

show signals which are consistent with slow  $S_xC-NMe_2$  bond rotation.<sup>11</sup>

The conversion of I into II by reaction with  $R_4tds$  demonstrates that the half-bridging  $S_5$  ligand is a likely intermediate in the formation of the half-bridging  $S_3CNR_2$  ligand. Presumably, the  $\mu-S$  atom of the  $S_5$  ligand is incorporated into the  $S_3CNR_2$  group. This is reasonable since the  $Os_2(\mu-S)_2$  bonding arrangement is very favorable and probably quite stable (vide supra). It is likely that the formation of the half-bridging  $S_3CNR_2$  ligand in these complexes results from initial activation of  $S_8$  by  $Os(S_2CNR_2)_3$ , subsequent loss of a  $S_2CNR_2$  radical, and dimerization into species which contain a  $Os(\mu-S_5)Os$  arrangement such as found in I. The formation of the half-bridging  $S_3CNR_2$  ligand could then proceed by the attack of a  $S_2CNR_2$  radical on the  $\mu-S$  followed by displacement of anionic sulfur radical species.  $R_4tds$  is well-known to produce  $S_2CNR_2$  radicals thermally,<sup>18</sup> and therefore the conversion of I into II by reaction with  $R_4tds$  is consistent with this mechanism. It is also noteworthy that reaction of I with  $S_2CNR_2^-$  does not lead to the formation of II. The recently discovered ability of  $Os(S_2CNR_2)_3$  to dimerize by expanding its coordination core<sup>19</sup> may be important in these reactions with  $S_8$ , and consequently in the formation of  $S_3CNR_2$  ligands. Once formed, the trithiocarbamate half-bridging ligand is very stable since 20% conversion of II into its "nonsulfur rich" analogue by reaction with nucleophiles such as  $P(n-C_4H_9)_3$  requires 4 h in refluxing  $CH_2Cl_2$  solutions. Work in progress is directed toward synthesizing trithiocarbamate complexes of different metals and coordination modes.

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**Supplementary Material Available:** Atom-labeling scheme, positional coordinates, and thermal parameters for  $Os_2(S_3CNET_2)(S_2CNET_2)_3$  and  $[Os_2(S_3CNMe_2)_2(S_2CNMe_2)_3] \cdot PF_6 \cdot C_7H_8$  (6 pages). Ordering information is given on any current masthead page.

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## Dimolybdenum: Nature of the Sextuple Bond

Sir:

Flash photolysis of  $Mo(CO)_6$  has been shown to generate gaseous dimolybdenum,  $Mo_2$ ,<sup>1</sup> a species which has also been trapped in inert gas matrixes.<sup>2</sup> Spectroscopic studies on the gas-phase species, which was presumed to have a  $^1\Sigma_g^+$  ground state, have led to the following molecular parameters:  $R_e = 1.929$  Å,  $\omega_e = 477$   $cm^{-1}$ ,  $\omega_e x_e = 1.51$   $cm^{-1}$ , and  $D_0^0 = 95 \pm 15$  kcal  $mol^{-1}$ . The reported molybdenum-molybdenum bond length in this molecule, if correct, is more than 0.1 Å shorter than that of any known Mo-Mo quadruple bond,<sup>3</sup> indicative of a bond order in  $Mo_2$  that is probably greater than four. An SCF- $X\alpha$ -SW calculation<sup>4</sup> on  $Mo_2$ , prior to its experimental detection, predicted

**Table I.** Calculated Molecular and Spectroscopic Parameters for  $Mo_2$

calcn	no. of config	$R_e$ , Å	$\omega_e$ , $cm^{-1}$	$\omega_e x_e$ , $cm^{-1}$
A	64	2.09	414	-1.5
B	151	1.94	588	1.1
C	3212	2.06	392	0.5
D	3212	1.97	475	2.3
exptl <sup>a</sup>		1.93	477	1.5

<sup>a</sup> Reference 1.

a bond order of six, corresponding to a  $...9\sigma_g^2 5\pi_u^4 2\delta_g^4 10\sigma_g^2$  valence configuration, in which one  $\delta$  bond and one  $\sigma$  bond have been "added to" the well-known  $\sigma_g^2 \pi_u^4 \delta_g^2$  quadruple bond. On the basis of overlap population distributions derived from a projected  $X\alpha$  ( $PX\alpha$ )<sup>5</sup> calculation on  $Mo_2$ , we have recently proposed<sup>6</sup> that the second  $\sigma$  bond in the molecule contributes significantly to the bond shortening whereas neither of the  $\delta$  bonds contributes very much.

The only previous ab initio calculation on  $Mo_2$  predicts a long bond length of 2.1 Å,<sup>7</sup> a value similar to that found for Mo-Mo quadruple bonds.<sup>8</sup> The authors neglect to explain the discrepancy between their result and the experimental one, leaving one to guess which value is in error. Furthermore, no attempt was made to discuss the relative importance of the different metal-metal bonding interactions. We now report the results of a calculation of the potential energy curve of  $^1\Sigma_g^+ Mo_2$  by a multiconfiguration self-consistent-field method with configuration interaction (CI). This technique provides an accurate determination of the potential curve near the equilibrium internuclear distance but is not appropriate at the dissociation limit. Our predicted spectroscopic constants,  $R_e = 1.97$  Å,  $\omega_e = 475$   $cm^{-1}$ , and  $\omega_e x_e = 2.3$   $cm^{-1}$ , provide excellent support for the experimental values. In addition, a natural orbital analysis confirms our previous proposal concerning the relative strengths of the various bonding interactions.

Four different calculations (A-D) are reported here. Linear combinations of Gaussian-type orbitals (GTOs) were obtained from a least-squares fit of near Hartree-Fock limit Slater atomic orbitals.<sup>9</sup> Three GTOs per atomic orbital were used, except for the Mo 3d and 4d orbitals for which four GTOs were used. The two most diffuse components of the 4d orbital were split off to form a triple- $\zeta$  representation. The most diffuse component of the 4p orbital was also split off, and an additional p GTO with an exponent of 0.10 was added to the basis, resulting in a set of (23s10p8d) primitive GTOs contracted to [9s5p4d] on each atom. This basis set has considerable flexibility in the valence region, but it is a poorer representation of the core regions. Calculations A-C used this basis while calculation D also had additional single s, p, and d GTOs, with exponents of 0.7, 0.4, and 0.4, respectively, at the midpoint of the bond (bond-centered functions). The generalized molecular orbital (GMO) method<sup>10-12</sup> was used to obtain an optimized set of strongly and weakly occupied valence orbitals. The metal-metal bonding  $9\sigma_g$ ,  $5\pi_u$ ,  $2\delta_g$ , and  $10\sigma_g$  orbitals (strongly occupied) and their corresponding antibonding orbitals (weakly occupied) were used to define a configuration space for the CI calculation.

A full CI calculation on  $^1\Sigma_g^+ Mo_2$  within this space of 12 orbitals would require more than 35 000 spin-adapted configurations and is computationally infeasible. Calculation A used all configurations involving paired excitations from the bonding orbitals to their corresponding antibonding orbitals. This set of 64

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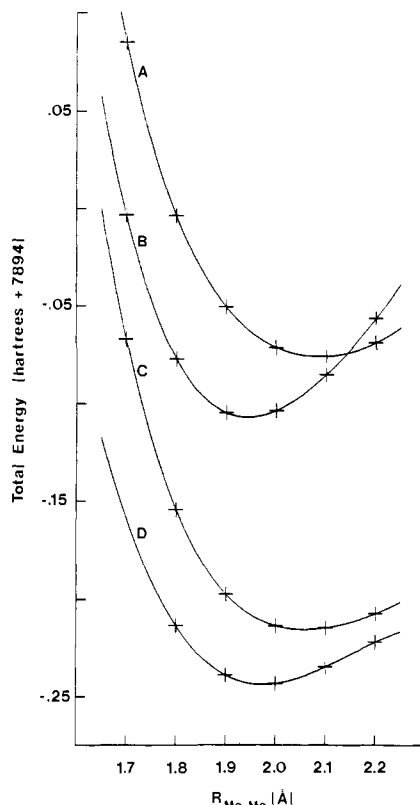
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**Figure 1.** Calculated potential curve for  $\text{Mo}_2$ ; + indicates a calculated energy. The arrow on the abscissa is at the experimental internuclear distance (from ref 1).

configurations contains those necessary for proper dissociation into neutral but not  $^7\text{S}$  Mo atoms. Within the orbital optimization afforded by the GMO method, this is the equivalent of a perfect-pairing generalized valence bond (GVB) calculation.<sup>13</sup> Calculation B included the 151 double excitations from the sextuply bonded ground configuration. The resultant wave function will not dissociate correctly, but all of the excited configurations can interact directly with the ground configuration, leading to a greater recovery of correlation energy near the equilibrium internuclear distance than in A. Calculations C and D include all single and double excitations out of the 64 configurations of A, a total of 3212 spin-adapted configurations.

The potential energy curves resulting from a least-squares fit to a fourth-order polynomial of calculations at  $R = 1.7, 1.8, 1.9, 2.0, 2.1,$  and  $2.2 \text{ \AA}$  (calculations A-C) and the latter five of these points (calculation D) are shown in Figure 1. The polynomial functions were analyzed by using the method of Dunham.<sup>14</sup> The calculated molecular constants are listed in Table I. Calculation A minimizes at the unsatisfactorily long bond length of  $R = 2.09 \text{ \AA}$ , in agreement with a recent GVB calculation on  $\text{Mo}_2$ .<sup>7</sup> Calculation B achieves the best agreement with the experimental bond distance, most likely due to a fortuitous cancellation of errors due to basis set incompleteness and a rather limited CI. Indeed, an increase in the number of configurations without a change in basis set size (C) has the expected effect of lengthening the Mo-Mo bond and decreasing  $\omega_e$ . Calculations C and D differ only in the addition of bond-centered functions in the latter, but the effect of the larger basis is quite dramatic; the calculated bond distance decreases by  $0.09 \text{ \AA}$ , and the predicted stretching frequency increases by  $83 \text{ cm}^{-1}$ . The equilibrium bond distance, stretching frequency, and first anharmonicity constant as derived from calculation D are all in excellent accord with experiment.

It is evident from the above that caution must be used when choosing a set of configurations to correlate orbitals based upon

a limited basis. Although calculation B is superior to A, it is expected that either an increase in basis set size or a better optimization of the orbitals used to construct the pair-correlated geminals would improve the results of the latter. Similarly, while calculation D achieves impressive agreement with the experimental results, it must be realized that the addition of more configurations or basis functions might change the results.<sup>15</sup> We expect, however, that any further changes would be small and that calculation D is a good representation of the potential near the equilibrium bond length.

The final electronic configuration for D at  $2.0 \text{ \AA}$  is

$$\dots 9\sigma_g^{1.88} 5\pi_u^{3.78} 2\delta_g^{3.42} 10\sigma_g^{1.92} 9\sigma_u^{0.08} 2\delta_u^{0.58} 5\pi_g^{0.22} 10\sigma_u^{0.12} \quad (1)$$

The sextuply bonded leading configuration comprises 61% of the total wave function for both calculations C and D at  $2.0 \text{ \AA}$ . It is interesting that this contribution is greater than that in A (46%) despite all of the configurations of A being included in C and D as well as excitations out of them. The source of this apparent anomaly will be discussed in a subsequent publication. Analysis of (1) indicates that the dominant excited configurations in the CI wave function are the result of excitations from the  $2\delta_g$  to the  $2\delta_u$  orbitals, representative of strong left-right correlation of the  $\delta$  electrons. By comparison, configurations representing excitations from the  $10\sigma_g$  to the  $9\sigma_u$  orbital make only a small (<4%) contribution to the CI wave function. Clearly, the comparative insignificance of the  $10\sigma_g$  to  $9\sigma_u$  correlation relative to the  $2\delta_g$  to  $2\delta_u$  correlation implies stronger bonding in the  $10\sigma_g$  MO than that found in the  $2\delta_g$  MO, i.e., the one-electron orbital description is more valid for the former. In fact, the  $10\sigma_g$  orbital, which is mostly 5s in character, correlates less than the  $9\sigma_g$  orbital, which is mostly  $4d_{z^2}$ , further evidence for the strong metal-metal interaction in the  $10\sigma_g$  orbital. This strongly supports our proposal<sup>6</sup> that the second  $\sigma$  bond in  $\text{Mo}_2$  has a far more important role than the second  $\delta$  bond in making the bond length of  $\text{Mo}_2$  shorter than those of the quadrupole Mo-Mo bonds. The formation of this second  $\sigma$  bond by using the s orbitals is restricted to the naked metal clusters, as the addition of ligands, with concomitant increase in oxidation number, will force the 5s atomic orbitals, and hence this molecular orbital, to higher energy.

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### Evidence for the Nonexistence of a ( $\eta^3$ -1-Silapropenyl)tricarbonyliron Complex. A Correction

Sir:

The extraordinary stability of transition-metal complexes of highly reactive species such as cyclobutadiene and trimethylenemethane has been well documented.<sup>1</sup> Recently, the preparation of two tricarbonyliron complexes of the 1-silapropenyl radical (**1a** and **b**) was reported and heralded as representing the preparation of the first stable compounds of doubly bonded silicon.<sup>2</sup>

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