

AN INVESTIGATION OF THE ELECTRONIC FACTORS THAT INFLUENCE STRUCTURAL DIFFERENCES BETWEEN *CIS*-(CpMoCl)₂(μ,η⁴-Ar₄C₄) (Ar = *p*-TOLYL OR PHENYL) AND *TRANS*-(CpNbCO)₂(Ph₂C₂)₂†

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Abstract—The influence of geometric factors, such as *cis/trans* isomerism, and electronic factors, such as π donor vs π acceptor ligands and coupled and uncoupled acetylene ligands, on the stability of *cis*-(CpMoCl)₂(μ,η⁴-Ar₄C₄) and *trans*-(CpNbCO)₂(Ph₂C₂)₂ is investigated through patterns in molecular orbital diagrams, size of HOMO/LUMO gap and total energies. The comparison between the two dimers involves rationalization of why the observed structures appear so different, when in fact both clusters have the same number of valence electrons. In the course of the investigation, other stable niobium chlorine complexes are discussed and the kinetic vs thermodynamic stability of *trans*-(CpNbCO)₂(Ph₂C₂)₂ is analysed.

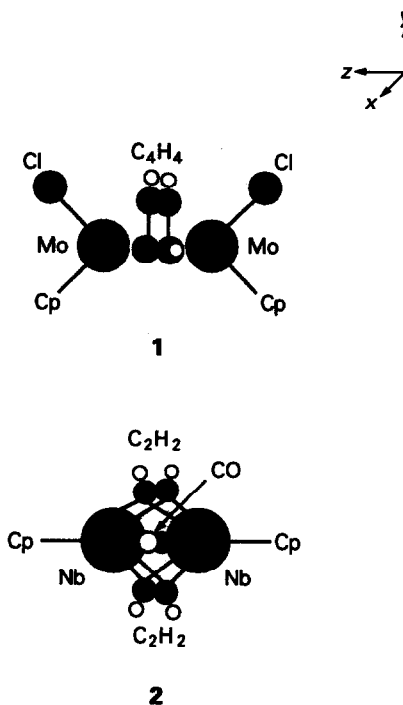
An interesting series of new organometallic dimers has been synthesized as part of an ongoing investigation of metal-metal multiple bonds.¹ This paper will focus on two of these dimers: they are of the type Cp₂M₂L₂R, where M = Mo or Nb, L = CO or Cl, and R = μ,η⁴-Ar₄C₄ or (Ar₂C₂)₂ (Ar = *p*-tolyl or phenyl).

More specifically, it is of interest to compare the structures of *cis*-(CpMoCl)₂(μ,η⁴-Ar₄C₄) (**1**) and *trans*-(CpNbCO)₂(Ph₂C₂)₂ (**2**).² These two complexes have identical electron counts: niobium has one less valence electron than molybdenum, but the carbonyl ligand is considered a two-electron donor, while chlorine is a one-electron donor [both (μ,η⁴-Ar₄C₄)²⁻ and (Ph₂C₂)₂ are eight-electron donors].³ Despite sharing the same number of valence electrons these two dimers have very different structures:^{4,§}

† Dedicated to Professor Richard F. Fenske in recognition of his contribution to theoretical organometallic chemistry and in appreciation of his guidance as my PhD adviser (M.C.M).

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§ The aryl and phenyl groups present in the dimers have been substituted by hydrogen atoms in order to simplify the molecular orbital calculations (see text).



The two molecules differ in their conformation (one is *cis* and the other *trans*) and in the molybdenum dimer the two alkyne ligands have coupled to form a (μ,η⁴-Ar₄C₄) ligand, while in the niobium complex two separate acetylene groups are present.

The structural and electronic features that distinguish the molybdenum from the niobium dimer can be grouped into three categories: *cis* or *trans* arrangement, Cl or CO ligands, coupled C_4H_4 or uncoupled $(C_2H_2)_2$ alkyne ligands. This paper will attempt to explain why the molybdenum dimer prefers one set of features and the niobium dimer the other by using non-empirical molecular orbital calculations. The three aspects will first be studied separately, and then taken into consideration simultaneously in order to justify the observed structures. The results of the calculations will be analysed in terms of the nature and energy of the valence molecular orbitals, as well as the relative total energies of the complexes.

COMPUTATIONAL PROCEDURE

Calculations have been carried out by using the Fenske–Hall non-empirical method⁵ on an IBM 3090-600 computer.⁶ Atomic basis functions were employed; for oxygen, carbon and chlorine Clementi's double- ξ functions were used,⁷ except for $1s$ and $2s$ functions, which were curve-fit to single- ξ by using the maximum overlap criterion.⁸ The hydrogen exponent was set to 1.16. Molybdenum(I) and niobium(I) functions were obtained by performing an atomic $X-\alpha$ calculation on a set of optimized, orthonormal Slater-type orbitals.⁹ In order to avoid working with metal outer functions that are too diffuse, the molybdenum $5s$ and $5p$ exponents were set to 1.85. The niobium $5s$ exponent was set to 1.602 and the $5p$ exponent to 1.259. The total energy for each molecule was calculated using the Hartree–Fock expression.^{10,11}

The geometrical parameters used for the experimentally observed compounds [*cis*-(CpMoCl)₂(μ,η^4 -Ar₄C₄),³ *trans*-(CpNbCO)₂(Ph₂C₂)₂^{2b} and *trans*-(MeCp)₂Nb₂(Ar₂C₂)₂(μ -Cl)₂¹²] were taken from the actual X-ray structures, but, for simplicity of interpretation and greater ease in the calculations, the phenyl and *p*-tolyl substituents on the

R ligands have been substituted by a hydrogen atom. Table 1 shows selected bond distances for the two basic dimer frames considered in this work: that of *cis*-(CpMoCl)₂(C₄H₄) and that of *trans*-(CpNbCO)₂(C₂H₂)₂. These two geometries are also used for the structures of *cis*-(CpNbCl)₂(C₄H₄) and *trans*-(CpMoCO)₂(C₂H₂)₂. For *cis*-(CpMoCO)₂(C₄H₄), the Mo—C_{CO} bond distance was taken to be 1.99 Å, which is the value found in a series of CpMo(CO)₃R complexes.¹³ In *trans*-(CpNbCl)₂(C₂H₂)₂, the Nb—Cl bond distance was set to 2.25 Å.¹⁴

The geometry of *trans*-(CpMoCl)₂(C₄H₄) cannot be made to match that of *trans*-(CpNbCO)₂(C₂H₂)₂ because the C₄H₄ ligand would be too close to the chlorine centres. Therefore, to obtain the geometry of the molybdenum dimer, half of the *cis*-(CpMoCl)₂(C₄H₄) dimer was rotated by 180° along the Mo—Mo axis, leaving the C₄H₄ ligand in place. On the other hand, the arrangement in *cis*-(CpNbCl)₂(C₂H₂)₂ can be made to resemble that of the experimentally observed molybdenum dimer by rotating half of *trans*-(CpNbCO)₂(C₂H₂)₂ by 180° along the Nb—Nb axis and leaving the C₂H₂ ligands in place. Furthermore, the two cyclopentadienyl rings are moved closer together at a 45° angle to the M—M axis and the two carbonyl ligands are pointed away from, rather than at, each other. Bond lengths and angles for the other dimers were extrapolated from the known geometries.

RESULTS AND DISCUSSION

The two experimentally observed dimers

In order to study the influence of the three geometrical factors on the electronic structure of the title compounds, it is best to start from an analysis of the MO diagram for each of the two molecules. Figure 1 shows the MO diagram for *cis*-(CpMoCl)₂(C₄H₄) (**1**). The HOMO/LUMO gap is fairly large (2.87 eV), pointing to the stability of the com-

Table 1. Selected bond distances for **1**, **2**, **11** and **12**^{3,2b}

	<i>cis</i> -(CpMCl) ₂ (C ₄ H ₄) ^a	<i>trans</i> -(CpMCO) ₂ (C ₂ H ₂) ₂ ^a
M—M	2.933	2.731
M—C _{Cp}	2.3	2.3
M—C _{CO}	—	2.107
M—Cl	2.4	—
M—C _{C₂H₂}	—	2.0
M—C _{C₄H₄}	2.0, 2.2 ^b	—

^a All distances in Å.

^b Distances for end and internal carbons.

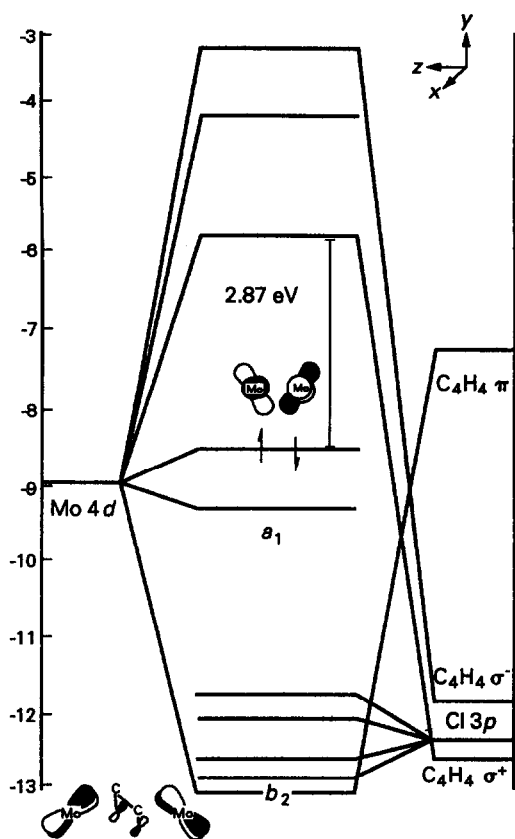


Fig. 1. Molecular orbital diagram for *cis*-(CpMoCl)₂(C₄H₄) (**1**).

plex.¹⁵ The five valence molecular orbitals (two occupied and three unoccupied) are in an e + t pattern and are largely metal-based. A fairly large gap separates the SHOMO (Second Highest Occupied Molecular Orbital) from the next set of occupied orbitals, which is comprised of in-phase and out-of-phase combinations of Cl 3p orbitals. The lowest-energy molecular orbital shown (*b*₂) is part of the atomic Mo—C₄H₄ bonding interaction: only the end carbons of the C₄H₄ ligand are participating in the bond via a hybrid orbital that is pointing toward one of the metal centres† [see Fig. 5(c)]. The metal centres are bonding with a combination of their *d*_{xy} and *d*_{xz} orbitals.

Figure 2 shows the MO diagram for the other dimer, *trans*-(CpNbCO)₂(C₂H₂)₂ (**2**). The HOMO/LUMO gap is not as large as the one in the molybdenum complex, but it still indicates that **2** is a stable molecule. The valence molecular orbitals do

† The C₄H₄ ligand also contributes some small amount of electron density from the internal carbons, but the contribution is too small to be shown. The *p* orbitals on the internal carbons form out-of-phase combinations with the *p* orbitals on the end carbons shown in Fig. 1.

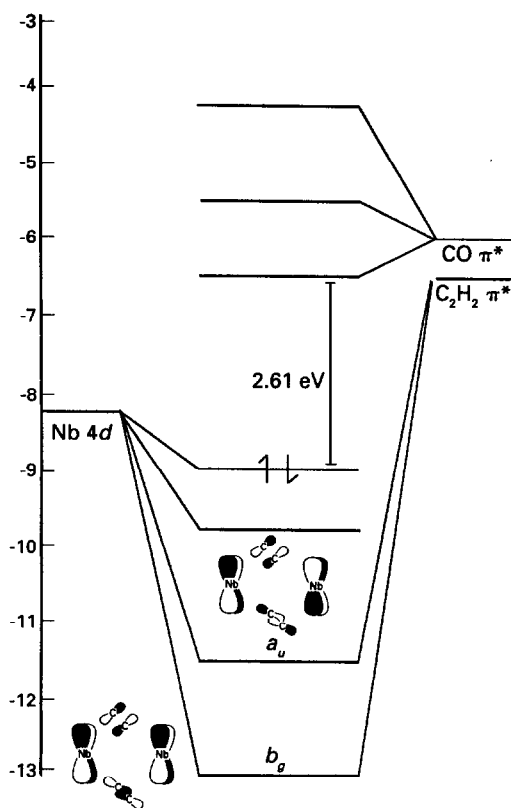


Fig. 2. Molecular orbital diagram for *trans*-(CpNbCO)₂(C₂H₂)₂ (**2**).

not show the e + t pattern present in **1** and they receive larger contributions from the ligand orbitals. The first three unoccupied molecular orbitals are mainly CO π* in character, as usual for molecules with carbonyl ligands.¹¹ The HOMO and the SHOMO are metal–metal bonding, which is consistent with the experimental observation of a Nb—Nb bond length characteristic of a double bond between the centres.^{2b,16} The two lowest levels shown in Fig. 2, *b*_g and *a*_u, contribute to the bonding between the metals and the acetylene ligands. This interaction can be compared to that between Mo and C₄H₄ in **1**, which was observed in the *b*₂ orbital of that molecule. In both molecular orbitals, the π* orbital on the acetylene ligand [see Fig. 6(c)] bonds with the *d*_{xy} orbital on niobium. In the *b*_g orbital, each of the acetylene ligands has an in-phase interaction with only one of the metals, while in the *a*_u level the ligands bond with both metal centres at the same time, forming a true bridge between them.

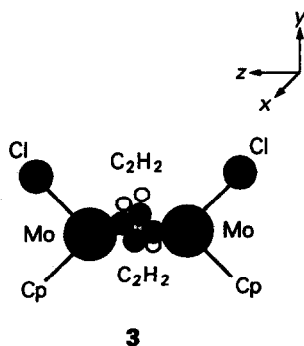
If the metal to R ligand interactions in the valence molecular orbitals of **1** and **2** are compared, a number of similarities become apparent. In both cases the bond occurs between one or more metal *d* orbitals of appropriate symmetry and the first empty level on the ligand. In the dimer, the resulting

bonding level or levels are filled, so that the net result is metal-to-ligand electron density donation. Furthermore, the ligand orbital participating in the interaction is a linear combination of two p orbitals on each of the carbon centres involved. This mixing of atomic orbitals is necessary in order to redirect the ligand orbitals toward the metal centres, since in neither **1** or **2** are the carbon atoms along the metal-metal axis.

Since the ligand orbitals that are on the accepting side of this backbonding interaction have varying degrees of antibonding character between carbon centres,[†] the metal-to-ligand interaction effectively weakens the C—C bond in the R ligand. Further weakening of such bonds occurs when the low-lying, filled, s and p orbitals of the R ligand (see Figs 5 and 6) donate electron density to the metal centres through additional bonding molecular orbitals. These molecular levels are at lower energies, buried in the group of M—L and L—L bonding orbitals below the valence sets shown in Figs 1 and 2. This hypothesis of a net weakening of ligand C—C bonds is verified by experimental observations of C—C bond lengths in the coordinated ligands, which are longer than the C—C bond lengths in the isolated alkenes and alkynes.^{2b}

C₄H₄ vs (C₂H₂)₂

The approach initially chosen to determine the role of the two different types of R ligand in the structure of the dimers was to consider a molybdenum complex with two acetylene ligands, *cis*-(CpMoCl)₂(C₂H₂)₂ (**3**) and a niobium complex with one C₄H₄ ligand, *trans*-(CpNbCO)₂(C₄H₄) (**4**). Unfortunately, it is not possible to place a ligand such as C₄H₄, which wraps around the dimer in the plane perpendicular to the one containing the metals, on a *trans* frame such as that of the niobium complex. There is no orientation of the ligand that would prevent it from coming in too close proximity to the carbonyl ligands. This in part explains why



the niobium dimer bonds to two distinct acetylene units, rather than one C₄H₄ ligand. To bond to the latter, the frame would have to adopt a *cis* configuration.

On the other hand, there are no difficulties in placing two acetylene units on the molybdenum *cis*-frame.

The molecular orbital diagram for **3** is shown in Fig. 3: the most striking feature of the diagram is the very small HOMO/LUMO gap (0.76 eV), combined with the comparatively large HOMO/SHOMO gap (1.32 eV). This suggests not only that **3** is an unstable complex, but also that oxidizing the molecule by two electrons might produce a more stable system. The fact that **3** is not stable is also confirmed by its total energy, which is higher than the total energy of **1** (see Table 2). Let us now investigate the electronic reasons why the *cis* molybdenum frame prefers one C₄H₄ to two C₂H₂ ligands.

Figures 1 and 3 show the same pattern of valence molecular orbitals consisting of five metal-based levels, two occupied and three unoccupied levels. The large gap that separates the metal-based orbitals from the Cl 3*p* orbitals in **1**, though, shrinks considerably in **3**. This is mostly due to the out-of-phase interaction of some of the chlorine p orbitals

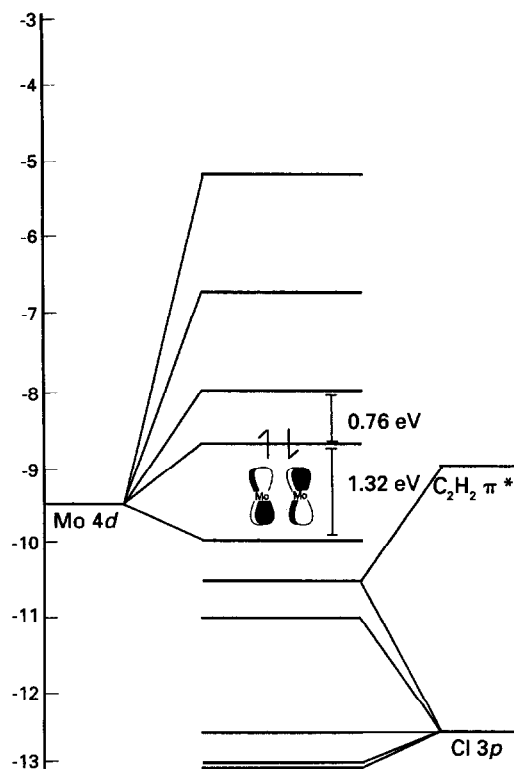


Fig. 3. Molecular orbital diagram for *cis*-(CpMoCl)₂(C₂H₂)₂ (**3**).

[†] See footnote [†] on p. 1857.

Table 2. Summary of energy considerations

	Total energy ^{a,b}	HOMO/LUMO gap ^a
<i>cis</i> -(CpMoCl) ₂ (C ₄ H ₄) (1)	-256,219	2.87
<i>cis</i> -(CpMoCl) ₂ (C ₂ H ₂) ₂ (3)	-256,201	0.76
<i>cis</i> -(CpMoCO) ₂ (C ₄ H ₄) (5)	-237,507	1.9
<i>cis</i> -(CpMoCO) ₂ (C ₂ H ₂) ₂ (7)	-237,472	1.69
<i>trans</i> -(CpMoCl) ₂ (C ₄ H ₄) (9)	-256,153	1.05
<i>cis</i> -(CpNbCl) ₂ (C ₄ H ₄) (12)	-244,162	0.96
<i>trans</i> -(CpNbCO) ₂ (C ₂ H ₂) ₂ (2)	-225,407	2.61
<i>trans</i> -(CpNbCl) ₂ (C ₂ H ₂) ₂ (6)	-244,115	3.43
<i>trans</i> -Cp ₂ Nb ₂ (C ₂ H ₂) ₂ (μ-Cl) ₂ (8)	-244,187	3.98
<i>cis</i> -(CpNbCO) ₂ (C ₂ H ₂) ₂ (10)	-225,438	1.61
<i>cis</i> -(CpNbCO) ₂ (C ₄ H ₄) (11)	-225,398	0.49
<i>trans</i> -(CpMoCO) ₂ (C ₂ H ₂) ₂ (13)	-237,467	1.50

^a Values in units of eV.

^b The total energy values for the molecules being analysed should not be taken literally but used for comparison with the other complexes.¹⁷

with the C₂H₂ π* level, which causes them to rise in energy, closer to the five valence orbitals.

The difference in the size of the HOMO/LUMO gap between **1** and **3** is due to two factors working together: a lowering in energy of the LUMO and a destabilization of the HOMO. In **1**, the LUMO is mostly metal-metal antibonding, but its energy is raised further by an out-of-phase interaction between the metals and the σ₋ orbital on C₄H₄. This interaction disappears in **3**, where there is no C₄H₄ ligand, and the LUMO is consequently lowered in energy. In both molecules, the HOMO contains an antibonding combination of metal-based orbitals. In **1**, it is a bent π interaction between d_{x²-y²} and d_{yz} orbitals on both centres, and as such it does not involve a large amount of overlap between the two metals. In fact, only one of the lobes on each centre actually participates in the interaction, and the orbital is not greatly destabilized with respect to the metal d atomic orbitals. In **3**, the interaction has δ symmetry and it is between d_{xy} orbitals. Even though δ-type overlap is usually not large, it is still greater than the bent π-type overlap just mentioned. Therefore, the HOMO in **3** is more destabilized than the HOMO in **1**, which contributes to closing the HOMO/LUMO gap.

CO vs Cl

In order to determine the influence of the carbonyl and chlorine ligands on the structure of the dimers, two complexes are considered: *cis*-(CpMoCO)₂(C₄H₄) (**5**) and *trans*-(CpNbCl)₂(C₂H₂)₂ (**6**). The dimers are identical to the

experimentally observed ones, except for having exchanged chlorine and carbonyl ligands.

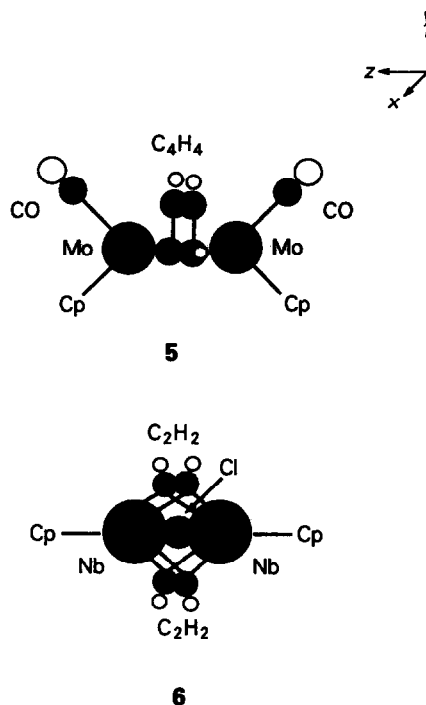


Figure 4 shows the influence of the carbonyl ligands on the molecular orbitals of the molybdenum dimer. It is immediately apparent that the empty CO π* orbitals participate in most of the valence molecular orbitals, both occupied and unoccupied. In particular, the low-lying empty orbitals in **1** are pushed to higher energies by an antibonding interaction between the metals and filled orbitals on the C₄H₄ ligand [σ₊ and σ₋; see

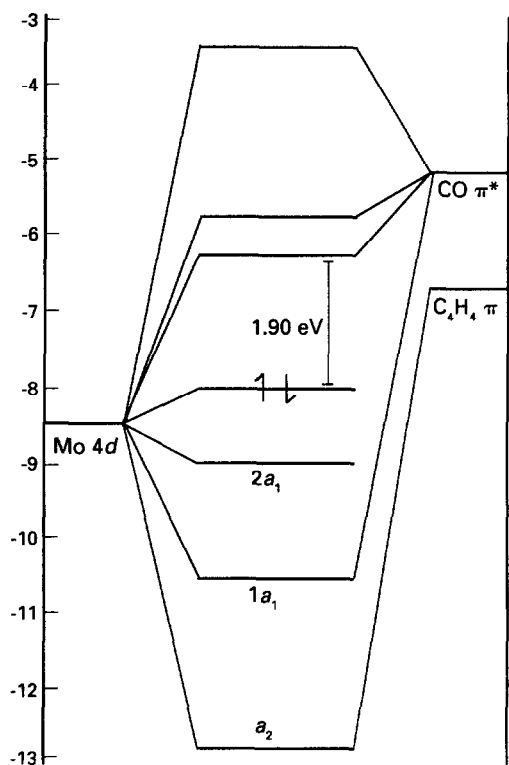


Fig. 4. Molecular orbital diagram for *cis*-(CpMoCO)₂ (C₄H₄) (5).

Fig. 5(a) and (b)]. In 5 these unoccupied orbitals are lowered in energy because of the participation of CO π^* levels, which substitute the C₄H₄ orbitals in the interaction with the metals. The C₄H₄ σ_+ and σ_- orbitals are instead greatly stabilized by ligand-

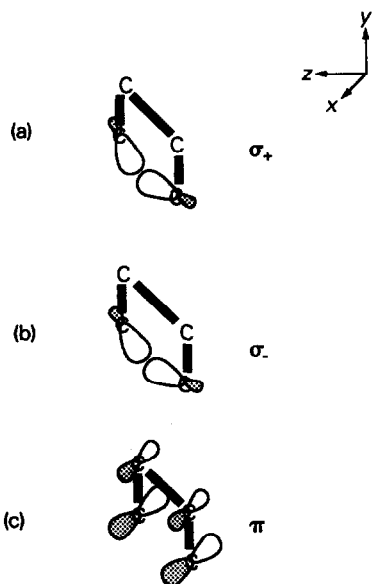


Fig. 5. Valence molecular orbitals of the (C₄H₄)²⁻ ligand which participate in bonding with the metal centres. Orbitals *a* and *b* are filled, orbital *c* is unoccupied.

ligand interaction with cyclopentadienyl π levels and they are found among the low-lying occupied orbitals of 5. The lowering of unoccupied molecular orbitals in 5 becomes most important in the LUMO, where it contributes to the decrease in the HOMO/LUMO gap. The decreased size of the gap points to the fact that the molybdenum dimer is more stable with chlorine than with carbonyl ligands.

Despite these differences between these two molybdenum dimers, some of the features of their molecular orbital diagrams are similar. Two of the valence orbitals in 5 are analogous to two orbitals in the diagram for 1: the M—C₄H₄, a_2 bonding orbital (b_2 in 1), and the SHOMO of the molecule ($2a_1$ in 5 and a_1 in 1), which is a Mo—Mo bonding interaction. The HOMO of 1, which has contributions from Mo $d_{x^2-y^2}$ orbitals, is greatly stabilized in 5 (a_1 level) by a bonding interaction with CO π^* levels.

To investigate the effect of coupling and decoupling the R ligand on the *cis*-(CpMoCO)₂ frame, an additional calculation was performed on the molecule *cis*-(CpMoCO)₂(C₂H₂)₂ (7).

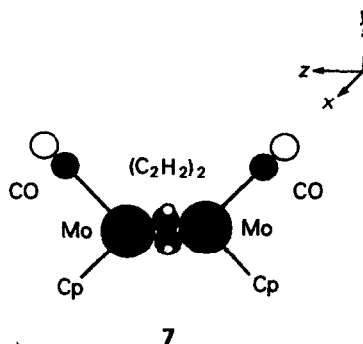


Table 2 shows that the dimer with the decoupled ligands (two C₂H₂ moieties) is less stable than its counterpart with the C₄H₄ ligand, both in terms of

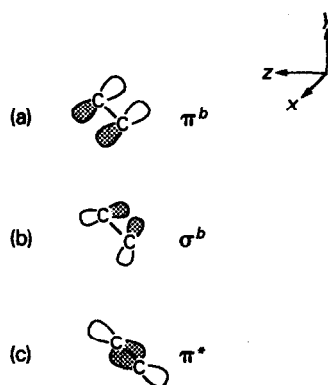


Fig. 6. Valence molecular orbitals of the C₂H₂ ligand which participate in bonding with the metal centres. Orbitals *a* and *b* are filled, orbital *c* is unoccupied.

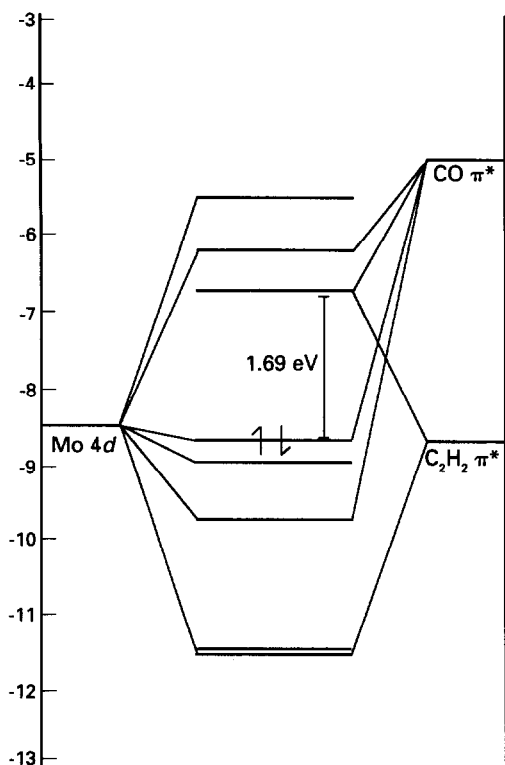
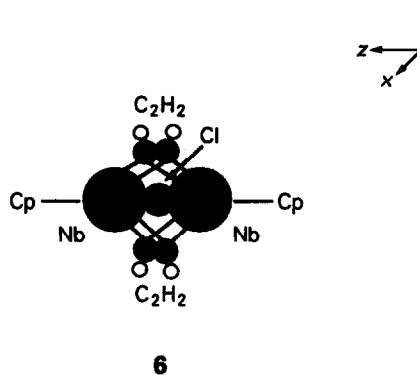


Fig. 7. Molecular orbital diagram for *cis*-(CpMoCO)₂(C₂H₂)₂ (7).



of CO π* levels, which tend to push all low-lying unoccupied orbitals, including the LUMO, to lower energies. Also peculiarly absent in Fig. 8 is the participation of the empty C₂H₂ π* level in bonding with the metals. In **2**, this bonding interaction is responsible for the stabilization of two valence molecular orbitals (*a_u* and *b_g* in Fig. 2); the lack of it causes the occupied valence orbitals of **6** (*1a_g* and *2a_g* in Fig. 8) to remain at higher energies. The C₂H₂ π* levels in **6** contribute instead to a high energy virtual orbital, in which they combine in an anti-bonding fashion with Nb *d_{x²-y²}* orbitals. In **2** this is not possible, since the *d_{x²-y²}* orbitals form an out-of-phase combination with the CO π* levels. There-

total energy and of HOMO/LUMO gap. Figure 7 is the molecular orbital diagram for **7**, which explains the stability trend just mentioned. Similarly to what is observed in Fig. 4, the diagram is dominated by the influence of the carbonyl π* levels on most of the valence molecular orbitals. This pushes the virtual orbitals to lower energies, contributing to the relatively small HOMO/LUMO gap. Also common to both Figs 4 and 7 is the presence of one or more M—R ligand bonding orbitals (involving C₄H₄ π in Fig. 4 and C₂H₂ π* in Fig. 7). In conclusion, then, the presence of a coupled or decoupled R ligand does not affect the electronic structure of dimers with frame *cis*-(CpMoCO)₂ as much as the presence of CO π* levels does: complexes **5** and **7** show more similarities than differences in their molecular orbital diagrams.

The effect of substituting Cl for CO ligands was also studied for the *trans*-(CpNbCO)₂(C₂H₂)₂ dimer.

The molecular orbital diagram of **6** is shown in Fig. 8. As indicated on the diagram, the HOMO/LUMO gap for this molecule is quite large, actually larger than the one found in **2**. This is not an entirely surprising result, since some preliminary experiments indicate that **6** might also be an observed structure.¹⁸ Again, the primary reason for the widening of the HOMO/LUMO gap is the absence

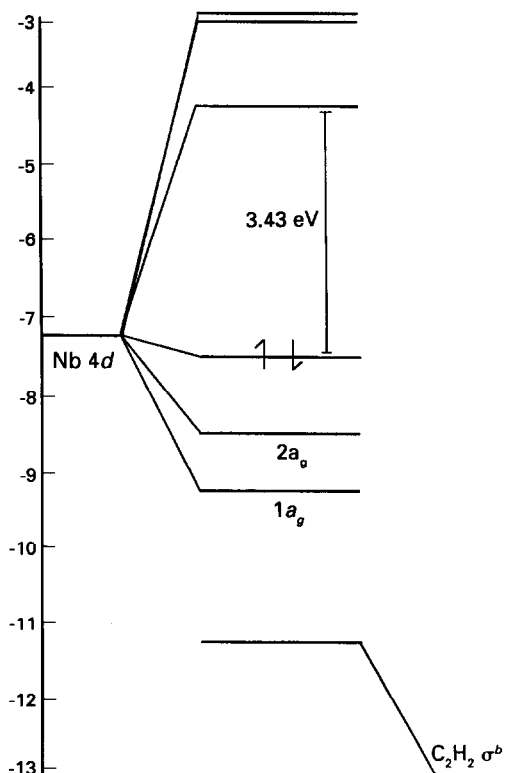
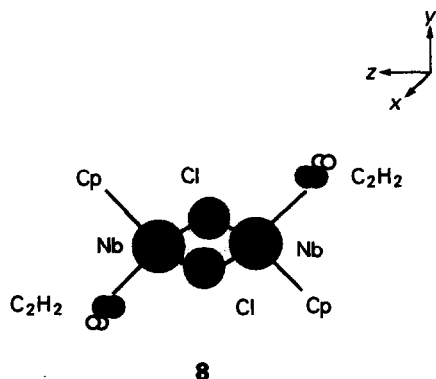


Fig. 8. Molecular orbital diagram for *trans*-(CpNbCl)₂(C₂H₂)₂ (**6**).

fore, the $C_2H_2 \pi^*$ levels in **2** are free to combine with other metal orbitals in a bonding fashion, as they do in levels a_u and b_g .

There is one other niobium dimer related to **6** that has been observed experimentally:¹² *trans*- $Cp_2Nb_2(C_2H_2)_2(\mu-Cl)_2$ (**8**).



In this complex, which is otherwise identical to **6**, the acetylene ligands are terminal and it is the chlorine ligands that are bridging the metals. Figure 9 illustrates the fact that **8** is a stable compound with a large HOMO/LUMO gap (see Table 2 for the total energy value). Figures 8 and 9 show general agreement between the molecular orbitals of these two acetylene chlorine niobium dimers. In both cases there are six valence molecular orbitals, three occupied and three unoccupied. In **8**, all three occupied orbitals are more stabilized with respect to those in **6**. In particular, the two lowest levels are stabilized by a bonding interaction between the metals and the π^* orbitals on the C_2H_2 ligands, since the Nb d_{xy} orbitals have the appropriate symmetry to bond with the π^* levels of the acetylenes in terminal positions. But the principal factor that contributes to the widening of the HOMO/LUMO gap is the stabilization of the HOMO in **8** with respect to that in **6**. The lowering of this molecular orbital is also caused, even though indirectly, by the fact that the acetylenes in their new terminal positions are ideally suited to interact with the Nb d_{xy} orbitals. In **6**, the HOMO is a bonding combination of metal d_{z^2} and d_{xy} orbitals; while in **8**, because the d_{xy} orbitals participate in levels $1a_2$ and $2a_2$, the HOMO is just d_{z^2} in character. Therefore, the HOMO in the dimer with the bridging acetylenes has bent- π symmetry with a small overlap between centres and little stabilization; while the HOMO in the dimer with the bridging chlorines has σ symmetry, which leads to a larger stabilization of the molecular orbital.

† For details on the geometries of these two complexes, see the Computational Procedure section of this paper.

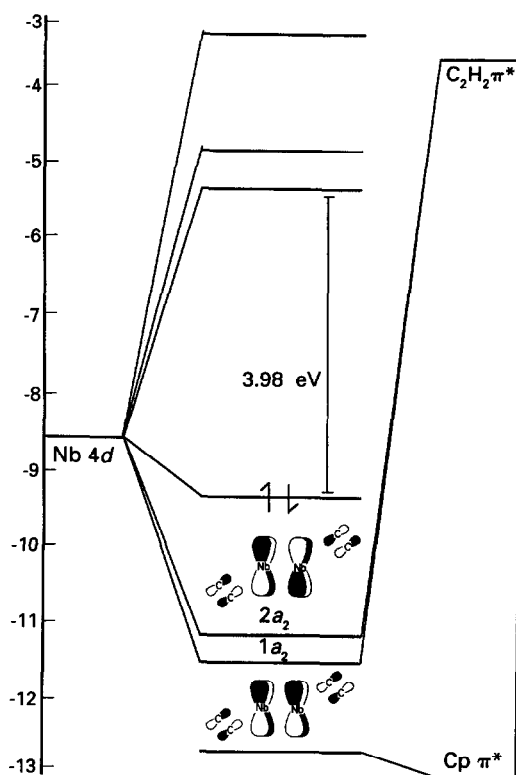
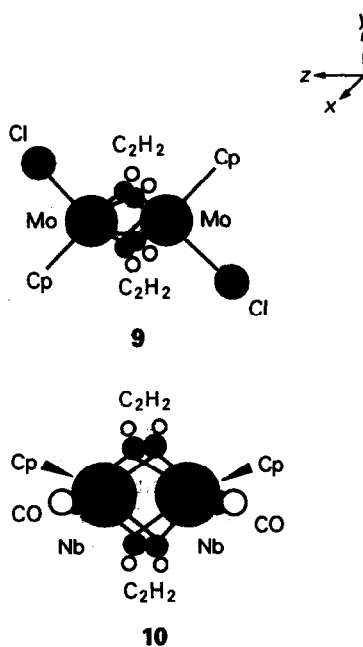


Fig. 9. Molecular orbital diagram for *trans*- $Cp_2Nb_2(C_2H_2)_2(\mu-Cl)_2$ (**8**).

Cis vs trans

The last factor to be considered is the *cis* vs *trans* conformation of the dimers. To this purpose, calculations on two additional complexes were carried out: *trans*-($CpMoCl$)₂(C_4H_4) (**9**) and *cis*-($CpNbCO$)₂(C_2H_2)₂ (**10**).†



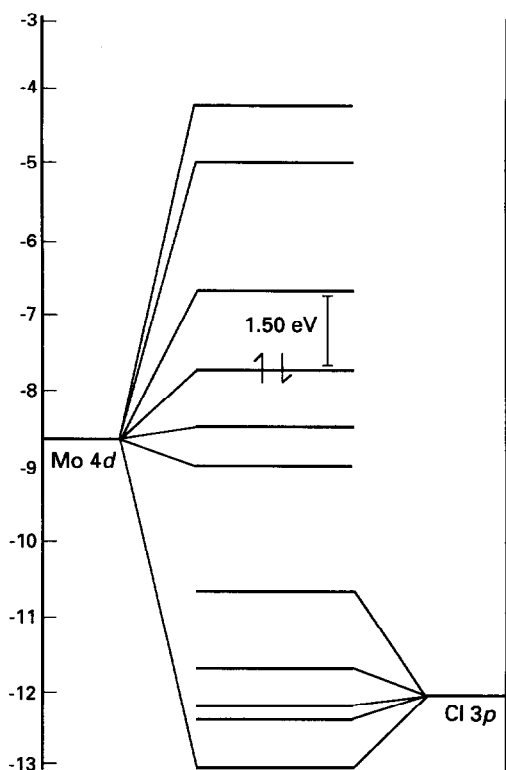


Fig. 10. Molecular orbital diagram for *trans*-(CpMoCl)₂(C₄H₄) (**9**).

Figure 10 shows the molecular orbital diagram for **9**: when it is compared to the diagram in Fig. 1, it becomes apparent that the gross features in the two diagrams are roughly the same. There is a series of low-lying, ligand-based orbitals separated by a gap from metal-based, occupied and unoccupied valence orbitals. Because of the change in symmetry from *cis* to *trans*, though, much mixing of the molecular orbitals occurs and it becomes difficult to follow how each level changes in going from Fig. 1 to 10. Figure 11 gives some indication of the mixing that is occurring: the HOMO and SHOMO of the *cis* complex loosely translate into levels 1a_g and 3a_g of the *trans* complex. Similarly, the two lowest unoccupied orbitals of the *cis* dimer are related to 5a_g and 6a_g levels in the *trans* dimer; level 2a_g in part (b) of the figure, the SHOMO of the complex, most resembles the highest unoccupied level shown for the *cis* complex. The LUMO of the *trans* dimer is the only level that seems to have no counterpart in the *cis* dimer: it is a mixture of d_{yz} orbitals on both metal centres. Actually, this orbital plays a big role in making the *trans* molecule less stable than the *cis* one: its position between the HOMO and LUMO of part (a) of the figure is responsible for the markedly decreased size of the HOMO/LUMO gap (see Table 2). In summary, then, the *trans* con-

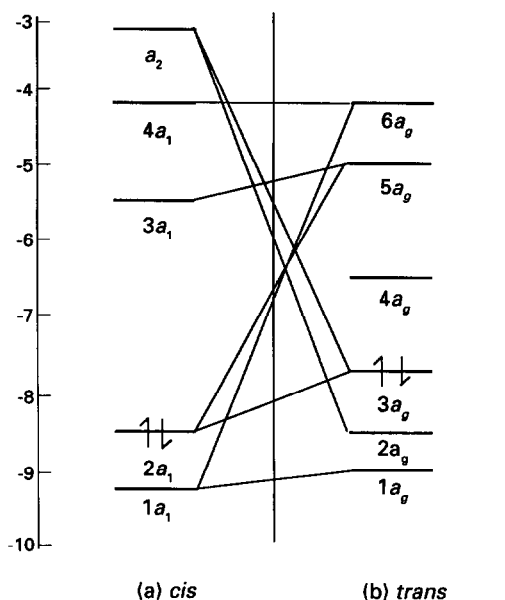


Fig. 11. Comparison of the valence molecular orbitals of **1** from Fig. 1(a) and those of **9** in Fig. 10(b). The lines between orbitals indicate how the orbitals in **a** mix give rise to the orbitals in **b**.

formation of the molybdenum dimer is less stable, according to both the total energy and the HOMO/LUMO gap, than the *cis* conformation. This arises from the presence of a new, metal-based level positioned between the HOMO and the LUMO. This orbital, which becomes the LUMO of the *trans* dimer, is mostly metal d_{yz} in character, but it is difficult to trace it back to the **1** dimer because of the extensive mixing occurring among the valence molecular orbitals.

Figure 12 shows the molecular orbital diagram for **10**, *cis*-(CpNbCO)₂(C₂H₂)₂. The overall pattern of orbitals in Figs 2 and 12 is similar: two, low-lying, metal-to-C₂H₂ π* bonding orbitals (one for each metal centre); HOMO and SHOMO orbitals that are close in energy, are stabilized with respect to the niobium *d* atomic levels only to a small extent, and are Nb—CO π* bonding in character; and three unoccupied orbitals that are mostly CO π* in character. Despite these similarities, the HOMO/LUMO gap in **10** is significantly smaller than that in **2** (see Table 2), pointing to the fact that the *cis* dimer is not as stable as the *trans* conformation. This happens mostly because in **10** the first two virtual orbitals are significantly lower in energy. Unfortunately, an in depth examination of the atomic orbital contributions to these molecular levels gives no indication of why the lowering in energy occurs. Again, the transformation from *trans* to *cis* involves a change in symmetry for the

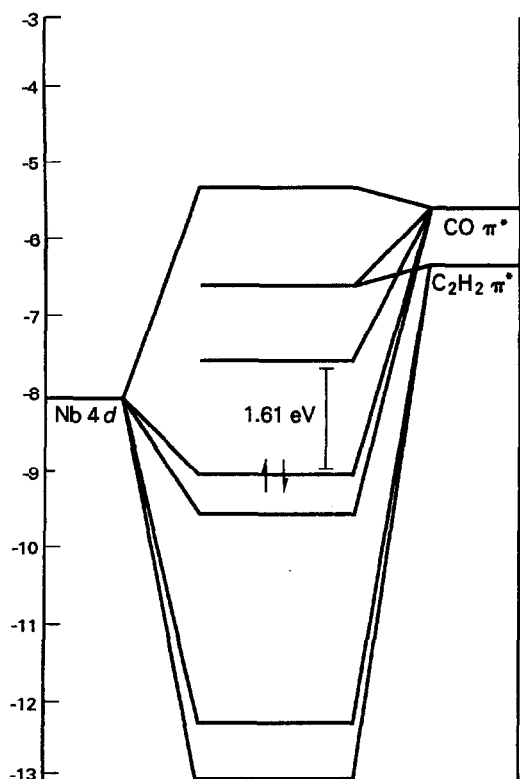


Fig. 12. Molecular orbital diagram for *cis*-(CpNbCO)₂(C₂H₂)₂ (**10**).

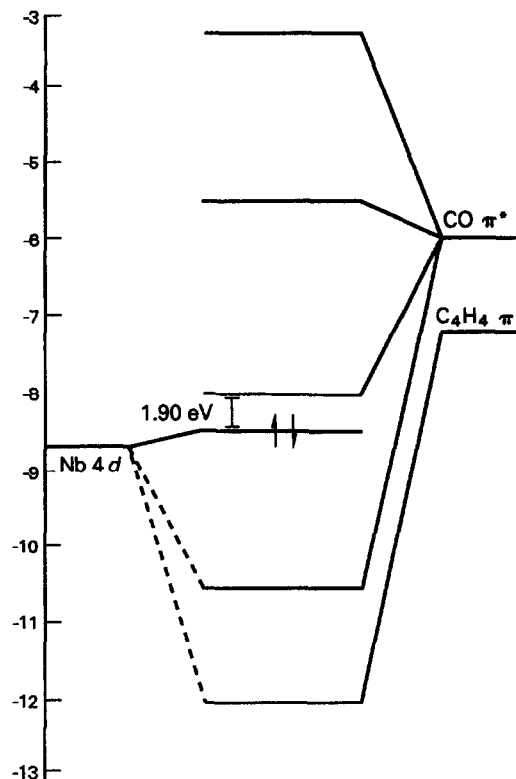
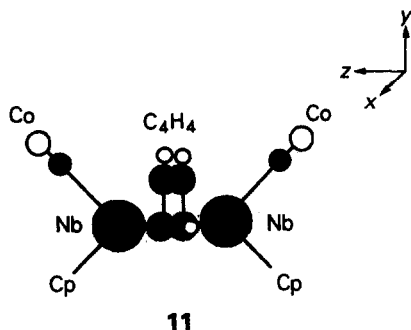


Fig. 13. Molecular orbital diagram for *cis*-(CpNbCO)₂(C₄H₄) (**11**). (Dotted lines indicate minor contributions.)

molecule and extensive mixing of the orbitals, which makes it difficult to trace changes in the composition of the levels. In addition, Table 2 shows that **10** has a lower total energy value than **2**, which is contrary to the trend in HOMO/LUMO gap mentioned above. This suggests that **2** might be a kinetically, but not thermodynamically, stable product.

One possible thermodynamic product would be *cis*-(CpNbCO)₂(C₄H₄) (**11**), where the acetylene ligands in **2** have been coupled.



11

As previously mentioned, because of steric hindrance, which makes it impossible for the C₄H₄ ligand to exist in a *trans* dimer, **11** has also been made *cis*. Figure 13 shows the molecular orbital diagram of this complex. Both the HOMO/LUMO gap and total energy of the compound (see Table

2) indicate that **11** is in fact very unstable, with the smallest gap and highest energy of all the niobium dimers in the table. This is mostly due to the low-lying LUMO, which is mainly CO π* in character. The carbonyl contribution pushes the molecular orbital particularly low in this complex because of the lack of metal *d* orbitals participation that usually destabilizes the virtual levels. It is a general trend, however, that the presence of carbonyl ligands in the dimers investigated in this work always causes the first few virtual orbitals to be low in energy because of contributions from CO π* levels. This lies at the root of the instability of such complexes. If the thermodynamically stable complex related to **2** contains one or more carbonyl ligands, then it is possible that its structure be radically different from that of the dimer, in order for the complex to remain stable.

Overall influence of the three geometric factors

The last set of calculations involves substituting molybdenum atoms in the frame of **2** and niobium atoms in the frame of **1**. Analysing the results of calculations on *cis*-(CpNbCl)₂(C₂H₄) (**12**) and *trans*-(CpMoCO)₂(C₂H₂)₂ (**13**) should help sum-

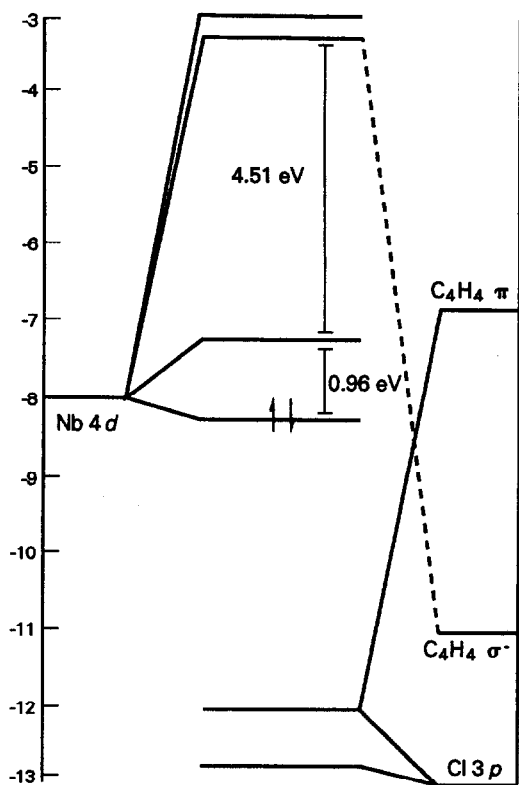


Fig. 14. Molecular orbital diagram for *cis*-(CpNbCl)₂(C₄H₄) (12).

marize the influence of all three geometric factors on the preferred geometry of the dimers and shed light on the reasons why molybdenum metals prefer a geometry like that in 1 and niobium metals prefer a 2-type frame. The geometries of 12 and 13 are identical to those of 1 and 2, except for the fact that the metals have been exchanged.†

Figure 14 is the molecular orbital diagram for 12: the pattern of two, closely spaced orbitals that are almost degenerate with the metal *d* levels, plus two (or three) high-lying orbitals is the same in the diagrams of both 1 and 12 (compare Figs 1 and 14). In the case of 12, though, the number of valence electrons is two less than that of 1, since the metal centres are niobium and not molybdenum. Therefore, in 12 the HOMO and LUMO are closely-spaced levels around the metal *d* orbitals and consequently the gap between them is only 0.96 eV. This leads to the conclusion that 12 would be a very unstable complex. In fact, the gap between the first- and second-lowest virtual orbitals is so large (4.51 eV) as to suggest that a reduced form of the complex might be stable.

When molybdenum centres are substituted into the frame of dimer 2, some changes occur in the

character of the valence molecular orbitals. Figure 15 shows the diagram for 13, which can be compared to that of 2, in Fig. 2. They both show two, low-lying, metal-to-C₂H₂ π* bonding orbitals and two, metal-based, moderately bonding orbitals. These last two levels are the HOMO and SHOMO of 2, but in 13, because of the extra valence electron in molybdenum with respect to niobium, there is an additional occupied level (*a_g* in Fig. 15). This orbital contributes to the bonding between the molybdenum centres and receives contributions from three molybdenum atomic orbitals. Since the *a_g* orbital comes between the HOMO and LUMO of Fig. 2, it substantially decreases the HOMO/LUMO gap of 13, which in turn results in an unstable system.

CONCLUSIONS

From this series of calculations, a number of conclusions about the title compounds and related dimers can be drawn. Patterns of orbital symmetries and energies become apparent and it can be determined how they are influenced by the geometric structure and the type of ligands on the dimers. The principal question asked in this paper is why the two dimers assume different geometric configurations,

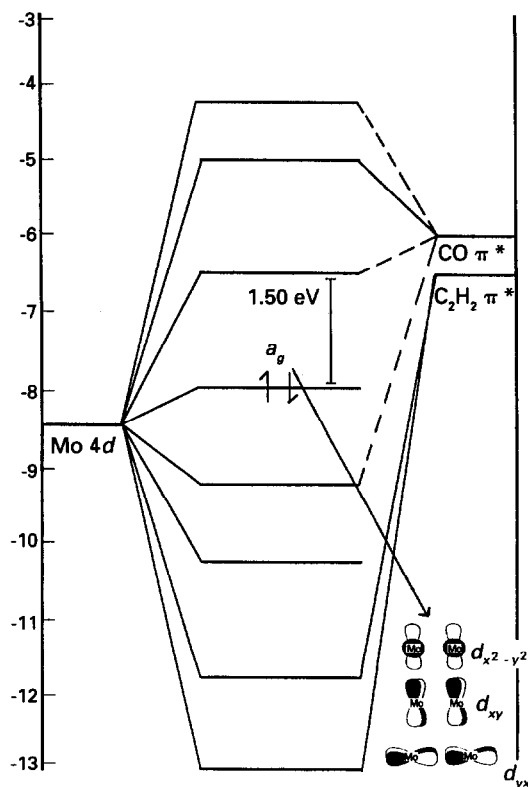


Fig. 15. Molecular orbital diagram for *trans*-(CpMoCO)₂(C₂H₂)₂ (13). (Dotted lines indicate minor contributions.)

† See footnote † on p. 1862.

when both clusters have the same number of valence electrons. The question is best answered by looking at Figs 14 and 15 and contrasting them with Figs 1 and 2. Such a comparison shows that each metal assumes the configuration that yields the largest HOMO/LUMO gap and therefore the most stable complex. If the metal is placed in the frame of the other complex, the difference in the number of metal valence electrons reduces the HOMO/LUMO gap drastically, which in turn diminishes the stability of the complex. Both the niobium and the molybdenum centres, therefore, assume the geometry that is appropriate to their number of valence electrons and type of ligands.

In examining the role of chlorine and carbonyl ligands in the dimers, it is also apparent that the π donor (Cl^-) has little influence on the valence molecular orbitals of the complex, since its p orbitals are found among the low-lying, filled levels of the molecule. On the other hand, the π acceptor ligand (CO) has a very strong influence on the molecular orbital composition of the complex, since its π^* virtual levels make up the majority of the low-energy, unoccupied orbitals of the molecule. The CO π^* influence usually leads to a lowering in the energy of such orbitals, and therefore it can potentially decrease the stability of the dimer.

When the coupled and decoupled forms of the R ligand (C_4H_4 and two C_2H_2) are compared, no dramatic differences are found. Both contribute to the bonding in the molecule with two, low-lying, filled levels that donate σ or π electron density to the metals and one virtual, π -type level that is used for metal-to-ligand backbonding (see Figs 5 and 6). The latter interaction gives rise to one (in the case of C_4H_4) or two (in the case of C_2H_2) markedly bonding molecular orbitals that have energies between those of the valence levels and those of the low-lying M—L and L—L levels.

The series of related compounds that has been investigated in this work could be augmented by additional, experimentally observed dimers which are variations on the basic geometries included in this paper.¹⁹ In addition, more could be predicted based on the electronic factors influencing stability which are discussed above.^{2b,12} Furthermore, there are other unanswered questions regarding these geometries, such as the relationship between substituent groups on the R ligands, their electron-withdrawing capabilities and bond angles and lengths in the complex.

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