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THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE AND REACTIONS OF $R_2W(\mu\text{-}CR)_2WR_2$*

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The electronic structure and reactions of $L_2W(\mu\text{-}CR)_2WL_2$, $\underline{\underline{1}}$, $(L = (CH_3)_3SiCH_2$, $R = CH_3)_3SiC$ are studied theoretically using the Fragment Molecular Orbital (FMO) approach on the model $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$, $\underline{\underline{7}}$. According to this the Molecular Orbitals (MOs) of $\underline{\underline{2}}$ are constructed from that of smaller fragments. The FMOs of $(CH_3)_2W$ are relatively simple. Interaction of two $W(CH_3)_2$ produces $(CH_3)_2WW(CH_3)_2$, This interacts with $(CH)_2$ fragments to give $\underline{\underline{7}}$.$\underline{\underline{7}}$ has a metal-metal single bond (d^1-d^1, W^{+5}). LUMO is a δ*MO so that d^2-d^2 system will not have a metal-metal double bond. The theoretical studies explain the following experimental observations. Reaction of $\underline{\underline{1}}$ with C_2R_2 leads to an initial complex $(L_2W(\mu\text{-}CR)_2WL_2(h^2\text{-}C_2R_2)$, $\underline{\underline{3}}$ whose electronic structure shows no metal-metal bond. $\underline{\underline{3}}$ reacts further to give $L_2W(\mu\text{-}C_3R_3)(\mu\text{-}CR)W(L_2)$, $\underline{\underline{2}}$, which regains the metal-metal bond. Ta and Nb analogs of $\underline{\underline{1}}$ do not react with acetylene. Acetylene and allene, but not ethylene and butadiene react with $\underline{\underline{1}}$. Only one equivalent of acetylene react with $\underline{\underline{1}}$, but two equivalents of allene reacts. The W_2C_2 ring in $\underline{\underline{1}}$ according to our analysis, is an unusual case of a four-membered ring with four π electrons and yet 'aromatic'. As most of the arguments developed here depend on symmetry, overlap, electron count and electronegativity differences, our conclusions should depend minimally on the method of calculation.

Key Words : Molecular Orbitals; Organometallic Reaction; Carbyne Complex.

INTRODUCTION

REACTIONS of carbyne ligands coordinated to transition metals are of current interest, as these species are implied in several catalytic reactions involving new C–C bond formation.[1] Several reactions of a bridging C–H(or C–R) group and alkynes are reported recently. Stone and coworkers found that μ–CR groups in Fe–W, and Co–W compounds reacted with alkynes to give dinuclear complexes with C_3R_3 units straddling the metal-metal bond (reaction 1).[2] Casey and co-workers recently discovered a hydrocarbation reaction where the bridged C–H group in $(C_5H_5)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(C_5H_5)^+$ reacts with alkynes (reaction 2).[3]

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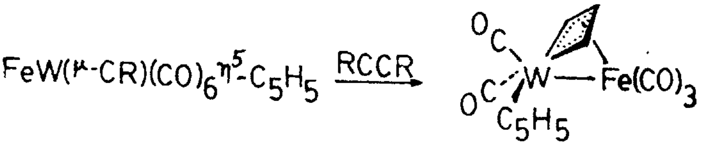

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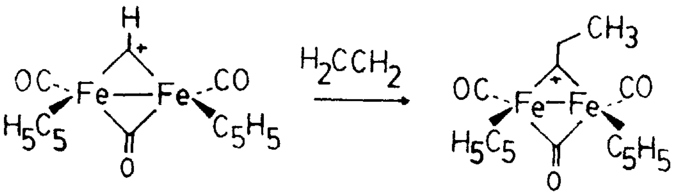

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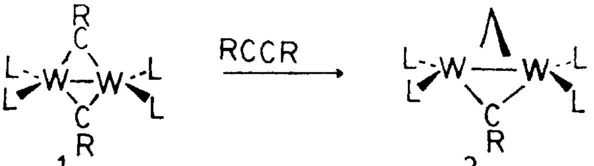
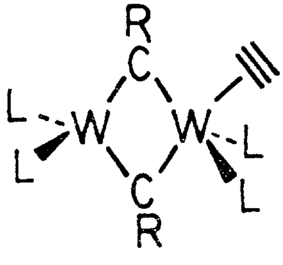


1 2

(3)[4]

Another reaction of the bridged carbynes was discovered by Chisholm and coworkers.[4] Reaction (3) is typical. The acetylene attaches itself to the μ–CR, forming a new C–C bond. The resulting C_3R_3 unit is similar to that in reaction(1). Reaction (3) proceeds through the formation of an intermediate, 3, where acetylene is attached to one of the metals. X-ray structures are available for representatives of 1, 2 and 3.[5] Formally the W in 1 is d^1. Isostructural Ta and Nb complexes (d^0–d^0) do not react with acetylene under similar conditions.[5] 1 reacts with acetylene and allene but not with ethylene and butadiene.[6] Again only one mole of acetylene reacts with 1 leading to 2 but allene reacts initially to give the 1 : 1 adduct 4 but, in some cases, produces a 1 : 2 complex.[6] Reaction (3) produces a kinetic product which rearranges in solution by scrambling the CR units of the C_3R_3 group to give the thermodynamically stable product. This process does not interchange the two bridging alkynes present initially. A bridged cyclopropene complex, 6, has been suggested as a possible intermediate for the C_3R_3 scrambling.[4] This rearrangment is slower when L = O–CH(CH$_3$)$_2$ than when L = CH$_2$Si(CH$_3$)$_3$. The geometry of (C_3R_3 in 2 is not symmetrical despite the symmetric disposition of the remaining part of the molecule. In the solid state, the middle CR unit of the C_3R_3 is closer to one of the metals so that the remaining metal forms an almost planar MC_3 metallocyclobutadiene ring, 5.[7] The M_2C_2 ring is often described as a 1,3-metallacyclobutadiene. Does it have the antiaromaticity associated with the organic equivalent cyclobutadiene? A detailed understanding of these reactions and structures are sought through molecular orbital theory so that better control of these reactions is possible through substituents on bridging carbons, replacement of ligands and variations of the metal and its oxidation state.



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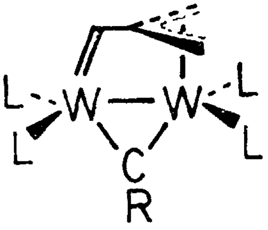

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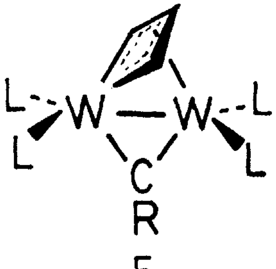

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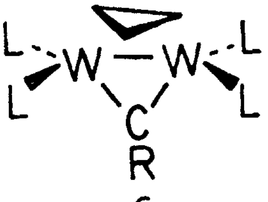

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Our approach is the following. The electronic structures of the stable compounds involved, 1, 2, and 3 will be analyzed first. Detailed pathways for the transformation of 1 → 3 and 3 → 2 will be studied to find the electronic requirements of the reaction. The suggested mechanism of scrambling of the C_3R_3 unit in 2 will be studied to find the influence of the substituents of the barrier. The Fragment Molecular Orbital (FMO) approach where the molecular orbitals (MOs) of larger fragments are constructed from that of the well-understood smaller fragments will be used throughout.[8] The Extended Huckel Method is used in generating wave functions.[9] As most of the arguments developed in the paper depend on symmetry, overlap, electron count and electronegativity differences our conclusion should depend minimally on the method of calculation.

RESULTS AND DISCUSSION

Electronic Structure of $L_2M(\mu\text{-}CR)_2\,ML_2$: Isostructural analogs of 1 are known for M = Ta, Nb, Ti, Re. The dependence of the M–M distances on the electron count has been described previously.[4] With d^0–d^0 metals the M–M distances is 2.897 Å (M = Nb, $L_2Nb(\mu\text{-}CR)_2\ NbL_2$, $L = (CH_3)_3\ SiCH_2$ $R = (CH_3)_3\ SiC$),[10] d^1–d^1 it is 2.548A(1).[4] Addition of two electrons (d^2–d^2) does not change the M–M distance considerably (2.557Å, $L_2Re(\mu\text{-}CR)_2\ ReL_2$).[11] Out of the multitude of structures we selected a model for our study, $(CH_3)_2\ W(\mu\text{-}CH)_2\ W(CH_3)_2$, 7. (The geometry and other parameters used in this and other Extended Huckel calculations are given in the appendix). 7 can be divided conceptually into $(CH_3)_2\ WW(CH_3)_2$ and $(CH)_2$. The MOs of the former fragment is familiar and can be constructed from the interaction of two $W(CH_3)_2$ fragments (Fig. 1).[12] The ML_2 fragment has a cluster of four orbitals $1a_1$, b_1, a_2 and $2a_1$ (C_{2v} point group). (Throughout this paper only the metal based orbitals (ns, $n+1$ s, p) are counted according to increasing serial number. The ligand-based orbitals will be mentioned with the symmetry labels, but these are not included in numbering the metal based MOs. Besides, a ligand based orbital label will be followed by (1) in parenthesis, e.g. $a_2(1)$. The d_{yz} orbital (b_2) lies above these four. In addition there is $3a_1$, a predominantly sp^n hybrid orbital, very high in energy.

When the ML_2 fragments are brought together the b_1, a_2 and b_2 orbitals give the bonding combinations b_{3u}, b_{2g}, b_{1g}, a_u, b_{2u} and b_{3g} (D_{2h} point group). The four orbitals resulting from the $1a_1$ and $2a_1$($1a_g$, $2a_g$, $1b_{1u}$, $2b_{1u}$), as well as a_u, b_{2u}, and b_{1g} are shown on the right hand side of Fig. 1. With W^{2+}, the lowest four MOs

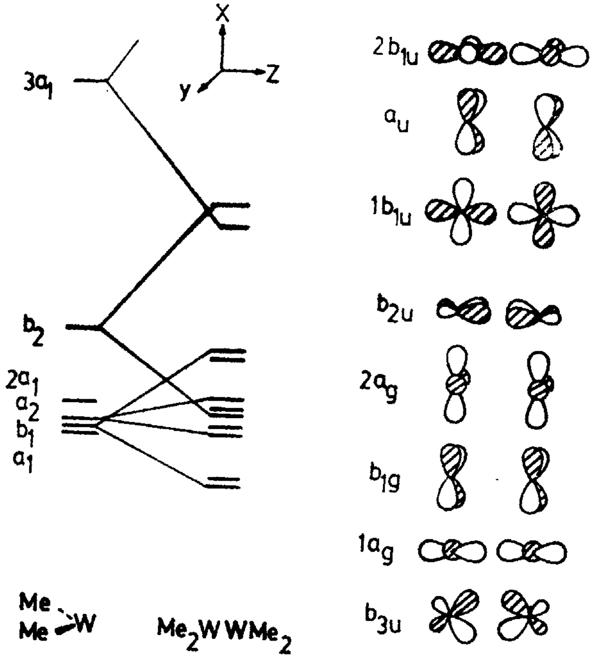


FIG 1 Interaction of two $W(CH_3)_2$ to give $(CH_3)_2\ WW(CH_3)_2$ in D_{2h} symmetry. Lowest four MOs are filled as the oxidation state of W is + 2 (d^4).

are filled in this fragment. These are all bonding and can be labelled as $\pi^2(b_{3u})$, $\sigma^2(1a_g)$, $\delta^2(b_{1g})$, $\delta^2(a_g)$.

The interaction of the $W_2(CH_3)_4$ fragment with $(CH)_2$ leads to the model $(CH_3)_2$ $W(\mu\text{-}CH)_2$ $W(CH_3)_2$, $\underline{\underline{7}}$. The frontier orbitals of $(CH)_2$ labelled according to the D_{2h} symmetry of the final complex is well known $\pi^*(b_{1g}, b_{2g})$, $\pi(b_{2u}, b_{1u})$, $\sigma^*(b_{3u})$ and $\sigma(a_g)$ given in Fig. 2. Since six electrons are required to fill these *M*Os, the interaction should result in a d^1–d^1 arrangement. Three metal orbitals are not changed at all in the process. The a_u and b_{3g} *M*Os of $W_2(CH_3)_4$ do not have *M*Os of the same symmetry in $(CH)_2$. The $2b_{1u}$ *M*O of $W_2(CH_3)_4$ is unaffected because the b_{1u} *M*O of $(CH)_2$ predominantly interacts with the lower $1b_{1u}$ of $W_2(CH_3)_4$. The $1a_g$, $2a_g$ and the $3a_g$ (sp hybrid) of $W_2(CO_3)_4$ and the a_g orbital of $(CH)_2$ interact to give one low lying a_g orbital mostly based on $(CH)_2$. This is too low in the scale to be seen in Fig. 2. Out of the antibonding (with respect to CH) combinations the lowest of the metal orbitals forms the highest occupied *M*O (HO*M*O), $1a_g$. This essentially corresponds to a metal-metal σ-bond. The highest a_g combination is mostly of metal *s* and *p* character and lies very high in energy

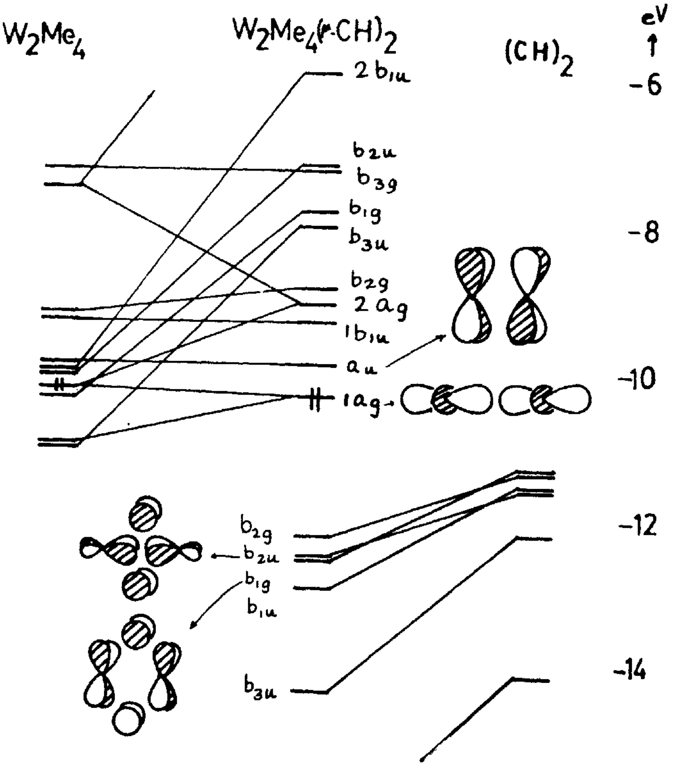
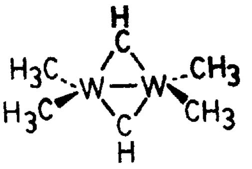


Fig 2 The interaction of the $W_2(CH_3)_4$ fragment with $(CH)_2$ giving $W_2(CH_3)_4$ $(\mu\text{-}CH)_2$ (D_{2h}). The oxidation state increases to +5 leading to one metal-metal bond (HO*M*O). Two occupied π-type *M*Os based on the $(CH)_2$ are shown.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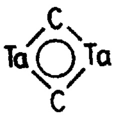
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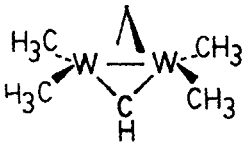
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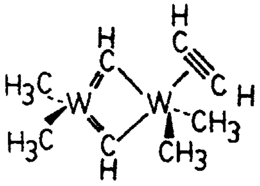
13 Cs

(not in the scale of Fig. 2). The remaining one, $2a_g$ corresponds to a δ bond, not occupied. Formally the oxidation state of W becomes +5, with one W–W σ-bond. W–W distance 2.548Å in 1, is indicative of a σ-bond.[4] Removal of two electrons should lengthen the M–M distance as is seen in the Nb and Ta analogs.[10] Since the lowest unoccupied MO(LUMO) of 1 is a δ^* orbital (a_u), increase of two electrons will only lengthen the metal-metal bond. The Re analog of 1 has an M–M distance comparable to that in 1.[11]

Often the M_2C_2 unit in 1 is represented as a metallacyclobutadiene with two MC double bonds. Occasionally a circle is drawn inside the M_2C_2 rhombus.[5] What is the extent of the π–type delocalization in $W_2(CH_3)_4$ (μ–$CH)_2$? This is an unusual example of a four-membered ring with four π–electrons and yet 'aromatic', if this term is taken to mean extra stabilization. The π–type orbitals involved are $b_{1g}(1)$ and $b_{2u}(1)$ (Fig. 3 shows the origin of the extra stabilization in comparison to cyclobutadiene). The degenerate nonbonding or slightly antibonding πMOs of cyclobutadiene are replaced by the b_{1g} orbital of $(CH)_2$ and the b_{3g} orbital of $W_2(CH_3)_4$. However, unlike in $(CH)_2$ there is another orbital on $W_2(CH_3)_4$ of b_{1g} symmetry so that the b_{1g} orbital of $(CH)_2$ is stabilized. Thus, there are two filled delocalized π type MOs imparting extra stability. The extra stabilization is due to the increased number of orbitals present (six π type orbitals are present in W_2C_2 in comparison to the four in C_4H_4). The bonding in the W_2C_2 unit in 1 may then be represented as 8 and that in the Nb or Ta analog as 9. Unlike in the organic counterpart a 1,3-σ bond between the metals does not detract much from the π delocalization. This metal-metal σ–bond plays a decisive role in the reactions of 1 with alkynes as discussed later.

Electronic Structure of 2, *$L_2W(\mu$–$CR)$ $(\mu$–$C_3RR'_2)$ WL_2)* : Several complexes of this general formula have been synthesized through reaction (3). Two of these

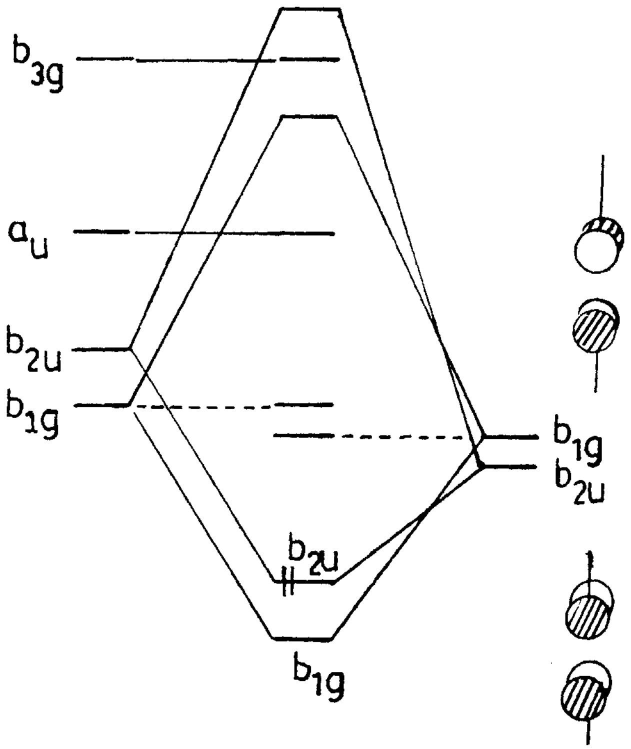

FIG 3 Illustration of the extent of π delocalization available in the π framework of W_2C_2. The dotted lines represent the energy of the b_{1g} *MO* of $(CH)_2$ which is what is expected in cyclobutadiene and the b_{1g} *MO* of W_2 of $W_2(CH_3)_4$. The interaction between these two orbitals leads to a stable b_{1g} (1) orbital which is even more stable than the b_{2u} (1). Thus the extra stabilization is due to the extra orbital (b_{1g}) present on the $W_2(CH_3)_4$ fragment.

compounds have been characterized by X-ray diffraction studies. In both of these the C_3R_3 unit straddles the W–W axis unsymmetrically so that the middle carbon of C_3R_3 is closer to one of the metals. In solution the C_3R_3 appears to have a C_2-axis, probably by a fast shifting between the two possible C_s structures, with a barrier so low that the process cannot be arrested even at very low temperatures. A model system $(CH_3)_2$ W(μ-CH) (μ-C_3H_3) $W(CH_3)_2$, 10, was considered in the C_{2v} geometry initially. Even though the *M*Os of 10 may be constructed from the fragments, a better picture emerges by tracing and correlating the metal *M*Os in $W_2(CH_3)_4$, 7 and 10. This is possible due to the small but definite difference between the orbitals of CH, and C_3H_3 fragments. The F*M*Os (11) of these show that though smaller in size CH has *M*Os of the same symmetry as that of C_3H_3 except for the a_2 orbital.[13] The a_u and the b_{3g} *M*Os of 7 reduce to a_2 symmetry in C_{2v} point group. Thus replacement of one CH by a C_3H_3 group should have maximum effect on these two *M*Os. Fig. 4 represents a correlation of the *M*Os of

$W_2(CH_3)_4$ with that of 7 and 10. The a_u and b_{3g} of 7 are pushed up to become $1a_2$ and $2a_2$ of 10. Thus 10 does not have the low energy δ* LUMO of 7. This reduces the π-acceptor character so that 10 does not react with π donors such as acetylene.

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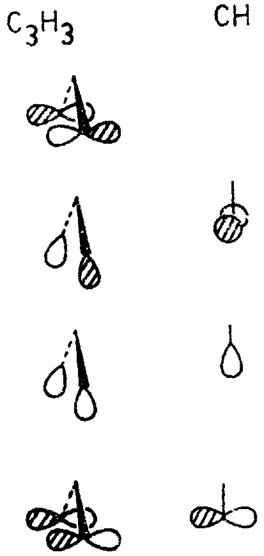

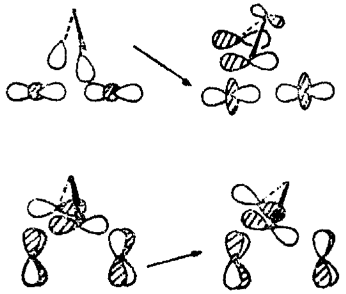

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The solid state structure of 2 is simulated by bending the C_3H_3 unit of 10 so that the central carbon atom of C_3 is closer to one of the metals. Extended Huckel calculations give nearly the same energy for the tilted structure. Fig. 4 extends the correlation to the tilted structure. The major changes in energy occur to the top two orbitals, 12 ($a_2(1)$, $1a_1$). $1a_1$ comes down in energy by 0.5 eV while the HOMO-1 goes up in energy by 0.35 eV. It should be possible to affect these two orbitals differently by substituents so that symmetrical structure may be made to lie high or low in energy. The low energy difference between the C_{2v} and the C_s structures coupled with the reported inability to arrest the conversion of the C_s structures *via* the C_{2v} geometry suggests possible contribution of the solid state packing effects reducing the symmetry to C_s from C_{2v}.

Electronic Structure of $R_2W(\mu\text{-}CR)_2(\eta^2\text{-}C_2R_2)WR_2$: The reaction between alkynes and $R_2W(\mu\text{-}CR)_2WR_2$ goes through an intermediate η^2 alkyne complex, 3.[4] One such intermediate 3 had been charaterized by X-ray diffraction. The molecular orbitals of a molecule, 13, is constructed in a stepwise fashion from that of 7 and of acetylene. 7 is distorted first to obtain a geometry similar to that found in 13. Here, the bridging CH groups will be closer to W_2. The methyl groups on W_1 are tilted to make way for the incoming acetylene. The geometric change reduces the symmetry to C_s. Many of the MOs, especially the ones that have π-type interac-

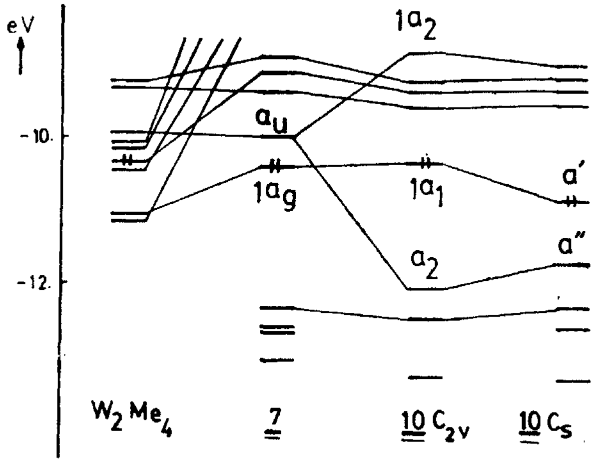


FIG 4 Correlation diagram between the *MO*s of $W_2Me_4(D_{2h})$, $W_2Me_4(\mu\text{-}CH)_2$ (D_{2h}) 7, $W_2Me_4(\mu\text{-}CH)(\mu\text{-}C_3H_3)$ 10 C_{2v}, and 10 C_s where the C_3H_3 group is tilted so that the central CH is closer to one of the metals. 7 has a metal-metal bond as HO*MO* and δ^* as LU*MO*. The non-bonding π *MO*o f C_3H_3 unit pushes this *LUMO* away in 10 so that in 10 the HO*MO*-LU*MO* difference increases. Bending of the C_3H_3 unit to give a C_s geometry lowers the energy ot the HO*MO* but raises that of the HO*MO*-I (*see 12*).

tion with the bridging CH groups, are polarized to one metal or the other (Fig. 5 left) $(CH_3)_2$ $W(\mu\text{-}CH)_2$ $W(CH_3)_2$ may also be considered as originating from a tetrahedral $(CH_3)_2$ $W(CH)_2$ group and $W(CH_3)_2$ group. The net effect is the following. The lowest metal orbitals, the $\sigma(1a_g)$ and the $\delta^*(a_u)$ are now mostly localized on W_2, so that an incoming alkyne will have maximum interaction. The major interaction is indeed between the hybrid π^* of acetylene, $2a'$ and the lowest W–W bonding orbital $1a'$. The resulting bonding combination is a highly delocalized orbital, 14. It is not appropriate to call it either a metal-based or ligand-based orbital, so that the assignment of C_2H_2 as a —2 ligand here is to be treated only as a formalism. The a_u orbital of 7 has a weak stabilizing interaction with the unhybridized π-orbital of acetylene, leading to some donation of π-electrons to the metal (15). A mulliken population analysis shows that the acetylene has a charge of -0.44 and that the reduced overlap population between the fragments is 0.654. Out of this 0.24 results from the HO*MO*-LU*MO* interaction and .08 from the LU*MO*-(HO*MO*-1) interaction, (15). The formation of this intermediate compound will not be possible if there are two electrons less (d^0-d^0) in the system. Similarly, with two electrons more (d^2-d^2) the formation of the intermediate complex will not be as facile even though there are still several metal d-orbitals empty. The explains the lack of reactivity of Ta, Nb analogs. The Re analog of 1 may not react in the same way.

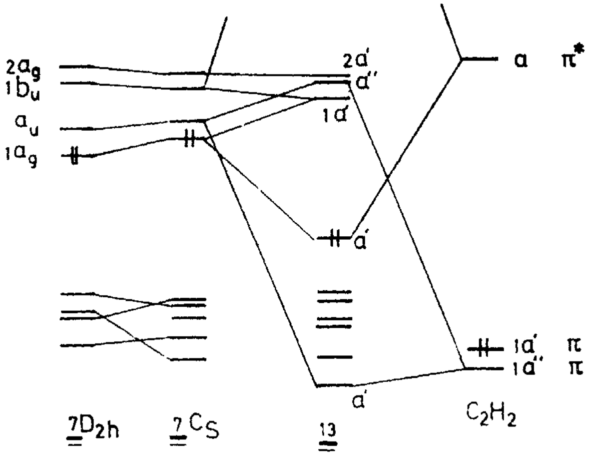
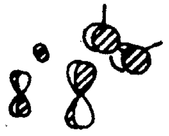


FIG 5 The changes in the MOs of 7 as its geometry is changed to conform to that of 13 is shown on the left hand side. The interaction of 7, (C_s), with acetylene has two major components. (*a*) The donation of the metal-metal bonding electrons to the 2a′ (π* ot C_2H_2) 14, and (*b*) the donation of the π-bonding electrons of 1*a*″ to the δ*MO, the LUMO of $W_2Me_4(\mu\text{-CH})_2$.

14a′



15a″

Since the donation of the metal-metal bonding electrons to the acetylene π*(2*a*′) and the reverse donation from the π-orbitals of acetylene (1*a*″) to the 1*a*″ orbital of the metal are involved in the formation of the intermediate, removal of one of them may stop the reaction. For example, the 1*a*″ orbital (a_u in 7) is not available in 10 as it is pushed up by the nonbonding π orbital of the C_3R_3 unit (1a_2 orbital of Fig. 4). Thus 10 does not react with acetylene. Similarly, only an acceptor or a donor interaction is available for ethylene and butadiene with 7 so that it does not react with either of them. On the other hand allene with a perpendicular set of orbitals do interact with 7. Details of these and the pathways that convert 7 to 13 and 10 will be discussed elsewhere. The scrambling of CR_s in the μ–C_3R_3 unit of 10 as well as the effect of varying the ligand are studied.

CONCLUSIONS

The electronic structure of 7$(CH_3)_2W(\mu\text{–}CH)_2W(CH_3)_2$, allows the description of a M–M σ-bond with a delocalized central W_2C_2 unit. The metal-metal bond as well as the δ* LU*M*O act as donor and acceptor orbitals respectively with systems having pairs of orbitals to each other. Thus acetylene and allene, but not ethylene and butadiene react with 7. Similarly, if two electrons are removed as it happens in Nb and Ta analogs of 7, the Metal-Metal bond disappears so that these cannot react with acetylene. The product of the reaction of 7 with acetylene is 10, which has a C_3H_3 unit The δ* orbital which was LU*M*O in 7 is pushed up in energy in 10 since there is an *M*O of appropriate symmetry in C_3H_3 so that the δ* acceptor orbital is not easily available in 10. Thus 10 dose not react further with acetylenes.

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APPENDIX

TABLE I

The geometric parameters adapted from the X-ray structures for 7, 10 and 13 used in the calculations

Parameter	Structure		
	7 D_{2h}	10 C_{2v}	13 C_s
W_1–W_2	2.55Å	2.55Å	2.915Å
W_1–$C(CH_3)$	2.10Å	2.10Å	2.10Å
W_1–$C(\mu\text{-}CH)$	1.91Å	1.91Å	
W_2–$C(\mu\text{-}CH)$	1.91Å	1.91Å	1.73Å
C–H	1.08Å	1.08Å	1.08Å
C_1–C_2	—	1.41Å	3.90Å
C_2–C_3	—	1.41Å	1.3Å
$< HC_2C_3$	—	127.0°	150.0°
$< W_1W_2C(CH_3)$	125.0°	125.0°	125.0°
$< C(CH_3)\ WC(CH_3)$	110.0°	110.0°	103.4°
$< W_2W_1C(CH_3)$	125.0°	125.0°	115.0°
$< W_2W_1C_2$	—	60.1°	131.6°
$< W_1W_2(\mu C_2)$	48.1°	48.1°	47.3°

The atomic parameters for carbon, hydrogen and tungsten are taken from previous studies.[14]