

## Is the C-Mo Bond in a Small Molybdenum Methylidyne Really a Triple Bond?

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High oxidation-state transition-metal complexes with multiple carbon-metal bond have been investigated extensively since the first discovery in early 1970's.<sup>1</sup> These complexes play important roles in alkane activation and metathesis reactions of alkene and cyclic alkanes.<sup>2</sup> Bulky substituents are normally required to stabilize the electron deficient metal center, and many of the carbene compounds are agostic.<sup>3</sup> Carbyne complexes, which are relatively rare, are mostly provided from reactions of Groups 5-9 heavy transition-metals.<sup>1</sup>

Recently a new breed of high oxidation-state transition-metal complexes have been introduced from direct reactions of metal atoms with small alkanes and their halides in excess Ar and Ne.<sup>4</sup> Particularly the methylidenes and methylidyne ( $CX_2=MX_2$ ,  $XCMX_3$ ) are the simplest possible cousins of the large transition-metal high oxidation-state complexes with multiple carbon-metal bond. They show unique structures such as agostic and Jahn-Teller distortions and interesting photochemical behaviors including photo-reversibility.<sup>4</sup> They are also considered as model systems to study the ligand effects and electronic structures of the large complexes because they are much more amenable to the higher level of theoretical methods.<sup>5</sup>

While the C-M multiple bond normally carries a high *d*-contribution and plays a key role for determination of the structure and reactivity of a complex,<sup>5</sup> previous studies showed that single configuration treatments often ended up with unrealistic answers.<sup>4</sup> For instance, B3LYP based natural bond orbital<sup>6</sup> (NBO) analyses underestimate the C-M bond

orders of Groups 9 and 10 metal methylidenes and the small Fe compounds reflect mixed characteristics of more than one electronic state.<sup>4b-d</sup> Complete active space multiconfiguration SCF (CASSCF) methods<sup>7</sup> turned out to be an efficient means to overcome the limits of single configuration approaches, and it has also been successfully used to examine the carbon-metal bonds of small transition-metal complexes.<sup>4b</sup>

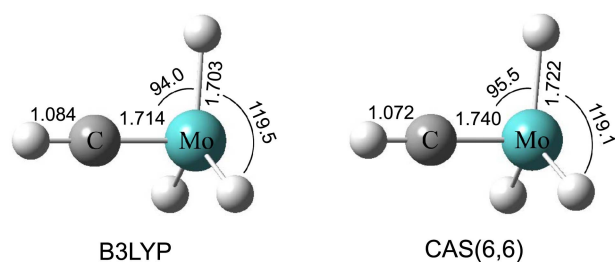
Recently small molybdenum methylidyne have been prepared along with the insertion and methylidene products from reactions of laser-ablated Mo atoms with alkanes and haloalkanes.<sup>4</sup> Halogen substitution increases the stability of the methylidyne relative to the other products due to the preference of metal-halogen bond. The C-Mo bond has been assumed to be a triple bond on the basis of its short bond-length and high stretching frequency while  $HC\equiv MoH_3$  with a simple  $C_{3v}$  structure provides a good testing ground for theoretical means. The previous studies also reveal the high natural *s*-character from C in the C-H bond.<sup>4c</sup> In this study, the C-Mo bonds of the small molybdenum methylidyne hydride ( $HC\equiv MoH_3$ ) and its halides have been examined with NBO<sup>6</sup> and CASSCF<sup>7</sup> computations using the Gaussian 09 package.<sup>8</sup>

The B3LYP hybrid density functional was incorporated with NBO analyses, while the 6-311++G(3df,3pd) basis was employed for C and H and the SDD pseudopotential and basis set for Mo.<sup>8</sup> Geometry was fully relaxed during optimization and the optimized geometry was confirmed by vibrational analysis. The minimum active space to investigate the C-Mo bond includes the  $\sigma$  and  $\sigma^*$  and two sets of  $\pi$  and  $\pi^*$

**Table 1.** C-Mo Bondlengths, Natural Occupation Numbers, and Effective Bond Orders of the C-Mo bond for Small Mo carbynes Computed with B3LYP

Complexes	r(C-Mo) <sup>a</sup>	$\sigma$ (C-Mo) <sup>b</sup>	$\pi_x$ (C-Mo) <sup>b</sup>	$\pi_y$ (C-Mo) <sup>b</sup>	$\sigma^*$ (C-Mo) <sup>b</sup>	$\pi_x^*$ (C-Mo) <sup>b</sup>	$\pi_y^*$ (C-Mo) <sup>b</sup>	EBO <sup>c</sup>	Q <sup>e</sup>
HCCH	1.196	1.992	1.999	1.999	0.009	0.000	0.000	2.991	0.0
HCMoH <sub>3</sub>	1.714	1.958	1.980	1.980	0.081	0.016	0.016	2.764	0.0
HCMoH <sub>2</sub> F	1.725	1.941	1.980	1.971	0.081	0.030	0.066	2.858	0.0
HCMoH <sub>2</sub> Cl	1.717	1.950	1.983	1.968	0.093	0.033	0.055	2.860	0.0
HCMoH <sub>2</sub> Br	1.723	1.901	1.928	1.795	0.095	0.035	0.074	2.707	0.0
HCMoH <sub>2</sub> I	1.715	1.953	1.985	1.947	0.115	0.035	0.048	2.843	0.0
FCMoH <sub>3</sub>	1.740	1.966	1.979	1.979	0.069	0.108	0.108	2.820	0.0
CICMoH <sub>3</sub>	1.737	1.956	1.975	1.975	0.088	0.128	0.128	2.781	0.0
FCMoF <sub>3</sub> <sup>d</sup>	1.716	0	0	0	0	0	0	0	28.0
CICMoCl <sub>3</sub> <sup>d</sup>	1.706	0	0	0	0	0	0	0	44.0

<sup>a</sup>C-Mo bondlength in Å. <sup>b</sup>Occupation number. <sup>c</sup>Effective bond order. <sup>d</sup>NBO calculations treated the small tetra halo Mo carbyne as a collection of six groups (atoms), gave unreasonable atomic charges, failed to give the bond orders (see text). <sup>e</sup>Total natural charge.



**Figure 1.** Optimized structures of  $\text{CHMoH}_3$  with 6-311++G(3df,3pd) at the levels of B3LYP and CAS(6,6). They have almost identical  $C_{3v}$  structures while the C-Mo bond is slightly longer in the CAS structure.

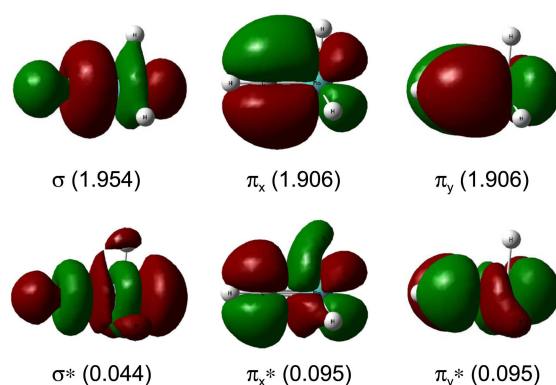
molecular orbitals (CAS(6,6)), and in order to investigate the effects of the neighboring bonds, active space is later expanded to (8,8), (12,12), and (14,14) by including C-H and Mo-H bonds.

The B3LYP C-Mo bond lengths, natural occupation numbers, and effective bond orders (EBO) for  $\text{C}_2\text{H}_2$  and  $\text{HC}\equiv\text{MoH}_3$  and its halides are listed Table 1. The computed C-C bond length of 1.196 Å for acetylene is slightly shorter than the observed value of 1.203 Å in gas phase.<sup>9</sup> The  $\sigma$  and  $\pi$  orbitals are almost fully occupied while the anti-bonding orbitals empty, leading to the natural bond order of 2.991. Shown in Figure 1 are the B3LYP and CAS(6,6) optimized structures of  $\text{HC}\equiv\text{MoH}_3$ , both having  $C_{3v}$  symmetry. The C-Mo bond length of 1.714 Å for  $\text{HC}\equiv\text{MoH}_3$  is slightly shorter than those of 1.743 and 1.754 Å measured for  $(\text{AdO})_3\text{Mo}\equiv\text{CR}$  complexes<sup>1a,10</sup> and that of 1.762 Å recently determined for  $(\text{R}_1\text{R}_2\text{N})_3\text{Mo}\equiv\text{CPPh}$ .<sup>11</sup>

The natural electron configuration of Mo for  $\text{HC}\equiv\text{MoH}_3$  ( $[\text{core}]4d^{5.03}5s^{0.59}5p^{0.28}$ ) indicates an  $sd^5$  hybridization, consistent with the Mo's ground state electron configuration ( $4d^55s^1$ ).<sup>12</sup> The C-Mo bonding orbitals are slightly less occupied than the C-C bonding orbitals of acetylene and the anti-bonding orbitals more occupied as shown in Table 1, resulting in a slightly lower bond order (2.764) than that of acetylene. The NBO results evidently show that the carbon-molybdenum bond is indeed a triple bond.

However, Table 1 shows that halogen substitution generally lengthens the C-Mo bond and also increases the natural bond order (2.707–2.858). In addition, the effects of electronegativity are not clear.  $\text{HC}\equiv\text{MoH}_2\text{F}$ ,  $\text{HC}\equiv\text{MoH}_2\text{Cl}$ , and  $\text{HC}\equiv\text{MoH}_2\text{I}$  show higher bond orders (2.858, 2.860, and 2.843), but  $\text{HC}\equiv\text{MoH}_2\text{Br}$  gives a lower value (2.707). Moreover, NBO computations produce irrational results for the tetrahalo Mo methylidyne ( $\text{FC}\equiv\text{MoF}_3$  and  $\text{ClC}\equiv\text{MoCl}_3$ ); the trials treat the compound as a collection of six independent groups (atoms) and yield unreasonable natural charges, the total natural charges of 28 and 44 for  $\text{FC}\equiv\text{MoF}_3$  and  $\text{ClC}\equiv\text{MoCl}_3$ .

In order to supplement the DFT based NBO analyses, CASSCF(6,6) calculations were carried out for acetylene,  $\text{HC}\equiv\text{MoH}_3$ , and the halide derivatives. The active space consists of the  $\sigma$  and  $\sigma^*$  C-Mo bonds and the two sets of  $\pi$  and  $\pi^*$  bonds, and six electrons (three from C and three from Mo) occupying the 6 CAS orbitals as shown in Figure 2.



**Figure 2.** Calculated CAS(6,6) orbitals involved in the carbon-molybdenum bond. Occupation numbers are given in parentheses, and the effective bond order (EBO) = 2.767, showing that the carbon-molybdenum bond in the carbyne complex is a triple bond.

Table 1 shows the optimized C-Mo bond length, occupation numbers for the bonding and anti-bonding orbitals, and net bond orders. Similar CAS(6,6) computation for acetylene leads to the C-C bond length for acetylene (1.214 Å) slightly longer than the observed<sup>9</sup> and B3LYP values of 1.203 and 1.196 Å, and the bond order of 2.859 well reflects the C-C triple bond.

The C-Mo bond length is 1.714 Å for  $\text{HC}\equiv\text{MoH}_3$ , and the net bond order 2.767 from the occupation numbers of the bonding and *anti*-bonding orbitals as shown in Figure 2  $[(1.954 + 1.906 + 1.906 - 0.044 - 0.095 - 0.095)/2]$ . The CAS(6,6) orbitals clearly show the large contribution of Mo 4d orbitals ( $sp^5$  hybridization). The net C-Mo bond order, which is comparable to that for the acetylene C-C bond, confirms that the C-Mo bond is a true triple bond. In order to explore the effects of the C-H and Mo-H bonds to the C-Mo triple bond, the active space was expanded in a series to (8,8), (12,12), and (14,14).

Addition of the  $\sigma$  and  $\sigma^*$  C-H bonds and two more electrons forms the active space (8,8), and the energy decreases 65 kJ/mol. It also gives a C-Mo bond length of 1.739 Å and bond order of 2.764. On the other hand, addition of the three pairs of the  $\sigma$  and  $\sigma^*$  Mo-H bonds and six more electrons to the original active space leads to CAS(12,12), and the energy decreases 180 kJ/mol. The optimized carbon-molybdenum bond length and net bond order are 1.750 Å and 2.752. Furthermore, addition of the  $\sigma$  and  $\sigma^*$  C-H bonds as well as three sets of  $\sigma$  and  $\sigma^*$  Mo-H bonds and eight more electrons to the original active space lowers energy by 249 kJ/mol, but the C-Mo bond length and bond order vary only slightly (1.747 Å and 2.750). The CAS(14,14) orbitals and occupation numbers are shown in Figure S1.

The relatively small changes in the C-Mo bond order with the expanded active spaces suggest that the minimum active space (6,6) is in fact sufficient to examine the carbon-metal bond order. The CAS(6,6) bond orders for the Mo methylidyne shown in Table 2, all of which are higher than 2.7, verify that the methylidyne C-Mo bond is a true triple bond regardless of halogen substitutions. They are apparently more consistent than the B3LYP based natural bond orders

**Table 2.** C-Mo Bondlengths, Occupation Numbers, and Effective Bond Orders for the C-Mo bond of Small Mo carbynes Computed with CAS(6,6)

Complexes	r(C-Mo) <sup>a</sup>	σ(C-Mo) <sup>b</sup>	π <sub>x</sub> (C-Mo) <sup>b</sup>	π <sub>y</sub> (C-Mo) <sup>b</sup>	σ*(C-Mo) <sup>b</sup>	π <sub>x</sub> *(C-Mo) <sup>b</sup>	π <sub>y</sub> *(C-Mo) <sup>b</sup>	EBO <sup>c</sup>
HCCH	1.214	1.982	1.939	1.939	0.019	0.061	0.061	2.859
HCMoH <sub>3</sub>	1.740	1.954	1.906	1.906	0.044	0.095	0.095	2.767
HCMoH <sub>2</sub> F	1.743	1.955	1.900	1.907	0.044	0.100	0.094	2.762
HCMoH <sub>2</sub> Cl	1.739	1.954	1.905	1.907	0.044	0.096	0.094	2.766
HCMoH <sub>2</sub> Br	1.739	1.954	1.906	1.907	0.044	0.095	0.094	2.767
HCMoH <sub>2</sub> I	1.737	1.954	1.907	1.907	0.044	0.094	0.094	2.768
FCMoH <sub>3</sub>	1.758	1.957	1.908	1.908	0.039	0.094	0.094	2.773
ClCMoH <sub>3</sub>	1.738	1.956	1.904	1.904	0.041	0.097	0.097	2.765
FCMoF <sub>3</sub>	1.754	1.956	1.901	1.901	0.040	0.101	0.101	2.757
ClCMoCl <sub>3</sub>	1.745	1.954	1.905	1.905	0.043	0.097	0.097	2.764

<sup>a</sup>C-Mo bondlength in Å. <sup>b</sup>Occupation number. <sup>c</sup>Effective bond order.

(Table 1). For example, those for HC≡MoH<sub>2</sub>X are 2.762, 2.766, 2.767, and 2.768 for X = F, Cl, Br, and I, and the tetrahalo methylidyne also bear consistent values. F substitution to C increases the value (2.773) while substitution to Mo decreases it (2.762). The CASSCF values, which are in general comparable to the B3LYP based NBO results, indicate that the small Mo methylidyne is essentially a single configuration problem.

In summary, the carbon-molybdenum bond of XC≡MoX<sub>3</sub> (H = H or X) has been investigated with the B3LYP based NBO and CASSCF methods, and the both methods clearly indicate that the C-Mo bond is a true triple bond. NBO trials gave unreasonable atomic charges and failed to give bond orders for tetra halo Mo methylidyne, whereas CASSCF computations with minimum active space (6,6) produce more consistent C-Mo bond orders for the Mo methylidyne including the tetrahalo methylidyne. Expansion of the active space brings only negligible changes to the C-Mo bond order. A small Mo methylidyne is essentially a single configuration problem on the basis of the similarity between the B3LYP based NBO and CASSCF results.

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