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Communications to the Editor

Addition of Alkynes to Hexaalkoxydimolybdenum $(M\equiv M)$ Compounds and Structure of μ-Ethyne-hexaisopropoxydipyridinodimolybdenum

Malcolm H. Chisholm,* John C. Huffman, and
Ian P. Rothwell

*Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405*

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Although hydrocarbon solutions of $Mo_2(OR)_6$ $(M\equiv M)$ compounds and alkynes have been noted to react, no simple addition products were isolated: only viscous gums, characteristic of polymerized alkynes were obtained.[1] We wish now to report that in the presence of pyridine, simple alkyne adducts, $Mo_2(OR)_6(py)_2(\mu\text{-}C_2R)$, can be isolated and that these compounds are involved in sequences leading to alkyne oligomerization.

The compounds $Mo_2(OR)_6(py)_2(ac)$, where R = *i*-Pr, ac = HCCH, MeCCH, and MeCCMe and R = Ne (neopentyl), ac = HCCH, were precipitated as crystalline solids when 1 equiv of the appropriate acetylene was added, by use of a calibrated vacuum manifold, to a near saturated solution of $Mo_2(OR)_6$ dissolved in hexane–pyridine solvent mixtures.[2] The crystal and molecular structure of the ethyne adduct, $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(HCCH)$, was determined[3] and an ORTEP view of the central skeleton of the molecule is shown in Figure 1. Pertinent bond distances and angles are given in Table I.

The acetylene bridges the two molybdenum atoms in a crosswise manner, which is common in dinuclear organometallic chemistry.[4] The C–C distance, 1.368 (6) Å, is longer than that in ethylene [1.337 (3) Å][5] and, indeed, is amongst the longest known for $M_2(\mu\text{-}C_2R_2)$-containing compounds.[6] The Mo–C distances, on the other hand, are short, 2.09 Å (average). These values may be compared with C–C = 1.337 (5) Å and Mo–C = 2.18 Å (average) associated with the $Mo_2(\mu\text{-}C_2H_2)$ unit in $Cp_2Mo_2(CO)_4(C_2H_2)$.[7]

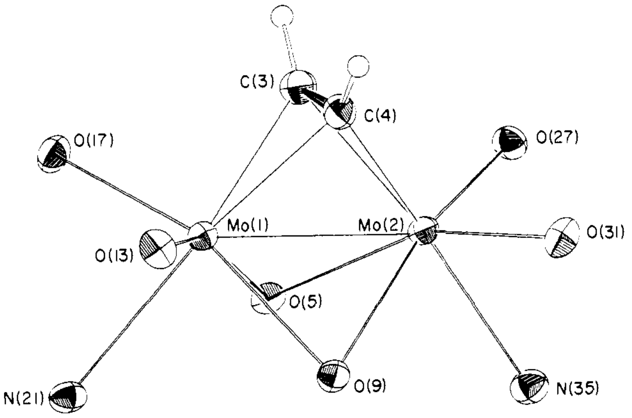

Figure 1. ORTEP view of the central skeleton of the $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(C_2H_2)$ molecule showing the atom numbering scheme used in Table I. The central skeleton of the molecule approximates to a cofacial bioctahedron if the μ_2-C_2 group is considered to occupy one position.

Table I. Bond Distances Associated with the Central $Mo_2O_6N_2C_2$ Skeleton of the $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(C_2H_2)$ Molecule

A	B	distance, Å
Mo(1)	Mo(2)	2.554 (1)
Mo(1)	O(5)	2.182 (3)
Mo(1)	O(9)	2.111 (3)
Mo(1)	O(13)	1.949 (3)
Mo(1)	O(17)	1.923 (3)
Mo(1)	N(21)	2.303 (3)
Mo(1)	C(3)	2.068 (4)
Mo(1)	C(4)	2.104 (4)
Mo(2)	O(5)	2.187 (3)
Mo(2)	O(9)	2.106 (3)
Mo(2)	O(27)	1.930 (3)
Mo(2)	O(31)	1.964 (3)
Mo(2)	N(35)	2.321 (3)
Mo(2)	C(3)	2.089 (4)
Mo(2)	C(4)	2.091 (4)
C(3)	C(4)	1.368 (6)

The NMR spectra of these compounds reveal downfield shifts of the acetylenic protons and carbons[8] and, furthermore, show that these compounds are fluxional on the NMR time scale, though low-temperature-limiting spectra are observed which are consistent with structures akin to that found in the solid state for the ethyne adduct. For example, the ^1H NMR spectrum of the propyne adduct, $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCH)$, recorded at 220 MHz and −45 °C in toluene-d_8, shows four types of isopropoxy groups in the ratio 1:1:2:2 assignable to the two different types of bridging and terminal O-*i*-Pr ligands which are expected, on the basis of solid-state structure of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(HCCH)$. Furthermore, the isopropyl methyl groups associated with the two types of terminal O-*i*-Pr ligands are diastereotopic. The two bridging O-*i*-Pr ligands, though different, do not have diastereotopic methyl groups, since these ligands are contained within the molecular plane of symmetry. At room temperature, bridge $\rightleftharpoons$ terminal OR group exchange is rapid. In the presence of added pyridine, all the acetylene adducts show rapid exchange of free and coordinated pyridine at room temperature. Both exchange processes can be frozen out on the NMR time scale, and added pyridine does not appear to influence the rate of bridge $\rightleftharpoons$ terminal OR group exchange. Nor does added pyridine displace the coordinated alkyne. Indeed, with the one exception noted below,

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[1] Chisholm, M. H.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 2321.

[2] All manipulations were carried out by using dry and oxygen-free atmospheres and solvents in a Vacuum Atmospheres Co. Dri-Lab assembly or on a vacuum manifold. The preparation of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(C_2H_2)$ outlined below is typical of the general procedure adopted for the preparations of the alkyne adducts. $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.50 g) was dissolved in degassed hexane (20 mL) and pyridine (0.4 mL) was added. The solution was frozen at liquid nitrogen temperature and, by use of a calibrated vacuum manifold, C_2H_2 (1 mmol, 1.1 equiv) was condensed into the flask. The system was sealed and allowed to warm slowly to room temperature, yielding a dark green solution. The flask was placed in the refrigerator at −15 °C. Within 24 h, dark green crystals had formed (ca. 300 mg, 60% yield based on Mo) which were collected by filtration and used in the X-ray structural determination. Anal. Calcd C, 49.3; H, 7.45; N, 3.83. Found: C, 49.1; H, 7.90; N, 3.85.

[3] X-ray data: Space group *P*21/*a* with $a = 19.183$ (5), $b = 15.677$ (4), $c = 12.165$ (3) Å; $\beta = 108.16$ (1)° at −165 °C. A total of 6166 unique intensities were collected at low temperature by using θ–2θ scan technique with a rate of 3°/min over a 2° + dispersion range and 5-s stationary background counts. Experimental and data reduction details are as previously described (Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755). The structure was solved by direct methods and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were located and refined isotropically. Final residues are $R(F) = 0.036$ and $Rw(F) = 0.037$.

[4] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th Ed.; Interscience: New York, 1980; p 1156.

[5] Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

[6] Muetterties, E. L.; Pretzer, W. R.; Thomas, M. G.; Beier, B. F.; Thorn, D. L.; Day, V. W.; Anderson, A. B. *J. Am. Chem. Soc.* **1978**, *100*, 2090 and references cited therein.

[7] Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

[8] For $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(C_2H_2)$ in toluene-d_8 at 16 °C, $\delta(C_2H_2)$ 7.26 and $\delta(C_2H_2)$ 162.7, which may be compared with the values of δ(H) 2.04 and δ(C) 71.6 for free HCCH. δ values are downfield from Me_4Si.

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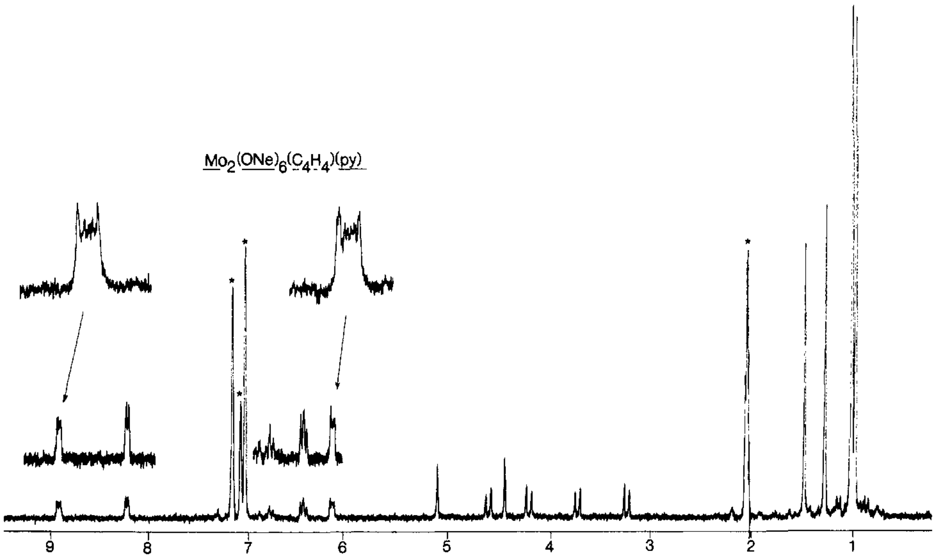

Figure 2. ^{1}H NMR spectrum of $Mo_2(ONe)_6(py)(C_4H_4)$ recorded in toluene-d_8 at 220 MHz, 16 °C. The peaks denoted by an asterisk arise from protio impurities in toluene-d_8. The methylene proton resonances of the neopentoxy ligands fall in the range δ 3.25–5.25 and appear as singlets (O2, O4) and AB quartets (O1, O3), since the former, but not the latter, are contained in a molecular plane of symmetry, see Figure 3. The signals arising from the C_4H_4 moiety appear as an AA′XX′ spectrum and are shown at scale expansion.

sealed NMR tube samples appear indefinitely stable when stored at room temperature.

Freshly prepared solutions of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCMe)$ in toluene-d_8 showed the presence of trace quantities of free dimethylacetylene, $Mo_2(O\text{-}i\text{-}Pr)_6$ and pyridine. With time, the relative concentrations of $Mo_2(O\text{-}i\text{-}Pr)_6$ and free pyridine increased at the expense of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCMe)$; a new resonance assignable to hexamethylbenzene grew in intensity. At room temperature, the disappearance of $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(MeCCMe)$ was complete in ca. 4 weeks.

It seems likely that steric factors influence the lability and reactivity of the coordinated alkyne ligand, and this is supported by the differing reactivities of the ethyne adducts of the isopropoxy and neopentoxy compounds. Both react rapidly with excess ethyne to give dark polymerized materials along with small quantities of benzene. When a tenfold excess of acetylene was condensed into NMR tubes containing the $Mo_2(OR)_6(py)_2(HCCH)$ compounds in toluene-d_8 frozen at liquid nitrogen temperature and the tubes were sealed and allowed to warm to room temperature, all the acetylene was consumed within 5–10 min. ^{1}H NMR spectra revealed the formation of benzene (ca. 5% of the added acetylene) and the starting material, when R = *i*-Pr. The neopentoxide, however, was converted to a new compound, $Mo_2(ONe)_6(py)(C_4H_4)$. This compound has been prepared as an analytically pure crystalline solid from preparative scale reactions involving the addition of acetylene (1 equiv) to hexane solutions of $Mo_2(ONe)_6(py)_2(HCCH)$. $Mo_2(ONe)_6(py)(C_4H_4)$ is not fluxional on the NMR time scale and does not show rapid exchange between free and coordinated pyridine. In the ^{1}H NMR spectrum, the coordinated C_4H_4 moiety appears as an AA′XX′ spectrum, and there are four types of alkoxy groups in the integral ratio 2:2:1:1 as shown in Figure 2. The NMR spectrum is consistent with the structure found in the solid state[9] (see Figure 3).

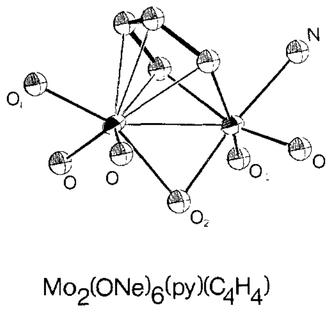

Figure 3. ORTEP view of the central $Mo_2O_6NC_4$ skeleton of the $Mo_2(OCH_2CMe_3)_4(py)(C_4H_4)$ molecule showing the four types of alkoxy ligands, two of which (O2 and O4) are contained in the molecular plane of symmetry. All atoms have been assigned artificial thermal parameters. See ref 9 for some pertinent bond distances.

The following points are worthy of consideration: (1) Acetylene addition to $Mo_2(OR)_6$ compounds may be viewed as oxidative-addition and the μ-C_2R_2 group counted as a $C_2R_2^{2-}$ ligand. The net transfer of electron density increases the Lewis acidity of the molybdenum atoms and promotes formation of alkoxy bridges and pyridine coordination. The Mo-to-Mo distance of 2.554 (1) Å may be viewed as a Mo-to-Mo double bond and compared with the distances 2.498 (1), 2.511 (1), and 2.523 (1) Å found in $Mo_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO)$,[10] MoO_2,[11] and $Mo_2(O\text{-}i\text{-}Pr)_8$,[12] respectively. (2) The central Mo_2C_2 unit differs little from those found in classical organometallic complexes, such as $Co_2(CO)_6(C_2Ph_2)$, $Ni_2(COD)_2(C_2Ph_2)$, and $Cp_2Mo_2(CO)_4(C_2H_2)$, where the metal atoms are in low oxidation states and an interesting comparison can be made with the structurally related compound, $Ta_2Cl_6(THF)_2(C_2\text{-}t\text{-}Bu_2)$, recently reported by Cotton and Hall.[13] (3) A catalytic sequence for the oligomerization of acetylenes is implicated: $M_2C_2 \rightarrow M_2C_4 \rightarrow M_2C_6 \rightarrow$ etc. This sequence has been seen before in organometallic dinuclear chemistry,[14] though in the present instance, the typical ligands of organometallic systems are absent, except for the reacting hydrocarbon fragment.

Further work is in progress.[15]

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(9) X-ray data: Space group *Pnam* with a = 23.190 (23), b = 11.369 (10), and c = 16.650 (15) Å at −163 °C. A total of 2985 unique intensities were collected to $2\theta = 45°$ at low temperature by using θ–2θ scan techniques with a rate of 3°/min over a 2° + dispersion range and 3-s stationary background counts. Intensity data dropped dramatically beyond $2\theta = 25°$ (Mo Kα radiation), with only 2025 of the data being "observed". The structure was solved by direct methods and Fourier techniques and refined to present residuals of $R(F) = 0.12$ and $Rw(F) = 0.10$. Attempts are now being made to resolve a slight disorder problem encountered with the neopentoxide ligands. Pertinent distances at this stage of the refinement are Mo–Mo = 2.685 (5), Mo–O = 1.90 (3) (av), Mo–μ_2O = 2.09 (3) (av), Mo–N = 2.17 (3), Mo–μ^1C = 2.11 (3), Mo–μ^4C = 2.37 (3) Å (av).

(10) Chisholm, M. H.; Cotton, F. A.; Kelly, R. L.; Extine, M. W. *J. Am. Chem. Soc.* **1978**, *100*, 2256; **1979**, *101*, 7645.

(11) Brandt, B. G.; Skapski, A. G. *Acta Chem. Scand.* **1967**, *21*, 661.

(12) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 2944.

(13) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.

(14) (a) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221. (b) Slater, S.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 946.

(15) We thank the Department of Energy, Office of Basic Research, and the Wrubel Computing Center for financial support. M.H.C. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant, 1979–1984.