

## COUPLING METHYLENES, METHYNES AND OTHER $\pi$ SYSTEMS ON ONE OR TWO METAL CENTERS

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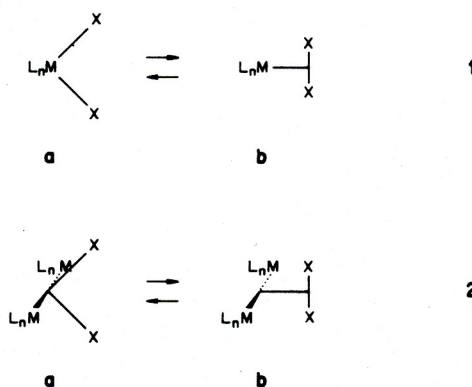
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**RÉSUMÉ.** — De nombreux complexes de métaux de transition existent sous deux formes isomériques. Dans l'une, deux (ou plus) fragments organiques sont liés par des liaisons multiples au squelette métallique. Dans l'autre, les deux fragments sont couplés par une liaison multiple et la molécule organique insaturée qui en résulte est elle-même liée au même squelette métallique. Les caractéristiques électroniques de la réaction de couplage des deux fragments ou de la réaction inverse, rupture de la liaison insaturée, a été étudiée tout d'abord pour un centre métallique dépourvu de tout autre ligand. A partir de cette étude élémentaire, la restauration des ligands permet de comprendre dans quelle mesure le changement de métal, le nombre d'électrons sur le métal, le squelette métallique, la nature des ligands, la géométrie des ligands ou le fragment organique lui-même affecte le cours général de la réaction. Cette étude a été faite pour quatre types de complexes ayant : (1) un centre métallique et des fragments organiques à un système  $\pi$  (2) un centre métallique et des fragments organiques cylindriques ayant deux systèmes  $\pi$  (3) deux centres métalliques et des fragments organiques ayant un seul système  $\pi$  (4) deux centres métalliques et des fragments organiques à deux systèmes  $\pi$ .

**ABSTRACT.** — There are many isomeric pairs among organometallic complexes in which one complex contains two (or more) organic fragments multiply bonded to a metal framework while another isomeric complex contains the composite multiply bonded organic molecule bound to the same framework. The electronic requirements for the forward coupling reaction, or of the reverse dismantling reaction, are explored for the metal stripped of its ligands. From this basic picture, the restoration of the ligands leads to an understanding of the effects that a change of metal, electron count, metal framework, ligand, ligand geometry, or organic fragment has upon the overall reaction. The reaction is studied for four types of complexes: (1) single-metal, single-faced organic  $\pi$ -ligands; (2) single-metal, two-faced or cylindrical organic  $\pi$ -ligands; (3) two-metal, single-faced or binuclear organic  $\pi$ -ligands; and (4) two-metal, two-faced organic  $\pi$ -ligands.

When two organic fragments are found on a metal framework, the possibility of coupling them becomes an attractive prospect, 1 and 2<sup>1</sup>. A systematic examination of the Walsh correlation diagrams for these complexes reveals that a group of frontier orbitals behaves in a consistent way when the number or geometry of the ligands varies. These complexes are arranged into four classes: (1) single-metal, single-faced  $\pi$ -ligands; (2) single-metal, cylindrical  $\pi$ -ligands; (3) two-metal or binuclear single-faced  $\pi$ -ligands; and (4) two-metal, cylindrical  $\pi$ -ligands<sup>2</sup>. Within each group of complexes, an examination of the naked metal case reveals the essence of the coupling reaction (as well as the dismantling reaction). This is not to say that the arrangement and nature of the ligands are not important influences on the course of the reaction but rather that the effects of the ligands may be factored conceptually from the reaction and treated separately. These two pieces can then be fit together to give a more thorough understanding of reactions 1 and 2.



X = single-face  $\pi$ -ligands — CR<sub>2</sub>, bent NR, etc.  
two-face  $\pi$ -ligands — CR, linear NR, N, O, CO, CNR, etc.

Single-Metal, Single-Faced Organic  $\pi$ -Ligand Complexes

The coupling of two methylenes on a single metal center is an example of a bond formation between two single-faced organic fragments, **3**. A Walsh correlation diagram for the coupling reaction is shown in Figure 1.

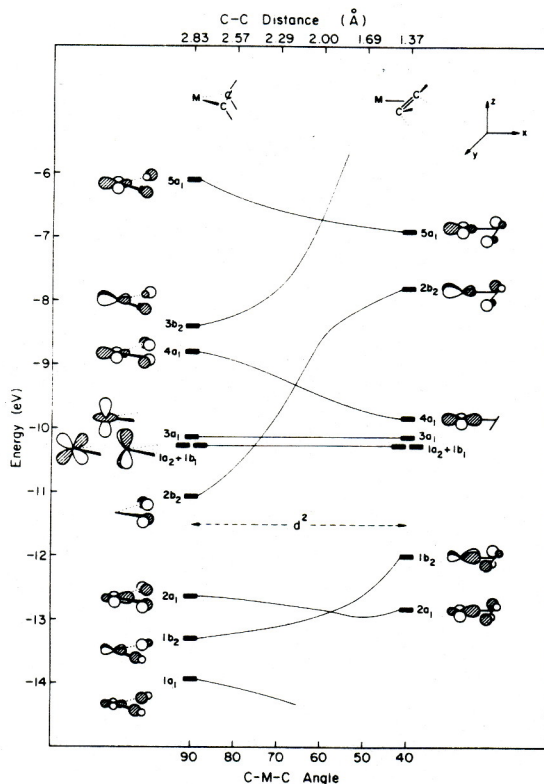
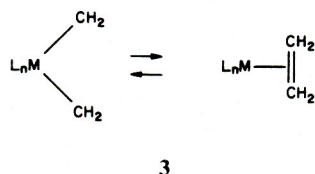
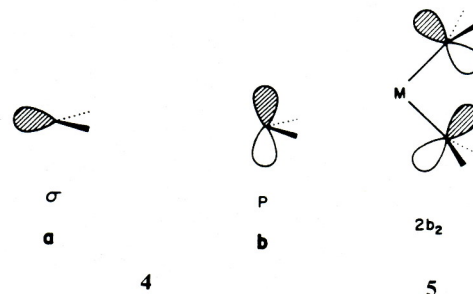


Figure 1. — The evolution of energy levels for  $W(CH_2)_2$  along an idealized coupling coordinate. Note the linear C—M—C angle scale at bottom and the corresponding nonlinear C—C distance at top.

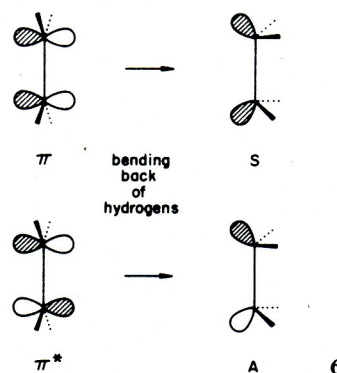


A methylene has two orbitals available for bonding to a metal: a filled  $\sigma$  lone pair, **4a**, and an empty  $p$  orbital, **4b**.<sup>3</sup> A pair of methylenes placed in a coupling geometry<sup>4, 5</sup> contribute in- and out-of-phase combinations of these  $\sigma$  and  $p$  orbitals. Three of these four orbitals,  $1a_1$ ,  $1b_2$  and  $2a_1$ , find a symmetry match among the metal orbitals. The fourth,  $2b_2$ ,<sup>5</sup> has the wrong pseudosymmetry to mix with any available  $s$ ,  $p$  or  $d$  metal orbital. Three of the metal  $d$  orbitals do not interact strongly with any methylene orbital and are nonbonding,  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$ ;  $1a_2$ ,  $1b_1$  and  $3a_1$ , respectively (left side of Fig. 1).

In the product with coupled methylenes, a metal olefin complex, the olefinic carbons do not lie in the same plane as the hydrogens. This bending back of the hydrogens



rehybridizes the HOMO and LUMO orbitals of the olefin, **6**. A planar olefin bonds to a metal through a filled  $\pi$  and an empty  $\pi^*$ . An olefin with bent-back hydrogens bonds with a filled symmetric lone pair, **S**, and an empty antisymmetric orbital, **A**. This rehybridization does not change the nodal structure of the olefin orbitals with respect to the metal. These orbitals, **S** and **A**, mix with a metal  $sp$  hybrid and  $d_{xy}$ ,  $a_1$  and  $1b_2$ . Four of the metal orbitals remain nonbonding:  $d_{xz}$ ,  $d_{yz}$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$ ;  $1a_2$ ,  $1b_1$ ,  $3a_1$  and  $4a_1$ , respectively.



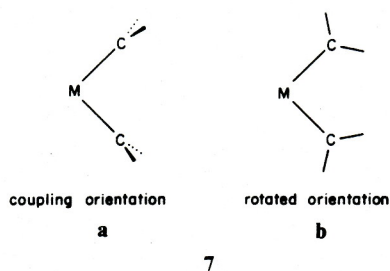
As the two methylenes approach one another along a least motion pathway, orbitals which are symmetric to the motion (the  $xz$  plane), those of  $a_1$  or  $b_1$  symmetry, should be stabilized; orbitals which are antisymmetric,  $b_2$  and  $a_2$ , should be destabilized. This assumes the orbitals in question place some electron density on the methylenes which approach each other, i. e. we would not expect much change in metal localized orbitals. By and large these expectations are fulfilled, but sometimes obscured by avoided crossings. The methylene  $\sigma$  orbitals,  $1a_1$  and  $1b_2$ , try to correlate to the olefin carbon-carbon  $\sigma$  and  $\sigma^*$ ,  $1a_1$  and  $3b_2$ ; the methylene  $p$  orbitals,  $2a_1$  and  $2b_2$ , try to correlate to the olefin  $\pi$  and  $\pi^*$  levels  $2a_1$  and  $1b_2$ . This picture, however, is complicated by the avoided crossing among the  $b_2$  orbitals. The  $1b_2$ , methylene  $\sigma$ , eventually correlates to the  $1b_2$  in the product, the olefin antisymmetric  $\pi^*$  level; the  $2b_2$ , methylene  $p$ , correlates to the  $2b_2$ ; and the  $3b_2$ , the olefin carbon-carbon  $\sigma^*$  orbital. And finally, the three nonbonding metal orbitals  $1a_2$ ,  $1b_1$  and  $3a_1$ , are unaffected by the motion of the methylenes.

A neutral methylene has a filled  $\sigma$  orbital, **4a**, and an empty  $p$  orbital, **4b**. A metal electron count of  $d^2$  fills through the  $2a_1$  (left side of Figure 1; the  $1b_2$  on the right). No crossing occurs between filled and unfilled orbitals and so the reaction is "allowed". For a metal electron count of  $d^4$  or higher, the  $2b_2$  becomes occupied for the bismethylene complex. As the

methylene carbons approach one another, this orbital rises sharply in energy and becomes unoccupied. An orbital crossing between filled and unfilled levels results and so the reaction is "forbidden".

### Oriental Preferences of the Bismethylene Complex

Since a methylene is a single-faced  $\pi$  acceptor the orientation of the two ligands is very important. In the coupling orientation, **7a**, the methylene  $p$  orbitals point toward one another, anticipating the forming olefin carbon-carbon bond. In the rotated orientation, **7b**, they do not. In any case, whatever the initial orientation of the methylenes, the complex must adopt the coupling orientation somewhere early along the coupling reaction coordinate. This would avoid the steric interaction of the methylene hydrogens, and also orient the methylene  $p$  orbitals properly.

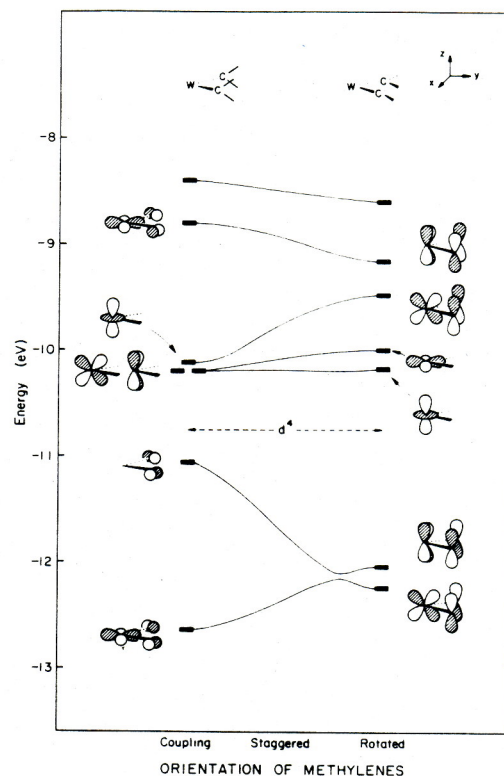


A Walsh correlation diagram for rotation of the methylenes is shown in Figure 2. In the coupling orientation only one of the two methylene  $p$  orbitals mixes with a metal orbital (see also Fig. 1). The other orbital,  $2b_2$ , **5**, has the wrong pseudosymmetry to interact strongly with the metal. In the rotated orientation, both of the methylene  $p$  orbitals,  $a_2$  and  $b_1$ , interact well with the metal. The coupling orientation has three metal nonbonding orbitals, the rotated orientation has only two.

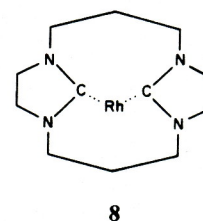
Our calculations show that for  $W(CH_2)_2$  with neutral methylenes: for an electron count of  $d^2$  or  $d^{10}$ , the coupling orientation is preferred; for an electron count of  $d^4$  or  $d^6$ , the rotated orientation is preferred and for an electron count of  $d^8$ , the staggered orientation is preferred. The presence of ligands *does* change this picture since the metal nonbonding orbitals may lie high in energy due to interaction with other metal ligands. A full analysis of the carbene orientation problem should include a discussion of the disrotatory mode, which we have not presented here, as well as the conrotatory one shown in Figure 2.

There are several examples of bismethylene complexes. Most of these complexes, containing electron-rich methylenes, have neither the coupling nor the rotated orientation. Instead the methylenes adopt a staggered orientation **6**. For the range of electron counts of these compounds, the staggered conformation is often close in energy to the preferred orientation. The steric interaction of the bulky substituents may effect the rotation of the methylenes. An example of this is the tetrakisbismethylene complex  $Ru(\overline{C}(NR)CH_2CH_2(NR))_4Cl_2$  which has all four methylenes in a propeller arrangement **6**. A very interesting exception to the staggered conformation is  $Rh(COD)L_2^{cyclam}$ , **8**. The

$(CH_2)_n$  bridges prevent the methylenes from rotating and so the complex adopts the coupling orientation ( $\angle C-Rh-C = 79^\circ$ ) **8**.



**Figure 2.** — The evolution of energy levels for the conrotatory motion of two methylenes of  $W(CH_2)_2$ .



When the effects of the orientational preferences are combined with those of the coupling reaction, a clear picture of the overall process emerges. For an electron count of  $d^2$ , not only do the methylenes adopt the coupling orientation, but also the coupling reaction is "allowed". The bismethylene and olefin complexes should be in equilibrium. For an electron count of  $d^4$ , the methylenes adopt a rotated orientation with a calculated rotation barrier of about 1 eV. Also, the coupling reaction itself is "forbidden". A large barrier separates the bismethylene and olefin complexes.

### Affecting the barrier for the $d^4$ -coupling reaction

The forbidden nature of the coupling reaction, for electron counts of  $d^4$  or higher, arises directly from the sharp increase

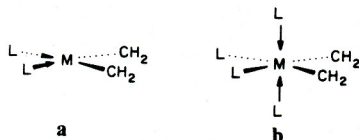
in energy of the  $2b_2$  orbital, **5**, (see Fig. 1). This orbital must cross the flat metal nonbonding orbitals,  $1a_2$ ,  $1b_1$  and  $3a_1$ . If for the bismethylene complex the energy of the  $2b_2$  orbital were raised, or if the energy of the metal orbitals were lowered, then there would be no orbital crossing.

There are four ways to lower the barrier of the coupling reaction. Since the  $2b_2$  orbital, **5**, is exclusively on the methylenes and the metal nonbonding orbitals are exclusively on the metal, it is possible to affect one of these orbitals without affecting the other. The following four chemical substitutions will reduce the barrier: (1) a more electronegative metal will push the metal orbitals down; (2) acceptor ligands on the metal will also push the metal orbitals down; (3) donor substituents on the methylene carbon push the  $2b_2$  up in energy; or (4) a more electropositive atom substituted for the methylene carbon will also push the  $2b_2$  up in energy.

If any or all of these prescriptions for chemical substitution are applied with sufficient impact so that the  $2b_2$  orbital is found above the metal nonbonding orbitals of the naked metal bismethylene complex, then for electron counts of  $d^2$ - $d^8$ , the coupling reaction is "allowed".

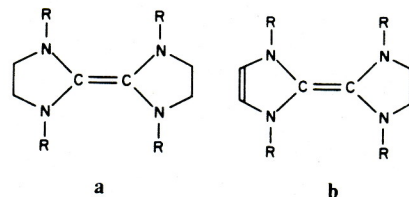
### Restoring the Metal Ligands

From the basic naked picture, it is possible to restore the metal ligands and predict the orbital evolution of a fully coordinated complex. If two equatorial ligands are added to the metal, **9a**, they bring two  $\sigma$ -donor orbitals,  $a_1$  and  $b_2$ . These orbitals interact with the high-lying metal  $sp$  hybrid orbitals,  $4a_1$  and  $3b_2$  (Fig. 1), pushing them up in energy. The ligand-only orbital,  $2b_2$ , **5**, and the metal nonbonding orbitals are not affected by the new equatorial ligands. If two axial ligands are also added to the metal, **9b**, with their two  $\sigma$ -donor orbitals,  $a_1$  and  $b_2$ , the metal orbitals  $d_{z^2}$  and  $p_z$  are pushed up in energy. The only relevant modification of the naked metal picture upon octahedral coordination is the removal of the  $3a_1$  orbital,  $d_{z^2}$ , from the frontier orbital region. In general any number or arrangement of metal ligands will push up in energy some combination of the metal  $sp$  hybrid and nonbonding orbitals. The  $2a_1$  and  $2b_2$  orbitals remain low in energy and for the coupling reaction, an electron count of  $d^2$  is "allowed", and  $d^4$  is "forbidden".



9

Of the thousands of known olefin complexes, only a handful have shown any reactivity towards cleavage of the olefin carbon-carbon bond. Electron-rich olefins react with a variety of metal complexes to yield mono, bis, tris and tetrakis-methylene complexes <sup>6-12</sup>. The electron-rich olefin used by Lappert, **10a**, and the related olefin used by Öfele, **10b**, react with a wide range of metal complexes to form stable carbene complexes. The electron-donating nature of the ligand is apparent. In a number of related biscarbene complexes, the carbene carbon has been replaced by a more electropositive atom such as tin, lead or germanium <sup>13</sup>.



10

### Single-metal, cylindrical or two-faced organic $\pi$ -ligand complexes

When a hydrogen is removed from a methylene, a second  $p$  orbital is freed for interaction with a metal. A Walsh correlation diagram for the coupling of two cylindrical  $\pi$ -ligands, methynes, **11**, is shown in Figure 3.

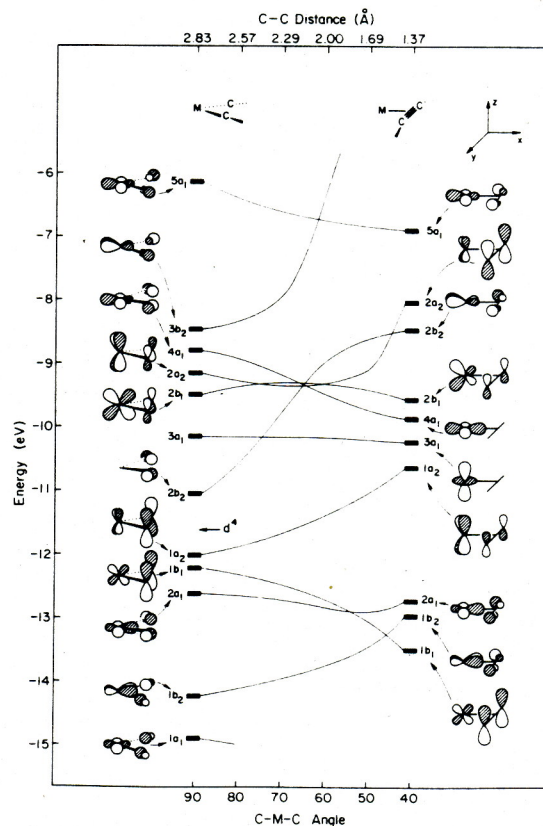
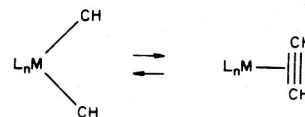
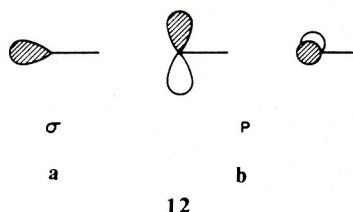


Figure 3. — The evolution of energy levels for  $W(CH)_2$  along an idealized coupling coordinate. Note the linear C—M—C angle scale at bottom and the corresponding nonlinear C—C distance at top.



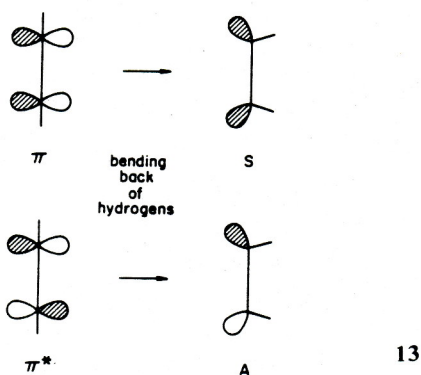
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A methyne has three orbitals available for bonding to a metal: a filled  $\sigma$  lone pair, **12a**, and a pair of perpendicular  $p$  orbitals, **12b**, containing only one electron. A pair of methynes contributes in- and out-of-phase combinations of these  $\sigma$  and  $p$  orbitals for bonding to a metal. The  $\sigma$  and one of the  $p$  orbitals are present from the methylene case; three of these four orbitals find a symmetry match among the metal orbitals. The fourth orbital,  $2b_2$ , **5**, has the wrong pseudosymmetry to interact with the metal. The other two  $p$  orbitals,  $1b_1$  and  $1a_2$ , interact with the metal  $d_{xz}$  and  $d_{yz}$  orbitals, respectively. The two electrons from the methylene  $p$  orbitals occupy the  $2a_1$  orbital. The metal electrons fill the  $1b_1$  orbital and on up in energy. An electron count of  $d^4$  fills through the  $1a_2$  orbital.



The orientation of a single-faced  $\pi$ -ligand determines with which metal orbital the  $p$  orbitals interact, Figure 2. A cylindrical  $\pi$ -ligand does not have an orientation preference. The acceptor  $p$  orbitals can interact with  $d_{xz}$ ,  $d_{yz}$  and  $d_{x^2-y^2}$  simultaneously and one set of the  $p$  orbitals is always prepared to form the carbon-carbon bond. While for the methylene case in a coupling orientation there were three nonbonding metal orbitals, now only the  $d_{z^2}$ ,  $3a_1$ , remains nonbonding.

In the product with coupled methynes, a metal-acetylene complex, the acetylene hydrogens are bent back away from the metal. This bending back rehybridizes one set of  $\pi$  and  $\pi^*$  orbitals, **13**. The other set of  $\pi$  orbitals is orthogonal to the bending hydrogens and remains pure  $\pi$  and  $\pi^*$ .



The rehybridization does not change the nodal character of the acetylene orbitals with respect to the metal. These orbitals, S and A, mix with  $d_{x^2-y^2}$  and  $d_{xy}$ ,  $2a_1$  and  $1b_2$ . The remaining acetylene  $\pi$  bond is  $1b_1$ ;  $\pi^*$  is  $1a_2$ .

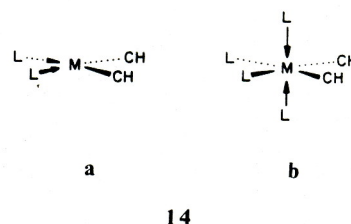
As the two methynes approach one another along a least motion pathway, orbitals which are symmetric to the motion (the  $xz$  plane), those of  $a_1$  or  $b_1$  symmetry, are stabilized; orbitals which are antisymmetric,  $b_2$  or  $a_2$ , are destabilized. The methyne  $1a_1$  and  $1b_1$  orbitals become the acetylene  $\sigma$  and  $\pi$  bonds, respectively; the  $1a_2$  becomes the  $\pi^*$  stabilized  $d_{yz}$ ; the  $2b_2$  rises sharply in energy; the  $d_{z^2}$ ,  $3a_1$ , remains

unaffected. The metal-methyne antibonding orbitals,  $2b_1$ ,  $2a_2$ ,  $4a_1$ ,  $3b_2$  and  $5a_1$  correlate similarly to the bonding orbitals, Figure 3.

A metal electron count of  $d^2$  occupies up to the  $1b_1$  orbital, and upon coupling no crossing between filled and unfilled levels occurs. The reaction is "allowed". For a metal electron count of  $d^4$ , the  $1a_2$  orbital is occupied. This orbital rises in energy since the methyne-methyne interaction is antibonding. There is, however, no orbital crossing, and the coupling is "allowed". The  $d^4$  electron count should be the favored metal count for a bismethyne complexes. For electron counts of  $d^6$  or higher, the  $2b_2$  is occupied and a level crossing occurs. The reaction is "forbidden".

### Restoring the metal ligands

The restoration of the metal ligands parallels the methylene case. Two equatorial ligands,  $a_1$  and  $b_2$ , push up in energy the  $5a_1$  and  $3b_2$  orbitals, **14a**. Two axial ligands, also  $a_1$  and  $b_1$ , push up in energy the  $3a_1$  orbital (as well as the metal  $p_z$  orbital, **14b**). The essential nature of the coupling reaction is left intact.



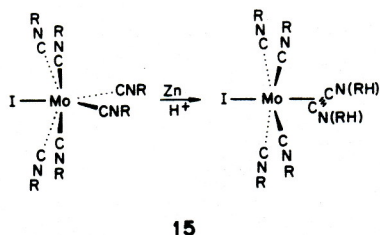
### Affecting the barrier for the $d^6$ -coupling reaction

Of the four prescriptions used to reduce the barrier of coupling two single-face  $\pi$ -ligands, not all are effective for the coupling of two cylindrical  $\pi$ -ligands. For a six coordinate bismethyne complex, there are no metal nonbonding orbitals. The  $d_{z^2}$  has been pushed up in energy by the axial ligands; the  $d_{xz}$  and  $d_{yz}$  have been pushed down by the acceptor methylene  $p$  orbitals. Consequently the  $1b_1$  and  $1a_2$  orbitals are now below the  $2b_2$  in energy. This is why an electron count of  $d^4$  is "allowed" for methyne coupling and "forbidden" for methylene coupling.

If, for example, a donor substituent on the methylene carbon is used, the  $2b_2$  orbital will rise up in energy, but so also will the  $2b_1$  and  $2a_2$  orbitals. The barrier remains the same. The same applies to the substitution of a more electropositive atom for the methyne carbon. The remaining two prescriptions will reduce the barrier: (1) a more electronegative metal will lower the  $2b_1$ ,  $2a_2$ ,  $1b_1$  and  $1a_2$  orbitals while leaving the  $2b_2$  unaffected; or (2) acceptor ligands on the metal will also push the  $2b_1$ ,  $2a_2$ ,  $1b_1$  and  $1a_2$  orbitals down in energy; leaving the  $2b_2$  alone.

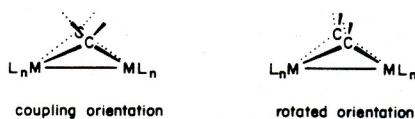
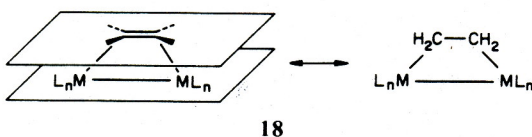
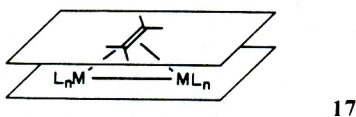
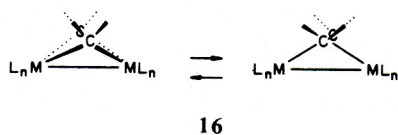
This analysis of methyne coupling can be extended to include nitrenes, oxides and isocyanides if proper attention is paid to electron counting. In non-interconvertible isomeric  $\text{PhNO}^{14}$  and  $(\text{PhN})(\text{O})^{15}$  complexes, more electronegative atoms, nitrogen and oxygen, have replaced the methyne carbon. Separate  $(\text{NR})_2^{16}$  and  $\text{RNRR}^{17}$  complexes,  $(\text{NR})(\text{CR}_2)$  and  $\text{RNCR}_2$ ,  $^{18}$   $(\text{N})(\text{CR})$  and  $\text{NCR}^{19}$ ,  $(\text{O})(\text{CR})$  and  $\text{OCR}^{20}$ ,  $(\text{O})(\text{CR}_2)$  and  $\text{OCR}_2^{21}$  are also of this type. So

is the photochemical cleavage of molecular oxygen to a *cis* dioxo complex in (TPP) Mo(O<sub>2</sub>)<sub>2</sub><sup>22</sup>. There are suggestions of incipient coupling of SR ligands<sup>23</sup>. Of particular interest is the coupling of two isocyanides to a diaminoacetylene on a seven-coordinate Mo(II) complex, **15**<sup>24</sup>. The net addition to two hydrogen atoms to the nitrogens accompanies the coupling reaction. The presence of the zinc complicates the overall reaction, but the first step is undoubtedly a coupling of two of the isocyanides. We have analyzed this reaction, as well as the prospects for carbonyl coupling, elsewhere<sup>25 a</sup>. Coupling of CO and CR has been achieved<sup>25 b, c</sup>.



### Single-faced $\pi$ -ligands on a binuclear framework

The coupling of two prototypical ligands, methylenes, in a binuclear complex is shown in **16**. Orientational problems are acute in both the "reactant" and in the product. First, no ethylene complexes of the "perpendicular" type, **17**, so common in acetylene chemistry, appear to be known. Only "parallel" complexes, **18**, and not too many at that, are available<sup>26</sup>. Second, the least-motion "coupling" orientation, **19**, is not a likely equilibrium geometry for a bridging carbene complex. Instead the rotated conformation, **20**, with locally tetrahedral carbons, is found in all the known bis-carbene complexes<sup>27</sup>.



No simple motion will take the favored bis-carbene **20** to the normal coordinated olefin **18** geometry. In this initial study we avoided the question of the correct complete pathway for carbene coupling. Instead we assumed that the "rotated" geometry **19** must be reached first in the reaction, that it is then transformed to the "perpendicular" olefin **17**, which then might rotate to a better geometry. The real pathway is probably of lower symmetry, but we hope that some insight can be gained from this model reaction. The evolution of the energy levels on going from **19** to **17** is shown in Figure 4.

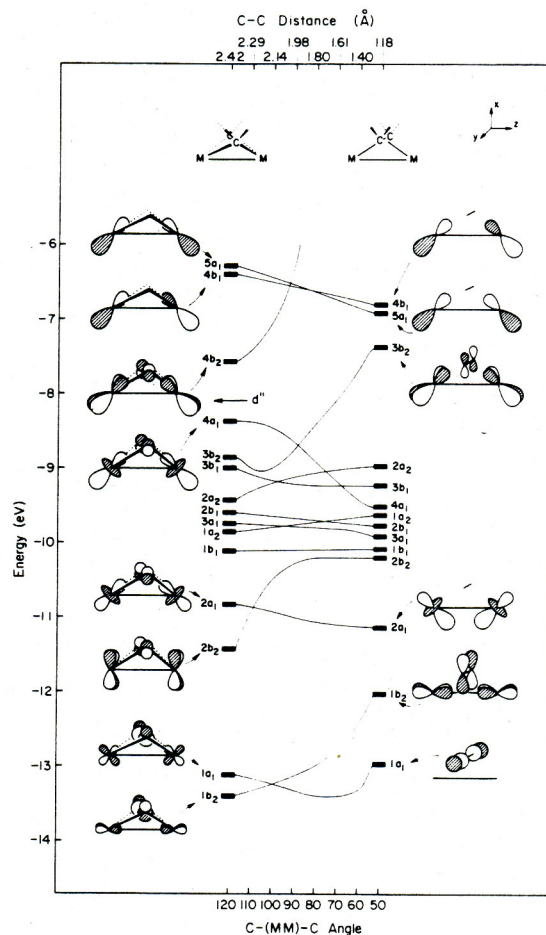
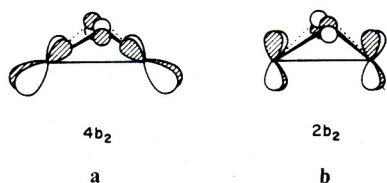


Figure 4. — The evolution of energy levels in W<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>. Note the linear C-(MM)-C angle scale at bottom and the corresponding nonlinear C-C distance at top.

The orbitals for methylene, **4**, form symmetric and antisymmetric combinations. For a single metal, the 2b<sub>2</sub> orbital, **5**, finds no symmetry match among the metal orbitals. For a d<sup>4</sup> bismethylene complex, this ligand-only orbital, lying below the metal nonbonding orbitals, is occupied. For a two metal framework, however, a metal orbital with the correct symmetry can mix with the methylene b<sub>2</sub>, **21**. The 4b<sub>2</sub> orbital, in **21**, is an antibonding admixture of methylene b<sub>2</sub> and metal b<sub>2</sub> orbitals. This high-lying orbital has an energy above the framework metal-metal orbitals.

Even though Figure 4 contains many more orbitals than the single-metal case, many of the orbitals follow roles similar to

those described above. The low-lying  $1a_1$  and  $1b_2$  are the bonding combinations of the methylene  $\sigma$  orbitals, **4a**, and the metal; the  $2a_1$  and  $2b_2$  orbitals are the methylene  $p$  orbitals, **4b**. The next seven orbitals,  $1b_1$ ,  $1a_2$ ,  $3a_1$ ,  $2b_1$ ,  $2a_2$ ,  $3b_1$  and  $3b_2$  are all metal-metal orbitals. The  $4a_1$  and  $4b_2$  orbitals are the antibonding partners of  $2a_1$  and  $2b_2$ . Finally, the  $4b_1$  and  $5a_1$ , metal  $sp$  hybrid orbitals, point away from the methylene carbons.



21

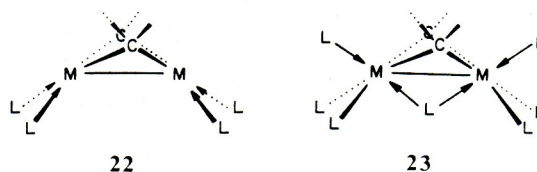
For the coupled olefin complex, only two olefin orbitals, the symmetric and antisymmetric lone pairs, **6**, have a large overlap with the metal. The  $1a_1$  orbital is the olefin carbon-carbon bond. The  $1b_2$  orbital has been stabilized by the antisymmetric lone pair. The symmetric lone pair has spread out among the  $a_1$  orbitals of the nine metal-metal orbitals,  $2a_1$ ,  $2b_2$ ,  $1b_1$ ,  $3a_1$ ,  $2b_1$ ,  $1a_2$ ,  $4a_1$ ,  $3b_1$  and  $2a_2$ . The  $3b_2$  orbital is the antibonding partner of the  $1b_2$  orbital. The  $5a_1$  and  $4b_2$  orbitals are still metal  $sp$  hybrids which point away from the methylene carbons.

#### Restoration of metal ligands

If four ligands approach the bare metal complex, **22**, such that each metal is locally square planar, they push up in energy some of the naked metal orbitals. The new ligand orbitals are of  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  symmetries. The high-lying metal  $sp$  hybrids,  $4b_1$  and  $5a_1$ , are directed toward the new ligands; the other two orbitals must come from the block of metal-metal orbitals. One is the  $2a_2$  orbital, the other, the  $4b_2$  orbital. The  $3b_2$  orbital must now correlate to the olefin  $\sigma^*$ . Since two previously occupied orbitals (for " $d^{11}-d^{11}$ ") are emptied, and an electron count of  $d^9-d^9$  leaves the  $3b_2$  unoccupied.

If three additional ligands approach the complex, **23**, such that each metal is locally octahedral, two  $a_1$  and one  $b_1$  orbitals appear. Three previously occupied orbitals bond to the ligands, two are emptied; the third is not pushed up high enough in energy to empty and becomes the HOMO. An electron count of  $d^7-d^7$  does not fill the  $3b_2$  orbital. For this electron count, our calculations show the olefin complex to be more stable. For  $d^8-d^8$ , however, the bismethylene complex is calculated to be more stable. On the olefin side the extra electrons must occupy a high-lying orbital, while for the bismethylene complex a gap is opened. Once formed, the  $d^8-d^8$  bismethylene complex will rotate.

As we mentioned above, only a few known olefin complexes bridge two metals. All of these have the structure shown in **18**<sup>26</sup>. Complexes with two or more bridging substituted methylenes are also known<sup>27</sup>. All of these complexes have the methylenes in a rotated orientation. King and Harmon, using an electron-rich olefin similar to those used by Lappert and Öfele, **10**, reacted it with  $\text{Fe}_3(\text{CO})_2$  or  $\text{Fe}(\text{CO})_5$ , found one of the products to be a bismethylene complex<sup>28</sup>. In general there is evidence of reluctance to form ethylene from the bismethylene complexes<sup>27k</sup>.



#### Cylindrically symmetric $\pi$ -ligands on a binuclear framework

When a hydrogen is removed from a methylene, a second  $p$  orbital is freed for interaction with the metal framework. The correlation diagram for the coupling of two methylenes on a binuclear framework, **24**, is in Figure 5.

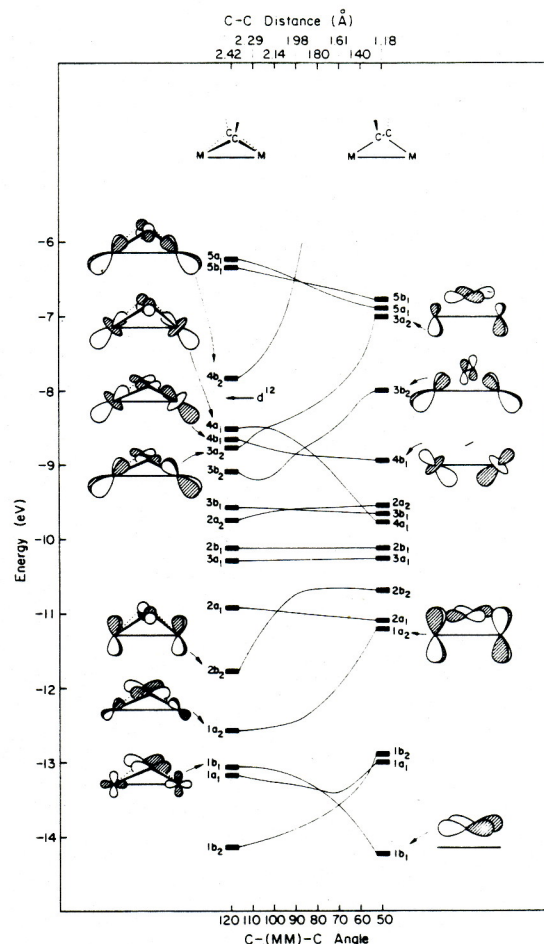
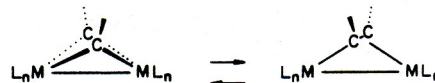


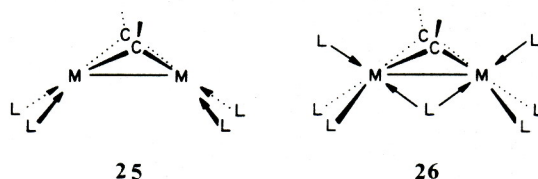
Figure 5. — The evolution of energy levels in  $\text{W}_2(\text{CH})_2$ . Note the linear  $\text{C}-(\text{MM})-\text{C}$  angle scale at bottom and the corresponding nonlinear  $\text{C}-\text{C}$  distance at top.



24

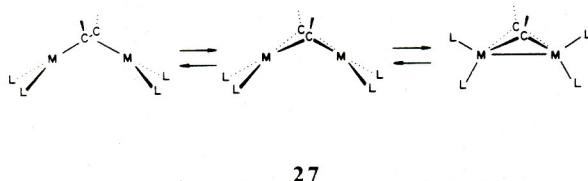
The two new methyne orbitals,  $a_2$  and  $b_1$ , interact with two metal-metal orbitals. The bonding combinations remain filled the antibonding empty. For neutral methynes, a metal electron count of " $d^{12}-d^{12}$ " leaves the  $4b_2$  empty and thus the coupling reaction is "allowed".

When four ligands approach the metal framework, **25**, such that each metal is locally square planar, four high-lying metal hybrid orbitals,  $5a_1$ ,  $3a_2$ ,  $5b_1$  and  $4b_2$  are used to bind the new ligands. Two of these orbitals are emptied and an electron count of  $d^{10}-d^{10}$  leaves the  $3b_2$  orbital empty. When three additional ligands approach the metal framework, **26**, two  $a_1$  and one  $b_1$  orbitals appear. Three previously occupied metal-metal orbitals bind to the ligands; two are emptied, and the third becomes the HOMO. An electron count of  $d^8-d^8$  leaves the  $3b_2$  empty. For this electron count, our calculations show the uncoupled complex ( $L=H^-$ , **26**) lies 1 eV above the acetylene complex in energy with no barrier to their interconversion.



There are many examples of both parallel and perpendicular acetylenes bridging two metals <sup>29</sup>, but relatively few examples of biscarbene complexes <sup>28,30-31</sup>, Separate  $(NR)_2$  <sup>32</sup> and RNNR <sup>33</sup> complexes as well as  $(NR)(O)$  <sup>34</sup> complexes are also known.

Stone and coworkers have observed fluxionality of a two-metal acetylene complex, **27**, ( $M=Pt$ ,  $L=PR_3$ , COD) <sup>35</sup>. The experimental evidence shows the equalencing of the two acetylene carbons. For a  $d^{10}-d^{10}$   $L_4Pt_2(C_2R_2)$  complex, the splitting of the acetylene is an "allowed" process <sup>36</sup>. Once split, the  $ML_2$  moiety can rotate, and upon reformation of the acetylene carbon-carbon bond, the effective rotation of the acetylene has occurred.



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#### Appendix

All calculations were performed using the extended Hückel method <sup>37</sup> with weighted  $H_{ij}$ 's <sup>38</sup>. The parameters are given in the Table below. Idealized geometries were used to provide a bridge among the known experimental structures.

For  $M(CH_2)_2$ , the  $\angle HCH$  of methylene was always  $120^\circ$ . As the two  $CH_2$ 's are coupled the hydrogens are bent back by  $25^\circ$ . For  $M(CH)_2$ , the hydrogens are bent back by  $30^\circ$ . The reaction coordinate is the  $C-M-C$  angle. The bond distances are:  $M-C$  2.0 Å;  $C-H$  1.09 Å;  $M-L(H^-)$  1.8 Å.

For  $M_2(CH_2)_2$ , the  $\angle HCH$  is  $120^\circ$ . As the two  $CH_2$ 's are coupled the hydrogens are bent back by  $30^\circ$ . For  $M_2(CH)_2$ , the hydrogens are also bent back by  $30^\circ$ . The reaction coordinate is the  $C-(M-M \text{ bond center})-C$  angle. The bond distances are:  $M-M$  2.6 Å;  $M-C$  2.03 Å;  $C-H$  1.09 Å;  $M-L(H^-)$  1.8 Å.

Table. — Extended Hückel Parameters

Orbital	$H_{ij}$ (eV)	$\zeta_1$	$\zeta_2$	$C_1^*$	$C_2^*$	
W	5d	-10.37	4.982	2.068	0.668 54	0.542 43
	6s	-8.26	2.341			
	6p	-5.17	2.309			
C	2s	-21.4	1.625			
	2p	-11.4	1.625			
H	1s	-13.6	1.3			

\* These are the double-zeta expansion coefficients.

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