parameters. Relatively large values for the latter indicated some positional disorder and/or appreciable thermal movement. A nonlinear decay of -22.6% of the reflection intensities of **5** during the data collection might have been caused by loss of interstitial benzene and could have contributed as well to the large displacement parameters. The decay was corrected for isotropically on the basis of the intensity variation of three mutually orthogonal standard reflections. A decay of -0.7% for **4** was not corrected for. Due to the platelike single crystals of **4** an empirical absorption correction was necessary, which was based on scans around the diffraction vectors of nine selected reflections near $\chi = 90°$ (relative transmission 0.72-1.00).

For **4** all hydrogen atoms could be located in difference syntheses after the anisotropic refinement of the non-H atoms. For **5** only five hydrogen atoms could be located; the remainder were calculated at idealized geometrical positions. The benzene hydrogen atoms were neglected. For both structures the H atoms were included as fixed-atom contributions in structure factor calculations, while all other atoms were refined anisotropically. Tables VI and VII contain the atomic coordinates of the non-H atoms.

Acknowledgment. We thank J. Riede for collecting the X-ray data sets, Drs. J. Blümel and N. Hertkorn for some NMR spectra, and Dr. Ch. Habarta for assistance in the CV work. We also thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and BASF AG for support.

Supplementary Material Available: Complete tables of hydrogen atom parameters and thermal parameters for **4** and **5** (6 pages); listings of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

Chemistry of Metal Oxo Alkyl Complexes. Mechanistic Studies on the Anaerobic and Aerobic Decompositions of Molybdenum(VI) Dioxo Dialkyl Complexes

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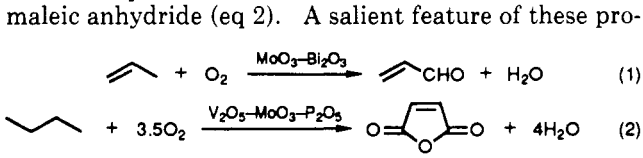
The anaerobic and aerobic decompositions of $L_2Mo(O)_2R_2$ [L_2 = 4,4'-dimethyl-2,2'-dipyridyl, R = CH_2Ph, **1**; R = $CH_2C_6H_4CH_3$-*p*, **2**; R = $(CH_2)_4CH{:}CH_2$, **3**; R = CH_2CHMe_2, **4**; R = CH_2CMe_3, **5**; R = CH_2CMe_2Ph, **6**] were studied. The anaerobic decomposition mode chosen by a given $L_2Mo(O)_2R_2$ complex is a sensitive function of the hydrocarbyl group, R. If accessible β-hydrogens are present on R (as in **3** and **4**), equal amounts of alkane and alkene are formed through a β-hydrogen abstraction pathway. In the case of **4**, an additional pathway involving Mo-R bond homolysis accounts for 10% of the products formed. When β-hydrogens are absent from R (as in **1**, **2**, and **6**), the free radical, R$^\bullet$, formed by Mo-R bond homolysis is the predominant product. However, in every case there is an additional minor pathway for the formation of the alkane, RH, that involves α-hydrogen abstraction from the neighboring hydrocarbyl group. Because of the expected low stability of the primary neopentyl radical, the α-hydrogen abstraction pathway, rather than Mo-R bond homolysis, predominates in the decomposition of **5**. The reaction of the $L_2Mo(O)_2R_2$ complexes with O_2 appears to proceed almost exclusively through the intermediacy of the free radical, R$^\bullet$. In inert solvents, the principal organic product is the corresponding aldehyde, and the role of O_2 in its formation from $L_2Mo(O)_2R_2$ is 2-fold: (a) O_2 promotes the homolysis of the Mo-R bond to form R$^\bullet$, and (b) O_2 traps the resultant radical to yield the aldehyde. Labeling studies indicated that O_2, rather than the Mo=O group, was the predominant source of oxygen for the aldehydes. Mechanistic implications of our observations for the heterogeneous oxidation of alkanes and alkenes by Mo(VI)- and V(V)-oxo species are discussed.

MoO_3 and V_2O_5, either alone or in combination with other acidic oxides, catalyze a number of selective oxidations of alkenes and alkanes.[1] Many of these are of commercial interest, such as the oxidation of propylene to acrolein (eq 1) for the remarkable conversion of butane to maleic anhydride (eq 2). A salient feature of these processes is the rate-limiting direct interaction of the substrate with the metal-oxo species.[1a,d,e] For propylene oxidation, the initial formation of a symmetrical allyl intermediate has been established.[2] Moreover, experiments with $^{18}O_2$ and ^{18}O-labeled catalysts have revealed that the source of oxygen for acrolein is adsorbed or free O_2 at lower reaction temperatures and the metal-oxo group at higher temperatures.[3] Thus, the general features of these oxidations indicate that an intermediate alkyl (or allyl) species is formed initially and that this is followed by oxygen transfer from either O_2 or a metal-oxo species. In order to gain a detailed understanding of the latter step, i.e., the conversion of the metal-bound hydrocarbyl group to the corresponding oxidized organic products, we have initiated an examination of the chemistry of Mo(VI) oxo alkyl complexes.[4] As detailed blow, our results allow us to



(1) Reviews: (a) Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55. (b) Hodnett, B. K. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 373. (c) Cullis, C. F.; Hucknall, D. J. *Catalysis* **1982**, *5*, 273. (d) Keulks, G. W.; Krenzke, L. D.; Notermann, T. M. *Adv. Catal.* **1978**, *27*, 183. (e) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; Chapter 6.

(2) (a) Adams, C. R.; Jennings, T. J. *J. Catal.* **1964**, *3*, 549; **1963**, *2*, 63. (b) McCain, C. C.; Gough, G.; Godin, G. W. *Nature* **1963**, *198*, 989.

(3) Sancier, K. M.; Wentrcek, P. R.; Wise, H. *J. Catal.* **1975**, *39*, 141.

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delineate (a) the anaerobic and aerobic decomposition pathways for the cleavage of the Mo–hydrocarbyl bond and (b) the role of O_2 in the latter decomposition.

Results

Synthesis and General Properties. The molybdenum(VI) compounds, $L_2Mo(O)_2R_2$ [L_2 = 4,4′-dimethyl-2,2′-dipyridyl, R = CH_2Ph, **1**; $CH_2C_6H_4Me$-*p*, **2**; $(CH_2)_4CH{:}CH_2$, **3**; CH_2CHMe_2, **4**; CH_2CMe_3, **5**; CH_2CMe_2Ph, **6**] were prepared by the action of the corresponding Grignard reagents on $L_2Mo(O)_2Br_2$, followed by aerobic oxidation of the resultant reaction mixture (eq 3). A similar prep-

$$L_2Mo(O)_2Br_2 \xrightarrow[(2)\ O_2/H_2O,\ 25\ °C]{(1)\ 2RMgX/THF,\ -78\ °C} L_2Mo(O)_2R_2 \quad (3)$$

arative pathway had been previously reported for the synthesis of the dipyridyl analogues of these compounds,[5] although the specific procedures described were generally unsuccessful for the compounds reported herein. The 4,4′-dimethyl-2,2′-dipyridyl complexes were chosen for the present study because of their enhanced solubility when compared to their unsubstituted dipyridyl analogues.

The success of the synthetic procedure was found to be very dependent on the experimental details. This appears to be due to the differences in air and moisture sensitivities of the products and the reaction intermediates when they are in solution and in the solid phase. We have found the following procedure to be reliable. When 2 equiv in a Grignard reagent was added to a suspension of $L_2Mo(O)_2Br_2$ in THF at −78 °C under an inert atmosphere and then the resultant mixture was allowed to warm up to 25 °C, a black solution was formed. Removal of the solvent by vacuum transfer resulted in a black residue. The residue was crushed into a powder and added to a large volume of water and stirred for 3 days, while freely exposed to air. During this period, the suspension turned from black to yellow or tan. The solid was collected, washed with water, and then dried under vacuum. Afterwards, the solid was washed with petroleum ether to remove the organic coupling product that was invariably formed from the Grignard reagent. The solid was then extracted with THF and filtered under an inert atmosphere to leave a gray residue and a brown filtrate. The filtrate was then cooled to −78 °C, and the yellow or orange solid that was formed was collected. Yields were generally in the range 15–30%. The reason for the especially low yield of **1** is not obvious. The use of 1 equiv of the Grignard reagent resulted in a lowered yield. Likewise, 3 equiv of the Grignard reagent gave reduced yields, and 4 equiv resulted in failure.

Compounds **1** and **2** are orange, while the dialkyl complexes, **3–6**, are yellow. All are soluble in chlorinated hydrocarbons, THF, diglyme, and aromatic hydrocarbons. They are insoluble in alkanes, diethyl ether, and water. All of the complexes are air-stable as solids but decompose at varying rates in solution in the presence of oxygen.

The ^1H NMR spectra of **1–6** show four absorptions, due to the coordinated 4,4′-dimethyl-2,2′-dipyridyl ligand. The methyl singlet in the complexes is shifted upfield compared to that in the free ligand (1.65–1.80 from 1.90 ppm). The doublet arising from the protons closest to the nitrogens (H6,H6′) is shifted downfield from 8.51 to 9.11–9.67 ppm upon coordination. Indeed, the observation of resonances in this region may be considered as strong evidence for the presence of a coordinated dimethyldipyridyl moiety. The other aromatic proton absorptions are shifted from 8.70 to 6.77–7.33 ppm (H3, H3′) and 6.61 to 6.28–6.50 ppm (H5, H5′). The coordinated hydrocarbyl group in these complexes exhibits the appropriate resonances in the ^1H and ^{13}C NMR spectra. All of the NMR spectra show one set of absorptions arising from equivalent hydrocarbyl groups and another set arising from a dimethyldipyridyl ligand in a bilaterally symmetric coordination environment. This observation may be explained by an octahedral coordination geometry wherein the two oxo ligands and the hydrocarbyl ligands are cis and trans, respectively. Such a structure has been demonstrated by single-crystal X-ray diffraction studies on several related compounds.[5]

The IR spectra of all of the dioxo compounds show at least two bands in the 860–930-cm^{-1} region. These may be attributed to the Mo=O bonds.

Decomposition Reactions. Compounds **1–6** decomposed in solution under an inert atmosphere at varying rates. **1** and **2** decomposed at 25 °C over a period of several days, while the alkyl complexes, **3–6**, required extensive heating to decompose on the same time scale. As the decomposition progressed, a brown, insoluble precipitate formed whose major component was presumably the oxides of molybdenum. The soluble products were free 4,4′-dimethyl-2,2′-dipyridyl and organic compounds that arose from the hydrocarbyl ligands. The yields of hydrocarbons that were obtained were essentially quantitative, based upon the amount of metal complex. After approximately 20% decomposition, the reaction mixture became too heterogeneous to follow by NMR spectroscopy, and the organic products were most conveniently analyzed by GC techniques. The course, or rates, of the reaction was not appreciably affected by the nature of the solvent. The decomposition was observed in CH_2Cl_2, $CHCl_3$, THF, diglyme, MeCN, PhH, and PhMe.

Compounds **1** and **2** thermally decomposed to a mixture of RH and RR (R = CH_2Ph, **1**; $CH_2C_6H_4Me$-*p*, **2**). For example, the decomposition of **2** in toluene at 110 °C led to the formation of 22% *p*-xylene and 78% 1,2-di-*p*-tolylethane (dixylyl) by mass (33% and 67%, respectively, by mole).

When **2** was refluxed in toluene-d_8 for 3 days to ensure completion of the decomposition, the xylene present showed only a trace, 0.64%, of deuterium incorporation. Clearly, the molybdenum compound, rather than the solvent, was the source of the hydrogen atom. To ascertain the origin of this hydrogen atom, compounds $L_2Mo(O)_2(CD_2C_6H_4CH_3\text{-}p)_2$ and $L_2Mo(O)_2(CH_2C_6H_4CD_3\text{-}p)_2$ were synthesized. Upon decomposition in refluxing toluene-d_0, both produced xylene-α,α,α-d_3 in approximately 100% D. Thus, neither the methyl group of the xylyl ligand nor the dimethyldipyridyl ligand was the source of the hydrogen. Rather, xylene was formed through α-hydrogen abstraction from the methylene group of the second xylyl ligand (eq 4). While there is a trans arrangement of the hydrocarbyl

$$L_2Mo(O)_2(CH_2R')_2 \xrightarrow{\text{major}} R'CH_2^{\bullet} \longrightarrow \text{disproportionation and dimerization}$$
$$L_2Mo(O)_2(CH_2R')_2 \xrightarrow[\alpha\text{-H abs.}]{\text{minor}} R'CH_3 + [L_2Mo(O)_2(CHR')] \longrightarrow \text{decomposition} \quad (4)$$

(4) Reviews of previous work on metal–oxoalkyl complexes: (a) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.

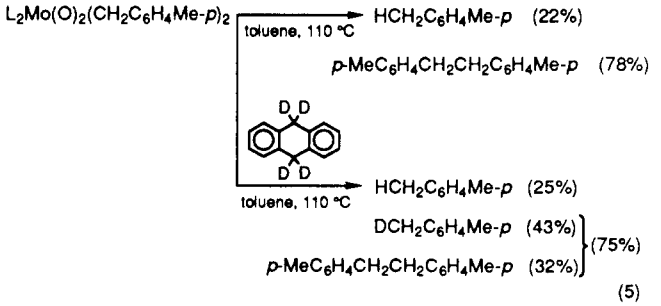
(5) Recent references: (a) Schrauzer, G. N.; Zhang, X.; Liu, N. H.; Schlemper, E. O. *Organometallics* **1988**, *7*, 279. (b) Schrauzer, G. N.; Schlemper, E. O.; Liu, N. H.; Wang, Q.; Rubin, K.; Zhang, X.; Long, X.; Chin, C. S. *Organometallics* **1986**, *5*, 2452. (c) Schrauzer, G. N.; Hughes, L. A.; Schlemper, E. O.; Ross, F.; Ross, D. *Organometallics* **1983**, *2*, 1163. References 4b and 4c contain very brief reports concerning the anaerobic and aerobic decompositions of such compounds. However, no mechanistic information if given.

ligands in the starting compound, the dissociation of the 4,4′-dimethyl-2,2′-dipyridyl ligand would allow a trans–cis isomerization, thus making the α-hydrogen abstraction step possible. Note that the 4,4′-dimethyl-2,2′-dipyridyl ligand is released from the metal in the course of the decomposition.

The formation of RH should logically be accompanied by the simultaneous formation of a molybdenum–carbene species (eq 4). Since RH and RR were the only observed decomposition products, the hydrocarbyl group that underwent α-hydrogen abstraction must end up as a part of the insoluble decomposition product. Attempts were made to detect organic products that may form through the reaction of the metal–carbene species. Reactions that have been observed for carbene complexes are insertion into C–H bonds, coupling to form an alkene, and the formation of cyclopropanes with alkenes.[6] Solutions of **2** refluxed in toluene when analyzed by GC–MS techniques showed no traces of 1-*p*-tolyl-2-phenylethylene, which would be the product of a *p*-tolylcarbene inserting into a benzylic C–H bond of toluene. Neither were isomers of 1,2-di-*p*-tolylethylene formed—the expected carbene coupling products. In an attempt to observe cyclopropanation, **2** was refluxed in toluene in the presence of a large excess of 1,1-diphenylethylene. 1,1-Diphenyl-2-*p*-tolylcyclopropane was not detected in the products. These failures may be due to the insolubility or the unreactivity of the proposed molybdenum–carbene species.

RR formed in the thermal decompositions of **1** and **2** must have originated through a mechanism different from that observed for RH. To determine whether this product was formed through a radical mechanism, attempts were made to trap the intermediate radical, R•. As noted above, when **2** was decomposed in toluene-d_8, very little (0.64%) deuterium was incorporated into the *p*-xylene formed. Toluene-d_8 likely fails as a deuterium source because the benzyl radical that would result is somewhat less stable than a xylyl radical. Hence, deuterium donors that would form very stable radicals upon abstraction were used subsequently. When **2** was decomposed in toluene in the presence of a large excess of Ph_3CD, there was 2.3% incorporation of deuterium in the xylene produced. In contrast, a similar experiment with 9,10-dihydroanthracene-*9,9,10,10*-d_4 replacing Ph_3CD resulted in the formation of *p*-xylene-d_1 58% D. 9,10-Dihydroanthracene-d_4 is a significantly more efficient deuterium donor than Ph_3CD, presumably because the deuterium atom(s) is more accessible in the former compound.

When **2** was decomposed in toluene in the presence of a large excess of 9,10-dihydroanthracene-*9,9,10,10*-d_4, 25% *p*-xylene-d_0, 43% *p*-xylene-α-d_1, and 32% dixylyl by mass were produced (eq 5). In the absence of 9,10-dihydroanthracene, the products were 22% *p*-xylene-d_0 and 78% dixylyl by mass. *These data show that the amount of p-xylene-d_1 produced in the presence of a deuterium donor was almost exactly equal to the amount of xylyl radicals diverted from the formation of dixylyl.*



(5)

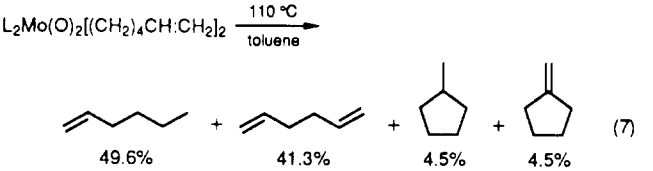
An equimolar ratio of **1** and **2** was decomposed at 64 °C in THF over a period of 6 days to ensure complete reaction. The products formed were dibenzyl, 8%; benzylxylyl (1-*p*-tolyl-2-phenylethane), 44%; and dixylyl, 48%. When the solution concentration of the molybdenum complexes was increased 100-fold (from 2.1×10^{-3} to 2.2×10^{-1} M), the products were dibenzyl, 9%; benzylxylyl, 46%; and dixylyl, 44%. That the amount of the crossover product, benzylxylyl, does not increase with increasing concentration of the molybdenum complexes appears to rule out an additional parallel bimolecular mechanism for its formation. Rather, the available evidence indicates that RR is formed by the dimerization of the radical, R•, that is freely released into solution (eq 4).

We have assumed that two distinct pathways are responsible for the formation of RH and RR, respectively (eq 4). However, it may be argued that both products arise through a common pathway involving Mo–R bond homolysis followed by competition between R• dimerization, α-hydrogen abstraction, and escape from the solvent cage. However, if R• does abstract a hydrogen from a second hydrocarbyl group, then it is difficult to see why in the case of the *p*-xylyl complex, **2**, the hydrogens on the more accessible *p*-Me group are not attacked.

With the dialkyl complexes, **3**–**6**, the anaerobic decomposition pathway chosen depended on whether accessible β-hydrogens were present on the alkyl group. If β-hydrogens were present (as in **3** and **4**), equal amounts of alkane and alkene were formed through the pathway outlined in eq 6. For example, the decomposition of **4** in

$$L_2Mo(O)_2(CH_2CHR'_2)_2 \xrightarrow[-R'_2C=CH_2]{\beta\text{-H abs.}} [L_2Mo(O)_2(H)(CH_2CHR'_2)] \xrightarrow{\text{red elim.}} R'_2CHCH_3 \quad (6)$$

refluxing toluene-d_8 resulted in the formation of 51% isobutane and 49% isobutylene. The same product distribution was also obtained when the decomposition was carried out in the presence of an excess of 9,10-dihydroanthracene. The decomposition of **3** in toluene-d_8 yielded 1-hexane, 49.6%; 1,5-hexadiene, 41.3%; methylcyclopentane, 4.5%; and methylenecyclopentane, 4.5% (eq 7).



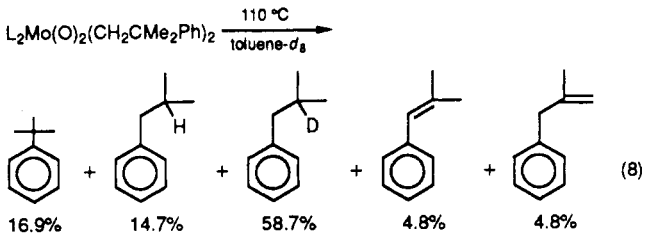
(7)

The formation of the latter two products supports an additional small contribution from a homolysis pathway leading to the formation of the 5-hexenyl free radical. This radical is known to rearrange rapidly to the corresponding cyclopentylmethyl radical ($k = 1.0 \times 10^5$ s^{-1}).[7]

As with compounds **1** and **2**, the decomposition of the dialkyl complex, **6**, which lacks β-hydrogens, led primarily to the formation of radicals. Upon refluxing in toluene-d_8, **6** gave the following products: *tert*-butylbenzene-d_0, 16.9%; isobutylbenzene-d_0, 14.7%; isobutylbenzene-d_1, 58.7%; 2-methyl-1-phenylpropene, 4.8%; and 2-methyl-3-phenylpropene, 4.8% (eq 8). All but the first product clearly arose from the arrangement of the neophyl radical,

(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 119, 783.

(7) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.



(8)

$PhMe_2CCH_2^{\bullet}$, by 1,2-phenyl migration (k = 59 s^{-1}).[7] Following rearrangement, the resultant radical either underwent disproportionation to isobutylbenzene-d_0 and the alkenes or, preferably, abstracted a deuterium from the solvent to yield isobutylbenzene-d_1. The lack of deuterium incorporation into *tert*-butylbenzene would appear to rule out the participation of the unrearranged neophyl radical. As with **1** and **2**, *tert*-butylbenzene may instead arise by α-hydrogen abstraction from a neighboring neophyl ligand (see eq 4). Again, no reaction product of the resultant molybdenum–carbene species was detected.

The dineopentyl complex, **5**, which also possesses no β-hydrogens, gave neopentane-d_0 as the only organic product after weeks of reflux in toluene-d_8. This is not unexpected for a member of the class of compounds whose thermolytic decomposition is dominated by radical reactions and whose alkyl group forms a primary radical of low stability. Presumably, the α-hydrogen abstraction pathway is the only favorable decomposition mode for **5**. While the 1,2-phenyl shift occurs for both the neophyl cation and the radical, 1,2-methyl migration occurs only for the neopentyl cation and not for the corresponding radical.[8] Hence, the observation of neopentane as the sole decomposition product for **5** also rules out a role for carbocations in these decompositions.

Solutions of the complexes **1** and **2**, when freely exposed to oxygen at 25 °C, gradually discolored over a period of hours and deposited a white precipitate. In this way, mixtures uncontaminated with the products of the thermal decomposition reaction could be obtained. The reactions of the dialkyl complexes, **3–6**, with oxygen were more sluggish, and the products obtained were always contaminated with thermal decomposition products. Precipitates that were formed were brown or gray. Mechanistic studies of aerobic decompositions were generally conducted in THF solution to ensure sufficient solubility of the compounds at 25 °C.

The decomposition of **1** and **2** in THF in an oxygen atmosphere resulted in the formation of the corresponding aldehyde and free 4,4′-dimethyl-dipyridyl as the only organic products (eq 9). The white, insoluble product

$$L_2Mo(O)_2(CH_2R')_2 \xrightarrow{O_2} R'CHO \qquad (9)$$

presumably consisted of oxides of molybdenum. In the case of **2**, *p*-methylbenzaldehyde was formed. Use of *p*-$MeC_6H_4CD_2$ as the hydrocarbyl ligand resulted in the exclusive formation of *p*-methylbenzaldehyde-d_1, labeled at the aldehydic hydrogen. Oxygen exposure of equimolar amounts of $L_2Mo(O)_2(CH_2C_6H_4Me\text{-}p)_2$ and $L_2Mo(O)_2(CD_2C_6H_4Me\text{-}p)_2$ in THF for a period long enough for 3% reaction to occur generated *p*-methylbenzaldehyde-d_0 and -d_1 in a 40:60 ratio. This product ratio amounts to an inverse deuterium isotope effect (k_H/k_D = 0.67). The aerobic decomposition of **2** in $CHCl_3$ resulted in the formation of 15% α-chloro-*p*-xylene, along with *p*-methylbenzaldehyde. The former product was presumably formed by chlorine abstraction from the solvent by free xylyl radical.

When **2** was allowed to decompose in THF under O_2 96% ^{18}O, *p*-methylbenzaldehyde 86% ^{18}O was obtained. The reaction was stopped at approximately 90% completion, and unreacted **2** was isolated from the reaction mixture. This sample of **2** was analyzed by mass spectroscopy, using the fast atom bombardment technique (MS-FAB), and was found to contain approximately 10% ^{18}O. This indicated that the exchange of the oxo ligands with external O_2 was slow under the reaction conditions and that >90% of the oxygen in *p*-methylbenzaldehyde was derived from external O_2, rather than the Mo=O group.

The aerobic decomposition of **3** resulted in a mixture of organic products consisting of the thermal decomposition products noted above, as well as cyclopentylformaldehyde. The latter product was clearly formed through cyclization of the 5-hexenyl radical prior to its reaction with oxygen. Complexes **4–6**, when allowed to sit under an oxygen atmosphere for several months, were found to yield small quantities of isobutyraldehyde, trimethylacetaldehyde, and 2-methyl-2-phenylpropanaldehyde, respectively.

In summary, the data on aerobic oxidations appear to indicate that the aldehyde is formed by the reaction of the free radical, R•, with external O_2 in solution. The formation of free radicals during aerobic oxidation rules out an alternative mechanism involving the following series of steps: (a) the conversion of the alkyl group to alkoxy ligand by interaction with a metal–peroxy species[9] and (b) the β-hydrogen abstraction from the resultant alkoxy ligand to generate the aldehyde.[10] Curiously, qualitative rate measurements for **2** revealed that the reaction with O_2 proceeded significantly faster and was essentially complete in 24 h, while under the same conditions, the anaerobic decomposition was only approximately 20% complete *although both reactions involve the intermediacy of the p-xylyl radical.*

Discussion

The anaerobic decomposition mode chosen by a given $L_2Mo(O)_2R_2$ complex is a sensitive function of the hydrocarbyl group, R. If accessible β-hydrogens are present on R (as in **3** and **4**), equal amounts of alkane and alkene are formed through a β-hydrogen abstraction pathway (eq 6). In the case of **4**, an additional pathway involving Mo–R bond homolysis accounts for 10% of the products formed. When β-hydrogens are absent from R (as in **1**, **2**, and **6**), the free radical, R•, formed by Mo–R bond homolysis is the predominant product (eq 4). However, in every case there is an additional minor pathway for the formation of the alkane, RH, that involves α-hydrogen abstraction from the neighboring hydrocarbyl group (eq 4). Because of the expected low stability of the primary neopentyl radical, the α-hydrogen abstraction pathway, rather than Mo–R bond homolysis, predominates in the decomposition of **5**.

The reaction of the $L_2Mo(O)_2R_2$ complexes with O_2 appears to proceed almost exclusively through the intermediacy of the free radical, R•. In inert solvents, the principal organic product is the corresponding aldehyde (eq 9) and the role of O_2 in its formation from $L_2Mo(O)_2R_2$ is *2-fold*:

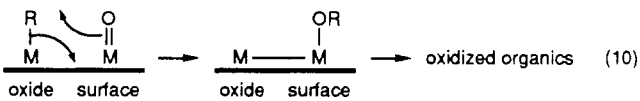
(8) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; 942.

(9) Recent reports on the formation of MOR from MR + O_2: Bottomley, F.; Magill, C. P.; White, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3070. (b) Parkin, G.; Bercaw, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 391. (c) van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 8254. (d) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424.

(10) Review: Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(a) O_2 promotes the homolysis of the Mo–R bond to form R•, and (b) O_2 traps the resultant radical to yield the aldehyde.[11] In support of the first step, the aerobic decomposition of **2** was found to proceed significantly faster than the anaerobic decomposition, although both reactions involve the intermediacy of the *p*-xylyl radical. In principle, other oxidants should also be able to promote the homolysis of the Mo–R bond and, indeed, the addition of $Cp_2Fe^+PF_6^-$ to **2** at 25 °C in MeCN resulted in the rapid formation of the radical-derived products, xylene and dixylyl. At first glance, the homolytic cleavage of metal–carbon bonds in a d^0-metal–hydrocarbyl complex promoted by oxidation may be surprising. However, Jordan has demonstrated similar oxidation-induced metal–carbon bond cleavage in d^0-zirconium complexes.[12] Presumably, oxidation weakens the metal–carbon bonds by removal of electrons from the σ-bonding orbitals.

The dual role of O_2 has important implications for the heterogeneous oxidation of alkenes and alkanes by Mo(VI)- and V(V)–oxo species. Thus, in the heterogeneous oxidations, it is possible that an alkyl (or allyl) radical is formed by O_2-promoted homolysis of the initially formed metal–alkyl (or allyl) bond. The resultant organic radical is then captured either by adsorbed or free O_2 at lower temperatures or by a lattice oxygen at higher temperatures. While the allyl radical has been detected in propylene oxidations,[1d,13] the oxidation-induced homolysis of metal–carbon bonds has never been invoked as a step in these catalytic reactions. This is surprising in view of numerous examples in the organometallic literature, indicating that metal–alkyl bond homolysis can be promoted by oxidation.[14] Moreover, our observation of enhanced rate for metal–alkyl bond homolysis in the presence of O_2 parallels observations[13] of increased concentration of surface-generated radicals in the presence of O_2 for reactions of hydrocarbons with metal oxides. The alternative to the stepwise transfer of oxygen to the metal-bound alkyl (or allyl) group postulated above would involve a concerted uni- or bimolecular process (eq 10). However, such a transfer of a metal-bound hydrocarbyl fragment to a metal–oxo group has never been directly observed.[15]



(10)

Experimental Section

General Procedures. Reactions involving Grignard reagents, moisture-sensitive synthetic reagents, or $L_2Mo(O)_2R_2$ complexes were handled under a dry N_2 atmosphere by using Schlenk techniques or in a Vacuum Atmospheres glovebox equipped with a Dri-train. Occasions where air exposure is involved as a preparative step in the synthesis of $L_2Mo(O)_2R_2$ complexes are specified below. Tetrahydrofuran, diethyl ether, toluene, and diglyme were dried by reflux over sodium benzophenone ketyl. Hexane was dried by reflux over CaH_2. Chloroform-d_1 was dried by reflux over P_2O_5. Benzene-d_6, toluene-d_8, and *p*-xylene-d_{10} were dried by reflux over Na–K alloy. $MoL_2(CO)_4$,[16] *p*-$MeC_6H_4CD_2Cl$,[17] *p*-$CD_3C_6H_4CO_2H$,[18] 1-phenyl-2-*p*-tolylethane,[19] Ph_3CD,[20] methyl 2-bromobenzoate,[21] benzylmagnesium chloride,[22] *p*-xylylmagnesium chloride,[23] $CH_2{:}CH(CH_2)_4MgCl$,[24] Me_2CHCH_2MgCl,[25] Me_3CCH_2MgBr,[26] and Me_2PhCCH_2MgCl[27] were prepared according to literature methods. Concentrations of Grignard reagents were determined by titration with 0.1 N aqueous HCl followed by backtitration with 0.1 N aqueous NaOH. 1,2-Di-*p*-tolylethane, 1,2-di-*p*-tolylethane-*ethylene*-d_4, 1,2-di-*p*-tolylethane-*methyl*-d_6, and dineophyl were recovered from petroleum ether washings of reaction mixtures obtained during the preparations of the $L_2Mo(O)_2R_2$ complexes described below. *p*-Xylene-α-d_1 was prepared by quenching *p*-xylylmagnesium chloride in THF with D_2O, followed by extraction and fractional distillation of the organic products. *p*-Xylene-α,α-d_2 and *p*-xylene-α,α,α-d_3 were similarly prepared by quenching *p*-$MeC_6H_4CD_2MgCl$ in THF with 10% aqueous HCl and D_2O, respectively. *p*-Xylene-$\alpha,\alpha,\alpha,\alpha'$-$d_4$ was prepared in a similar manner by quenching *p*-$CD_3C_6H_4CH_2MgCl$ in THF with D_2O. $LiAlH_4$, $LiAlD_4$, *n*-BuLi (1.6 M solution in hexane), and bromine were obtained from Aldrich. Thionyl chloride was obtained from Baker. MoO_2Cl_2 was purchased from Strem and twice sublimed. 4,4′-Dimethyl-2,2′-dipyridyl was obtained from Aldrich and twice sublimed.

Analytical Instrumentation. IR spectra were recorded on a Perkin-Elmer Model 281B spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Brüker AM300 FT-NMR spectrometer. UV–vis spectra were recorded with a Hewlett-Packard Model 8450A UV–vis spectrometer. Routine gas chromatograms were conducted with a Varian 3700 gas chromatograph equipped with a flame ionization detector using a 10 ft × $^1/_8$ in. stainless steel column packed with 10% SP-2100 on 80/100-mesh Supelcoport using N_2 as the carrier gas. Gas chromatograms of the decomposition products of **4** (isobutane and isobutylene) were taken on the same instrument using a 4 m × $^1/_8$ in. stainles steel column packed with 20% ethylene glycol/silver nitrate on 45/60-mesh Chromosorb PNAW. GC–mass spectra were obtained with a Kratos MS-25 GC–mass spectrometer equipped with a 25-m J & W DB5 capillary column. When CI spectra were observed with this instrument, isobutylene was used as the reagent gas. Fast atom bombardment mass spectra (MS-FAB) were taken with a Kratos MS-50 spectrometer using a 3:1 18-crown-6/tetraglyme matrix for –FAB and *p*-nitrophenyl ether matrix for +FAB.

Synthetic Procedures. 9,10-Dihydroanthracene-*9,9,10,10*-d_4. A solution of 69.81 g (0.325 mol) of methyl 2-bromobenzoate in 150 mL of THF was added to 10.31 g (0.246 mol) of $LiAlD_4$ in 150 mL of THF dropwise while stirring over 2 h. The reaction mixture was refluxed for 3 h and then allowed to stir overnight. One-hundred milliliters 10% aqueous NaOH was added to form a white precipitate, after which 20 mL of cold 25% aqueous H_2SO_4 was added to dissolve the precipitate. THF was removed by rotary evaporation, and diethyl ether was added to the residue. The solution was washed exhaustively with saturated aqueous $NaHCO_3$ until gas evolution ceased and then with distilled water. The ethereal phase was dried with anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation to leave 41.49 g (0.220 mol, 89.4% yield) of white crystalline *o*-$C_6H_4(Br)CD_2OH$. ^1H NMR ($CDCl_3$) (ppm): 2.45 (s, 1 H), 7.14 (td, 1 H, J_{H-H} = 7.6, J_{H-H} = 1.8 Hz), 7.31 (m, 1 H), 7.44 (dd, 1 H, J_{H-H} = 8.6, J_{H-H} = 1.8 Hz), 7.52 (dd, 1 H, J_{H-H} = 7.9, J_{H-H} = 1.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 64.15 (5-plet, J_{D-C} =

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22.2 Hz), 122.45, 127.58, 128.79, 129.00, 132.46, 139.56. IR (KBr pellet): 2051, 2085, 2098, 2116, 2205, 3210, 3310 cm^{-1}.

Fifty milliliters (0.696 mol) of thionyl chloride was added dropwise to 41.49 g (0.220 mol) of o-$C_6H_4(Br)CD_2OH$ in 300 mL of diethyl ether over 20 min and was allowed to stir overnight. Solvent and excess thionyl chloride were distilled off at ambient pressure, while protecting the reaction mixture from atmospheric moisture with a Drierite drying tube. Residual liquid was fractionally distilled under reduced pressure through an 18-cm Vigreux column to obtain 30.11 g (0.145 mol, 66.1% yield) of white transparent liquid o-$C_6H_4(Br)CD_2Cl$ (bp 120–121 °C/35 Torr). ^1H NMR ($CDCl_3$) (ppm): 7.17 (td, 1 H, J_{H-H} = 1.8, J_{H-H} = 7.8 Hz), 7.30 (td, 1 H, J_{H-H} = 1.0, J_{H-H} = 7.3 Hz), 7.46 (dd, 1 H, J_{H-H} = 1.7, J_{H-H} = 7.6 Hz), 7.57 (d, 1 H, J_{H-H} = 8.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 45.62 (5-plet, J_{D-C} = 23.2 Hz), 124.09, 127.83, 130.05, 130.86, 133.10, 136.54.

n-BuLi (90.7 mL, 6 M) in hexane was added dropwise over 20 min to a solution of 30.11 g (0.145 mol) of o-$C_6H_4(Br)CD_2Cl$ in 940 mL of THF/290 mL of hexane cooled in an acetone slush bath. The reaction mixture was allowed to come to room temperature and stir for 3 h and was then quenched with 25 mL of distilled water. Solvent was then removed by rotary evaporation, and 100 mL of diethyl ether was added to the residue. It was washed with 7 × 100 mL of distilled water, after which the ethereal phase was dried with anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to leave a slushy residue, which was recrystallized from petroleum ether to yield 6.05 g (32.8 mmol, 45.2% yield) of white crystalline 9,10-dihydroanthracene-*9,9,10,10-d_4*. ^1H NMR ($CDCl_3$) (ppm): 7.19 (m, 4 H), 7.28 (m, 4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 35.43 (5-plet, J_{D-C} = 19.8 Hz), 126.01, 127.36, 136.62. MS(EI): m/e (intensity) 50 (17), 51 (28), 52 (25), 53 (15), 64 (12), 78 (37), 84 (18), 90 (25), 91 (58), 92 (29), 168 (14), 180 (15), 181 (29), 182 (50), 183 (79), 184 (100), 185 (15). IR (KBr pellet): 2046, 2074, 2100, 2114, 2194, 2207 cm^{-1}.

p-$CD_3C_6H_4CH_2OH$. p-$CD_3C_6H_4CO_2H$ (31.96 g, 0.231 mol) was suspended in 450 mL of diethyl ether and added to 8.78 g of $LiAlH_4$ suspended in 400 mL of diethyl ether over 1 h while stirring and then refluxed for 3 h. One-hundred milliliters of 10% aqueous NaOH was added to the reaction mixture slowly, and then 300 mL of 25% aqueous H_2SO_4 was added to dissolve the precipitate formed. The mixture was poured into a 1-L separatory funnel, and the ethereal phase was removed. The aqueous phase was extracted with 2 × 200 mL of diethyl ether. All ethereal fractions were combined and washed with 2 × 150-mL portions of saturated aqueous $NaHCO_3$ and 150 mL of distilled water. Upon drying with anhydrous Na_2SO_4 and removal of solvent by rotary evaporation, 19.84 g (0.160 mol, 69.1% yield) of white crystalline solid was obtained. ^1H NMR ($CDCl_3$) (ppm): 3.32 (s, 1 H), 4.35 (s, 2 H), 6.98 (d, 2 H, J_{H-H} = 8.0 Hz), 7.07 (d, 2 H, J_{H-H} = 8.4 Hz). $^{13}C\{^1H\}$ ($CDCl_3$) (ppm): 65.08, 127.08, 129.15, 137.17, 137.80. IR (KBr pellet): 2053, 2127, 2221, 3305 cm^{-1}.

p-$CD_3C_6H_4CH_2Cl$. A solution of 60 mL of thionyl chloride in 60 mL of diethyl ether was added dropwise to 19.84 g (0.160 mol) of p-$CD_3C_6H_4CH_2OH$ in 100 mL of diethyl ether while stirring at 0 °C. The resultant mixture was allowed to stir overnight at room temperature, and then the solvent was distilled away at ambient pressure while being protected from atmospheric moisture with a Drierite drying tube. Residual liquid was fractionated with an 18-cm Vigreux column at reduced pressure. Transparent liquid (12.8 mL, 94.8 mmol, 59.3% yield, bp 86 °C/35 Torr) was obtained. ^1H NMR ($CDCl_3$) (ppm): 4.55 (s, 2 H), 7.15 (d, 2 H, J_{H-H} = 8.1 Hz), 7.26 (d, 2 H, J_{H-H} = 8.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 46.22, 128.50, 129.36, 134.52, 138.13.

p-$CD_3C_6H_4CH_2MgCl$. p-$CD_3C_6H_4CH_2Cl$ (12.8 mL, 94.8 mmol) dissolved in 100 mL of THF was added slowly to 2.31 g of magnesium turnings stirred in 30 mL of THF over 20 min. The mixture was stirred at room temperature for 45 min and then refluxed for 20 min. The concentration of Grignard reagent was determined by titration with 0.1 M aqueous HCl, followed by backtitration with 0.1 M aqueous NaOH. p-$CD_3C_6H_4CH_2MgCl$ (130 mL, 0.634 M) in THF (8.24 mmol, 86.9% yield) was obtained.

p-$MeC_6H_4CD_2MgCl$. p-$MeC_6H_4CD_2Cl$ (13.94 g, 97.8 mmol) dissolved in 180 mL of THF was reacted with 2.38 g of magnesium turnings in 20 mL of tetrahydrofuran as above. p-$MeC_6H_4CD_2MgCl$ (180 mL, 0.506 M) in THF (91.1 mmol, 93.1% yield) was obtained.

$L_2Mo(O)_2Br_2$ (L = 4,4′-Dimethyl-2,2′-dipyridyl). Ten grams (25.5 mmol) of $MoL_2(CO)_4$ was dissolved in 1000 mL of methylene chloride/1000 mL of absolute ethanol in a 4-L Erlenmeyer flask open to air. Seven milliliters (136 mmol) of bromine was added in one portion while stirring. Vigorous gas evolution occurred immediately, and the color lightened briefly and then turned to a dark red brown. After 10 min of stirring, gas evolution ceased, and the reaction mixture was warmed to reflux temperature for 20 min, during which the solution lightened and a precipitate formed. Insoluble yellow–orange product (10.81 g, 22.9 mmol, 89.9% yield) was collected on a Büchner funnel after cooling. IR (KBr pellet): 878, 910 cm^{-1}.

$L_2Mo(O)_2(CH_2C_6H_4Me$-$p)_2$, 2. $L_2Mo(O)_2Br_2$ (10.51 g, 22.3 mmol) suspended in 40 mL of THF was stirred in an acetone slush bath under a dry nitrogen atmosphere. Eighty milliliters of 0.592 M (47.4 mmol) p-xylylmagnesium chloride in THF was added dropwise over 45 min. The reaction mixture was allowed to come to room temperature slowly, after which solvent was removed by vacuum transfer and the black residue was dried under dynamic high vacuum overnight. The residue was air-exposed and scraped into 1 L of distilled water in a large beaker and stirred for 3 days while exposed to air, during which a dirty yellow suspension formed. The solid was collected on a Büchner funnel and then dried under vacuum. The solid was then washed with 500 mL of petroleum ether in a 150-mL M-fritted Büchner funnel to free the residue of 1,2-di-p-tolylethane. The residue was extracted with 150 mL of THF under a dry nitrogen atmosphere and filtered through the funnel. The filtrate was placed in a recrystallizer with a 5-cm M-fritted disk and cooled in an acetone slush bath for 1.5 h. The product was collected, and the solvent was removed from the dark brown filtrate by vacuum transfer. The contents of the recrystallizer were dried under dynamic high vacuum overnight. Fine orange needles (2.25 g, 4.31 mmol, 19.3% yield) were obtained. ^1H NMR (C_6D_6) (ppm): 1.76 (s, 6 H), 2.02 (s, 6 H), 3.30 (s, 2 H), 6.26 (d, 4 H, J_{H-H} = 8.0 Hz), 6.31 (d, 2 H, J_{H-H} = 5.6 Hz), 6.45 (d, 4 H, J_{H-H} = 7.8 Hz), 6.87 (d, 2 H, J_{H-H} = 0.6 Hz), 9.26 (d, 2 H, J_{H-H} = 5.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 20.65, 21.21, 46.24, 121.61, 125.90, 127.40, 127.55, 131.60, 144.47, 148.82, 149.64, 150.58. IR (KBr pellet): 899, 913 cm^{-1}. Anal. Calcd for $C_{28}H_{30}N_2O_2Mo$: C, 64.44; H, 5.79. Found: C, 64.26; H, 5.83.

$L_2Mo(O)_2(CD_2C_6H_4Me$-$p)_2$. $L_2Mo(O)_2Br_2$ (10.10 g, 21.4 mmol) in 60 mL of THF was reacted as above with 84.6 mL of 0.506 M (42.8 mmol) p-$MeC_6H_4CD_2MgCl$ in THF. Fine orange needles (2.46 g, 4.67 mmol, 21.8% yield) were obtained. ^1H NMR (C_6D_6) (ppm): 1.75 (s, 6 H), 2.13 (s, 6 H), 6.26 (d, 4 H, J_{H-H} = 8.1 Hz), 6.30 (d, 2 H, J_{H-H} = 7.2 Hz), 6.45 (d, 4 H, J_{H-H} = 8.5 Hz), 6.86 (s, 2 H), 9.27 (d, 2 H, J_{H-H} = 5.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 20.58, 21.13, 45.45 (5-plet, J_{D-C} = 17.5 Hz), 121.67, 125.85, 127.34, 127.42, 131.54, 144.32, 148.74, 149.71, 150.38. IR (KBr pellet): 878, 898, 2104, 2174, 2192 cm^{-1}.

$L_2Mo(O)_2(CH_2C_6H_4CD_3$-$p)_2$. $L_2Mo(O)_2Br_2$ (10.02 g, 21.2 mmol) in 60 mL of THF was allowed to react as above with 66.9 mL of 0.634 M (42.4 mmol) p-$CD_3C_6H_4CH_2MgCl$ in THF. Fine orange needles (3.17 g, 6.00 mmol, 28.3% yield) were obtained. ^1H NMR (C_6D_6) (ppm): 1.74 (s, 6 H), 3.31 (s, 4 H), 6.26 (d, 4 H, J_{H-H} = 8.0 Hz), 6.29 (d, 2 H, J_{H-H} = 7.3 Hz), 6.44 (d, 4 H, J_{H-H} = 8.0 Hz), 6.86 (s, 2 H), 9.27 (d, 2 H, J_{H-H} = 5.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 19.69 (7-plet, J_{D-C} = 19.2 Hz), 21.09, 46.19, 121.68, 125.82, 127.30, 127.41, 131.40, 144.30, 148.70, 149.73, 150.29. IR (KBr pellet): 878, 896, 2008, 2084, 2160, 2185 cm^{-1}.

$L_2Mo(O)_2(CH_2Ph)_2$, 1. Ten grams (21.2 mmol) of $L_2Mo(O)_2Br_2$ in 30 mL of THF was allowed to react as above with 60.8 mL of 0.697 M (42.4 mmol) benzylmagnesium chloride in THF. A yellow solid (0.38 g, 0.77 μmol, 3.6% yield) was obtained. ^1H NMR (C_6D_6) (ppm): 1.72 (s, 6 H), 3.33 (s, 4 H), 6.27 (m, 6 H), 6.55 (m, 6 H), 6.80 (s, 2 H), 9.21 (d, 2 H, J_{H-H} = 5.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 21.26, 46.14, 121.62, 122.25, 126.16, 126.75, 127.60, 147.60, 148.74, 149.84, 150.58. IR (KBr pellet): 861, 873, 892 cm^{-1}.

$L_2Mo(O)_2(CH_2CHMe_2)_2$, 4. $L_2Mo(O)_2Br_2$ (10.19 g, 21.6 mmol) in 50 mL of THF was allowed to react as above with 51.6 mL of 0.837 M (43.2 mmol) Me_2CHCH_2MgCl in THF. A pale yellow solid (2.64 g, 6.19 mmol, 28.7% yield) was obtained. ^1H NMR (C_6D_6) (ppm): 1.33 (d, 12 H, J_{H-H} = 6.5 Hz), 1.43 (d, 4 H, J_{H-H} = 6.3 Hz), 1.71 (s, 6 H), 2.78 (7-plet, 2 H, J_{H-H} = 6.5 Hz), 6.41 (d, 2 H, J_{H-H} = 5.4 Hz), 7.06 (s, 2 H), 9.63 (d, 2 H, J_{H-H} = 5.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 21.46, 26.28, 33.86, 61.13, 122.74,

126.05, 149.04, 150.00, 150.66. IR (KBr pellet): 871, 898, 2840–2960 cm^{-1}. Anal. Calcd for $C_{20}H_{30}N_2O_2Mo$: C, 56.33; H, 7.09. Found: C, 56.09; H, 7.03.

$L_2Mo(O)_2(CH_2CMe_3)_2$, 5. $L_2Mo(O)_2Br_2$ (10.39 g, 22.0 mmol) in 50 mL of THF was allowed to react as above with 40.0 mL of 1.10 M (44.0 mmol) Me_3CCH_2MgBr in THF. A pale yellow solid (2.47 g, 5.44 mmol, 24.7% yield) was obtained. ^1H NMR (C_6D_6) (ppm): 1.48 (s, 22 H), 1.67 (s, 6 H), 6.38 (d, 2 H, J_{H-H} = 5.5 Hz), 7.00 (s, 2 H), 9.60 (d, 2 H, J_{H-H} = 5.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 21.50, 32.90, 35.34, 67.55, 122.81, 125.85, 149.06, 149.98, 151.08. IR (KBr pellet): 896, 921, 930, 2850–2940 cm^{-1}. Anal. Calcd for $C_{22}H_{34}N_2O_2Mo$: C, 58.14; H, 7.54. Found: C, 57.92; H, 7.50.

$L_2Mo(O)_2(CH_2CMe_2Ph)_2$, 6. $L_2Mo(O)_2Br_2$ (9.44 g, 20.0 mmol) in 50 mL of THF was allowed to react as above with 33.3 mL of 1.20 M (40.0 mmol) $PhMe_2CCH_2MgCl$ in THF. An off-white solid (0.97 g, 1.68 mmol, 8.4% yield) was obtained. ^1H NMR (C_6D_6) (ppm): 1.65 (s, 6 H), 1.66 (s, 4 H), 1.90 (s, 12 H), 6.28 (d, 2 H, J_{H-H} = 5.5 Hz), 6.88–7.04 (m, 10 H), 7.33 (d, 2 H, J_{H-H} = 7.1 Hz), 9.14 (d, 2 H, J_{H-H} = 5.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (ppm): 21.36, 31.26, 41.51, 67.28, 122.64, 124.36, 125.57, 125.72, 127.33, 148.59, 149.71, 150.84, 153.41. IR (KBr pellet): 888, 900, 920, 927, 2850–2940 cm^{-1}.

$L_2Mo(O)_2[(CH_2)_4CH{:}CH_2]_2$, 3. $L_2Mo(O)_2Br_2$ (14.03 g, 29.7 mmol) in 50 mL of THF was allowed to react as above with 68.0 mL of 0.874 M (59.4 mmol) $CH_2{:}CH(CH_2)_4MgBr$ in THF. A dirty yellow solid (4.99 g, 10.4 mmol, 17.6% yield) was obtained. ^1H NMR (C_6D_6) (ppm): 1.41–1.56 (br, 8 H), 1.80 (s, 6 H), 1.95 (q, 4 H, J_{H-H} = 5.4 Hz), 2.28 (5-plet, 4 H, J_{H-H} = 7.7 Hz), 4.85 (m, 2 H), 4.86 (m, 2 H), 5.70 (m, 2 H), 6.50 (d, 2 H, J_{H-H} = 5.3 Hz), 7.24 (s, 2 H), 9.67 (d, 2 H, J_{H-H} = 5.5 Hz). $^{13}C\{^1H\}$NMR ($CDCl_3$) (ppm): 21.44, 33.41, 33.38, 35.45, 49.34, 113.51, 122.72, 126.17, 139.43, 149.07, 150.19, 150.44. IR (KBr pellet): 872, 894, 2880–2940 cm^{-1}. Anal. Calcd for $C_{24}H_{34}N_2O_2Mo$: C, 60.24; H, 7.16. Found: C, 59.55; H, 7.55.

Decomposition Procedures. Thermal Decomposition of 1–6. In the cases of complexes **1**, **2**, and **6**, 0.10 g of the compound and 5.0 mL of toluene or toluene-d_8 were placed in a 10-mL round-bottomed flask equipped with a Liebig condenser and refluxed under N_2 for 3 days. Volatiles were separated for GC–MS analysis by vacuum transfer. In cases where nonvolatile products were studied, the metal complex was refluxed in toluene-d_8 in the same way, but metal compounds were separated by addition of the reaction mixture to 15 mL of hexane or pentane, followed by centrifugation. In cases where lower boiling products were possible, a different procedure was followed. **5** (0.10 g) was refluxed at 120 °C in 2.0 mL of toluene-d_8 for 10 days in a Carius tube placed in a mineral oil bath. The reaction mixture was vacuum transferred, and the volatiles were analyzed by GC–MS(CI). **4** (25 mg) was heated in 0.50 mL of toluene for 5 days at 120 °C in a Carius tube. After cooling, the reaction mixture was analyzed by GC. **3** (0.25 g) in 0.50 mL of toluene-d_8 was heated at 120 °C in a Carius tube for 3 days. The volatiles were vacuum transferred and analyzed by ^{13}C NMR using a relaxation delay of 10 s. Relative concentrations of the components were determined by integrating methylene carbon absorption.

Thermal Decomposition of 1 and 2, Together in Solution. **1** (0.214 g, 433 μmol) and **2** (0.226 g, 433 μmol) were added to 2.00 mL of THF (0.217 M) in a 5-mL flask fused to a condenser as one piece, and 0.051 g (103 μmol) of **1** and 0.054 g (103 μmol) of **2** were added to 50.00 mL of THF (2.06 mM) in a 100-mL flask similarly joined to a condenser. The flasks were heated to reflux for 5 days in the same mineral oil bath under a N_2 atmosphere to ensure complete decomposition. Solvent was removed from each by vacuum transfer, and the residue was washed with 300 mL of petroleum ether. Removal of solvent from the filtrates by rotary evaporation left small amounts of crystalline residue. The residues were analyzed by GC.

Thermal Decomposition of 2 in the Presence of 9,10-Dihydroanthracene-*9,9,10,10*-d_4. **2** (0.100 g) in 2.0 mL of toluene in a 10-mL round-bottomed flask equipped with a Liebig condenser and another identical reaction vessel containing the same solution, except for the addition of 1.00 g of 9,10-dihydroanthracene-*9,9,10,10*-d_4, were refluxed for 36 h in the same mineral oil bath. After cooling, the reaction mixtures were each added to 10 mL of pentane, and the solids were separated by centrifugation. The residues collected were extracted with 2 × 10-mL portions of pentane that were then combined with the supernatants. These were analyzed by GC. A portion of the second solution was vacuum transferred, and the volatiles were analyzed by GC–MS to determine deuterium incorporation into *p*-xylene.

Thermal Decomposition of 4 in the Presence of 9,10-Dihydroanthracene. **4** (25 mg) and 9,10-dihydroanthracene (0.25 g) in 0.50 mL of toluene were sealed in a Carius tube and heated for 5 days at 120 °C. The product mixture was analyzed by GC.

Decomposition of 2 in the Presence of 9,10-Diphenylethylene. **2** (0.100 g) was placed in a 10-mL round-bottomed flask with 2.0 mL of 1,1-diphenylethylene and 5.0 mL of toluene. The flask was fitted with a Liebig condenser, and the reaction mixture was refluxed under N_2 for 2.5 days. After cooling, the reaction mixture was added to 10 mL of pentane and centrifuged. The organic products were then analyzed.

Decomposition of 1–6 in the Presence of O_2. In the cases of **1** and **2**, a solution of 50 mg of the compound in 3.0 mL of solvent was placed in a Schlenk tube and closed with a rubber pipet bulb. Dry O_2 was flushed through the side tube for 10 min with a stainless steel needle, after which the valve was closed and the pipet bulb was inflated with O_2 pressure. The reaction mixtures were allowed to stand for several days in this way and then centrifuged. This technique was sufficient for **1** and **2**, which react readily with oxygen.

The more air-stable compounds, **3–6**, which require very long reaction times, demanded a more careful method to obtain samples that contained sufficient concentrations of aldehydes and were free of contaminating plasticizers. One of the compounds (0.10 g) was placed in a 2-dram vial equipped with a Teflon-lined screw cap under an N_2 atmosphere. One milliliter of dried, degassed THF was added, and then the vial was closed. The vial was opened and freely exposed to a dry O_2 atmosphere inside a glovebag. Afterward, the vial was closed and stirred until decomposition was evident. The volatiles were removed by vacuum transfer.

Decomposition of 2 in the Presence of $^{18}O_2$. Two-hundred milligrams (3.83 μmol) of **2** and 10.0 mL of THF was added to a 25-mL three-necked flask inside a dry N_2 filled glovebox. A vacuum adapter was fitted to the center neck, and a 10-mL round-bottomed flask was attached to a side neck with a 75° bent distillation adapter. To the other side neck was attached a 50-mL gas bulb equipped with a breakseal containing 96% $^{18}O_2$ (2.2 mmol) purchased from MSD Isotopes. After the apparatus was attached to a Schlenk manifold, the solution was allowed to thaw, the breakseal was ruptured, and the reaction mixture was stirred for 4 days. Following this period, a white precipitate and a faint yellow supernatant were formed. The solution was freeze–pump–thaw degassed, and then the volatiles were vacuum transferred into the round-bottomed flask. The adapter and flask containing the volatiles were removed under N_2 flush and replaced with a glass stopper. The residue was dried under vacuum overnight and then scraped out, extracted with 20 mL of petroleum ether, and collected on a 2-mL F-fritted Büchner funnel. The funnel containing the residue was extracted with 15 mL of THF under a dry N_2 atmosphere, and the solvent was removed under reduced pressure to leave a small amount of **2**. The volatiles collected were analyzed by GC–MS, and the **2** was analyzed by +FAB MS.

Decompositions of 2 and $L_2Mo(O)_2(CD_2C_6H_4Me\text{-}p)_2$, Together in Solution in the Presence of O_2. **2** (0.100 g, 191 μmol) and $L_2Mo(O)_2(CD_2C_6H_4Me\text{-}p)_2$ (0.100 g) were dissolved in 20 mL of THF in a 25-mL round-bottomed flask. The flask was closed with a Schlenk adapter covered with a rubber pipet bulb. The apparatus was flushed with O_2 as described above, and the bulb was inflated. The reaction mixture was stirred for 90 min, and afterward, the adapter was removed. The flask was attached to a short path distillation apparatus and freeze–pump–thaw degassed, and then the volatiles were removed. The volatiles were analyzed by GC–MS(EI). From the amount of *p*-toluenealdehyde present, it was evident that the reaction had progressed ≈3% toward completion.

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