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Reaction of $L_2W(\mu\text{-}CR)_2WL_2$ with C_2R_2. A Theoretical Study[1]

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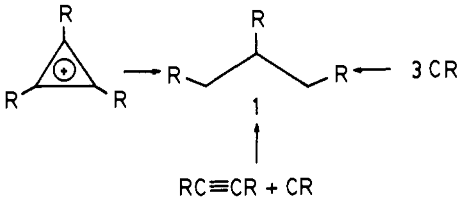
Abstract: The electronic structure and reactions of $L_4W_2(\mu\text{-}CR)_2$ are studied theoretically with the fragment molecular orbital approach within the extended Hückel method on the model $L_2W(\mu\text{-}CH)_2WL_2$ (L = CH_3, OCH_3, CN). $L_2W(\mu\text{-}CH)_2WL_2$ has a metal–metal single bond (d^1–d^1, W^{5+}). The LUMO is a δ^* MO (a_u) so that a d^2–d^2 system does not possess a metal–metal double bond. The donation of electrons from the π MO of an incoming ligand to the LUMO of the complex and the back-donation of the M–M bonding electrons to a π^* MO lying in a plane perpendicular to that of the donor π MO trigger the reaction of ligands with $L_2W(\mu\text{-}CR)_2WL_2$. Thus alkynes, allenes, CO, CO_2, RN_3, RCN, RNC, and ketones but not ethylene and butadiene are expected to react. The Ta and Nb analogues do not react as there is no M–M bond to donate electrons to the π^* MO of the incoming ligand. The Re analogue also is not expected to react in the same fashion since the δ^* acceptor orbital is already occupied. The μ-CH in $L_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)WL_2$ does not react with another molecule of acetylene as the δ^* acceptor orbital has been pushed up by the μ-C_3H_3 ligand.

Among the many unusual organic fragments that are stabilized by transition metals is C_3R_3, the 1,3-didehydroallyl, **1**. It was initially obtained from the cyclopropenyl ligand by breaking one of the C–C bonds assisted by transition metals.[2] Recently **1** has also been obtained from a more constructive process of forming a new C–C bond between an alkyne and a carbyne ligand.[3-9] The details of the bond-breaking pathway to **1** have been studied theoretically before.[10] The current study focusses on a one-bond formation pathway to **1** effected on a binuclear transition-metal template. A study of the two-bond formation pathway to **1** will be given later.[11]



The reactions of carbyne ligands coordinated to transition metals are of current interest as these species are implied in several catalytic reactions.[12] Several reactions of bridging C–H or C–R groups have been reported recently. Stone and co-workers found that μ-CR groups in heterobinuclear complexes reacted with alkynes to give dinuclear complexes with C_3R_3 units straddling the metal–metal bond.[3] Casey and co-workers recently discovered a hydrocarbation reaction where the bridged C–H group in $(\eta^5\text{-}Cp)OCFe(\mu\text{-}CH)(\mu\text{-}CO)Fe(\eta^5\text{-}Cp)CO^+$ reacts with alkyne.[13] Chisholm and co-workers discovered another reaction where $L_2W(\mu\text{-}CR)_2WL_2$ (**2**) reacts with RCCR to give $L_2W(\mu\text{-}CR)(\mu\text{-}C_3R_3)WL_2$ (**4**) (L = OR, R; R = alkyl).[4] The reaction proceeds through an intermediate alkyne complex (reaction 1). We selected this reaction for study from among these for the following reasons. Detailed experiments of the Chisholm group have opened up a series of puzzles about this reaction.[4b] Even though **2** has two μ-CR groups, only 1 mol of alkyne reacts with it; the second μ-CR is spared even when an excess of alkyne is used. The reaction is facile with alkyne and allene but does not go with ethylene or

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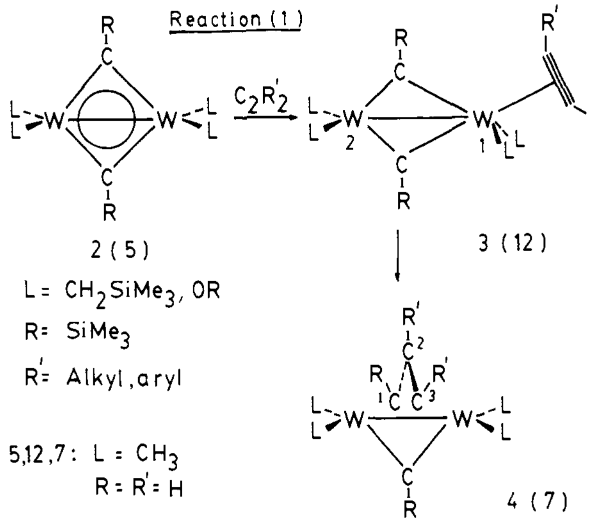


butadiene. Isostructural Ta and Nb complexes which have two electrons less do not react with alkynes under similar reaction conditions.[4a] Single-crystal X-ray structures are available for representatives of **2**, **3**, and **4**.[4] The C_3R_3 in **4** is not symmetrical in the solid state with respect to the metals, despite the symmetric disposition of the rest of the molecule. The middle CR unit is closer to one of the metals so that the remaining metal forms part of an almost planar MC_3 unit. However, in solution the C_3R_3 group is fluxional, leading to overall C_{2v} symmetry with the C_3R_3 plane bisecting the M–M bond, **4**. We analyze, explain, and predict several aspects of this reaction.

Our approach is the following. The electronic structures of the stable species involved, **2**, **3**, and **4**, will be analyzed first. Correlations will be made between the molecular orbitals of **2**, **3**, and **4** to obtain the electronic requirement of the reaction. The fragment molecular orbital (FMO) approach where the MOs of the larger fragments are constructed from those of the well-understood small fragments will be used within the extended Hückel method.[14,15] Our arguments depend mainly on symmetry, overlap, electron count, and electronegativity differences and hence should depend minimally on the method of calculation.

Electronic Structure of $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$ (5)[16]

$(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$ (**5**) has been used as a model for **2** with the geometry given in the Appendix (Table I). **5** is thought to be constructed from $W_2(CH_3)_4$ and $(CH)_2$. The MOs of $(CH_3)_2WW(CH_3)_2$ are constructed from those of the two $W(CH_3)_2$ units (Figure 1). Here, the correlations of the a_1 orbitals of $W(CH_3)_2$ to the a_g orbitals of $W_2(CH_3)_4$ have been omitted for clarity. The oxidation state of W in the fragment is 2+ with d^4 electron count. The electronic configuration (frontier MOs) of $W_2(CH_3)_4$ is $\pi^2(b_{3u})$, $\sigma^2(1a_g)$, $\delta^2(b_{1g})$, $\delta^2(2a_g)$. The $(CH)_2$ group orbitals are essentially similar to that of HCCH except for feeble interaction between the two carbon atoms due to the large CC distance. Within D_{2h} symmetry the $\pi(b_{2u},b_{1u})$ and the $\pi^*(b_{1g},b_{2g})$ orbitals of HC···CH lie close to each other but above $\sigma^*(b_{3u})$. Each of the frontier orbitals of $(CH)_2$ finds a partner in the $W_2(CH_3)_4$ set so that there is a formal charge transfer to $(CH)_2$ of 6 electrons. Thus the interaction diagram (right side of Figure 1) justifies the classification of CH as 3–, leading to an oxidation state of W^{5+} in **5**. The two remaining "metal electrons" go to the W–W σ bonding orbital. The nonbonding or slightly antibonding nature of LUMO (a_u, δ^*) has been pointed out earlier.[4b] The M–M bond length variation in $M_2L_4(\mu\text{-}CR)_2$ with M = Ta, Nb (d^0–d^0 no M–M bond), W (d^1–d^1, σ^2 M–M bond), and Re (d^2–d^2, σ^2, δ^{*2}) is explained on this basis.[17] This a_u orbital should be followed carefully as it turns out to be the key for the reactivity or the lack of it for the μ-CH groups with alkyne. The HOMO–LUMO gap in **5** is rather small. This can be increased by varying the metal parameters, but optimum metal parameters do not change our arguments and hence were not sought.

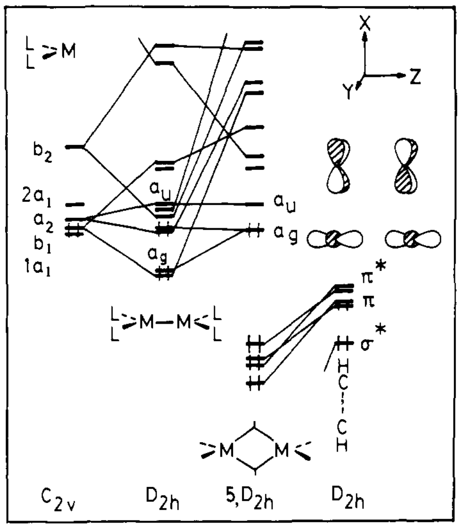
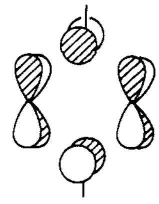
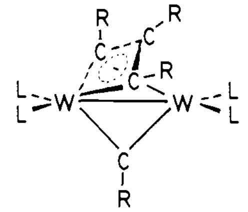


Figure 1. The construction of molecular orbitals of $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2$, (**5**) from smaller fragments. Two $(CH_3)_2W$ are brought together (left) to give the MOs of $(CH_3)_2WW(CH_3)_2$. This is interacted with the MOs of HC···CH leading to the MOs of **5**.

The W_2C_2 unit in **2** is often represented as a metallacyclobutadiene with two WC double bonds. Occasionally a circle is drawn inside the W_2C_2 rhombus, implying a four membered ring system with four π electrons and yet, unlike cyclobutadiene, aromatic.[4,16,17] The saving grace to avoid the antiaromaticity of cyclobutadiene comes via the b_{1g} orbital, **6**, which is stabilized by metal contributions. Without this it would have been one of the degenerate π MOs of a square cyclobutadiene.



6, b_{1g}



9, C_s (**10**, R=H, L=CH_3)

A Comparison of CH and C_3H_3 Fragments. The Electronic Structure of $(CH_3)_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)W(CH_3)_2$ (7)

Replacement of one of the CR groups in **2** by C_3R_3 gives **4**. The electronic structure of the corresponding model, $(CH_3)_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)W(CH_3)_2$, (**7**), is easily understood because the difference between **5** and **7** is only that of μ-CH vs. μ-C_3H_3. The frontier molecular orbitals of C_3H_3 and CH are similar, with the exception of the extra a_2 orbital of C_3H_3 shown in **8**. Thus the MOs of **7** should be very similar to that of **5** except for the changes in the a_2(a_u and b_{3g} in D_{2h}) orbitals. The correlation of the MOs of **5** to **7** shows that the a_u orbital (LUMO in **5**) forms bonding and antibonding combinations with the a_u orbital of C_3H_3 (Figure 2a,b). Consequently the vacant metal based δ^* MO is now rather high in energy. This, as will be seen below, decides the reactivity of **5** over **7**. In these calculations, **7** was assumed to have C_{2v} symmetry where the C_3H_3 plane bisects the W–W bond. However, in the solid state, **4** is found to have less symmetrical disposition

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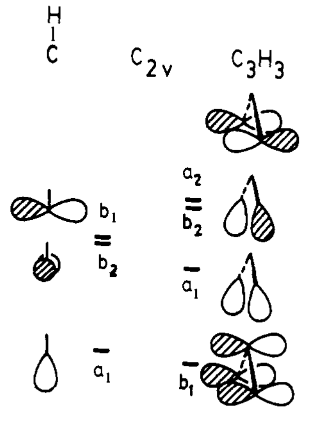
of the C_3R_3 group, with the middle carbon atom closer to one of the metals, **9**. The C_3R_3 group shows dynamic behavior at room temperature, giving an effective symmetry of **7**. Extended Hückel calculations gave nearly the same energy for **7** and **10**. The major changes in energy occur to HOMO and HOMO-1 (Figure 2b,e), HOMO comes down in energy by 0.5 eV while HOMO-1 goes up in energy by 0.35 eV. Since the variations are in opposite directions the only conclusion to be drawn is that the energy difference between **7** and **10** will be small.



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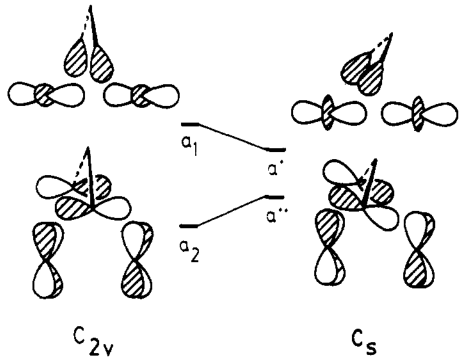
Despite similarities between CH and C_3H_3 valence MOs, they differ in detail. One factor is the greater extension in space of the orbitals of C_3H_3 in relation to the MOs of the same symmetry of CH. The immediate consequence of this is seen in the LWL angle in **2** and **4**. For the $W(CH_3)_2$ fragment orbitals to be oriented for better overlap with the μ-C_3R_3 ligand, the LWL angle in **4** should be smaller than that in **2**. This is indeed found to be true (the average values are 114.9° in $W_2(\mu\text{-CSiMe}_3)_2(\text{O-ipr})_4$ and 102.4° in $W_2[\mu\text{-CHCHC(SiMe}_3)](\text{CSiMe}_3)(\text{O-iPr})_4)$.[4] Such correlations exist between the cone angle and n in $C_nH_nM(CO)_3$ complexes.[18]



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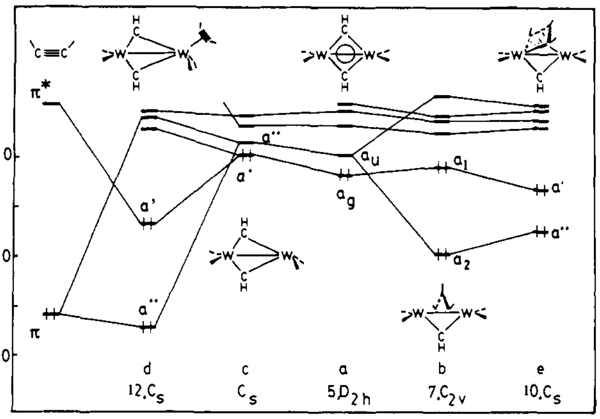

Figure 2. This forms the central part of our arguments. (a) The lower lying metal orbitals of **5** are from Figure 1. (b) A correlation is made here from part a since the difference between the two stems from the $a_u(a_2$ in $C_{2v})$ orbital of C_3H_3 which is absent in CH. (c) This part represents a distortion of **5** to a geometry found in the intermediate complex **12**. (d) Together with part c and the MOs of acetylene, extreme left, we have the interaction of HCCH with distorted **5** leading to the MOs of the intermediate, **12**. Only the two stabilizing donor-acceptor interactions are shown. This indicates that the M-M bond donation to π^* is probably stronger than the π donation to M-M δ^* (LUMO). (e) (b→e) shows the correlation diagram for the distortion of **7** (C_{2v}) to **10** (C_s) which is the geometry observed in the solid state.

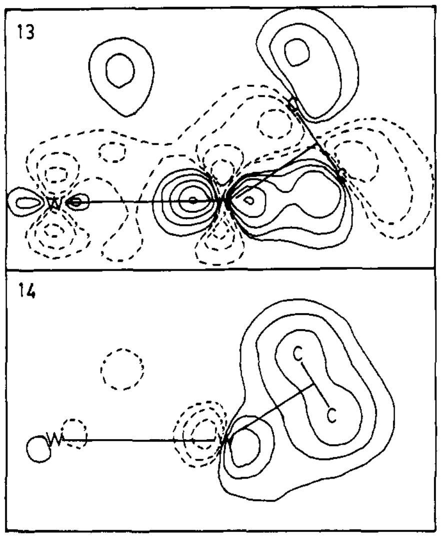

Figure 3. Cross section of the MO corresponding to π (alkyne) to metal δ^* donation (**14**) and the metal to π^* (alkyne) donation **13**. **14** was plotted in a plane 0.5 Å above the plane of the drawing in **13**. The contours used are ±0.4, ±0.2, ±0.1, ±0.05, and ±0.025.

Electronic Structure of the Intermediate, $L_2W(\mu\text{-CR})_2W(\eta^2\text{-RCCR})L_2$ (3), and the Requirements for Its Formation

The intermediate **3** formed during the reaction **2** → **4** is modelled by $(CH_3)_2W(\mu\text{-CH})_2W(\eta^2\text{-HCCH})(CH_3)_2$ (**12**). The molecular orbitals of **12** are constructed from those of **5** and of acetylene. **5** is distorted first to a geometry close to that found in **12**. The two bridging groups are closer to one of the metals and the methyl ligands on the other metal are tilted to give way for an incoming acetylene. Figure 2a,c shows the variation in the MOs during this distortion. Consequently the metal-metal bond is broken, the symmetry is reduced, and the metal-based MOs are polarized on one or the other metal. The important interactions involved in the complexation with alkyne are the following. What was originally the M-M bond is now localized on one metal and donates electrons to the in-plane π^* MO of acetylene, **13**. The δ^* LUMO in the new geometry is an ideal acceptor orbital to the π bond of acetylene perpendicular to the C_2H_2 plane, **14** (Figure 2d and 3). The in-plane π bond (a') of acetylene is involved in destabilizing four-electron two-orbital interactions while the perpendicular π^* of acetylene (a'') interacts only with the empty orbitals of the metal fragment (these are not shown in the diagram). Thus the requirement on the π ligands for the formation of the intermediate complex is the availability of one acceptor and one donor orbital in orthogonal planes. The metal requires corresponding donor and acceptor orbitals. The Ta or Nb analogues of **2** do not have the two electrons of the M-M bond for donation to the π^* of alkyne to trigger the reaction. Re analogues of **2**(d^2-d^2) should also not favor the initial complex formation as the acceptor orbital δ^* is already filled. Fully knowing the limitations of the approach, we have plotted the total energy as a function of the reaction coordinates designed to get the intermediate complex **12** from **5** for W and for two electrons less and two electrons more (Figure 4). The energy goes down after initial increase for the d^1-d^1 system (W_2) while it goes up for d^0-d^0 or

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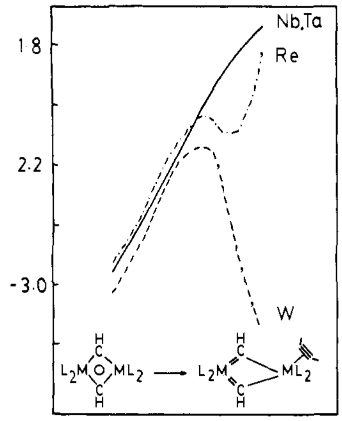

Figure 4. The variation of the sum of one-electron energies along the reaction coordinate leading to intermediate complex **12**. Nb, Ta, and Re curves are approximated by adding and subtracting two electrons from that of $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2(\eta^2\text{-}HCCH)$.

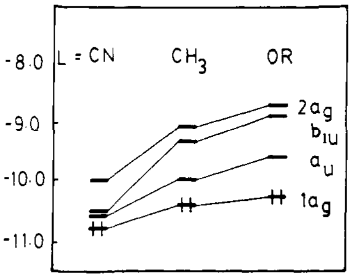

Figure 5. The variation of the frontier orbital energies of **5** with terminal ligands.

d^2–d^2 electron count without any minima corresponding to the intermediate complex.

The absence of reactivity of **4** with further alkynes can also be explained on the basis of Figure 2 The δ^* orbital of **5** which accepts electrons from the π orbital of alkyne is not the LUMO in **7**; this has been pushed away by the a_2 orbital of C_3H_3 (Figure 2b). Thus a second acetylene does not have the same advantage along the reaction coordinate to form the intermediate complex. This protects the second μ-CR group from reacting. Ethylene, butadiene, and other ligands with π MOs in one plane alone are not expected to react with **2** under similar conditions. This is supported by experimental observations. In addition to alkynes CO, CO_2, allenes, ketenes, HCN, HNC, RN_3, and to a certain extent ketones should react with **2**. Some of these are already known,[4c,19] and others are worth trying.

Experimentally the stability of the intermediate complex **3** is found to be less for L = OR than for L = R.[4] At the same time **3** with L = OR reacts faster to give the final product **4**. Any contribution from direct electronic effects to these observations was searched by calculations on **2** and **3** (L = OCH_3 and CN, R = H). The replacement of CH_3 by CN or any π acceptor ligand lowers the energy of metal orbitals of π symmetry in the ML_2 fragment. Similarly OCH_3 ligands push the d orbitals up in energy. These are reflected in the energies of the MOs of **2** for L = CN, CH_3, and OCH_3 (Figure 5). The acceptor orbital (LUMO) in **2** is higher for L = OCH_3, leading to decreased interaction between the π donor MO of acetylene and the δ^*. The MO corresponding to the metal–metal bond also goes up with L = OCH_3. This helps in increasing the back-donation to the π^* of the incoming acetylene. Since these are opposing each other we hesitate to draw any conclusions in the absence of more quantitative study.

Table I. Bond Lengths (Å) and Bond Angles (deg)

parameter	structure		
	5, D_{2h}	**7**, C_{2v}	**12**, C_s
W_1–W_2	2.550	2.550	2.915
W–C(CH_3)	2.100	2.100	2.100
W_1–C(μ-CH)	1.910	1.910	2.158
W_2–C(μ-CH)	1.910	1.910	1.730
C–H	1.080	1.080	1.080
C_1–C_2		1.410	3.900
C_2–C_3		1.410	1.300
W–O	1.873		1.873
(W)O–C(H_3)	1.410		1.470
W–C(N)	2.150		2.150
C–N	1.170		1.170
∠C_2–C_3–H		127.0	150.0
∠W_1–W_2–C(CH_3)	125.0	125.0	125.0
∠W_2–W_1–C(CH_3)	125.0	125.0	115.0
∠C(CH_3)–W–C(CH_3)	110.0	110.0	103.0
∠W_1–W_2–(μ-C_2)	48.1	48.1	47.3
∠W–W–O	125.0		125.0
∠W–O–C(H_3)	145.0		145.0
∠W–W–C(N)	125.0		125.0
∠W–C–N	180.0		180.0

The reaction pathway for transforming **12** to **7** or **10** does not retain any symmetry. There is bonding overlap population between carbyne carbon and adjacent carbon of acetylene in **12**. We have studied two pathways for the conversion of **12** to **7**. One involved the formation of the C_3R_3 unit, which together with the two metals and the other carbon formed a plane, C_3M_2C, and subsequent rotation of C_3R_3 to give **7**. The latter process involved substantial barrier. The second pathway involved the direct formation of **7** from **12**. This was a low-energy process with no symmetry at all. Analysis of this process did not provide any additional useful information and hence was not pursued.

Conclusions

The reaction of $L_2W(\mu\text{-}CR)_2WL_2$ with C_2R_2 has been studied theoretically with extended Huckel calculations on model compounds (L = CH_3, OCH_3, CN; R = H). The donation of π electrons of an alkyne to the δ^* orbital of the metals and the back donation of the metal-metal bonding electrons to the π^* orbital of alkyne in a plane perpendicular to that of the donating π bond trigger the formation of the intermediate complex, $(CH_3)_2W(\mu\text{-}CH)_2W(CH_3)_2(\eta^2\text{-}C_2H_2)$. This explains the lack of reactivity of ethylene and butadiene which do not have π MOs in perpendicular planes and of the Nb, Ta analogues which do not have the metal–metal bond electrons for back-donation. The Re analogue is also not expected to react as its δ^* MO is already occupied and hence cannot act as an acceptor orbital. The δ^* MO is pushed up in energy in the final product $(CH_3)_2W(\mu\text{-}CH)(\mu\text{-}C_3H_3)W(CH_3)_2$ so that the remaining μ-CH group does not react with acetylene.

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Appendix

The geometric parameters given in Table I are used in the calculations performed. The atomic parameters for carbon, hydrogen, nitrogen, oxygen, and tungsten are taken from previous studies.[20] Weighted H_{ij} were used in all calculations.

The transformation pathway for the process **5** ⟶ **12** is designed as follows. In the starting point, acetylene is kept, in-plane, at a distance of 3.0 Å from one of the metal atoms of **5** and the midpoint of acetylene. The M–M–midpoint of acetylene angle is taken as 150°. From this stage, the geometry of the system is distorted in six regular intervals, of all the parameters involved, to get to the geometry of **12**.

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