Organometallics **1993,** *12,* 4267–4268

Structure of μ-S$_2$CPR$_3$ Complexes. Direction of Tilting and Compatibility of Fragment Orbitals

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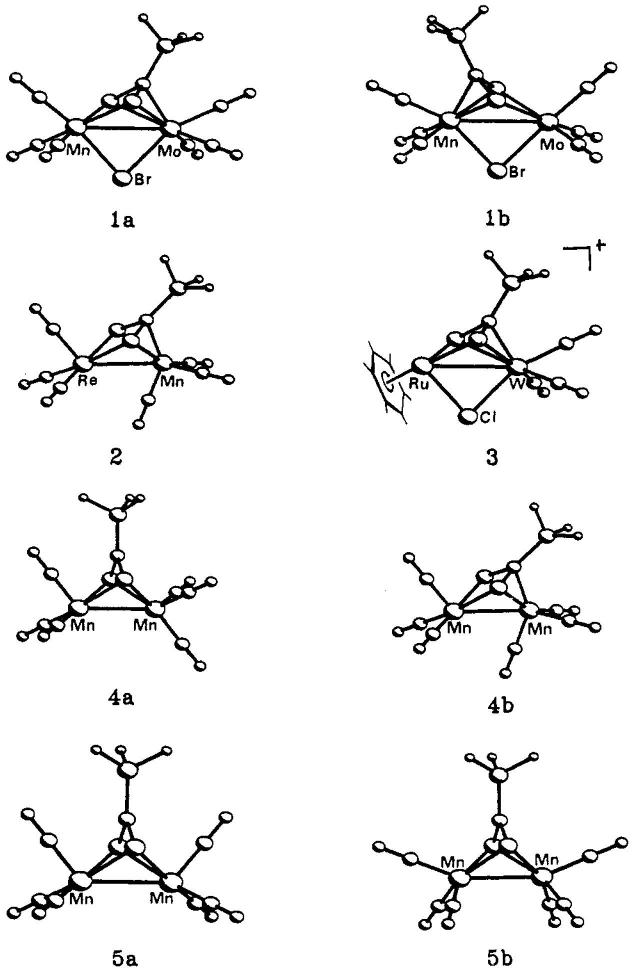
Received May 13, 1993[●]

Summary: The concept of compatibility of orbitals in overlap has been used to explain the observed preferential tilting of the μ-S$_2$CPR$_3$ ligand on a bimetallic template toward the metal that provides more diffuse orbitals.

Recently in this journal, the synthesis and X-ray structure of [(CO)$_3$Mn(μ-Br)(μ-S$_2$CPR$_3$)Mo(CO)$_3$] (R = Pr^i, Cy; **1a**) with a μ_3-bridging substituent were published.[1] The straddling μ-S$_2$CPR$_3$ group was tilted toward Mo, even though it was equally possible for the bridging group to tilt toward Mn (**1b**). In contrast, the μ-S$_2$CPR$_3$ group in [(CO)$_3$Mn(μ-S$_2$CPCy$_3$)Re(CO)$_3$] (**2**) prefers to tilt toward Mn rather than Re,[2] "the reasons for such discrimination remaining, so far, unclear".[1a] Another example along this line is [(η^6-C$_6$Me$_6$)Ru(μ-Cl)(μ-S$_2$CPCy$_3$)M(CO)$_3$]$^+$ (M = Mo, W; **3**) where the μ-S$_2$CPCy$_3$ group tilts toward Mo or W.[3] In homobinuclear complexes, the bridging group tends to be symmetrical if the metal coordinations are symmetrical.[4] A model based on the optimization of overlap was used to explain the preference of the μ-S$_2$CR group in homodinuclear complexes for symmetrical and tilted structures.[5] An apparent failure of this model came to light with the synthesis of [(CO)$_3$Mn(μ-S$_2$CPCy$_3$)Mn(CO)$_3$][6a] (**4b**) and [(CO)$_2$Mn(μ-S$_2$CPCy$_3$)(μ-dppm)Mn(CO)$_2$].[6b] Though a symmetrically bridged structure (**5**) was anticipated for **4b**, the observed structure had the bridging group tilted toward one of the Mn atoms.

In this communication, we provide a simple qualitative explanation for the specificity shown in the tilting of μ-S$_2$CPR$_3$ ligands in **1**–**3**. We also predict the direction of tilting in yet to be characterized systems. The reasons for the discrepancy between the experimental geometry and that anticipated by the bonding model for **4** are also analyzed. Extended Hückel calculations,[7] supported by symmetry and overlap of orbitals involved, are used in arriving at these results. The geometric parameters used are taken from reported crystal structures, approximated to C_s symmetry.[8]

Chart I



1a 1b 2 3 4a 4b 5a 5b

We have shown that the σ and π parts of the allyl type ligands such as C$_3$R$_3$ and S$_2$CR have very different orbital spans.[5] The σ orbitals in a bridging situation are hybridized toward the metal–metal axis, while the π-MO's are pure p orbitals not well directed toward the metal. When the metal environments are different, as in heterobinuclear complexes, the metal fragment with more diffuse orbitals would prefer to interact with the π face of the S$_2$CR ligand. The σ type orbitals, which are more directed, would interact with the metal fragment that has more contracted orbitals.

In complexes **1**–**3**, the two metals in each are different. In **1**, the bridging ligand is tilted toward molybdenum. Extended Hückel calculation on **1a** and the hypothetical structure **1b** showed **1b** to be less favored by 0.6 eV. Single-point ab initio calculation using the LANL1MB basis[9a] also follows the same trend (**1a** is more stable by 4.7 eV than **1b**).[9b] An idea of the diffuse nature of the MO's

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[●] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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(8) For the purposes of calculation, where performed, the PH$_3$ ligand was considered instead of PR$_3$.

0276-7333/93/2312-4267$04.00/0

Table I. s- and d-Orbital (Double-ζ) Exponents for Various Metals in Complexes 1–3

atom	exponent		ref
	s	d1, d2	
Mn	1.800	5.150, 1.900	10a
Mo	1.960	4.540, 1.900	10a
Re	2.398	5.343, 2.277	10b
Mn	1.800	5.150, 1.900	10a
Ru	2.080	5.380, 2.300	10a
W	2.341	4.982, 2.068	10b

obtained from their respective d-orbital exponents (Table I)[10] could also serve as a rationale for the observed selectivity without any effort put into computation. A larger exponent indicates the orbital to be less diffuse. Thus, Mn with d-orbital exponents larger than Mo (Table I) prefers to interact in a σ fashion with the bridging ligand so that **1a** is formed exclusively. In **2**, Mn provides more diffuse orbitals than Re and, hence, the π face of the S_2CPR_3 ligand binds to Mn (Table I).[11] Similarly, W with more diffuse orbitals than Ru prefers structure **3**. Obviously these arguments work best when the terminal ligands on the two metals are similar. Further evidence for this overlap control on the direction of tilting can be obtained from the structures of $[(\eta^5\text{-}C_5R_5)Ni(\mu\text{-}C_3Cl_3)Ni(\eta^4\text{-}C_4R_4)]$ (**6**).[5,12] The frontier orbitals of C_5R_5Ni are less diffuse than the frontier orbitals of C_4R_4Ni.[5b] Thus, the C_3R_3 group tilts to the side of C_4R_4Ni, as is found experimentally.

While two different ligands on the homobinuclear complex **6** make the metal centers different from each other, leading to an unsymmetrically bridged complex, the tilted structure in **4b**, where the two sets of ligands are identical, is puzzling. A closer analysis of the crystal structure is revealing.

The crystal structure of **4b** clearly indicates a staggered arrangement of the M_2L_6 unit, while the other reported crystal structures in the literature with symmetrical bridging units have their M_2L_n bimetallic template in the eclipsed form.[5,10a] Such a change in conformation from the eclipsed to the staggered form alters the symmetrical nature of the frontier orbitals of the M_2L_6 frame. Another aspect revealed by the crystal structure of **4b** is that one of the $Mn(CO)_3$ units is bent significantly from the idealized staggered geometry. In all the reported complexes with symmetrical bridging groups, both metal centers pyramidazlize to the same extent. However, in **4b** only one of the metal centers is pyramidalized. The unsymmetrical nature of the metal environment forces the S_2CPR_3 unit to tilt toward the ML_n unit that provides maximum bonding. This situation is obtained by the π-allyl type interaction with the metal that has more diffuse orbitals, in this case Mn(2). A correlation between the MO's of **4a** (hypothetical structure where the $\mu\text{-}S_2CPR_3$ ligand is considered to be bridging symmetrically) and **4b** shows that there is a strong avoided crossing. The sum of one-electron energies indicates **4b** to be more favored by 3.4 eV and hence its exclusive formation.

The possibility of symmetrical bridging by the S_2CR ligand with the bimetallic template was probed by a Walsh analysis (**5a** → **5b**) for the pyramidalization around both metal centers (with the bimetallic unit in the eclipsed arrangement). When the $Mn(CO)_3$ ligands are bent by about 50° from the metal–metal axis (close to a sawhorse geometry), **5b** was favored by 2.8 eV over **5a**. Thus, in a symmetrical structure pyramidalization at both metal centers brings down the energy. With appropriate chelating ligands that can force a symmetrical bimetallic unit, symmetrically bridging complexes similar to **5b** should be possible.

Such orientational preferences (**4b** compared to **4a**) and pyramidalization around the metal center (**5b**) are not unusual for a $\mu\text{-}S_2CPR_3$ bridging ligand on a bimetallic template. A series of complexes with bridging ligands such as C_2R_2, C_4R_4, C_6R_6, and other π-electron systems have been synthesized, and a rationale for their preferential tilting has been provided by Hoffmann.[10a]

To conclude, the compatibility of orbitals in overlap accounts for the discrimination observed in the formation of complexes **1–3**. We also predict that in yet to be synthesized complexes analogous to **1** the following preferential tilting of the bridging groups may be observed. For example, in $(CO)_3Mn(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)W(CO)_3$ and $(CO)_3Re(\mu\text{-}Br)(\mu\text{-}S_2CPR_3)M(CO)_3$ (M = Mo, W), the $\mu\text{-}S_2CPR_3$ bridging ligand would tilt toward Mo and W preferentially.

Acknowledgment. E.D.J. thanks the Department of Science and Technology, New Delhi, India, for financial support. G.S. thanks the Council of Scientific and Industrial Research, New Delhi, India, for a Senior Research Fellowship.

OM9303212

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(9) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 284, 299. (b) The energy difference is large, because **1b** is a hypothetical structure with the geometrical parameters of **1a**. Further, **1** is not an optimized structure at this level. This calculation was done mainly to show that the trends are reproduced at various levels of theory.

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(11) The observed crystal structure is favored over the hypothetical complex (where the bridging ligand is tilted towards Re) by 0.4 eV by EH calculation.

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