

# Molecular Routes to Metal–Carbides, –Nitriles, and –Oxides. 3.<sup>1</sup> Chemical Vapor Deposition Employing $X_3W\equiv^*CCMe_3$ , Where $X = CH_2CMe_3$ , $O^tBu$ , and $O^tBu-d_0$ and $^*C = ^{12}C$ or $^{13}C$ , and a Comparison with the Chemistry of $(^tBuO)_3W\equiv N$

Ziling Xue,<sup>†</sup> Shiow-Huey Chuang, Kenneth G. Caulton, and Malcolm H. Chisholm\*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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Low-pressure ( $10^{-3}$  Torr) chemical vapor deposition (LPCVD) employing a hot-walled quartz reactor (300–360 °C) and silica/quartz or silicon substrates have been carried out with  $X_3W\equiv^*C^tBu$ , where  $X = CH_2CMe_3$ ,  $O^tBu$ , and  $O^tBu-d_0$  and  $^*C = ^{12}C$  and  $^{13}C$ . Thin films formed on  $SiO_2$  or Si have been examined by XPS, RBS, XRD, SEM, and SIMS. The volatile components evolved under the LPCVD conditions were trapped in an  $N_2(l)$ -cooled U-tube packed with glass beads and examined by GC–MS and  $^1H$  and  $^{13}C$  NMR spectroscopy. Gray-black reflective films of amorphous tungsten carbide were formed (320–360 °C), when  $X = Me_3CCH_2$ , contaminated with 5–9 atom % oxygen. The  $^{12}C:^{13}C$  ratio in the film was ca. 7:1, and the volatile components were  $Me_4C$ ,  $Me_3C^{13}CH_3$  (54 mol % combined),  $Me_2C=CH_2$  (35 mol %),  $Me_3C^{13}C\equiv CMe_3$  (6 mol %), and  $Me_3C^{13}CH=CHCMe_3$  (5 mol %) for the LPCVD employing the  $^{13}C$ -labeled alkylidyne carbon. Films grown from  $(^tBuO)_3W\equiv CMe_3$  were  $WO_2$  (determined by XRD after annealing) contaminated with some carbon. The volatile components were  $Me_2C=CH_2$  (45 mol %),  $^tBuOH$  (38 mol %), and  $Me_4C$  (5 mol %), together with  $Me_3CC\equiv CMe_3$ ,  $Me_3CCH=CHCMe_3$ , and  $Me_3CCH_2CH_2CMe_3$  (totaling ca. 10 mol %). Reactions employing  $(^tBu-d_0O)_3W\equiv C(CH_3)_3$  yielded perdeuterated isobutylene and *tert*-butyl alcohol together with  $(CH_3)_3CCD_3$ ,  $(CH_3)_3CCD=CDC(CH_3)_3$ , and  $(CH_3)_3CCD_2-CD_2C(CH_3)_3$ . Reactions employing  $(^tBuO)_3W\equiv N$  were less clean because the precursor was less volatile and it decomposes with sublimation. Nevertheless, the films obtained were predominately  $WO_2$  contaminated with small amounts of C and N (<4%), and the volatile components revealed the presence of  $NH_3$ , isobutylene, and  $^tBuOH$ . Collectively these results show that the metal–ligand multiple bond is labile to hydrogen-transfer reactions, which may lead to loss of the  $W\equiv X$  atom. In the case of WC formation, the elimination of  $Me_3CC\equiv CMe_3$  and  $Me_3CCH=CHCMe_3$  implicate surface chemistry involving C–C coupling of alkylidyne and alkylidene ligands.

## Introduction

Although the origins of the sol–gel process  $[Si(OEt)_4 + H_2O \rightarrow SiO_2 + EtOH]^2$  and CVD [chemical vapor deposition, as in the Mond process,  $Ni(CO)_4 \rightarrow Ni(m) + CO]^3$  date back to work of the last century, only more recent studies have started to elucidate the chemical pathways involved. Particularly noteworthy in the area of CVD leading to metallic films has been the production of thin films of Al,<sup>4</sup> Cu,<sup>5</sup> Au,<sup>6</sup> and Pd,<sup>7</sup> where the nature of the ligand loss has been elucidated with great detail. In the synthesis of binary materials, much attention has

been directed toward the use of complexes where the element–element bonds are present in the precursor and may be retained in the product. For example,<sup>8</sup> in the production of GaAs, the use of a volatile precursor complex of the form  $R_2Ga-AsR_2'$  could afford the advantage of avoiding the use of  $AsH_3$ . Similarly the use of metal–silyl complexes<sup>9</sup> in the preparation of metal silicides could avoid the use of  $SiH_4$ . The potential advantages of using such single source precursors

\* Corresponding author. E-mail: chisholm@indiana.edu.

<sup>†</sup> Present address: Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600.

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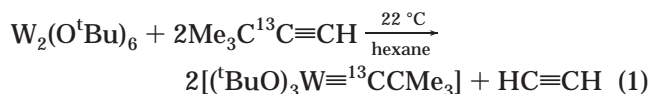
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have been well-promoted in the recent literature, and in some instances success has been achieved in that high-purity films with low levels of undesirable impurities have been obtained. In general, however, this has not been the case, and the complex reaction pathways involved in the CVD production of binary materials remain poorly understood. This is not surprising because the reactions involve gas-gas, gas-surface, and surface-surface reactions and only the nature of the precursor molecule is known. Following the pioneering synthesis by Girolami<sup>10</sup> and co-workers of TiC thin films at temperatures as low as 150–200 °C (10<sup>-2</sup> Torr), we have explored the use of volatile organotungsten compounds for the synthesis of WC films. Tungsten carbide is, of course, one of the most important constituents of modern cemented materials due to its very high hardness and its exceptional inertness to chemical attack. Chemical vapor deposition employing precursors<sup>11</sup> such as W(CO)<sub>6</sub> or WF<sub>6</sub> was known to give films of WC but only with high impurities of heteroatoms such as oxygen or halogens, while the use of organometallic compounds<sup>12a-c</sup> such as ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>W, (allyl)<sub>4</sub>W, CpW(CO)<sub>3</sub>H, and Cp<sub>2</sub>WH<sub>2</sub> gave films with high graphite content. An ingenious attempt to reduce the latter was attempted by employing a trace amount of a volatile organoplatinum compound in the presence of H<sub>2</sub> gas whereby the Pt could assist in the hydrogenation of the unwanted carbon.<sup>12d</sup> This approach met with some success but, of course, led to incorporation of Pt in the films. We were attracted to the use of (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>W=CCMe<sub>3</sub>,<sup>13</sup> which is volatile, contains a relatively high H:C internal ratio, and a thermodynamically strong W-C triple bond. In an initial report in this journal we disclosed that this compound did indeed lead to tungsten carbide films with the near ideal 1:1 W to C ratio.<sup>13</sup> In an attempt to follow the nature of the reaction chemistry, we were determined to use the isotopically labeled compound (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>W=CCMe<sub>3</sub>. We report herein the results of these studies together with the use of another volatile precursor, (tBuO)<sub>3</sub>W=CCMe<sub>3</sub>.

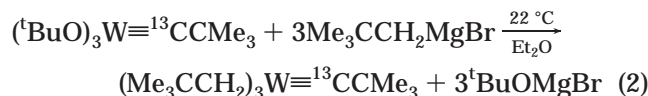
## Results and Discussion

**Synthesis of Precursors.** The introduction of the alkylidyne <sup>13</sup>C label was achieved through the synthesis of Me<sub>3</sub>C<sup>13</sup>C≡CH (see Experimental Section) and its subsequent use in the metathesis reaction shown in eq 1,



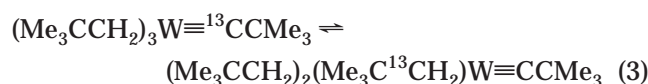
originally discovered by Schrock.<sup>14</sup>

The preparation of (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>W=CCMe<sub>3</sub> employed the alkyl for alkoxide exchange reaction developed earlier in this lab (eq 2),



where the subsequent addition of F<sub>3</sub>B:OEt<sub>2</sub> facilitates the removal of the Mg salts.<sup>15</sup>

Purification of the tris(neopentyl)tungsten neopentylidyne complex by vacuum sublimation (10<sup>-2</sup> Torr, 70 °C) onto a coldfinger at ca. -10 °C leads to alkyl-alkylidyne scrambling, eq 3.



In benzene-*d*<sub>6</sub> at 60 °C, the statistical mixture (no significant <sup>13</sup>C:<sup>12</sup>C isotope effect is observed) of (Me<sub>3</sub>C\*CH<sub>2</sub>)<sub>3</sub>W=CCMe<sub>3</sub> is reached in 24 h. That is to say, the <sup>13</sup>C label is present in the α-carbon atoms in the <sup>13</sup>CH<sub>2</sub>:≡<sup>13</sup>C groups in a 3:1 ratio. This scrambling can easily be seen by <sup>1</sup>H NMR spectroscopy due to the <sup>1</sup>J<sub>C-H</sub> coupling in the methylene protons and <sup>3</sup>J<sub>C-H</sub> ~ 5 Hz for the neopentylidyne ligand. The scrambling by intramolecular C-H to W=C transfer is consistent with our previous studies of the related scrambling involving (Me<sub>3</sub>-SiCH<sub>2</sub>)<sub>3</sub>W=CCMe<sub>3</sub>.<sup>16</sup> The compound (tBuO)<sub>3</sub>W=CCMe<sub>3</sub> was prepared from the "chop-chop Schrock" reaction involving W<sub>2</sub>(O<sup>t</sup>Bu)<sub>6</sub> and MeC≡N.<sup>17</sup>

**Low-Pressure Chemical Vapor Deposition Studies.** The CVD studies employed the use of a hot-walled quartz reactor of a local construction design previously described.<sup>13</sup> The substrates upon which the films were grown were p-type Si(100) wafers, SiO<sub>2</sub>/Si(100), Pyrex, or quartz slides. They were subjected to a standard treatment of washing with acetone/2-propanol followed by deionized water prior to drying in the hot zone of the reactor under vacuum. The LPCVD employed a base pressure of 4 × 10<sup>-3</sup> Torr with the temperature of the reactor at 360 °C (±15 °C). The precursor complex was heated to 50–80 °C and this resulted in film growth rates on the substrates of ca. 3 μm/h. At 360 °C no precursor complex passed through the reactor zone. Decomposition was essentially complete within the first 10–15 cm of the 20 cm tube. The volatile gases were collected in a N<sub>2</sub>(l)-cooled U-tube filled with glass beads which was placed directly following the furnace and prior to the usual N<sub>2</sub>(l) trap and vacuum pump. For studies where the detailed analysis of the volatile components was essential, quartz substrates were used so that both the reactor wall and substrate were the

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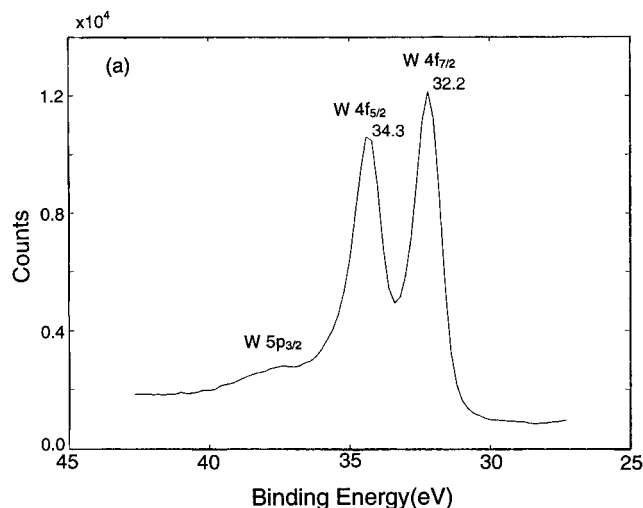
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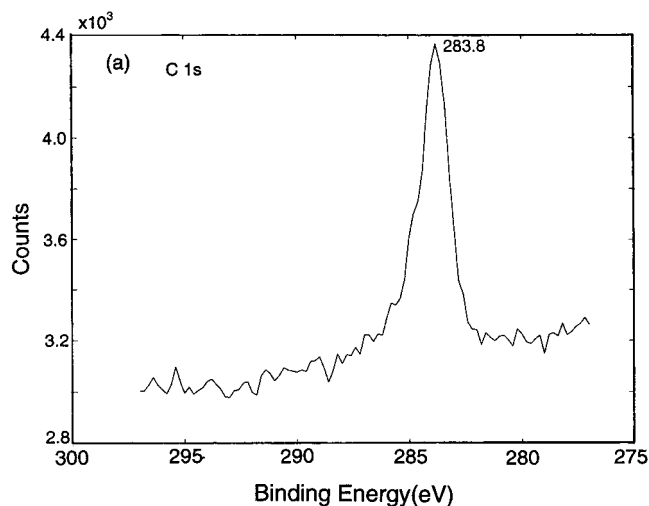


**Figure 1.** XPS spectra on  $W_{4f}$  region of the tungsten carbide film deposited on Si(100) under vacuum at 623 K with a precursor temperature of 323 K.

same. However, in our analyses of the thin films formed by this CVD we observed no selectivity of deposition on Si(100).

The thin films produced were examined by XPS, RBS, XRD, SEM, and in some instances SIMS. The volatile components were collected in a  $N_2(l)$ -cooled U-trap, transferred by vacuum pump from the cold trap, and examined by GC–MS and NMR spectroscopy. By mass balance, >95% of the anticipated organic material was collected. The setup described would not have been able to trap  $H_2$  or  $CH_4$ .

**( $Me_3CCH_2$ ) $_3W\equiv CMe_3$ .** As reported in the preliminary account of this work, gray, shiny films are formed on quartz, Pyrex, Si(100), and  $SiO_2/Si(100)$ . These films are strongly bound to the substrate, passing the Scotch tape test and being resistant to scratching with a file. They are also inert to acid (aqua regia) and alkali (1 N NaOH) for extended periods (>weeks). The XPS data for the films shown in Figure 1 of 32.2 ( $W_{4f_{7/2}}$ ) and 34.3 eV ( $W_{4f_{5/2}}$ ) may be compared with WC standards of 32.2 and 34.4 eV binding energies for  $W_{4f_{5/2}}$  and  $4f_{7/2}$ , respectively. Similarly for the C1s, the binding energy of 283.8 eV (half-width 2.1 eV) compares with that of WC standard (283.2 eV) and is notably different from that of graphite (284.6 eV). See Figure 2. SEMs of the films deposited on Si(100) revealed very smooth surfaces with particle sizes ranging from 300 to 1000 Å. Depth profile analysis by XPS and RBS indicated that the bulk composition of the film was uniform with a carbon-to-tungsten ratio of close to 1:1. RBS indicated the presence of oxygen in the films in the range 5–9 atom %. Very little nitrogen was detected  $\leq 1\%$ , which contrasts with the relatively high N atom content of tungsten oxide films grown in LPCVD employing  $(RO)_4W=O$  under similar conditions.<sup>18</sup> Given the relatively poor background vacuum pressure ( $10^{-2}$ – $10^{-3}$  Torr) and the relative slow rate of film growth, incorporation of O and N is understandable. However, surface sites on the growing film must be able to activate (cleave  $N_2$ ) for N incorporation in  $WO_3$  films and similarly active sites are not apparently present



**Figure 2.** XPS spectra on  $C_{1s}$  region of the tungsten carbide film deposited on Si(100) under vacuum at 623 K with a precursor temperature of 323 K.

**Table 1. Summary of Volatile Components from CVD Reactions Using ( $BuCH_2$ ) $_3W\equiv CMe_3$**

|                      | integral       | integral/no. of hydrogen | mol % |
|----------------------|----------------|--------------------------|-------|
| $CMe_4$              | 55             | $55/12 = 4.6$            | 54    |
| $Me_2C=CH_2$         | 24             | $24/8 = 3$               | 35    |
| $Me_3CC\equiv CMe_3$ | 9              | $9/18 = 0.5$             | 6     |
| $Me_3CCH=CHCMe_3$    | 8 <sup>a</sup> | $8/20 = 0.4$             | 5     |

<sup>a</sup> Based on  $CMe_3$  signal.

during WC film growth. [Activation of  $O_2$  ( $D = 118$  kcal/mol) is expected to be easier than that of  $N_2$  ( $D = 225$  kcal/mol)]. The films did not show any XRD patterns, which leads us to propose that the films are amorphous tungsten carbide with only a small quantity of graphitic carbon. The films remain amorphous after heating under vacuum to 900 °C for 2 h, as determined by XRD.

The volatile components liberated in the preparation of the above films were predominantly neopentane ( $CMe_4$ ) and isobutylene. However, careful examination of these gases also revealed the presence of *trans*- $Me_3CCH=CHCMe_3$  and even  $Me_3CC\equiv CMe_3$ . The volatile components derived from use of the  $\alpha$ - $^{13}C$ -enriched samples revealed the extensive scrambling of the  $^{13}C$  label in the products. Notably, the presence of  $Me_3C^{13}CH=CHCMe_3$  and  $Me_3C^{13}C\equiv CMe_3$  are suggestive of surface C–C bond forming reactions. The liberation of  $Me_3C^{13}CH_3$  surely arises from  $\alpha$  C–H transfer to a  $W^{13}CH_2CMe_3$  moiety. A summary of volatile components analyzed by GC–MS and NMR spectroscopy is given in Table 1.

The relative  $^{12}C:^{13}C$  ratio in the WC films derived from the  $\alpha$ - $^{13}C$ -labeled compounds was examined by SIMS. The ratio was essentially invariant with film depth and was close to 7:1.  $\alpha$ - $^{13}C$  enrichment in the sample was 1:3, indicating that only ca. 50% of the  $\alpha$ -carbon atoms account for the carbon content in the tungsten carbide film. This further attests to the active surface organometallic chemistry that must be occurring during film growth. On the basis of the established organometallic chemistry of metal–neopentyl ligands, one can speculate that  $\alpha$ -CH activation<sup>16,19–21</sup> occurs on

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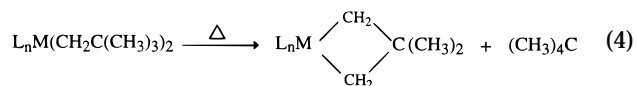
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**Table 2. Summary of Volatile Components from CVD Reactions Using  $({}^t\text{BuO})_3\text{W}\equiv\text{CCMe}_3$** 

|  | integral         | integral/no. of hydrogen | mol % |
|--|------------------|--------------------------|-------|
| $\text{Me}_2\text{C}=\text{CH}_2$                | 32.0             | 32.0/8 = 4               | 45    |
| ${}^t\text{BuOH}$                                | 34.3*            | 34.3/10 = 3.4            | 38    |
| $\text{CMe}_4$                                   | 5.7              | 5.7/12 = 0.48            | 5     |
| $\text{Me}_3\text{CC}\equiv\text{CCMe}_3$        | 3.3              | 3.3/18 = 0.18            | 2     |
| $\text{Me}_3\text{CCH}=\text{CHCMe}_3$           | 7.4 <sup>a</sup> | 7.4/20 = 0.37            | 4     |
| $\text{Me}_3\text{CCH}_2\text{CH}_2\text{CMe}_3$ | 10.0*            | 10.0/22 = 0.46           | 5     |

<sup>a</sup> Based on  $\text{CMe}_3$  signal.

the surface and that this leads to the loss of the original meaning of  $\alpha$  and  $\gamma$ , as both become equivalent. As seen in the chemistry of Th(IV) and Pt(II), for example, dineopentyl complexes liberate neopentane (sometimes reversibly) with the formation of a metallacycle<sup>22–26</sup> (eq 4).



**$({}^t\text{BuO})_3\text{W}\equiv\text{CCMe}_3$ .** This alkoxy alkylidyne complex decomposed in the hot-wall reactor at 300–320 °C,  $10^{-2}$ – $10^{-3}$  Torr, to yield black, highly reflective films. By SEM these appeared to be dense with small particle size (<1000 Å). They did not reveal clear diffraction lines (XRD) as formed, but upon annealing at 600–700 °C, diffraction data consistent with that of  $\text{WO}_2$  were obtained. RBS data revealed that the films contained significant amounts of carbon, up to 25 atom %. We cannot with certainty claim that this is graphitic, since we did not detect this by XRD. It could be incorporated in the film in what is sometimes referred to as WOC. We did not pursue characterization of these films since it was clear that the alkylidyne moiety is for the most part eliminated as neopentane. The major volatile organic molecule is, however,  $\text{Me}_2\text{C}=\text{CH}_2$ , and this is derived from decomposition of the  ${}^t\text{BuO}$  ligands. Reactions employing  $(d_9\text{-Bu}^t\text{O})_3\text{W}\equiv\text{CCMe}_3$  gave overwhelmingly  $(\text{CD}_3)_2\text{C}=\text{CD}_2$ ,  $(\text{CD}_3)_3\text{COD}$ , and neopentane that was partially deuterated ( $d_3$ ,  $d_2$ , and a trace of  $d_1$ ). There could also have been some  $\text{Me}_4\text{C}-d_4$ , which is difficult to detect in its various isotopic forms, e.g.  $(\text{CH}_3)_2\text{C}(\text{CHD}_2)_2$  and  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{D})(\text{CD}_3)$ , in the presence of  $(\text{CH}_3)_3\text{C}(\text{CHD}_2)$  and  $(\text{CH}_3)_3\text{CCD}_3$ . The formation of  $\text{Me}_3\text{CC}\equiv\text{CCMe}_3$ ,  $\text{Me}_3\text{CCD}=\text{CDCMe}_3$ , and  $\text{Me}_3\text{CCD}_2\text{-CD}_2\text{CMe}_3$  are again suggestive of surface chemistry involving alkylidyne, alkylidene, and alkyl groups. Decomposition of  $({}^t\text{BuO}-d_9)_3\text{W}\equiv\text{CCMe}_3$  did not yield protio  $\text{Me}_2\text{C}=\text{CH}_2$ . A summary of the organic products formed in CVD reactions employing  $({}^t\text{BuO})_3\text{W}\equiv\text{CCMe}_3$  is given in Table 2.

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The SIMS analysis of the film formed from  $({}^t\text{BuO})_3\text{W}\equiv{}^{13}\text{CCMe}_3$  showed a near 1:1 ratio for  ${}^{13}\text{C}:{}^{12}\text{C}$  of the carbon contained in the film. Thus the carbon content of the film is 50%, derived from the alkylidyne moiety. Again scrambling of the  $\alpha$  and other carbon atoms of the neopentylidyne ligand must occur during decomposition.

**$({}^t\text{BuO})_3\text{W}\equiv\text{N}$**  was also used as a precursor molecule in LPCVD experiments. This, however, is not a good precursor since it sublimes with decomposition. One cannot therefore distinguish from product analysis of the organic materials those which are formed by CVD from those which are formed by solid-state thermolysis. Black, metallic films formed at ca. 300 °C,  $10^{-3}$  Torr were found to have low C and N content (<4 atom %), and upon annealing,  $\text{WO}_2$  was identified by XRD. Analysis of the volatile components revealed the formation of isobutylene,  ${}^t\text{BuOH}$ , and ammonia as the major carbon and nitrogen containing products.

## Concluding Remarks

$(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$  provides a good molecular precursor for inert thin films on  $\text{SiO}_2$  and  $\text{Si}(100)$ . These are formulated as WC based on stoichiometry and XPS data, though they do not show XRD patterns characteristic of crystalline WC. Oxygen impurities (5–9 atom %) presumably arise from the background atmosphere at the relatively low pressures employed in the LPCVD. Undoubtedly better reactor design with a much lower base pressure would dramatically lower the oxygen contamination. The labeling studies reveal that the tungsten-bound alkylidyne carbon is kinetically labile to a variety of scrambling processes, including in the case of  $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$ , a relatively facile C–H atom transfer which interconverts alkyl and alkylidyne ligands. The SIMS analysis of the  ${}^{13}\text{C}:{}^{12}\text{C}$  ratio in the WC film shows that C atoms other than  $\alpha$ -carbons are incorporated as carbide. From an examination of the volatile components, we see products derived from C–C coupling reactions. These are suggestive of surface-bound alkylidene and alkylidyne species. Some of these are responsible for the loss of the alkylidyne carbon. The LPCVD reactions employing both  $({}^t\text{BuO})_3\text{W}\equiv\text{CCMe}_3$  and  $({}^t\text{BuO})_3\text{W}\equiv\text{N}$  show that elimination of the  $\text{W}\equiv\text{E}$  heteroatom occurs with ease as a result of hydrogen atom transfer and that the predominant product is in both cases  $\text{WO}_2$ .

To stress the positive, use of  $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$  provides a low-temperature route in the synthesis of WC films. Relative to the reactions employing  $\text{Cp}_2\text{WH}_2$ ,  $(\text{allyl})_4\text{W}$ ,  $(\text{crotyl})_4\text{W}$ , and  $\text{CpW}(\text{CO})_3\text{X}$ , where X = Me and H,<sup>12</sup> which yield a mixture of WC and graphite (ca. 50:50), the success of  $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$  may rest with its relatively high internal H to C content. Thus  $(\text{Me}_3\text{CCH}_2)_3\text{W}\equiv\text{CCMe}_3$  may provide a useful low-temperature precursor for coatings and/or catalysts employing thin films of WC.

## Experimental Section

All preparations and handling procedures employed the use of dry, oxygen-free atmospheres ( $\text{N}_2$ ) and solvents.  $\text{W}_2(\text{O}^-$

Bu)<sub>6</sub>,<sup>27</sup> (<sup>t</sup>BuO)<sub>3</sub>W≡\*CCMe<sub>3</sub>,<sup>14</sup> (<sup>t</sup>BuO)<sub>3</sub>W≡N,<sup>17</sup> and (Me<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>W≡CCMe<sub>3</sub><sup>15</sup> were prepared by literature procedures. Me<sub>3</sub>C<sup>13</sup>C≡CH was prepared as outlined below.

(1)  $\text{Bu}^t\text{MgCl} + {}^*\text{CO}_2 \xrightarrow{+\text{H}^+} \text{Bu}^t\text{COOH}$ . In a flame-dried 300 mL Schlenk flask was added 24 mL of 2 M (0.48 mol) Bu<sup>t</sup>MgCl/Et<sub>2</sub>O (Aldrich) solution. The solution was subjected to four freeze–pump–thaw cycles and then kept at –12 °C under the vapor of Et<sub>2</sub>O (130 mmHg).

The flask was then opened to another flask containing 1 L of \*CO<sub>2</sub> gas (Cambridge Isotope Laboratories) at ambient pressure (41.1 mmol). The \*CO<sub>2</sub> was transferred to the flask containing the Grignard solution. After 45 min when the pressure of the system was steady at 130 mmHg, the flask containing the Grignard reagent was cooled by liquid N<sub>2</sub> to condense the remaining \*CO<sub>2</sub> gas into the reaction flask. The sealed flask was then kept at 0 °C and stirred for 2 h.

Nitrogen gas at the ambient pressure was then introduced to the flask. At 0 °C, 43 mL of 25% H<sub>2</sub>SO<sub>4</sub> was added dropwise. Then in air, Et<sub>2</sub>O was added and the ether layer was collected. The water layer was extracted with 4 × 30 mL of Et<sub>2</sub>O and the Et<sub>2</sub>O solution was dried by MgSO<sub>4</sub>. The Et<sub>2</sub>O was removed first by distillation till the solution reached 60 °C and then by a water aspirator at –15 °C to give 4.41 g of crude Bu<sup>t</sup>COOH as a white solid at 0 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 1.22 (s, CH<sub>3</sub>, <sup>3</sup>J<sub>C–H</sub> = 4.4), the –OH peak was not resolved; <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 183.6 (\*C=O), 38.4 (d, CMe<sub>3</sub>, <sup>1</sup>J<sub>C–C</sub> = 54.8), 27.0 (d, CMe<sub>3</sub>, <sup>2</sup>J<sub>C–C</sub> = 1.0).

(2)  $\text{Bu}^t\text{COOH} + \text{SOCl}_2 \rightarrow \text{Bu}^t\text{COCl}$ . Bu<sup>t</sup>COOH (4.41 g) was added to 4.6 mL (1.5-fold excess) of freshly distilled SOCl<sub>2</sub> and the solution was refluxed under N<sub>2</sub> for 2.5 h. The clear liquid was then pumped at 70 °C to give a mixture of Bu<sup>t</sup>COCl and unreacted SOCl<sub>2</sub> (total weight, 7.06 g). The mixture was used in the following reaction without further purification: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 1.31 (s, CH<sub>3</sub>, <sup>3</sup>J<sub>C–H</sub> = 6.2); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 180.6 (\*C=O), 49.2 (d, CMe<sub>3</sub>, <sup>1</sup>J<sub>C–C</sub> = 50.7), 27.1 (d, CMe<sub>3</sub>, <sup>2</sup>J<sub>C–C</sub> = 0.6).

(3)  $\text{Bu}^t\text{COCl} + \frac{1}{2}\text{Me}_2\text{CuLi} \rightarrow \text{Bu}^t\text{COMe}$ . Half of the Bu<sup>t</sup>COCl liquid prepared above (3.53 g) was added to 30 mL of dry Et<sub>2</sub>O. The solution was then degassed by three freeze–pump–thaw cycles and then cooled to –78 °C.

CuI (16.7 g, 0.0878 mol) in a 500 mL flask was flame-dried under vacuum for 5 min. The flask was cooled to 0 °C and added to 125 mL of 1.4 M MeLi (Aldrich). The gray solution was stirred for 15 min at 0 °C and cooled to –78 °C and the Bu<sup>t</sup>COCl/SOCl<sub>2</sub> in Et<sub>2</sub>O was added. The mixture was stirred for 15 min at –78 °C. Subsequently, 9.9 g MeOH was added. The solution was warmed to 23 °C overnight. Then the solution was poured into 150 mL of saturated NH<sub>4</sub>Cl/H<sub>2</sub>O solution.

The organic layer was separated and the water layer was extracted with 3 × 100 mL of Et<sub>2</sub>O. The combined Et<sub>2</sub>O solution was dried over MgSO<sub>4</sub>. The volume of the solution was reduced through Et<sub>2</sub>O distillation. The solution was used in the following reaction without further purification: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 2.06 (d, COMe, <sup>2</sup>J<sub>C–H</sub> = 5.6), 1.07 (d, CMe<sub>3</sub>, <sup>3</sup>J<sub>C–H</sub> = 4.1); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 214.1 (\*C=O), 44.2 (d, CMe<sub>3</sub>, <sup>1</sup>J<sub>C–C</sub> = 39.2), 26.3 (d, CMe<sub>3</sub>, <sup>2</sup>J<sub>C–C</sub> = 0.5), 24.5 (COMe, <sup>1</sup>J<sub>C–C</sub> = 39.4).

(4)  $\text{Bu}^t\text{COMe} + \text{PCl}_5 \rightarrow \text{Bu}^t\text{CCl}_2\text{Me}$ . To an oven-dried Schlenk flask was added 6.1 g of finely ground PCl<sub>5</sub>. The Bu<sup>t</sup>COMe/Et<sub>2</sub>O solution was degassed by three freeze–pump–thaw cycles and added dropwise to the PCl<sub>5</sub> powder at 0 °C. The mixture was slowly warmed to 23 °C with stirring. The suspension was then poured into 100 g of ice. NaHCO<sub>3</sub> was added to the mixture until the pH was 8. The Et<sub>2</sub>O was collected, and the water layer was extracted with 3 × 100 mL of Et<sub>2</sub>O. The Et<sub>2</sub>O solution was dried over CaCl<sub>2</sub>. Et<sub>2</sub>O was removed by distillation to leave a clear solution of Bu<sup>t</sup>CCl<sub>2</sub>–

Me with some remaining Et<sub>2</sub>O. The solution was used in the following reaction without further purification.

(5)  $\text{Bu}^t\text{CCl}_2\text{Me} + \text{KOBu}^t \rightarrow \text{Bu}^t\text{C}\equiv\text{CH}$ . The Bu<sup>t</sup>CCl<sub>2</sub>–Me/Et<sub>2</sub>O prepared above was degassed by three freeze–pump–thaw cycles, and 2 mL of anhydrous DMSO (Aldrich) was added. The solution was added dropwise to KOBu<sup>t</sup> (4.84 g, 0.0431 mol) in 12 mL of anhydrous DMSO and subsequently stirred at 23 °C for 4 h.

Subsequent distillation and pumping (by water aspirator) at 70 °C gave 9.0 g of a mixture of Bu<sup>t</sup>C≡CH and Et<sub>2</sub>O collected at –78 °C. The mixture was found to contain 0.92 g of Bu<sup>t</sup>C≡CH (11.1 mmol) by <sup>1</sup>H NMR spectroscopy. The solution was used without further purification to make (Bu<sup>t</sup>O)<sub>3</sub>W≡\*C<sup>t</sup>Bu: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 2.04 (d, ≡CH, <sup>2</sup>J<sub>C–H</sub> = 48.2), 1.22 (d, CMe<sub>3</sub>, <sup>3</sup>J<sub>C–H</sub> = 5.2); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 93.2 (Bu<sup>t</sup>C), 66.3 (d, ≡C–H, <sup>1</sup>J<sub>C–C</sub> = 166.4), 30.9 (d, CMe<sub>3</sub>, <sup>2</sup>J<sub>C–C</sub> = 1.6), 27.2 (Me<sub>3</sub>C, <sup>1</sup>J<sub>C–C</sub> = 65.5).

(7)  $\frac{1}{2}\text{W}_2(\text{O}^t\text{Bu})_6 + \text{Bu}^t\text{C}\equiv\text{CH} \rightarrow (\text{Bu}^t\text{O})_3\text{W}\equiv\text{C}^t\text{Bu}$ . To W<sub>2</sub>(OBu<sup>t</sup>)<sub>6</sub> (7.39 g) in 150 mL of pentane was added the Bu<sup>t</sup>C≡CH/Et<sub>2</sub>O solution which had been degassed by three freeze–pump–thaw cycles. After being stirred overnight at 23 °C, all the volatile components were removed. Sublimation gave 2.7 g of (Bu<sup>t</sup>O)<sub>3</sub>W≡\*C<sup>t</sup>Bu (5.7 mmol or 27.7% from \*CO<sub>2</sub>). Note: Only half of the Bu<sup>t</sup>COCl liquid was used in the preparation: <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 1.46 (s, OCMe<sub>3</sub>), 1.37 (d, ≡\*CCMe<sub>3</sub>, <sup>3</sup>J<sub>C–H</sub> = 4.3); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm, 23 °C, *J* in Hz) δ 271.4 (≡\*CCMe<sub>3</sub>, <sup>1</sup>J<sub>W–C</sub> = 296.2), 79.0 (d, OCMe<sub>3</sub>, <sup>3</sup>J<sub>C–C</sub> = 0.7), 49.8 (d, ≡\*CCMe<sub>3</sub>, <sup>1</sup>J<sub>CC</sub> = 32.5), 34.2 (s, Me<sub>3</sub>CO), 32.6 (d, ≡\*CCMe<sub>3</sub>, <sup>2</sup>J<sub>C–C</sub> = 0.7).

(8)  $(\text{Bu}^t\text{O})_3\text{W}\equiv\text{C}^t\text{Bu} + 3^t\text{BuCH}_2\text{MgX} \rightarrow (\text{Bu}^t\text{CH}_2)_3\text{W}\equiv\text{C}^t\text{Bu}$  (X = Br, Cl). (Bu<sup>t</sup>O)<sub>3</sub>W≡\*C<sup>t</sup>Bu (0.10 g, 0.21 mmol) was added dropwise to a total of 3.0 mL of 0.286 M BuCH<sub>2</sub>–MgCl at –78 °C. The solution was slowly warmed to 23 °C overnight. After the volatile components were removed under vacuum, the residue was extracted with pentane. The pentane solution was filtered. Sublimation (70 °C, 10<sup>–2</sup> Torr) of the extract gave 25 mg (0.053 mmol, 25% yield) of yellow (BuCH<sub>2</sub>)<sub>3</sub>W≡\*C<sup>t</sup>Bu. <sup>1</sup>H NMR (through the integration of the ≡CCMe<sub>3</sub> peaks) analysis indicated that the alkylidyne carbon was 45% <sup>13</sup>C-enriched.

In a separate experiment, (Bu<sup>t</sup>O)<sub>3</sub>W≡\*C<sup>t</sup>Bu (0.20 g, 0.42 mmol) in 10 mL of Et<sub>2</sub>O was added dropwise a total of 3.0 mL of 0.507 M BuCH<sub>2</sub>MgBr at –78 °C. The solution was slowly warmed to 23 °C overnight, after which the volatile components were removed under vacuum. The sublimation of the residue (60 °C, 10<sup>–2</sup> Torr) gave 100 mg of yellow (BuCH<sub>2</sub>)<sub>3</sub>W≡\*C<sup>t</sup>Bu (50%). <sup>1</sup>H NMR analysis indicated that the alkylidyne carbon was ca. 62% <sup>13</sup>C enriched. Heating a benzene-*d*<sub>6</sub> solution of the <sup>13</sup>C labeled complex at 100 °C, 24 h, produced what appeared to be a statistical mixture of α-<sup>13</sup>C labels according to eq 3.

**Thin Film Production.** In a locally constructed apparatus (previously described)<sup>13</sup> the volatile organometallic precursor was heated to its sublimation temperature, 80–100 °C (X<sub>3</sub>W≡CCMe<sub>3</sub>, where X = BuO and Me<sub>3</sub>CCH<sub>2</sub>), under a dynamic vacuum and the vapor passed into the quartz tube containing the substrates within the oven heated to 300–360 °C, the required decomposition temperature of the sample (X = CH<sub>2</sub>CMe<sub>3</sub>, 360 °C; X = BuO, 300–320 °C). The volatile materials were passed through a U-tube containing glass beads cooled in liquid nitrogen. The condensable materials so collected were analyzed by GC–MS and by NMR spectroscopy.

The Si(100), quartz, SiO<sub>2</sub>/Si(100), or silica substrates were cleaned in an acid wash, followed by deionized water and EtOH, and then dried at 150 °C prior to use.

The compound (Bu<sup>t</sup>O)<sub>3</sub>W≡N, which is an infinite polymer,<sup>28</sup> sublimed with decomposition at 100–120 °C and was decomposed in the furnace at 300 °C. The background pressure for all reactions was ca. 10<sup>–3</sup> Torr.

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**Analysis of the Thin Films.** The SIMS  $^{13}\text{C}:^{12}\text{C}$  analyses were performed at the University of Minnesota, Materials Research Lab on a PHI SIMS II instrument operating at 5 kV with an ion raster area of  $4 \times 4$  mm. The  $^{13}\text{C}:^{12}\text{C}$  ratio was determined throughout the film.

XPS was carried out on a Surface Science Lab SSX-100 system or PHI-560 equipped with a 3 keV  $\text{Ar}^+$  sputter gun. The electron energy analyzer was calibrated to the  $\text{Au}4f_{7/2}$  line at 84 eV. XPS spectra were collected in the unscanned mode by using monochromatized  $\text{Al K}\alpha$  excitation with a spot size of  $600 \mu\text{m}$  and the electron-energy analyzer set for a pass energy of 150 eV. The experimental detector width is 18.6 eV in this configuration. The base pressure was  $10^{-7}$  Torr with the  $\text{Ar}^+$  gun on.

RBS analyses were obtained on a General Ionics Model 4117 using a beam of  $\text{He}^+$  of energy 2.0 MeV for films deposited on silicon.

SEM images were obtained by using a Cambridge Instruments Stereoscan 250 Mk2 microscope.

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