

# Metal Alkoxides: Models for Metal Oxides. 2.<sup>1</sup> Addition of Ethyne, Propyne, and 2-Butyne to Mo<sub>2</sub>(OR)<sub>6</sub> (M≡M) Compounds (R = *t*-Bu, *i*-Pr, and Ne). Characterization of μ-Alkyne and μ-C<sub>4</sub>H<sub>4</sub> Adducts and an Evaluation of Their Role in Alkyne Oligomerization Reactions

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

Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405. Received October 21, 1981

**Abstract:** Hydrocarbon solutions of Mo<sub>2</sub>(OR)<sub>6</sub> (M≡M) compounds, where R = *t*-Bu, *i*-Pr, and Ne (Ne = CH<sub>2</sub>CMe<sub>3</sub>), react rapidly with the alkynes C<sub>2</sub>H<sub>2</sub>, MeC<sub>3</sub>H, and MeC<sub>2</sub>Me. In the presence of pyridine, μ-alkyne adducts Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub>(μ-RC<sub>2</sub>R'), where R = R' = H, D, Me and R = Me, R' = H, and Mo<sub>2</sub>(ONE)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>) have been isolated and characterized. A single-crystal X-ray diffraction study shows that acetylene in Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>) bridges the two molybdenum atoms in a crosswise manner. In addition, there is a pair of alkoxy bridging ligands. The central Mo<sub>2</sub>O<sub>6</sub>N<sub>2</sub>(μ-C<sub>2</sub>) skeleton may be viewed as a confacial bioctahedron. Pertinent bond distances are Mo-Mo = 2.554 (1) Å, Mo-O (terminal) = 1.94 Å (averaged), Mo-O (bridging) = 2.14 Å (averaged), Mo-N = 2.31 Å (averaged), Mo-C = 2.09 Å (averaged), and C-C = 1.368 (6) Å. The pyridine ligands are trans to the μ-C<sub>2</sub>H<sub>2</sub> ligands. <sup>1</sup>H NMR studies show that all these molecules are fluxional: bridge ⇌ terminal OR group exchange and exchange between free and coordinated pyridine are rapid at room temperature, but exchange between free and coordinated alkyne is not. Low-temperature limiting <sup>1</sup>H NMR spectra are attained at ca. -40 °C at 220 MHz and are consistent with those expected on the basis of the solid-state structure of Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>). Addition of 1 equiv of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub> to Mo<sub>2</sub>(ONE)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>) leads to Mo<sub>2</sub>(ONE)<sub>6</sub>(μ-X)(py) compounds where X = C<sub>4</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>2</sub>D<sub>2</sub>, respectively. The bridging C<sub>4</sub> ligand is akin to that seen in dinuclear metal carbonyl chemistry and commonly called a "flyover" bridge. The <sup>1</sup>H NMR spectrum of the μ-C<sub>4</sub>H<sub>2</sub>D<sub>2</sub>-containing compound reveals that the Mo-C<sub>4</sub> metallacycle is formed by the direct coupling of two acetylenes without subsequent or concomitant scrambling of C-H/C-D groups. A single-crystal diffraction study reveals that each molybdenum atom is in a pseudooctahedral geometry and both metal atoms share a common face formed by the μ-C<sub>4</sub>H<sub>4</sub> ligand and one bridging ONe ligand. One molybdenum atom is coordinated to two terminal OR groups and forms two Mo-C η<sup>1</sup> bonds to the μ-C<sub>4</sub>H<sub>4</sub> moiety, while the other molybdenum atom has three terminal OR ligands and is π bonded (η<sup>4</sup>) to the μ-C<sub>4</sub>H<sub>4</sub> ligand. <sup>1</sup>H NMR studies reveal that this asymmetry is preserved in solution and the molecule is not fluxional on the NMR time scale at temperatures below 70 °C; above this temperature, alkoxy group scrambling is observed. By <sup>1</sup>H NMR studies, the aforementioned μ-C<sub>2</sub>R<sub>2</sub> and μ-C<sub>4</sub>H<sub>4</sub> compounds have been shown to be intermediates in alkyne cyclotrimerization reactions. These findings are compared with well-established organometallic compounds and reaction pathways. Crystal data for Mo<sub>2</sub>(O-*i*-Pr)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>): space group = P2<sub>1</sub>/a with a = 19.183 (5) Å, b = 15.677 (4) Å, c = 12.165 (3) Å, β = 108.16 (1)°, and Z = 4; for Mo<sub>2</sub>(ONE)<sub>6</sub>(py)<sub>2</sub>(μ-C<sub>4</sub>H<sub>4</sub>): space group = Pnam with a = 23.19 (2) Å, b = 11.37 (1) Å, c = 16.56 (2) Å, and Z = 4.

In the previous paper<sup>1</sup> we drew attention to the structural similarities in the compounds [Ti(OR)<sub>4</sub>]<sub>2</sub><sup>2</sup> and W<sub>4</sub>(OR)<sub>16</sub>,<sup>3</sup> where R = Me and Et, Mo<sub>4</sub>O<sub>8</sub>(O-*i*-Pr)<sub>4</sub>(py)<sub>4</sub>, Ag<sub>8</sub>W<sub>4</sub>O<sub>16</sub>,<sup>4</sup> and Ba<sub>1.13</sub>-Mo<sub>8</sub>O<sub>16</sub>.<sup>5</sup> All these compounds share a common M<sub>4</sub>X<sub>16</sub> unit in which the metal atoms attain an octahedral geometry through the agency of oxygen bridges (μ<sub>2</sub> and μ<sub>3</sub>). This unit readily accommodates 0, 4, 8, and 10 electrons into metal-metal bonds that systematically change M-M distances in the centrosymmetric M<sub>4</sub> frame.<sup>6</sup> The similarity of structures found in metal alkoxide and metal oxide chemistry was first generally recognized several years ago after Bradley proposed a structural theory for metal alkoxide polymers<sup>7</sup> and metal oxide-alkoxide polymers.<sup>8,9</sup> Our interest in this area has been stimulated by the notion that other similarities in the chemistry of metal alkoxides and oxides might exist. Specifically, with respect to reactivity, might certain metal alkoxides act as hydrocarbon-soluble catalysts for reactions

presently known for heterogeneous metal oxide systems? Catalytic processes involving metal oxides are particularly important in the petrochemical industry. Presumably, metal-carbon and metal-hydrogen bonds are involved in most of these reactions, and one might wonder how the metal oxide environment influences the reactivity of these bonds. In contrast to the ligands commonly used in organometallic chemistry (e.g., carbonyl, phosphines, cyclopentadienes, arenes, alkenes, etc.), which are π acceptors, oxo and alkoxy ligands are strong π donors and promote metal-metal bonding when the d<sup>n</sup> configuration permits. Both of these factors could be important in organic transformations at metal oxide surfaces, which must surely provide very different environments from those commonly found in organometallic chemistry.

In the chemistry of molybdenum and tungsten, the threshold for metal-metal bonding occurs in the oxidation state 5+ when there are oxo<sup>10</sup> or alkoxy bridges.<sup>11</sup> In oxidation state 4+, there are M≡M bonds in MoO<sub>2</sub><sup>12</sup> and Mo<sub>2</sub>(O-*i*-Pr)<sub>8</sub><sup>13</sup> and Mo-Mo single bonds in Zn<sub>2</sub>Mo<sub>3</sub>O<sub>8</sub>,<sup>14</sup> Mo<sub>3</sub>O(OR)<sub>10</sub><sup>15</sup> (R = *i*-Pr and Ne), and dozens of other triangulo M<sub>3</sub>-containing compounds.<sup>16</sup> In

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the lower oxidation states of 3+ and 2+, metal-metal bonding may be in the form of discrete multiple bonds, as in  $M\equiv M$ <sup>17,18</sup> and  $M^4-M$ -containing compounds,<sup>19,20</sup> or may be delocalized in cluster molecular orbitals as in  $M_6X_8^{4+}$ -containing compounds of which  $Na_2Mo_6(OMe)_{14}$  is a member.<sup>21</sup> In all of these compounds, the metal-metal bonds provide a reservoir of electrons that are potentially available for oxidative-addition reactions. The microscopic reverse, reductive elimination, could proceed with the return of electrons to metal-metal bonding molecular orbitals. It certainly not difficult to visualize how metal-metal-bonded compounds could be incorporated into catalytic cycles that parallel those so well-known for mononuclear complexes wherein square-planar  $d^8$  and octahedral  $d^6$  complexes are interconverted.<sup>22</sup>

Presently, rather little is known about the role of strongly  $\pi$ -donating ligands in organometallic chemistry. It is, of course, well-known that they decrease  $\Delta_0$  values in octahedral complexes by raising the energy of the metal  $t_{2g}$  d orbitals,<sup>23</sup> and furthermore,  $\pi$  donation can greatly influence the rate of substitution as, for example, is seen in the base hydrolysis of  $Co^{III}$ -amine complexes.<sup>24</sup> Oxo and alkoxy ligands can also act as terminal and bridging ligands ( $\mu_2$  and  $\mu_3$ ) and can thus accommodate a variety of possible coordination geometries and fluxional processes.

Our recent characterization of  $Mo(O-t-Bu)_2(py)_2(CO)_2$ <sup>25</sup> and  $Mo(O-i-Pr)_2(bpy)_2$ <sup>26</sup> is illustrative of how the  $\pi$ -donor properties of RO ligands can influence the ground states of other ligands. The former compound has anomalously low  $\nu_{CO}$  values, 1906 and 1776  $cm^{-1}$ , for a *cis*-(CO)<sub>2</sub>Mo<sup>2+</sup> compound,<sup>27</sup> and in the latter, the 2,2'-bipyridyl ligands are partially reduced. Both of these observations reflect the fact that the RO-Mo  $\pi$  bonding raises the energy of the  $t_{2g}$  orbitals and thus enhances backbonding to CO  $\pi^*$  and bpy  $\pi^*$  orbitals.

With these general considerations in mind, we decided to investigate the reactions of small alkynes ( $HC\equiv CH$ ,  $MeC\equiv CH$ , and  $MeC\equiv CMe$ ) with  $Mo_2(OR)_6$  ( $M\equiv M$ ) compounds.<sup>28</sup> Here, a central  $Mo_2^{6+}$  unit is surrounded by six oxygen donors in a distorted octahedral ( $D_{3d}$ ) environment. Access to the metal atoms can be controlled by varying the steric properties of R, and the adducts  $Mo_2(OSiMe_3)_6(HNMe_2)_2$ ,<sup>29</sup>  $Mo_2(O-i-Pr)_6(py)_2$ ,<sup>30</sup> and  $Mo_2(ONe)_6(py)_2$ <sup>30</sup> have been structurally characterized. Addition of alkynes to  $Cp_2Mo_2(CO)_4$  ( $M\equiv M$ ) to give  $Cp_2Mo_2(CO)_4(RC_2R')$  ( $M-M$ ) compounds is well-known.<sup>31,32</sup> Furthermore in these or related  $Mo_2^{6+}$ -containing compounds, stepwise transformations in M-M bond order from three to four<sup>33</sup> and from three to two to one<sup>11</sup> have been achieved by reductive-elimination

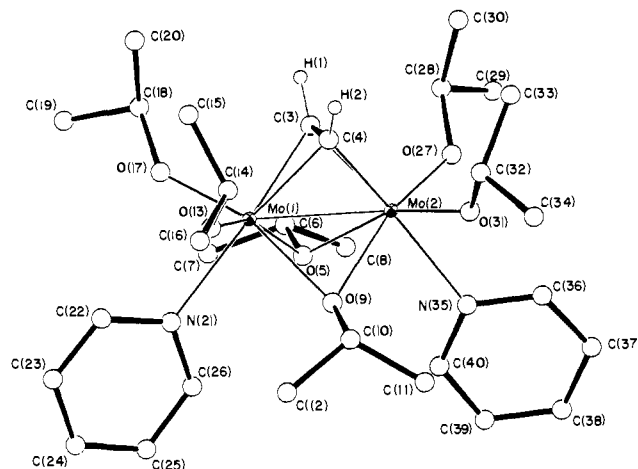


Figure 1. Ball-and-stick drawing of the  $Mo_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$  molecule giving the atom numbering scheme used in the tables.

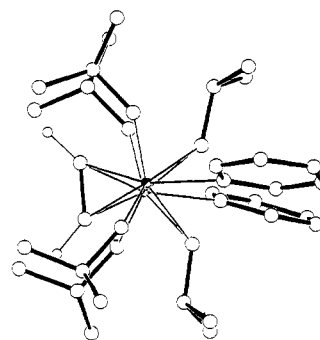


Figure 2. Ball-and-stick drawing of the  $Mo_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$  molecule viewed along the Mo-Mo axis emphasizing the pseudo-octahedral geometry about each molybdenum atom and the similarity with the confacial bioctahedral geometries of the  $M_2Cl_5^{3-}$  ions ( $M = Cr, Mo,$  and  $W$ ).

and oxidative-addition reactions. A preliminary report of some of this work has appeared.<sup>34</sup>

## Results and Discussion

**Synthesis of  $Mo_2(OR)_6(py)_2(\mu-RCCR')$  Compounds.** Hydrocarbon solutions of  $Mo_2(OR)_6$  ( $M\equiv M$ ) compounds were previously noted to react rapidly with alkynes at room temperature, but simple addition products were not isolated.<sup>35</sup> In an attempt to moderate the reaction, we carried out the slow addition of 1 equiv of the alkyne ( $HCCCH$ ,  $MeCCH$ , and  $MeCCMe$ ), by using a calibrated vacuum manifold, to a hexane solution of  $Mo_2(OR)_6$  compounds (ca. 0.1 mmol in hexane, 20 mL) cooled at  $-78^\circ C$  in the presence of pyridine (ca. 1 mL). The solutions were warmed to ca.  $-20^\circ C$ , whereupon the alkyne adducts  $Mo_2(OR)_6(py)_2(\mu-R'C'CR'')$ ,  $R = i-Pr$  and  $Ne$ ,  $R' = R'' = H$ ,  $R' = Me$ ,  $R'' = H$  or  $Me$ , crystallized from solution. Elemental analyses and other characterization data for the new compounds are given in the Experimental Section. The new compounds are very soluble in benzene and toluene but less soluble in hexane and pentane and may readily be recrystallized from hexane solutions. The compounds are air-sensitive and must be stored and handled in dry and oxygen-free atmospheres and solvents.

It should be noted that the above synthetic procedure does not allow the isolation of  $Mo_2(O-t-Bu)_6(py)_2(HCCH)$ . This, we believe, results from steric factors. In related reactions involving  $Mo_2(OR)_6$  compounds with CO, it has been possible to isolate  $Mo_2(OR)_6(py)_2(\mu-CO)$  compounds where  $R = i-Pr$  and  $Ne$ ,<sup>36</sup>

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for the  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  Molecule<sup>a</sup>

atom	x	y	z	$B_{\text{iso}}^b$
Mo(1)	3292.2 (2)	2285.0 (2)	3192.4 (3)	9
Mo(2)	3104.6 (2)	3295.3 (2)	1477.6 (3)	9
C(3)	2800 (2)	2015 (3)	1459 (3)	13
C(4)	2322 (2)	2501 (3)	1821 (3)	12
O(5)	4128 (1)	2647 (2)	2407 (2)	11
C(6)	4494 (2)	2048 (3)	1887 (4)	14
C(7)	5038 (3)	1530 (3)	2824 (4)	20
C(8)	4882 (3)	2525 (3)	1160 (4)	20
O(9)	3474 (1)	3615 (2)	3247 (2)	12
C(10)	3158 (3)	4246 (3)	3818 (4)	15
C(11)	3301 (3)	5129 (3)	3422 (4)	22
C(12)	3483 (3)	4166 (3)	5119 (4)	18
O(13)	2716 (1)	2357 (2)	4255 (2)	13
C(14)	1954 (2)	2450 (3)	4104 (4)	12
C(15)	1570 (3)	1599 (3)	3780 (4)	18
C(16)	1884 (3)	2783 (4)	5240 (4)	21
O(17)	3490 (2)	1087 (2)	3454 (2)	14
C(18)	3427 (2)	323 (3)	2803 (4)	16
C(19)	3966 (3)	-321 (3)	3518 (5)	25
C(20)	2646 (3)	9987 (3)	2489 (4)	20
N(21)	4219 (2)	2309 (2)	4934 (3)	12
C(22)	4156 (2)	1809 (3)	5795 (4)	14
C(23)	4656 (2)	1830 (3)	6889 (4)	19
C(24)	5239 (3)	2377 (3)	7117 (4)	20
C(25)	5318 (2)	2882 (3)	6236 (4)	19
C(26)	4801 (2)	2827 (3)	5154 (4)	16
O(27)	3112 (1)	3167 (2)	-97 (2)	12
C(28)	3023 (2)	2475 (3)	-881 (4)	14
C(29)	3398 (3)	2704 (3)	-1776 (4)	20
C(30)	2213 (3)	2298 (3)	-1465 (4)	17
O(31)	2364 (2)	4206 (2)	1104 (2)	15
C(32)	1610 (2)	4240 (3)	1007 (4)	17
C(33)	1158 (3)	3891 (4)	9845 (4)	24
C(34)	1408 (3)	5155 (3)	1154 (7)	35
N(35)	3850 (2)	4428 (2)	1333 (3)	14
C(36)	1592 (2)	4993 (3)	474 (4)	17
C(37)	4021 (3)	5655 (3)	285 (4)	22
C(38)	4737 (3)	5729 (3)	1001 (4)	24
C(39)	5000 (3)	5156 (3)	1892 (4)	22
C(40)	4538 (2)	4514 (3)	2027 (4)	17

<sup>a</sup> Fractional coordinates are  $\times 10^4$  for non-hydrogen atoms.  $B_{\text{iso}}$  values are  $\times 10$ . <sup>b</sup> Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

whereas for  $R = t\text{-Bu}$ , only the extremely reactive compound  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  has been isolated.<sup>37</sup> The latter compound is labile in solution toward both loss of CO and attack by CO, and it is likely that a related compound,  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-C}_2\text{R}_2)$ , would be similarly reactive.

**Synthesis of  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ .** Addition of a further equivalent of  $\text{C}_2\text{H}_2$  to a hexane solution of  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  or the direct addition of 2 or more equiv of  $\text{C}_2\text{H}_2$  to  $\text{Mo}_2(\text{ONE})_6(\text{py})_2$  in hexane yields  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  in essentially quantitative yield. This purple crystalline compound is appreciably less soluble in hexane and pentane than in benzene and toluene. Characterization data are given in the Experimental Section.

Addition of 2 or more equiv of propyne to  $\text{Mo}_2(\text{ONE})_6(\text{py})_2$  results in the formation of products that, by <sup>1</sup>H NMR spectroscopy, may be reasonably assigned to the isomers of  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{Me}_2\text{H}_2)(\text{py})$  resulting from the three possible C-C couplings of the two MeCCH units in a  $\text{Mo}_2$  flyover compound. At this time no attempt has been made to separate these. We have restricted our attention to the  $\mu\text{-C}_4\text{H}_4$  compound and its reactivity.

**Solid-State Structure of  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ .** Fractional coordinates and isotropic thermal parameters are given in Table I. Anisotropic thermal parameters are available in the

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Table II. Bond Distances (Å) for the  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  Molecule

A	B	distance	A	B	distance
Mo(1)	Mo(2)	2.554 (1)	N(35)	C(36)	1.342 (6)
Mo(1)	O(5)	2.182 (3)	N(35)	C(40)	1.333 (5)
Mo(1)	O(9)	2.111 (3)	C(3)	C(4)	1.368 (6)
Mo(1)	O(13)	1.949 (3)	C(6)	C(7)	1.518 (6)
Mo(1)	O(17)	1.923 (3)	C(6)	C(8)	1.518 (6)
Mo(1)	N(21)	2.303 (3)	C(10)	C(11)	1.518 (6)
Mo(1)	C(3)	2.068 (4)	C(10)	C(12)	1.515 (6)
Mo(1)	C(4)	2.104 (4)	C(14)	C(15)	1.516 (6)
Mo(2)	O(5)	2.187 (3)	C(14)	C(16)	1.522 (6)
Mo(2)	O(9)	2.106 (3)	C(18)	C(19)	1.512 (6)
Mo(2)	O(27)	1.930 (3)	C(18)	C(20)	1.520 (6)
Mo(2)	O(31)	1.964 (3)	C(22)	C(23)	1.376 (6)
Mo(2)	N(35)	2.321 (3)	C(23)	C(24)	1.369 (7)
Mo(2)	C(3)	2.089 (4)	C(24)	C(25)	1.377 (7)
Mo(2)	C(4)	2.091 (4)	C(25)	C(26)	1.382 (6)
O(5)	C(6)	1.433 (5)	C(28)	C(29)	1.524 (6)
O(9)	C(10)	1.447 (5)	C(28)	C(30)	1.518 (6)
O(13)	C(14)	1.422 (5)	C(32)	C(33)	1.512 (7)
O(17)	C(18)	1.420 (5)	C(32)	C(34)	1.510 (7)
O(27)	C(28)	1.420 (5)	C(36)	C(37)	1.386 (6)
O(31)	C(32)	1.415 (5)	C(37)	C(38)	1.383 (7)
N(21)	C(22)	1.344 (5)	C(38)	C(39)	1.376 (7)
N(21)	C(26)	1.338 (5)	C(39)	C(40)	1.385 (6)

supplementary material. Bond distances and pertinent bond angles are given in Tables II and III, respectively. An ORTEP view of the molecule, giving the atom numbering scheme used in the tables, is shown in Figure 1 and a view of the molecule looking down the Mo-Mo axis is shown in Figure 2.

The molecule has virtual  $C_{2v}$  symmetry. Each molybdenum can be considered to attain pseudooctahedral coordination if the  $\mu\text{-C}_2\text{H}_2$  ligand is counted as a monodentate ligand. The two octahedral units are joined by a common face involving a pair of RO bridges and the  $\text{C}_2\text{H}_2$  moiety. An analogy with the confacial bioctahedral structures of the  $\text{M}_2\text{Cl}_3^{3-}$  ions ( $M = \text{Cr}, \text{Mo}, \text{W}$ )<sup>38</sup> can be seen, and this point is emphasized in the view of the molecule shown in Figure 2.

The crosswise bridging mode of the  $\text{C}_2\text{H}_2$  group is common in dinuclear chemistry, and a comparison of the internuclear distances associated with the central pseudotetrahedral  $\text{M}_2\text{C}_2$  units in previously reported organometallic compounds is given in Table IV. The C-C distance, 1.368 (6) Å, is longer than that in ethylene (1.337 (3) Å)<sup>45</sup> and, indeed, is among the longest known in  $\text{M}_2(\mu\text{-C}_2\text{R}_2)$ -containing compounds of this type. The Mo-C distances on the other hand are short, 2.09 Å (averaged). These distances may be compared with C-C = 1.337 (5) Å and Mo-C = 2.18 Å (averaged) in  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$ .<sup>31</sup> Thus, despite the high formal oxidation state associated with the  $(\text{Mo}=\text{Mo})^{6+}$  unit, the molybdenum atoms act as a source of electrons and the bridging  $\text{C}_2\text{H}_2$  moiety may be counted (considered) as a  $\text{C}_2\text{H}_2^{2-}$  ligand. The addition of the alkyne may then be viewed as an oxidative addition to the Mo=Mo bond. The Mo-Mo distance of 2.554 (1) Å may be viewed as a double bond ( $d^2-d^2$ ) and compared with the distances 2.498 (1), 2.511 (1), and 2.523 (1) Å found in  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$ ,<sup>37</sup>  $\text{MoO}_2$ ,<sup>12</sup> and  $\text{Mo}_2(\text{O}-i\text{-Pr})_8$ ,<sup>13</sup> respectively, all of which for reasons previously given can be considered as Mo=Mo-containing compounds.

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Table III. Pertinent Bond Angles, in Degrees, for the  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  Molecule

A	B	C	angle	A	B	C	angle
Mo(2)	Mo(1)	O(5)	54.3 (1)	O(5)	Mo(2)	C(3)	76.2 (1)
Mo(2)	Mo(1)	O(9)	52.6 (1)	O(5)	Mo(2)	C(4)	101.8 (1)
Mo(2)	Mo(1)	O(13)	122.7 (1)	O(9)	Mo(2)	O(27)	159.2 (1)
Mo(2)	Mo(1)	O(17)	135.3 (1)	O(9)	Mo(2)	O(31)	93.0 (1)
Mo(2)	Mo(1)	N(21)	127.8 (1)	O(9)	Mo(2)	N(35)	82.9 (1)
Mo(2)	Mo(1)	C(3)	52.5 (1)	O(9)	Mo(2)	C(3)	104.1 (1)
Mo(2)	Mo(1)	C(4)	52.3 (1)	O(9)	Mo(2)	C(4)	88.4 (1)
O(5)	Mo(1)	O(9)	67.7 (1)	O(27)	Mo(2)	O(31)	94.3 (1)
O(5)	Mo(1)	O(13)	157.2 (1)	O(27)	Mo(2)	N(35)	79.0 (1)
O(5)	Mo(1)	O(17)	101.1 (1)	O(27)	Mo(2)	C(3)	88.7 (1)
O(5)	Mo(1)	N(21)	86.4 (1)	O(27)	Mo(2)	C(4)	111.4 (1)
O(5)	Mo(1)	C(3)	76.7 (1)	O(31)	Mo(2)	N(35)	81.1 (1)
O(5)	Mo(1)	C(4)	101.6 (1)	O(31)	Mo(2)	C(3)	121.1 (1)
O(9)	Mo(1)	O(13)	92.5 (1)	O(31)	Mo(2)	C(4)	88.1 (1)
O(9)	Mo(1)	O(17)	159.5 (1)	N(35)	Mo(2)	C(3)	155.7 (1)
O(9)	Mo(1)	N(21)	83.3 (1)	N(35)	Mo(2)	C(4)	165.6 (1)
O(9)	Mo(1)	C(3)	104.6 (1)	C(3)	Mo(2)	C(4)	38.2 (2)
O(9)	Mo(1)	C(4)	87.9 (1)	Mo(1)	O(5)	Mo(2)	71.5 (1)
O(13)	Mo(1)	O(17)	94.1 (1)	Mo(1)	O(5)	C(6)	123.5 (2)
O(13)	Mo(1)	N(21)	79.9 (1)	Mo(2)	O(5)	C(6)	124.2 (2)
O(13)	Mo(1)	C(3)	121.0 (1)	Mo(1)	O(9)	Mo(2)	74.5 (1)
O(13)	Mo(1)	C(4)	88.4 (1)	Mo(1)	O(9)	C(10)	126.9 (2)
O(17)	Mo(1)	N(21)	78.9 (1)	Mo(2)	O(9)	C(10)	126.5 (2)
O(17)	Mo(1)	C(3)	88.4 (1)	Mo(1)	O(13)	C(14)	133.9 (2)
O(17)	Mo(1)	C(4)	111.6 (1)	Mo(1)	O(17)	C(18)	138.9 (3)
N(21)	Mo(1)	C(3)	156.6 (1)	Mo(2)	O(27)	C(28)	135.2 (3)
N(21)	Mo(1)	C(4)	164.9 (1)	Mo(2)	O(31)	C(32)	133.9 (3)
C(3)	Mo(1)	C(4)	38.3 (2)	Mo(1)	N(21)	C(22)	118.5 (3)
Mo(1)	Mo(2)	O(5)	54.1 (1)	Mo(1)	N(21)	C(26)	123.4 (3)
Mo(1)	Mo(2)	O(9)	52.8 (1)	C(22)	N(21)	C(26)	118.0 (4)
Mo(1)	Mo(2)	O(27)	134.7 (1)	Mo(2)	N(35)	C(36)	118.5 (3)
Mo(1)	Mo(2)	O(31)	123.2 (1)	Mo(2)	N(35)	C(40)	122.8 (3)
Mo(1)	Mo(2)	N(35)	127.1 (1)	C(36)	N(35)	C(40)	118.6 (4)
Mo(1)	Mo(2)	C(3)	51.7 (1)	Mo(1)	C(3)	Mo(2)	75.8 (1)
Mo(1)	Mo(2)	C(4)	52.7 (1)	Mo(1)	C(3)	C(4)	72.3 (2)
O(5)	Mo(2)	O(9)	67.7 (1)	Mo(2)	C(3)	C(4)	71.0 (2)
O(5)	Mo(2)	O(27)	100.5 (1)	Mo(1)	C(4)	Mo(2)	75.0 (1)
O(5)	Mo(2)	O(31)	157.7 (1)	Mo(1)	C(4)	C(3)	69.5 (2)
O(5)	Mo(2)	N(35)	85.4 (1)	Mo(2)	C(4)	C(3)	70.8 (2)

Table IV. Internuclear Distances (Å) Associated with the Central Pseudotetrahedral  $\text{M}_2\text{C}_2$  Unit in Some Dinuclear Metal Acetylene Complexes

complex <sup>a</sup>	M-M	M-C	C-C	ref
$\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2$ - (HCCH)	2.554 (1)	2.09 (av)	1.368 (6)	this work
$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{HCCH})$	2.980 (1)	2.18 (av)	1.337 (5)	31
$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{EtCCEt})$	2.977 (1)	2.19 (av)	1.335 (8)	31
$\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{PhCCPh})$	2.956 (1)	2.19 (av)	1.329 (6)	31
$\text{Fe}_2(\text{CO})_6(t\text{-Bu-CC-}t\text{-Bu})$	2.316 (1)	2.09 (av)	1.311 (10)	39
$\text{Co}_2(\text{CO})_6(t\text{-Bu-CC-}t\text{-Bu})$	2.463 (1)	2.00 (av)	1.335 (6)	39
$\text{Rh}_2(\text{PF}_3)_4(\text{PPh}_3)_2$ - (PhCCPh)	2.740 (1)	2.12 (av)	1.369 (7)	40
$\text{Cp}_2\text{Ni}_2(\text{HCCH})$	2.345 (3)	1.884 (4)	1.341 (6)	41
$\text{Cp}_2\text{Ni}_2(\text{PhCCPh})$	2.329 (4)	1.89 (av)	1.35 (3)	42
$(\text{COD})_2\text{Ni}_2(\text{PhCCPh})$	2.617 (2)	1.93 (av)	1.386 (11)	43
$(\eta^5\text{-C}_5\text{Ph}_5)_2\text{Pd}_2$ - (PhCCPh)	2.639 (1)	2.05 (av)	1.33 (?)	44
$\text{Ta}_2\text{Cl}_6(\text{THF})_2$ - ( <i>t</i> -Bu-CC- <i>t</i> -Bu)	2.667 (1)	2.31 (av)	1.35 (2)	47

<sup>a</sup> py = pyridine; Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; COD = 1,5-cyclooctadiene; THF = tetrahydrofuran.

The assignment of M-M bond order is, however, somewhat arbitrary and certainly subject to debate whenever there are bridging groups present, since a mixing of metal-metal and metal-ligand (bridging) interactions is inevitable.<sup>46</sup> An alternate description of the Mo-Mo bond can be based on the view that the bridging alkyne merely acts as a four-electron donor to the dimetal center. This leaves the Mo-Mo bond order formally at three, and an interesting comparison can be made with the

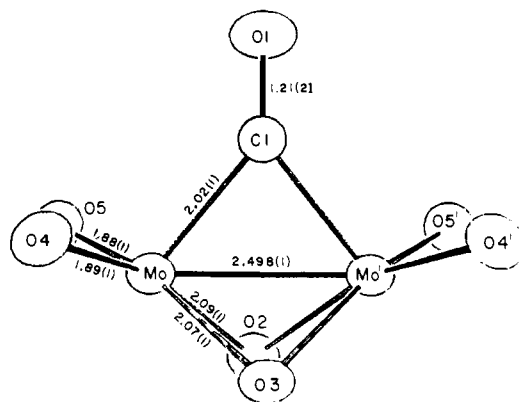


Figure 3. Central  $\text{Mo}_2\text{O}_6(\mu\text{-CO})$  skeleton of the  $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\mu\text{-CO})$  molecule showing pertinent distances for comparison with  $\text{Mo}_2(\text{O}-i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ .

structurally related compound  $\text{Ta}_2\text{Cl}_6(\text{THF})_2(\mu\text{-C}_2\text{-}t\text{-Bu}_2)$  recently reported by Cotton and Hall.<sup>47</sup> The two structures are related by the formal substitutions, Ta for Mo, Cl for O-*i*-Pr, THF for py, and *t*-BuCC-*t*-Bu for HCCH. The Ta-Ta distance of 2.677 (1) Å, which is longer than the Mo-Mo distance of 2.554 (1) Å, may be viewed as representing a Ta=Ta bond.

The Mo-O distances associated with the terminally bonded OR ligands are notably shorter than those associated with the bridging OR ligands. This is general in metal alkoxide structures, and an interesting comparison can be made with the  $\text{Mo}_2(\text{O}-i\text{-Bu})_6(\mu\text{-CO})$  structure (see Figure 3). The positions trans to the bridging

Table V. Fractional Coordinates and Isotropic Thermal Parameters for the  $\text{Mo}_2(\text{ONE})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$  Molecule<sup>a</sup>

atom	x	y	z	$B_{\text{iso}}^b$
Mo(1)	1809 (1)	1744 (3)	2500* <sup>c</sup>	22
Mo(2)	674 (1)	1255 (3)	2500*	21
C(3)	1447 (9)	475 (9)	3292 (14)	21
C(4)	1116 (11)	-489 (22)	2068 (17)	36
N(5)	2583 (12)	704 (27)	2500*	30
C(6)	2609 (17)	-533 (31)	2500*	36
C(7)	3149 (19)	-1163 (34)	2500*	43
C(8)	3607 (16)	-561 (31)	2500*	17
C(9)	3628 (14)	671 (42)	2500*	33
C(20)	3155 (10)	1323 (42)	2500*	57
O(11)	2110 (8)	2398 (14)	3498 (13)	39
C(12)	2424 (14)	1967 (24)	4102 (19)	57
C(13)	2500 (11)	2887 (22)	4838 (15)	24
C(14)	2852 (17)	3908 (33)	4488 (24)	85
C(15)	1951 (18)	3512 (42)	5120 (22)	90
C(16)	2795 (15)	2319 (30)	5559 (26)	64
O(17)	1130 (10)	2918 (20)	2500*	28
C(18)	1072 (30)	3934 (46)	2500*	273
C(19)	1241 (18)	5125 (30)	2500*	29
C(20)	1926 (21)	5024 (29)	2500*	48
C(21)	1052 (18)	5767 (44)	3219 (18)	108
O(22)	379 (9)	1791 (19)	3491 (12)	53
C(23)	390 (21)	1932 (49)	4169 (27)	140
C(24)	-61 (16)	2524 (27)	4715 (17)	50
C(25)	316 (13)	3353 (28)	5179 (23)	56
C(26)	-473 (10)	3331 (23)	4130 (16)	33
C(27)	9550 (14)	1716 (32)	5286 (27)	77
O(28)	3 (18)	231 (28)	2500*	87
C(29)	-342 (22)	-467 (38)	2500*	120
C(30)	-992 (22)	-434 (33)	2500*	46
C(31)	-1202 (14)	-1064 (21)	3219 (15)	41
C(32)	-1228 (22)	855 (41)	2500*	65

<sup>a</sup> Fractional coordinates are  $\times 10^4$  for non-hydrogen atoms and  $\times 10^3$  for hydrogen atoms.  $B_{\text{iso}}$  values are  $\times 10$ . <sup>b</sup> Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609. <sup>c</sup> Parameters marked by an asterisk were not varied.

Table VI. Bond Distances (Å) for the  $\text{Mo}_2(\text{ONE})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$  Molecule

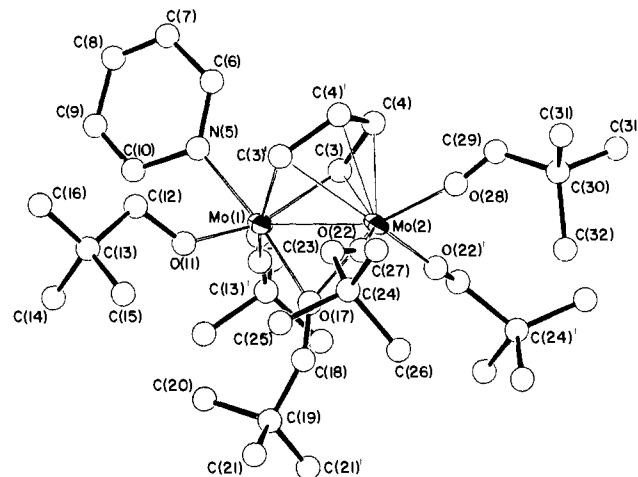
A	B	distance	A	B	distance
Mo(1)	Mo(2)	2.69 (1)	C(6)	C(7)	1.44 (5)
Mo(1)	O(11)	1.94 (2)	C(7)	C(8)	1.26 (5)
Mo(1)	O(17)	2.06 (2)	C(8)	C(9)	1.40 (5)
Mo(1)	N(5)	2.15 (3)	C(9)	C(10)	1.32 (5)
Mo(1)	C(3)	2.12 (2)	C(12)	C(13)	1.61 (4)
Mo(2)	O(17)	2.17 (2)	C(13)	C(14)	1.53 (4)
Mo(2)	O(22)	1.88 (2)	C(13)	C(15)	1.53 (4)
Mo(2)	O(28)	1.94 (4)	C(13)	C(16)	1.52 (4)
Mo(2)	C(3)	2.39 (2)	C(18)	C(19)	1.41 (6)
Mo(2)	C(4)	2.34 (2)	C(19)	C(20)	1.59 (6)
O(11)	C(12)	1.33 (3)	C(19)	C(21)	1.46 (3)
O(17)	C(18)	1.16 (5)	C(23)	C(24)	1.54 (5)
O(22)	C(23)	1.13 (4)	C(24)	C(25)	1.50 (4)
O(28)	C(29)	1.13 (5)	C(24)	C(26)	1.64 (3)
N(5)	C(6)	1.41 (4)	C(24)	C(27)	1.60 (5)
N(5)	C(10)	1.50 (5)	C(29)	C(30)	1.51 (6)
C(3)	C(4)	1.47 (3)	C(30)	C(31)	1.47 (4)
C(4)	C(4)	1.43 (6)	C(30)	C(32)	1.56 (5)

carbonyl group as vacant whereas in the  $\mu\text{-C}_2\text{H}_2$  compound the pyridine ligands are relatively weakly coordinated as evidenced by the long Mo-N bond distances, 2.31 Å (averaged). The substitution of *i*-Pr for *t*-Bu allows the isolation of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-CO})$  with Mo-N = 2.32 Å (averaged). It is thus likely that in the absence of pyridine reactive  $\text{Mo}_2(\text{OR})_6(\mu\text{-C}_2\text{R}_2)$  compounds are formed.

**Solid-State Structure of  $\text{Mo}_2(\text{ONE})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$ .** Fractional coordinates and isotropic thermal parameters are given in Table V. Anisotropic thermal parameters are available in the supplementary material. Bond distances and pertinent bond angles are given in Tables VI and VII, respectively. A view of the

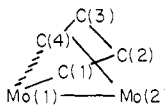
Table VII. Pertinent Bond Angles, in Degrees, for the  $\text{Mo}_2(\text{ONE})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$  Molecule

A	B	C	angle
Mo(2)	Mo(1)	O(11)	115.5 (6)
Mo(2)	Mo(1)	O(17)	52.3 (7)
Mo(2)	Mo(1)	N(5)	134.7 (8)
Mo(2)	Mo(1)	C(3)	58.2 (6)
O(11)	Mo(1)	O(11)	116.6 (11)
O(11)	Mo(1)	O(17)	91.5 (6)
O(11)	Mo(1)	N(5)	84.9 (7)
O(11)	Mo(1)	C(3)	82.9 (9)
O(17)	Mo(1)	N(5)	173.1 (11)
O(17)	Mo(1)	C(3)	98.0 (8)
N(5)	Mo(1)	C(3)	87.5 (9)
C(3)	Mo(1)	C(3)	76.3 (13)
Mo(1)	Mo(2)	O(17)	48.8 (6)
Mo(1)	Mo(2)	O(22)	106.8 (7)
Mo(1)	Mo(2)	O(28)	155.1 (9)
Mo(1)	Mo(2)	C(3)	48.9 (5)
Mo(1)	Mo(2)	C(4)	75.4 (7)
O(17)	Mo(2)	O(22)	84.0 (8)
O(17)	Mo(2)	O(28)	156.0 (10)
O(17)	Mo(2)	C(3)	87.6 (7)
O(17)	Mo(2)	C(4)	121.7 (9)
O(22)	Mo(2)	O(22)	121.6 (12)
O(22)	Mo(2)	O(28)	84.4 (8)
O(22)	Mo(2)	C(3)	150.7 (8)
O(22)	Mo(2)	C(4)	99.6 (9)
O(28)	Mo(2)	C(3)	112.2 (9)
O(28)	Mo(2)	C(4)	81.0 (11)
C(3)	Mo(2)	C(3)	66.5 (11)
C(3)	Mo(2)	C(4)	36.1 (8)
C(4)	Mo(2)	C(4)	35.5 (13)
Mo(1)	O(11)	C(12)	134.1 (16)
Mo(1)	O(17)	Mo(2)	78.9 (8)
Mo(1)	O(17)	C(18)	137.0 (39)
Mo(2)	O(17)	C(18)	144.1 (39)
Mo(2)	O(22)	C(23)	154.3 (26)
Mo(2)	O(28)	C(29)	172.1 (37)
Mo(1)	N(5)	C(6)	125.8 (24)
Mo(1)	N(5)	C(10)	118.7 (22)
C(6)	N(5)	C(10)	115.5 (29)
Mo(1)	C(3)	Mo(2)	72.9 (7)
Mo(2)	C(3)	C(4)	70.2 (14)
Mo(2)	C(4)	C(3)	73.7 (13)
Mo(2)	C(4)	C(4)	72.2 (7)

Figure 4. Ball-and-stick drawing of the  $\text{Mo}_2(\text{ONE})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$  molecule giving the atom numbering scheme used in the tables.

molecule, giving the atom numbering scheme used in the tables, is shown in Figure 4.

The molecule contains a crystallographically imposed mirror plane that contains the atoms of the pyridine ligand, the two molybdenum atoms, the oxygen atoms of the bridging ONE ligand, one terminally bonded ONE ligand, and three of the five carbon atoms of each of their respective neopentyl groups. The mirror

Table VIII. Internuclear Distances (Å) Associated with the Central  $M_2(\mu-C_4)$  Moiety in Some Flyover Compounds


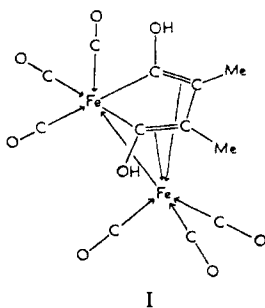
A-B	$Mo_2(O\dot{N}e)_6(py)(\mu-C_4H_4)$	$Cp_2Cr_2(\mu-C_4Ph_4)CO$	$(CO)_6Fe_2(\mu-C_4Me_2(OH)_2)$	$(CO)_6Fe_2(\mu-C_{12}H_{10})$
M(1)-M(2)	2.69 (1)	2.337 (2)	2.439 (?)	2.462 (3)
M(1)-C(1)	2.12 (2)	2.024 (7)	1.943 (?)	1.935 (13)
M(1)-C(4)	2.12 (2)	2.020 (7)	1.948 (?)	1.987 (14)
M(2)-C(1)	2.39 (2)	2.032 (7)	2.111 (?)	2.087 (14)
M(2)-C(4)	2.39 (2)	2.023 (7)	2.121 (?)	2.066 (12)
M(2)-C(2)	2.34 (2)	2.229 (7)	2.150 (?)	2.172 (12)
M(2)-C(3)	2.34 (2)	2.232 (7)	2.142 (?)	2.189 (13)
C(1)-C(2)	1.47 (3)	1.42 (1)	1.413 (?)	1.41 (2)
C(3)-C(4)	1.47 (3)	1.42 (1)	1.424 (?)	1.40 (2)
C(2)-C(3)	1.43 (6)	1.43 (1)	1.430 (?)	1.43 (2)

plane bisects the  $\mu-C_4H_4$  moiety.

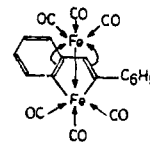
Regretably, the quality of the reflection data did not allow a very precise structural determination for this compound. Nevertheless, the structural parameters are meaningful, and the solid-state structure is consistent with the structure present in solution as deduced from  $^1H$  NMR studies.

The gross structural features of the  $Mo_2(\mu-C_4H_4)$  moiety are comparable to those previously seen in organometallic flyover compounds. A comparison with three other compounds, namely,  $(CO)_6Fe_2(\mu-C_4(OH)_2Me_2)$ ,<sup>48</sup>  $(CO)_6Fe_2(\mu-C_{12}H_{10})$ ,<sup>49</sup> and  $Cp_2Cr_2(\mu-C_4Ph_4)CO$ ,<sup>50</sup> is given in Table VIII ( $\mu-C_{12}H_{10}$  is the metallocycle derived from 1,7-cyclododecadiyne). Though other  $M_2(\mu-C_4R_4)$ -containing compounds have been structurally characterized, the three chosen for comparison with  $Mo_2(O\dot{N}e)_6(py)(\mu-C_4H_4)$  are sufficient and particularly appropriate.

The 1961 paper by Hock and Mills<sup>48</sup> is of historic significance. It provided the first structural characterization of a flyover compound isolated from the reaction between but-2-yne and "...alkaline solutions of ironhydroxycarbonyl:  $MeCCMe-H_2Fe_2(CO)_8$ ". The authors noted, "The structure exhibits a number of novel features which include (i) a four-carbon chain chelated on to one of the iron atoms with which it forms single metal-carbon bonds, (ii)  $\pi$ -bonds between this four-carbon chain and the second iron atom, (iii) the probability that one of the six  $Fe-C\equiv O$  linkages is non-linear ( $168^\circ$ )". The valence bond description of Hock and Mills is shown in I. Note the formal classification of one iron as  $Fe(2+)$ , the other as  $Fe(0)$ , and the presence of the  $Fe \rightarrow Fe$  bond.

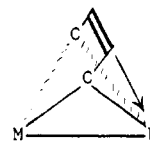


The Chin and Bau<sup>49</sup> structural characterization of  $(CO)_6Fe_2(\mu-C_{12}H_{10})$ , where  $\mu-C_{12}H_{10}$  is the metallocycle derived from 1,7-cyclododecadiyne, provides a modern-day characterization of essentially the same situation, namely, a metallocyclopentadiene  $\pi$  bonded to the other metal, despite the rather fancy nature of the cyclic ligand. A further example of the  $FeC_4-\pi-Fe$  bonding depicted in I is seen in  $(CO)_5Fe_2(PhC_2Ph^*)$ ,<sup>51</sup> where one of the phenyl rings ( $Ph^*$ ) volunteers two of its carbon atoms to form the metallocycle as shown in II.



II

By contrast, Stone et al.<sup>50</sup> suggest that the characterization of  $Cp_2Cr_2(\mu-C_4Ph_4)CO$ , which reveals C(1) and C(2) symmetrically bridging the chromium atoms with very low-field chemical shifts ( $\delta$  C(1) and C(2) = 310 relative to  $Me_4Si$ , which may be compared with  $\delta$  C(1), C(2)  $\sim$  160 in the  $Fe_2(\mu-C_4)$  compounds),<sup>52</sup> is indicative of significant bridging carbene-like character (see III). This chromium compound has, formally, a



III

$Cr\equiv Cr$  bond in compliance with the 18-electron rule, and the short  $Cr-Cr$  distance may bias the  $M-C$  distances in favor of III relative to I. Muetterties et al.<sup>53,54</sup> have recently reported the preparation of  $Cp_2Mo_2(\mu-C_4R_4)CO$  and  $Cp_2Mo_2(\mu-C_4R_4)(CO)_3$ , where  $R = Et$ . The structural comparison of the two compounds would be interesting; in the former, there should be a  $Mo\equiv Mo$  bond whereas a  $Mo-Mo$  single bond is expected in the latter.

With this brief discourse on structural properties of organometallic  $M_2(\mu-C_4R_4)$  compounds, it is easy to recognize that  $Mo_2(O\dot{N}e)_6(py)(\mu-C_4H_4)$  fits the classical description:  $Mo(1)$  is incorporated in the metallocyclopentadiene and  $Mo(2)$  is the recipient of the  $\pi$  interaction as implied by I. Each molybdenum atom is in a distorted octahedral environment if the  $\mu-C_4H_4$  ligand is considered to occupy cis sites for each molybdenum, with two  $Mo-C$   $\sigma$  bonds for  $Mo(1)$  and two  $\pi$  bonds for  $Mo(2)$ . Formally, the  $Mo_2^{6+}$  center has been oxidized to  $Mo_2^{8+}$ . If the terminal OR ligands are counted as 1- and the bridging OR ligand as 0.5-,  $Mo(1)$  is formally in oxidation state 4.5+ whereas  $Mo(2)$  is in 3.5+. This is, of course, only a formalism, but it should be noted that the pyridine nitrogen to  $Mo(1)$  distance, 2.15(3) Å, is much shorter than the  $Mo-N$  distances, 2.31 Å (averaged), found in  $Mo_2(O-i-Pr)_6(py)_2(\mu-C_2H_2)$ . Furthermore, the  $Mo-O$  distances associated with the bridging ONe ligand are notably different:  $Mo(1)-O(17) = 2.06(2)$  Å,  $Mo(2)-O(17) = 2.17(2)$  Å. Both of these observations may be rationalized in terms of oxidation of  $Mo(1)$ .

**$^1H$  NMR Studies of  $Mo_2(OR)_6(py)_2(\mu-RCCR')$  Compounds.** At +35 °C and 220 MHz the  $^1H$  NMR spectrum of  $Mo_2(O-i-$

(48) Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

(49) Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5068.

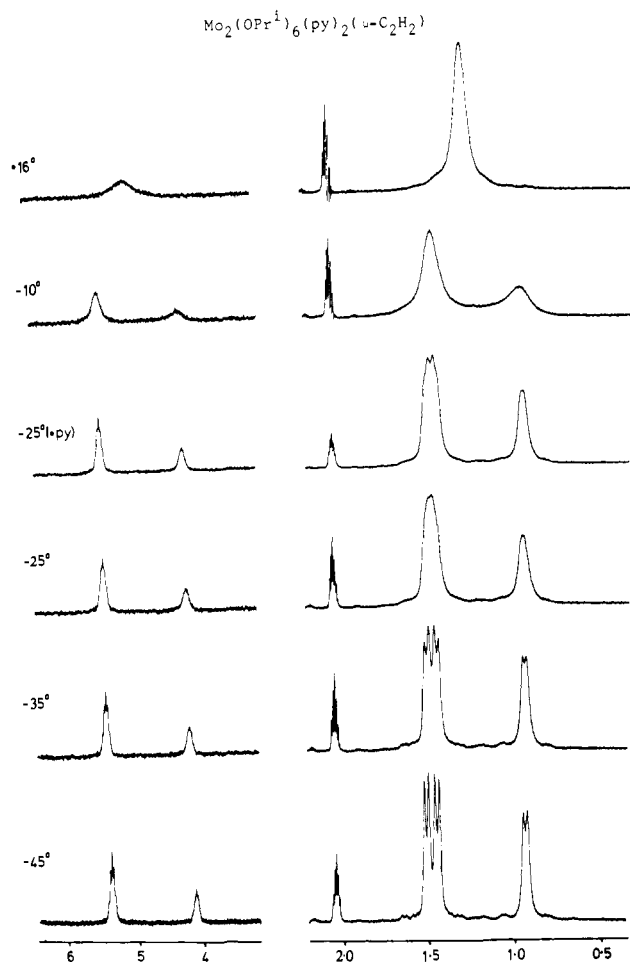
(50) Knox, S. A. R.; Stansfield, R. F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1978**, 221.

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(53) Slater, S.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 3337.

(54) Slater, S.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 946.

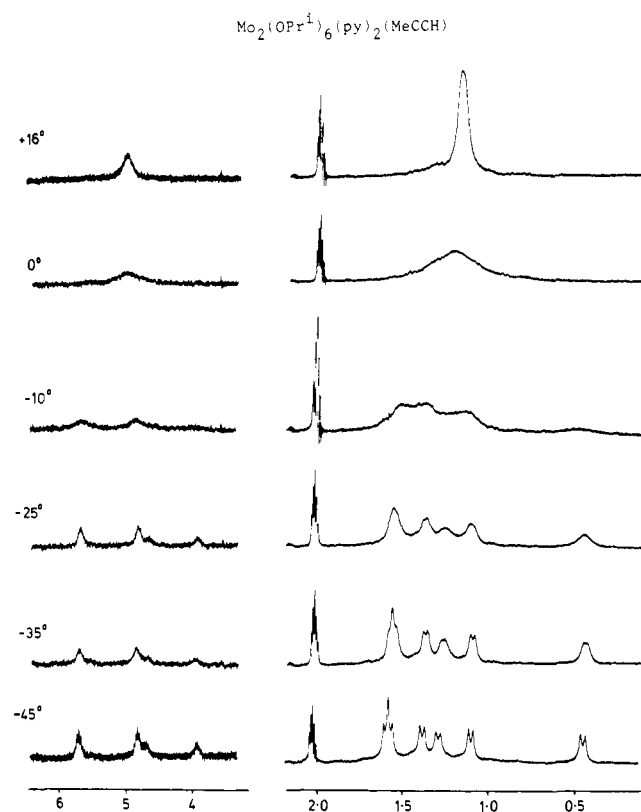


**Figure 5.**  $^1\text{H}$  NMR spectra at various temperatures recorded in toluene- $d_8$  at 220 MHz showing the isopropoxy resonances of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-HCCH})$ .

$\text{Pr})_6(\text{py})_2(\text{HCCH})$  in toluene- $d_8$  shows a septet and a doublet for the O- $i$ -Pr ligands, a singlet at 7.26 ppm (relative  $\text{Me}_4\text{Si}$ ), assignable to the ethyne protons, and resonances assignable to the pyridine ligands. After the temperature is lowered, the isopropoxy resonances initially broaden and then split. These changes with temperature are shown in Figure 5. The low-temperature limiting spectrum is entirely consistent with the solid-state structure. There are two types of O- $i$ -Pr ligands in the 2:1 ratio corresponding to terminal and bridging groups, respectively, and the former, but not the latter, contain diastereotopic methyl groups.

The  $^1\text{H}$  NMR spectra associated with the propyne adduct are even more interesting. The introduction of an unsymmetrically substituted acetylene reduces the symmetry of the molecule from  $C_{2v}$  to  $C_s$ . There are now four types of O- $i$ -Pr ligands: the terminal O- $i$ -Pr ligands are related in a pairwise manner by the mirror plane that bisects the molecule and contains the two bridging O- $i$ -Pr ligands. Though both of the bridging ligands are contained in the plane, they are different from each other because of the unsymmetrical crosswise bridge,  $\mu\text{-MeCCH}$ . The low-temperature limiting spectrum for the  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-MeCCH})$  compound (O- $i$ -Pr resonances) is shown in Figure 6. Note, as expected, that there are four methyne septets in the integral ratio 2:2:1:1 and there are six isopropylmethyl doublets. (The two at low-field overlap to yield a three-line pattern.) After the temperature is raised, these resonances broaden, collapse, and give a sharp septet and doublet above  $+35^\circ\text{C}$ .

These changes are not affected by added pyridine, though exchange between free and coordinated pyridine is rapid on the  $^1\text{H}$  NMR time scale at room temperature. This exchange is frozen out at low temperatures. These observations are all explainable in terms of Mo-py bond rupture as the rate-determining step for both pyridine exchange and O- $i$ -Pr group exchange. Previously it was shown that  $\text{Mo}_2(\text{O-}i\text{-Bu})_6(\mu\text{-CO})$  was fluxional and



**Figure 6.**  $^1\text{H}$  NMR spectra recorded at various temperatures, 220 MHz, of the isopropoxy resonances of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-MeCCH})$ . The spectrum recorded with the presence of excess pyridine (10 equiv) is also shown at  $-25^\circ\text{C}$ .

bridge-terminal OR exchange was not frozen out on the NMR time scale. The compounds  $\text{M}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-CO})$ , where  $\text{M} = \text{Mo}$  and  $\text{W}$ , which are fluxional at room temperature, are frozen out at low temperatures, however.<sup>36</sup>

Freshly prepared solutions of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCMe})$  in toluene- $d_8$ , which showed similar dynamic solution behavior on the  $^1\text{H}$  NMR time scale, showed the presence of trace quantities of free dimethylacetylene and  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$  and pyridine. With time, the relative concentrations of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$  and free pyridine increased at the expense of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCMe})$ , and a new resonance, identified as hexamethylbenzene, grew in intensity. At room temperature, the disappearance of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCMe})$  was essentially complete in 4 weeks. In addition to  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ , pyridine, and  $\text{Me}_6\text{C}_6$ , there were some unidentified O- $i$ -Pr signals, implying that some new molybdenum compound is also formed.

**$^1\text{H}$  NMR Studies on  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$ .** The  $^1\text{H}$  NMR spectrum of  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  in toluene- $d_8$  at 220 MHz,  $+16^\circ\text{C}$ , shows four types of neopentoxo ligands and is consistent with retention in solution of the structure found in the solid state. The signals of the neopentyl methylene protons appear as two AB quartets and two singlets; the latter are assignable to the bridging and terminal ONe ligands that are contained in the molecular plane of symmetry. A specific assignment of resonances for the ONe ligands is not possible. The  $^1\text{H}$  NMR spectrum of the  $\mu\text{-C}_4\text{D}_4$ - and the pyridine- $d_5$ -substituted compounds together with the spectrum of the protio compound in the region 3–8 ppm are shown in Figure 7. This allows an unequivocal assignment of the  $\mu\text{-C}_4\text{H}_4$  resonances that correspond to an AA'XX' spectrum. The spectrum is unaffected by added pyridine, although chemical exchange between free and coordinated pyridine is quite rapid (but not on the NMR time scale), as is evidenced by the fact that addition of  $\text{py-}d_5$  to a solution of the protio compound readily forms  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_4)(\text{py-}d_5)$  and free pyridine.

Upon raising the temperature, we observed little change in the  $^1\text{H}$  NMR spectrum below  $+75^\circ\text{C}$ . From  $+75$  to  $+95^\circ\text{C}$  the neopentoxo signals broaden and at  $+100^\circ\text{C}$  are approaching coalescence. At this temperature, exchange between free and

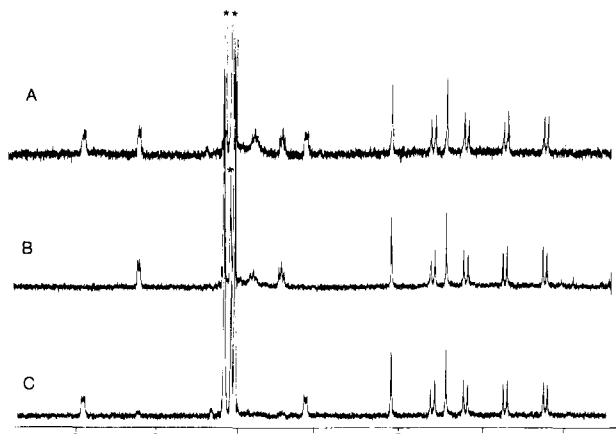


Figure 7.  $^1\text{H}$  NMR spectra recorded in toluene- $d_8$  at  $+16^\circ\text{C}$  and 220 MHz of the compounds  $\text{Mo}_2(\text{ONe})_6(\text{py})(\mu\text{-C}_4\text{H}_4)$  (A) and the  $^2\text{H}$ -labeled compounds containing  $\text{py-}d_5$  (B) and  $\mu\text{-C}_4\text{D}_4$  (C) ligands in the region  $\delta = 3\text{--}8$ .

coordinated pyridine is fast on the NMR time-scale.

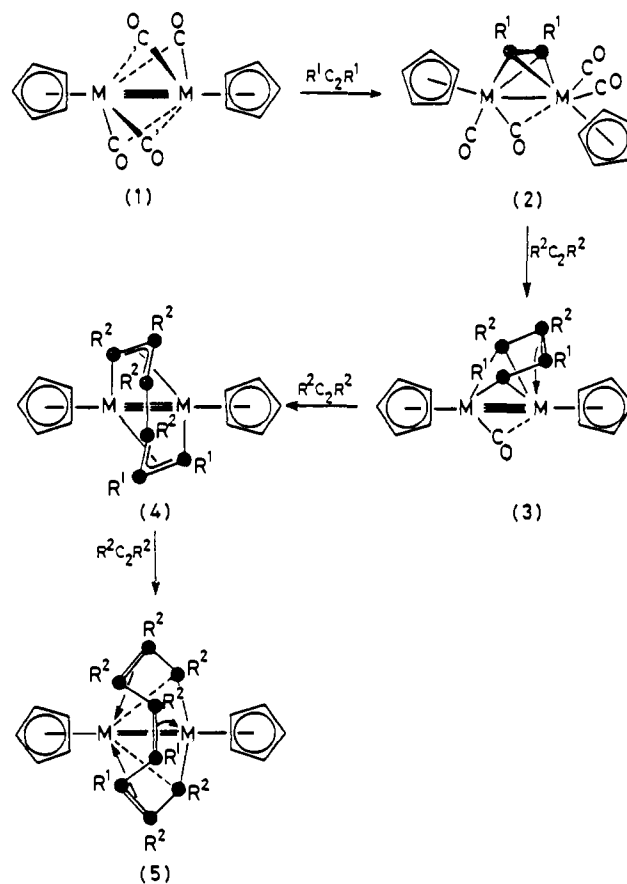
It is thus evident that the rate of alkoxy group scrambling is very different in the acetylene adducts and the flyover compound. The coalescence temperatures differ by  $100^\circ\text{C}$ , which, if one assumes the rate doubles for each  $10^\circ\text{C}$  temperature increase, implies an ca.  $2^{10}$  difference in the rate of OR group scrambling.

We believe that alkoxy group scrambling requires prior pyridine dissociation in both types of compounds and that in the flyover compound the pyridine ligand is more strongly bound. This is also indicated by the observed Mo-N bond distances, 2.15 and 2.32 Å, found in the flyover compound and acetylene adduct, respectively. This conclusion regarding Mo-py bond dissociation and OR group scrambling is also supported by some recent work using phosphine ligands.<sup>55</sup> Addition of  $\text{PMe}_2\text{Ph}$  (1 equiv) to  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  in toluene- $d_8$  gives  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{PMe}_2\text{Ph})$  and free pyridine, indicating a thermodynamic preference for the phosphine adduct. This compound is not fluxional at  $+100^\circ\text{C}$  and does not show rapid (NMR time scale) exchange between free and coordinated  $\text{PMe}_2\text{Ph}$  at this temperature.

**Alkyne Oligomerization.** As noted previously, hydrocarbon solutions of  $\text{Mo}_2(\text{OR})_6$  compounds ( $\text{R} = t\text{-Bu}$ ,  $i\text{-Pr}$ , and  $\text{Ne}$ ) react rapidly with sterically unencumbered alkynes at room temperature. The compounds appear to act as alkyne polymerization catalysts, though the detailed nature of the polymers has not yet been determined. Ethyne yields a black, metallic-looking powder, propyne yields a yellow powdery solid, and but-2-yne yields a gelatinous rubber-like material. An indication of the activity of the system is seen in the following. When  $\text{Mo}_2(\text{ONe})_6$  (50 mg, 0.07 mmol) dissolved in hexane (50 mL) was exposed to 1 atm of propyne, within 10 min 143 equiv of propyne was consumed (removed from the gas phase); in 90 minutes 331 equiv (23 mmol) of propyne had been taken up. Subsequent workup using the Katz procedure<sup>56</sup> (which involves dissolving the polymer in  $\text{CH}_2\text{Cl}_2$  followed by precipitation with MeOH and a repetition of the same) gave 0.42 g, 10.5 mmol, of yellow polymer in 46% yield based on alkyne absorbed into the system. On this scale of reaction, loss of polymer may arise from handling of small samples because of the intractable nature of the polymer that coats the wall of the flask.

It is difficult to compare the catalyst activity of  $\text{Mo}_2(\text{OR})_6$  compounds with other alkyne catalysts because few have been reported and, for those that have, the reaction conditions are dissimilar. For example, Katz and Lee<sup>56</sup> recently reported alkyne polymerization using the metal carbene complexes  $(\text{CO})_5\text{W}=\text{C}(\text{X})\text{Ph}$ , where  $\text{X} = \text{OMe}$  and  $\text{Ph}$ . The experimental conditions were 1% metal complex in neat alkyne at  $40^\circ\text{C}$ . When  $\text{X} = \text{OMe}$ , after 45 h, 44% yield of polypropyne was recovered by using the  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ -workup procedure. When  $\text{X} = \text{Ph}$ , after 22 h,

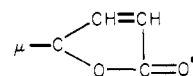
Scheme 1



75% polypropyne was recovered. Since 1% catalyst was used, the percentage polymer represents the number of turnovers of catalyst. It is thus evident that  $\text{Mo}_2(\text{ONe})_6$  dissolved in hexane (*not* neat propyne) at room temperature achieves comparable catalyst turnover numbers in shorter times and lower temperatures.

Though no simple molybdenum-containing compounds have been isolated in the absence of added pyridine or other donor ligands, it is natural to question what role, if any, compounds of the type  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  and  $\text{Mo}_2(\text{ONe})_6(\mu\text{-C}_4\text{H}_4)(\text{py})$  might play in a catalytic cycle. We have demonstrated that the pyridine ligands are labile to exchange reactions, and thus one might speculate that, in their absence, alkyne coordination and coupling reactions might be rapid.

Alkyne oligomerization about a dimetal center has been previously noted, and in 1959 the first alkyne adduct formed in reactions involving  $\text{Co}_2(\text{CO})_8$  was structurally characterized:  $\text{Co}_2(\text{CO})_6(\text{PhCCPh})$ .<sup>57</sup> In the same year, Mills and Robinson<sup>58</sup> reported the partial structure of a compound of empirical formula  $\text{Co}_2(\text{CO})_9(\text{HCCH})$ , which was shown to contain a bridging carbene ligand:



In 1961, Hubel et al.<sup>59</sup> showed that compounds formulated as flyover compounds  $\text{Co}_2(\text{CO})_4(\text{RCCR}')_3$  could, upon thermolysis or bromination, yield benzenes, and in 1964, Mills and Robinson<sup>60</sup> provided the partial structure of  $(\text{CO})_4\text{Co}_2[(t\text{-BuCCH})_2(\text{HCCH})]$ , a compound formed from the reaction between  $t\text{-BuCCH}$  and  $\text{Co}_2(\text{CO})_6(\text{HCCH})$ . Further studies on the reactions between alkynes and  $\text{Co}_2(\text{CO})_8$  by Dickson et al.<sup>61</sup> provided additional structural characterization of a similar compound,  $\text{Co}_2(\text{CO})_4(\text{C-}$

(57) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18.

(58) Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1964**, 187.

(59) Hubel, W.; Krueker, U.; Hoogzand, C. *Chem. Ber.* **1961**, *94*, 2817.

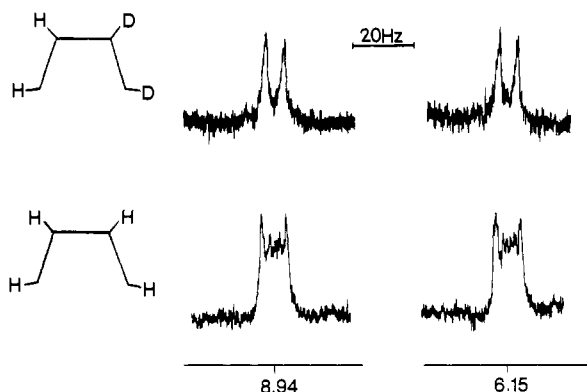
(60) Mills, O. S.; Robinson, G. *Proc. Chem. Soc., London* **1964**, 187.

(61) Dickson, R. S.; Frazer, P. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278.

(55) Chisholm, M. H.; Rothwell, I. P., results to be published.

(56) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.





**Figure 8.**  $^1\text{H}$  NMR spectrum of the  $\mu\text{-C}_4\text{H}_4\text{D}_2$  ligand formed in the reaction between  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-HCCH})$  and DCCD (1 equiv) compared to that of the  $\mu\text{-C}_4\text{H}_4$ -containing compound.

$\text{F}_3\text{CCH})_3$ . More recently, Knox, Stone, and co-workers<sup>50</sup> established a stepwise sequence of alkyne additions involving  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M}=\text{M}$ ) compounds, where  $\text{M} = \text{Cr}$  and  $\text{Mo}$ , and structurally characterized the compound  $\text{Cp}_2\text{Mo}_2\text{-}[(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})(\text{HC}_2\text{H})(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})_2]$ , which has a four-acetylene linkage wrapped around the dimetal center; see Scheme I. The reaction conditions necessary to induce alkyne oligomerization about these dimetal centers require heat or photolysis, since carbonyl dissociation must occur prior to acetylene addition. The reactions involving  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{RCCR})$  and additional acetylenes have been shown to require temperatures in excess of  $100^\circ\text{C}$  to initiate significant thermal expulsion of  $\text{CO}$ .<sup>53,54</sup> The lability of the pyridine ligands in the alkyne and flyover compounds reported here might be responsible for their higher reactivity.

As is evident from the sequence shown in Scheme I, alkyne oligomerization about the  $\text{Mo}_2$  center proceeds with stepwise expulsion of the  $\text{CO}$  ligands. If the  $\text{Mo}_2$  center is involved in a catalytic cycle for alkyne polymerization, the alkyne polymer must at some step leave the dimetal center. If this does not happen, the  $\text{Mo}_2$  unit will remain embedded in the polymer, and after some number of turnovers, polymerization will cease. The same line of reasoning must apply to  $\text{Mo}_2(\text{OR})_6$  alkyne polymerization, and we have found that after ca. 1000 turnovers the catalyst system dies. To investigate what role the compounds  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  and  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  played in alkyne oligomerization, we carried out the following reactions in NMR tubes and monitored the course of the reaction by  $^1\text{H}$  NMR spectroscopy.

(1)  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-HCCH})$  was allowed to react with ca. 20 equiv of  $\text{HCCH}$ . Within 30 min or less, all the acetylene had reacted, as evidenced by the disappearance of the signal at 1.49 ppm. The only  $^1\text{H}$  NMR signals arose from  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{HCCH})$  and benzene, which had been formed in ca. 5% yield based on added acetylene.

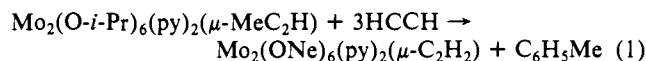
(2)  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\text{HCCH})$  was allowed to react with 1 equiv of DCCD. Within the time required to obtain an  $^1\text{H}$  NMR spectrum, the compound  $\text{Mo}_2(\text{ONE})_6(\mu\text{-C}_4\text{H}_2\text{D}_2)(\text{py})$  had been formed. The  $^1\text{H}$  NMR signals for the  $\mu\text{-C}_4\text{H}_2\text{D}_2$  moiety appear as an AX spectrum since spin coupling to  $^2\text{H}$  is negligible compared to  $^1\text{H-}^1\text{H}$  coupling (see Figure 8). The observed spectrum for the  $\mu\text{-C}_4\text{H}_2\text{D}_2$  ligand establishes the stereochemistry of the C-C coupling and shows that no subsequent scrambling of hydrogen atoms occurs.

(3)  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  was allowed to react with ca. 20 equiv of  $\text{HCCH}$ . Polyacetylene was precipitated, and a small quantity of benzene was formed. The polymerization rate was notably slower than that observed for (1) above involving  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ . Using carefully recrystallized (superpure)  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ , we found that ethyne polymerization was even slower, and some free  $\text{HCCH}$  could be detected by  $^1\text{H}$  NMR spectroscopy even after 24 h. More benzene was formed, however.

(4)  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  was allowed to react with ca. 20 equiv of DCCD. Polyacetylene was precipitated from solution, but only ca. 30% of the  $^1\text{H}$  signal intensity of  $\mu\text{-C}_4\text{H}_4$  was lost, implying formation of  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{D}_4)$ . Significantly, it appeared that the  $\text{C}_4\text{H}_4$  hydrogen atoms were exclusively converted to benzene protons, based on relative signal intensities. The experiment involving the inverse use of labels was also carried out: the  $\mu\text{-C}_4\text{D}_4$  compound was allowed to react with  $\text{HCCH}$ , ca. 20 equiv. Signals associated with the  $\mu\text{-C}_4\text{H}_4$  moiety grew with time, but only ca. 30% replacement was achieved before consumption of the excess  $\text{HCCH}$ . A small signal from benzene protons was observed.

(5)  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  was allowed to react with DCCD. Polyacetylene was precipitated. The signal associated with the  $\mu\text{-C}_2\text{H}_2$  protons decreased, implying formation of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{D}_2)$ . Significantly, a benzene proton resonance appeared, and within the limits of  $^1\text{H}$  NMR integration, the intensity of this signal corresponded to the loss of the  $\mu\text{-C}_2\text{H}_2$  signal, which implies that the  $\mu\text{-C}_2\text{H}_2$  moiety is exclusively involved in the formation of benzene and is not involved in the formation of the insoluble polymer. In this experiment, as in (4), it is possible to balance proton signal intensities, but we cannot distinguish between the signals associated with  $\text{C}_6\text{H}_2\text{D}_4$  and  $\text{C}_6\text{H}_4\text{D}_2$  or any other  $\text{C}_6\text{H}_n\text{D}_{6-n}$  species.

(6)  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-MeC}_2\text{H})$  was allowed to react with ca. 20 equiv of  $\text{HCCH}$ . Formation of toluene and  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  was observed. The integral ratio of the  $\mu\text{-C}_2\text{H}_2$  and toluene- $\text{CH}_3$  signals was 2:3, which establishes the stoichiometry of the reaction shown in eq 1.



The  $^1\text{H}$  NMR spectrum recorded immediately after addition of ethyne showed the formation of an intermediate, presumably  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_4\text{H}_3\text{Me})$  and toluene. No propyne adduct was visible.

We conclude from the above findings that the compounds  $\text{Mo}_2(\text{OR})_6(\text{py})_2(\text{RC}_2\text{R}')$  and  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  are only active toward alkyne cyclotrimerization to give benzenes. The species responsible for the polymerization of the alkynes to the yet-uncharacterized polymers is unknown. This polymerization sequence is kinetically more facile than cyclotrimerization since only a small fraction of alkyne is converted to benzenes. Recently, attention has been drawn to the fact that mononuclear<sup>56</sup> carbene complexes and dinuclear<sup>62</sup> bridging carbene complexes may act as alkyne polymerization initiators. We have no evidence that carbene ligands are formed in these reactions, though it is not altogether unlikely that they could be formed. For example, the bridging vinylidene ligand found in  $\text{Cp}_2\text{Mn}_2(\text{CO})_3(\mu\text{-C}=\text{CH}_2)$  is formed from the reaction between  $\text{CpMn}(\text{CO})_2(\text{THF})$  and  $\text{CH}=\text{CH}$ .<sup>63</sup> Furthermore, some years ago it was found that terminal alkynes can react with alcohols within the coordination sphere of  $\text{Pt}^{2+}$  to give alkoxy carbene ligands.<sup>64</sup>

Prompted by the recent findings by Katz et al.<sup>65</sup> that olefin metathesis can be induced by the addition of alkynes to carbene metal complexes that are themselves inactive in the olefin metathesis reaction, we initiated acetylene polymerization by  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  in the presence of an excess of 1-butene. No olefin metathesis was observed, but this observation by no means excludes the possibility of a carbene-promoted reaction. Other polymerization pathways are also possible;<sup>66</sup> the carbene-metal-promoted reaction is merely one that has received recent attention.

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### Concluding Remarks

(1) The  $(\text{Mo}\equiv\text{Mo})^{6+}$  unit supported by alkoxy ligands in  $\text{Mo}_2(\text{OR})_6$  compounds provides a coordinatively unsaturated center to which, despite the relatively high formal oxidation state of the metal atoms, alkynes may readily coordinate.

(2) The structural properties and chemical reactivity of the  $\mu\text{-C}_2\text{R}_2$  and  $\mu\text{-C}_4\text{R}_4$  groups have direct parallels with those of classical organometallic compounds. This leads us to believe that (i) similar coordination and reactivity could be found in molybdenum oxide-alkyne chemistry and (ii) that alkoxide ligands may support a new branch of organometallic chemistry that has thus far been overlooked.

(3) The fact that  $\text{Mo}_2(\text{OR})_6(\text{py})_2(\mu\text{-C}_2\text{R}_2)$  and  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  compounds are active in the cyclotrimerization of alkynes establishes that addition and elimination from the dimetal center can occur readily. The formation of cyclotrimers must reflect steric and energetic factors, not least of which is the stability of the aromatic ring.

(4) Future studies will be aimed toward elucidating the nature of the other alkyne oligomers formed in the reactions between  $\text{Mo}_2(\text{OR})_6$  compounds and alkynes, along with an identification of the catalytically active species.

### Experimental Section

General procedures and the preparation of  $\text{Mo}_2(\text{OR})_6$  compounds have been described.<sup>28</sup> The compounds  $\text{Mo}_2(\text{OR})_6(\text{py})_2$ , where  $\text{R} = i\text{-Pr}$  and  $\text{Ne}$  ( $\text{Ne} = \text{CH}_2\text{CMe}_3$ ), were prepared by the addition of pyridine ( $\gg 2$  equiv) to a near-saturated solution of the  $\text{Mo}_2(\text{OR})_6$  compounds in hexane. Upon cooling the solutions to ca.  $-5^\circ\text{C}$ , large dark purple crystals,  $\text{Mo}_2(\text{OR})_6(\text{py})_2$ , were formed and were collected by filtration and dried in vacuo. Complete characterization of the  $\text{Mo}_2(\text{OR})_6(\text{py})_2$  compounds, including studies of the equilibrium reaction  $\text{Mo}_2(\text{OR})_6 + 2\text{py} \rightleftharpoons \text{Mo}_2(\text{OR})_6(\text{py})_2$ , will be reported elsewhere.<sup>30</sup>

$^1\text{H}$  NMR spectra were recorded on a Varian HR220 spectrometer equipped with a variable temperature probe.  $^{13}\text{C}$  NMR spectra were obtained by using a Varian XL100 spectrometer. Infrared spectra were obtained from Nujol mulls between CsI plates on a Perkin-Elmer 283 spectrophotometer.

The alkynes HCCH and MeCCH were purchased from Matheson, MeCCMe from Farchan, and were used without purification.

**$\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{HCCH})$ .** A solution of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$  (0.50 g) in hexane/pyridine (20/0.40 mL) was frozen at liquid- $\text{N}_2$  temperature, and with a calibrated vacuum manifold,  $\text{C}_2\text{H}_2$  (1 mmol, 1.1 equiv) was condensed into the flask. On warming to room temperature, a dark green solution was obtained. The flask was placed in a refrigerator at  $-15^\circ\text{C}$  for 24 h, yielding dark green crystals,  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{HCCH})$  (0.35 g, 60% yield based on Mo), which were collected by filtration and dried in vacuo. Anal. Calcd for  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{HCCH})$ : C, 49.3; H, 7.45; N, 3.83. Found: C, 49.1; H, 7.90; N, 3.85.

$^1\text{H}$  NMR at  $-40^\circ\text{C}$  in toluene- $d_6$ :  $\delta$  ( $\text{OCHMe}_2$ ) 5.23 (terminal OR), 4.05 (bridging OR) as septets with  $J_{\text{HH}} = 7$  Hz;  $\delta$  ( $\text{OCHMe}_2$ ) 1.51, 1.40 (terminal OR), and 0.92 (bridging OR) as doublets with  $J_{\text{HH}} = 7$  Hz;  $\delta$  (py) 9.42 b (2 H), 6.95 t (4 H), 6.79 (3 H);  $\delta$  ( $\text{H}_2\text{C}_2$ ) 7.26 (s) ( $\delta$  in ppm relative to  $\text{Me}_4\text{Si}$ ). The  $^{13}\text{C}$  NMR spectrum showed  $\delta$  (HCCH) 162.7 with  $^1J_{^{13}\text{C}-^1\text{H}} = 202$  Hz. IR ( $\text{cm}^{-1}$ ): 1602 m, 1570 w, 1480 m, 1328 m, 1319 w, 1258 w, 1218 m, 1212 m, 1170 m, 1120 vs, 1069 mw, 1039 mw, 980 s, 938 s, 840 s, 827 ms, 755 m, 690 ms, 665 w, 625 m, 590 s, 559 m, 545 m, 460 m, 422 mw, 320 m.

**$\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCH})$ .** Essentially identical procedures using MeCCH yielded red crystalline samples of  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCH})$ . Anal. Calcd for  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCH})$ : C, 50.0; H, 7.58; N, 3.76. Found: C, 49.8; H, 8.25; N, 3.83.

$^1\text{H}$  NMR at  $-40^\circ\text{C}$ , toluene- $d_6$ :  $\delta$  ( $\text{OCHMe}_2$ ) 5.81, 4.90 (terminal OR), 4.78, and 4.05 (bridging OR) as septets,  $J_{\text{HH}} = 7$  Hz;  $\delta$  ( $\text{OCHMe}_2$ ) 1.68, 1.62, 1.40, 1.30, 1.12, and 0.35 as doublets,  $J_{\text{HH}} = 7$  Hz;  $\delta$  (py) 9.59 b (2 H), 6.94 t (4 H), 6.75 t (3 H);  $\delta$  (HCCMe) 7.15 s;  $\delta$  (HCCMe) 3.0, s.

IR ( $\text{cm}^{-1}$ ) 1600 m, 1568 w, 1480 m, 1375 m, 1365 m, 1354 m, 1315 m, 1260 mw, 1216 m, 1212 m, 1160 m, 1110 vs, 1070 mw, 1042 mw, 1010 mw, 975 s, 935 m, 835 m, 755 m, 698 m, 625 mw, 605 mw, 590 m, 540 mw, 440 ms, 305 m.

**$\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCMe})$**  was prepared similarly by using 2-butyne and isolated as a red crystalline compound that was not stable indefinitely at room temperature in sealed ampules. The  $^1\text{H}$  NMR spectrum of freshly prepared samples showed the presence of free MeCCMe and  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ , and with time, a resonance corresponding to hexamethylbenzene (identified by comparison with an authentic sample) grew in intensity. After 21 days at room temperature in toluene- $d_6$ ,

all the starting butyne adduct had been converted to hexamethylbenzene,  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ , pyridine, and some other Mo-O- $i\text{-Pr}$ -containing compound that was not pursued further.

**$\text{Mo}(\text{ONE})_6(\text{py})_2(\mu\text{-HCCH})$ .**  $\text{Mo}_2(\text{ONE})_6(\text{py})_2$  (0.50 g) was dissolved in hexane (20 mL), and the solution was then frozen at liquid- $\text{N}_2$  temperature. By use of a calibrated vacuum manifold,  $\text{C}_2\text{H}_2$  (0.6 mmol) was added. The flask was allowed to warm to  $0^\circ\text{C}$ , giving a green microcrystalline precipitate that was collected by filtration and dried in vacuo.  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$  (0.35 g, ca. 60% yield based on Mo). Anal. Calcd C, 56.1; H, 8.74; N, 3.11. Found: C, 56.0; H, 8.60; N, 3.28.

$^1\text{H}$  NMR  $-45^\circ\text{C}$  in toluene- $d_6$ :  $\delta$  ( $\text{OCH}_2\text{CMe}_3$ ) 4.83 d, 4.59 d (terminal OR), 3.87 s (bridging OR);  $\delta$  ( $\text{OCH}_2\text{CMe}_3$ ) 1.16 s (terminal OR), 0.81 s (bridging OR);  $\delta$  (py) 9.57 b (2 H), 6.80 b (3.4 H);  $\delta$  (HCCH) 7.74 s.

**$\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ .**  $\text{Mo}_2(\text{ONE})_6(\text{py})_2$  (0.50 g) was dissolved in hexane (20 mL), and the solution was frozen at liquid- $\text{N}_2$  temperature. By use of a calibrated vacuum manifold,  $\text{C}_2\text{H}_2$  (1.4 mmol, 2.2 equiv) was added, and the solution was warmed to room temperature. The flask was then placed in the refrigerator at  $-15^\circ\text{C}$ , yielding dark red-green crystals,  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$  (ca. 35 g, 60% yield based on Mo), which were collected by filtration and dried in vacuo. Evaporation of the mother liquor gave a dark solid that, by  $^1\text{H}$  NMR spectroscopy, was found to be slightly impure  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ .

Addition of 1 equiv of HCCH to a hydrocarbon solution of  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\text{HCCH})$  also gave good yields of  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ , and the  $\mu\text{-C}_4\text{H}_2\text{D}_2$ -labeled compound was made by this route, employing DCCH (from Merck, Sharpe, and Dohme). Anal. Calcd for  $\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ : C, 55.3; H, 8.93; N, 1.66. Found: C, 55.2; H, 8.79; N, 1.84.

$^1\text{H}$  NMR,  $-45^\circ\text{C}$  in toluene- $d_6$ :  $\delta$  ( $\text{OCH}_2\text{CMe}_3$ ) 5.10 s, 4.45 s, 4.65 d, 4.21 d with  $J_{\text{HH}} = 12$  Hz, 3.80 d, 3.24 d with  $J_{\text{HH}} = 12$  Hz;  $\delta$  ( $\text{OCH}_2\text{CMe}_3$ ) 1.45 s, 1.30 s, 1.04 s, 0.96 s;  $\delta$  (py) 8.15 d (2 H), 6.80 t (4 H), 6.44 t (3 H);  $\delta$  ( $\text{C}_4\text{H}_4$ ) 8.95 m, 6.18 m. For the  $\mu\text{-C}_4\text{H}_2\text{D}_2$  compound,  $\delta$  ( $\text{C}_4\text{H}_2\text{D}_2$ ) 8.94, 6.15 d,  $J_{\text{HH}} = 7$  Hz.

**$^1\text{H}$  NMR Studies of Alkyne Oligomerization Reactions.** These reactions were all carried out by using a similar procedure. Approximately 10–25 mg of the  $\text{Mo}_2$  compound dissolved in ca. 1 mL of toluene- $d_6$  or benzene- $d_6$  was placed in an NMR tube, and acetylene ( $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{D}_2$ ), 10–50 equiv, was condensed into the tube by using a calibrated vacuum manifold. The NMR tube was sealed with a torch and allowed to warm to room temperature slowly. Solid polyacetylene was deposited along the sides of the tube, but this did not cause any serious loss of  $^1\text{H}$  NMR sensitivity.

In a typical experiment,  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-MeCCH})$  (50 mg) was dissolved in benzene- $d_6$  (2 mL). The sample was split into two equal portions and placed into two NMR tubes. One was sealed under vacuum, while the other was allowed to react with  $\text{C}_2\text{H}_2$  (40 equiv) as described above. After warming to room temperature, the  $^1\text{H}$  NMR spectrum of the latter was recorded and the reaction followed with time. Within 30 min the spectrum corresponded to  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-HCCH})$ , and the methyl signal of the propyne ligand had been transformed to the methyl signal of toluene. From integral comparisons with the blank and with the internal standards of Me signals due to O- $i\text{-Pr}$  ligands, all the propyne had been converted to toluene as indicated by the stoichiometric reaction 1.

**X-ray Structural Determinations.** General procedures were as described previously.<sup>67</sup>

**$\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-HCCH})$ .** A well-formed green crystal of dimensions  $0.36 \times 0.24 \times 0.32$  mm was transferred to the cold stream of the goniostat under an atmosphere of dry nitrogen. The cell dimensions obtained from 40 reflections at  $-165^\circ\text{C}$  with Mo  $K\alpha$  ( $\lambda$  0.71069 Å) were  $a = 19.183$  (5) Å,  $b = 15.677$  (4) Å,  $c = 12.165$  (3) Å,  $\beta = 108.16$  (1)°,  $V = 3476.1$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.400$  g cm<sup>-3</sup>, with space group =  $P2_1/a$ .

A total number of 6166 unique reflections were collected by using standard moving-crystal, moving-detector techniques with the following values: scan speed =  $4.0^\circ$  min<sup>-1</sup>, scan width =  $2.0 +$  dispersion, single background time at extremes of scan = 5 s, and aperture size =  $3.0 \times 4.0$  mm. The limits of data collection were  $5^\circ \leq 2\theta \leq 50^\circ$ . The number of reflections with  $F > 2.33\sigma(F)$  was 5186.

The structure was solved by direct methods and refined by full-matrix techniques including all hydrogen atoms to give final residuals:  $R(F) = 0.036$  and  $R_w(F) = 0.038$ . The goodness of fit for the last cycle was 1.154 and the maximum  $\Delta/\sigma$  was 0.05.

**$\text{Mo}_2(\text{ONE})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ .** A red crystal of dimensions  $0.14 \times 0.20 \times 0.20$  mm was transferred to the cold stream of the goniostat under an atmosphere of dry nitrogen. The cell dimensions obtained from 40 re-

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lections at  $-162\text{ }^\circ\text{C}$  were  $a = 23.19\text{ (2) } \text{\AA}$ ,  $b = 11.37\text{ (1) } \text{\AA}$ ,  $c = 16.56\text{ (1) } \text{\AA}$ ,  $V = 4366\text{ (2) } \text{\AA}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.287\text{ g cm}^{-3}$ , with space group = *Pnam*.

A total number of 3305 reflections were collected by using standard moving-crystal, moving-detector techniques with the following values: scan speed =  $4.0^\circ\text{ min}^{-1}$ , scan width =  $2.0 + \text{dispersion}$ , single background time at extremes of scan = 3 s, and aperture size =  $3.0 \times 4.0\text{ mm}$ . The limits of data collection were  $6^\circ \leq 2\theta \leq 45^\circ$ . Of the 3305 reflections, 2982 were unique, and the number with  $F > 2.33\sigma(F)$  was 2025. It should be pointed out that the crystal was a poor scatterer of X-rays, and of the 3305 measurements, only 2102 has a net count greater than twice the background count.

The structure was solved easily by direct methods and Fourier techniques. During refinement, several atoms in the neopentoxy ligands acquired nonpositive definite thermal parameters. To resolve this problem, we first assumed that the space group was incorrect, and the molecule was placed in the corresponding noncentric space group. While the residuals, as expected, were slightly less in the noncentric space group, the same atoms were nonpositive definite, indicating other problems were responsible. Careful examination of Fourier and difference-Fourier maps indicated that disorder might be present, although attempts to resolve the disorder were unsuccessful. Our final conclusion is that most of the neopentoxy ligands are undergoing large vibratory motion, which may or may not be disorder. This conclusion is supported in part by the large number of reflections that were less than twice their background values (an unusual occurrence for low-temperature data) and experience with

other compounds containing the neopentoxy ligand.

The following full-matrix refinement utilized only those data that were observed by using the criteria  $I(\text{net count}) > 2.0 \times (\text{background count})$ . The final residuals are  $R(F) = 0.093$  and  $R_w(F) = 0.109$ . The goodness of fit for the last cycle was 2.345, and the maximum  $\Delta/\sigma$  was 0.05.

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**Registry No.**  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{HCCH})$ , 78736-93-3;  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCH})$ , 78736-94-4;  $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\text{MeCCMe})$ , 78750-14-8;  $\text{Mo}_2(\text{ONe})_6(\text{py})_2(\mu\text{-HCCH})$ , 81987-91-9;  $\text{Mo}_2(\text{ONe})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ , 82010-06-8;  $\text{Mo}_2(\text{O-}i\text{-Pr})_6$ , 62521-20-4;  $\text{Mo}_2(\text{ONe})_6(\text{py})_2$ , 81987-92-0.

**Supplementary Material Available:** Tables of observed and calculated structure factors and anisotropic thermal parameters (60 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports No. 8066 ( $\text{Mo}_2(\text{O-}i\text{-Pr})_6(\text{py})_2(\mu\text{-C}_2\text{H}_2)$ ) and No. 81018 ( $\text{Mo}_2(\text{ONe})_6(\text{py})_2(\mu\text{-C}_4\text{H}_4)$ ), are available, in microfiche form only, from the Indiana University Library.

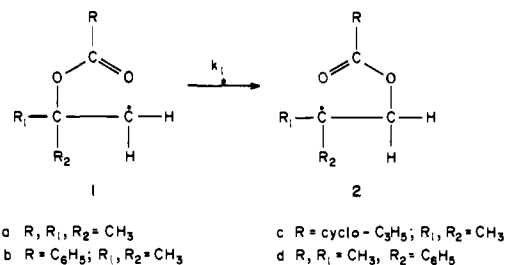
## Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 38. Rearrangement of $\beta$ -(Acyloxy)alkyl and $\beta$ -(Benzoyloxy)alkyl Radicals<sup>1</sup>

L. R. C. Barclay,<sup>\*2</sup> D. Griller,<sup>3</sup> and K. U. Ingold<sup>3</sup>

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada, and the Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada. Received December 28, 1981

**Abstract:** Rate constants for the free-radical rearrangement,  $\text{RC}(\text{O})\text{OCMe}_2\text{CH}_2 \rightarrow \text{RC}(\text{O})\text{OCH}_2\text{CMe}_2$ , and for the ring-opening reaction,  $\text{RCOCH}_2\text{CMe}_2\text{O} \rightarrow \text{RC}(\text{O})\text{OCH}_2\text{CMe}_2$ , have been measured by kinetic EPR spectroscopy. In hydrocarbon solvents at  $75\text{ }^\circ\text{C}$  with  $\text{R} = \text{methyl}$  and  $\text{phenyl}$ , the 1,2-acyloxy migrations are slower ( $k = 5.1 \times 10^2\text{ s}^{-1}$  and  $2.5 \times 10^2\text{ s}^{-1}$ , respectively) than the corresponding 1,3-dioxolan-2-yl ring openings ( $k = 7.6 \times 10^3\text{ s}^{-1}$  and  $1.0 \times 10^3\text{ s}^{-1}$ , respectively). The formation of a 1,3-dioxolan-2-yl radical as an intermediate in these two rearrangements could not, therefore, be ruled out. However, with  $\text{R} = \text{cyclopropyl}$ , the rearrangement proceeded normally ( $k \approx 1.2 \times 10^2\text{ s}^{-1}$  at  $75\text{ }^\circ\text{C}$ ), but the corresponding 1,3-dioxolan-2-yl radical underwent opening of the cyclopropyl ring rather than the dioxolanyl ring. Since this process occurred at a much faster rate ( $k = 8.7 \times 10^5\text{ s}^{-1}$  at  $75\text{ }^\circ\text{C}$ ) than the rearrangement, the dioxolanyl radical cannot, in this case at least, be an intermediate in this acyloxy migration. The possible role of charge separation in the transition state for acyloxy migration is considered.

There has been a continuing interest in the 1,2 migration of the acyloxy group ( $1 \rightarrow 2$ ) in  $\beta$ -(acyloxy)alkyl radicals<sup>4</sup> since this



reaction has no direct intermolecular analogue. This rearrangement was originally observed during radical addition to the

acetate of 2-methylbut-3-en-2-ol.<sup>5</sup> Subsequently, it was detected during the free-radical-induced decarbonylation of  $(\text{CH}_3)_2\text{C}[\text{O}-\text{C}(\text{O})\text{CH}_3]\text{CH}_2\text{CHO}$ , which was found to give both  $(\text{CH}_3)_3\text{CO}-\text{C}(\text{O})\text{CH}_3$  and  $(\text{CH}_3)_2\text{CCHCH}_2\text{OC}(\text{O})\text{CH}_3$ .<sup>6</sup> It was suggested that the reaction proceeded through the 1,3-dioxolan-2-yl radical, **3a**, which could serve as "a transition state, or an unreactive intermediate".<sup>6</sup> Subsequent kinetic and product studies by Beckwith and co-workers<sup>7,8</sup> led to the conclusion that **3** did not lie on the rearrangement pathway, although labeling experiments with <sup>18</sup>O showed a clean inversion of the positions of the two acyloxy oxygens. A cyclic transition state of ill-defined structure,<sup>9</sup> **4**, was proposed.<sup>8</sup>

The evidence that **3** was not involved in these rearrangements came from kinetic studies.<sup>7,8</sup> In the first place, reaction of *tert*-butyl acetate with HO• radicals in water in an EPR spec-

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(2) Mount Allison University.

(3) N.R.C.C.

(4) For a review of this and other free-radical rearrangements, see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Chapter 4, pp 162-283.

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(9) Structure **4** differs slightly from the original representation.