(w), 1248 (w), 1215 (sh), 1165 (sh), 1148 (vs), 1108 (sh), 953 (w), 890 (m), 855 (m), 828 (m), 770 (w, br), 705 (m), 680 (w), 581 (w), 480 (w) cm^{-1}. Mass spectrum: M^+, 189; $M - C_2H_4^+$, 161; $M - CF_3^+$, 120; $CH_2CH_2S^+$, 60. NMR: $\phi(CF_3)$ −77.4 (pentet, $J_{F\text{-}CH} \simeq 1$ Hz); $\delta(NH_2)$ 2.47; $\delta(CH_2S)$ 3.45 ($J_{NH\text{-}CH} \simeq 1$ Hz). Anal. Calcd: C, 25.49; H, 3.15; N, 7.37; S, 33.96. Found: C, 25.40; H, 3.17; N, 7.41; S, 33.86.

Acknowledgment. J.M.S. is grateful to the Alexander von Humboldt Stiftung for a U.S. Senior Scientist Award.

Registry No. $CF_3C(NH_2)OCH_2CH_2O$, 70247-62-0; $CF_3C(NH_2)N{=}C(CF_3)OCH_2CH_2O$, 70247-63-1; $CF_3C(NH_2)OCH_2CH_2S$, 70247-64-2; $CF_3C(NH_2)SCH_2CH_2S$, 70247-65-3; $HOCH_2CH_2OH$, 107-21-1; $HOCH_2CH_2SH$, 60-24-2; $HSCH_2CH_2SH$, 540-63-6; CF_3CN, 353-85-5; NaF, 7681-49-4.

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Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Addition of Dimethylcyanamide to Hexakis(alkoxy)dimolybdenum Compounds

Malcolm H. Chisholm* and Raymond L. Kelly

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Prior work has established that the triple bond (M≡M) in $Cp_2Mo_2(CO)_4$ forms 1:1 adducts with a number of unsaturated molecules. The latter act as four electron donor ligands and span the Mo–Mo bonds in the manner shown schematically in Figure 1. The Mo-to-Mo distance increases from 2.448 (1) Å in $Cp_2Mo_2(CO)_4$ (M≡M)[1] to 2.974 (1), 3.015 (1), and 3.117 (1) Å in the adducts $Cp_2Mo_2(CO)_4{\cdot}(un)$, when un = $HC{\equiv}CH$,[2] Me_2NCN,[3] and $CH_2{=}C{=}CH_2$,[4] respectively. This is tantamount to a M–M triple to single bond transformation[5] and is in keeping with the maintenance of an 18-valence-shell electron count per molybdenum atom.

The compounds Mo_2X_6,[6] where X = R (alkyl), NR_2, and OR, also contain Mo-to-Mo triple bonds. However, in these compounds the molybdenum atoms do not attain 18-valence-shell configurations and have been shown to be capable of undergoing reactions which lead to a net donation of four electrons to the central $(M{\equiv}M)^{6+}$ moiety without disruption of the M–M multiple bond. The previously reported preparations of $Mo_2(OSiMe_3)_6{\cdot}2HNMe_2$[7] and $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$[8] from $Mo_2(OR)_6$ compounds provide two examples of structurally characterized compounds having triple bonds (M≡M) between four-coordinated molybdenum atoms.[9] We are currently extending our studies of the reactions of $Mo_2(OR)_6$ compounds to include reactions involving small unsaturated molecules of the type known to form adducts with $Cp_2Mo_2(CO)_4$ and report here studies involving dimethylcyanamide, Me_2NCN.

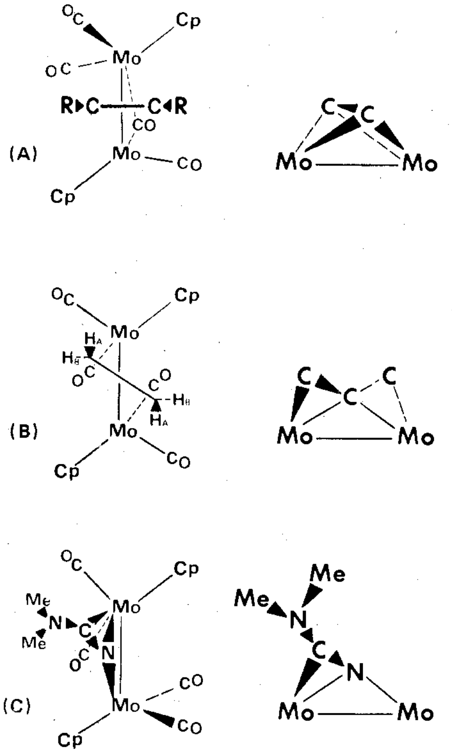

Figure 1. Schematic representations of the $Cp_2Mo_2(CO)_4{\cdot}un$ molecules (A, un = $RC{\equiv}CR$; B, un = allene; C, un = Me_2NCN) emphasizing the coordination of the central Mo_2un group.

Results and Discussion

Hydrocarbon solutions of $Mo_2(OR)_6$ compounds (R = Bu-*t* and Pr-*i*) react with Me_2NCN to give intense purple solutions from which dark crystals can be obtained by careful crystallizations. (Regrettably no crystals have proved suitable for detailed X-ray studies thus far.[10]) The dark, air- and moisture-sensitive crystals are formulated as 1:1 adducts $Mo_2(OR)_6{\cdot}NCNMe_2$ on the basis of analytical and spectroscopic data (vide supra).

Formation of these adducts is reversible and, the Me_2NCN ligand is readily lost when these compounds are heated in vacuo: only $Mo_2(OR)_6$ compounds sublime. However, in the mass spectrometer weak molecular ions are observed, $Mo_2(OR)_6{\cdot}NCNMe_2^+$, followed by loss of Me_2NCN to give $Mo_2(OR)_6^+$ which are the most intense ions in the spectra. In solution $Mo_2(OBu\text{-}t)_6{\cdot}NCNMe_2$ exists in equilibrium with $Mo_2(OBu\text{-}t)_6$ and the free cyanamide whereas $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ appears stable with respect to this type of ligand loss. This difference we attribute to the greater steric bulk of the *tert*-butyl group and parallels previous observations on the formation of amine adducts of $Mo_2(OR)_6$ compounds.[11]

In the IR spectrum of $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ there is an intense band at 1582 cm^{-1} assignable to a stretching mode of the coordinated Me_2NCN molecule. This is reduced from a free ligand value for $\nu(C{\equiv}N)$ of 2205 cm^{-1}. There is also a strong broad asymmetric band at 634 cm^{-1} which we assign to $\nu(Mo\text{–}O)$ of terminal Mo–OPr-*i* ligands. We find no evidence in the IR spectrum for bridging OPr-*i* ligands.

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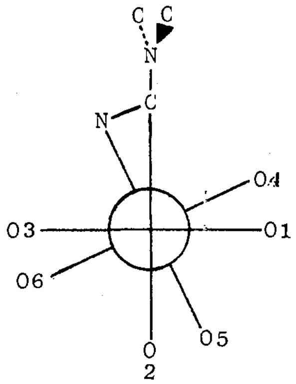

Figure 2. Schematic representation of the proposed ground-state structure of the $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ molecule viewed down the molybdenum-to-molybdenum bond.

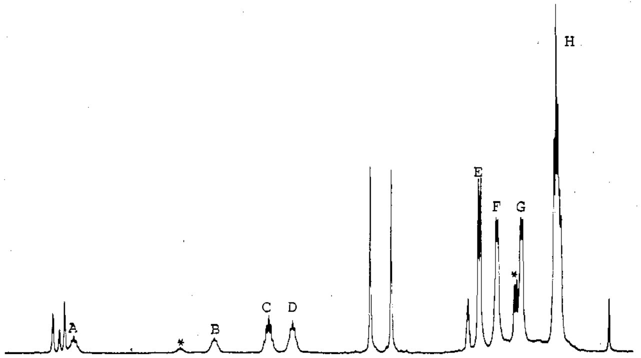

Figure 3. ^1H NMR spectrum of $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ at 220 MHz and −40 °C. Methyne proton resonances are indicated A, B, C, and D and methyl signals E, F, G, and H. Signals marked with an asterisk are due to $Mo_2(OPr\text{-}i)_6$ (M≡M). The solvent is toluene-d_8.

The $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ compound shows fascinating ^1H NMR spectra which vary with temperature but which may readily be rationalized in the following manner.

We propose that the Me_2NCN ligand acts as a four-electron donor and spans the Mo–Mo bond in a manner similar to that found in $Cp_2Mo_2(CO)_4{\cdot}NCNMe_2$.[4] The cyanamide ligand can be considered to form an N σ bond to one molybdenum atom and a CN π bond to the other. Furthermore, we suggest that in the ground state (solid-state structure) the alkoxy groups are not eclipsed but adopt a partially staggered conformation. This is the situation for both $Mo_2(OSiMe_3)_6{\cdot}2HNMe_2$[7] and $W_2(OPr\text{-}i)_6{\cdot}2py$.[12] Thus the ground-state structure would consist of two enantiomers which schematically may be represented as shown in Figure 2. Here for the sake of clarity a fully eclipsed form of the molecule is drawn. Enantiomerization could occur by a simple rotation about the Mo–Mo bond causing an apparent plane of symmetry containing the two molybdenum atoms, the oxygen atoms labeled 2 and 5 in Figure 2, and the C_2NCN atoms of the coordinated cyanamide ligand. This apparent plane of symmetry would lead to four types of OPr ligands ($O1 = O3 \neq O4 = O6 \neq O2 \neq O5$) which fall into two classes with respect to the bridging $NCNC_2$ ligand, namely, cis (O1, O3, O4, O6) and trans (O2, O5) groups.

The low-temperature limiting ^1H NMR spectrum, which is shown in Figure 3, is entirely consistent with the above description of the molecule. There are four methyne proton resonances, labeled A, B, C, and D in Figure 3, in the integral ratio 1:1:2:2, respectively. The methyl region of the spectrum is more complex and consists of three well-separated doublets, E, F, and G, and three overlapping doublets, labeled H in Figure 3. Six methyl resonances are expected for our proposed structure since rapid enantiomerization still leaves the isopropoxy ligands which are cis to the bridging $NCNMe_2$ with diastereotopic methyl groups. There are two signals of equal intensity for the *N*-methyl protons which is expected for a planar C_2NCN moiety with restricted rotation about the central N–C bond (this is directly analogous to the low-temperature limiting spectrum observed for $Cp_2Mo_2(CO)_4{\cdot}NCNMe_2$). The only other resonances seen in the spectrum (Figure 3) are assignable to (i) a small amount of $Mo_2(OPr\text{-}i)_6$ which is present as an impurity and (ii) residual protons in the toluene-d_8 solvent.

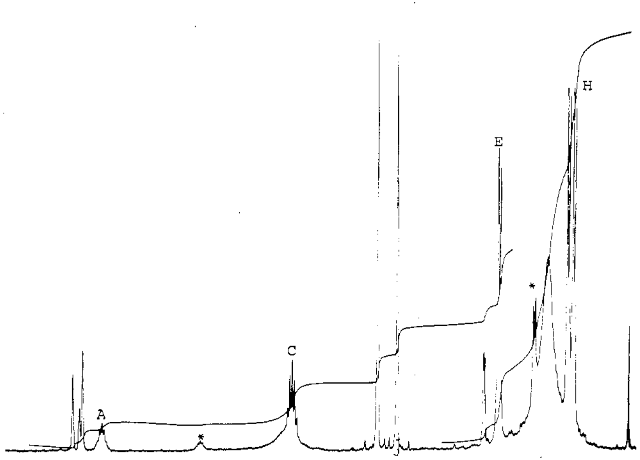

Figure 4. ^1H NMR spectrum of $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ at 220 MHz and 16 °C in toluene-d_8. Signals marked with an asterisk are from $Mo_2(OPr\text{-}i)_6$ (M≡M).

When the temperature is raised, the methyne proton resonances B and D start to broaden and then coalesce as do three of the methyl doublets, namely, the doublets indicated by F and G and one from H in Figure 3. The ^1H NMR spectrum obtained at 16 °C is shown in Figure 4. At this temperature site exchange of three of the OPr-*i* ligands is fast while the other three are still frozen out on the NMR time scale. There are still two signals of equal intensity for the *N*-methyl protons which implies that the $Mo_2(NCNC_2)$ unit is not fluxional. We believe the most reasonable interpretation of the dynamic behavior of the molecule at 16 °C is that alkoxy group exchange is occurring rapidly at one molybdenum atom but not at the other one. Furthermore, it is reasonable to suppose that the rapid site exchange involves the alkoxy group represented by O4, O5, and O6 in Figure 2 since these are coordinated to the least sterically crowded molybdenum atom.

When the temperature is raised above 16 °C, site exchange between the other set of OPr-*i* ligands sets in, and finally (>80 °C) all OPr-*i* ligands become equivalent and the *N*-methyl resonances collapse to a single resonance. This is consistent with the view that the Mo_2NCNC_2 unit becomes fluxional in a manner which equivalences both molybdenum atom: this was found for $Cp_2Mo_2(CO)_4{\cdot}NCNMe_2$. All these temperature-dependent processes do not involve free $Mo_2(OPr\text{-}i)_6$, which is present in solution, and are thus most likely intramolecular processes.

We conclude that all the experimental data for the $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ molecule is at least consistent with the view that the Me_2NCN ligands acts as a four-electron donor in a manner analogous to that previously established for the $Cp_2Mo_2(CO)_4{\cdot}NCNMe_2$.

Experimental Section

General procedures, including the preparation of $Mo_2(OR)_6$ compounds (R = Bu-*t* and Pr-*i*) have been previously described.[12] Note the use of anaerobic conditions and dry, oxygen-free solvents. Me_2NCN was purchased from Columbia Organics. Analyses were performed by the Alfred Bernhard Co. Mass spectral results were obtained on an AEI MS9 by the method of direct insertion. Infrared spectra were obtained from Nujol mulls between CsI plates with a Perkin-Elmer 283 spectrometer.

Preparation of $Mo_2(OPr\text{-}i)_6\cdot Me_2NCN$. To $Mo_2(OPr\text{-}i)_6$ (0.17 g, 0.31 mmol) in hexane (10 cm^3) was added Me_2NCN (20 μL, 0.4 mmol (=25% excess)). On addition, the red solution instantly turned deep purple. The reaction mixture was allowed to stand for 12 h and then cooled to −20 °C. Deep purple crystals were subsequently filtered off from the mother liquor; yield 0.12 g, 63% based on $Mo_2(OPr\text{-}i)_6$.

Anal. Calcd for $H_{48}C_{21}N_2Mo_2$: C, 40.91; H, 7.85; N, 4.54. Found: C, 40.64; H, 7.72; N, 4.50. IR (Nujol mull between KBr plates): 1582 (vs), 1415 (m), 1320 (m), 1265 (w), 1168 (m), 1110 (vs), 970 (vs), 851 (s), 836 (s), 730 (s), 634 (br, s), 455 (m), 430 (m) cm^{-1}. ^1H NMR (220 MHz; toluene-d_8; −40 °C; low temperature limiting spectrum, i.e., Figure 3): δ(CH) A = 6.84, B = 5.16, C = 4.50, D = 4.20; $\delta(CH_3)$ E = 1.95, F = 1.74, G = 1.44, H = 1.02; δ(*N*-methyls) 3.27, 3.02. The δ values were measured relative to Me_4Si.

Preparation of $Mo_2(OBu\text{-}t)_6\cdot NCNMe_2$. $Mo_2(OBu\text{-}t)_6\cdot NCNMe_2$ was prepared in the manner described above by using $Mo_2(OBu\text{-}t)_6$ in place of $Mo_2(OPr\text{-}i)_6$. Anal. Calcd for $H_{54}C_{27}N_2Mo_2$: C, 46.28; H, 8.63; N, 4.00. Found: C, 46.04; H, 8.48; N, 3.79.

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Registry No. $Mo_2(OPr\text{-}i)_6Me_2NCN$, 70576-08-8; $Mo_2(OBu\text{-}t)_6Me_2NCN$, 70576-09-9; $Mo_2(OPr\text{-}i)_6$, 62509-78-8; $Mo_2(OBu\text{-}t)_6$, 62509-80-2.

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(5) Mo–Mo single bonds vary greatly in distance depending on the formal oxidation state of molybdenum and the nature of the ligands (F. A. Cotton, *J. Less-Common Met.*, **54**, 3 (1977)). The single bond distance found in $Cp_2Mo_2(CO)_6$ is 3.235 (1) Å which serves here as a good comparison (R. D. Adams, D. M. Collins, and F. A. Cotton, *Inorg. Chem.*, **13**, 1086 (1974)).

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(9) There is also a recent report of another example of a structurally characterized molecule containing a Mo-to-Mo triple bond between four-coordinated molybdenum atoms, $Mo_2(O_2POH)_4$ (A. Bino and F. A. Cotton, *Angew. Chem., Int. Ed. Engl.*, in press).

(10) We thank Dr. Michael W. Extine and Phillip E. Fanwick of Professor F. A. Cotton's Laboratory at Texas A&M University and Dr. John Huffman of the Molecular Structure Center at Indiana University for their time and trouble in this regard.

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Correspondence

Reassignment of the Satellites in the X-ray Photoelectron Spectra of Chromium Hexacarbonyl

Sir:

Bancroft, Boyd, and Creber have recently reported high-resolution, gas-phase, X-ray photoelectron spectra (XPS) of group 6B hexacarbonyls.[1] The authors interpreted the extensive satellite structure in terms of the allowed (monopole) excitations of the ground-state molecules.[2] While this may be adequate for the satellites of the metal core ionizations, we believe it is preferable to interpret the satellites of the carbon and oxygen core ionizations in terms of localized hole states. In fact, we believe that the reduction to C_{4v} symmetry in forming these localized hole states is responsible for the stronger satellite structure observed by Bancroft et al. for the carbon and oxygen core ionizations. In addition, transitions which are forbidden in O_h symmetry may have appreciable intensities in the lower, C_{4v}, symmetry of the localized hole states. In order to test our assumptions, we have carried out parameter-free molecular orbital (MO) calculations[3] on various hole states and calculated the intensity of the satellites via the sudden approximation.[4]

Since the satellite structure for all three metals is similar, we have calculated only that for $Cr(CO)_6$. The atomic basis set of Clementi was used for C and O[5] and the s functions were reduced to a single exponent.[6] Richardson's atomic functions were used for the Cr[7] and the 4s and 4p exponents were 1.70.[8] Final core hole states were calculated by removing the electron of interest and converging the localized or delocalized hole states. In accord with the equivalent core model,[9] the atomic basis functions of the photoionized atom with nuclear charge Z were replaced by functions for an atom with nuclear charge $Z + 1$, i.e., F for photoionized O(O*) and Mn for photoionized Cr(Cr*). Results obtained for unrelaxed basis sets were in qualitative agreement. The method for calculating satellite intensities has been described previously.[10] We have used the orbital numbering scheme of Beach and Gray,[2] as did Bancroft et al.

When the symmetry of the core hole state was forced to remain octahedral by delocalizing the C or O 1s hole, no satellites were found. The probability of the main peak, calculated from the overlap of the initial and final states, was greater than 99%. When the symmetry was reduced to C_{4v} by localizing the hole, four relatively intense satellites were found, which correspond well to the four observed satellites. The carbon and oxygen satellites are similar in structure and arise from the same transitions, so we will limit our discussion to the oxygen satellites.

The satellite intensities for 35 C_{4v}, symmetry-allowed transitions were calculated. Only four of these transitions showed appreciable intensities. The satellite assignments and their octahedral parentage are given in Table I. The molecular orbital diagram, Figure 1, shows how the important orbitals in C_{4v} symmetry arise from the O_h orbitals. The first and strongest satellite is due to the $7e \rightarrow 8e$ transition and involves charge transfer from the chromium–carbonyl π bonds, mainly M–C–O*, to the 2π orbitals of the photoionized carbonyl. The 7e orbital is derived primarily from the $2t_{2g}$ (96%), while the 8e is 40% $2t_{2u}$, 40% $4t_{1u}$, and 10% $3t_{2g}$. The second satellite arises from the $7e \rightarrow 10e$ and $2b_2 \rightarrow 3b_2$ and is again $M \rightarrow L^*$, in which the 10e involves the 2π of the trans carbonyl and some CO* 2π contribution and the $3b_2$ involves the 2π of the four cis carbonyls. The 10e and $3b_2$ orbitals both contain significant metal character (40%). These transitions have their parentage in the $2t_{2g} \rightarrow 3t_{2g}$ O_h transition, which was assigned by Bancroft et al. to the primary satellite. The third satellite corresponds to the $6e \rightarrow 8e$ transition, where the 6e is a component of the $3t_{1u}$ (98%). This satellite is primarily a $5\sigma \rightarrow 2\pi$ transition from the cis OC–Cr–CO framework to the photoionized carbonyl and, again, both orbitals have a significant metal character. The fourth peak is assigned as the $1e \rightarrow 8e$, where the 1e is an equal mixture

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