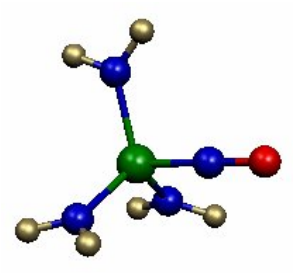
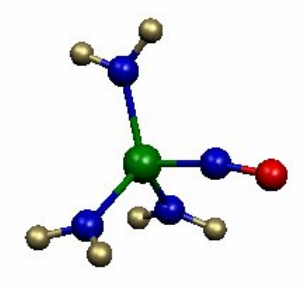
C_{3v} symmetry

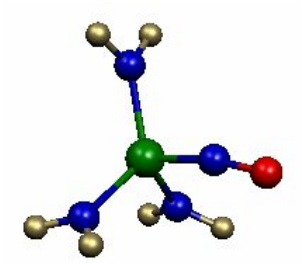


C_s symmetry



C_s symmetry

one $[NH_2]$ ligand rotated



C_s symmetry

two $[NH_2]$ ligands rotated

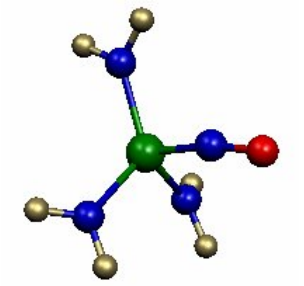
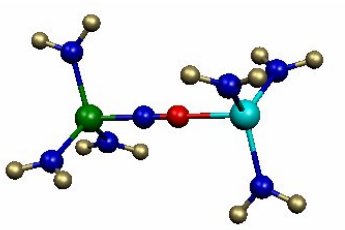
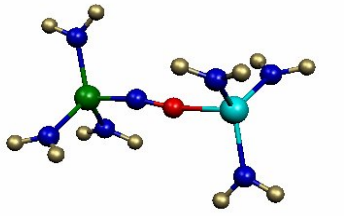


Figure S1. Initial structures used in geometry optimizations of encounter complexes. In addition, a C_1 symmetry calculation was carried by enforcing no symmetry constraints on the (otherwise) C_s configuration.

C_{3v} symmetry



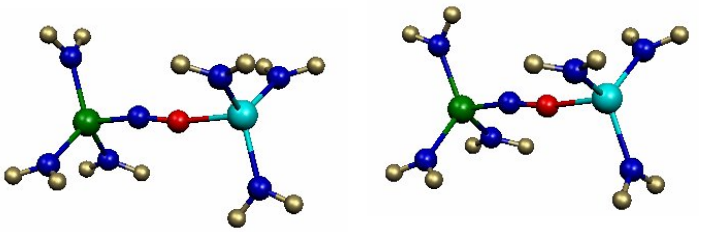
C_s symmetry



C_s symmetry

one $[NH_2]$ ligand rotated

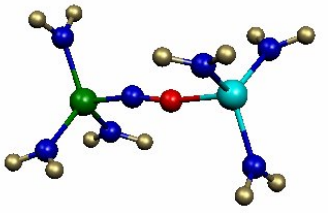
either end



C_s symmetry

one $[NH_2]$ ligand rotated

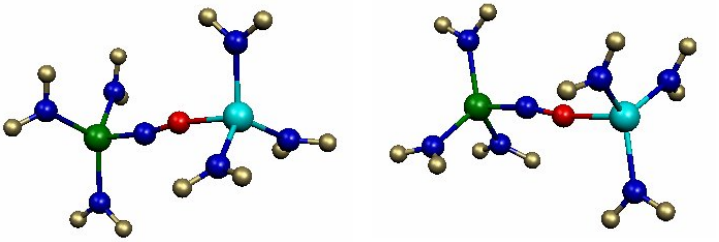
both ends



C_s symmetry

two $[NH_2]$ ligands rotated

either end



C_s symmetry

two $[NH_2]$ ligands rotated

both ends

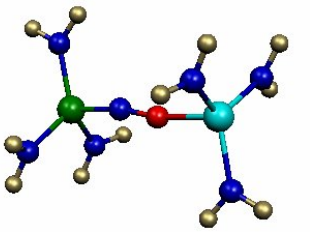


Figure S2. Initial structures used in geometry optimizations of dinuclear species. In addition, a C_1 symmetry calculation was carried by enforcing no symmetry constraints on the (otherwise) C_s configuration.

Table S1. Calculated bonding energy values ($kJ \cdot mol^{-1}$) for the reactants, encounter complex, dinuclear species, and products.

	Cr-V	**Mo-Nb**	**W-Ta**	**Mo-V**	**Mo-Mo**
Reactants	-11749	-11786	-11757	-11715	-11761
Encounter Complex	-12012	-12155	-12175	-12079	-12129
Dinuclear Species	-12104 (C_1) -12012 (C_{3v})	-12230 (C_1) -12150 (C_{3v})	-12272 (C_s)	-12142 (C_1) -12079 (C_{3v})	-12125 (C_{3v})
Products	-12293	-12552	-12661	-12393	-12401

Table S2. Calculated free energy values ($kJ \cdot mol^{-1}$) for the reactants, encounter complex, dinuclear species, and products.

	Cr-V	**Mo-Nb**	**W-Ta**	**Mo-V**	**Mo-Mo**
Reactants	-11584	-11628	-11603	-11553	-11600
Encounter Complex	-11780	-11935	-11962	-11860	-11907
Dinuclear Species	-11819 (C_1) -11729 (C_{3v})	-11963 (C_s) -11888 (C_{3v})	-12006 (C_s)	-11864 (C_1) -11803 (C_{3v})	-11848 (C_{3v})
Products	-12054	-12328	-12435	-12159	-12177