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Insights into the Schrock 'chop-chop' reaction gained from density functional theory and preparation and structure of $W_2(\mu\text{-PhCCPh})(SC_6H_4\text{-2-Me})_6$†

Malcolm H. Chisholm,*[a] Ernest R. Davidson,*[b] Maren Pink[c] and Kristine B. Quinlan[c]
[a] *Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, Ohio 43210, USA. E-mail: chisholm@chemistry.ohio-state.edu; Fax: 614 292 0368; Tel: 614 292 7216*
[b] *Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195, USA. E-mail: erdavid@u.washington.edu; Fax: 206 543 8621; Tel: 206 685 1617*
[c] *Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, Indiana 47405, USA*

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Computations employing density functional theory on the reactions between ethyne and the model compounds $(HE)_3M{\equiv}M(EH)_3$, where M = Mo and W and E = O and S, predict that the alkyne adducts $M_2(\mu\text{-}C_2H_2)(EH)_6$ are thermodynamically favored with respect to the metathesis products $HC{\equiv}M(EH)_3$ except when M = W and E = O; the reaction between $(^tBuO)_3W{\equiv}CPh$ and 2-MeC_6H_4SH (> 3 equiv.) yields $W_2(\mu\text{-PhCCPh})(SC_6H_4\text{-2-Me})_6$ consistent with expectations based on the calculations.

Nearly twenty years ago Schrock reported the 'chop-chop' reaction wherein C≡C or C≡N bonds undergo a metathesis with W≡W bonds, eqn. 1 and eqn. 2.[1]

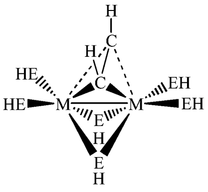
$$W_2(O^tBu)_6 + RC{\equiv}CR \rightarrow 2(^tBuO)_3W{\equiv}CR, \quad \text{where } R = \text{Me, Et, Pr} \tag{1}$$

$$W_2(O^tBu)_6 + RC{\equiv}N \rightarrow (^tBuO)_3W{\equiv}N + (^tBuO)_3W{\equiv}CR, \quad \text{where } R = \text{alkyl or aryl} \tag{2}$$

Schrock and coworkers extended these reactions in the preparation of $(RO)_3M{\equiv}CR'$ compounds where M = Mo and W and R, R′ = alkyl or aryl and investigated their reactivity towards alkyne metathesis and other reactions.[2] The 'chop-chop' reaction is, however, very sensitive to the nature of the metal, Mo *versus* W, and the attendant ligands. For example, $Mo_2(O^tBu)_6$ appears quite inert to MeC≡N and PhC≡N even though the products of the metathesis are known: $(^tBuO)_3Mo{\equiv}N$[3] and $(^tBuO)_3Mo{\equiv}CR$.[4] Similarly, we have found that the introduction of S^tBu groups at a $(W{\equiv}W)^{6+}$ center shuts down the reactivity with alkynes and organic nitriles.[5] These results lend themselves to speculation concerning thermodynamics and kinetics. In an attempt to evaluate some of those factors, we have turned to the use of electronic structure calculations employing density functional theory on the model compounds $M_2(EH)_6$, where M = Mo and W and E = O and S, and their reactions with ethyne. We report here some findings from these computational studies together with an experimental observation that was prompted by the theoretical work.

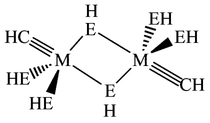
In the first instance we have examined the thermodynamics involved in the reaction between ethyne and the ethane-like model compounds which yield ethyne adducts of the type shown in **A**.

In all instances the ethyne adduct is predicted to be enthalpically favored, although for M = Mo and E = O, at 298 K the ΔG^o is slightly positive. See Table 1. While we do not wish to place undue emphasis on the absolute numerical predictions for the reaction, we do note that experimentally the compounds $M_2(O^tBu)_6$ react with ethyne at 25 °C to form ethyne adducts reversibly in the case of molybdenum and irreversibly in the case of tungsten.[6,7] Moreover, only for M = W do we observe the formation of the methylidyne complex $(^tBuO)_3W{\equiv}CH$.[7]



A

We proceeded to calculate the thermodynamics for the reaction interconverting the alkyne adduct, **A**, to the alkylidyne, **B**. Only in the case when M = W and E = O is the reaction product **B** favored (Table 1).



B

In addition for the reaction where M = Mo and W and E = O we have calculated a reaction pathway for the interconversion of **A** and **B**. The highest lying transition state involves an asymmetric structure with one bridging and one terminal alkylidyne group as shown in **C** for molybdenum. At 298 K, the $\Delta G^{\neq}$ for the forward reaction is 34 kcal mol^{-1} for M = Mo and 19 kcal mol^{-1} for M = W. Again these calculated values find relevance to the observation that the Schrock 'chop-chop' reaction proceeds rapidly for tungsten at ambient temperatures, but only occurs for $Mo_2(O^tBu)_6$ with terminal alkynes in low yield and under more forcing conditions as in the preparation of $(^tBuO)_3Mo{\equiv}CPh$ in the reaction between $Mo_2(O^tBu)_6$ and PhC≡CH.[2]

Perhaps what is most striking from these calculations is the prediction of the stability of the W_2-thiolate alkyne adduct. Surprisingly, no such compound had been made. This implicates a significant kinetic effect both in the reactions involving $M_2(SAr)_6$ and $M_2(O^tBu)_2(S^tBu)_4$ compounds with

Table 1 ΔG^o (at 298 K, kcal mol^{-1}) for the reactions involved in acetylene cleavage by dinuclear $M_2(EH)_6$ complexes, where M = Mo and W and E = O, S

	Mo, O	Mo, S	W, O	W, S
$M_2(EH)_6 + HC{\equiv}CH \rightarrow M_2(EH)_6(\mu\text{-}C_2H_2)$	4.5	−1.0	−0.8	−13.3
$M_2(EH)_6(\mu\text{-}C_2H_2) \rightarrow [(HE)_3M{\equiv}CH]_2$	5.0	21.0	−6.3	18.3
$M_2(EH)_6 + HC{\equiv}CH \rightarrow [(HE)_3M{\equiv}CH]_2$	9.5	20.0	−7.1	5.0

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† Dedicated to Roald Hoffmann on the occasion of his 65th birthday.

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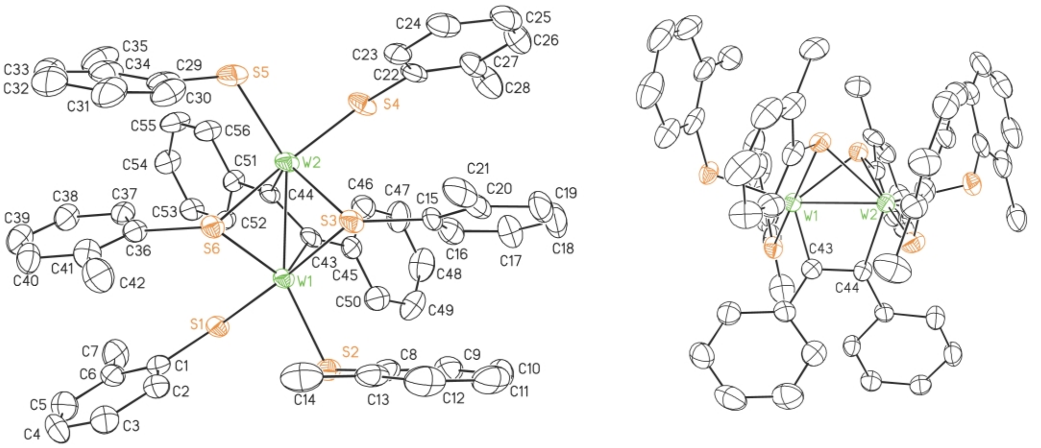
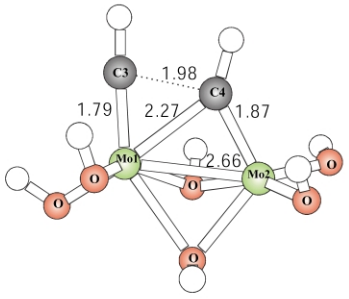


Fig. 1 ORTEP drawings of $W_2(\mu\text{-}C_2Ph_2)(\mu\text{-}SAr)_2(SAr)_4$ with atoms at 50% probability.



C $Mo_2(CH)(\mu\text{-}CH)(OH)_6$ with Selected Bond Lengths (Å).

alkynes and in the back reaction involving thiolato metal alkylidynes such as $(ArS)_3M{\equiv}C^tBu$,[8] where Ar = 2,4,6-$Me_3C_6H_2$ and 2,4,6-$^iPr_3C_6H_2$, and $(^tBuS)_3M{\equiv}C^tBu$.[9] Of course, computations involving the model compounds with SH ligands and CH for the alkylidyne negate what are obviously significant steric considerations. No $^tBuCC^tBu$ alkyne adduct of a $M_2(OR)_6$ compound, for example, has ever been seen. We reasoned, however, that the use of a benzylidyne ligand in combination with 2-MeC_6H_4S ligands should allow steric access to the alkyne adduct in $W_2(\mu\text{-}PhCCPh)(SC_6H_4\text{-}2\text{-}Me)_6$. Use of the aryl thiolate ligand also obviates facile C–S bond cleavage reactions which commonly occur for alkyl thiolates. The reaction between 2-MeC_6H_4SH (>3 equiv.) and $(^tBuO)_3W{\equiv}CPh$ proceeds at room temperature in toluene to give a green solution from which green crystals are obtained of the alkyne adduct $W_2(\mu\text{-}PhCCPh)(SC_6H_4\text{-}2\text{-}Me)_6$ in 60% isolated yield. The molecular structure seen in the solid state is shown in Fig. 1.‡ There are two bridging thiolate ligands and a twisted bridging alkyne ligand. The W–W distance 2.662(1) Å and C–C distance 1.420(8) Å are comparable to those seen in the alkyne adducts of $W_2(OR)_6$ compounds, though the skewed bridge is rather exceptional. The W–C distances of 1.980(8) Å (ave) and 2.559(8) Å (ave) are approaching W–C double and non-bonding distances, respectively. The C–C/W–W twist angle is 43.0(3)°, where 90° represents a μ-perpendicular and 0° a μ-parallel alkyne adduct.[10] The calculated structure for $W_2(\mu\text{-}C_2H_2)(SH)_6$ is shown in Fig. 2 which can be seen to closely represent that observed for the arylthiolate with the μ-PhCCPh bridge. Most notably, the skewed orientation of the C–C bridge of the alkyne is reproduced, despite the lack of steric bulk in the model compound.

The ^1H NMR spectrum of the $W_2(\mu\text{-}PhCCPh)(SC_6H_4\text{-}2\text{-}Me)_6$ in benzene-d_6 reveals three methyl signals in the ratio 1 : 1 : 1, indicative of the maintenance of the skewed-C_2 structure in solution.

In conclusion, we believe that the DFT calculations have provided insight into the Schrock 'chop-chop' reaction and can be useful in the design of new experiments involving these types of reagents as we have shown here in the synthesis of the first alkyne adduct of a $W_2(SAr)_6$ compound.

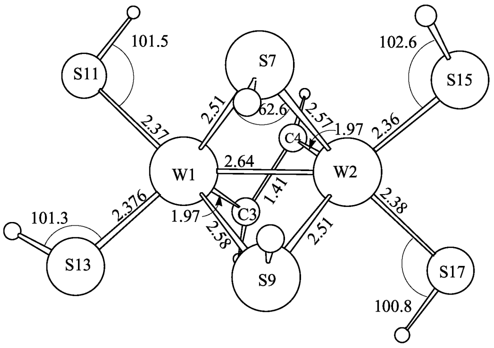


Fig. 2 Optimized structure of $W_2(\mu\text{-}C_2H_2)(\mu\text{-}SH)_2(SH)_4$ with selected bond lengths (Å) and angles (deg).

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Notes and references

‡ B3LYP DFT calculations were done using the Gaussian 98 program.[11] 6-31G* was used for O, S, C and H and LANL2DZ was used for Mo and W. CCDC 192708. See http://www.rsc.org/suppdata/cc/b2/b208819c/ for crystallographic data in CIF or other electronic format.

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