Molecular Routes for the Synthesis of Metal Carbides, Nitrides, and Oxides. 1. Studies of the Thermal Decomposition of $M_2(OR)_6$ and $M_2(CH_2Ph)_2(OR)_4$ Compounds Where M = Mo and W

David V. Baxter, Malcolm H. Chisholm,* Vincent F. DiStasi, and
Scott T. Haubrich

Departments of Chemistry and Physics, Indiana University, Bloomington, Indiana 47405

Thermolysis of the homoleptic alkoxides $M_2(OR)_6$ and the mixed benzyl alkoxides $M_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$, where M = Mo and W, have been studied under a purified helium flow by a coupled thermogravimetric analyzer/mass spectrometer (TGA-MS) system installed in a VAC atmosphere Dri-Lab. Under rigorously purified He, $Mo_2(OR)_6$, where R = *t*-Bu and *i*-Pr, sublimed without decomposition at ca. 100–200 °C, 1 atm. In the presence of a trace of O_2/H_2O, $Mo_2(O\text{-}t\text{-}Bu)_6$ gave MoO_2. The related $W_2(OR)_6$ compounds were transformed to WO_2 when R = *t*-Bu at ca. 200 °C and when R = *i*-Pr to a mixture of WO_2 and W(m) after heating to 750 °C. In contrast, the cyclohexoxides $M_2(O\text{-}c\text{-}C_6H_{11})_6$ gave upon heating Mo_2C and W(m), respectively, by way of a metastable amorphous phase of approximate composition $M_2C_4O_4$. The introduction of two benzyl ligands in the compound $M_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ significantly alters the molecular decomposition. For instance, for M = Mo the addition of the benzyl ligands causes the compound to decompose prior to sublimation and gives Mo_2C with traces of Mo(m). For M = W the decomposition pathway is altered considerably, with the initial decomposition temperature range lower than that of the homoleptic alkoxide $W_2(O\text{-}i\text{-}Pr)_6$ by ca. 100–250 °C. This decomposition gives the product W_2C (>65%) with traces of W(m) and WC as the only detectable products by X-ray diffraction (XRD) powder patterns. The formation of the residues after thermal decomposition is based on XRD and the precentage weight retained in the TGA experiments. A variety of isotopically labeled compounds were prepared and the gases evolved during thermolysis were analyzed by MS, GC-MS, and ^1H and ^{13}C NMR spectroscopy. On the basis of these studies, some insights into the initial mechanisms of the thermolyses are proposed.

Introduction

The molecular precursor strategy for the synthesis of solid-state materials has gained considerable momentum within recent years. Sol–gel[1] and organometallic chemical vapor deposition (OMCVD),[2] whose origins date back well over a century, are currently employed in the synthesis of a wide range of materials—from metal oxide-based ceramics[3] to thin films of metals and semiconductors.[4] The concept of a "single-source precursor" has gained popularity based on the hypothesis that a molecule may be designed (selected) so as to contain the correct ratio of atoms needed in the desired product.[5] There is no need for mixing since the desired stoichiometry is built in at the atomic level. There is, however, the necessity that all other unwanted atoms present in the molecule leave during the transformation of molecule to material. Herein lies the rub and the

challenge to the synthetic and mechanistic chemist. While much has been learned over the past several decades in the *construction* of intricate organometallic and metalloorganic compounds, relatively little is known concerning their *destruction*. However, the synthesis of GaAs from molecules containing Ga–As bonds has been a prolific area of research within recent years and has led to high-purity thin films,[6] thereby fueling the "single-source precursor" concept.

Metal alkoxides, $[M(OR)_x]_y$, are commonly used as molecular precursors for the formation of metal oxides of high purity in the electronic and ceramics industries. The transformation of metal alkoxides to oxides can presently be obtained by hydrolysis and subsequent polycondensation reactions (sol–gel) and OMCVD techniques. Another viable route to metal oxides is by thermolysis of homoleptic alkoxides, e.g.,[7] as in the preparation of TiO_2 from $Ti(OR_4)$. However, relatively little is known about the thermolytic decomposition pathways[8] for these compounds.

* To whom correspondence should be addressed at the Department of Chemistry.
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In this series of papers we shall be studying the chemical transformations of molecules (molecular precursors) to metal carbides, nitrides, and oxides by a variety of procedures. We start here with a study of the thermolysis of a series of homoleptic alkoxides of molybdenum and tungsten $M_2(OR)_6$ that contain redox active $(M\equiv M)^{6+}$ centers. A preliminary account of this work was published in this journal.[9] In an attempt to introduce an Achilles heel, or low-energy pathway of decomposition, we also have examined the thermolytically labile benzyl ligands and examined the thermolyses of $M_2(CH_2Ph)_2(O-i-Pr)_4$. We show that the selection of a specific alkoxide or the introduction of the benzyl group may alter the initial mechanism of the thermal decomposition and this in turn determines the nature of the final product.

Experimental Section

General Procedures. All manipulations were carried out by using standard Schlenk and drybox techniques under prepurified helium or nitrogen. Aromatic and aliphatic hydrocarbon solvents were dried and distilled from sodium or potassium benzophenone ketyl. Polar solvents were stored over 3-Å molecular sieves, while nonpolar solvents were stored over 4-Å molecular sieves. NMR solvents benzene-d_6 and toluene-d_8 were dried over molecular sieves and degassed with dry nitrogen. Azeotropes of *tert*-butyl alcohol-d_6/benzene and *tert*-butyl alcohol/benzene were dried and distilled from CaH_2, subjected to three freeze−pump−thaw cycles and stored over 3-Å molecular sieves. 2-Propanol and cyclohexanol were dried and distilled from magnesium turnings and stored over 3-Å sieves. *tert*-Butyl alcohol-d_9, cyclohexanol-d_{12}, 2-propanol-d_6, and 1-propanol-d_7 were purchased from Cambridge Isotopes, stored over 3-Å sieves, and used without any further purification. *tert*-Butyl alcohol-d_6 was prepared by the reaction of $(CD_3)_2CO$ with CH_3MgBr, followed by hydrolysis with a saturated NH_4Cl aqueous solution, isolation via distillation, and subsequent formation of the benzene azeotrope. $W_2(O-t-Bu)_6$, $W_2(O-c-C_6H_{11})_6$, $W_2(O-i-Pr)_6$, $W_2(bz)_2(O-i-Pr)_4$, $W_2(bz)_2(O-i-Pr-d_6)_4$, $W_2(bz)_2(O-i-Pr-d_7)_4$, $Mo_2(O-t-Bu)_6$, $Mo_2(O-c-C_6H_{11})_6$, $Mo_2(O-i-Pr)_6$ and $Mo_2(bz)_2(O-i-Pr)_4$ were prepared via literature methods.[10] The compounds were purified by recrystallization from hexane. Recrystallization was performed twice for ultrapurity. Only highly pure compounds were used for thermolytic studies.

Samples of $W_4(\mu-C)(O-i-Bu)_{14}$ and $W_4(\mu-{}^{13}C)(O-i-Bu)_{14}$ were supplied by Dr. Victor Johnston.

Physical Techniques. ^1H and ^{13}C NMR spectra were recorded on Varian XL300 (300 and 75 MHz, respectively) and Bruker AM500 (500 and 124 MHz) spectrometers in dry and oxygen-free toluene-d_8 or benzene-d_6. All ^1H NMR chemical shifts are reported in ppm relative to the CHD_2 quintet of toluene-d_8 set at δ 2.09 or the ^1H impurity in benzene-d_6 set at δ 7.15. All ^{13}C NMR chemical shifts are reported in ppm relative to the ipso carbon of toluene-d_8 set at δ 137.5.

GC/MS data were recorded on a departmental HP5890 gas chromatograph coupled to a HP5971 mass selective detector interfaced to a Hewlett-Packard Chem Station. The GC column used was a Supelco SPB5 (60 m long, 0.25 mm i.d.).

Room-temperature powder X-ray diffraction (XRD) studies were performed on a Scintag XDS 2000 powder diffractometer (Cu Kα) equipped with a solid-state (Ge) detector.

Thermogravimetric Mass Spectral Analysis (TG-MS). Thermogravimetric studies are carried out in a coupled TG-MS[11] system with a prepurified helium flow. This type of system offers a simultaneous sampling of the volatile decomposition products, which provides a powerful method for investigating the thermal decomposition of a material, as well as elucidating the mechanism. The thermobalance of the thermogravimetric analyzer (TGA), as well as the quadrupole mass spectrometer inlet, have been installed inside a modified VAC Atmosphere Dri-Lab equipped with a dual Dri-Train and oxygen analyzer. The glovebox is operated under a helium atmosphere in order to eliminate problems in sample loading arising from static electricity. The oxygen level in the glovebox is kept below 1 ppm (a typical atmosphere contains 0.66 ppm O_2). The flow of the purge gas is regulated by using a ball-tube flow meter. To remove any trace impurities of water or oxygen, the purge gas is sent through a water/oxygen scrubber.

The DuPont 951 TGA typically requires samples sizes in the range 5−100 mg and heating rates in the range 5−50 °C min^{-1}. Gas flow rates typically were 50 cm^3 min^{-1}. Faster flow rates often blow the sample off the platinum boat giving erroneous weight loss data. The VG Micromass PC quadrupole mass spectrometer (QMS) has an enclosed ion source with triple $^1/_4$-in. filter analyzers and contains dual Faraday and secondary electron multiplier (SEM) detectors. The QMS is operated under vacuum with an ultimate pressure of 1×10^{-8} mbar (typically our instrument is run at 1×10^{-7} mbar). The electron energy on the ionizer of the mass spectrometer is factory set at 70 eV. The capillary inlet samples continuously with a bleed rate of 12 cm^3 min^{-1}. The mass range of the QMS is from 1 to 300 amu. Although this instrument works well qualitatively, quantitative work is not possible because of the varying ionization yields of the volatile components.

Thermolysis of Labeled Compounds. *Solution Thermolysis of $W_2(OC(CH_3)(CD_3)_2)_6$.* To an NMR tube containing 0.5 mL of toluene-d_8 was added approximately 20 mg of the homoleptic alkoxide. The NMR tube was then flame sealed under vacuum. Inverted, the NMR tube was placed in a 98 °C silicon oil bath up to the level of the alkoxide solution. After the thermolysis was complete a clear colorless solution with a brown/black precipitate remained. A ^1H NMR spectrum was taken once the thermolysis was complete. A GC-MS was taken of the NMR solution once NMR studies were complete.
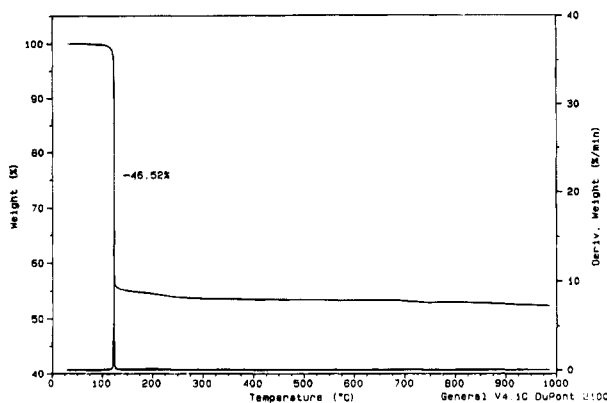
Solid-State Thermolysis of $W_2(OC(CH_3)(CD_3)_2)_6$. A glass tube blown to a bulb at one end and equipped with a 14/20 ground glass joint was charged with 20 mg of the homoleptic alkoxide. A Kontes valve equipped with a 14/20 joint and a 5 mm NMR tube containing 0.5 mL of toluene-d_8 was connected to the glass tube containing the solid. The NMR tube was submerged in liquid N_2 and subjected to three freeze−pump−thaw cycles. After the last freeze−pump−thaw cycle the NMR tube was again placed in liquid N_2 and the bulb containing the alkoxide was placed in a 200 °C silicon oil bath. As the thermolysis occurred the volatile components were vacuum transferred into the submerged NMR tube. After 2 h the NMR tube was flame sealed. ^1H NMR spectroscopy was performed on the collected volatile gases. GC-MS studies were also completed on the sample.

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Figure 1. Thermogram of $W_2(O\text{-}t\text{-}Bu)_6$ showing the percent weight loss (left) and the derivative weight loss (right).

Results and Discussion

$M_2(O\text{-}t\text{-}Bu)_6$ Compounds. Thermogravimetric analysis of $Mo_2(O\text{-}t\text{-}Bu)_6$ under a rigorously dried He flow reveals a thermogram with two plateaus and a sample weight loss of ca. 90% beginning at approximately 130 °C. The trace shows a long slow sample weight loss which, in conjunction with the slope of the reaction interval, is consistent with simultaneous sublimation and decomposition Sublimation occurs at the beginning of the weight loss, while decomposition occurs toward the end of the reaction interval. Sublimed material Mo_2-$(O\text{-}t\text{-}Bu)_6$ was collected on the cool section of the quartz furnace tube and was clearly visible. Because of the limited amu range of the QMS, a parent molecular ion $Mo_2(O\text{-}t\text{-}Bu)_6^+$ was not observed. The residue in the pan after annealing to 1000 °C was determined to contain MoO_2 by XRD. When the thermolyses were carried out by using helium gas that had not been vigorously dried, the amount of sublimed material was much less and more MoO_2 was formed.

The thermolysis of $W_2(O\text{-}t\text{-}Bu)_6$ gave a qualitatively similar thermogram. See Figure 1. In this instance there was no evidence for sublimation. The average sample weight loss between 80 and 500 °C over nine consecutive experiments was 46.52 ± 0.07%. As is evident from an inspection of Figure 1 the thermal decomposition of $W_2(O\text{-}t\text{-}Bu)_6$ occurs with great rapidity at ca. 120 °C and is essentially complete by 200 °C. From the weight loss one can anticipate that the product is WO_2. The XRD of samples prepared by the thermolysis of $W_2(O\text{-}t\text{-}Bu)_6$ with heating to 300 °C showed very diffuse patterns. Only upon heating (800–1000 °C) is the well-defined XRD of WO_2 observed.[12] See Figure 2.

The mass spectral analysis of the gases evolved during the thermolyses of $M_2(O\text{-}t\text{-}Bu)_6$ reveals 2-methyl-2-propanol (t-BuOH), 2-methyl-1-propene (Me_2C=CH_2) and 2-methylpropane (Me_3CH). We shall return to consider how these are formed later in this paper.

For a comparison, we also investigated the nature of the thermolysis of $Al_2(O\text{-}t\text{-}Bu)_6$ which, of course, contains what may be viewed as a non-redox-active Al_2^{6+} core. Under high-purity He flow $Al_2(O\text{-}t\text{-}Bu)_6$ sublimes cleanly at 180–240 °C, 1 atm. In the presence of H_2O and O_2,
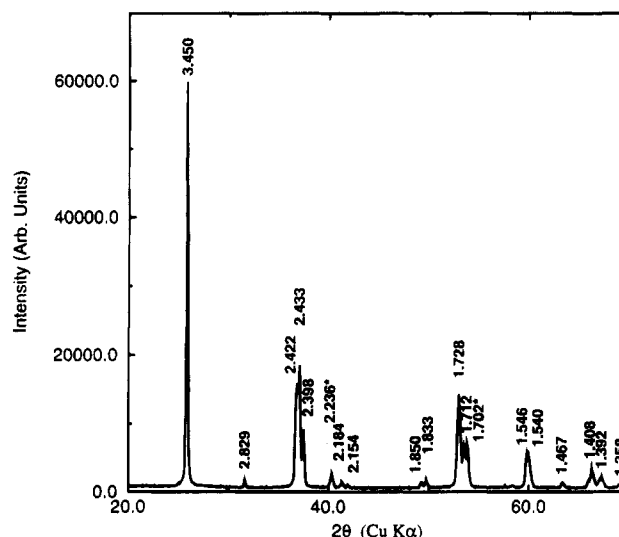
Figure 2. Powder X-ray diffraction of products formed by the thermolysis of $W_2(O\text{-}t\text{-}Bu)_6$. All peaks index to monoclinic WO_2 except the two indicated by asterisks. Of these, the peak at 2.236 Å is probably due to W metal while the origin of the peak at 1.702 Å is unknown.

i.e., with nonpurified helium, the behavior is similar to that of $Mo_2(O\text{-}t\text{-}Bu)_6$ in that decomposition occurs (with partial sublimation) and γ-Al_2O_3 is formed as the residue.
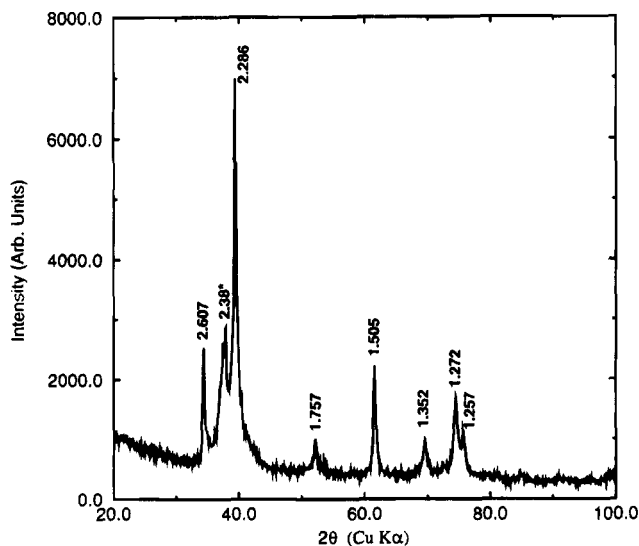
The markedly different thermal stabilities of the M_2-$(O\text{-}t\text{-}Bu)_6$ compounds where M = Al, Mo, and W underlies the fact that the M≡M bond is important in significantly altering the decomposition properties of these otherwise homoleptic alkoxides.

$M_2(O\text{-}i\text{-}Pr)_6$ Compounds. The compound $Mo_2(O\text{-}i\text{-}Pr)_6$ is very volatile, subliming at ca. 60 °C, 10^{-2} Torr, and under a rigorously pure helium flow sublimed at 1 atm at 180 °C. The compound $W_2(O\text{-}i\text{-}Pr)_6$ is extremely air-sensitive and difficult to isolate rigorously free from $W_4(O\text{-}i\text{-}Pr)_{12}$.[13] This having been stated the thermolysis of $W_2(O\text{-}i\text{-}Pr)_6$ was examined. The onset of decomposition occurred at ca. 85 °C whereupon a 37.7 wt % loss occurred, giving an amorphous (by XRD) material that was thermally stable from 375 to 700 °C. The volatile components lost in the first stage of the thermolysis were propane and propene with small amounts of acetone and 2-propanol. From 700 to 750 °C a ca. 5 wt % loss was observed with the evolution of CO. The resultant material was seen to be a mixture of WO_2 and W(m) by XRD.

$M_2(O\text{-}c\text{-}C_6H_{11})_6$ Compounds. Both compounds showed superficially similar behavior and were very different from the $M_2(O\text{-}t\text{-}Bu)_6$ compounds described above. The first weight loss begins at 210 °C, and the changing slope of the thermogram trace indicates that more than one process is involved. The sample weight loss from the first to the second plateau is 61.7 ± 0.3%. The mass spectral analysis of the gases evolved reveal that the major species are cyclohexanone, cyclohexanol, cyclohexane, and cyclohexene. These compounds were also identified by GC-MS from the thermolyses of M_2-$(O\text{-}c\text{-}C_6H_{11})_6$ compounds carried out at 250 °C on the

(12) All comparisons to known crystalline phases in this paper refer to the diffraction patterns tested by the Joint Committee on Powder Diffraction Standards (JCPDS), International Center for Diffraction Data, Swarthmore, PA.

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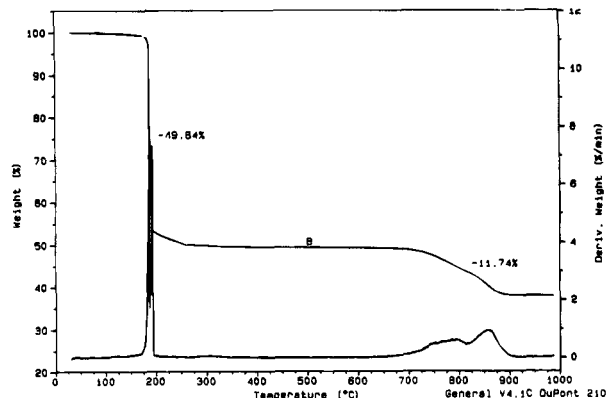
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Figure 3. Powder X-ray diffraction of α-Mo$_2$C formed as the final product in the thermolysis of Mo$_2$(O-*c*-C$_6$H$_{11}$)$_6$. The peak near 2.38 Å is broad and does not index to the α phase as well as the other peaks which may indicate the presence of a second phase.
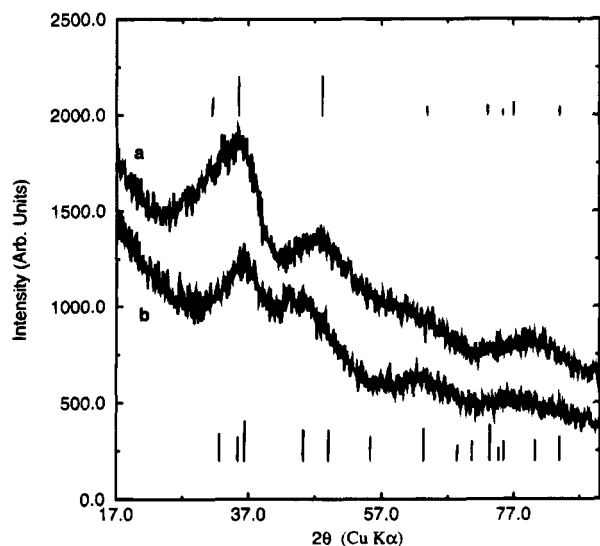
Figure 4. Powder X-ray diffraction pattern of the sample formulated as "M$_2$C$_4$O$_4$" with (a) M = W and (b) M = Mo. The vertical lines at the top and bottom of the figure indicate the positions and relative intensities of the major peaks in hexagonal WC and moC, respectively.

Figure 5. Thermogram of W$_2$(O-*c*-C$_6$H$_{11}$)$_6$ showing the percent weight loss on the left and the derivative weight loss on the right. The plateau "B" has a composition approximating "M$_2$C$_4$O$_4$".

bench top with a helium flow and a cold trap: cyclohexane, 5.83%; cyclohexene, 20.17%; cyclohexanol, 47.40%; cyclohexanone, 26.60%. [The percentages quoted are based on the integral areas of the GC curves.] Some other minor products with higher column retention times were evolved but were not identified.
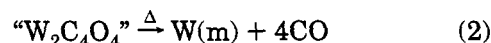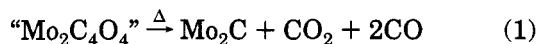
From the initial mass loss we can estimate that the composition of the 2nd plateau is "Mo$_2$C$_4$O$_4$". We have no way of estimating its hydrogen content. We attempted solid-state ^{13}C NMR spectroscopy (Cp-MAS) but did not detect any carbon signal. The material "Mo$_2$C$_4$O$_4$" is thermally stable to ca. 650 °C whereupon from 650 to 750 °C there is a second weight loss and CO and CO$_2$ are evolved. The resultant material formed at 750 °C is predominantly α-Mo$_2$C. See Figure 3. Figure 4 shows X-ray diffraction patterns from the "M$_2$C$_4$O$_4$" intermediate material for both M = W and

M = Mo. The shape and position of the diffuse peaks in the tungsten intermediate pattern strongly suggest that this sample contains a significant amount of hexagonal WC in the form of very small and/or disordered crystallites together with some amorphous material. The Mo intermediate is also consistent with very small particles of hexagonal MoC in an amorphous matrix, although here the correspondence with the associated crystalline pattern is less strong. In addition the solid-state (KBr matrix) IR spectra of this material derived from Mo$_2$(O-*c*-C$_6$H$_{11}$)$_6$ and Mo$_2$(O-*c*-C$_6$D$_{11}$)$_{12}$ were recorded. No absorption band that could be assigned to ν(OH), ν(OD), ν(C−H), ν(C−D), or CO groups was detected. The IR was virtually silent between 4000 and 400 cm^{-1}. This rules out the existence of terminal, bridging, or semibridging carbonyl ligands and also oxalate ligands. Furthermore, no aromatic or olefinic absorptions were observed. Certainly the hydrogen content of the material must be very low.

The thermogram of W$_2$(O-*c*-C$_6$H$_{11}$)$_6$ is shown in Figure 5 and is very similar to that of Mo$_2$(O-*c*-C$_6$H$_{11}$)$_6$ except in that (i) the initial onset of thermal decomposition occurs at just below 200 °C, (ii) the metastable product W$_2$C$_4$O$_4$ that is formed by 250 °C and is persistent to temperatures of 700 °C, and (iii) in the final weight loss, which occurs from 700 to 900 °C, carbon monoxide is evolved. The stoichiometric equations (1) and (2) can therefore be written for molybdenum and tungsten, respectively.

$$\text{"Mo}_2\text{C}_4\text{O}_4\text{"} \xrightarrow{\Delta} \text{Mo}_2\text{C} + \text{CO}_2 + 2\text{CO} \quad (1)$$

$$\text{"W}_2\text{C}_4\text{O}_4\text{"} \xrightarrow{\Delta} \text{W(m)} + 4\text{CO} \quad (2)$$

The XRD of the final product formed in the thermal decomposition of W$_2$(O-*c*-C$_6$H$_{11}$)$_6$ is W(m), as shown in Figure 6. Only a trace quantity of WO$_2$ is detectable, in sharp contrast to the previously discussed decomposition of W$_2$(O-*t*-Bu)$_6$ (see Figure 2).

Despite the formal similarities in the initial decomposition modes of the Mo and W compounds, a derivative plot of the *first* weight loss reveals differences as is shown in Figure 7a. For tungsten the decomposition proceeds in two distinct steps, while for molybdenum the decomposition is more complicated. Because of the proximity of these thermal decompositions, it is difficult to determine what gases are evolved first. However, for
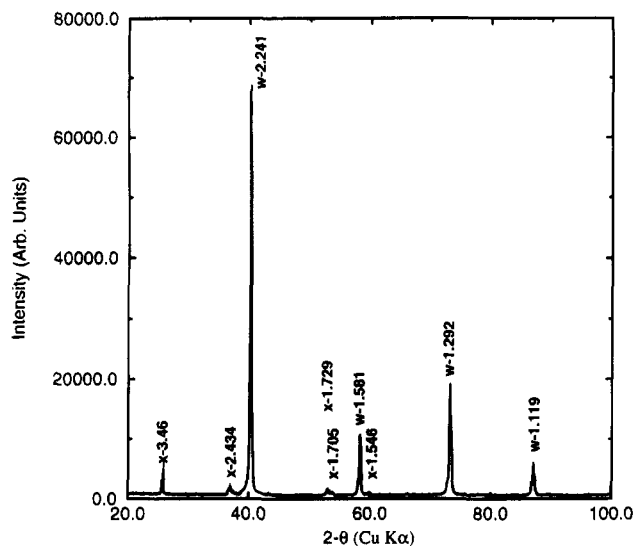
Figure 6. Powder X-ray diffraction of the final product obtained from the thermolysis of $W_2(O\text{-}c\text{-}C_6H_{11})_6$ showing the formation of $W(m)$ and traces of WO_2. Labels give the measured d spacings of the oxide (x) and metallic phases (w).
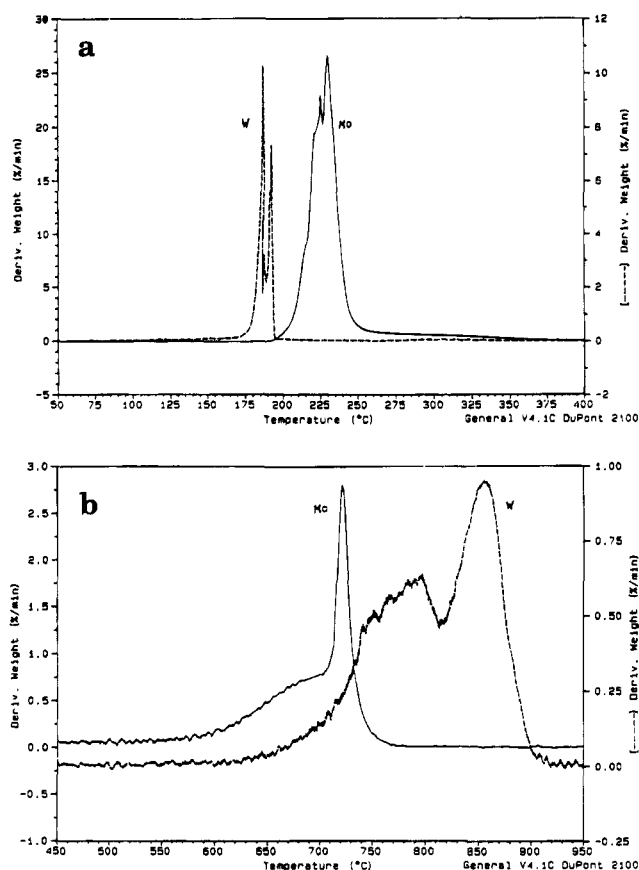
Figure 7. (a) Top: superimposed derivative plot for the first reaction interval (50 → 400 °C) in the thermolysis of $W_2(O\text{-}c\text{-}C_6H_{11})_6$ and $Mo_2(O\text{-}c\text{-}C_6H_{11})_6$, marked Mo and W, respectively, (b) for the second stage of the thermolysis in the temperature range 600 → 900 °C.

tungsten the initial step involves elimination of cyclohexene, cyclohexane, and cyclohexanol; in the second step these gases are observed along with cyclohexanone. In the case of molybdenum all four gases were detected. Unfortunately, the order in which they evolve could not be determined. The second step of the thermolysis also proceeds in two steps as shown in Figure 7b. In the
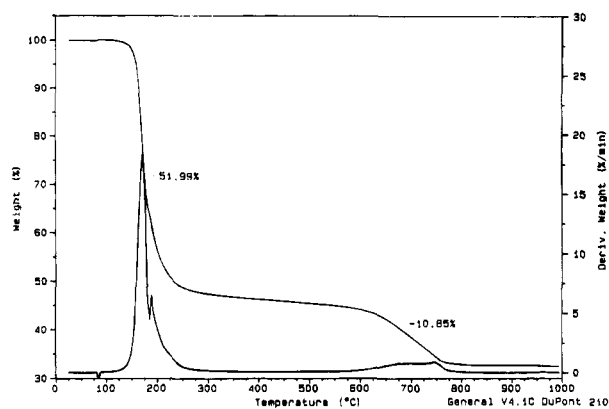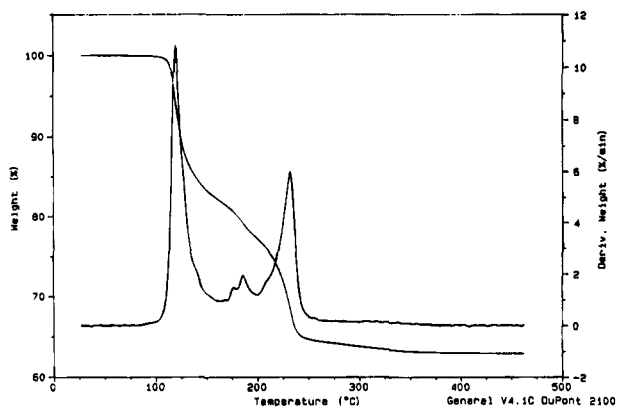

Figure 8. Thermogram showing the percent weight loss (left) and derivative weight loss (right) for $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ in the temperature range 22–1000 °C.

case of molybdenum the first weight loss involves the elimination of CO and the second both CO and CO_2. For tungsten both steps involve the loss of CO.

$M_2(OCH_2R)_6$ Compounds. It would have been desirable to include the thermal decomposition of primary alkoxides. However, we were unable to obtain a pair of related complexes for such a comparison. In general $M_2(OCH_2R)_6$ complexes are prone to form tetranuclear clusters $M_4(OCH_2R)_{12}$, e.g., ref 10g for R = i-Pr, c-C_4H_7, c-C_5H_9, and c-C_6H_{11}. In the case of R = t-Bu (the neopentoxides), the molybdenum compound sublimed and the tungsten compound upon thermal decomposition formed a foam that overflowed the pan and thus rendered a meaningless TGA.

$M_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ Compounds. To introduce a thermally labile ligand that might facilitate decomposition, we prepared the 1,2-dibenzyl compounds $M_2(CH_2\text{-}Ph)_2(O\text{-}i\text{-}Pr)_4$. Neither have been structurally characterized in the solid state, but both are probably very similar to $1,2\text{-}W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ that exists as an ethanelike dimer with an anti-$W_2C_2O_4$ core.[10b] [In solution 1,2-$M_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ compounds exist as a rapidly interconverting mixture of anti and gauche rotamers.]

As is shown in Figure 8 the thermogram of $Mo_2(CH_2\text{-}Ph)_2(O\text{-}i\text{-}Pr)_4$ occurs in two stages. The first stage begins at 145 °C where ca. 52% weight loss occurs by 250 °C. A calculation of the molecular formula for the species that is first formed and that is stable up until 625 °C is again "$Mo_2C_4O_4$". Upon heating from 600 to 775 °C, a further weight loss occurs as CO_2 and CO are evolved and the XRD of the resulting material corresponds to Mo_2C with $Mo(m)$ as a very minor product. The thermolysis process is thus very similar to that for $Mo_2(O\text{-}c\text{-}C_6H_{11})_6$ once decomposition sets in. However, in the case of $Mo_2(O\text{-}i\text{-}Pr)_6$ this does not occur—sublimation occurs prior to thermal decomposition. The introduction of the benzyl ligands serves as an Achilles heel in the $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ molecule causing initial decomposition at lower temperatures. The volatile components eliminate in the initial thermolysis, 140–200 °C, were toluene, propane, and propene along with relatively small amounts of acetone and 2-propanol. As is evident from the derivative plot of the thermogram, the initial decomposition of $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ occurs in more than one step, but the narrow temperature range of the decomposition prevented us from an analysis of the initial and final phases. However, the decomposition of $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$, which is qualitatively
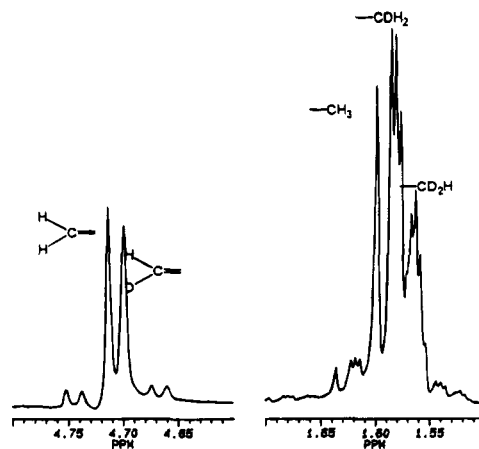
Figure 9. Thermogram of the initial decomposition of $W_2(CH_2\text{-}Ph)_2(O\text{-}i\text{-}Pr)_4$ showing the percent weight loss (left) and the derivative weight loss (right) in the temperature range 22–500 °C.

similar, has an initial decomposition that is spread out over a wide temperature range. See Figure 9. In the initial decomposition that begins at 100 °C (continuing to 250 °C), there is a 38.4 wt % loss, resulting in a material "$W_2C_4O_4$" (from mass balance) that is thermally persistent to 635 °C and amorphous (XRD). The second stage of the thermal decomposition leads to an 11.7 wt % loss and the attainment of a plateau at 750 °C and above of a phase that might be anticipated to be W_2C based on residual weight. Both CO and CO_2 are lost in the second stage of the thermolysis. By XRD, the final product formed after annealing at 1000 °C is W_2C (>65%) with W(m) and WC as the only other detectable species present.

It should therefore be noted that the introduction of the benzyl groups has altered the decomposition pathway considerably, and changed the stoichiometry of the final product relative to the thermolysis of $M_2(O\text{-}i\text{-}Pr)_6$.

Isotopic Labeling Studies. To try to interrogate some of the pathways of the initial thermal decompositions a number of deuterium labeling studies were carried out. We recently have reported[14] that the thermal decomposition of $[W_2(O\text{-}t\text{-}Bu)_7]^-$ which yields $[W_2(\mu\text{-}H)(\mu\text{-}O)(O\text{-}t\text{-}Bu)_6]^-$ and isobutylene, shows a significant deuterium isotope effect k_H/k_D (30 °C) = 3.5(1). The kinetic isotope effect on the rate of the reaction was measured in two ways: (1) by comparing the rate of the thermal decomposition of $[W_2(OC(CH_3)_3)_7]^-$ with that of $[W_2(OC(CD_3)_3)_7]^-$ in toluene-d_8 and (2) by determining the relative propensity for the formation of $(CD_3)_2C{=}CH_2$ and $(CH_3)(CD_3)C{=}CD_2$ in the decomposition of $[W_2(OC(CH_3)(CD_3)_2)_7]^-$. The ratio k_H/k_D = 3.5(1) at 30 °C was found to be the same in both experiments, thereby establishing that C–H bond breaking is involved in the rate-determining step.

$W_2(O\text{-}t\text{-}Bu)_6$. The thermolyses of $W_2(OC(CH_3)_3)_6$ and $W_2(OC(CD_3)_3)_6$ have been carried out under helium flow (TGA-MS) and in sealed NMR tubes in toluene-d_8 as solvent. The deuterated compounds are somewhat more thermally persistent. However, it is impossible to compare rates.[15] In both instances the decomposition

(14) Budzichowski, T. A.; Chisholm, M. H.; Huffman, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 389.

(15) The thermal decomposition of $OC(CH_3)_3$ and $OC(CD_3)_3$ on a Rh(111)–p(2 × 1)–O surface have also been found to show a kinetic preference for the decomposition of the protio compound Xu, Xi: Friend, C. M. *Langmuir* **1991**, *113*, 6686.

Figure 10. ^{1}H NMR spectrum of the 2-methyl-1-propene formed in the thermal decomposition of $W_2(OC(CH_3)(CD_2)_2)_6$ in a sealed NMR tube. The solvent is toluene-d_8 and the spinning sidebands are present due to an imbalance in the NMR tube from the flame sealing procedure.
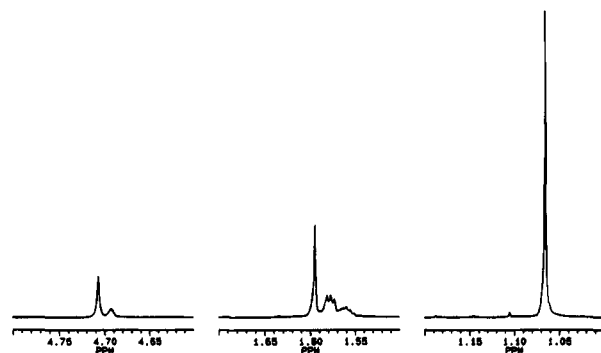
Figure 11. ^{1}H NMR spectrum of the gases evolved in the thermal decomposition of $W_2(OC(CH_3)(CD_3)_2)_6$ carried out in vacuo. The signals at γ 4.7 and 1.55–1.60 reveal the lesser degree of H/D scrambling relative to that seen in Figure 10 and the signal at γ 1.07 corresponds to $(CH_3)(CD_3)_2COH/D$.
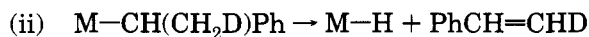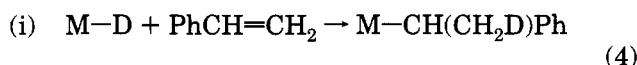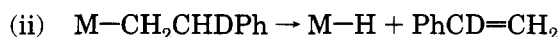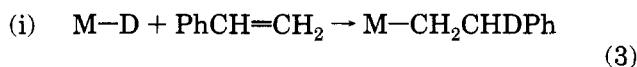
appears autocatalytic. This is indicated from a kinetics program that analyzes the derivative of the weight loss on the TGA experiment. Following our earlier successful use of the partially labeled *tert*-butoxide ligand, OC-$(CH_3)(CD_3)_2$, we studied the thermal decomposition of $W_2(OC(CH_3)(CD_3)_2)_6$. In solution we observed a remarkable finding: there was a statistical scrambling of H and D over the olefinic and methyl positions in 2-methyl-1-propene (isobutylene). This was determined by ^{1}H NMR spectroscopy that revealed an upfield shift for CH resonances attached to carbon atoms that were simultaneous deuterated. See Figure 10. Note the methylenic proton in the =CHD group does not show a gem J_{HD} coupling, but the methyl groups CHD_2 and CH_2D do. This is because of the relative magnitudes of the J_{HH} couplings and because the gyromagnetic ratio of ^{2}H is roughly one-sixth that of ^{1}H. Absent from the solution phase decomposition was tert-butyl alcohol. However, when the thermolysis was carried out in a vacuum and the volatile components were collected as they were evolved, $t\text{-}(CH_3)(CD_3)_2COH$ was seen along with 2-methyl-1-propene. The latter showed now only a relatively small, but still quite easily detectable, amount of H/D scrambling. See Figure 11. This clearly indicates that in the closed system some species is present that catalyzes the thermal decomposition of *tert*-butyl alcohol and facilitates H/D exchange in the 2-methyl-1-propene.
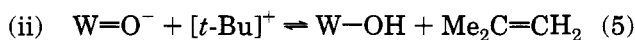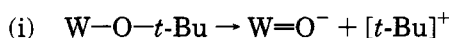
Furthermore, when $W_2(OC(CD_3)_3)_6$ was decomposed in toluene-d_8 in the presence of added free protio-2-methyl-1-propene the ^1H NMR spectrum revealed that deuterium incorporation into the added olefin occurred in a statistical manner.

In toluene-d_8 solution the thermal decomposition of $W_2(O-t-Bu)_6$ was also studied in the presence of styrene. No polystyrene was formed. In the presence of an excess of styrene (10 equiv) the deuterium from $W_2(OC-(CD_3)_3)_6$ was only sparsely incorporated into the styrene despite the absolute ratio 54D:30H (from olefinic $PhCH=CH_2$). However, when only 1 equiv of styrene was added deuterium was clearly seen in the formation of $PhCD=CH_2$ and $PhCH=CHD$ (cis and trans) by ^1H NMR spectroscopy (there the absolute D:H ratio was 54D:3H). A careful examination of the ^2H incorporation into the styrene in these reactions revealed that this was statistically distributed between the α- and β-carbon atoms. This result argues against a metal–hydride mechanism for scrambling of the H/D isotopes since insertion and elimination would be expected to occur much more facilely for the *n*-alkyl relative to the *sec*-alkyl. See eqs 3 and 4. A reviewer raised the point that

$$\text{(i)}\quad M-D + PhCH=CH_2 \rightarrow M-CH_2CHDPh$$
$$\text{(ii)}\quad M-CH_2CHDPh \rightarrow M-H + PhCD=CH_2 \tag{3}$$

$$\text{(i)}\quad M-D + PhCH=CH_2 \rightarrow M-CH(CH_2D)Ph$$
$$\text{(ii)}\quad M-CH(CH_2D)Ph \rightarrow M-H + PhCH=CHD \tag{4}$$

if reactions 3 and 4 are fast compared to the time scale of the experiment, both sites would be scrambled and thus our argument would be invalid. However, the reader should note that deuterium incorporation into the styrene was very sparse when an excess of styrene was present. Only when 1 equiv of styrene was present was any significant deuterium incorporation observed and by ^2H NMR spectroscopy that which was incorporated was statistical. Therefore we argue that incorporation of D into the styrene occurs under kinetic control.
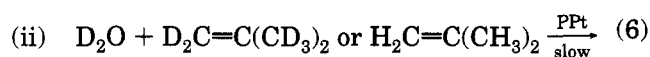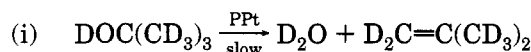
We propose that a carbenium ion mechanism is at work and probably involves an acidic hydroxyl group that is formed upon the initial decomposition of $W_2(O-t-Bu)_6$, such as that shown in eq 5.

$$\text{(i)}\quad W-O-t-Bu \rightarrow W=O^- + [t-Bu]^+$$

$$\text{(ii)}\quad W=O^- + [t-Bu]^+ \rightleftharpoons W-OH + Me_2C=CH_2 \tag{5}$$

$$\text{(iii)}\quad W-OH + \text{alkene} \rightleftharpoons W=O^- + [\text{alkyl}]^+$$

Furthermore in a closed system such as a sealed NMR tube the acidic functionality would cause the dehydration of any *tert*-butyl alcohol formed. Under vacuum the alkene or *tert*-butyl alcohol evolved would have less chance of reacting with the acidic hydroxyl group and would therefore be liberated with less scrambling. The ultimate fate of the hydroxyl group is most likely the formation of H_2O, which is always detected in trace quantities, and formation of the metal oxide. In addition, 5 mg of the precipitate formed from the thermolysis of $W_2(O-t-Bu)_6$ in toluene-d_8 was collected. This sample

was placed in an NMR tube with 0.21 mmol of protio-2-methyl-1-propene and 0.21 mmol of $DOC(CD_3)_3$ and toluene-d_8 as solvent. This mixture was then heated for 24 h at 90 °C. After heating, the products were analyzed by ^1H and ^{13}C NMR and GC-MS. It was determined that only trace amounts of deuterium incorporation had occurred in 2-methyl-1-propene. An appreciable amount of the tertbutanol-d_{10} was dehydrated to form 2-methyl-1-propene-d_8, and a small amount of $DOC(CH_3)_2(CH_2D)$ was also detected. Several conclusions can be made from this experiment. First, the final decomposition product (solid precipitate) from the thermolysis of $W_2(O-t-Bu)_6$ in solution is not the catalyst for deuterium scrambling between olefins. The scrambling must take place during the decomposition not after it is complete.

Second, the solid slowly dehydrates *tert*-butyl alcohol and may cause some deuterium scrambling (eq 6), where

$$\text{(i)}\quad DOC(CD_3)_3 \xrightarrow[\text{slow}]{PPt} D_2O + D_2C=C(CD_3)_2$$

$$\text{(ii)}\quad D_2O + D_2C=C(CD_3)_2 \text{ or } H_2C=C(CH_3)_2 \xrightarrow[\text{slow}]{PPt} \tag{6}$$

$$DOC(CD_3)_3 \text{ or } DOC(CH_3)_2(CH_2D)$$

PPt = decomposition product. However, this must be extremely slow, since after 24 h only trace amounts of protio-*tert*-butyl alcohol are observed. Furthermore, we did not find that WO_2 (annealed at 1000 °C) induced H/D scrambling in the presence of labeled and unlabeled olefins under related conditions.

These results can be contrasted with the thermal decomposition of $W_2(OC(CH_3)(CD_3)_2)_6$ that yields a statistical distribution of H/D in the 2-methyl-1-propene.
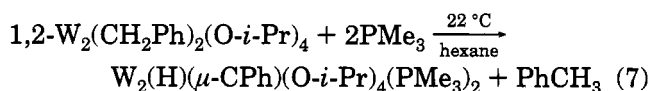
$W_2(CH_2Ph)_2(O-i-Pr)_4$. As shown in Figure 9 the thermogram of $W_2(CH_2Ph)_2(O-i-Pr)_4$ proceeds in steps in the temperature range 100–250 °C. It is therefore possible to probe the initial products of elimination and by the use of isotopic labels obtained some information pertaining to their formation. The following compounds were used in the study $W_2(CH_2C_6H_5)_2(OCH(CH_3)_2)_4$, $W_2-(CH_2C_6H_5)_2(OCH(CD_3)_2)_4$, and $W_2(CH_2C_6H_5)_2-(OCD-(CD_3)_2)_4$. Under a helium flow, the samples were heated to 150 °C. This effected the first weight loss, and the volatile components were collected and analyzed. The samples were cooled to room temperature and then reheated to 150 °C. No further weight loss was observed. However, the samples were then heated to 300 °C to effect the second stage of the thermal decomposition. Again the gases evolved were analyzed. These experiments were run both by TGA-MS and also on the bench top. In the latter case the volatile components were collected and analyzed by ^1H NMR, ^{13}C NMR, and by GC-MS spectroscopy.

The results of these experiments are summarized in Table 1. A key point is that toluene is given off in the first step of the decomposition [benzyl ligands were introduced to facilitate decomposition] and furthermore the toluene is protiotoluene even when the *i*-Pr ligands are *i*-Pr-d_7. This implicates an α-hydrogen atom transfer reaction wherein one benzyl ligand abstracts an α-hydrogen from another benzyl ligand. While the present study can not distinguish between intra- and intermolecular reactions, the elimination of toluene is

Table 1. ^{1}H NMR and GC/MS Data for the Volatile Components Derived from the Thermal Decomposition of $W_2(bz)_2(O^iPr)_4$-d_0, $W_2(bz)_2(OCH(CD_3)_2)_4$-d_8, and $W_2(bz)_2(OCD(CD_3)_2)_4$-d_7

compound/step	compiled ^{1}H NMR and GC/MS data (relative ratios)
d_0/step 1	toluene (1):propene (1):propane (1): acetone (0.5):isopropyl alcohol (0.5): C_6H_{12} (trace)
d_0/step 2	propene (1):acetone (0.5):isopropyl alcohol (0.5):propane (small): toluene (small):C_6H_{12} (trace)
d_8/step 1	toluene-d_0 (1):propene-d_5 (1): propane-d_7 (1):acetone-d_6 (0.5): isopropyl alcohol-d_6 (0.5): $C_6D_{10}H_2$ (trace)
d_8/step 2	propene-d_5 (1):acetone-d_6 (0.5): isopropyl alcohol-d_6 (0.5): propane-d_7 (small):toluene-d_n (0.5): $C_6D_{10}H_2$ (trace)
d_7/step 1	toluene-d_0 (1):propene-d_6 (1): propane-d_8 (1):acetone-d_6 (0.5): isopropyl alcohol-d_8 (0.5): $C_6D_{10}H_2$ (trace)
d_7/step 2	propene-d_6 (1):acetone-d_6 (0.5): isopropyl alcohol-d_8 (0.5): propane-d_8 (small): toluene-d_n (small):C_6D_{12} (trace)

very reminiscent of the phosphine induced intramolecular reaction shown in eq 7.[16] In reaction 7 all the

$$1,2\text{-}W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4 + 2PMe_3 \xrightarrow[\text{hexane}]{22\ °C}$$
$$W_2(H)(\mu\text{-}CPh)(O\text{-}i\text{-}Pr)_4(PMe_3)_2 + PhCH_3 \quad (7)$$

available evidence points to a phosphine induced 1,2-benzyl migration as seen for $1,2\text{-}Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ in its reaction with PMe_3, followed by C−H activations generating the μ-alkylidyne hydride complex.

In the first step, in addition to toluene, propene, and propane are evolved in equal quantities along with a small amount of acetone and 2-propanol. From the labeling studies it is also evident that the formation of propene, propane, acetone, and 2-propanol are exclusively due to the decomposition of the O-i-Pr ligands.

In the second step propene is the major component followed by roughly equal amounts of acetone and 2-propanol with smaller amounts of propane and toluene. In both stages of the reaction there is a trace of C_6H_{12} that appears to be formed by the coupling of two C_3 fragments derived from the O-i-Pr ligands.

It is difficult to try to piece together any detailed understanding of how these products are formed and why the thermal decomposition should proceed in the two major stages as is found. However, the labeling studies do suggest that the initial elimination of toluene occurs by an α-CH transfer between two benzyl ligands. It seems that this triggers the decomposition of some but not all of the O-i-Pr ligands. The remnant of the benzyl ligand that has given up a hydrogen atom in the elimination process seems likely to be a benzylidene species that is labile to further C−H activation processes. The toluene evolved in the second step from the labeled compounds showed a range of deuterium incorporation. For example, the decomposition of W_2-

Table 2. Summary of Thermolytic Studies of $M_2(OR)_6$ and $M_2(CH_2Ph)_2(O^iPr)_4$ Compounds

| compounds | temp, °C | | "intermediate" | product(s) |
	1st transition	2nd transition		
$W_2(O^tBu)_6$	120			WO_2
$W_2(O^iPr)_6$	85	700		WO_2, W(m)
$W_2(OCy)_6$	180	700	"$W_2C_4O_4$"	W(m)
$W_2(bz)_2(O^iPr)_4$	75–100	650	"$W_2C_4O_4$"	W_2C, WC, W
$Mo_2(O^tBu)_6$				sublimes
$Mo_2(O^iPr)_6$				sublimes
$Mo_2(OCy)_6$	210	600	"$Mo_2C_4O_4$"	Mo_2C
$Mo_2(bz)_2IO^iPr)_4$	145	625	"$Mo_2C_4O_4$"	Mo_2C, Mo(m)

$(CH_2C_6H_5)_2(OCH(CD_3)_2)_4$ gives in the second step C_6H_5-CH_2D, $C_6H_5CHD_2$, and $C_6H_5CD_3$, and for $W_2(CH_2C_6H_5)_2$-$(OCD(CD_3)_2)_4$ gives $C_6H_5CHD_2$ and $C_6H_5CD_3$. These results suggest that the additional protons may come from either the methyl groups or the α-carbon on the isopropyl ligands. The presence of $C_6H_5CD_3$ also suggests that proton scrambling may take place at this elevated temperature ($\approx$250 °C). We are not able to monitor H_2 evolution and cannot tell whether or not this is transformed into a benzylidyne and/or undergoes cyclometalation. However, the formation of toluene-d_n suggests to us that such processes are operative and that the hydrogen atoms required for elimination of toluene in the second stage are in part provided by the O-i-Pr ligands.

$W_4(C)(O\text{-}i\text{-}Bu)_{14}$ and $W_4(^{13}C)(O\text{-}i\text{-}Bu)_{14}$. As a final check of molecular precursor control over the course of the reaction, we studied the thermal decompositions of $W_4(C)(O\text{-}i\text{-}Bu)_{14}$ compounds that are prepared from the reaction between $W_4(O\text{-}i\text{-}Bu)_{12}$ and carbon monoxide.[10c,18] In these reactions the μ_4-carbido atom is derived from CO and can therefore easily be labeled a (^{13}C)carbide. The thermolyses proceeded in a two-step process with the final product being a roughly 50:50 mixture of W_2C and W(m) as determined by XRD and percentage weight loss. In the second step of the reaction, as with $W_2(O\text{-}c\text{-}C_6H_{11})_6$ and $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$, carbon monoxide was evolved. When the ^{13}C-labeled compound $W_4(\mu\text{-}^{13}C)(O\text{-}i\text{-}Bu)_{14}$ was employed, both ^{12}CO and ^{13}CO were evolved as determined by mass spectroscopy. We were not able to determine the relative ^{12}C:^{13}C ratio in the W_2C residue. However, it is clear that some of the ^{13}C is lost in a reforming reaction.

Concluding Remarks

A summary of the thermolytic studies is presented in Table 2. It is evident that the selection of a specific $M_2(OR)_6$ compound can have an influence in the formation of the final product. Specifically the tertiary alkoxides $M_2(O\text{-}t\text{-}Bu)_6$ are prone to decomposition to give MO_2, although the molybdenum compound is more thermally robust and in part sublimes without decomposition. These decompositions appear autocatalytic as was first noted by Bradley and Factor.[8e,f] The labeling studies imply that a carbonium ion mechanism may well be operative wherein oxygen−carbon bond cleavage is an important step. Oxygen-to-metal π-bonding could facilitate this, and this might explain why the ther-

(16) Blau, R. J.; Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C.; Kramer, K. S., results to be published.

(17) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kramer, K. S.; Tatz, R. J. *Organometallic* **1992**, *11*, 4029.

(18) Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E.; Huffman, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 7056.

molytic stability of $M_2(O\text{-}t\text{-}Bu)_6$ compounds follow the order $M = Al \gg Mo > W$.[19]

The nonvolatile secondary alkoxides $M_2(O\text{-}c\text{-}C_6H_{11})_6$ and the thermally sensitive $W_2(O\text{-}i\text{-}Pr)_6$ and $W_2(CH_2\text{-}Ph)_2(O\text{-}i\text{-}Pr)_4$ do not give metal oxides upon thermolysis but rather metal carbides or W(m). This difference can be traced to the early stages in the thermolysis of the compounds. It seems that metal−carbon bonds can be formed by either cyclometalation or addition of a ketone (formed by β-CH activation) across the M≡M bond (to generate alkylidene−oxo ligands).[20] We have not been able to characterize the phase "$M_2C_4O_4$" beyond noting that it is consistent with an amorphous material together with some hexagonal very fine crystals of metal carbide. Upon heating to 650−750 °C the evolution of CO_2 and/or CO in a re-forming reaction leads to metal carbides or, in the case of tungsten, tungsten metal.

That one can start with a molecule having six tungsten−oxygen bonds and in the final thermolysis product none remains in quite remarkable. The introduction of the thermally labile benzyl ligands promotes decomposition at a lower temperature and changes the stoichiometry of the final product.

Collectively these studies reveal that the thermal decomposition of $M_2(OR)_6$ compounds, where $M = Mo$ and W, is dependent on both M and R. These studies emphasize that much needs to be learned concerning the complexities of thermal decomposition reactions where a wide variety of bonds may be broken and formed and various thermodynamically favorable products such as WO_2, WC, W_2C, or W(m) may be accessed from a starting material of generic formula such as $W_2(OR)_6$.

(19) For a theoretical and computational analysis of O to M π-bonding for M = Al and Mo see: Chisholm, M. H.; Davidson, E. R.; DiStasi, V. F.; Ping, Du; Huffman, J. C. *Inorg. Chem.* **1991**, *30*, 1020.

(20) (a) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallic* **1990**, *9*, 602. (b) Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.