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 (48) The Löwdin process of defining net atom charges is not as arbitrary as the partitioning process used in defining Mulliken net atom charges. Thus Löwdin net atom charges are employed here. The two charge quantities generally parallel each other.
 (49) Destabilization energies are calculated as the difference in total energy (eV) between the azolium ion and conjugate base. Relative destabilization energies reflect the positive change in internal energy that accompanies deprotonation.
 (50) The average d population for each orbital was 0.0501 and 0.0377, respectively.
 (51) The average Q_{net} value for the N -methyl protons of the imidazolium is 0.0341, while the average C -methyl proton charge is 0.0435. The average Q_{net} of imidazole N -methyl protons is 0.0114.

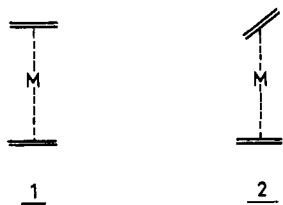
Stereochemistry of *trans*- $\text{MoX}_4(\text{C}_2\text{H}_4)_2$ and $\text{MoX}_4(\text{O}_2)_2$ Complexes

C. Bachmann, J. Demuyck, and A. Veillard*

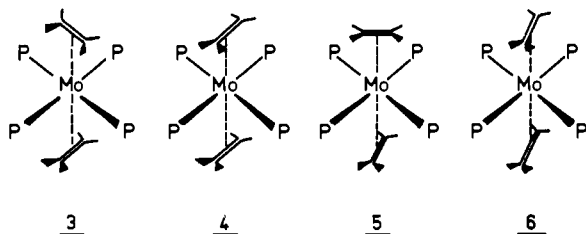
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Abstract: The relative energies of the different conformations for the complex $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ are discussed on the basis of ab initio LCAO-MO-SCF calculations of double- ζ quality at the level of the valence shells. The most stable conformation has the two ethylene ligands mutually perpendicular and eclipsing the Mo-P bonds. This is rationalized on the basis of the metal-ligand electronic interactions $4d-\pi^*$ and $4d-\pi$ and of the steric effects. The computed barrier of 16 kcal/mol for the rotation about the metal-olefin bond compares well with the reported experimental value of 15.3 kcal/mol. The relative stabilities of the various conformations are also discussed as a function of the number of d electrons and of the nature of the equatorial ligands (with CO replacing PH_3). Similar arguments are used to rationalize the stereochemistry of the diperoxomolybdenum-(VI) porphyrin.

Transition metal complexes with *trans* olefinic ligands may show a variety of structures, with the olefinic ligands either eclipsed (**1**) or staggered (**2**). Furthermore, if the metal



atom is hexacoordinated with a quasi-octahedral structure, the relative orientation of the axial olefinic ligands with respect to the equatorial ligands may be either eclipsed or staggered as in the four structures 3-6. We denote these structures se (for



staggered-eclipsed, **3**), ee (eclipsed-eclipsed, **4**), ss (**5**), and es (**6**). Osborn et al. assigned a se structure to the molecule *trans* $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$ (diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) on the basis of the ^1H and ^{31}P NMR spectra, with the ethylene ligands staggered but eclipsing the *trans* P-Mo-P vectors.¹ They reported an estimated barrier of 15.3 kcal/mol for the

rotation about the metal-olefin bond, but did not specify the nature of the rotation motion (one may consider either a process where the two ethylene ligands remain mutually staggered such as **3** \rightarrow **5** or a process where each ethylene ligand rotates independently, for instance, **3** \rightarrow **4**). A *trans* structure has been assigned to $\text{W}(\text{CO})_4(\text{C}_2\text{H}_4)_2$ on the basis of the infrared spectra,² but detailed information regarding the stereochemistry of the ethylene ligands is lacking to our knowledge. The matrix synthesis of $\text{Cu}(\text{C}_2\text{H}_4)_2$ and $\text{Ni}(\text{C}_2\text{H}_4)_2$ has been reported recently but their structure remains unknown.^{3,4} Rösch and Hoffmann addressed the question of the relative orientation of the two ethylene ligands in bis(ethylene)nickel(0).⁵ They found the D_{2d} structure **2** favored over the D_{2h} structure **1** by 1.5 kcal/mol on the basis of an extended Hückel calculation, a consequence of the fact that the stabilization produced by the two interactions of **7** is slightly greater than the stabilization associated with **8**. However, the lack of discrimination

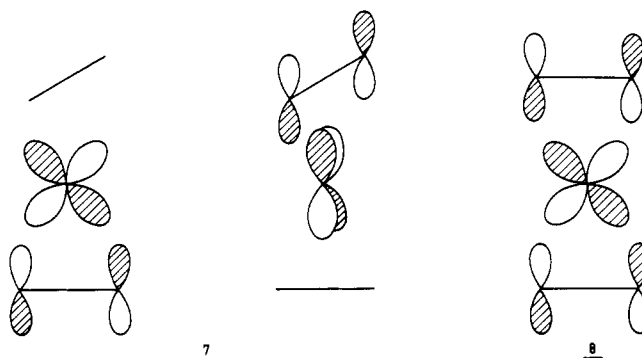


Table I. Total Energies (au) and Relative Energies (kcal/mol) of the Different Conformations

	Conformation	Total energy	Rel energy
$\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$	se	-5489.9144	0.
	ee	-5489.8922	13.9
	ss	-5489.8841	18.8
	es	-5489.8654	30.7
$\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$	se	-4572.8738	0.
	ee	-4572.8640	6.3
	ss	-4572.8659	5.0
$\text{MoCl}_4(\text{C}_2\text{H}_4)_2$	se	-5957.4130	0.
	ee	-5957.4121	0.6

in total energy was traced to the large energy gap between the metal d orbitals and the ethylene π^* orbitals (on the basis of perturbation theory, the same stabilization through d- π^* back-bonding is found when the levels d and π^* are far apart in energy, whereas structure **2** is preferred when they are close in energy). Rösch and Hoffmann reported that a reduction in the 3d- π^* energy separation produces an increasing favoring of the D_{2d} structure. Such a reduction in the d- π^* energy separation is expected when Mo(0) compounds are considered rather than Ni(0) compounds.

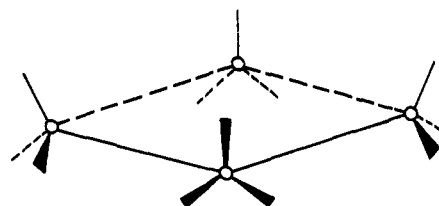
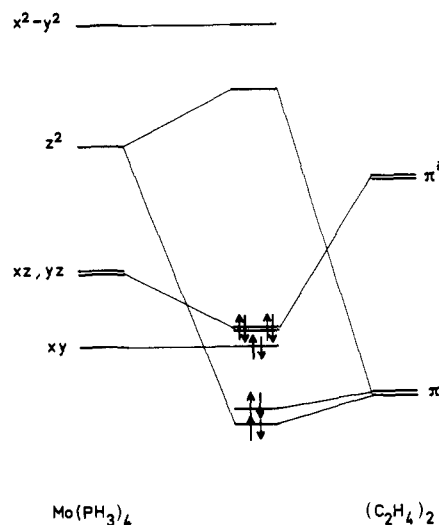
The same choice of structures may be expected for other ligands with a perpendicular mode of coordination such as the dioxygen ligand or the diazene ligand (a limited number of π complexes of diazenes have been reported⁶). The diperoxomolybdenum(VI) porphyrin shows two dioxygen ligands mutually perpendicular and eclipsing the N-Mo-N bonds.⁷ The dioxygen ligand of the peroxotitaniumoctaethylporphyrin eclipses one trans N-Ti-N vector.⁸ From an ab initio calculation for TiPO_2 (P = porphine dianion), this eclipsed structure was found more stable, by 5 kcal/mol, than the staggered structure where the projection of the dioxygen ligand in the equatorial plane bisects the cis N-Ti-N vectors.^{9,10} A D_{2d} structure with the dioxygen ligands mutually perpendicular has been proposed for tetraoxycopper, $\text{Cu}(\text{O}_2)_2$.¹¹

We report here ab initio LCAO-MO-SCF calculations for $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ (**1**) (considered as a model for $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$), $\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$ (**2**), and $\text{MoCl}_4(\text{C}_2\text{H}_4)_2$ (**3**) in order (1) to ascertain the relative stabilities of the four configurations **3-6** for Mo(0) and Mo(IV) complexes; (2) to separate the steric effects associated with the relatively bulky ligands diphos or PH_3 from the electronic effects at the level of the metal d orbitals.

Calculations

LCAO-MO-SCF calculations were carried out with the system of programs Asterix¹² using the following Gaussian basis sets: (13,9,7) contracted to [5,4,3] for molybdenum,¹³ (10,6) contracted to [4,3] for phosphorus and chlorine,¹⁴ (8,4) contracted to [3,2] for first-row atoms,¹⁵ and (4) contracted to [2] for hydrogen¹⁶ (the contracted basis set is a minimal set for the inner shells and the 5s and 5p shells of molybdenum and a double- ζ set for the valence shells).

We have used the following bond lengths and bond angles, based on the corresponding values in related molecules: Mo-P 2.50 Å (2.517 Å in $\text{Mo}(\text{CO})_4$ (*cis*-PP),¹⁷ PP = *o*-(*cis*-propenyl)phenyldiphenylphosphine, and 2.50 Å in $\text{Mo}(\text{PH}_3)_4\text{N}_2$ ¹⁸), Mo-C(ethylene) 2.40 Å (2.45 Å in $\text{Mo}(\text{CO})_4$ (*cis*-PP)¹⁷), C-C 1.40 Å (1.39 Å in $\text{Mo}(\text{CO})_4$ (*cis*-PP)¹⁷), C-H 1.10 Å, Mo-C(carbonyl) 2.06 Å (1.96-2.05 Å in $\text{Mo}(\text{CO})_4$ (*cis*-PP)¹⁷ and 2.06 Å in $\text{Mo}(\text{CO})_6$,¹⁹ C-O 1.15 Å (1.11-1.20 Å in $\text{Mo}(\text{CO})_4$ (*cis*-PP)¹⁷), P-H 1.42 Å,²⁰ Mo-Cl 2.26 Å (2.27 Å in MoCl_5 ,²⁰ 2.28 Å in MoO_2Cl_2 ,²⁰ 2.24 and 2.25 Å in $\text{Mo}_2\text{Cl}_{10}$ ²⁰). The HPH angle in the PH_3 ligand was assumed tetrahedral. For computational reasons, a rigid structure with


Figure 1. The assumed conformation for the four equatorial PH_3 ligands in $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$.

Figure 2. A simplified interaction diagram for $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$.

a C_{4v} symmetry (Figure 1) was assumed for the set of equatorial ligands in $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$, namely, the phosphine ligands were not allowed to rotate freely about the Mo-P bond. It is worth noting that, in the structures se and ee of $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$, the shortest distance between a hydrogen atom of a phosphine ligand and a hydrogen atom of an ethylene ligand is 2.20 Å but falls to 1.72 Å in the structures ss and es. This latter distance is much shorter than the estimated sum of 2.4 Å of the van der Waals radii.^{21,22} The x and y axes correspond to the equatorial bonds and the z axis passes through the midpoints of the two C-C bonds.

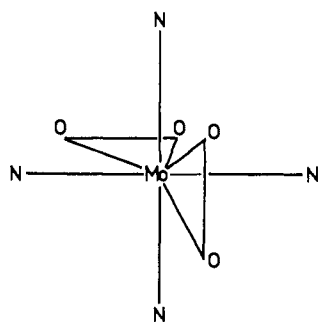
The computed total energies and the relative energies of the different conformations are reported in Table I for the three systems considered.

Discussion

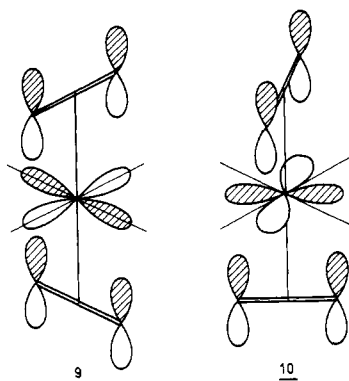
The most stable conformation for $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ is se with the two ethylene ligands mutually perpendicular and eclipsing the Mo-P bonds. This is in agreement with the proposal by Osborn et al. for $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$.¹ The conformation ee, where the two ethylene ligands retain the same orientation with respect to the equatorial ligands but eclipse each other, is 13.9 kcal/mol higher. This is in marked contrast with the small energy difference of 1.5 kcal/mol found by Rösch and Hoffmann for the two conformations D_{2h} and D_{2d} of $\text{Ni}(\text{C}_2\text{H}_4)_2$.^{5,24} Examination of the orbital energies indicates that in the molybdenum complex **1** the metal d_{xz} and d_{yz} orbitals and the ethylene π^* orbitals are rather close in energy (a molecular interaction diagram is shown in Figure 2) and this results in a strong discrimination in energy between the two conformations se and ee. This analysis is substantiated by the results of the population analysis in Table II which indicate a large back-donation from the metal orbitals d_{xz} and d_{yz} to the π^* orbitals of the ethylene ligand. The increased stability of the conformation ss compared to es has the same origin (the destabilization of es compared to ss amounts to 12 kcal/mol

Table II. Some Orbital Populations for $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ and $\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$

Orbital populations	$\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$				$\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$		
	se	ee	ss	es	se	ee	ss
4d _{xy}	1.75	1.69	1.73	1.67	1.39	1.38	1.37
4d _{xz}	1.40	1.17	1.42	1.53	1.46	1.30	1.47
4d _{yz}	1.40	1.88	1.42	1.53	1.46	1.69	1.47
4d _{z²}	0.34	0.31	0.35	0.33	0.44	0.44	0.45
4d _{x²-y²}	0.38	0.35	0.38	0.36	0.52	0.51	0.52
C2p _z (C ₂ H ₄)	1.15	1.10	1.14	1.10	1.00	0.98	0.99
Net charge of Mo	+0.65	+0.57	+0.63	+0.56	+0.56	+0.53	+0.57
Net charge of C ₂ H ₄	-0.30	-0.21	-0.27	-0.18	-0.01	+0.03	0.

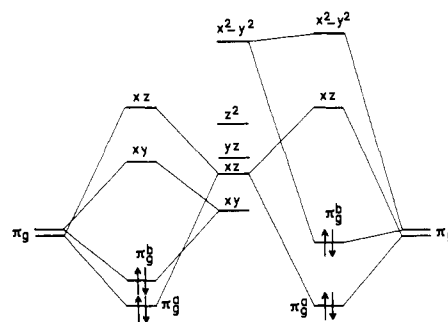
**Figure 3.** The structure of the core MoN_4O_4 in the *trans*-diperoxo-molybdenum(VI) porphyrin (from ref 7).

and is similar to the destabilization of ee compared to se). It is more difficult to assess the origin of the large destabilization (18.8 kcal/mol) computed for the structure ss. Both steric and electronic effects may contribute. We have already mentioned that in the structure ss, the proton(ethylene)-proton(phosphine) distance is shorter than the sum of the van der Waals radii of the two hydrogen atoms; this would account for the steric effects. Electronic effects may originate from two interactions, namely, a $4d_{x^2-y^2}-(\pi_1 + \pi_2)$ interaction **9** in the se structure and a $4d_{xy}-(\pi_1 + \pi_2)$ interaction **10** in the ss



structure ($\pi_1 + \pi_2$ stands for the appropriate combination of the π orbitals of the ligands). According to the diagram of Figure 2, interaction **9** is stabilizing since the π orbitals are filled and $4d_{x^2-y^2}$ is empty (however, it is expected to be a weak stabilization since $d_{x^2-y^2}$ is much higher in energy than the π orbitals). Interaction **10** will be a four-electron destabilizing interaction. Thus electronic factors will also tend to destabilize the ss structure comparative to se.

The results for $\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$ allow us to separate the electronic and the steric factors, since the steric requirements of the equatorial ligands are kept to a minimum in this molecule. We find again that the ee structure is destabilized comparative to the se structure; however, this destabilization is much reduced (from 13.9 to 6.3 kcal/mol) in the case of carbonyl equatorial ligands. This relative stabilization of the ee

**Figure 4.** A metal-dioxygen interaction diagram for $\text{MoP}(\text{O}_2)_2$ (P = porphine dianion) with the dioxygen ligands either eclipsed (left) or staggered (right) with respect to the Mo-N bonds (for the sake of simplicity we have represented the interactions with only one dioxygen ligand).

structure can be traced to a decrease in the electron-donor ability of the metal atom toward the ethylene ligands when the phosphine ligands are replaced by the carbonyl ligands. The carbonyl being a better π acceptor than the phosphine, the extent of π back-donation to the ethylene ligands is decreased upon substitution of the phosphine ligands by the carbonyl ligands. This analysis is substantiated by the changes in the orbital populations of Table II. The difference of 5 kcal/mol in the relative stabilities of the se and ss structures represents now a purely electronic effect associated with the interactions **9** and **10**. Since these two interactions should not be very different for $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ and $\text{Mo}(\text{CO})_4(\text{C}_2\text{H}_4)_2$, most of the destabilization of the ss structure in $\text{Mo}(\text{PH}_3)_4(\text{C}_2\text{H}_4)_2$ can be ascribed to the steric effects.

One may now address the question of whether the rotation about the metal-olefin bond observed by Osborn et al. for the $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$ molecule corresponds to a process where the two ethylene ligands rotate independently or whether their motion is synchronous, the two ligands remaining perpendicular. If each ligand rotates freely, one may consider a rotation of the upper ligand which proceeds from se to ee through conformation **11** (the planes containing the metal atom and

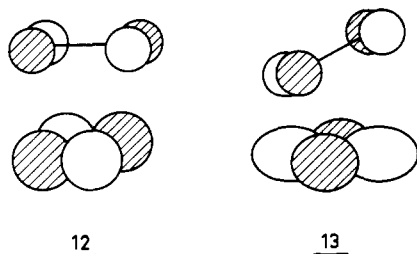
**11**

each C-C axis being at 45°). The relative stability of **11** will probably correspond to a mean value between ee and ss, with a relative energy of 16-17 kcal/mol.²⁵ The transition state for a synchronous rotation of the two ligands corresponds to ss, with a rotation barrier of 18.8 kcal/mol. A process where each ethylene ligand rotates independently appears slightly more

favorable. The above value of 16–17 kcal/mol for the rotation barrier compares favorably with the estimated barrier of 15.3 kcal/mol.¹ The above discussion relies implicitly on the assumption that the steric requirements of the diphos and phosphine ligands are not too different.

One can also address the question of how the relative stabilities of the various conformations will change with the number of d electrons. For $\text{MoCl}_4(\text{C}_2\text{H}_4)_2$ we have assumed a closed-shell configuration d_{xy}^2 for the Mo(IV) atom²⁶ and the stabilities of the two conformations *se* and *ee* are practically equal. This is expected since the orbitals d_{xz} and d_{yz} involved in the back-bonding interaction **7** and **8** are now empty. Thus the two conformations will have comparable stabilities for d^0 – d^2 , and the stabilization of *se* relative to *ee* will increase from d^3 to d^6 as a consequence of increased back-bonding ability, then should decrease from d^7 to d^{10} as a consequence of increased d – π^* energy separation (since the d orbitals sink toward the end of the transition series). Conformation *ss* should be less stable than *se* within d^2 – d^8 , and the difference in stability will be reduced for d^9 – d^{10} (although it should not completely disappear since a four-electron interaction $d_{x^2-y^2}$ –($\pi_1 + \pi_2$) will be less destabilizing than the four-electron interaction d_{xy} –($\pi_1 + \pi_2$) as long as $d_{x^2-y^2}$ will be much higher than d_{xy}). Thus it is expected that axial ethylenic ligands should always eclipse the equatorial bonds, at least when the electronic effects are not dominated by steric effects.

We may ask what is the relationship of the above discussion for the case of *trans* ethylenic ligands to the case of *trans* dioxygen ligands. The *trans*-diperoxomolybdenum(VI) porphyrin shows the same structural features found in $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$, namely, the two dioxygen ligands are mutually perpendicular and eclipse the equatorial Mo–N bonds (Figure 3).⁷ The same arguments used above hold, except that *the relative roles of the metal d and ligand π^* or π orbitals are now exchanged*. To assign the electronic ground state of the diperoxomolybdenum porphyrin, we rely on (1) the crystal structure with an oxygen–oxygen bond length of 1.40 Å indicative of the peroxo nature of the two dioxygen ligands; (2) our previous treatment of the peroxotitanium porphyrin TiPO_2 with the electronic configuration of the ground state assigned as $d^0(\pi_g^a)^2(\pi_g^b)^2$.^{9,30} Thus we may describe formally the ground state of $\text{MoP}(\text{O}_2)_2$ through the electronic configuration $d^0(\pi_{g1})^4(\pi_{g2})^4$ where we denote by π_{g1} and π_{g2} the π antibonding orbitals of the two dioxygen ligands. The mutually perpendicular orientation of the two dioxygen ligands results now from the two-electron stabilizing interactions π_{g1} – $4d_{xz}$ and π_{g2} – $4d_{yz}$ (Figure 4). The conformation *se* with the dioxygen ligands eclipsing the Mo–N bonds is more stable than the conformation *ss* since both interactions **12** (π_g^b – $4d_{xy}$) (for the eclipsed structure) and **13** (π_g^b – $4d_{x^2-y^2}$) (for the staggered



structure) are stabilizing, but the stabilization corresponding to **12** will be larger since the energy separation between π_g^b and $4d_{xy}$ is smaller (Figure 4) (thus the role assigned previously to the π orbital of ethylene is here assigned to the π^* orbital of dioxygen³²).

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- (25) An independent SCF calculation for conformation 11 gives a relative energy of 16.3 kcal/mol with respect to *se*.
- (26) For the ground state of $\text{MoCl}_4(\text{C}_2\text{H}_4)_2$ we had a choice between the two electronic configurations d_{xy}^2 (closed shell, singlet state) and $d_{xz}^1 d_{yz}^1$ (open shell, triplet state). The corresponding energies are not comparable at the SCF level because of the correlation error. A number of calculations indicate that in the complexes of C_{4v} or D_{4h} symmetry the d_{xy} orbital is lower in energy than d_{xz} and d_{yz} .²⁷⁻²⁹
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- (30) We denote by π_g^a the π_g antibonding orbital of dioxygen which is symmetrical with respect to the metal–dioxygen plane and by π_g^b the π_g orbital which is antisymmetrical with respect to the same plane.³¹
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