The Molybdenum–Molybdenum Triple Bond. 4.[1] Insertion Reactions of Hexakis(alkoxy)dimolybdenum Compounds with Carbon Dioxide and Single-Crystal X-Ray Structural Characterization of $Mo_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$

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Abstract: $Mo_2(OR)_6$ compounds, where R = Me_3Si, Me_3C, Me_2CH, and Me_3CCH_2, react readily and reversibly both in solution and in the solid state with CO_2 (>2 equiv) to give insertion products which, on the basis of analytical data, spectroscopic studies (IR, ^1H and ^{13}C NMR, and mass spectroscopy), and x-ray crystallography of one product, are formulated as dinuclear compounds $Mo_2(OR)_4(O_2COR)_2$. For the case where R = Me_3C, the product crystallizes in the monoclinic system, space group $P2_1/c$ with $Z = 4$ and the following unit cell dimensions: a = 10.676 (2) Å, b = 10.890 (1) Å, c = 31.515 (4) Å, β = 97.34 (1)°, and V = 3634.1 (8) Å^3. The bridging carbonato groups are cis and the molecule has an approximate twofold axis of symmetry which is a perpendicular bisector of the Mo–Mo bond. The Mo–Mo distance is 2.241 (1) Å. The Mo–O distances vary, with an average of 2.13 Å for the carbonato oxygen atoms, 1.906 Å for two of the alkoxy oxygen atoms, and 1.865 Å for the other two alkoxy groups. The Mo–Mo–O angles are about 90° for carbonato oxygen atoms, about 102° for the longer two Mo–OR bonds, and about 112° for the shorter two Mo–OR bonds. The dihedral angle between the mean carbonato planes is 75°. The rotational conformation with respect to the Mo–Mo bond is essentially eclipsed. The mechanism of CO_2 insertion/deinsertion in the solid state proceeds via a direct attack of CO_2 on $Mo_2(OR)_6$ compounds while in solution evidence is presented for the availability of a kinetically more labile pathway involving an alcohol-catalyzed chain reaction: ROH + CO_2 ⇄ ROCOOH, MoOR + ROCOOH ⇄ MoO_2COR + ROH. These findings are compared with earlier studies involving the reactions between $M_2(NMe_2)_6$ compounds (M = Mo and W) and CO_2.

Introduction

Concerns about alternate petrochemical feedstocks have stimulated interest in the chemistry of carbon dioxide, and the potential for CO_2 activation via coordination to a transition metal complex has been recognized.[4] At present there are two crystallographically characterized transition metal–carbon dioxide adducts[5,6] and several reports relating to the insertion of CO_2 into transition metal–hydrogen,[7-10] -carbon,[11-16] -nitrogen,[17-19] and -oxygen[22-25] bonds. In general little is known concerning the mechanisms of these insertion reactions. Insertion could occur by a direct attack on the metal–ligand bond with or without formation of a transition metal–CO_2 adduct as an intermediate. Alternatively a catalyzed reaction sequence could lead to insertion. The latter was established[19] in the reaction of $W(NMe_2)_6$ and $W_2Me_2(NEt_2)_4$ with CO_2 which yield $W(NMe_2)_3(O_2CNMe_2)_3$ and $W_2Me_2(O_2CNEt_2)_4$, respectively. Insertion into the tungsten–nitrogen bond occurs by the amine-catalyzed sequence shown in eq 1. The

$$\text{(a)}\quad R_2NH + CO_2 \rightleftarrows R_2NCOOH \qquad (1)$$
$$\text{(b)}\quad M{-}NR_2 + R_2NCOOH \rightarrow M{-}O_2CNR_2 + HNR_2 + X$$

possibility for a general catalytic sequence leading to insertion, eq 2, should be recognized whenever the organic molecule X–H

$$\text{(a)}\quad X{-}H + CO_2 \rightleftarrows XCOOH \qquad (2)$$
$$\text{(b)}\quad M{-}X + XCOOH \rightarrow M{-}O_2CX + X{-}H$$

contains an active hydrogen (i.e., one capable of reacting according to eq 2a) and the reaction is carried out in the presence of the organic substrate X–H, either wittingly or unwittingly as may be the case when the M–X bond is susceptible to hydrolysis.

We report here our studies of the reaction between CO_2 and $Mo_2(OR)_6$ compounds. Brief mention of this work was made in previous reports describing the preparation and characterization of the dinuclear alkoxides, $Mo_2(OR)_6$, which contain triple bonds between the molybdenum atoms and have a central Mo_2O_6 core of D_{3d} symmetry (ethanelike).[20,26]

Results and Discussion

$Mo_2(OR)_6$ compounds, where R = Me_3Si, Me_3C, Me_2CH, and Me_3CCH_2, react in hydrocarbon solvents to give $Mo_2(OR)_4(O_2COR)_2$ compounds according to eq 3.

$$Mo_2(OR)_6 + 2CO_2 \rightleftarrows Mo_2(OR)_4(O_2COR)_2 \qquad (3)$$

For R = Me_3C and Me_2CH the bis(alkylcarbonato)tetrakis(alkoxy) compounds have been isolated as crystalline solids by low-temperature crystallizations carried out under an atmosphere of CO_2. These compounds are moisture and oxygen sensitive but are quite stable in the solid state at room temperature. They may be stored in vacuo at room temperature without losing CO_2, but when heated to ca. 90 °C at 10^{-4} cmHg, sublimation and decarboxylation occur simultaneously, leading to $Mo_2(OR)_6$ sublimates. In the mass spectrometer the peak of highest m/e corresponds to $Mo_2)or)_6^+$.

When samples of finely divided $Mo_2(OR)_6$ compounds are placed in sealed tubes under 5 atm of CO_2, the insertion reaction 3 also occurs and the CO_2 insertion products may be isolated in this manner.

A comparison of the speed of insertion was made for both the homogeneous (solution) and the heterogeneous (solid state/gas) reactions. The heterogeneous reaction was considerably slower, but for both the homogeneous and heterogeneous reactions the following rate dependence on alkoxy ligand was observed: $Me_3CCH_2O > Me_2CHO > Me_3CO$. (See Experimental Section for details.)

In solution the progress of the insertion reaction is readily followed by ^1H NMR spectroscopy and may be qualitatively observed by the eye since these reactions are accompanied by striking color changes. For example, $Mo_2(OCHMe_2)_6$ is a pale-yellow solid and gives pale-yellow solutions in hydrocar-

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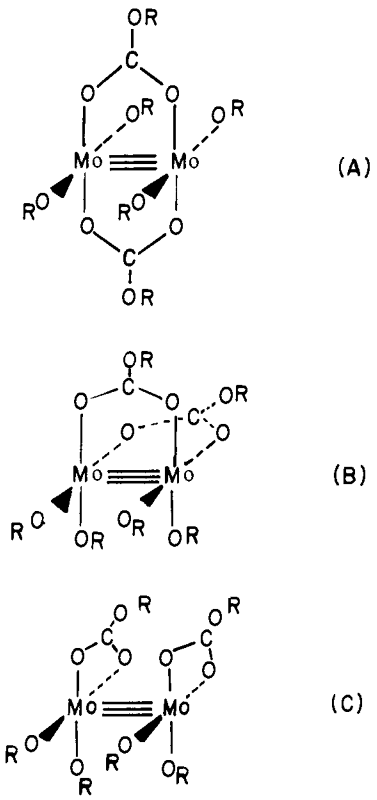


Figure 1. Proposed structures for $Mo_2(OR)_4(O_2COR)_2$.

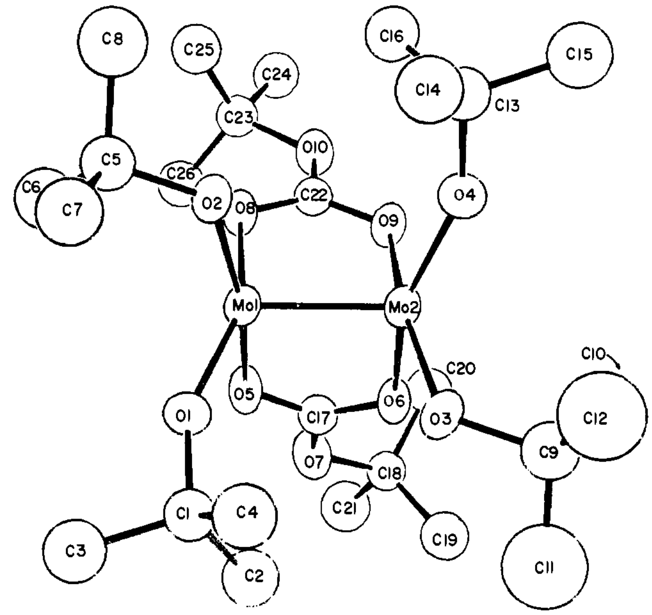


Figure 2. An ORTEP drawing of the $Mo_2(O_2COCMe_3)_2(OCMe_3)_4$ molecule using 40% probability ellipsoids and showing the atom labeling scheme. The view is along the virtual twofold symmetry axis of the molecule. The four $OCMe_3$ groups are above and the two O_2COCMe_3 groups are below the plane of the paper.

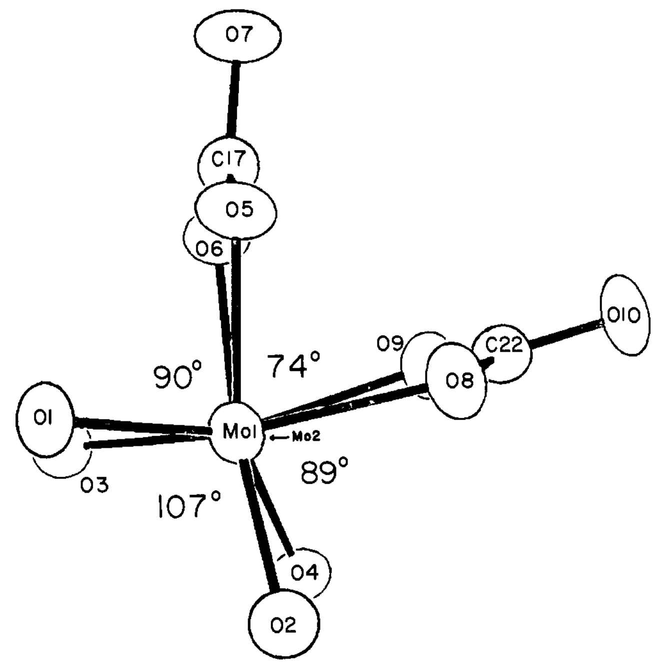


Figure 3. An ORTEP of the central $Mo_2(O_2COC)_2(OC)_4$ portion of the molecule viewed directly down the Mo(1)–Mo(2) bond showing the near-eclipsed configuration and listing some of the dihedral angles. Mo(2) is hidden by Mo(1).

bon solvents. On exposure to CO_2 these solutions turn deep red with the formation of $Mo_2(OCHMe_2)_4(O_2COCHMe_2)_2$. However, it is not clear that this intense color is due to $Mo_2(OCHMe_2)_4(O_2COCHMe_2)_2$ since in the crystalline state this compound is a cream or a bleached-bone color. It could be that the intense red color arises from an intermediate in reaction 3, such as $Mo_2(OR)_5(O_2COR)$, which is not present in sufficient concentration to be detected by ^1H NMR spectroscopy.

Infrared and NMR (^1H and ^{13}C) data for the insertion products, together with other characterization data, are given in the Experimental Section. We observe only one type of O_2COR ligand and one type of M–OR group in these compounds. We conclude that in solution these molecules must have a plane of symmetry, a twofold axis or a center of inversion. Since the methylene protons in $Mo_2(OC\mathit{H}_2CMe_3)_4(O_2COCH_2CMe_3)_2$ and the methyl protons in $Mo_2(OCH\mathit{Me}_2)_4(O_2CHMe_2)_2$ are diastereotopic, there must not be a plane containing the Mo_2O_4 moiety. Thus the cis-bridged structure B, which could have C_2, C_s, or C_{2v} symmetry, but not the trans-bridged structure A (see Figure 1), is possible. Alternatively, structure C, or one of its rotamers, is possible. It may be noted that both B and C have some precedence in the chemistry of metal–metal triple bonded compounds. Both $W_2(O_2CNMe_2)_6$ and $W_2Me_2(OCNEt_2)_4$ have cis-bridged $W_2(O_2CNR_2)_2$ moieties, while $Mo_2(OSiMe_3)_6(HNMe_2)_2$ has a central $Mo_2O_6N_6$ skeleton based on a staggered $Re_2Cl_8^{2-}$ geometry.[28]

The ready reversibility of reaction 3 both in solution and in the solid state, the diamagnetic nature of the insertion products (this clearly rules out a mononuclear species), and the well-established dinuclear chemistry surrounding $M_2(NMe_2)_6$ compounds (M = Mo and W) with regard to ligand substitution and CO_2 insertion reactions all led us to conclude that the CO_2 insertion products are dinuclear, in solution and in the solid. In the latter case we have obtained direct evidence by x-ray crystallography.

The entire molecule of $Mo_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$ constitutes the crystallographic asymmetric unit and thus has no rigorous symmetry. However, as Figure 2 shows, there is an approximate twofold symmetry axis, which lies perpendicular to the plane of the drawing and bisects the Mo–Mo line. As expected, two molecules of CO_2 have been inserted into Mo–OR bonds, converting the OR groups to O_2COR, monoalkylcarbonato, ligands which then serve as bridging, bidentate ligands. The other four alkoxy groups remain nonbridging ligands so that each molybdenum atom forms four Mo–O bonds. This molecule thus provides the second

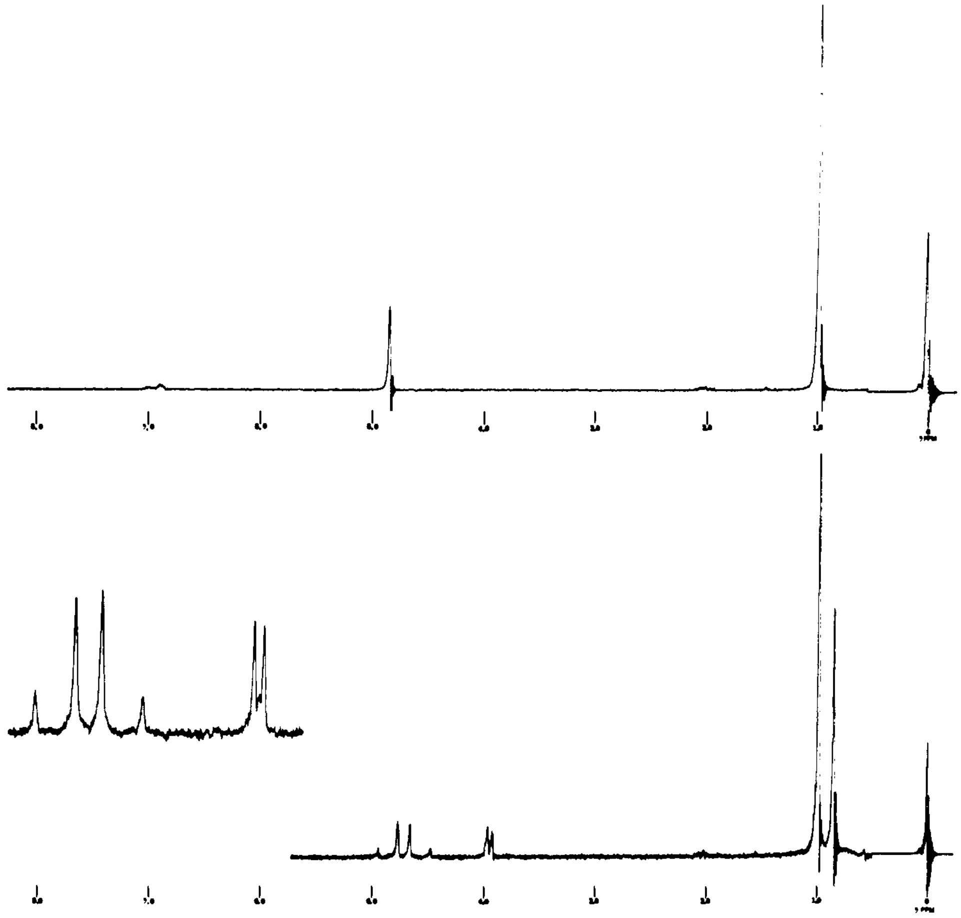


Figure 4. Lower: ^1H NMR spectrum of $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ formed in a sealed NMR tube reaction: $Mo_2(OCH_2CMe_3)_6 + {}^{13}CO_2$ (6 equiv), in toluene-d_8, 40 °C, 60 MHz. The region of the spectrum showing the methylene protons is presented with scale expansion; $^3J_{^{13}C-H} = 3$ Hz in $O_2{}^{13}COCH_2CMe_3$. Top: ^1H NMR spectrum of a sample of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2 + CO_2$ (1 atm) in an NMR tube in toluene-d_8 at 94 °C. The spectrum corresponds to that of $Mo_2(OCH_2CMe_3)_6$.

structurally characterized example of a dimolybdenum compound having a triple M–M bond and four ligand atoms attached to each metal atom. The one previous example is $Mo_2(OSiMe_3)_6(NHMe_2)_2$, but there is a major, quantitative difference between the two structures.

In the $Mo_2(OSiMe_3)_6(NHMe_2)_2$ structure, where all eight ligand atoms are separate and independent, the rotational conformation is staggered, as would be expected for a triple M–M bond. As Figure 3 shows, the rotational conformation in the present case is essentially eclipsed, which may be attributed to the restraint on rotation imposed by the bridging carbonato groups. The Mo–Mo distances in these two molecules are essentially identical, at 2.241 (1) Å.

The Mo–OR distances here have an average value of 1.89 (2) Å, which is the same as that, 1.88 (2) Å, found in the pure alkoxy compound, $Mo_2(OCH_2CMe_3)_6$.[20] The Mo–O distances to the carbonato groups are very much longer, averaging 2.13 (2) Å. This is comparable to those found in $Mo_2(O_2CR)_4$ type compounds, which are normally in the range 2.10–2.14 Å.

The arrangement of Mo–O bonds about each metal atom deviates markedly from fourfold symmetry in other ways as well. The RO–Mo–OR angles average 101.2 ± 0.8° whereas the O–Mo–O angles involving carbonato oxygen atoms are 76.6 ± 0.3°. The other angles are in the range 86.7–89.6°. While it is not possible to say with certainty why there is such a great disparity, doubtless steric factors are important. The spreading of the RO–Mo–OR angles may be caused in part by repulsion between cis oxygen atoms so close (~1.9 Å) to the metal atom, and the steric requirements of the *tert*-butyl groups on those atoms may also contribute to this result. The carbonato oxygen atoms lie at greater distances from the metal atoms and the CMe_3 groups of the carbonato ligands are so far from each other that they offer no resistance to closer approach of the carbonato groups to each other.

The variations in distances and angles so far mentioned are all within the scope of C_{2v} symmetry, but there is still another set of variations that are responsible for degrading the symmetry to only C_2, namely, variations in the Mo–Mo–O angles. For the carbonato oxygen atoms these are all about equal (ca. 90°) which conforms to C_{2v} symmetry, but where the alkoxy groups are concerned there is a clear dichotomy. For two of the alkoxy groups the Mo–Mo–O angles are relatively large, 112.2 (6)°, while the Mo–O distances are 1.865 (5) Å, whereas for the other two, the angles are considerably smaller, 102.7 (2)°, and the Mo–O distances are somewhat longer, 1.906 (5) Å. Once again, it is likely that intramolecular steric effects are responsible for these variations.

Mechanistic Considerations. Reaction 3 is kinetically facile and reversible. At room temperature the position of equilibrium lies to the right, but at higher temperatures, lies to the left. These statements are exemplified by observations of the reaction between $Mo_2(OCH_2CMe_3)_6$ and $^{13}CO_2$ carried out in NMR tube experiments. Within 5 min of condensing $^{13}CO_2$ (>2 equiv) into an NMR tube of $Mo_2(OCH_2CMe_3)_6$ in toluene-d_8 frozen in liquid nitrogen, the tube was sealed with a torch and the ^1H NMR spectra were recorded at ca. 35 °C. The spectrum (see Figure 4) corresponded to $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$. The presence of $^3J_{^{13}C-H} = 3$ Hz clearly identifies the $O_2{}^{13}COCH_2CMe_3$ ligand. On raising the temperature to 80 °C, the ^1H NMR spectra corresponded to $Mo_2(OCH_2CMe_3)_6$ (see Figure 4). The sample was removed from the probe and was observed to be a pale yellow color. Within moments, the solution turned a deep purple color as the sample cooled. The tube was returned to the probe of the NMR spectrometer and cooled to 35 °C, and the spectrum corresponding to $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ was obtained.

Clearly the reaction is kinetically facile and totally reversible, and must have a small value of ΔG. Why ΔG should apparently change sign with temperature is not obvious and not pertinent to the subsequent discussion of mechanism.

The fact that the compounds $Mo_2(OR)_4(O_2COR)_2$ decarboxylate (and $Mo_2(OR)_6$ sublimes) at 90 °C (10^{-4} cmHg) indicates that $\Delta G^{\ddagger}$ for decarboxylation must be equal to, or less than, the enthalpy of sublimation. This we may reasonably estimate to be ca. 22 kcal mol^{-1}.[29] A catalyzed mechanism of the type 2 cannot be operative under these experimental conditions. By the law of microscopic reversibility, we conclude that a direct insertion process is operative with $\Delta G^{\ddagger}$ comparable to, or less than, the enthalpy of sublimation (ca. 22 kcal mol^{-1}).

As a further proof of a direct insertion process, solid samples of $Mo_2(OCH_2CMe_3)_6$ and $Mo_2(OBu\text{-}t)_6$ were mixed and placed in a sealed tube under 5 atm of CO_2. When insertion had occurred, the tube was opened and the insertion products were examined by mass spectroscopy. No ligand crossover products, i.e., $Mo_2(OBu\text{-}t)_x(OCH_2CMe_3)_{6-x}{}^+$, were detected.

While these experiments demonstrate the existence of a direct insertion mechanism, they do not demand that in solution a mechanism involving alcohol catalysis, eq 2, X = OR, is not possible. It may even be kinetically more facile.

We attempted numerous sealed NMR tube experiments in which alcohol scavengers were added to hydrocarbon solutions of $Mo_2(OR)_6$. These included lithium alkyls, methyl Grignard, sodium metal, and lithium aluminum hydride. All scavengers failed to suppress the rate of insertion to any detectable extent. These findings do not, however, rule out a catalyzed reaction sequence for the following reasons: (1) the alcohol scavengers react with the M–OR bonds, (2) addition of CO_2 removes the ROH scavenger, and (3) sealing the NMR tube by flame torch may liberate trace quantities of H_2O, either from the glass or by decomposition of $Mo_2(OR)_6$ compounds located on the walls of the glass.

At this point we undertook a reaction involving freshly sublimed $Mo_2(OPr\text{-}i)_6$ and $Mo_2(OBu\text{-}t)_6$ under the most rigorous vacuum and anaerobic conditions at our disposal (see Experimental Section). Upon addition of CO_2 no color change was observed over a period of 30 min. The solvent was stripped and the solids were analyzed by mass spectroscopy. Crossover ions, $Mo(OBu\text{-}t)_x(OPr\text{-}i)_{6-x}{}^+$, were observed.

The following day the reaction was repeated using $Mo_2(OPr\text{-}i)_6$ and $Mo_2(OBu\text{-}t)_6$ (now 1 day old) which had been stored in the drybox. (The sample of $Mo_2(OPr\text{-}i)_6$ was noticeably a darker yellow than it was when freshly sublimed.) Within 5–10 min of the addition of CO_2 the solution was brown ($Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ and $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$ are green and red, respectively, in solution). The solvent was stripped and the solids were analyzed by mass spectroscopy. Crossover products, $Mo_2(OBu\text{-}t)_x(OPr\text{-}i)_{6-x}{}^+$, were again detected.

Blank reactions, which involved the mixing of the two dinuclear alkoxides, adding pentane by vacuum distillation, stirring for 30 min at room temperature, stripping the solvent, and analyzing the solids by mass spectroscopy, were carried out on both occasions, and crossover products were found in the mass spectrometer. Thus $Mo_2(OBu\text{-}t)_x(OPr\text{-}i)_{6-x}$ compounds must have been formed in solution in the absence of added CO_2 (mixing the solids directly does not lead to crossover ions $Mo_2(OBu\text{-}t)_x(OPr\text{-}i)_{6-x}{}^+$ in the mass spectrometer).

An unequivocal conclusion cannot be reached from these observations. It is known that $Mo_2(OR)_6$ compounds are coordinatively unsaturated and will reversibly add donor ligands such as amines. With alcohols, $Mo_2(OR)_6$ compounds react to give alkoxy-group exchange which is rapid on the NMR time scale (see Experimental Section). Thus the formation of $Mo_2(OBu\text{-}t)_x(OPr\text{-}i)_{6-x}$ may readily be accounted for in the absence of CO_2. The observations with regard to color changes parallel those previously noted.[16] Freshly prepared $W_2Me_2(NEt_2)_4$ was reacted in hexane with CO_2 (25% excess) at 25 °C for 24 h and no reaction was observed. Upon addition of a small amount of $HNEt_2$ (ca. 0.005 equiv), CO_2 insertion occurred and was complete within 10 min. However, since we have no way of establishing that insertion did not occur in the first reaction, the observations remain equivocal.

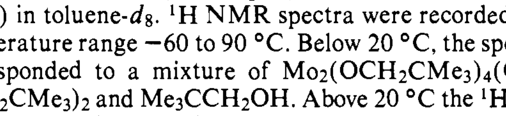
The relative speed of CO_2 insertion follows the order $Me_3CCH_2O > Me_2CHO > Me_3CO$, which may be accounted for by steric considerations. The reaction between $Mo_2(OBu\text{-}t)_6$ and CO_2 in toluene-d_8 or benzene may be followed by ^1H NMR spectroscopy over a period of ca. 30–45 min (t_∞ spectrum) at probe temperature ca. 35 °C. We decided to carry out the insertion reaction in the presence of added t-BuOH and compared the speed of insertion with a blank sample (see Experimental Section). The sample containing added t-BuOH reacted significantly faster to give the insertion product.

In another NMR tube experiment, $Mo_2(OCH_2CMe_3)_6$ was reacted with $^{13}CO_2$ (ca. 6 equiv) and Me_3CCH_2OH (ca. 3 equiv) in toluene-d_8. ^1H NMR spectra were recorded in the temperature range −60 to 90 °C. Below 20 °C, the spectrum corresponded to a mixture of $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ and Me_3CCH_2OH. Above 20 °C the ^1H NMR spectra showed that exchange between MoOR, MoO_2COR, and ROH groups was occurring on the NMR time scale. At 90 °C only two sharp resonances were observed (integral ratio 2:9) corresponding to the fast exchange limit. These observations offer further support for the occurrence of reaction 2, X = OR, as well as the direct observation of the alcohol exchange reaction: Mo–OR + R′OH $\rightleftharpoons$ MoOR′ + ROH.

Conclusions

1. $Mo_2(OR)_6$ compounds react reversibly both in solution and in the solid state with CO_2 to give insertion products which are dinuclear compounds containing molybdenum-to-molybdenum triple bonds, $Mo_2(OR)_4(O_2COR)_2$. The free-energy change for this reaction is very small and the free energy of activation for the insertion reaction in the solid state is less than or comparable to the enthalpy of sublimation of $Mo_2(OR)_6$ compounds (ca. 22 kcal mol^{-1}).

2. The mechanism for CO_2 insertion (deinsertion) in the solid state proceeds via a direct attack. Whether this involves a direct attack by CO_2 on the Mo–OR bond as depicted in eq 4, or whether this proceeds via a Mo–CO_2 intermediate, remains unknown. In solution there is good evidence to support the view that a kinetically more labile pathway exists, namely, that involving an alcohol-catalyzed chain mechanism, eq 2, X = OR.



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Experimental Section

Materials. $Mo_2(OR)_6$, where R = t-Bu, i-Pr, CH_2CMe_3, and $SiMe_3$ were prepared as previously described.[20] "Bone-dry" carbon dioxide was purchased from Matheson. $^{13}CO_2$ (90% ^{13}C) was purchased from Merck and Co. Lithium alkyls, LiR, where R = Me, *n*-Bu, and *t*-Bu were purchased from Alfa. $LiCH_2SiMe_3$ was prepared by published procedures.[31] $LiAlH_4$ was purchased from Aldrich.

General Procedures. Owing to the highly reactive nature of $Mo_2(OR)_6$ and $Mo_2(OR)_4(O_2COR)_2$, all preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo, using standard Schlenk-type techniques.[32] Solvents (pentane, hexane, benzene, and toluene) were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, phenyl ether, and sodium. When not needed for immediate use, solvents were stored over calcium hydride under nitrogen. Samples were stored and handled in a Vacuum Atmospheres Dri Lab system.

Carbon dioxide was measured (ca. 2% accuracy) on a calibrated vacuum manifold, then condensed into the reaction flask with liquid N_2.

Isotopically Labeled Compounds. Labeled compounds, $Mo_2(OR)_4(O_2{}^{13}COR)_2$ were prepared similarly to the respective unlabeled compounds.

Physical and Analytical Methods. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques.

Infrared spectra were obtained from Nujol mulls between CsI plates using a Perkin-Elmer IR 283 spectrometer.

^1H and ^{13}C NMR measurements were made on Varian Associates A-60 and XL-100 spectrometers, respectively. Both instruments were equipped with a variable temperature probe. Toluene-d_8 was used as the solvent and chemical shifts are reported as parts per million downfield from hexamethyldisiloxane (HMDS) (for ^1H NMR data) or as parts per million downfield from Me_4Si (for ^{13}C NMR data).

Mass spectra were obtained using an AEI MS9 mass spectrometer and the method of direct insertion (90–120 °C).

Preparation of $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$. CO_2 (7.86 mmol) was condensed into a solution of $Mo_2(OBu\text{-}t)_6$(0.826 g, 1.31 mmol) in hexane (30 mL). The solution was warmed to room temperature and stirred for 4 h. During this time the solution turned from red to green. The solution was cooled to −60 °C. A blue precipitate came out of solution. Excess solution was syringed off and the last traces of solvent were removed in vacuo at −60 °C. The blue solid (0.45 g), $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$, was then dried (30 min, 10^{-3} Torr). Anal. Calcd: C, 43.46; H, 7.75. Found: C, 43.19; H, 7.46.

Infrared data (Nujol mull between CsI plates): 292 (m), 310 (m), 355 (m), 367 (w), 384 (m), 416 (m), 425 (m), 475 (m), 552 (s), 592 (s), 620 (s), 742 (s), 768 (vs), 784 (s), 800 (s), 810 (m), 864 (sh), 896 (vs), 910 (vs), 979 (vs, br), 1026 (s), 1092 (s), 1168 (vs, br), 1232 (s), 1260 (m), 1357 (s), 1408 (s), and 1540 cm^{-1} (s).

A parent ion at *m/e* 630 in the mass spectrum corresponds to $Mo_2(OB\text{-}t)_6{}^+$ (based on ^{96}Mo).

If an NMR sample of $Mo_2(OBu\text{-}t)_4(O_2COB\text{-}t)_2$ is dissolved in toluene-d_8 and sealed in vacuo, the resulting spectra correspond to that of $Mo_2(OBu\text{-}t)_6$.[20]

$Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$, when heated to 100 °C (10^{-3} Torr), sublimes with loss of CO_2 to yield $Mo_2(OBu\text{-}t)_6$.

$Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ can also be prepared in the following manner. CO_2 (5 atm) was condensed into a sample tube containing a finely divided sample of $Mo_2(OBu\text{-}t)_6$ (100 mg). After 3 days, the red solid had become a blue, powdery solid which was identified as $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ by IR spectroscopy. Note: $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ can be sealed under vacuum at room temperature without loss of CO_2 as indicated by the analytical data.

Preparation of NMR Solution of $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$. CO_2 (0.5 mmol) was condensed into a NMR tube containing a solution of $Mo_2(OBu\text{-}t)_6$ (ca. 20 mg) in toluene-d_8. The tube was sealed with a torch. After a period of 30 min, the previously orange solution turned green. NMR data (^1H and ^{13}C) are reported in Table IV.

A solution of $Mo_2(OBu\text{-}t)_6$ (36.0 mg) in toluene-d_8 (1.0 mL, with HMDS as internal reference) was prepared. Aliquots (0.5 mL, measured via syringe) were placed in two NMR tubes. Additionally, ca. 0.05 mL of 36% *t*-BuOH/benzene azeotrope was syringed into one NMR sample. CO_2 (0.5 mmol was condensed into each NMR tube (sample A, $Mo_2(OBu\text{-}t)_6 + CO_2$; sample B, $Mo_2(OBu\text{-}t)_6 + CO_2 +$ trace of *t*-BuOH). NMR measurements were used to follow the rates of the reaction. Within 5 min of warming to probe temperature, ca. 35 °C, sample A contained $Mo_2(OBu\text{-}t)_6$ and to a very small extent, $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$. After a period of 15 min, $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ were present in almost equal quantities. After 30 min, only $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ was detectable. However, for sample B, upon warming to probe temperature, $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ were detected in almost equal quantities. After 10 min, only $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ was detectable.

Preparation of $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$. CO_2 (12 mmol) was condensed into a solution of $Mo_2(OPr\text{-}i)_6$ (1.08 g, 1.98 mmol) in hexane (30 mL). The yellow solution, upon warming to room temperature, turned red. The reaction mixture was stirred for 30 min and then cooled to −60 °C. A cream-colored solid precipitated out of solution. Excess solution was removed via syringe and the last traces of sovent were removed in vacuo at −60 °C. The cream solid (0.50 g), $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$, was then dried (30 min, 10^{-3} Torr). Anal. Calcd: C, 37.86; H, 6.67. Found: C, 37.46; H, 6.46. To determine if CO_2 deinsertion occurs over a period of time, $Mo_2(OPr\text{-}i)_4(O_2COPR\text{-}i)_2$ which had been stored under N_2 for 2 weeks was submitted for analysis and analyzed as $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$. Anal. Calcd: C, 37.86; H, 6.67. Found: C, 37.53; H, 6.70. Samples submitted for analysis were sealed for several days under vacuum without loss of CO_2.

Infrared data (Nujol mull between CsI plates): 304 (m), 323 (w), 454 (m(, 624 (s), 653 (m), 840 (w), 833 (s), 852 (s), 944 (vs), 980 (vs), 1110 (vs), 1128 (s), 1167 (s), 1262 (m), 1327 (s), 1362 (s), 1412 (s), and 1560 cm^{-1}.

A parent ion at *m/e* 546 in the mass spectrum corresponds to $Mo_2(OPr\text{-}i)_6{}^+$ (based on ^{96}Mo).

Cream-colored $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$, when heated to 70 °C ($10^{-3}$ Torr), sublimes with loss of CO_2 to yield yellow $Mo_2(OPr\text{-}i)_6$.

If an NMR sample of $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$ is dissolved in toluene-d_8 and selaed in vacuo, the resulting spectra correspond to that of $Mo_2(OPr\text{-}i)_6$.[20]

$Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$ can also be prepared by sealing a finely divided sample of $Mo_2(OPr\text{-}i)_6$ under 5 atm of CO_2.

Preparation of NMR Solution of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$. CO_2 (0.5 mmol) was condensed into an NMR tube containing a solution of $Mo_2(OCH_2CMe_3)_6$ (ca. 20 mg) in touene-d_8. Upon warming, the yellow solution immediately turned red. NMR data (^1H and ^{13}C), which are reported in Table IV, indicated the formation of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$.

In a similar manner, $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ was prepared. The methylene protons on the neopentyl carbonate ligand appeared as a doublet: $^3J_{^{13}C\text{-}H} = 3$ Hz.

At 90 °C, the NMR spectra of a solution of the $Mo_2(OCH_2CMe_3)_6$ and CO_2 showed only the presence of $Mo_2(OCH_2CMe_3)_6$.

Reaction of $Mo_2(OSiMe_3)_6$ with CO_2. CO_2 (7.0 mmol) was condensed into a solution of $Mo_2(OSiMe_3)_6$ (0.85 g, 1.17 mmol) in hexane (30 mL). The red solution, upon warming to room temperature, turned green immediately. A solid product was not isolated.

Reactions of $Mo_2(OR)_6 + 2CO_2$ in the Presence of Alcohol Scavengers. CO_2 insertion reactions of $Mo_2(OCH_2CMe_3)_6$ and $Mo_2(OBu\text{-}t)_6$ in the presence of alcohol scavengers were investigated. The alcohol scavengers were lithium alkyls LiR (where R = Me, *t*-Bu, *n*-Bu, CH_2SiMe_3, and CPh_3), MeMgBr, $LiAlH_4$, and Na metal. Typically in an NMR experiment, $Mo_2(OR)_6$ (ca. 20 mg) was placed in an NMR tube and a small trace of the alcohol scavenger added. Toluene-d_8 (with HMDS as an internal reference) was then added as solvent. In the case of LiBu-*n*, which is a liquid, the lithium alkyl was added to toluene-d_8 before addition to the molybdenum alkoxide in the NMR tube. All solutions were homogeneous except those with MeMgBr, $LiAlH_4$, and Na. When CO_2 was condensed into the NMR tubes, the $Mo_2(OR)_6$ complexes reacted to form $Mo_2(OR)_4(O_2COR)_2$; i.e., insertion of CO_2 was not quenched. Furthermore, it was observed that LiR also reacted with CO_2 to form insoluble precipitates. Additionally, the lithium alkyls reacted with $Mo_2(OR)_6$. For example, an NMR investigation of a solution of $Mo_2(OBu\text{-}t)_6$ in the presence of a trace of LiBu-*t* gave peaks corresponding to the formation of isobutylene and LiOBu-*t*, besides the peak corresponding to unreacted $Mo_2(OBu\text{-}t)_6$.

Insertion Reactions of Mixtures of $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OPr\text{-}i)_6$ with CO_2. CO_2 was condensed into pentane solutions of $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OPr\text{-}i)_6$ mixtures in order to determine if insertion was occurring by a direct insertion mechanism, thereby leading to a nonexchange of ligands, or by an alcohol-catalyzed mechanism, thereby leading to an exchange of ligands.

(a) Pentane, which had been freshly distilled from benzophenone and sodium, was stored over $LiAlH_4$ and placed through a freeze-

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.088 95 (8)	0.132 33 (9)	0.13045 (3)	0.005 68 (8)	0.007 28 (9)	0.000 75 (1)	−0.0009 (2)	0.000 35 (5)	0.000 51 (6)
Mo(2)	0.297 56 (8)	0.126 85 (9)	0.127 69 (3)	0.005 96 (8)	0.007 28 (9)	0.000 77 (1)	−0.0006 (2)	0.000 98 (5)	−0.000 18 (6)
O(1)	0.0067 (7)	8.2484 (7)	0.0936 (2)	0.0083 (8)	0.0078 (8)	0.000 93 (9)	−0.000 (1)	−0.0007 (5)	0.0015 (4)
O(2)	0.0315 (6)	−0.0153 (7)	0.1021 (2)	0.0055 (7)	0.0087 (7)	0.001 08 (9)	−0.002 (1)	−0.0004 (4)	0.0002 (5)
O(3)	0.3160 (6)	0.2302 (7)	0.0800 (2)	0.0081 (7)	0.0090 (8)	0.001 08 (9)	−0.003 (1)	0.0025 (4)	0.0005 (5)
O(4)	0.3488 (7)	−0.0256 (7)	0.1087 (2)	0.0093 (8)	0.0074 (7)	0.001 07 (9)	0.000 (1)	0.0012 (5)	−0.0005 (5)
O(5)	0.1214 (6)	0.2768 (7)	0.1764 (2)	0.0056 (6)	0.0101 (8)	0.001 05 (9)	−0.001 (1)	0.0007 (4)	−0.0021 (5)
O(6)	0.3262 (6)	0.2819 (7)	0.1683 (2)	0.0060 (7)	0.0089 (8)	0.001 09 (9)	−0.000 (1)	0.0019 (4)	−0.0010 (5)
O(7)	0.2453 (7)	0.4012 (7)	0.2163 (2)	0.0085 (8)	0.0106 (9)	0.001 29 (10)	0.000 (1)	0.0004 (5)	−0.0035 (5)
O(8)	0.1102 (6)	0.0378 (7)	0.1894 (2)	0.0059 (6)	0.0106 (8)	0.000 91 (8)	0.001 (1)	0.0009 (4)	0.0015 (5)
O(9)	0.3213 (6)	0.0494 (7)	0.1907 (2)	0.0058 (7)	0.0099 (8)	0.001 07 (9)	−0.001 (1)	0.0004 (4)	0.0013 (5)
O(10)	0.2464 (7)	−0.0304 (8)	0.2454 (2)	0.0086 (8)	0.0124 (9)	0.000 84 (8)	0.002 (1)	0.0016 (4)	0.0030 (5)
C(1)	0.002 (1)	0.352 (1)	0.0664 (4)	4.5 (3)					
C(2)	0.090 (1)	0.453 (1)	0.0872 (4)	5.8 (3)					
C(3)	−0.139 (1)	0.394 (1)	0.0589 (5)	6.6 (4)					
C(4)	0.046 (1)	0.309 (1)	0.0226 (4)	6.0 (3)					
C(5)	−0.099 (1)	−0.056 (1)	0.0945 (4)	4.9 (3)					
C(6)	−0.169 (1)	0.003 (1)	0.1290 (5)	6.8 (4)					
C(7)	−0.153 (1)	−0.015 (1)	0.0493 (5)	6.6 (4)					
C(8)	−0.094 (2)	−0.198 (2)	0.1019 (5)	8.0 (4)					
C(9)	0.439 (1)	0.261 (1)	0.0664 (4)	5.6 (3)					
C(10)	0.546 (2)	0.235 (2)	0.1014 (5)	8.0 (4)					
C(11)	0.434 (2)	0.399 (2)	0.0586 (7)	12.1 (7)					
C(12)	0.452 (2)	0.186 (2)	0.0275 (7)	11.3 (6)					
C(13)	0.334 (1)	−0.152 (1)	0.0989 (4)	4.8 (3)					
C(14)	0.254 (1)	−0.164 (1)	0.0531 (5)	6.5 (4)					
C(15)	0.472 (1)	−0.202 (1)	0.0984 (5)	7.1 (4)					
C(16)	0.269 (1)	−0.216 (1)	0.1336 (4)	5.3 (3)					
C(17)	0.231 (1)	0.317 (1)	0.1856 (4)	3.7 (2)					
C(18)	0.374 (1)	0.442 (1)	0.2368 (4)	4.2 (3)					
C(19)	0.442 (1)	0.510 (1)	0.2046 (4)	5.8 (3)					
C(20)	0.450 (1)	0.331 (1)	0.2567 (4)	5.9 (3)					
C(21)	0.339 (1)	0.532 (2)	0.2713 (5)	7.5 (4)					
C(22)	0.224 (1)	0.020 (1)	0.2080 (3)	3.4 (2)					
C(23)	0.140 (1)	−0.075 (1)	0.2694 (4)	4.7 (3)					
C(24)	0.219 (1)	−0.130 (1)	0.3098 (5)	6.1 (3)					
C(25)	0.064 (1)	−0.174 (1)	0.2438 (4)	5.7 (3)					
C(26)	0.062 (1)	0.035 (1)	0.280 (4)	6.0 (3)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table II. Bond Distances (Å)[a]

Atoms		Distance	Atoms		Distance	Atoms		Distance
Mo(1)	Mo(2)	2.241 (1)	0(5)	C(17)	1.25 (1)	C(5)	C(7)	1.53 (1)
Mo(1)	O(1)	1.860 (5)	O(6)	C(17)	1.27 (1)	C(5)	C(8)	1.56 (2)
Mo(1)	O(2)	1.903 (6)	O(7)	C(17)	1.32 (1)	C(9)	C(10	1.52 (2)
Mo(1)	O(5)	2.136 (6)	O(7)	C(18)	1.51 (1)	C(9)	C(11)	1.52 (2)
Mo(1)	O(8)	2.111 (6)	O(8)	O(9)	2.252 (8)	C(9)	C(12)	1.49 (2)
Mo(2)	O(3)	1.908 (6)	O(8)	C(22)	1.29 (1)	C(13)	C(14)	1.58 (1)
Mo(2)	O(4)	1.869 (6)	O(9)	C(22)	1.28 (1)	C(13)	C(15)	1.58 (1)
Mo(2)	O(6)	2.117 (6)	O(10)	C(22)	1.29 (1)	C(13)	C(16)	1.54 (1)
Mo(2)	O(9)	2.142 (6)	O(10)	C(23)	1.52 (1)	C(18)	C(19)	1.51 (1)
O(1)	C(1)	1.41 (1)	C(1)	C(2)	1.54 (1)	C(18)	C(20)	1.54 (1)
O(2)	C(5)	1.45 (1)	C(1)	C(3)	1.56 (1)	C(18)	C(21)	1.55 (1)
O(3)	C(9)	1.47 (1)	C(1)	C(4)	1.58 (1)	C(23)	C(24)	1.56 (1)
O(4)	C(13)	1.42 (1)	C(5)	C(6)	1.54 (1)	C(23)	C(25)	1.52 (1)
O(5)	O(6)	2.234 (8)				C(23)	C(26)	1.51 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

pump-thaw cycle three times. Subsequently it was distilled (ca. 20 mL) into a flask cooled in liquid nitrogen which contained freshly sublimed $Mo_2(OBu\text{-}t)_6$ (0.263 g, 0.42 mmol) and $Mo_2(OPr\text{-}i)_6$ (0.210 g, 0.38 mmol). CO_2 (12.0 mmol) was condensed into the reaction flask. Upon warming, the reaction mixture remained a yellow color for 20 min, indicative of no insertion of CO_2. Additional CO_2 (6.0 mmol) was condensed into the reaction flask, followed once again by no color change for 10 min. The solvent was removed in vacuo. Mass spectral analysis indicated that ligand exchange had occurred, with a peak of highest m/e 616 ($Mo_2(OBu\text{-}t)_6$ has a parent peak at m/e 630), corresponding to $Mo_2(OBu\text{-}t)_5(OPr\text{-}i)^+$ (based on ^{96}Mo).

The same procedure and conditions as described above were followed for a mixture of $Mo_2(OBu\text{-}t)_6$(0.243 g, 0.39 mmol) and $Mo_2(OPr\text{-}i)_6$ (0.256 g, 0.47 mmol); however, no CO_2 was added. The solution was stirred for 30 min and the solvent was stripped. Mass spectral analysis indicated that ligand exchange had occurred with a parent peak at m/e 602 (corresponding to $Mo_2(OBu\text{-}t)_4(OPr\text{-}i)_2{}^+$, based on ^{96}Mo).

(b) The two samples of freshly sublimed $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OPr\text{-}i)_6$ were then stored in the drybox overnight where atmospheric impurities caused the samples to darken slightly. The same procedure and conditions as described above were applied to a mixture

Table III. Bond Angles (deg)[a]

Atoms			Angle	Atoms			Angle	Atoms			Angle
Mo(2)	Mo(1)	O(1)	112.7 (2)	Mo(1)	O(5)	C(17)	118.9 (6)	O(4)	C(13)	C(14)	108.4 (8)
Mo(2)	Mo(1)	O(2)	102.8 (2)	Mo(2)	O(6)	C(17)	116.1 (6)	O(4)	C(13)	C(15)	104.8 (8)
Mo(2)	Mo(1)	O(5)	88.3 (2)	C(17)	O(7)	C(18)	121.9 (7)	O(4)	C(13)	C(16)	109.5 (8)
Mo(2)	Mo(1)	O(8)	91.4 (2)	Mo(1)	O(8)	C(22)	117.6 (6)	C(14)	C(13)	C(15)	111.0 (9)
O(1)	Mo(1)	O(2)	100.5 (3)	Mo(2)	O(9)	C(22)	119.3 (6)	C(14)	C(13)	C(16)	111.8 (9)
O(1)	Mo(1)	O(5)	86.9 (3)	C(22)	O(10)	C(23)	121.4 (7)	C(15)	C(13)	C(16)	111.0 (9)
O(1)	Mo(1)	O(8)	150.5 (3)	O(1)	C(1)	C(2)	109.8 (8)	O(5)	C(17)	O(6)	124.5 (9)
O(2)	Mo(1)	O(5)	162.8 (2)	O(1)	C(1)	C(3)	106.6 (8)	O(5)	C(17)	O(7)	115.4 (8)
O(2)	Mo(1)	O(8)	89.6 (2)	O(1)	C(1)	C(4)	107.4 (3)	O(6)	C(17)	O(7)	120.1 (8)
o)5)	Mo(1)	O(8)	76.9 (2)	C(2)	C(1)	C(3)	112.3 (9)	O(7)	C(18)	C(19)	110.1 (8)
Mo(1)	Mo(2)	O(3)	102.6 (2)	C(2)	C(1)	C(4)	110.6 (8)	O(7)	C(18)	C(20)	110.0 (8)
MO(1)	Mo(2)	O(4)	111.6 (2)	C(3)	C(1)	C(4)	110.1 (8)	O(7)	C(18)	C(21)	101.2 (8)
Mo(1)	Mo(2)	O(6)	91.3 (2)	O(2)	C(5)	C(6)	107.5 (8)	C(19)	C(18)	C(20)	112.9 (9)
Mo(1)	Mo(2)	O(9)	88.6 (2)	O(2)	C(5)	C(7)	107.7 (8)	C(19)	C(18)	C(21)	110.0 (9)
O(3)	Mo(2)	O(4)	102.0 (3)	O(2)	C(5)	C(8)	105.3 (8)	C(20)	C(18)	C(21)	112.0 (9)
O(3)	Mo(2)	O(6)	89.1 (3)	C(6)	C(5)	C(7)	112.1(9)	O(8)	C(22)	O(9)	122.4 (8)
O(3)	Mo(2)	O(9)	161.9 (2)	C(6)	C(5)	C(8)	108 (1)	O(8)	C(22)	O(10)	122.3 (8)
O(4)	Mo(2)	O(6)	151.1 (2)	C(7)	C(5)	C(8)	115 (1)	O(9)	C(22)	O(10)	115.3 (8)
O(4)	Mo(2)	O(9)	86.7 (3)	O(3)	C(9)	C(10)	111.(9)	O(10)	C(23)	C(24)	99.7 (7)
O(6)	Mo(2)	O(9)	76.3 (2)	O(3)	C(9)	C(11)	105 (1)	O(10)	C(23)	C(25)	110.0 (8)
Mo(1)	O(1)	C(1)	153.9 (6)	O(3)	C(9)	C(12)	107 (1)	O(10)	C(23)	C(26)	109.4 (8)
Mo(1)	O(2)	C(5)	125.5 (6)	C(10)	C(9)	C(11)	108 (1)	C(24)	C(23)	C(25)	110.8 (9)
Mo(2)	O(3)	C(9)	123.4 (6)	C(10)	C(9)	C(12)	111 (1)	C(24)	C(23)	C(26)	111.7 (9)
Mo(2)	O(4)	C(13)	154.6 (6)	C(11)	C(9)	C(12)	114 (1)	C(25)	C(23)	C(26)	114.3 (9)

[a] Numbers in parentheses are esd's in the least significant digits.

Table IV. ^1H and ^{13}C NMR Data for $Mo_2(OR)_4(O_2COR)_2$[a]

Compd	Temp, °C	^1H (multiplicity, rel intensity)	^{13}C (rel intensity)
$Mo(OC(CH_3)_3)_4(O_2COC(CH_3)_3)_2$[b]	38	β 1.43 (2, s)	× 173.5 (2)
α β × α′ β′		β′ 1.38 (1, s)	α′ 82.3 (2)
			α 81.3 (4)
			β 32.1 (12)
			β′ 28.3 (6)
$Mo_2(OCH(CH_3)_2)_4(O_2COCH(CH_3)_2)_2$	38 to	β′ 1.13 (2, d)	× 173.2 (2)
α β × α′ β′	−60	β 1.32 (4, d)	α′ 73.7 (2)
		α′ 4.90 (1, sept)	α 72.6 (4)
		α 5.72 (2, sept)	β 26.2 (8)
			β′ 25.4 (4)
$Mo_2(OCH_2C(CH_3)_3)_4(O_2COCH_2C(CH_3)_3)_2$	38 to	γ 0.83 (18, s)	× 174.0 (2)
α β γ × α′ β′ γ′	−60	γ 0.95 (36, s)	α 82.6 (4)
		α 3.95 (4, s)	α′ 79.5 (2)
		α 4.70 (8, AB, spectrum)	β 34.3 (4)
			β′ 32.0 (2)
			γ 26.9 (12)
			γ′ 26.3 (6)

[a] ^1H NMR spectra are reported in parts per million relative to HMDS (hexamethyldisiloxane). ^{13}C NMR spectra are reported in parts per million relative to Me_4Si. The solvent is toluene-d_8. s = singlet; d = doublet; sept = septet. [b] $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$ is very sparingly soluble in hydrocarbon solvents at low temperatures.

of $Mo_2(OBu\text{-}t)_6$ (0.238 g, 0.38 mmol) and $Mo_2(OPr\text{-}i)_6$ (0.264 g, 0.48 mmol) when CO_2 (12.0 mmol) was condensed into the reaction mixture. Upon warming, the solution turned dark brown after 10 min. The solvent was then removed in vacuo and the products were analyzed by mass spectroscopy. A parent peak occurred at *m/e* 588 (corresponding to $Mo_2(OBu\text{-}t)_3(OPr\text{-}i)_3^+$, based on ^{96}Mo), indicative of ligand exchange. Similarly, a mixture of $Mo_2(OBu\text{-}t)_6$ (0.249 g, 0.40 mmol) and $Mo_2(OPr\text{-}i)_6$ (0.263 g, 0.48 mmol) with no addition of CO_2, but treated with the same conditions as above, was prepared and the solvent was removed in vacuo after 10 min. The products were analyzed by mass spectroscopy and a parent peak occurred at *m/e* 588 (corresponding to $Mo_2(OBu\text{-}t)_3(OPr\text{-}i)_3^+$, based on ^{96}Mo) indicative of ligand exchange.

CO_2 Insertion into a Solid Mixture of $Mo_2(OBu\text{-}t)_6$ and $Mo_2(OCH_2CMe_3)_6$. CO_2 (5 atm) was condensed into a tube containing $Mo_2(OBu\text{-}t)_6$ (ca. 20 mg) and $Mo_2(OCH_2CMe_3)_6$ (ca. 20 mg). The solid mixture turned red after 1 h. After 1 day, the products were collected and analyzed by mass spectroscopy. Two intense peaks at *m/e* 714 and 630 were observed, corresponding to $Mo_2(OCH_2CMe_3)_6^+$ and $Mo_2(OBu\text{-}t)_6^+$, respectively (based on ^{96}Mo). No evidence of ligand exchange was present.

NMR Study of Exchange between $Mo_2(OCH_2CMe_3)_6$ and Free Neopentyl Alcohol. A 1-mL stock solution of $Mo_2(OCH_2CMe_3)_6$ (29.7 mg, 0.04 mmol) and Me_3CCH_2OH (12.8 mg, 0.15 mmol) in toluene-d_8 (with HMDS as an internal reference) was prepared. A 0.5-mL portion of this solution was placed in an NMR tube to determine the rate of exchange of free neopentyl alcohol with $Mo_2(OCH_2CMe_3)_6$. From 80 to −60 °C, there are two peaks in the NMR, δ 0.9 and 4.23 ppm (relative to HMDS), indicative of rapid exchange on the NMR time scale.

NMR Study of Exchange between $Mo_2(OCH_2CMe_3)_6$, Free Neopentyl Alcohol, and CO_2. A 0.5-mL portion of the stock solution of $Mo_2(OCH_2CMe_3)_6$ and neopentyl alcohol described immediately above was placed in an NMR tube. $^{13}CO_2$ (0.25 mmol, 6 equiv) was condensed into the NMR tube. NMR analysis was made of the mixture. From 60 to 90 °C, there are two peaks in the NMR, δ 0.9 and 4.23 ppm (relative to HMDS), indicative of rapid exchange between $Mo_2(OCH_2CMe_3)_6$ and neopentyl alcohol. From 20 to 60 °C, there is exchange between $Mo_2(OCH_2CMe_3)_6$, Me_3CCH_2OH, and $^{13}CO_2$ leading to broadened peaks in the NMR. At 20 to −40 °C, the spectrum corresponds to a mixture of $Mo_2(OCH_2CMe_3)_4(O_2{}^{13}COCH_2CMe_3)_2$ and Me_3CCH_2OH.

Preparation of NMR Solution of $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$. CO_2 (0.5 mmol) was condensed into an NMR tube containing a solution of $Mo_2(OPr\text{-}i)_6$ (ca. 20 mg) in toluene-d_8. After a period of 10–15 min (time varying with different samples), the yellow solution turned red. NMR data (^1H and ^{13}C), which are reported in Table IV indicated the formation of $Mo_2(OPr\text{-}i)_4(O_2COPr\text{-}i)_2$.

Preparation of $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$. Attempts to isolate $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$ at low temperatures from hexane solutions of $Mo_2(OCH_2CMe_3)_6$ and CO_2 were complicated by the formation of polymeric $(Mo(OCH_2CMe_3)_3)_x$[17]. However, $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$ was prepared in a reaction between solid $Mo_2(OCH_2CMe_3)_6$ and CO_2. CO_2 (5 atm) was condensed into a sample tube containing a finely divided sample of $Mo_2(OCH_2CMe_3)_6$ (ca. 50 mg). After 1 h, the yellow solid had transformed into a red solid $Mo_2(OCH_2CMe_3)_4(O_2COCH_2CMe_3)_2$.

Infrared data (Nujol mull between CsI plates): 325 (w, br), 396 (m), 419 (m), 486 (m), 642 (s), 680 (m), 722 (m), 758 (m), 936 (m), 972 (s), 995 (s), 1019 (s), 1045 (s), 1122 (m), 1168 (m), 1218 (m), 1261 (m), 1295 (w), and 1562 cm^{-1} (m).

X-Ray Crystallography. A crystal of $Mo_2(O_2COBu\text{-}t)_2(OBu\text{-}t)_4$ measuring approximately 0.2 × 0.3 × 0.55 mm was wedged in a Nujol-filled, thin-walled glass capillary. The peak widths at half-height were ca. 0.2° for ω scans of several intense low-angle reflections. Cell constants and axial photographs indicated that the crystal belonged to the monoclinic system with $a = 10.676$ (2) Å, $b = 10.890$ (1) Å, $c = 31.515$ (4) Å, $\beta = 97.34$ (1)°, $V = 3634.1$ (8) Å^3. The observed volume was consistent with that expected for $Z = 4$.

Data were collected at 23 ± 2 °C on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite crystal monochromator and using Mo Kα (λ 0.710 730 Å) radiation. The θ–2θ scan technique was used with scans ranging from 0.9° above to 0.9° below the calculated Kα_1–Kα_2 doublet, variable scan rates of from 4.8 to 24.0°/min, and with a scan to background time ratio of 2.0. The intensities of three standard reflections, monitored frequently throughout data collection, showed an average decrease of 11.4%. The integrated intensities of 4765 unique, nonsystematically absent reflections, having $0° < 2\theta(\text{Mo K}\alpha) < 45°$, were recorded. A correction for crystal decay was applied to these data, which were then reduced to relative $|F_o|^2$ values.[33] No correction for absorption ($\mu = 7.23$ cm^{-1}) was applied. The 2796 observations having $|F_o|^2 > 3\sigma(|F_o|^2)$ were retained as observed and used in subsequent structure solution and refinement. The systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) were noted and uniquely determined the space group to be $P2_1/c$.

The structure was solved using conventional heavy atom methods and it was refined to convergence using anisotropic thermal parameters for the 2 Mo and 10 O atoms and isotropic thermal parameters for the 26 C atoms. The final residuals were $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$, $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.081$. A value of 0.07 was used for p in the calculation[1] of the weights, w. The esd of an observation of unit weight was 1.702. The largest peaks in a final difference Fourier map could be assigned to methyl-group hydrogen atoms, but no effort was made to include them in refinement.

The atomic positional and thermal parameters are listed in Table I, and the bond distances and angles are given in Tables II and III.

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Supplementary Material Available: A table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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