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Rotational isomerism in *bis* carbene MoL_4 complexes: A theoretical study

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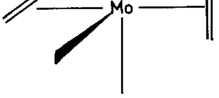
LCAO-MO-SCF calculations are reported for the different stereoisomers of the $Mo(CO)_4(CH_2)_2$ and $Mo(CO)_4[C(NH_2)_2]_2$ systems. The substitution of the hydrogen atoms by the amino groups in the carbene ligands leads to an almost zero rotational barrier. Steric interactions are therefore expected to govern the barrier for diaminocarbene ligands which are more bulky than $C(NH_2)_2$. The rotational isomerism in these *bis* carbene MoL_4 systems is also discussed in connection with the isolobal analogy between CH_2 and C_2H_4.

Key words: Carbene rotational barriers—Isolobal analogy—*Ab-initio* SCF calculations.

Introduction

There have recently been some theoretical and experimental studies devoted to the stereochemistry of *bis* olefin- and *bis* carbene-ML_4 complexes, where M is a d^6 metal atom [1]. More specifically the theoretical prediction [1] that the most stable conformation for $Mo(PH_3)_4(C_2H_4)_2$ and $Mo(CO)_4(C_2H_4)_2$ has the two ethylene ligands mutually perpendicular and eclipsing the Mo—P bonds as in **1** has been corroborated very recently by the X-ray crystal structure of the



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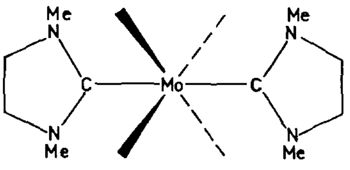
$Mo(PMe_3)_4(C_2H_4)_2$ system [2] ($Me{=}CH_3$). Since the carbene ligand CR_2 is isolobal [3] to the olefin C_2H_4 or C_2R_4, the same stereochemistry was anticipated for *bis* carbene ML_4 complexes [4]. Yet an X-ray crystal structure determination [5] of the *bis* carbene system *trans*-$Mo(CO)_4[CN(Me)CH_2CH_2NMe]_2$ has revealed the opposite stereochemistry, the two carbene ligands being mutually eclipsed and staggering the Mo—C bond, as shown in **2**. This striking result therefore calls for a more thorough theoretical study of the carbene case (as opposed to the ethylene case) to account for the experimental result and for the apparent failure of the isolobal analogy concept. A better understanding of alcene and carbene rotational barriers is also desirable in connection with the olefin metathesis reaction. Here we report the results of LCAO-MO-SCF calculations [6] carried out on the *trans*-$Mo(CO)_4(CH_2)_2$ and the *trans*-$Mo(CO)_4[C(NH_2)_2]_2$ systems [11], the latter one being a closer model of the *trans*-$Mo(CO)_4[CN(Me)CH_2CH_2NMe]_2$ complex. We first proceed through the determination of the rotational barriers of the carbene ligands in these two systems. The comparison between the corresponding results is used to trace the role of the heteroatom in the carbene ligand. This is analyzed in terms of orbital interactions. The confrontation of the stereochemistry, as determined by the calculations, with the experimental one obtained from the X-ray crystal structure is then used to single out the steric factors.



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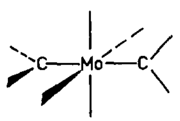
Results and discussion

There are four possible stereoisomers for the $Mo(CO)_4(CR_2)_2$ system. For the sake of comparison we shall adopt the same notations which were used in the previous theoretical study of the $MoL_4(C_2H_4)_2$ system [1], namely staggered-eclipsed (**3**), eclipsed-eclipsed (**4**), staggered-staggered (**5**) and eclipsed-staggered (**6**). As evidenced from the corresponding relative stabilities for the



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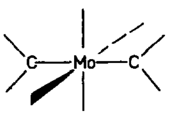

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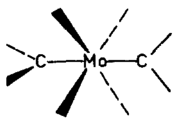

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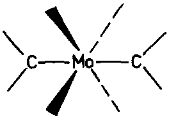

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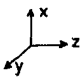
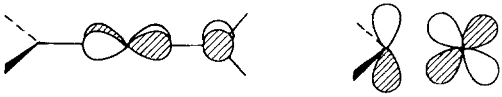


Table 1. Relative energies (in kcal/mole) for the different stereoisomers of the $Mo(CO)_4(CH_2)_2$, $Mo(CO)_4(C_2H_4)_2$ and $Mo(CO)_4[C(NH_2)_4]_2$ systems

Conformation		$Mo(CO)_4(CH_2)_2$ [a]	$Mo(CO)_4(C_2H_4)_2$ [b]	$Mo(CO)_4[C(NH_2)_2]_2$ [a]
3	*se*	0	0	—
4	*ee*	11.0	6.3	—
5	*ss*	0.4	5.0	0
6	*es*	10.9	—	0.3

[a] Present computation
[b] Values quoted in Ref. [1]

$Mo(CO)_4(CH_2)_2$ system (see Table 1 [12]) the most stable conformation is *se*, i.e. with the two carbene ligands mutually perpendicular and eclipsing the Mo—C bonds. The same result was obtained for the $Mo(CO)_4(C_2H_4)_2$ and $Mo(PH_3)_4(C_2H_4)_2$ systems [1]. As for the $MoL_4(C_2H_4)_2$ case, the rationale behind the mutually staggered conformation of the two carbene ligands lies in a greater stabilization obtained from the two interactions between the empty π orbital of each carbene ligand and the occupied d_π orbitals of the metal atom (see **7**), compared to the stabilization obtained from the interaction of the two π carbene ligand orbitals and one d_π metal orbital of appropriate symmetry (see **8**). This feature of the two acceptor orbitals which avoid to share the same donor orbital is now well recognized [1, 13].



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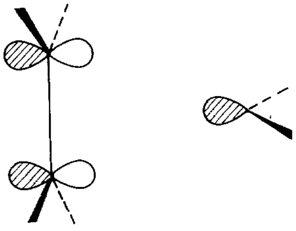
That the same type of orbital interactions were put forth to explain the preference for the mutually staggered C_2H_4 ligands in the $MoL_4(C_2H_4)_2$ system is an illustration of the isolobal analogy between C_2H_4 and CH_2 which is based on the similarity of the $\pi_{C_2H_4}$ and σ_{CH_2} occupied orbitals (**9**) on one hand, and of the



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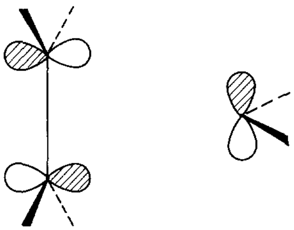

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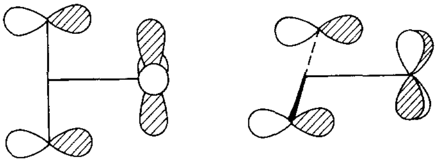
$\pi^*_{C_2H_4}$ and π_{CH_2} empty orbitals (**10**) on the other hand. The interaction diagram for the staggered-eclipsed structure (**3**) of the $Mo(CO)_4(CH_2)_2$ system shown on the Fig. 1 is indeed similar to the diagram derived for the *bis* ethylene case [1]. There is a difference however between the $\pi_{C_2H_4}$ orbital and the σ_{CH_2} orbital since the former may interact with *d* metal orbitals of δ symmetry as shown in **11** whereas the latter which is of cylindrical symmetry has no overlap and hence



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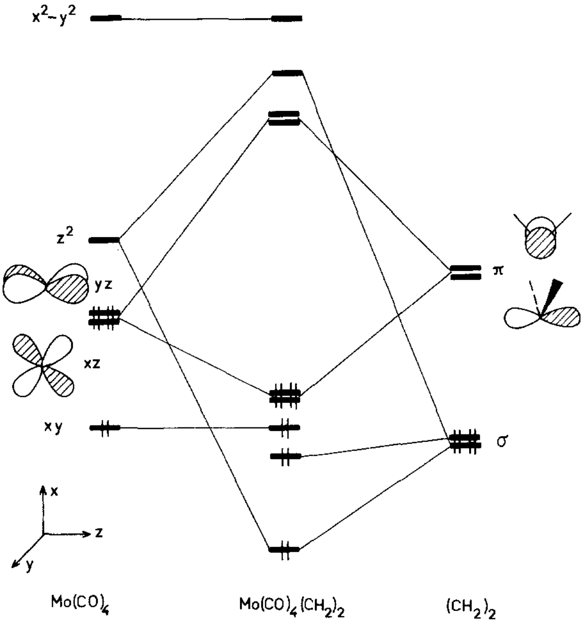


Fig. 1. Orbital interaction diagram between the valence orbitals of the planar $Mo(CO)_4$ fragment and the two CH_2 fragments

does not interact with the δ metal *d* orbitals. Indeed such interactions of δ type could explain the destabilization of the *ss* stereoisomer with respect to the *se* stereoisomer of the $Mo(CO)_4(C_2H_4)_2$ system (Table 1) but are not present in the $Mo(CO)_4(CH_2)_2$ system, therefore leading to the same relative stability for the *ss* and *se* stereoisomers and for the *ee* and *es* stereoisomers as well (Table 1).

The calculations of the $Mo(CO)_4(CH_2)_2$ system therefore account for the quasi absence of rotational barrier of the carbene ligands with respect to the equatorial carbonyl ligands. But they fail to predict the mutual orientation of the two axial $[CN(Me)CH_2CH_2NMe]$ ligands. The validity of the CH_2 model ligand is therefore questionable. Calculations were carried out on the $Mo(CO)_4[(C(NH_2)_2]_2$ system in order to test this hypothesis on the two structures **5** and **6** having both the two carbene ligands staggered with respect to the equatorial carbonyl ligands (as experimentally found) but being different in their mutual orientation. As seen from Table 1, both stereoisomers are almost equal in energy [14], the *ss* conformation being still slightly more stable. The decrease in the rotational barrier, when

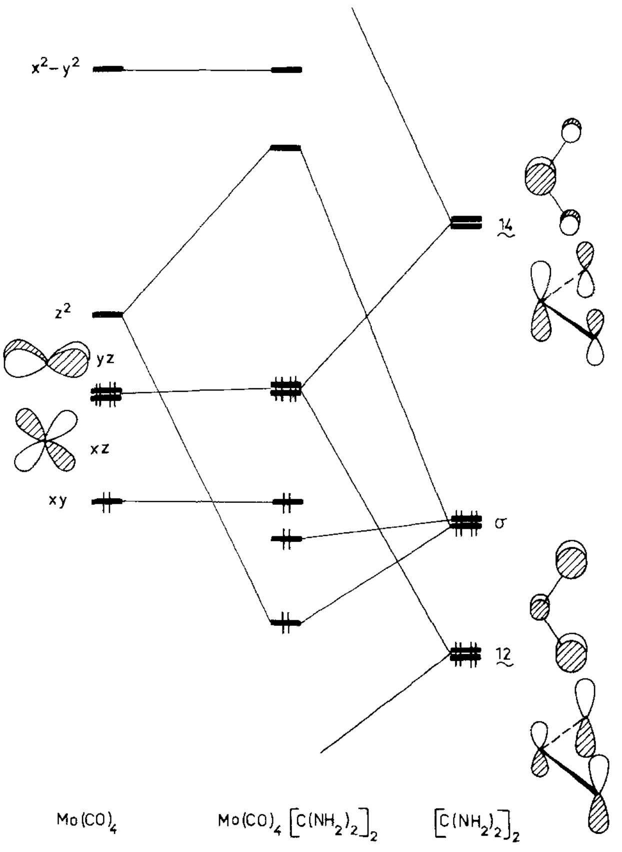
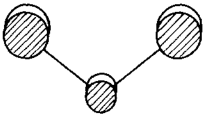


Fig. 2. Orbital interaction diagram between the valence orbitals of the planar $Mo(CO)_4$ fragment and the two $C(NH_2)_2$ fragments

going from CH_2 to $C(NH_2)_2$, is traced to the interaction of the π orbitals of the heteroatoms with the π orbital on the carbon atom. The result is the familiar allyl-like three orbital pattern shown in **12–14**, where **12** and **13** are occupied and **14** empty [15]. Of these three orbitals, **12** and **14** interact with the occupied



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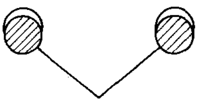

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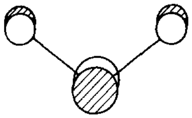

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d_π orbital of corresponding symmetry within again a three orbital mixing pattern shown on the interaction diagram of the Fig. 2 (for the eclipsed-staggered case). The middle orbital (i.e. the d_π orbital, the energy variation of which is crucial for the rotational barrier, changes little in energy, whatever the conformation of the two carbene ligands is. The consequence of this feature is an almost zero rotational barrier.

It follows that the eclipsed staggered conformation of the *trans*-$Mo(CO)_4[CN(Me)CH_2CH_2NMe]_2$ system is probably governed by the steric interaction between the methyl ends of the carbene ligand and the equatorial ligands: as pointed out by Lappert et al. [5] the unequal C—Mo—C equatorial angles minimize these interactions. But this holds only for the eclipsed arrangement of the two carbene ligands since the staggered arrangement should lead to equal C—Mo—C equatorial angles, hence with greater steric carbonyl-methyl interactions.

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6. The *ab-initio* calculations were carried out with the Asterix system of programs [7] using the following basis set: (15, 10, 8) contracted to 6, 4, 4 for Mo [8], (9, 5) contracted to 3, 2 for the first row atoms [9] and (4) contracted to 2 for H [10]. The contracted basis set is a minimal set for the inner shells, a double-zeta set for the valence shell and a triple-zeta for the 4*d* of Mo
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11. The geometries were set as follows: for the $Mo(CO)_4$ moeity, an idealized D_{4h} geometry was chosen. The Mo—C(CO) and Mo—C (carbene) bond lengths were set to 2.001 and 2.232 Å respectively on the basis of the experimental structure of the $Mo(CO)_4CN(Me)CH_2CH_2NMe_2$ system [5]. For the $C(NH_2)_2$ ligand the C—N bond lengths and the N—C—N bond angle were set respectively to 1.34 Å and 106.6° (this is also based on the experimental structure of Ref. [5]). The C—H and N—H bonds were fixed at 1.13 and 1.0 Å in CH_2 and NH_2 respectively
12. The corresponding total energies (in a.u.) are the following: *se*, −4496.3444; *ee*, −4496.3268; *ss*, −4496.3438; *es*, −4496.3271
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14. The corresponding total energies (in a.u.) are; *ss*, −4716.4295; *es*, −4716.4290
15. The polarization of the bonding orbital Scheme 12 is reversed however, due to the greater electronegativity of the nitrogen atom as compared to the carbon atom

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