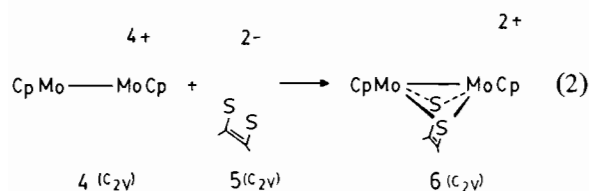


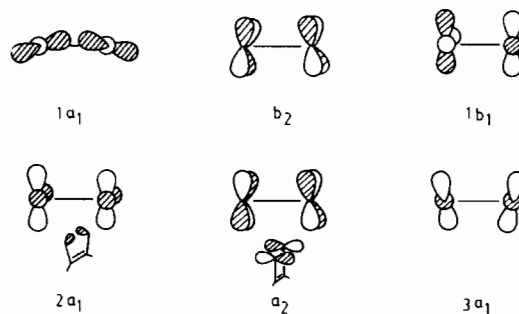
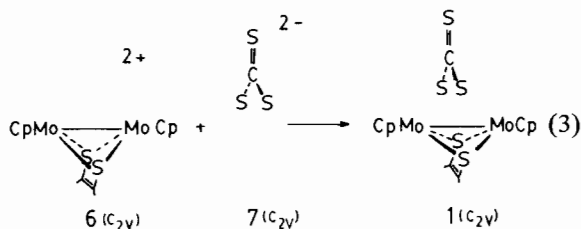
Fig. 1. Interaction diagram for the construction of molecular orbitals of fragment 6 from smaller fragments 4 and 5.

1 and 2 based on the well known MO pattern of CpMo–MoCp [12] using the fragment molecular orbital (FMO) approach. Molecular orbitals of fragment 6 are constructed from smaller fragments 4 and 5 (eqn. (2)).



4 (d^3-d^3) has a metal–metal σ and two δ orbitals. The HOMO (δ)–LUMO (δ^*) gap is small. Figure 1 shows the interaction diagram for the construction of fragment 6. All the energy levels are labelled according to the C_{2v} point group. Two major interactions are observed. $2b_1(\sigma^*)$ of 4 interacts with $1b_1$ (non-bonding π) of 5 and gets destabilized to give a metal based MO, $2b_1$, of 6. $2a_1(\delta)$ of 4 gets a slight push upwards, due to its interaction with $1a_1$ of 5, to become LUMO ($2a_1$) in fragment 6. Another major interaction is between $2b_2(\delta)$ of 4 and $1b_2$ (non-bonding σ^*) of 5 but without much contribution to the frontier range of 6. Finally the bimetallic system in fragment 6 is left with the following frontier orbitals. $1a_1(\sigma)^2$, $b_2(\delta)^2$, $1b_1(\delta^*)^2$, $2a_1(\delta)^0$, $a_2(\delta^*)^0$, $3a_1(\pi)^0$ and $2b_1(\pi^*)$ (Scheme 1). The HOMO and LUMO are very close in energy.

Molecular orbitals of 1 are constructed as shown in eqn. (3). Fragment 7 ($\eta\text{-S}_2\text{C}=\text{S}$) has a high lying



Scheme 1. Frontier MOs of the fragment 6.

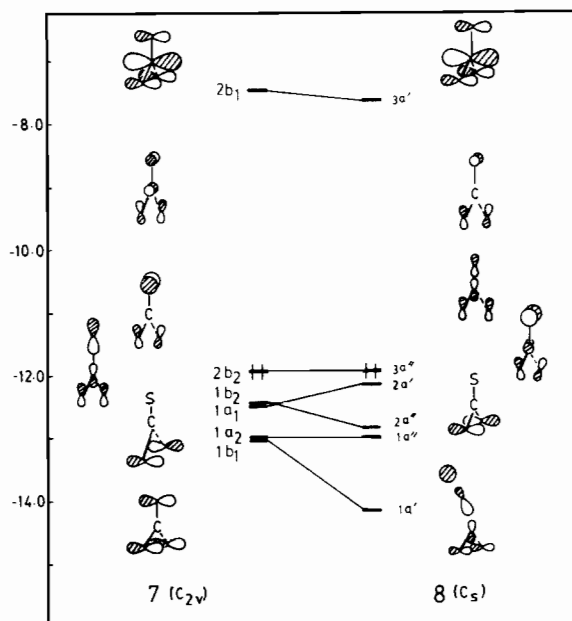


Fig. 2. Correlation between the MOs of fragments 7 and 8.

LUMO ($2b_1$) orbital with the remaining orbital pattern as shown on the left hand side of Fig. 2. Its interaction with 6 is shown on the left hand side of Fig. 3. LUMO $2a_1$ of 6 gets destabilized due to its interaction with $1a_1$ of 7, to become HOMO in 1. $2b_1$ (HOMO) in 6 gets slightly stabilized because of its interaction with $2b_1$ of 7. $1a_2$ of 7 interacts with $1a_2$ of 6 resulting in the high lying LUMO of compound 1. $2b_2(\delta)$ of 6 is pushed up in energy. Compound 1 has a metal–metal σ bond with the following d electron configuration, $1b_1(\delta^*)^2$, $1a_1(\sigma)^2$, $2a_1(\delta)^2$, $1a_2(\delta^*)^0$, $2b_1(\sigma^*)^0$, $2a_2(\pi^*)^0$ in the frontier region.

Electronic Structure of CpMo($\mu\text{-S}_2(\text{CSCH}_3)$ – $(\mu\text{-S}_2\text{C}_2\text{H}_2)\text{MoCp}^*$ (2) (symm.))

Methylation of complex 1 leads to 2 [4]. The interaction diagram for the construction of compound 2 (symmetric bridging) as represented by eqn. (4) (Fig. 3, right) is essentially similar to that in

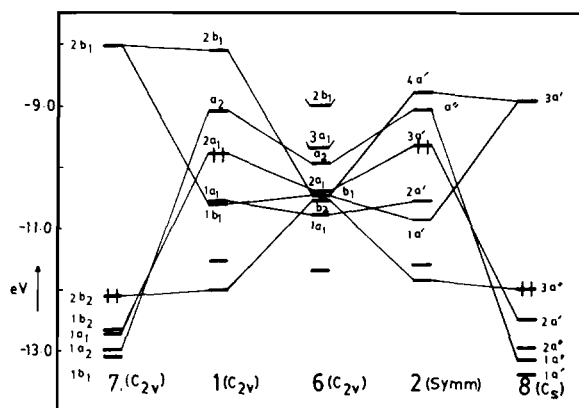
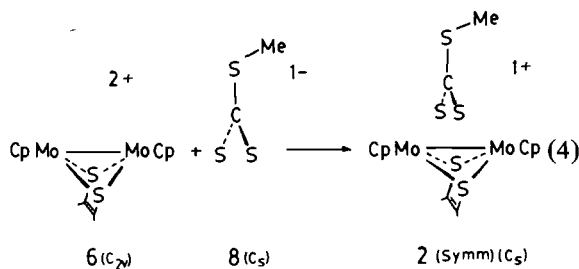


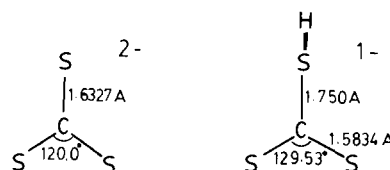
Fig. 3. Interaction diagram showing the construction of the MOs of compounds 1 and 2 (symm.).



the construction of compound 1. This is evident from Fig. 3. Small differences observed in the interaction diagrams (Fig. 3 left and right) arise from the differences in the ligand orbital patterns (Fig. 2). Increase in the energy of a_1 in 8 over that in 7 causes destabilization of HOMO in compound 2 (symm). Energy of LUMO is unchanged. $2b_2(\delta)$ of 6 is pushed out of the frontier range in this case also. Other interactions do not produce any major changes.

Nature of the Bridging Ligands

MNDO calculations [10] are performed on $(S_2C=S)^{-2}$ and the model $(S_2C-SH)^{-}$ to find out the deviations from the trigonal planar arrangement in the $S_2C=S$ group on methylation. In S_2C-SH^- , the $(H)S-C-S$ angle decreases and the $S-C-S$ angle increases to 130.2° . This is mainly due to the decrease in negative charge and the localization of the charge in the two free C-S bonds. A similar increment in the $S-C-S$ angle is expected when compound 1 is methylated at the terminal sulfur atom (eqn. (1)). Scheme 2 shows the optimized geometries of S_3C^{-2} and $(S_2CSH)^{-}$ ligands in the absence of metallic template. Figure 2 gives a correlation between the orbitals in the two ligands. The energies used in Fig. 2 are obtained using EH calculations. MNDO calculations on $S_2CH_2^{-2}$ and S_2CH^- , as expected, gave a larger $S-C-S$ angle in the latter due to the conversion from sp^3 to sp^2 hybridization around carbon. Thus ligand 8 should provide a larger claw size than ligand 7.



Scheme 2. Optimized (MNDO) geometric parameters for ligands 7 and 8.

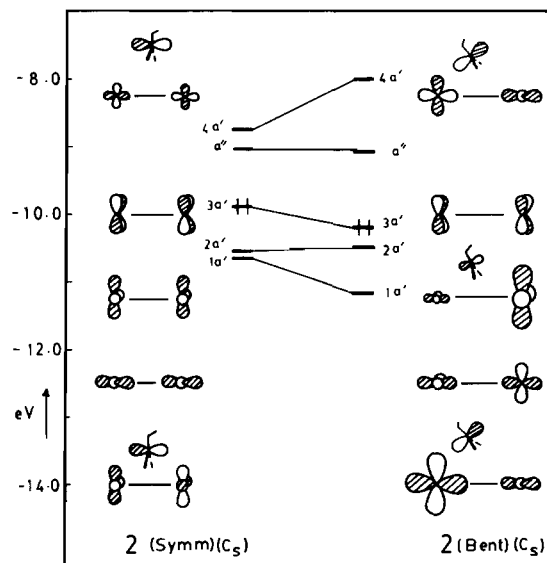


Fig. 4. Walsh diagram showing the tilting process of the bridging ligand in 2 (symm.) to 2 (bent).

Since the bimetallic template is symmetric, a trihapto bridge which is symmetrical along the M-M axis is anticipated in compound 2. However the X-ray structure of 2 indicates that the bridging ligand is tilted towards one of the metals [4]. This tilt in compound 2 can be explained on the basis of molecular orbital picture as follows. On methylating the terminal sulfur atom, the π lone pair on the sulfur of the SCH_3 group is orthogonal to the p orbital on carbon. The π system of the $CS_2(SR)$ will be more free to bind as a hapto-3 ligand, by bending towards one of the metals [7] (Fig. 4). However, the donation from the two sulphur atoms to the remaining metal demands a decrease in the SCS angle, leading to the experimental value of 108.4° [4]. The stabilization of 2 (bent) arises mainly because of the increased metal-carbon(p) π type of coordination. On bending the bridging ligand, the carbon atom of the bridging ligand comes close to one of the metals and this increases the interaction between the HOMO of fragment 6 and LUMO of the fragment 8. As a result, in the compound, $4a'$ goes up in energy and $1a'$ gets stabilized resulting in strong metal carbon interaction (Fig. 4). HOMO $3a'$ also gets stabilized due to development of the bonding interaction

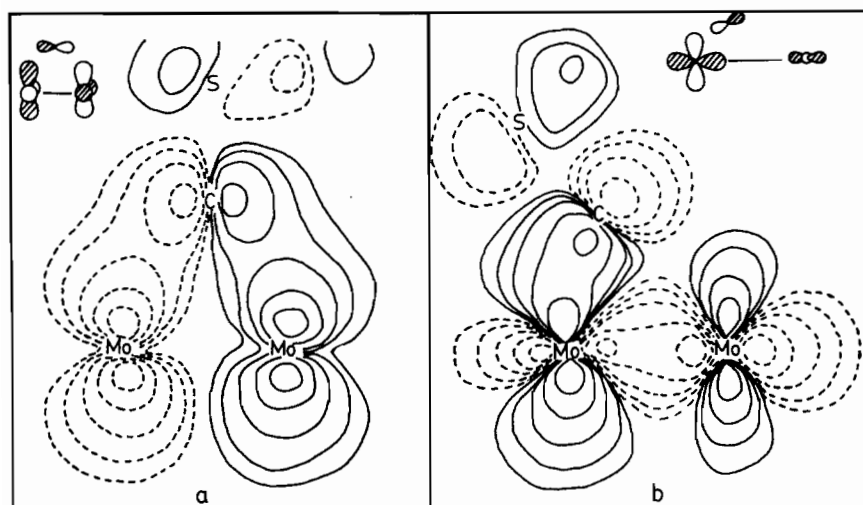


Fig. 5. Contour plots showing the metal carbon interactions in **2** (symm.) and **2** (**1a'** of Fig. 4): (a) **2** (symm.) (b) **2** (bent).

between the bridging ligand and fragment **6**. The metal carbon bonding interaction in **1a'** is clearly shown in the contour diagram (Fig. 5). This also shows an additional benefit obtained from bending. There is a definite increase in the M–M bonding. The amount of stabilization in **2** on tilting is not very large as shown by the sum of one electron energies. This supports the fluxional behaviour of the bridging ligand in solution [4]. Moreover, the carbon atom in **2** does not adopt the sp^3 hybridization [4]. This clearly indicates the Mo–C bond is not a pure M–C σ bond but an η^3 type (π interaction) of bonding between M_1 and $S_2C-SCH_3^-$. This would facilitate the fluxional behaviour of the bridging ligand. Bending the bridging ligand ($\mu-S_2C=S$) in compound **1** leads to destabilization. This is mainly due to the development of antibonding interaction between metal and the terminal sulfur atom.

This argument for the tilting is further supported by the fact that in the compound $CpMo(\mu-S_2CCH_3)(\mu-S_2CH_2)MoCp^+$ (**3**) $S_2C-CH_3^-$ is tilted towards one of the metals while $S_2CH_2^{2-}$ is symmetrical with respect to the M–M bond [6]. With the sp^2 hybridization around carbon, the π orbitals of $S_2CSCH_3^-$ are more diffused. Because of the rigid nature of the metal terminal ligand environment, the bridging ligand has to bend to gain stability [7]. This clearly indicates that a more diffuse bridging ligand like **8** prefers a bent geometry rather than a symmetric one as in **2** and bridging ligands $S_2C=S$ and S_2CR_2 prefer a symmetric arrangement.

Conclusions

Study of the electronic structure of compounds **1**, **2** and **3** shows that unsymmetrical nature of the η^3 bridging units in **2** and **3** is due to overcrowding of

the terminal ligand environment. The strong interaction developed between carbon and the metal orbitals is assisting the tilt. The sp^2 hybridization present on the carbon atom in the bridging unit facilitates the fluxional behaviour.

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Appendix

The geometric parameters used in the calculations are as follows. Mo–Mo: 2.624 Å; Mo–Cp: 2.000 Å; C₁–S₁: 1.752 Å; C₁–S₂: 1.620 Å (in 1) and 1.755 Å (in 2); C₁–C₂: 1.243 Å (in 3) S₂–C₁–S₂: 108.0° (in 1), 108.4° (in 2) and 108.9° (in 3). Tilting of the bridging unit in 2 and 3 is performed so as to get almost planar arrangement of Mo₁ and the three atoms (S–C–S) of the bridging unit. The Extended Hückel parameters are adopted from the literature [11j].