, we suggest (*vide supra*) that **I** is *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (Sch. 1)<sup>1</sup>. Two compounds isoelectronic to  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ , namely  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SBU}^t)_2]$ <sup>2</sup> and  $[\text{W}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SCHMe}_2)_2]$ <sup>3</sup>, have been structurally characterised by X-ray diffraction techniques. These two compounds adopt the *trans*-conformation in the solid state.  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SBU}^t)_2]$  has been shown to adopt the *syn* conformation for the SR groups and has a molecular symmetry close to  $C_s$  (in particular, significantly different values are found between the two CpMoMo angles and between the MoMoCO angles)<sup>2</sup>. On the other hand,

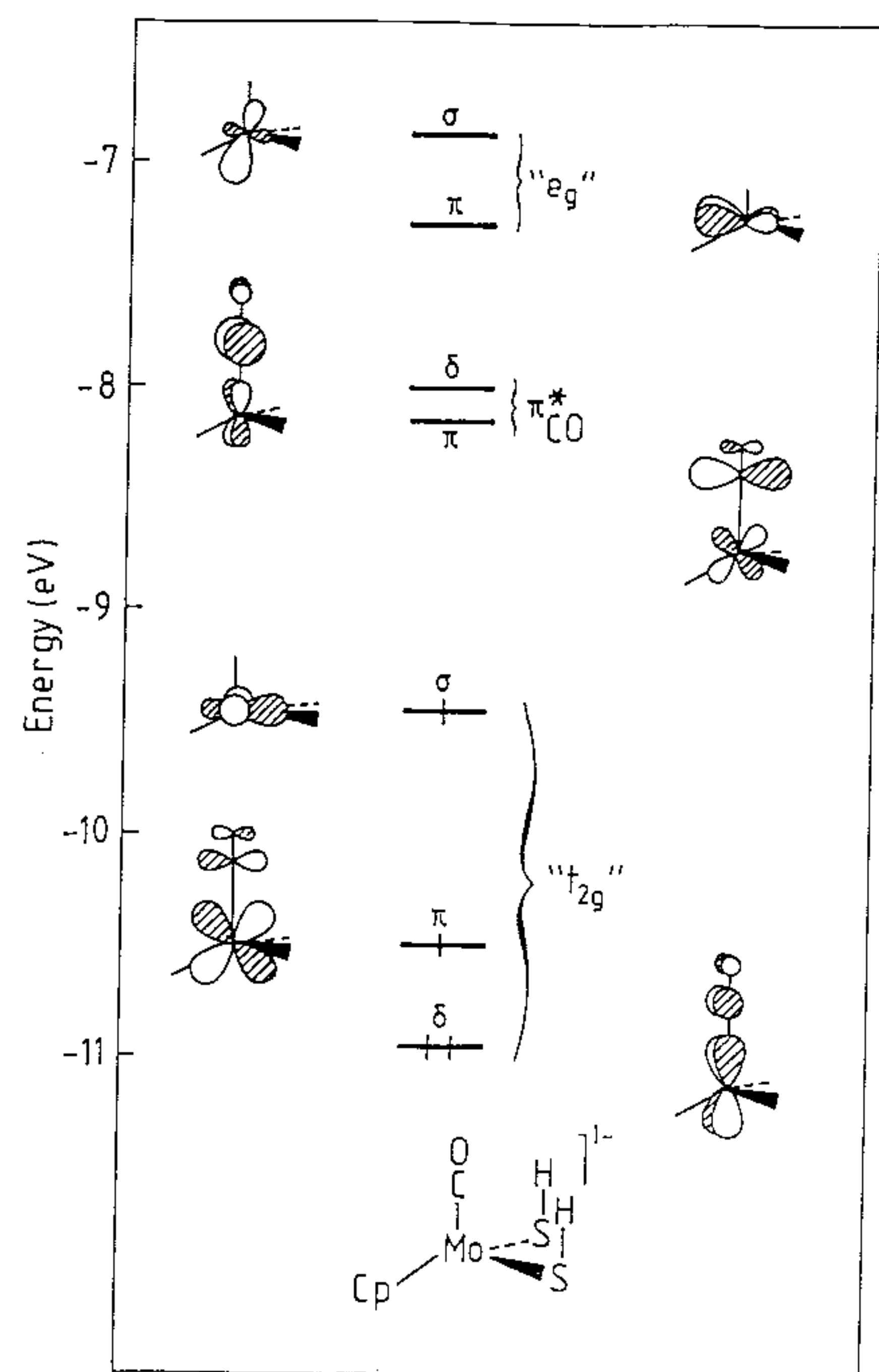
$[\text{W}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SCHMe}_2)_2]$  adopts the *anti* conformation with the  $C_{2h}$  symmetry in the crystal<sup>3</sup>. The closely related complex  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-PPh}_2)_2]$  adopts also the *trans* arrangement in the solid state<sup>4</sup>. In order to compare the stability and reactivity of *cis* and *trans* forms of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$ , we have undertaken calculations on the *cis-syn* ( $C_{2v}$ ) and the *trans-anti* ( $C_{2h}$ ) isomers of the model  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SH})_2]$ , respectively **4a** and **4b**, shown in Scheme 3.



Scheme 3

In order to investigate the *syn/anti* isomerisation process, we have also performed calculations on the *cis-anti* and *trans-syn* isomers of **4a** and **4b**. In the *cis* conformation, the *anti* isomer was found less stable than the *syn* isomer by only 0.14 eV. The energy barrier associated with the *cis-syn* to *cis-anti* transformation was calculated to be 0.38 eV, a peculiarly low value if one considers that extended Hückel calculations generally overestimate energy barriers. In the *trans* conformation, the two *syn/anti* isomers were found isoenergetic. The energy barrier associated to their interconversion was calculated to be 0.36 eV. Obviously, the *syn/anti* exchange appears easy. This finding is in agreement with the fact generally admitted that the *syn/anti* isomerisation is, for this type of compounds, a low-energy process in solution<sup>3,5</sup>. Moreover, a comparison of the electronic structure of these four isomers and of their tungsten analogues indicates that the choice of the *syn* or *anti*-conformation has little influence on the metal-metal and metal-ligand interactions. Other calculations on the "deprotonated" isoelectronic complex  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-S})_2]^{2-}$  confirm this

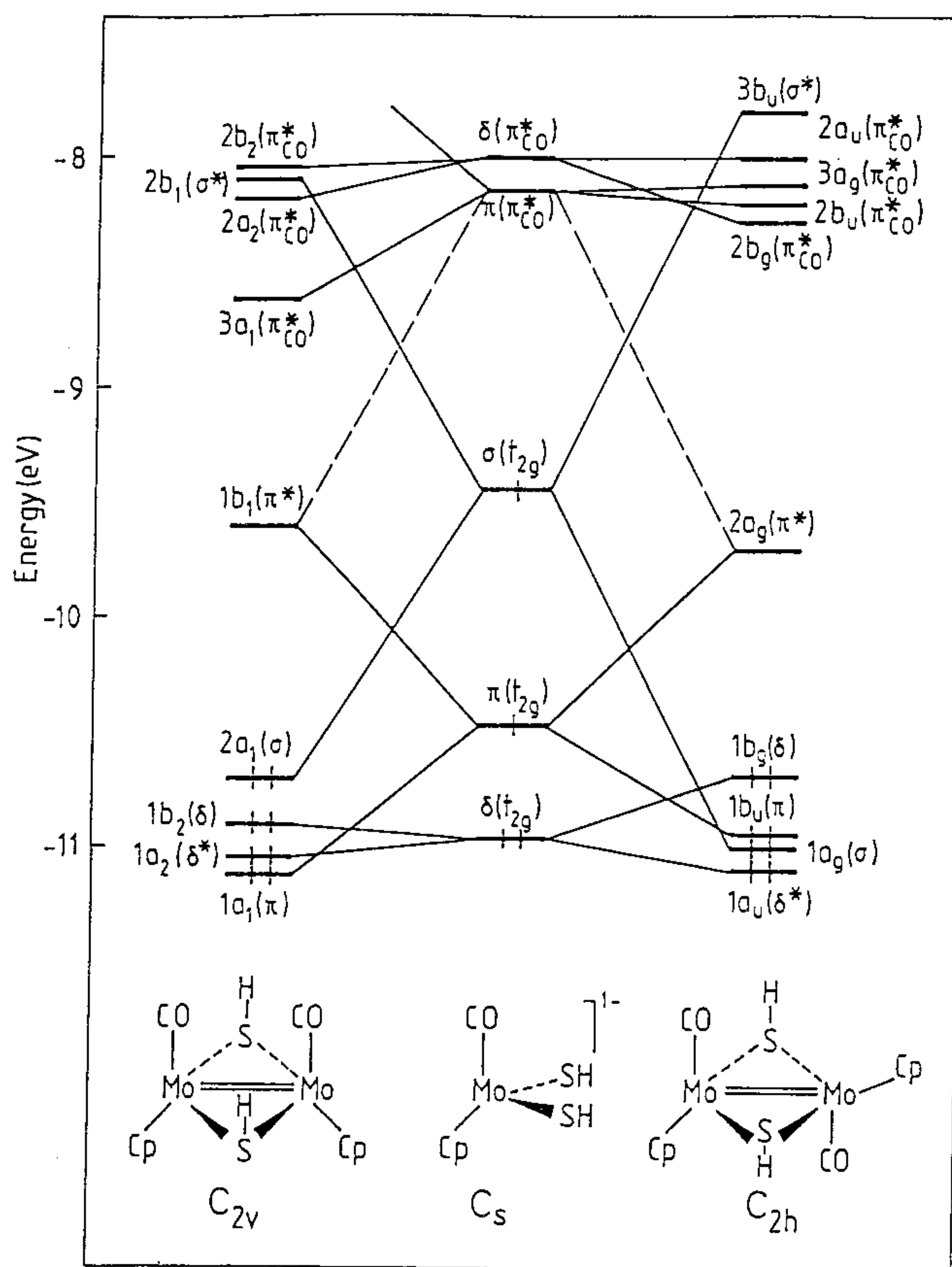
view. Therefore, we will concentrate now the discussion on the *cis/trans* isomerism.



**Figure 1.** – Frontier orbitals of the  $d^4$   $[\text{CpMo}(\text{CO})(\text{SH})_2]^-$  fragment. The  $\pi$ ,  $\sigma$  and  $\delta$  labels refer to the future Mo–Mo bond.

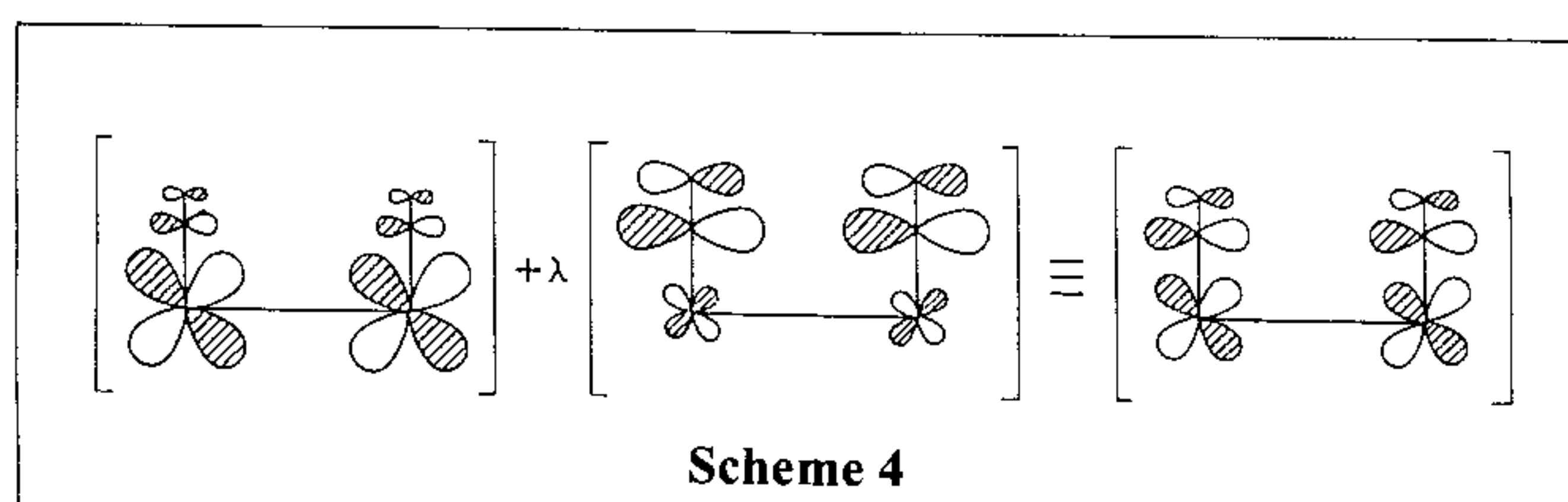
The metal-metal bonding interaction in these complexes can be conceptually constructed from the interaction of two  $d^4$   $\text{CpMo}(\text{CO})(\text{SH})_2$  “monomeric” units<sup>6</sup>. These mononuclear fragments are of the general pseudo-octahedral  $\text{ML}_6$  type and exhibit the general pattern of a group of three low-lying d-type orbitals, the  $t_{2g}$  set, situated below two antibonding d-type orbitals, the  $e_g$  set (see Fig. 1, where the levels are labelled  $\sigma$ ,  $\pi$  or  $\delta$  with respect to the future Mo–Mo bond). Of course, because of the lower real symmetry of the compound, the degeneracy is significantly splitted inside the  $t_{2g}$  and  $e_g$  sets, but the two groups of levels remain well separated in energy. A typical feature of these fragments is the presence, between the  $t_{2g}$  and  $e_g$  sets, of two levels derived from the  $\pi^*(\text{CO})$  antibonding orbitals. This is the consequence of the closeness in energy of the Mo 4d atomic orbitals (–10.5 eV) with the  $\pi^*$  levels of free CO (–9.4 eV for the same interatomic distance as in **4**). This proximity in energy induces also a significant intermixing between the  $\pi^*(\text{CO})$  orbitals and the  $\pi$  and  $\delta$  components of the  $t_{2g}$  set. This mixing confers a Mo–CO antibonding character to the  $\pi^*(\text{CO})$  levels and a bonding one to the  $t_{2g}$   $\pi$  and  $\delta$  components. This is a situation which, among others, can happen in carbonyl complexes of early second- or third-row transition metals.

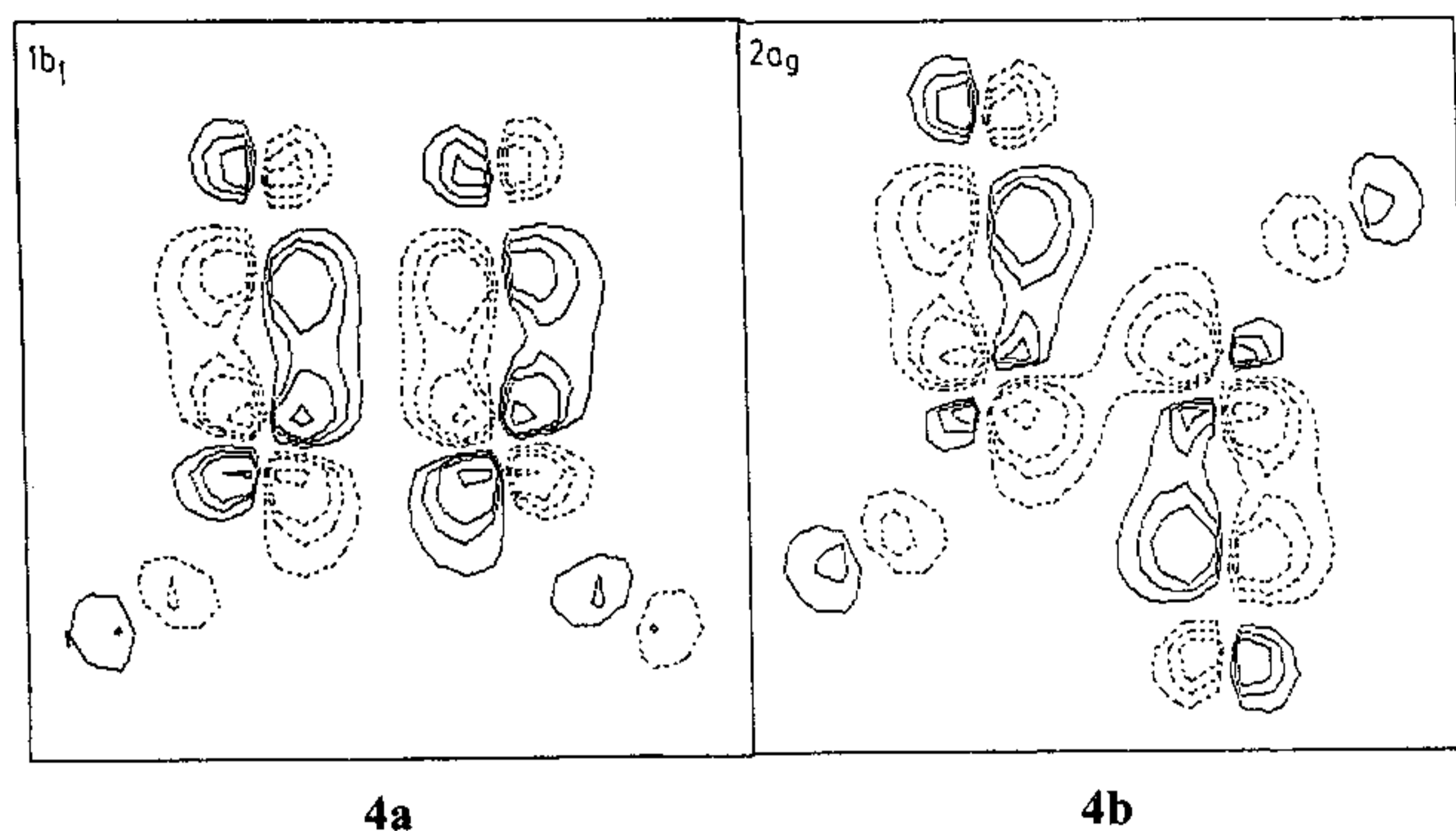
The MO diagrams of the **4a** and **4b** dimers (Fig. 2) are now easy to understand: each monomeric level generates an in-phase and an out-of-phase combinations in the dimers. Among the  $t_{2g}$  set, only the  $\sigma$  and  $\pi$  combinations afford a significant splitting at the Mo–Mo distance of 2.62 Å, leading to the formal  $\delta^2\delta^*\sigma^2\pi^2$  metallic configuration, in agreement with the presence of a double bond. Both diagrams of **4a** and **4b** appear very similar in terms of energy levels, although there are some differences in the MO localisation and composition, consequences of structural differences and of different second-order mixing between levels of same symmetry. A typical feature of both MO diagrams is the presence of a rather low-lying LU-



**Figure 2.** – Molecular orbital diagram of the *cis-syn* (**4a**) and *trans-anti* (**4b**) isomers of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SH})_2]$ . The  $\pi$ ,  $\sigma$  and  $\delta$  labels refer to the Mo–Mo bond.  $\pi^*_{\text{CO}}$  indicates a level of predominant  $\pi$  antibonding character between carbon and oxygen.

MO, situated in the middle of a large energy gap. This LUMO can be identified as being the  $\pi^*(\text{Mo-Mo})$  orbital. Its low-lying situation arises from the  $\pi$  Mo–Mo nature of this level, but also from the interaction of the antibonding combination of the monomeric  $\pi$ -type  $t_{2g}$  component with the antibonding combination of the in-plane  $\pi^*(\text{CO})$  levels. Indeed, these two types of monomeric levels are rather close in energy (*vide supra*). This second-order mixing is indicated by dashed lines in Figure 2 and schematically shown in Scheme 4 for the *cis* conformation (the coefficient  $\lambda$  indicates a secondary participation). Its effects is to reduce the destabilization of the  $\pi^*(\text{Mo-Mo})$  level, by reducing its Mo–Mo antibonding character and increasing its Mo–CO bonding character. A plot of the LUMO's of **4a** and **4b** is given in Figure 3. This orbital is 57% metal centered, and has 34% of  $\pi^*(\text{CO})$  character in **4a**. The corresponding values for **4b** are 46% and 20%, respectively. The Mo–Mo overlap population of this LUMO is –0.173 and –0.075 for **4a** and **4b**, respectively. This situation might confer peculiar chemical and electrochemical properties to this type of complexes. In particular, their reduction is expected to be easy and to induce a (moderate?) weakening of the Mo–Mo bond and a strengthening of the Mo–CO bonds.





**Figure 3.** – Contour plots of the LUMO's of (**4a**) and (**4b**) in the (CO)MoMo(CO) symmetry plane.

The computed Mo–Mo overlap populations are similar in **4a** and **4b**: 0.336 and 0.320, respectively. **4b** is found to be more stable than **4a** by only 0.12 eV. This energy difference is not really significant at our level of accuracy. Reasonable structural modifications and angle optimisations do not change the order of magnitude of this energy difference. Therefore one can conclude that the EH calculations predict similar thermodynamic stabilities for **4a** and **4b**. This result is in contradiction with the fact that all the experimental structures of related dimers have the *trans* conformation (see above). A possible overestimation of the energy of **4b** with respect to the one of **4a** might have its origins in the difficulties that has the EH method to properly take into account long distance interactions. Indeed, steric repulsions might be stronger in the case of **4a**. Moreover, weak M...CO semi-bridging interactions are present in the molecular structures of the *trans* complexes [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SBu<sup>1</sup>)<sub>2</sub>]<sup>2</sup>, [W<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SCHMe<sub>2</sub>)<sub>2</sub>]<sup>3</sup> and [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>]<sup>4</sup> (M...C = 2.83–3.44 Å and M–C–O = 171–174°). Our calculations suggest that this M...C through-space interaction is favored in the *trans* conformation. Indeed the corresponding overlap population is found to be +0.034 in **4b** and only +0.008 in **4a**. This difference comes from the occupied π(Mo–Mo) bonding orbital which provides more M...C bonding character in **4b**. We think that this stabilizing interaction present in **4b** is underestimated in our calculations.

The **4a** → **4b** isomerisation cannot process by a simple rotation of a CpMo(CO) fragment. Indeed, the computed energy barrier for this rotation is very high (≈ 11 eV), mainly because of steric hindrance. It has been shown that in structurally related complexes similar *cis* → *trans* isomerisation proceeds *via* the opening of one the bridges<sup>6,7</sup>. Such a mechanism is in agreement with the fact that the **4a** → **4b** reaction is slow in the absence of CO.

#### The interaction of *cis*- and *trans*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SR)<sub>2</sub>] with CO

We now investigate the possibility for either **4a** and **4b** to add a CO ligand. This hypothetical reaction has been firstly modelised by taking the frozen geometries of **4a** and **4b** and adding a CO ligand at any terminal (*trans* to CO) and bridging possible position. The distance between Mo and the incoming carbonyl was fixed to be the same as for two normally bonded carbonyls, *i.e.* 1.94 Å (terminal) or 2.10 Å (bridging). Larger bonding distances have been also tested; they lead to the same general conclusions. The interaction energy between the entering CO and **4a** or **4b** was found highly positive (destabilizing) for any of the considered approaches, except for the bridging approach to **4a** shown in **5** (see Scheme 3), where it was calcu-

lated to be –2.2 eV. The reasons of this strong preference are of both steric and electronic origin. Any approach of the entering CO molecule in a terminal position is highly disfavored, because of very short non-bonding contacts [C(CO)...C(Cp) = 1.5 Å; O(CO)...H(Cp) = 1.1 Å]. The approach in bridging position on the same side as a CO ligand is also disfavored (CO...CO = 1.4 Å). Since the *trans* isomer **4b** has CO ligands on both sides, steric factors cannot be ruled out. On the other hand, it is clear that, because of its low energy, the LUMO of **4a** (or of **4b**) is expected to be strongly involved in the interaction with the incoming CO. In the particular case of **4a** it has perfect symmetry and spacial localisation for providing a strong overlap with one of the π\* orbitals of an additional bridging CO ligand (see plots in Fig. 3). The part taken by this LUMO in the stability of *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-SR)<sub>2</sub>] is discussed in the following section.

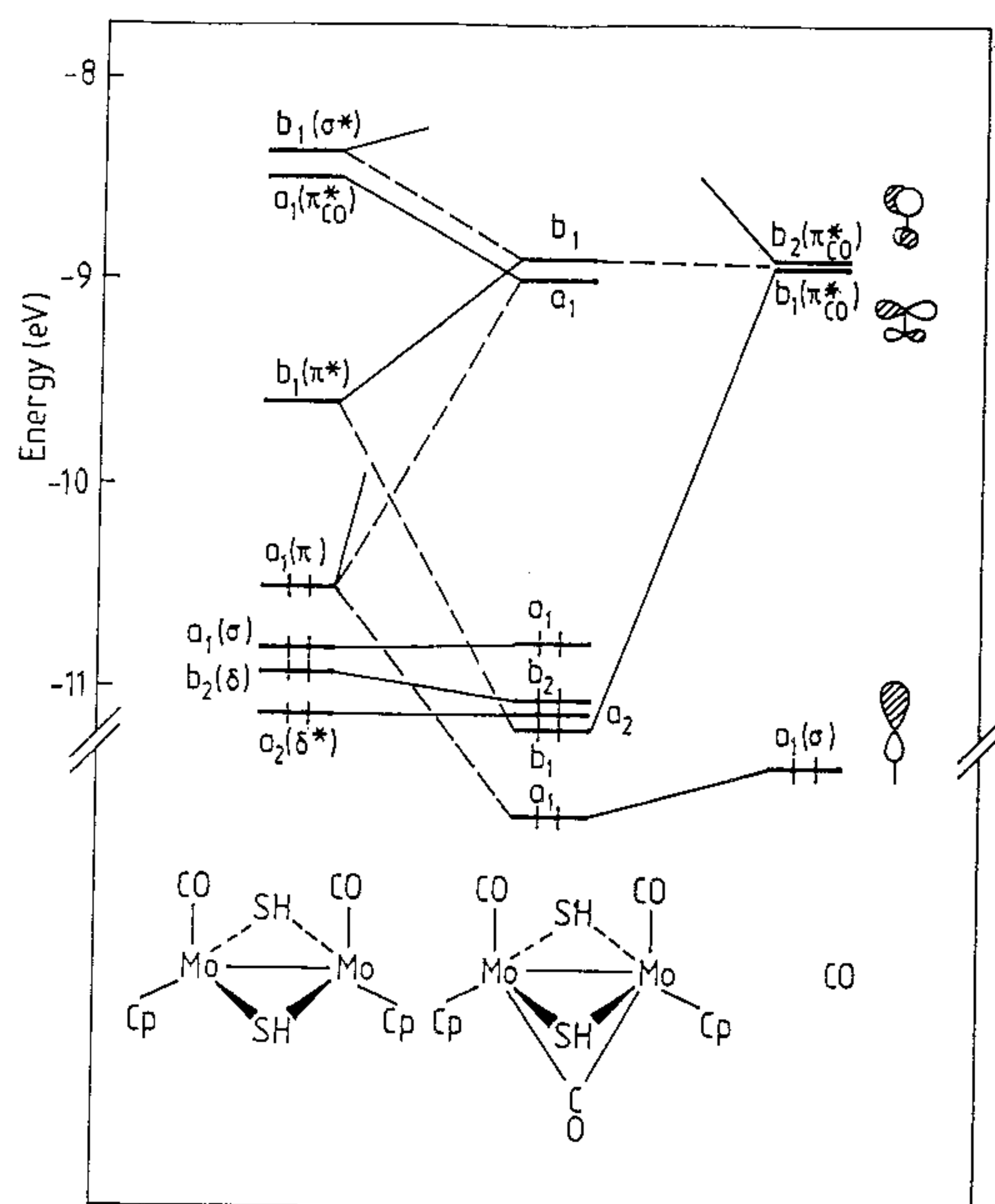
Since the molecular structure of *trans*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SBu<sup>1</sup>)<sub>2</sub>] presents two symmetrically different Mo atoms<sup>2</sup>, (*vide supra*) we similarly tested the different approaches of a CO molecule on a C<sub>s</sub> model of related structure, obtained by distortion of **4b**. As for the C<sub>2v</sub> model **4b**, all the tested approaches of CO to this C<sub>s</sub> structure (terminal and bridging) were found repulsive. We obtained the less disfavored approach (interaction energy = +1.7 eV) for one of the bridging positions. Clearly, the *cis* isomer **4a** appears to be able to bind efficiently carbon monoxide in the bridging position shown in **5**, without any important structural reorganisation. This result confirms our initial assumption<sup>1</sup> suggesting that the intermediate **I** of Scheme 1 is *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SMe)<sub>2</sub>].

#### MO analysis of *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-SR)<sub>2</sub>]

Starting from the hypothesis that a species such as **5** might be an intermediate structure in the process of Scheme 1, we then considered a more realistic geometry for this complex, based on the averaged X-ray molecular structure of the isoelectronic *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SMe)<sub>3</sub>]<sup>+</sup> cation<sup>5</sup> (see below for structural details). This former complex has the same molecular conformation as **5**, but with a SMe group in the place of the bridging carbonyl and a Mo–Mo single bond of 2.78 Å. The respective angular positions of the MoSMo and MoC(bridging)Mo wings of this “relaxed” structure **6** shown in Scheme 3, have been optimized by EH calculations which found that the two Mo– and the two S atoms lie approximately in the same plane, as in the related *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SMe)<sub>3</sub>]<sup>+</sup> compound. The MO diagram of **6** is shown in Figure 4. The bonding interaction between the bridging CO and the *cis*-[Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SH)<sub>2</sub>] fragment is then –2.7 eV, a value close to the one obtained with the “unrelaxed” model **5**. This is not surprising since the frontier MO diagram of the [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SH)<sub>2</sub>] fragment in **6** resembles the one of complex **4a** (compare Fig. 2 and 4), the main difference being the lower energy of the π\*(Mo–Mo) LUMO in the case of the longer Mo–Mo bond. Two major bonding interactions are responsible for the Mo–C(bridging) bonds. One, of a<sub>1</sub> symmetry, involves the σ non-bonding HOMO of CO and the π(Mo–Mo) bonding orbital of the dinuclear fragment. The other one is of b<sub>1</sub> symmetry and involves one of the π\*(CO) LUMO's and the low-lying π\*(Mo–Mo) frontier orbital (in addition, a secondary attractive interaction occurs, involving the occupied b<sub>1</sub> π(CO) which contributes to the destabilisation of the π\*(Mo–Mo) frontier orbital). The two (a<sub>1</sub>+b<sub>1</sub>) corresponding antibonding combinations are left vacant, while the two bonding combinations are occupied by four electrons, coming from the a<sub>1</sub> CO lone pair and from the occupied π(Mo–Mo) of a<sub>1</sub> symmetry orbital of the dinuclear Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(μ-SH)<sub>2</sub> fragment. There-

fore, it appears that the two  $(a_1+b_1)$  bonding electron pairs in **6** originate from two pairs of  $a_1$  symmetry in the fragments, implying a HOMO/LUMO level crossing for the symmetrical ( $C_{2v}$ ) approach of CO to **4a**. This will be discussed in the following section.

The result of the double  $(a_1+b_1)$  interaction is a population of  $\pi^*(\text{Mo-Mo})$  (by 0.69 electron) and a depopulation of  $\pi(\text{Mo-Mo})$  (by 1.18 electron) in the complex. Consequently, the metal-metal  $\pi$  bond is broken and the Mo-Mo overlap population (0.065) is significantly weaker than in **4** (note that, in the unrelaxed structure **5**, the Mo-Mo overlap population is even weaker: 0.046). Therefore this *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SR})_2]$  complex of the type **6**, with a large HOMO-LUMO gap of 1.8 eV, appears stable enough to be considered as a possible intermediate rather than a transition state in the reaction process of Scheme 1.



**Figure 4.** — Molecular orbital interaction diagram of *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SH})_2]$ . The  $\pi$ ,  $\sigma$  and  $\delta$  labels refer to the Mo-Mo bond.  $\pi^*$  indicates a level of predominant  $\pi$  antibonding character between carbon and oxygen.

The question which arises then is: can the *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$  isomer be also a possible reaction intermediate? Starting from the structure of the *cis* form **6**, we have performed various variations of bond and dihedral angles leading to possible *trans* or *transoid* conformations. The steric effects mentioned in the previous section remain in this “relaxed” structure. Consequently the energy of any *transoid* conformer that we calculated was found several eV’s above the energy of the *cis* form which appears to be the unique low-energy minimum on the potential energy surface.

#### The early stage of the approach of CO to *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$

As discussed above, when CO is approached to *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$  in a bridging way, such as the  $C_{2v}$  symmetry is maintained along the reaction path, a HOMO ( $a_1$ )/LUMO ( $b_1$ ) level crossing occurs at Mo-CO(bridging) distances of ca. 3.0 Å. Consequently, this reaction appears formally symmetry-forbidden. However, the computed barrier height is not very large (0.6 eV), indicating the possibility of a low-symmetry al-

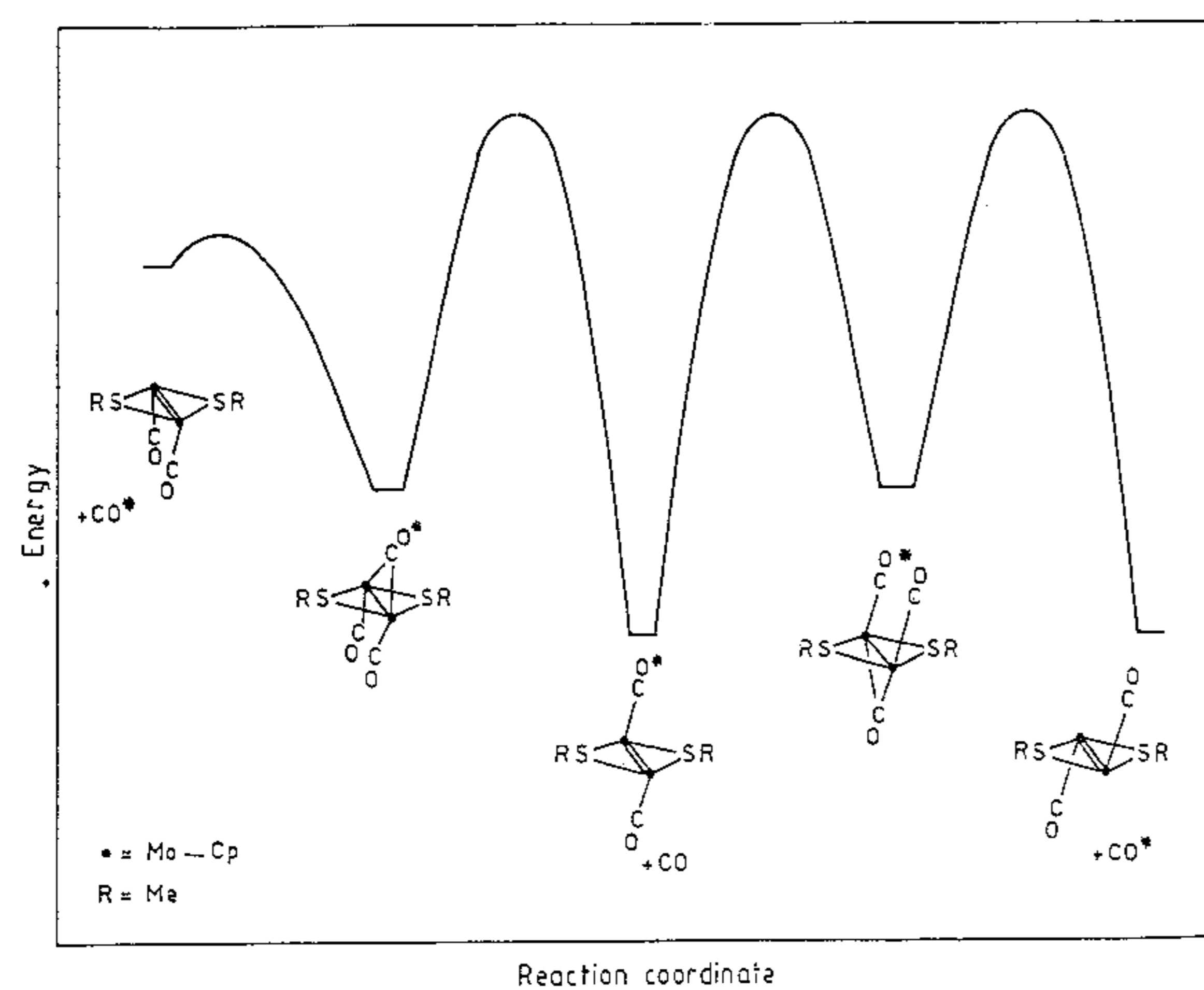
lowed process. Indeed, the computed energy barrier almost vanishes when the symmetry of the early stage approach is lowered in the following way: keeping both bridging Mo-CO distances equal to  $\approx 3.0$  Å, the CO ligand is bent so that its vector points approximately in the direction of one of the Mo atoms. In addition, the valence bond angles around the Mo atoms have to be somewhat adapted. In that situation, both  $\sigma$  non-bonding and  $\pi$  in-plane bonding orbitals of the incoming carbonyl participate to the interaction with the metallic LUMO. This unsymmetrical approach is followed by a rocking motion of the bridging CO, so that ideal  $C_{2v}$  symmetry is reached for the last step of the reaction. It is clear that a full exploration of the potential energy surface of such a reaction is beyond the capabilities of EH calculations and these findings have to be considered as approximate. However, our partial results indicate clearly that the only possible low energy pathway implies an unsymmetrical but bridging position of the entering CO during the early stage of the approach.

#### Electronic structure of $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$

We now examine the electronic structure of one of the starting products of the reactions of Scheme 1, namely  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$ . As said previously, this cation has been structurally characterised in its *cis* conformation<sup>5</sup> and is isoskeletal and isoelectronic to the *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SR})_2]$  intermediate. EH calculations on the model  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SH})_3]^+$  confirm that both compounds are electronically related. Once more, the *trans* conformation appears highly disfavored, mainly for steric reasons. A comparison of the Mo-S overlap populations indicates that the SH group situated on the same side of the Mo-Mo bond as the Cp ligands is slightly less strongly bonded to the metals than the other two thiolato ligands (corresponding values: 0.40 vs 0.44). Moreover, the LUMO, which can be identified as the  $\sigma^*(\text{Mo-Mo})$  orbital is somewhat antibonding between this unique sulfur and the metal atoms. These results agree well with the fact that the electrochemical elimination of a thiolato group from  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$  (first step of Scheme 1) leads to the formation of the *cis* rather than the *trans* isomer of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . This *cis* conformation of intermediate **I** was also suggested on the ground of our previous experiments.

#### Discussion on the ligand exchange mechanism of Scheme 1

Our EH calculations are in very good agreement with the mechanism proposed in Scheme 1. The starting compound  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$ , which is very likely to be the *cis* isomer, loses upon reduction the thiolato group which lies on the Cp side, generating the intermediate *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . In the absence of CO, this *cis* complex is stable and isomerises only slowly in its *trans* conformer. This reaction suggests that EH calculations underestimate the stability of the *trans* form with respect to the *cis* one. In the presence of CO, because of its good accepting capability (low-lying LUMO) and the presence of one uncongested side of the Mo-Mo bond, *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  adds readily one CO ligand to yield *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$ , isostructural with the starting cation, and which is unstable with respect to the dissociation into *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  and CO. This last step is understandable if one considers that the energy of *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SR})_2]$  is, for reasons exposed above, overestimated in the calculations.



**Figure 5.** – Qualitative energy profiles of the *cis* → *trans* (left) and *trans* → *trans* (right) isomerisation reaction of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  with CO exchange.

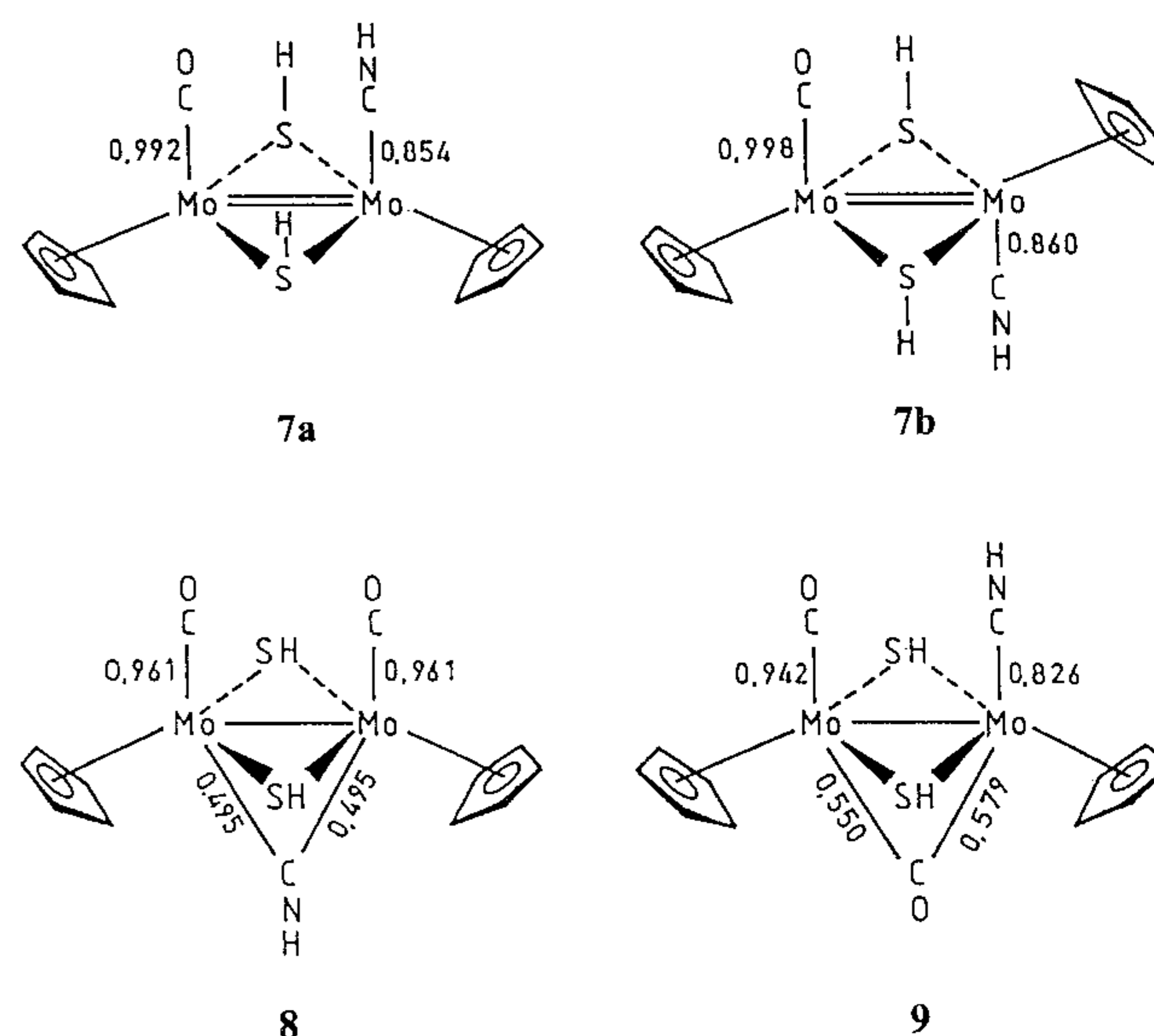
Our calculations suggest that, in the isomerisation process of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  under the presence of CO, *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$  is a reaction intermediate rather than a transition state. Therefore, for these last steps of the mechanism of Scheme 1, we propose the qualitative energy profile shown on the left side of Figure 5. The formation of *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$  from *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  is expected to occur with a low activation energy. Indeed, little structural reorganisation of the  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  moiety is required in this bond-forming process. Conversely, this is not the case for the formation of *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  from *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$ , which requires significant ligand motion, and for which we expect a significant activation energy.

We propose (*vide supra*) that if the *trans* → *cis* isomerisation reaction of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  is not observed, this is for thermodynamic reasons. In principle, if the activation energy of the *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  →  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$  reaction is sufficiently low, it is possible to imagine a *trans* → *trans* interconversion of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  under CO and with CO exchange, as schematised in the right side of Figure 5. Conversely, the mechanism we propose excludes the possibility of a similar *cis* → *cis* interconversion **with** CO exchange. It is noteworthy for the following that the CO exchange mechanism we propose on Figure 5 remains qualitatively valid if CO\* is replaced by any 2- electron ligand, such as an isocyanide ligand.

### Electronic structure of the isocyanide derivatives

In the ligand exchange mechanism of Scheme 2, two isomers of  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  are formed. As for the dicarbonyl analogue, the two *syn/anti* and *cis/trans* types of isomerism can be considered. Our calculations on the model  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNH})(\mu\text{-SH})_2]$  lead to similar results as those obtained for  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ : the energy difference between two *syn* and *anti* conformers is very low (less than 0.13 eV), as well as the energy barrier associated with their interconversion (less than 0.4 eV). Therefore, and for the same reasons as for the dicarbonyl analogue, we propose that the *syn/anti* exchange is present in solution at room-temperature and that the isomers named Type 1 and Type 2 differ by their *cis/trans* conformations. The corresponding molecular models we used in our calculations, namely **7a** and **7b**, are depicted in

Scheme 5. Their structures were simply derived from the ones of **4a** (*cis/anti*) and **4b** (*trans/syn*) by substitution of one CO ligand by CNH. In both isomers, the optimisation of the CNH angle leads to a linear isocyanide ligand. Most of the general characteristics concerning the electronic structure of **7a** and **7b** were found to be very similar to those obtained for the related complexes **4a** and **4b**. The Mo–Mo overlap populations are 0.354 and 0.346 for **7a** and **7b** respectively. The HOMO/LUMO gap is 1.2 and 1.0 eV, respectively. The energy difference between the two isomers is 0.22 eV in favor of **7b**. This value is probably meaningless, and EH calculations seem unable to reproduce the respective stabilities of the two isomers, as for the case of the dicarbonyl analogues (*vide supra*).



**Scheme 5**

As for isomers **4**, the LUMO is found to be isolated in the energy scale, and of Mo–Mo  $\pi^*$  dominant character mixed in a bonding way with  $\pi^*$  ligand orbitals (*see* Scheme 4). However, since CNR is a weaker  $\pi$ -acceptor than CO, its  $\pi^*$  orbitals lie at higher energy and mix to a lesser extent with the metallic orbitals in the LUMO. It results that in the case of complexes **7**, the loss of ligand  $\pi^*$  character on the isocyanide side increases the participation of the metal atom bonded to it. As a consequence, the LUMO's of **7a** and **7b** are significantly dissymmetrical. In the case of the *cis* isomer **7b**, the LUMO is 18% localised on the Mo atom bearing the CO ligand, and 47% localised on the Mo atom bearing the CNH ligand. The corresponding values for the *trans* isomer **7a** are 17% and 40%, respectively. Another consequence of the difference in the  $\pi$ -accepting abilities of CO and CNR is that CO is bonded more strongly to the metal than CNR. This is illustrated on Scheme 5, where the corresponding Mo–CO and Mo–CNH overlap populations are indicated. From these values, CNR appears to be a better leaving group than CO.

We have also carried out calculations on the two isocyanide derivatives of the tricarbonyl intermediate **6**, namely *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CNH})(\mu\text{-SH})_2]$  (**8**) and *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNH})(\mu\text{-CO})(\mu\text{-SH})_2]$  (**9**). These two hypothetical intermediates are shown in Scheme 5. Their geometries were derived from the one of **6** by simply substituting a CO ligand by CNH. Again, the optimisation of the CNH angle leads to a linear isocyanide. Results obtained for **8** and **9** are very similar to those obtained for **6**. In particular, their formation by addition of a bridging ligand to either **4a** or **7a** were found energetically very

favorable. The Mo–CO and Mo–CNH overlap populations for **8** and **9** are given in Scheme 5. One can see that, as in complexes **7**, the isocyanide ligand is bonded less tightly than the carbonyl. The energy difference between isomers **8** and **9** is rather large (1.1 eV in favour of **9**), suggesting that **9** is a more accessible intermediate than **8**.

### Discussion on the mechanism of Scheme 2

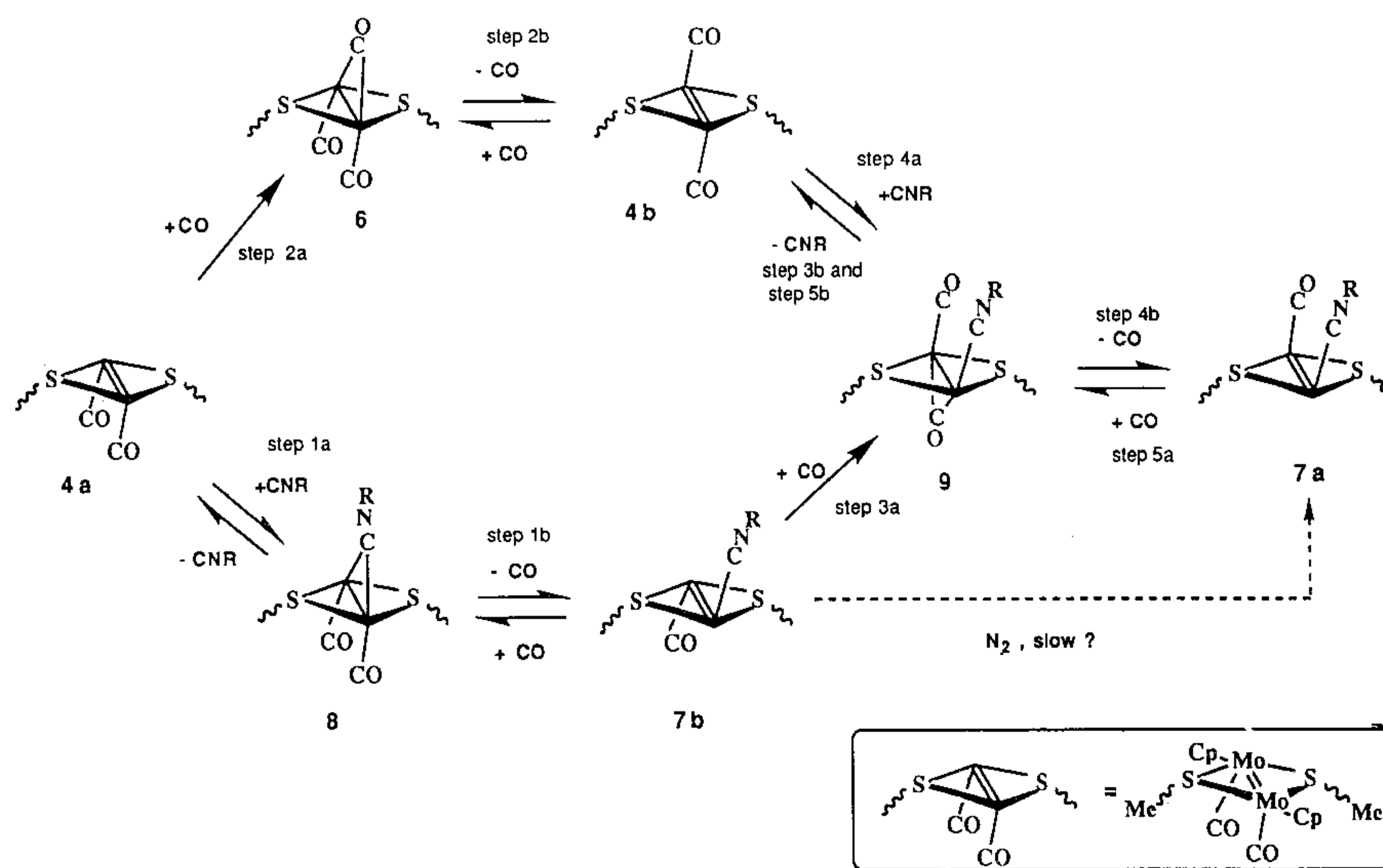
From our calculations, we are now able to complete and to modify the mechanism of Scheme 2, based on the electrochemical experiments<sup>1</sup>. This is done in Scheme 6, that we would like to comment as follows.

According to the ligand exchange mechanism we propose (*vide supra*), a *cis* complex cannot give rise to a substituted *cis* derivative. Consequently, in agreement with the conclusion we arrive at from the electrochemical experiments<sup>1</sup>, we suggest that isomer named Type 1 (Sch. 2) is *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$ . It is generated from *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  by a ligand exchange mechanism similar to that of the *cis/trans* isomerisation of the dicarbonyl complex  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . The intermediate species of step 1 is a compound of the type of **8** (Scheme 6, step 1a-b; in this scheme, the sulfur substituents are omitted: they are H in the calculations and Me in the experiments). The CO released in step 1, can react with the electrogenerated *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  to yield its thermodynamically stable *trans* conformer (Scheme 6, step 2a-b). CO can also react with *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  to produce either the starting species *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (via an intermediate of the type of **8**), or *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (via an intermediate of the type of **9**); this confirms our results concerning the generation of *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  by CO attack on either *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  (CO-catalysed isomerisation, Schemes 2 and 6, step 2), or *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  (Scheme 2 and 6, step 3). According to our calculations, in which **9** is found significantly more stable than **8**, the second pathway appears easier. Once formed, *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  reacts with CNR to give the isomer named Type 2 in Scheme 2<sup>1</sup>, which must be *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$ . This reaction also takes place via an intermediate of the type of **9**. Since **9** is a common intermediate in steps 3 and 4, one has to consider the possibili-

ty of the *trans*- to *cis*-conversion of  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$ , via **9** (Scheme 6, steps 3a-4b)<sup>11</sup>. From the observation of the metal-ligand overlap populations in **9** (Scheme 5), it is clear that the Mo–CNH bond is weaker than the Mo–CO bond. Moreover, the bridging carbonyl is more strongly bonded to the metal atom holding the isocyanide. From these results, it appears that if a ligand is more easily lost from **9**, it should be the isocyanide. Therefore, the formation of *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  from the reaction with an authentic sample of *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  suggests that, under an inert atmosphere in the presence of CNR<sup>11</sup>, CO loss from **9** (Scheme 6, step 4b) is kinetically more favoured than the isocyanide decoordination (Scheme 6, step 5b). Conversely, under a CO atmosphere, the conversion of *cis*- (and *trans*-)  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  to *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  is observed, in agreement with the results of our calculations.

### Conclusion

From the analysis of the electronic structure of the reactants, products and possible intermediates of the reactions shown in Schemes 1 and 2, we were able to show that the key intermediate **I**, generated from the electrochemical reduction of compounds **1**, **2** or **3**, is *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . Under the presence of CO, this compound is kinetically unstable with respect of its *trans* isomer. Our calculations indicated that the attack of CO on *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$  is very easy and gives rise to the formation of the very unstable (or possibly transition state) *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SMe})_2]$  which ultimately decomposes into CO and *trans*- $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_2]$ . From these theoretical results, one can predict that a *trans* → *trans* isomerisation process is also possible under the same conditions as the observed *cis* → *trans* process (CO exchange) and involves the same transition state (Fig. 5). The experiments made under the presence of isocyanide instead of CO (Scheme 2) can be interpreted in the same way, through ligand exchange reactions of the type  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{L})(\mu\text{-SMe})_2] + \text{L}' \rightarrow [\text{Mo}_2\text{Cp}_2(\text{CO})(\text{L}')(\mu\text{-SMe})_2] + \text{L}$ , accompanied with *cis* → *trans* or *trans* → *trans* ligand conformational rearrangements and involving bridged  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{L})(\text{L}')(\mu\text{-SMe})_2]$  intermediates. It was therefore possible to identify the isomers named Type 1 and Type 2 in Scheme 2 as being the *trans* and the *cis* isomers of  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$ , respectively.



Scheme 6



In addition, a reinterpretation of the experimental results (Sch. 2) is proposed (Sch. 6).

### Computational details

All the calculations were made within the extended Hückel formalism<sup>8</sup>, using the weighted  $H_{ij}$  formula<sup>9</sup>. The atomic parameters are taken from the literature<sup>10</sup>. The molecular structures of **4a**, **4b** and **5** have been idealised from the averaged experimental structure of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SBU}^t)_2]^2$  with the following bond distances (Å): Mo–Mo=2.62; Mo–C(Cp)=2.34; Mo–C(CO)=1.94; Mo–S=2.42; C–C=1.40; C–O=1.16; S–H=1.33 and bond angles (°): Mo–Mo–CO=90; Cp–Mo–CO=111. The distorted  $C_s$  structure of **4b** considered in one of the models for (**5**) (see text) differ from the  $C_{2h}$  structure by the following angles (°): Mo–Mo–CO=97 and 74; Cp–Mo–CO=120 and 112. Test calculations were also made on the W analogues of **4** and **5** by averaging the experimental structure of  $[\text{W}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SCHMe}_2)_2]^3$ . They lead to similar results as for the Mo complexes. The structures of **6** and  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SH})_3]^+$  have been idealised from the averaged experimental structure of  $[\text{Mo}_2\text{Cp}_2(\text{CO})_2(\mu\text{-SMe})_3]^+$ <sup>5</sup> with the following bond distances (Å): Mo–Mo=2.78; Mo–C(Cp)=2.32; Mo–C(CO)=1.94 (terminal) 2.02 (bridging), Mo–S=2.45; C–C=1.41; C–O=1.17, S–H=1.33 and bond angles (°): Mo–Mo–CO=90; Cp–Mo–CO=169. The geometries of **7**, **8** and **9** were derived from that of **4**, **5** and **6** by substituting one CO by CNH with the following bond distances for CNH (Å): C–N=1.14; N–H=1.01.

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- A diisocyanide intermediate of the type *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-CNR})(\mu\text{-SMe})_2]$  cannot be fully ruled out, although this is probably a higher energy species than **9**. The formation of such an intermediate could explain the fact that, even when CO is removed from the solution by  $\text{N}_2$  bubbling, a small amount of *cis*- $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  is detected<sup>1</sup>. Alternatively, this complex could also result from a direct *trans*  $\rightarrow$  *cis* isomerisation of  $[\text{Mo}_2\text{Cp}_2(\text{CO})(\text{CNR})(\mu\text{-SMe})_2]$  (Scheme 6, dotted arrow), similar to the slow *cis*  $\rightarrow$  *trans* isomerisation of the dicarbonyl derivative under an inert atmosphere (Scheme 1).