Supporting Information For

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

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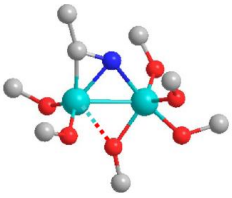
The calculated structures of minima and transition states associated with the reaction of $W_2(OMe_3)_6$ and MeCN.

I



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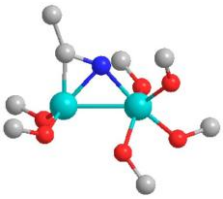

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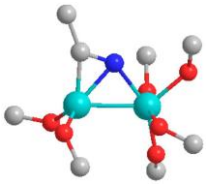

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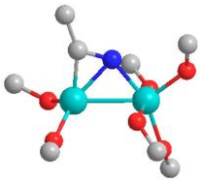

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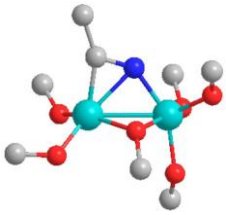

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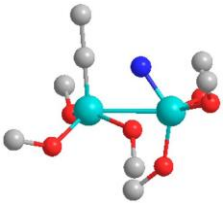

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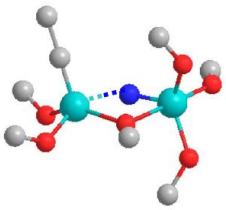

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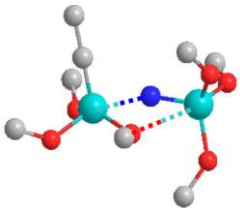

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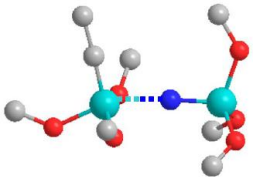

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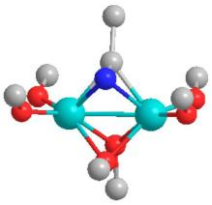

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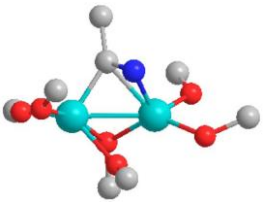

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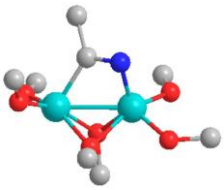

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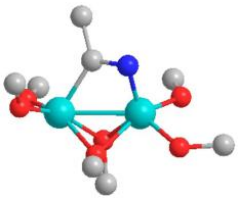

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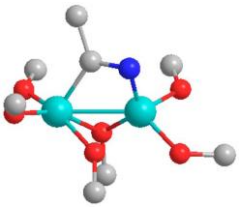

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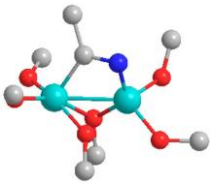

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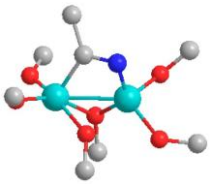

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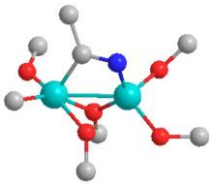

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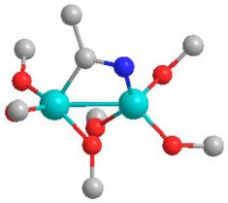

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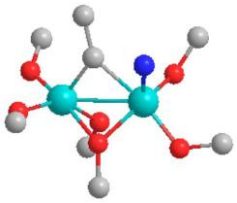

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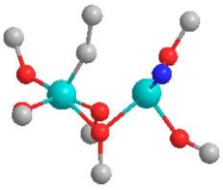

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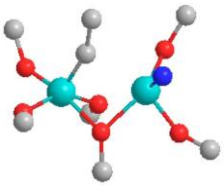

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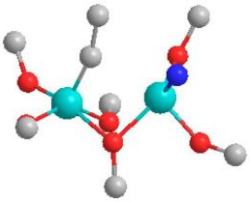

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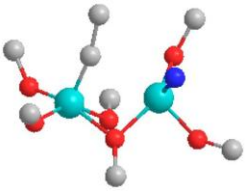

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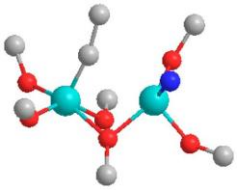

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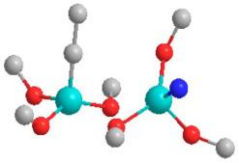

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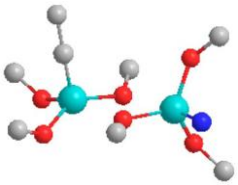

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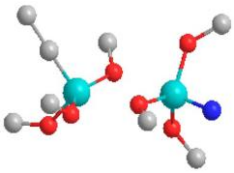

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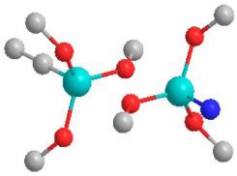

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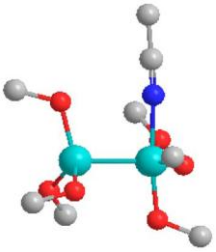

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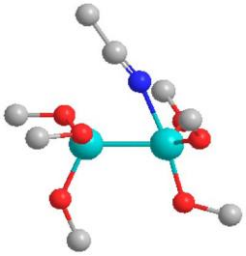

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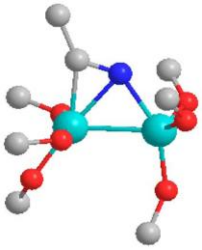

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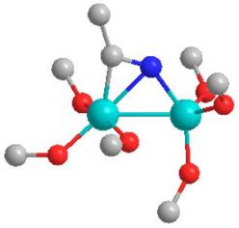

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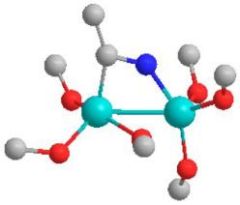

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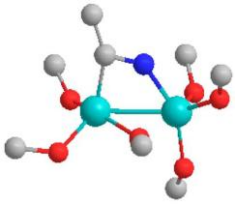

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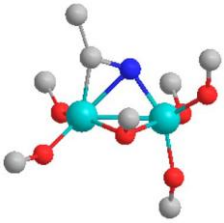

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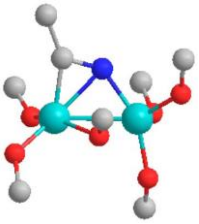

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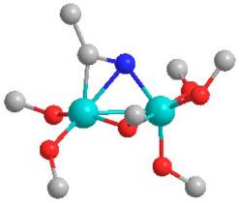

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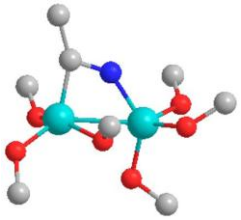

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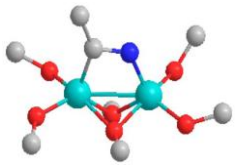

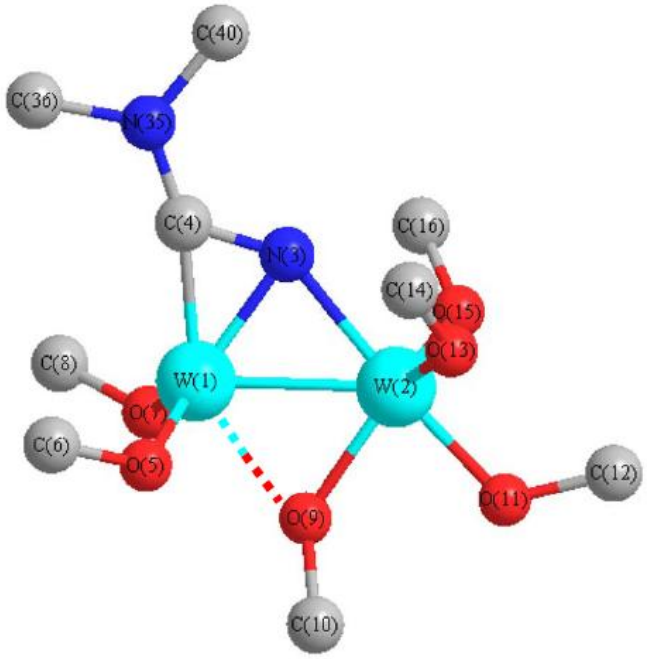

Figure S1. The optimized structure for 1:1 dimethylcyanamide tungsten adduct $W_2(OMe)_6(\mu\text{-}NCNMe_2)$. The hydrogen atoms are omitted for clarity. The calculated free energy (ΔG^o) is -8.7 kcal/mol relative to the starting materials ($W_2(OMe)_6$ and $NCNMe_2$).

Table S1. Slected bond distances (Å) and bond angles (deg) for the calculated structure of $W_2(OMe)_6(\mu\text{-}NCNMe_2)$.

A	B	Dist.	A	B	C	Angl.
W(1)	W(2)	2.503	N(3)	C(4)	N(35)	126.0
W(1)	N(3)	1.965	W(1)	C(4)	N(35)	165.7
W(1)	C(4)	2.008	W(1)	C(4)	N(3)	68.3
W(1)	O(5)	1.931	W(1)	W(2)	N(3)	49.2
W(1)	O(7)	1.926	W(2)	N(3)	C(4)	146.4
W(1)	O(9)	2.229	W(2)	W(1)	C(4)	96.0
W(2)	N(3)	2.155	W(1)	N(3)	W(2)	74.7
W(2)	O(9)	2.040	W(1)	O(9)	W(2)	71.6
W(2)	O(11)	1.955	O(9)	W(1)	N(3)	106.7
W(2)	O(13)	1.908	O(9)	W(2)	N(3)	106.8
W(2)	O(15)	1.902	W(1)	W(2)	O(11)	135.5
N(3)	C(4)	1.355	O(5)	W(1)	O(7)	120.6
C(4)	N(35)	1.352	O(13)	W(2)	O(15)	115.4

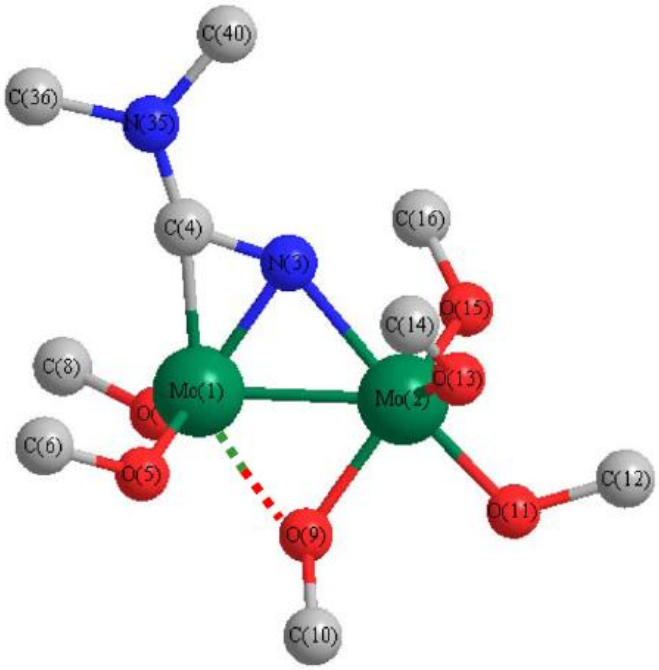

Figure S2. The optimized structure for 1:1 dimethylcyanamide molybdenum adduct $Mo_2(OMe)_6(\mu\text{-}NCNMe_2)$. The hydrogen atoms are omitted for clarity. The calculated free energy (ΔG^o) is -4.3 kcal/mol relative to the starting materials ($Mo_2(OMe)_6$ and $NCNMe_2$).

Table S2. Slected bond distances (Å) and bond angles (deg) for the calculated structure of $Mo_2(OMe)_6(\mu\text{-}NCNMe_2)$.

A	B	Dist.	A	B	C	Angl.
Mo (1)	Mo(2)	2.487	N(3)	C(4)	N(35)	126.2
Mo(1)	N(3)	1.950	Mo(1)	C(4)	N(35)	167.1
Mo(1)	C(4)	2.044	Mo(1)	C(4)	N(3)	66.6
Mo(1)	O(5)	1.942	Mo(1)	Mo(2)	N(3)	48.8
Mo(1)	O(7)	1.937	Mo(2)	N(3)	C(4)	147.8
Mo(1)	O(9)	2.196	Mo(2)	Mo(1)	C(4)	96.7
Mo(2)	N(3)	2.190	Mo(1)	N(3)	Mo(2)	73.6
Mo(2)	O(9)	2.050	Mo(1)	O(9)	Mo(2)	71.6
Mo(2)	O(11)	1.960	O(9)	Mo(1)	N(3)	109.0
Mo(2)	O(13)	1.920	O(9)	Mo(2)	N(3)	105.5
Mo(2)	O(15)	1.912	Mo(1)	Mo(2)	O(11)	135.0
N(3)	C(4)	1.340	O(5)	Mo(1)	O(7)	125.4
C(4)	N(35)	1.345	O(13)	Mo(2)	O(15)	117.0

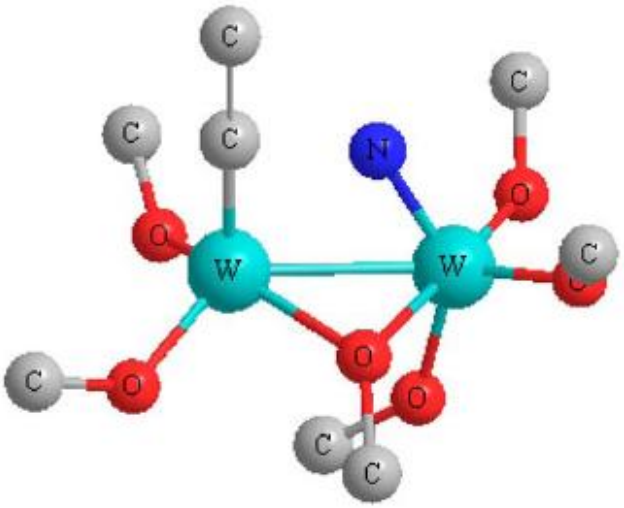

Figure S3. The calculated structure for the transition state (**P5**). The hydrogen atoms are omitted for clarity.

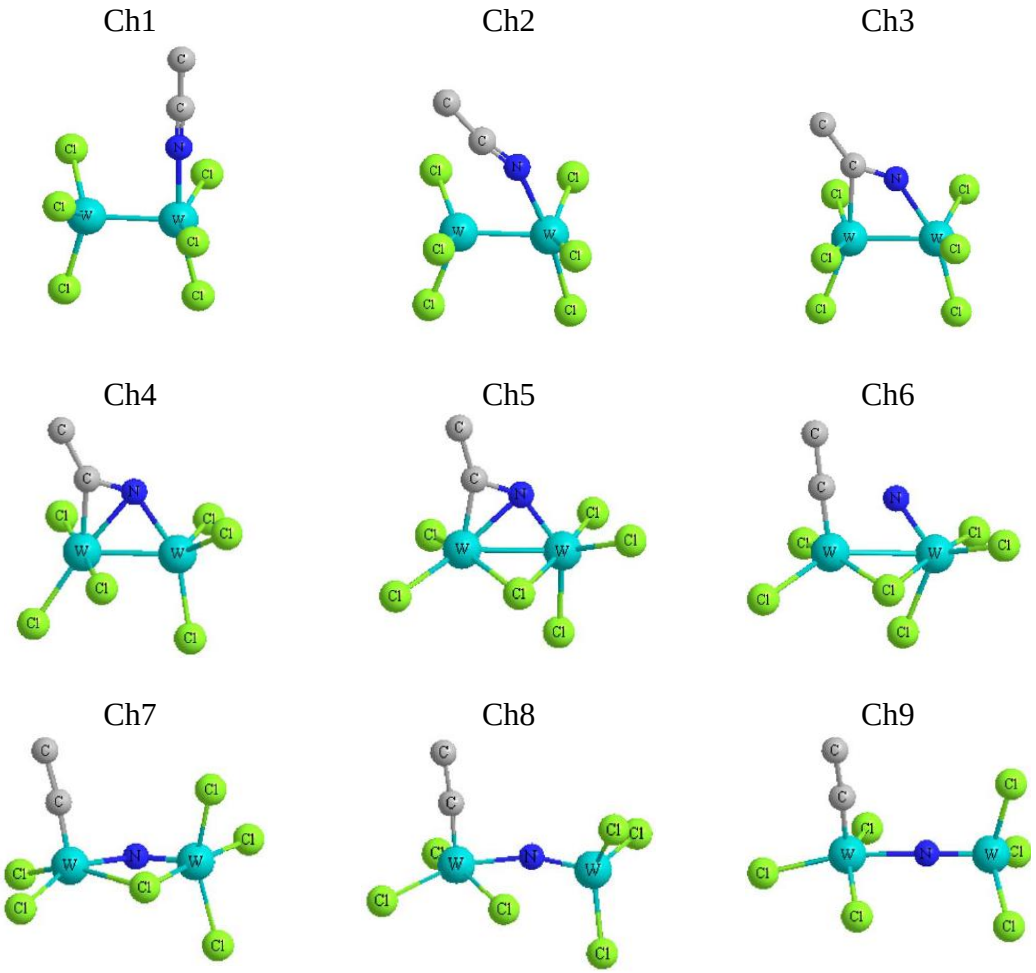

Figure S4. Free energy (kcal/mol)) profiles for the metathesis reaction between $Cl_3W{\equiv}WCl_3$ and MeCN and the optimized structures for the minima and transition states along the reaction pathway. **R** denotes the reactants, $Cl_3W{\equiv}WCl_3$ and MeCN. **P**

denotes the isolated species $Cl_3W{\equiv}N$ and $Cl_3W{\equiv}CMe$.

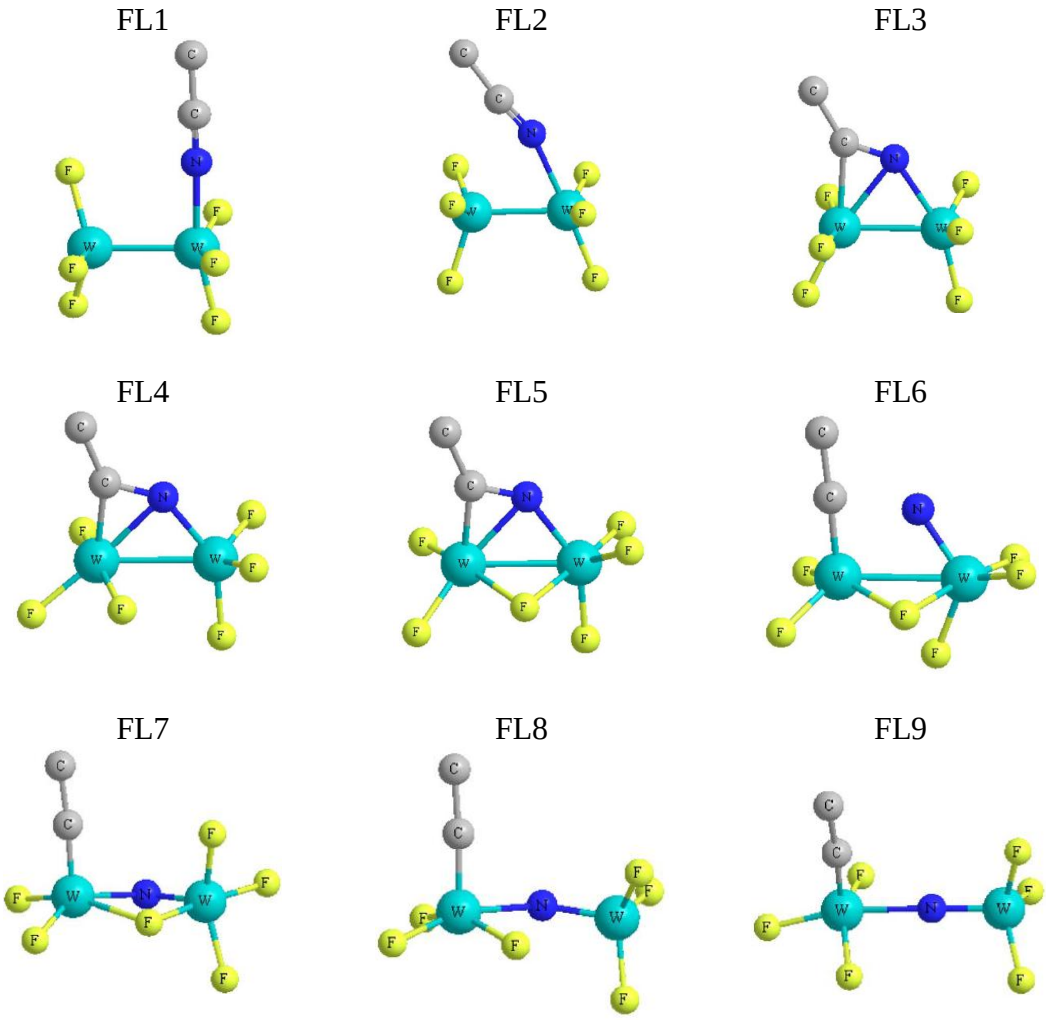

Figure S5. Free energy (kcal/mol)) profiles for the metathesis reaction between $F_3W{\equiv}WF_3$ and MeCN and the optimized structures for the minima and transition

states along the reaction pathway. **R** denotes the reactants, $F_3W{\equiv}WF_3$ and MeCN. **P** denotes the isolated species $F_3W{\equiv}N$ and $F_3W{\equiv}CMe$.