

Reactions of the Metal-Metal
Triple Bond of Molybdenum and Tungsten

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Literature Seminar

November 15, 1988

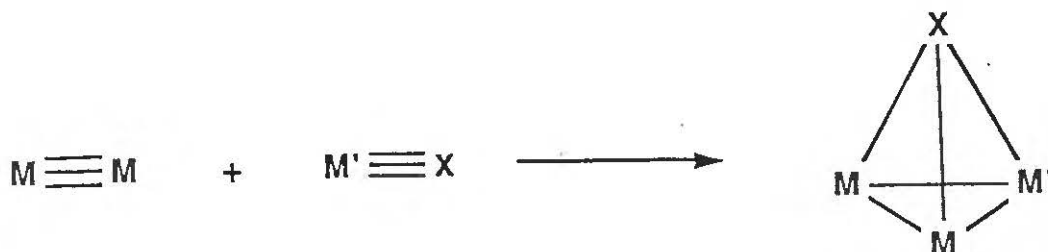
The formation of compounds that contain multiple bonds between transition metals has been documented extensively, and recently there has been growing interest in their reactivity [1,2]. To a first approximation, triple bonds in dimolybdenum and ditungsten compounds can have a variety of molecular orbital configurations: $\sigma^2\pi^4$, $\sigma^2\pi^2\delta^2$, $\pi^4\delta^2$, and $\sigma^2\pi^4\delta^2\delta^2$. However, the presence of bridging ligands complicates this simple bonding picture. A mixing of metal-metal and metal-ligand bonding orbitals may take place, and the metal-metal bonding scheme can be much more complex. Because of the variety of possible electron configurations, the reactivity of triply bonded compounds varies not only from metal to metal but from configuration to configuration.

All dimolybdenum and ditungsten compounds that form metal-metal triple bonds are either d^3-d^3 or d^5-d^5 dimers. The dimolybdenum and ditungsten hexa-alkoxides, $M_2(OR)_6$ [2,3], are the most extensively studied compounds of the d^3-d^3 series, and have a $\sigma^2\pi^4$ configuration [4]. The $Cp_2M_2(CO)_4$ compounds are the most extensively studied of the d^5-d^5 series [2,5]. The $Cp_2M_2(CO)_4$ compounds have semi-bridging carbonyls which complicate the bonding picture, and calculations show the presence of closely spaced M-M orbitals of σ , δ , δ^* , π_{xz} , and π_{yz} symmetry [6].

The molybdenum and tungsten metal-metal triple bonds, especially of the hexa-alkoxide series, have been called "inorganic functional groups" since they react with a variety of substrates [3]. Some of the most remarkable reactions of triply-bonded molybdenum and tungsten species are those with other molecules possessing triple bonds (C-C, C-N, C-O, M-C, M-N, and M-O). The reactions of the dimolybdenum and ditungsten hexa-alkoxide compounds with carbon monoxide, nitriles, and alkynes often lead to cleavage of the metal-metal triple bond [7]. In addition, reactions with alkynes and nitriles sometimes result in the metathesis of the metal-metal triple bonds [8]:



Metathesis reactions involving alkynes give alkylidyne complexes, which catalyze alkyne metathesis [9]. Reactions with metal-oxo, -carbyne, and -nitride give trinuclear clusters [10]:



Among the other reactions that triply-bonded transition metal dimers can undergo are ligand substitutions [1], dimerization to form tetranuclear clusters [11], and reductive-elimination to form quadruple bonds [12]. There is still much unexplored chemistry, and it remains to be seen in what other ways metal-metal triple bonds can serve as inorganic functional groups.

References

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