Theoretical Studies on $(\mu$ -S₂CR) Bridged Cyclopentadienyl Molybdenum Dimers

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Abstract

The electronic structures of $CpMo(\mu-S_2C_2H_2)(\mu S_2C=S)MoCp$, (1), $CpMo(\mu-S_2C_2H_2)(\mu-S_2CSMe)-MoCp^+$ (2) and $CpMo(\mu-S_2C_2H_2)(\mu-S_2CCH_3)MoCp^+$ (3) are studied. Electronic factors control the unsymmetrical bridging nature of the η^3 bridging units in 2 and 3.

Introduction

Binuclear transition metal complexes with small bridging groups are of current interest [1]. A three atom bridging group may adopt either a symmetrical or an unsymmetrical arrangement to the two metals [2-6]. The effect is particularly pronounced when the bridging ligand is C_3R_3 [3]. The group CS_3 also provides interesting dynamics in the compound $CpMo(\mu-S_2C_2H_2)(\mu-S_2C=S)MoCp$, (1) ($Cp = C_5H_5$) [4]. Reaction of this compound with methyl iodide gives an iodide salt 2 (eqn. (1)) [4]. In 1 the CS_3 group bridges the two metals symmetrically [5],



but in 2 the $CS_2(SCH_3)$ group tilts towards one of the metals. In fact in solution the bridging ligand in 2 shows some fluxional behaviour [4]. Similarly in compound $CpMo(\mu$ - $S_2C_2H_2)(\mu$ - $S_2CCH_3)MoCp^+$ (3) the bridging ligand S_2CMe , which is supposed to be obtained from a possible $(\mu$ - $S_2CR_2)$ bridging unit, also tilts towards one of the metals [6]. On the other hand, the S_2CH_2 unit in 3 adopts a perfectly symmetric disposition along the metal-metal axis. We have shown that the C_3R_3 bridging ligands tilt pre-



dominantly due to electronic factors [7]. In the unsymmetrical metal environments, the directional preferences of the bridging C_3R_3 unit are controlled by the diffused nature of the metal orbital lobes. The C₃R₃ group tilts towards the metal which provides more diffuse orbitals [7]. Hence in $(\eta^4 - C_4 Ph_4)Ni(\mu C_3Ph_3$)Ni(η^5 - C_5Ph_5) [2k], the bridging C_3Ph_3 unit tilts towards Ni(η^4 -C₄Ph₄). When the metal environment is symmetrical, the freedom available to the terminal ligands on the metal controls the tilt. When the terminal ligands are free to pyramidalize, the bridging unit adopts the symmetric disposition. When the freedom of the terminal ligands is restricted by another bridging unit, the C₃R₃ ligand prefers to bend in order to gain better overlap with the two metals [7]. For example, the C₃R₃ unit in (CH₂-SiMe₃)₂W(µ-CPhCPhCSiMe₃)(µ-CSiMe₃)W(CH₂- $SiMe_3)_2$ is bent towards one of the metals in the solid state [2s, t].

In this article we study the electronic structure of 1, 2 and 3 searching for the factors responsible for the bending of the η^3 bridging ligands observed in 2 and 3. The molecular orbitals from the fragment molecular orbital (FMO) method [8] within Extended Hückel formalism [9] is used in our analysis. MNDO calculations [10] are used to study the bridging units in detail.

Results and Discussion

Electronic Structure of $CpMo(\mu-S_2C_2H_2)(\mu-S_2C=S)$ -MoCp (1)

The molecular orbital patterns in bimetallic systems are well documented in the literature [11, 12]. We build the electronic structures of complexes

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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 $1b_2$ (nonbonding 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 (η -S₂C=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 (2b₁) 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 2a₁ of **6** gets destabilized due to its interaction with 1a₁ of 7, to become HOMO in **1**. 2b₁ (HOMO) in **6** gets slightly stabilized because of its interaction with 2b₁ of 7. 1a₂ of 7 interacts with 1a₂ of **6** resulting in the high lying LUMO of compound **1**. 2b₂(δ) of **6** is pushed up in energy. Compound **1** has a metal-metal σ bond with the following d electron configuration, 1b₁(δ^*)², 1a₁(σ)², 2a₁(δ)², 1a₂(δ^*)⁰, 2b₁(σ^*)⁰, 2a₂(π^*)⁰ in the frontier region.

Electronic Structure of $CpMo(\mu-S_2(CSCH_3)-(\mu-S_2C_2H_2)MoCp^+(2)$ (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 $(S_2C-SH)^{-1}$ 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 type lone pair on the sulfur of the SCH₃ group is orthogonal to the p orbital on carbon. The π system of the CS₂(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 la' 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 (la' 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 (μ -S₂C=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 $CpMo(\mu$ -S₂CCH₃)- $(\mu$ -S₂CH₂)MoCp⁺ (3) S₂C-CH₃⁻ is tilted towards one of the metals while S₂CH₂²⁻ is symmetrical with respect to the M-M bond [6]. With the sp² hybridization around carbon, the π orbitals of S₂CSCH₃⁻ 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 S₂C=S and S₂CR₂ 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.

Acknowledgements

UGC is thanked for financial assistance (SRF to B.V.P.). The Computer centre at the University of Hyderabad is thanked for computational facilities. C.S.R. thanks the Directorate of Higher Education, A.P. for permitting him to attend the M. Phil. programme.

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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; C_1-S_1 : 1.752 Å; C_1-S_2 : 1.620 Å (in 1) and 1.755 Å (in 2); C_1-C_2 : 1.243 Å (in 3) $S_2-C_1-S_2$: 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].