10358 *Inorg. Chem.* **2009**, *48*, 10358–10363
DOI: 10.1021/ic901528c

Inorganic Chemistry
Article

Concerning the Reaction Pathway of the Metathesis Reaction involving WW and CN Triple Bonds: A Theoretical Study

Shentan Chen and Malcolm H. Chisholm*

Department of Chemistry, The Ohio State University Columbus, Ohio 43210

Received July 31, 2009

The original "chop—chop" reaction reported by Schrock [*J. Am. Chem. Soc.* **1982**, *104*, 4291] involving $W_2(O^tBu)_6$ and organic nitriles, RC≡N to give the metal alkylidyne and nitride products $(^tBuO)_3WC{\equiv}R$ and $(^tBuO)_3WC{\equiv}N$, has been examined by a density functional theory based calculation where the bulky ^tBuO ligands have been substituted by MeO. The reaction between $W_2(OMe)_6$ and MeCN proceeds via a ditungstaazacyclobutadiene intermediate having a planar W_2CN core, **I**, with a structure related to that seen for $Mo_2(OCH_2{}^tBu)_6(\mu\text{-}NCNMe_2)$. Another possible intermediate having a pseudo tetrahedral W_2CN core, **II**, a ditungstaazatetrahedrane was examined and shown to have a higher energy. The interconversion of **I** and **II** was found to be energetically unfavorable with respect to their formation of metathesis products. The highest energy transition state involving the conversion of **I** to products was comparable to that for the conversion of **II** to products but the initial formation of **I** from the reaction between $W_2(OMe)_6$ and MeCN was favored over the formation of **II**. The related reaction between $Mo_2(OMe)_6$ and MeCN was shown to be thermodynamically unfavorable with respect to either adduct formation or metathesis products. However the reaction between $Mo_2(OMe)_6$ and Me_2NCN did yield a thermodynamically favored 1:1 adduct with a structure related to **I**.

Introduction

The original report by Schrock et al.[1] of the metathesis reaction involving the W≡W bond in $W_2(O^tBu)_6$ with alkynes and nitriles, eq 1 and 2 below, led to the facile synthesis of discrete molecular species $(^tBuO)_3W{\equiv}CR$ that were active in alkyne metathesis, a reaction that has found considerable synthetic utility.[2]

$$W_2(O^tBu)_6 + RCCR \rightarrow 2(^tBuO)_3WCR \qquad (1)$$

$$W_2(O^tBu)_6 + RCN \rightarrow (^tBuO)_3WCR + (^tBuO)_3WN \qquad (2)$$

Subsequently work in the Chisholm group established that in a number of instances there exists an equilibrium involving the tungsten alkylidyne and a dinuclear μ-alkyne adduct, a dimetallatetrahedrane.[3] This equilibrium could be driven in favor of the alkylidyne by donor ligands and toward the alkyne adduct by the addition of a π-acceptor ligand such as CO. In a formal sense the interconversion of the alkylidyne and alkyne adducts could be viewed as an internal redox reaction. Following on from this work, Chisholm and Davidson examined the reaction pathway involving the interconversion of the dimetallatetrahedrane and the alkylidyne metal complexes in a computational study involving density functional theory on the model reaction shown in eq 3,[4]

$$W_2(OH)_6(\mu\text{-}C_2H_2) \rightleftharpoons 2[(OH)_3WCH] \qquad (3)$$

More recently we have been interested in the chemistry of the metal nitrides of the group 6 elements, $(RO)_3M{\equiv}N$ and their reactivity toward nitrogen atom metathesis with organic nitriles.[5−7] This reaction, which proceeds more readily for M = W than for M = Mo[8] and does not occur for M = Cr, was found to proceed by way of a diazametallacyclobutadiene intermediate, a nitrogen analogue of the metallacyclobutadiene that is involved in alkyne metathesis. These studies led us to question whether or not the metathesis reaction involving W≡W and RC≡N bonds, eq 2, followed a similar

---

*To whom correspondence should be addressed. E-mail: chisholm@chemistry.ohio-state.edu.

(1) Schrock, R. R.; Listemann, M. L.; Strugeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(2) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748.

(3) (a) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794. (b) Chisholm, M. H.; Conroy, B. K.; Huffman, H. C.; Marchant, N. S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 446.

(4) Chisholm, M. H.; Davison, E. R.; Quinlan, K. B. *J. Am. Chem. Soc.* **2002**, *124*, 15351.

(5) Chisholm, M. H.; Delbridge, E. E.; Kidwell, A. R.; Quinlan, K. R. *Chem. Commun.* **2003**, 126.

(6) Burroughs, B. A.; Bursten, B. E.; Chen, S.; Chisholm, M. H.; Kidwell, A. R. *Inorg. Chem.* **2008**, *47*, 5377.

(7) Chen, S.; Chisholm, M. H.; Davidson, E. R.; English, J. B.; Lichtenberger, D. L. *Inorg. Chem.* **2009**, *48*, 828.

(8) Gdula, R. L.; Johnson, M. J. A.; Ockwig, N. W. *Inorg. Chem.* **2005**, *44*, 9140.

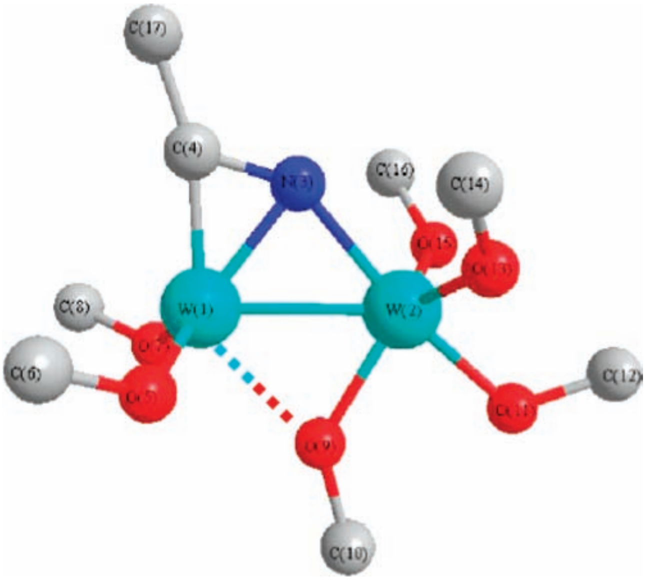


Figure 1. Optimized structure for the ditungstaazacyclobutadiene (**I**). The hydrogen atoms are omitted for clarity.

path to that of the W≡W + RC≡CR reaction in eq 1. We report here our findings that were prompted by this line of questioning.

Results and Discussion

1:1 Adducts. We started by comparing the calculated ground state structures for the ditungstaazacyclobutadiene, **I**, and the ditungstaazatetrahedrane, **II**.

A view of the optimized structure of **I** is given in Figure 1 where a striking similarity is seen with the molecular structure of $Mo_2(OCH_2{}^tBu)_6(\mu\text{-}NCNMe_2)$[9] found in the solid-state. A comparison of related bond distances and angles pertaining to the central core is given in Table 1. Of singular note is the asymmetric or semibridging alkoxide with W−O distances of 2.001 and 2.324 Å. The comparison of the metric parameters given in Table 1 is pertinent because the radii of molybdenum and tungsten are virtually identical due to the lanthanide contraction.

The W−W distance of 2.554 Å in **I** is shorter than that in dimetallatetrahedrane $W_2(\mu\text{-}C_2H_2)(O^tBu)_6(py)$[3] where W−W = 2.665(1) Å. In the latter molecule this distance has been compared to that of a W−W single bond with the ethyne being reduced to $C_2H_2{}^{4-}$. In the case of **I** the C−N bond distance is lengthened from 1.171 Å in free MeCN to 1.367 Å, essentially an increase of 0.2 Å. This together with N−C−C angle of 125.1° is a clear indication of the reduction of the C≡N bond and an oxidation of the $(WW)^{6+}$ center.

Finally, we note that the calculated free energy of **I** is 2.9 kcal/mol relative to the starting materials. However, the energies for the calculated structures for the dimethylcyanamide adducts $M_2(OMe)_6(\mu\text{-}NCNMe_2)$ molecules were found to be stable with respect to the starting materials: $\Delta G° = -8.7$ kcal/mol and -4.3 kcal/mol for M = W and Mo, respectively. The calculated structures for these two molecules are given in the Supporting Information.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for the Calculated Structure of $W_2(OMe)_6(\mu\text{-}NCMe)$ (**I**) and Those in the Solid State Structure of $Mo_2(OCH_2{}^tBu)_6(\mu\text{-}NCNMe_2)$[9]

A	B	dist (cal.)	dist (exp.)	A	B	C	angl (cal.)	angl (exp.)
M(1)	M(2)	2.554	2.449	N(3)	C(4)	C(17)[a]	125.1	127.1
M(1)	N(3)	1.970	1.908	M(1)	C(4)	C(17)[a]	164.5	167.0
M(1)	C(4)	1.948	2.014	M(1)	C(4)	N(3)	70.4	65.9
M(1)	O(5)	1.913	1.908	M(1)	M(2)	N(3)	49.0	48.6
M(1)	O(7)	1.913	1.918	M(2)	N(3)	C(4)	146.8	148.8
M(1)	O(9)	2.324	2.146	M(2)	M(1)	C(4)	93.8	96.7
M(2)	N(3)	2.081	2.134	M(1)	N(3)	M(2)	78.1	74.3
M(2)	O(9)	2.001	1.999	M(1)	O(9)	M(2)	71.9	72.3
M(2)	O(11)	1.959	1.954	O(9)	M(1)	N(3)	101.1	108.1
M(2)	O(13)	1.907	1.872	O(9)	M(2)	N(3)	108.9	105.2
M(2)	O(15)	1.907	1.870	M(1)	O(9)	C(10)	154.2	135.2
N(3)	C(4)	1.367	1.333	M(2)	O(9)	C(10)	133.9	128.6

[a] C(17) is a N atom in the solid state structure $Mo_2(OCH_2{}^tBu)_6(\mu\text{-}NCNMe_2)$.

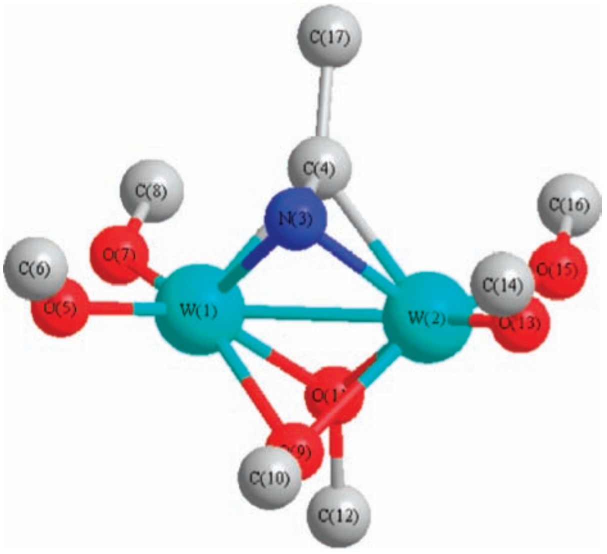


Figure 2. Optimized structure for the ditungstaazatetrahedrane (**II**). The hydrogen atoms are omitted for clarity.

The calculated structure for the ditungstaazatetrahedrane **II** is shown in Figure 2. The disposition of the six alkoxides around the W_2 center is very similar to that seen in the molecular structure of $W_2(O^iPr)_6(\mu\text{-}C_2H_2)(py)_2$[3] where the loosely bound py molecules are trans to the bridging ethyne. The W−W distance in **II** is 2.572 Å which is similar to that in the ethyne adduct 2.567(1) Å. A comparison of the metric parameters of the central cores of these molecules is given in Table 2. Again the lengthening of the C−N bond to 1.435 Å and the N−C−C = 126.1° is a clear indication of the reduction of the C≡N by the W_2 center. The calculated free energy of **II** is 10.0 kcal/mol, clearly indicating it is less stable than its isomer **I**.

Pathway to Cleavage. Starting from **I**, which has a structure related to $Mo_2(OCH_2{}^tBu)_6(\mu\text{-}NCNMe_2)$,[9] we have traced the path to cleavage yielding the isolated species $(MeO)_3W{\equiv}N$ and $(MeO)_3W{\equiv}CMe$ by the free energy profile shown in Figure 3. What becomes immediately obvious is that there are two intermediates that have a significantly lower energy than that of **I** and furthermore that one of them is lower in energy than

---

(9) Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *Organometallics* **1987**, *6*, 1073.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Calculated Structure of $W_2(OMe)_6(\mu\text{-}NCMe)$ (**II**) and Those in the Solid State Structure of $W_2(O^iPr)_6(\mu\text{-}C_2H_2)(py)_2$[3]

A	B	dist (cal.)	dist (exp)	A	B	C	angl (cal.)	angl (exp)
W(1)	W(2)	2.572	2.567	N(3)[a]	C(4)	C(17)	126.1	—
W(1)	O(5)	1.898	1.948	W(1)	C(4)	N(3)[a]	70.1	69.9
W(1)	O(7)	1.907	1.927	W(1)	W(2)	N(3)[a]	51.7	51.8
W(1)	O(9)	2.188	2.114	W(2)	N(3)[a]	C(4)	69.3	71.6
W(1)	O(11)	2.110	2.175	W(2)	W(1)	C(4)	51.4	52.9
W(1)	N(3)[a]	2.073	2.080	W(1)	C(4)	W(2)	77.2	75.1
W(1)	C(4)	2.061	2.096	W(1)	N(3)[a]	W(2)	76.7	75.9
W(2)	N(3)[a]	2.073	2.094	W(1)	O(9)	W(2)	72.0	75.1
W(2)	C(4)	2.061	2.118	C(4)	W(2)	O(9)	101.2	104.2
W(2)	O(9)	2.189	2.099	C(4)	W(1)	O(9)	101.2	104.5
W(2)	O(11)	2.110	2.183	C(4)	W(2)	O(11)	86.1	77.6
W(2)	O(13)	1.898	1.950	W(2)	O(11)	W(1)	75.1	72.2
W(2)	O(15)	1.907	1.940	C(4)	W(1)	O(11)	86.1	78.2
C(4)	N(3)[a]	1.435	1.394	O(5)	W(1)	O(7)	95.9	92.2
				O(13)	W(2)	O(15)	95.9	92.5

[a] N(3) is a C atom in the solid structure $W_2(O^iPr)_6(\mu\text{-}C_2H_2)(py)_2$.

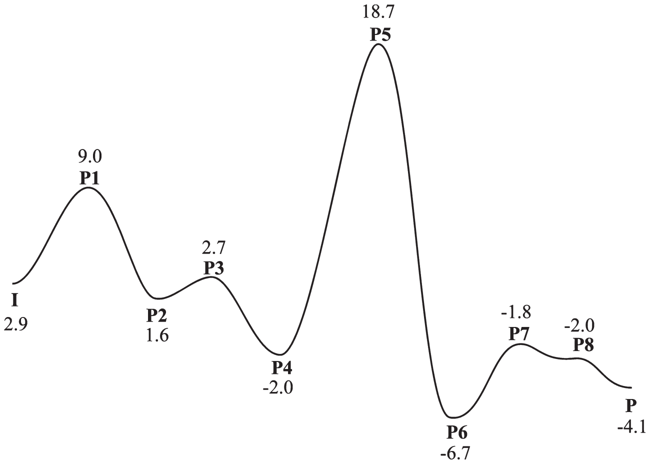


Figure 3. Free energy (calculated at 298 K in kcal/mol) profiles for the cleavage of ditungstaazacyclobutadiene (**I**). **P** denotes the isolated species $(MeO)_3W{\equiv}N$ and $(MeO)_3W{\equiv}CMe$.

the products, namely, **P6**. An examination of **P6** shows that it is simply an alkoxide bridged molecule in which the W≡N and W≡CMe bonds are already formed. There is an additional weak W···N interaction of 2.134 Å. It is not unreasonable that this should be lower in energy since, in the reaction between MeC≡N and $W_2(O^tBu)_6$, the nitride product $(^tBuO)_3W{\equiv}N$ is an infinite linear polymer involving alternating short and long W−N distances.[10] Also in the solid state the structure of $(^tBuO)_3W{\equiv}CMe$ is a dimer with a pair of alkoxide bridges that have alternating long and short W−O bonds with the long bonds being trans to the W≡CMe moiety.[10]

The structure of the other lower energy intermediate, **P4**, is shown in Figure 4 and is closely related to that of **I**, although the W−W distance is longer 2.653 Å, the W−C distance 1.929 Å is slightly shorter, and the W−N distances move in the direction of the cleavage, namely, one gets longer and the other shorter. The C−N bond distance is relatively unperturbed, but the bridging methoxide is more symmetrically bridging the two W atoms [W(1)−O(9) = 2.153 Å, W(2)−O(9) = 2.152 Å] and is more sp^3 hybridized such that the methyl carbon does not lie in the W_2O plane.

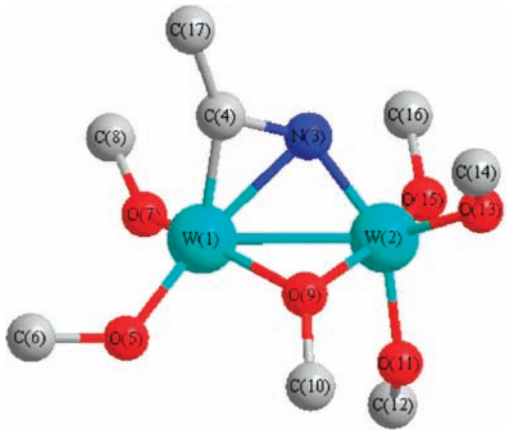


Figure 4. Optimized structure for **P4**. The hydrogen atoms are omitted for clarity.

The highest energy transition state, **P5** can be seen to be derived from **P4** by the rupture of the C−N bond, C···N = 2.016 Å, with an accompanying significant lengthening of the longer W−N distance, 2.158 to 2.293 Å, and a shortening of the other, 1.921 to 1.788 Å. The W−C distance similarly shortens form 1.929 to 1.800 Å and the W−C−C angle is enlarged from 153.7 to 177.2°. The W−W distance also increases to 2.653 to 2.782 Å, which is approaching a non-bonding distance with the two tungsten atoms being bridged by the single alkoxide. In the other transition states, the motion involves primarily W−O−C bending and rotation. Selected structural data for this reaction pathway are given in Table 3.

The reaction pathway for **II** leading to cleavage is more complex and is shown in Figure 5. There are many relatively inconsequential energy wells and saddle points that merely involve perturbation of W−O−C groups but the two key high energy transition states are represented by **V1** and **V9**. The change from **II** to **V1** represents a twisting of the μ-NCMe ligand from the perpendicular toward the parallel mode of bonding as is often seen for non-parallel, non-perpendicular alkyne bridges.[11] The structures of **V2** and **V8** are similar though **V8** is lower in energy and in both there are still two bridging alkoxides. In **V8** the central W_2CN moiety is not rigorously planar. The two W−C and W−N distances are distinctly asymmetric, and the C−N distance of 1.417 Å is effectively a single bond distance. Selected structural data for the intermediates and transition states for the reaction path shown in Figure 5 are given in Table 4.

Of note here is that the energy of **V8** is 5.4 kcal/mol higher than that of **I**. The reaction from **V8** to **V10** represents the cleavage of the C−N bond and proceeds via the transition state **V9**, and occurs with a twisting of the two halves of the molecule. The structure of the

---

(10) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(11) (a) Chisholm, M. H.; Click, D. R.; Gallucci, J. C.; Hadad, C. M.; Wilson, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 14518. (b) Hoffmann, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (c) Calhorda, M. J.; Hoffmann, R. *Organometallics* **1986**, *5*, 2181. (d) Cotton, F. A.; Feng, X. *Inorg. Chem.* **1990**, *29*, 3187. (e) Chisholm, M. H.; Lynn, M. A. *J. Organomet. Chem.* **1998**, *550*, 141.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Intermediates and Transition States on the Pathway Towards the Cleavage of Ditungstaazacyclobutadiene (**I**)

	W(1)−W(2)	C(4)−N(3)	W(1)−C(4)	W(1)−N(3)	W(2)−N(3)	W(1)−O(9)	W(2)−O(9)	C(17)−C(4)−N(3)	C(17)−C(4)−W(1)
I	2.554	1.367	1.948	1.970	2.081	2.324	2.001	125.1	164.5
P1	2.662	1.365	1.922	1.998	2.020	2.804	1.967	127.5	159.5
P2	2.602	1.331	1.951	2.032	2.041	3.285	1.962	129.5	156.7
P3	2.626	1.345	1.939	2.043	1.996	2.826	2.009	128.4	157.0
P4	2.653	1.364	1.929	2.158	1.921	2.153	2.152	126.4	153.7
P5	2.782	2.016	1.800	2.293	1.788	2.112	2.205	107.2	177.2
P6	3.265	3.039	1.768	2.134	1.741	2.176	2.150	136.5	179.0
P7	3.671	3.002	1.775	2.206	1.710	2.024	3.089	133.8	179.4
P8	2.999	3.903	1.772	2.206	1.707	1.957	4.070	135.4	177.6

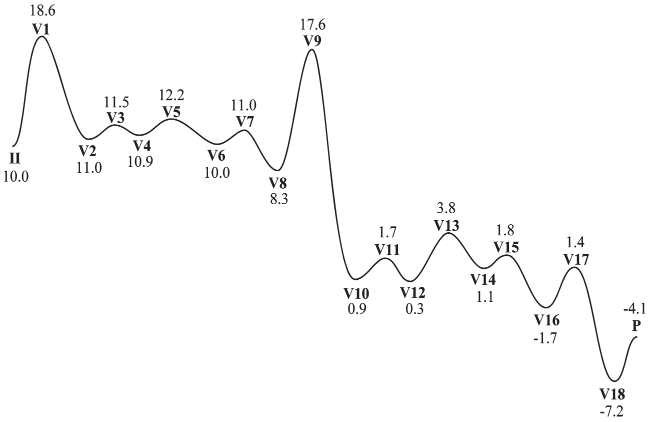


Figure 5. Free energy (calculated at 298 K in kcal/mol) profiles for the cleavage of ditungstaazatetrahedrane (**II**). **P** denotes the isolated species $(MeO)_3W{\equiv}N$ and $(MeO)_3W{\equiv}CMe$.

product of this C−N cleavage and twisting, **V10**, is interesting since, though it clearly has nitride and alkylidyne ligands on separate tungsten atoms, it is in other ways highly asymmetric. The molecule is shown in Figure 6, and structural data are given in Table 5. The asymmetry in the molecule is suggestive of a $[(MeO)_2W{\equiv}N]^+$ cation associating with a $[(MeO)_4W{\equiv}CMe]^-$ anion where the alkylidyne and two of the attendant OMe ligands are semibridging to the positively charged tungsten center of the $[(MeO)_2W{\equiv}N]^+$ cation. The reaction pathway leading from **V10** to **V18** involves further twisting and W−O−C maneuvering until the pseudo fused trigonal bipyramidal structure is attained wherein the W≡N and W≡CMe groups are mutually anti and occupy axial positions of a distorted trigonal bipyramid. This structure is analogous to that seen for the $(^tBuO)_3W{\equiv}CMe$ dimer.[9] As in the reaction for **II**, the last step in the reaction, the cleavage of the alkoxide bridged dimer, is endothermic.

In comparing the energetics of the two reaction pathways leading to cleavage we find that the highest energy transition states are comparable in energy. See **P5** in Figure 3 and **V1** in Figure 5. This is clearly not discriminating with respect to the pathway leading to C−N bond cleavage.

We next looked at the reaction pathway from the free reactants toward the formation of **P4** and **V8**.

Pathway to Adduct Formation. The reaction pathway from the free reactants to the lowest energy 1:1 adducts is shown in Figure 7. The formation of the perpendicular and parallel modes of bonding follows a common reaction path leading to **F5**. The local minimum **F1** corresponds to coordination of MeCN to one W atom via a weak W···N interaction. The transition state **F2** corresponds to the repositioning of the nitrile toward bridge formation. **F3**, **F5**, and **P4** all contain the planar ditungstaazacyclobutadiene geometry and only differ with respect to the conformations of the W−O−Me groups.

The reaction leading from **F5** to the μ−perpendicular intermediate **II** proceeds via the dotted pathway in Figure 7. From this it can be seen that the minimum, **V8**, which has the non-perpendicular/non-parallel bridge, is accessed before the intermediate **II**. However, what becomes obvious is that the transition state **T10** is higher in energy than the transition state for the cleavage of the C−N via the μ−parallel intermediate. The energy of **P5** is 18.7 kcal/mol relative to the reactants as shown in Figure 3. From this we can conclude that the μ−parallel intermediates are involved in the reaction leading to C≡N cleavage and not the μ−perpendicular ones.

$Mo_2(OMe)_6$ + MeC≡N. We have also considered the reaction between the molybdenum triple bonded complex $Mo_2(OMe)_6$ and MeC≡N. The reaction products $(MeO)_3Mo{\equiv}N$ and $(MeO)_3Mo{\equiv}CMe$ are higher in energy by 5.0 kcal/mol which is consistent with the lack of multiple bond metathesis involving Mo≡Mo and C≡N bonds. Moreover, if we consider a similar reaction pathway for molybdenum then the transition state involving the C−N bond rupture (**P5** in Figure 3) is calculated to be 33.3 kcal/mol which is 15 kcal/mol higher relative to when M = W.

$Mo_2(OMe)_6$ + $Me_2NC{\equiv}N$. For M = Mo, the formation of the 1:1 adduct of structure type **I** is calculated to be favorable by 4.3 kcal/mol relative to the starting materials and also favorable with respect to the cleavage products. For M = W, both the μ−parallel adduct of type **I** and the cleavage products are stable with respect to the reactants; $\Delta G° = -8.7$ and -7.8 kcal/mol, respectively. For tungsten, with the bulky ^{t}BuO ligands, only the cleavage products are observed. This may well reflect steric factors destabilizing a structure akin to **I** and/or that the products of the reaction are not monomeric but rather associate by either M≡N→M bonding or alkoxide bridge formation. Both factors clearly will favor the metathesis reaction over 1:1 adduct formation.

W_2X_6 + MeCN, where X = Cl and F. A clear complication in calculations employing alkoxide ligands is that they are variable π-donors. With an sp^2-hybridized oxygen, the RO^- ligand can be viewed as a $\sigma^2\pi^2$-single-faced π-donor whereas in the linear M−O−R group, the RO^- ligand is a cylindrical $\sigma^2\pi^4$ donor.[12] These two are clearly limiting descriptions and it is the variation and orientations of the

---

[12] (a) Chisholm, M. H. *Chemtracts-Inorganic Chemistry 4* **1992**, 273. (b) Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582. (c) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouveau J. Chim.* **1983**, *7*, 535.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for Intermediates and Transition States on the Pathway Towards the Cleavage of Ditungstaazatetrahedrane (**II**)

	W(1)−W(2)	C(4)−N(3)	W(1)−C(4)	W(2)−C(4)	W(1)−N(3)	W(2)−N(3)	W(1)−O(9)	W(2)−O(9)	W(1)−O(11)	W(2)−O(11)	C(17)−C(4)−N(3)	C(17)−C(4)−W(1)
II	2.572	1.435	2.061	2.061	2.073	2.073	2.188	2.188	2.110	2.110	126.1	140.3
V1	2.539	1.445	1.990	2.176	2.449	1.913	2.098	2.171	2.211	2.152	123.5	140.3
V2	2.601	1.418	1.997	2.293	2.895	1.843	2.101	2.107	2.160	2.126	117.0	127.4
V3	2.612	1.416	2.002	2.291	2.929	1.837	2.068	2.138	2.162	2.129	117.2	125.8
V4	2.618	1.411	2.010	2.291	2.947	1.834	2.048	2.153	2.160	2.118	117.2	124.9
V5	2.641	1.422	2.005	2.317	2.957	1.815	2.065	2.160	2.139	2.108	116.3	125.4
V6	2.633	1.413	2.012	2.323	2.949	1.822	2.057	2.162	2.146	2.110	117.2	125.1
V7	2.649	1.418	2.004	2.362	2.946	1.816	2.080	2.166	2.106	2.079	116.6	125.6
V8	2.628	1.417	2.000	2.346	2.925	1.822	2.060	2.168	2.164	2.098	116.5	126.8
V9	2.658	1.802	1.919	2.254	3.288	1.750	2.127	2.154	2.035	2.335	100.3	134.8
V10	2.949	2.953	1.808	2.481	4.020	1.696	2.141	2.159	1.994	2.564	83.6	159.6
V11	2.940	2.937	1.809	2.476	4.016	1.697	2.135	2.167	1.999	2.535	83.4	169.7
V12	2.931	2.950	1.802	2.561	3.966	1.700	2.115	2.142	2.043	2.507	82.4	164.7
V13	2.980	3.130	1.795	2.664	4.011	1.699	2.114	2.068	2.042	2.543	84.2	168.7
V14	3.050	3.217	1.782	2.905	3.965	1.701	2.193	2.068	2.055	2.385	83.5	174.8
V15	3.345	4.241	1.769	3.600	4.424	1.702	2.231	2.028	2.061	2.345	95.0	178.1
V16	3.564	5.444	1.766	4.298	4.873	1.702	2.278	1.992	2.067	2.365	117.5	177.8
V17	3.645	6.339	1.767	4.906	5.017	1.701	2.437	1.973	2.009	2.406	142.7	177.9
V18	3.635	6.697	1.779	5.156	5.044	1.698	2.451	1.945	1.956	2.502	161.0	179.7

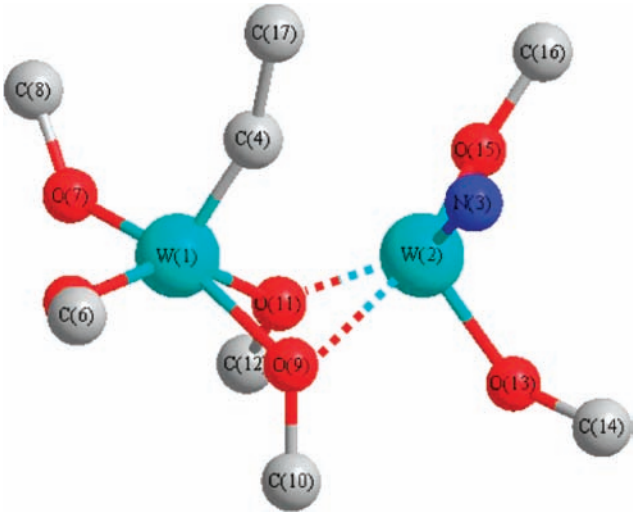


Figure 6. Optimized structure for **V10**. The hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for the Calculated Structure of **V10**

A	B	dist(cal.)	A	B	C	angl(cal.)
W(1)	W(2)	2.949	W(1)	C(4)	C(17)	159.6
W(1)	O(5)	1.909	W(1)	C(4)	N(3)	113.0
W(1)	O(7)	1.894	W(1)	W(2)	N(3)	117.3
W(1)	O(9)	2.141	W(2)	N(3)	C(4)	57.1
W(1)	O(11)	1.994	W(2)	W(1)	C(4)	57.0
W(1)	N(3)	4.020	W(1)	O(9)	W(2)	86.6
W(1)	C(4)	1.808	C(4)	W(2)	O(9)	72.5
W(2)	N(3)	1.696	C(4)	W(1)	O(9)	88.0
W(2)	C(4)	2.481	C(4)	W(2)	O(11)	71.6
W(2)	O(9)	2.159	W(2)	O(11)	W(1)	79.5
W(2)	O(11)	2.564	C(4)	W(1)	O(11)	101.8
W(2)	O(13)	1.908	O(5)	W(1)	O(7)	94.8
W(2)	O(15)	1.899	O(13)	W(2)	O(15)	103.3
C(4)	N(3)	2.953				

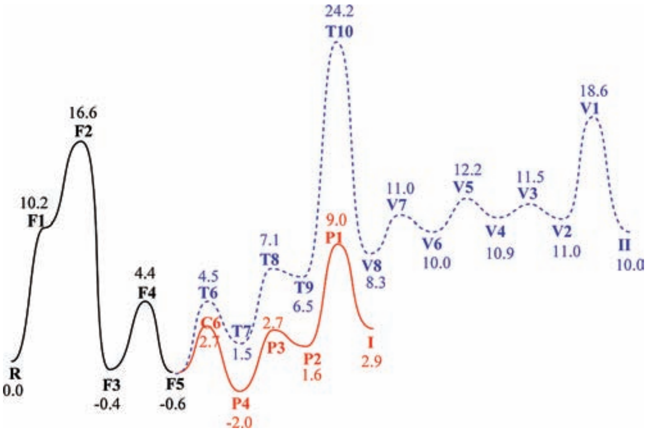
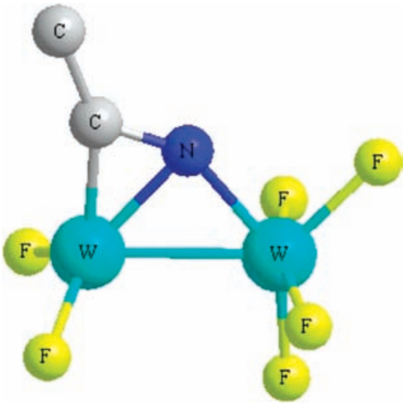


Figure 7. Free energy (calculated at 298 K in kcal/mol) profiles leading to the formation of ditungstaazacyclobutadiene (**I**) and ditungstaazatetrahedrane (**II**) from the starting materials. The red solid line is the pathway leading to the formation of **I**; the blue dash line is the pathway leading to the formation of **II**.

M−O−C angles that complicate the calculations presented above and, as seen in Figure 5 and 7, produce many local minima and transition states that are not "rate-limiting" in the overall reaction pathway. Consequently, we wondered if the key features of the reaction could be reproduced by replacing the methoxide by the halides, Cl^- and F^-, even though the W_2X_6 compounds (X = Cl, F) are not known as triply bonded molecules with D_{3d} symmetry. Starting with the optimized geometry for the $X_3W{\equiv}WX_3$ molecules, we probed the reaction with MeCN, and this is presented in detail in the Supporting Information. The cleavage products $X_3W{\equiv}CMe$ and $X_3W{\equiv}N$ are not thermodynamically favored in either case: $\Delta G° = 4.6$ and 6.9 kcal/mol for X = Cl and F, respectively. However, the transition state involving the C−N bond rupture was structurally similar to that for X = OMe and in both cases was the highest energy. In both cases the μ−parallel MeCN adduct akin to the ditungstaazacyclobutadiene was more stable than the μ−perpendicular adduct, the ditungstaazatetrahedrane, but the most stable 1:1 adduct ($\Delta G° = -21$ kcal/mol) had the structure shown below (X = F). In this structure one W atom is in a pseudo square pyramidal geometry and the fluoride ligands are terminal.



Given the high electronegativity of the fluoride ligands and the strong reducing power of the W≡W bond, it is not surprising that the 1:1 adduct of W_2F_6 with MeCN is more stable that its methoxide counterpart.

Concluding Remarks

It is interesting now to compare the reaction pathways involving the metathesis of C≡C and C≡N bonds in their reactions with M≡M triple bonds in $M_2(OR)_6$ compounds. The reaction favors the cleavage products only when M = W. This is probably a simple reflection of the greater stability of the M(6+) oxidation state for the third row transition metal and the strength of metal−ligand bonding: $5d > 4d > 3d$. In reactions involving alkynes, the μ−perpendicular 1:1 adduct, the dimetallatetrahedrane is more stable than the μ−dimetallacyclobutadiene but for nitriles the μ−parallel adducts, the dimetallaazacyclobutadiene intermediates, are thermodynamically favored over the μ−perpendicular, the dimetallaazatetrahedrane. It is in interesting to speculate why these 1:1 adducts are favored with differing structures. In our view the stability of the μ−parallel nitrile bonding bonding mode is favored for RCN because this maximizes metal−nitrogen bonding and in some ways this is similar to an acetylide which in a bridge bonding mode is often seen as μ-η^1,η^2. A nice example of this transformation is seen in the reaction of $W_2(\mu\text{-}C_2H_2)(OSiMe_2Bu^t)_6(py)$ which eliminates Me_2Bu^tSiOH with the loss of pyridine to give $W_2(\mu\text{-}CCH)(OSiMe_2Bu^t)_5$ with the conversion of the W_2C_2 moiety from perpendicular to parallel, μ-η^1,η^2.[13] However, despite this difference in preferential bonding, the lowest energy transition state for both C−C and C−N cleavage are rather similar with an asymmetric structure in which there is one terminal W-alkylidyne and a bridging alkylidyne or nitride ligand.

Computational Details

All calculations were performed using DFT as implemented in the Gaussian 03 suite of programs.[14] The PW91PW91[15−19] [Perdew and Wang's 1991 exchange and gradient-corrected correlation functional] density functional were used for all calculations. The LanL2DZ[20−22] was used for transition metal atoms, and the 6-31G* basis sets[23−27] were used for all other non-metal atoms in the model compounds. All the structures were fully optimized without symmetry constraints. Frequency calculations were also performed to confirm that all the stationary points were minima or transition states (no imaginary frequency for a minimum and one imaginary frequency for a transition state). Intrinsic reaction coordinates (IRC)[28,29] calculations were carried out on transition states to confirm these structures are indeed connecting two minima. The discussed energies are relative Gibbs free energies (ΔG_{298K}). All the relative energies were defined with respect to the starting materials.

Acknowledgment. We thank the National Science Foundation and the Ohio State University for financial support and the Ohio Supercomputer Center for computational resources. S.C. also thanks Dr. Bruce E. Bursten for his input toward the Ph.D.

Supporting Information Available: Calculated structures of minima and transition states associated with the reaction of $W_2(OMe_3)_6$ and MeCN. Calculated structures of the 1:1 dimethylcyanamide tungsten adduct $W_2(OMe)_6(\mu\text{-}NCNMe_2)$ and the molybdenum adduct $Mo_2(OMe)_6(\mu\text{-}NCNMe_2)$. Energy profiles and the structures of the minima and transition states along the reaction pathways for the metathesis reactions between W_2X_6 (X = Cl, F) and MeCN. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(13) Chisholm, M. H.; Cook, C. M.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Dalton Trans.* **1991**, 929.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Fresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G. Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challocombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(15) Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum: New York, 1998; pp 81−111.

(16) Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991; p 11.

(17) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Sing, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1992**, *46*, 6671.

(18) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B: Condens. Matter* **1993**, *48*, 4978.

(19) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B: Condens. Matter* **1996**, *54*, 1653.

(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(21) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(23) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(24) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(25) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209.

(26) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(27) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(28) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161.

(29) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.