Computational Study of the Gas Phase Reactions of Isopropylimido and Allylimido Tungsten Precursors for Chemical Vapor Deposition of Tungsten Carbonitride Films: Implications for the Choice of Carrier Gas

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Computational chemistry was employed to investigate possible gas phase decomposition pathways of the precursors $Cl_4(CH_3CN)W{=}NR$ (**2**: R = ^{i}Pr; **3**: R = C_3H_5) for MOCVD of tungsten carbonitride (WN_xC_y) thin films. The preferred pathways were demonstrated to be dependent on the presence of reactive species as a model for the selection of carrier gas in deposition experiments. For all gases, rapid dissociation of the acetonitrile ligand to generate $Cl_4W{=}NR$ (**2a**: R = ^{i}Pr; **3a**: R = C_3H_5) was assumed to be the first step. Calculations on a unimolecular pathway to generate WCl_4 from **2a** or **3a** via α-shift of hydrogen and subsequent W−N(imido) bond cleavage are consistent with mass spectrometric data on **2** and **3**. The presence of H_2 facilitated cleavage of the metal-chloride bonds via σ-bond metathesis, resulting in an increase in the strength of the W−N(imido) bond compared to the N(imido)−C bond. The presence of NH_3 led to exchange of the alkylimido ligand (NR) with NH via transamination and also to addition−elimination pathways that generated derivatives with an additional N-bound ligand (amido or imido) and concomitant loss of HCl. These reaction pathways had similar activation energies, suggesting that film growth and film properties could be altered by the choice of carrier gas.

Introduction

Tungsten nitride (WN_x) and tungsten carbonitrides (WN_xC_y) are promising barrier materials for prevention of copper migration in integrated circuits (ICs) with Cu-based metallization.[1−9] We recently reported the growth of WN_xC_y thin films by metal-organic chemical vapor deposition (MOCVD) using a series of related single source precursors: the phenylimido complex $Cl_4(CH_3CN)W{=}NPh$ (**1**),[10] the isopropylimido complex $Cl_4(CH_3CN)W{=}N^iPr$ (**2**),[11] and the allylimido complex $Cl_4(CH_3CN)W{=}NC_3H_5$ (**3**).[12] Since the precursors **1**−**3** were dissolved in benzonitrile for aerosol-assisted CVD, their acetonitrile ligands exchanged for benzonitrile during the course of the depositions,[13] but for simplicity here, we will refer to them as the acetonitrile complexes **1**−**3**. In conjunction with these experimental studies, we also reported density functional theory (DFT) calculations[13] showing that **1** has a stronger N(imido)−C bond and a slightly weaker W−N(imido) bond than **2** and **3**. The facile loss of the PhN moiety from **1** as a result of the weaker W−N and stronger N−C bonds manifested itself in the very low nitrogen content (maximum of 3 atom %) in films deposited from phenylimido complex **1**[10] compared to those from **2** and **3**. However, even with the more favorable bonding situations in **2** and **3**, the nitrogen contents of the WN_xC_y films deposited from **1**−**3** were generally low (maximum 11 atom % even with **2** and **3**) compared to those in the stoichiometric compound W_2N.[12] Efforts to increase nitrogen content in the deposited films by addition of ammonia (NH_3) to the carrier gas during depositions from **2** resulted in an increase in N content from 8 to 24 atom %

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for films deposited at 450 °C.[14] This effect was also manifested as an increase in N content (4 to 23 atom %) for depositions from **3** in the presence of ammonia.[15] Lower carbon content was obtained upon addition of ammonia to the carrier gas during depositions from **2** and **3** in the temperature range 450 to 650 °C. [14,15] We now report a computational investigation on the gas phase decomposition pathways of **2** and **3** in the presence of inert gas only, with H_2 carrier, and with the addition of NH_3, discussing the low nitrogen inclusion in the deposited films from **2** and **3** and the increase of nitrogen content when depositions are carried out in the presence of NH_3. The correlation of positive ion electron ionization (EI) MS data for **2** and **3** with the results of computational chemistry is consistent with a pathway for the unimolecular decomposition of **2** and **3** into WCl_4, a process that is a model system for loss of the imido ligand in the gas phase during CVD. Dissociation of the imido ligand by an analogous pathway would decrease nitrogen content in the films and does not require reducing agents such as hydrogen and NH_3. On the contrary, the presence of NH_3 during depositions enables two relatively low barrier pathways: transamination of the imido ligand with NH_3 and an addition−elimination sequence that results in net exchange of ancillary chloride ligands for NH_2. Both of these pathways generate N-bound ligands that could facilitate nitrogen incorporation into the films. These results suggest that the gas phase decomposition behavior of the precursors during MOCVD could be modified with the selection of carrier gas.

Computational Methods

All calculations were carried out with GAUSSIAN 03,[16] using the B3LYP DFT method and split basis sets (LanL2DZ for tungsten and 6-311G(d) for other elements).[16−18] Full geometry optimization was carried out for all species. The transition state (TS) was optimized using the Berny algorithm as implemented in GAUSSIAN 03.[16] Harmonic vibrational frequencies were calculated for each structure, and used to compute enthalpy. Materials Studio 4.2 was used for the visualization of the results.

Table 1. Summary of Relative Abundances for Positive Ion EI Mass Spectra of Tungsten Imido Complexes 2 and 3

		relative abundance[a]	
EI fragments	*m/z*	R = ^{i}Pr (**2**)	R = allyl (**3**)
$[Cl_3W({=}NR)]^+$	348/346	100	100
$[Cl_4W]^+$	326	26	34
$[Cl_3W({=}NH)]^+$	306	78	12
$[Cl_3W]^+$	291	30	58
$[CH_3CN]^+$	41	24	95

[a] Relative abundances were adjusted by summing the observed intensities for the predicted peaks of each mass envelope and normalizing the largest sum to 100%. Data are taken from refs 11 and 12.

Results and Discussion

Unimolecular Decomposition Pathways of 2 and 3 (Inert Carrier Gas). Since experimental data on the species obtained by gas phase pyrolysis of complexes **2** and **3** are not available, mass spectrometric fragmentation patterns were used to suggest possible cleavage pathways during thermal decomposition. The caveats associated with predicting CVD behavior by mass spectrometry have been discussed previously in the literature,[19,20] but we have found such data to be useful in understanding the fragmentation of precursors under deposition conditions.[10−12] The positive ion EI MS data for **2** and **3** are summarized in Table 1. The relative abundance of $[Cl_3W{=}NH]^+$ with respect to $[Cl_3W]^+$ shows different behavior for **2** and **3**. Isopropylimido complex **2** exhibits a much higher abundance of $[Cl_3W{=}NH]^+$, which results from cleavage of the N−C bond in the imido ligand, following initial chloride loss during the ionization process. The trend is reversed for **3**, which undergoes more extensive cleavage to $[Cl_3W]^+$.

On the basis of this information, two possible unimolecular pathways from the cationic complex $[Cl_3W{=}N^i\mathrm{Pr}]^+$ were constructed (Scheme 1). Although CVD conditions are not ionizing and these cations are thus not expected to play any role in film deposition, their reactions could be used to model possible mechanistic steps involving the imido ligand. In this way, the thermal reactions under CVD conditions could be discussed in the context of mass spectrometric data, as has been described in the literature.[21,22] In the first pathway (a-1, Scheme 1), a hydrogen is transferred from the methyl group of the isopropylimido moiety to the nitrogen with concomitant formation of $[Cl_3W({=}NH)]^+$ and propylene. In the second pathway (a-2), the methine hydrogen from the isopropyl is shifted to the nitrogen, releasing the imine $(CH_3)_2C{=}NH$ as the organic fragment to generate $[Cl_3W]^+$. For the allylimido complex $\mathbf{3}^+$, pathway b-1 (Scheme 1) involves transfer of the methine hydrogen to afford allene and $[Cl_3W({=}NH)]^+$, in a process analogous to pathway a-1. Note that pathways for conversion of titanium amido to imido complexes have been explored computationally,[23,24] but to

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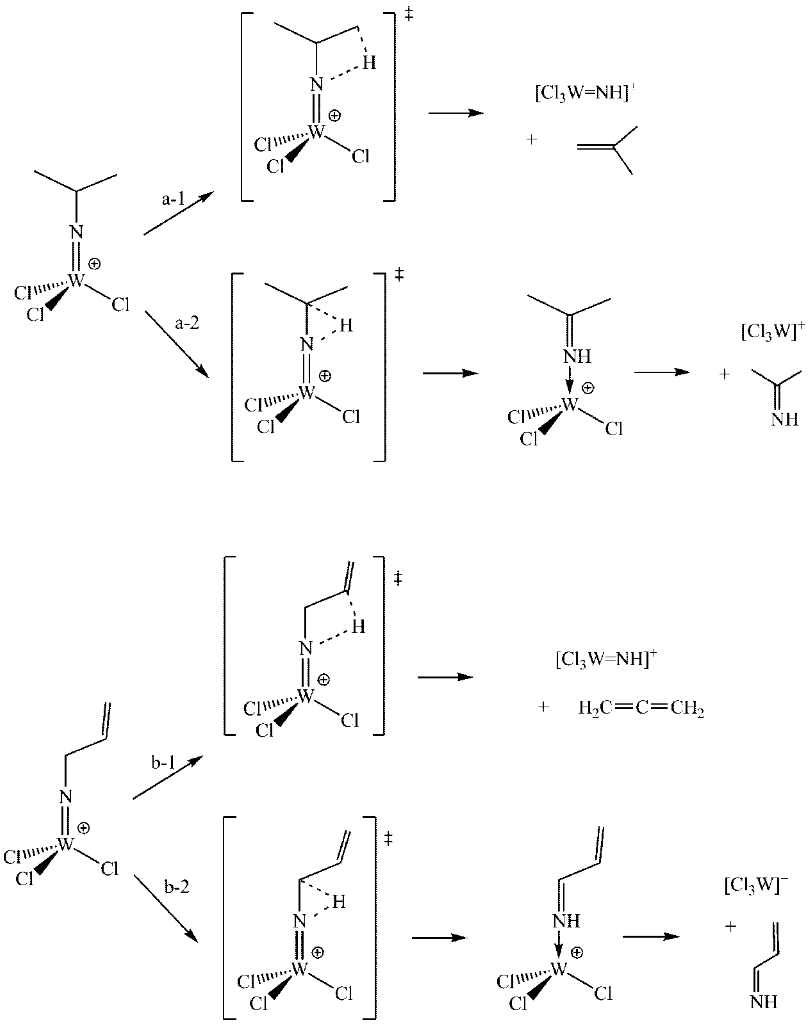
Scheme 1



our knowledge, these pathways for the fragmentation of imido ligands have not been reported.

To the extent that the Scheme 1 pathways are also valid for the imido ligands in the neutral molecules, the related complexes $Cl_4W{=}N^iPr$ (**2a**) and $Cl_4W{=}NC_3H_5$ (**3a**), which are the products of acetonitrile (CH_3CN) loss from **2** and **3**, can be used as starting points for a computational investigation of unimolecular decomposition mechanisms for **2** and **3**, which is a model system for CVD growth from **2** or **3** using only an inert carrier gas. The facile dissociation of acetonitrile from **1**−**3** has already been established both experimentally and computationally.[13] Energies of the important stationary points on the reaction surfaces for decomposition of the imido ligands of **2a** and **3a** by the Scheme 1 reactions are depicted in Figure 1. Note that the activation barriers for these pathways are high, consistent with the poor film quality observed experimentally when only inert carrier gases are present.[25] Formation of tungsten tetrachloride (WCl_4) and the corresponding imine is predicted to be preferred to pathways that retain the W−N bond for both cases. The activation energies ($\Delta H^{\ddagger,\circ}_{298}$) for WCl_4 formation are calculated to be 60.4 kcal/mol for **2a** and 55.1 kcal/mol for **3a**, respectively. A unimolecular pathway for loss of nitrogen from the precursor during the deposition is consistent with the low N/W ratios for the films deposited using **2** and **3**, both in the presence of H_2[12] and during the use of N_2 carrier gas.[25] Note that the nearly linear W=N−C geometry in imido complexes **2a** and **3a** would prevent the β-H elimination processes that have been invoked for early metal amides on the basis of computational[23] and experimental[26−32] studies. Direct hydrogen transfer to the chloride ligands would also be hindered by the geometry of the imido ligand, in contrast to the chemistry of early metal amides, where calculations suggest that direct H-transfer to a leaving group can be an accessible pathway.[23,24,33,34]

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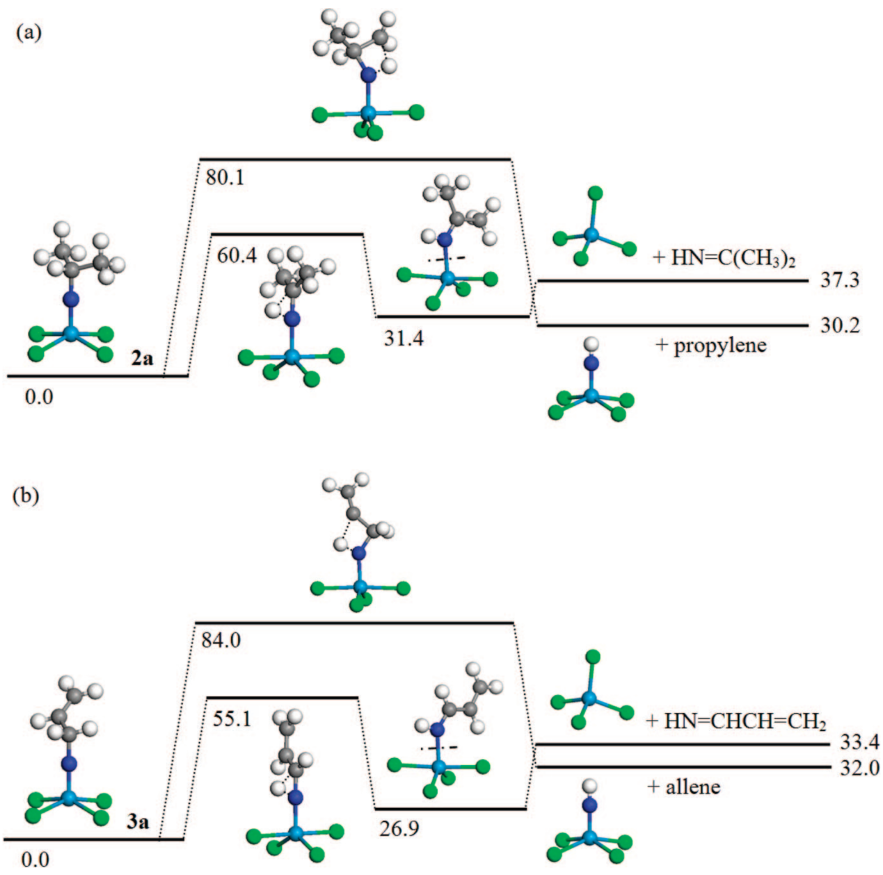

Figure 1. Energetics for two possible unimolecular decomposition pathways of (a) **2a** and (b) **3a**. Enthalpy values (ΔH°_{298}) have the unit of kcal/mol.

Table 2. Calculated Bond Dissociation Enthalpy (BDE, ΔH°_{298}) for the N(imido)—C and W—N(imido) bonds in 2a–3a and 2b–3b

compound	BDE (N(imido)—C) (kcal/mol)	BDE (W—N(imido)) (kcal/mol)
2a	98.4[a]	88.2[a]
2b	82.8	106.9
3a	82.7[a]	86.4[a]
3b	67.9	106.3

[a] Data are taken from ref 13.

Unimolecular Decomposition Pathways of 2 and 3 after Reaction with H_2 Carrier Gas. We have previously provided experimental and computational evidence for conversion of metal chloride bonds to metal hydrides during CVD from **2** and **3** in the presence of H_2 carrier gas.[13] Loss of acetonitrile and complete σ-bond metathesis of the metal-chloride bonds of **2** and **3** with H_2 would afford the hydride complexes $H_4W{=}N^iPr$ (**2b**) or $H_4W{=}NC_3H_5$ (**3b**), respectively. It is interesting that calculations on a pathway for WH_4 formation via shift of the methine hydrogen from **2b** or **3b** analogous to the Scheme 1 reactions did not result in location of a transition state. Although it is not clear how many of the chlorides would be removed by metathesis in the gas phase before surface reactions begin, it is interesting that the formation of metal hydride moieties appears to hinder the hydrogen transfer from the methine carbon to the imido nitrogen that results in release of the nitrogen in the imine product (Scheme 1, paths a-2 and b-2). As shown in Table 2, the σ-bond metathesis with H_2 renders the W—N(imido) bond stronger and N(imido)—C bond weaker both in $H_4W{=}N^iPr$ (**2b**) and $H_4W{=}NC_3H_5$ (**3b**) compared to those in **2a** and **3a**. Interestingly, the calculated N(imido)—C bond strengths for hydride complexes **2b** and **3b** are closer to the reported homolytic N—C bond dissociation energies of the corresponding organic amines RNH_2 (cf. $^iPrNH_2 = 84$ kcal/mol; $C_3H_5NH_2 = 73$ kcal/mol),[35,36] suggesting that the presence of the chlorides in **2a** and **3a** had strengthened the N(imido)—C bond. These results imply that replacement of chloride ligands by hydrides upon reaction with H_2 carrier gas will have a positive effect on cleavage of the N(imido)—C bond and preservation of the W—N(imido) bond during the deposition.

Reactions with NH_3: Transamination of the Imido Ligand and Loss of Chloride by Addition–Elimination. In the presence of NH_3, transamination of the imido ligand[37−39] provides another possible pathway for the gas phase reaction of precursors **2** and **3**. As described above, reaction of **2** and **3** is expected to begin with the facile dissociation of the acetonitrile ligand to generate intermediates **2a** and **3a**. Figure 2a illustrates the calculated energies along the pathway for the subsequent transamination of the isopropylimido ligand of **2a** with NH_3. Initial addition of NH_3 to the empty coordination site on W is exothermic, having a reaction enthalpy (ΔH°_{298}) of −20.8 kcal/mol.

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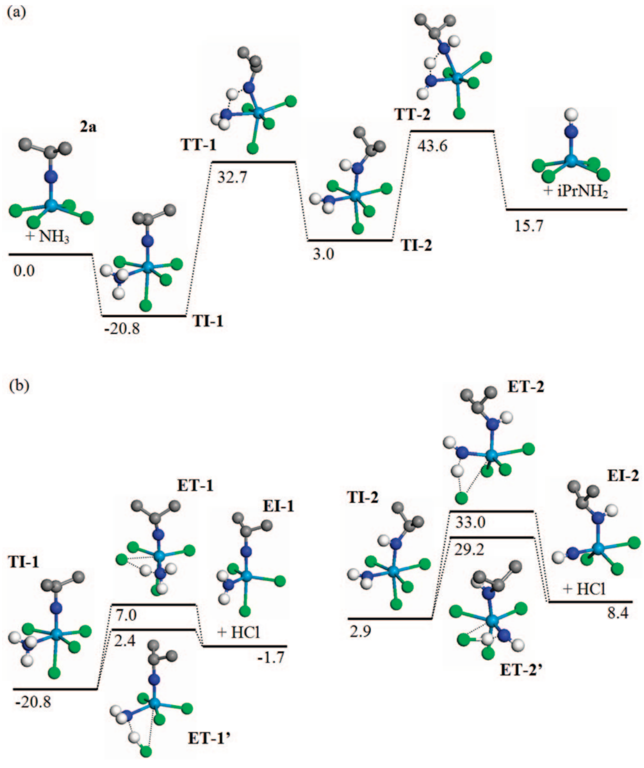

Figure 2. Energetics for (a) transamination of **2a** with NH$_3$ and (b) 1,2-elimination of HCl from **TI-1** and **TI-2**. Enthalpy values (ΔH°_{298}) are reported in kcal/mol. Hydrogens on the isopropyl groups are omitted for clarity.

Conversion of the isopropylimido ligand to isopropylamine is calculated to proceed via the (bis)amide complex **TI-2**, which ultimately affords Cl$_4$W═NH after a second proton transfer and loss of the isopropylamine ligand. The energies in this pathway are much lower than those calculated for unimolecular decomposition of Cl$_4$W═N^{i}Pr (Figure 1), consistent with transamination being the dominant pathway for alkyl loss during CVD in the presence of NH$_3$. This result is consistent with calculations previously reported for the reaction of NH$_3$ with (^{t}BuN)$_2$W(NH^{t}Bu)$_2$ under ALD conditions.[40] As this pathway preserves the W—N bond, it would be favorable for deposition of N-rich films, which is what is observed experimentally for both precursors **2** and **3**.[14,15]

The chlorides could then be removed either in the gas phase by addition of NH$_3$ followed by elimination of HCl[41−43] or via surface reaction with species generated from NH$_3$.[44,45] Figure 2b illustrates the calculated energetics for 1,2-elimination of HCl from ammonia adduct **TI-1** and bisamido complex **TI-2**, respectively. The activation barriers are lower than in the pathway of transamination of the isopropylimido ligand of **2a** with NH$_3$ (Figure 2a) at each corresponding step. This implies that loss of HCl from intermediates **TI-1** and **TI-2** is competitive with transamination (**TI-1** to **EI-1** has a particularly low barrier). Not only does this provide a route toward the experimentally observed chloride-free films, the resulting amido and imido ligands in **EI-1** and **EI-2** could facilitate the increase in N content for films deposited in the low temperature range in the presence of NH$_3$.[14] As the growth temperature increases, the transamination pathway (Figure 2a) will become increasingly competitive, providing a means of removing the isopropyl group as isopropylamine. The possibility of chloride removal by addition of ammonia followed by elimination of HCl contrasts with the situation in H$_2$ carrier gas where the gas phase chloride loss pathway has been calculated to be σ-bond metathesis with H$_2$.[13] Alternatively, reactions with surface hydrides derived from H$_2$ carrier gas could generate the HCl product under those conditions.

Table 3. Comparison of Calculated Pathways for Reaction of 2a with Carrier Gas

carrier gas	W product	activation energy ($\Delta H^{\ddagger,\circ}_{298}$, kcal/mol)	predicted film constitution (N/W ratio)
inert	Cl$_4$W	60.4	low
H$_2$	Cl$_3$HW═N^{i}Pr	37.2^a	intermediate
NH$_3$	Cl$_3$(NH$_2$)W═N^{i}Pr (**EI-1**)	2.4	high
	Cl$_3$(NH^{i}Pr)W═NH (**EI-2**)	29.2	
	Cl$_4$W═NH	43.6	

^{a} Data are taken from ref 13.

Dependence of Gas Phase Decomposition Pathways on the Choice of Carrier Gas. Possible decomposition pathways for loss of the alkyl moieties from precursors **2** and **3** in an inert gas and NH$_3$, respectively, are presented in Figures 1 and 2. In addition to the differences between the inert gas and NH$_3$ pathways, we have previously established the viability of exchange of chloride ligands for metal hydrides by σ-bond metathesis in hydrogen carrier gas.[13] It is clear that the choice of carrier gas for CVD will affect the course of the gas phase reactions. Because the amorphous nature of films deposited at low temperatures, as required for diffusion barrier applications, makes computational modeling of the surface difficult, we have not calculated models for the surface reactions in this study. However, it follows that surface reactions of the carrier gas (H$_2$ or NH$_3$) will also play critical roles in the deposition behavior. Table 3 compares the predicted pathways for the precursor **2** in various carrier gases after initial dissociation of the acetonitrile ligand to yield **2a**. Because there is an accessible route from **2** to WCl$_4$ in an inert gas, the presence of hydrogen or NH$_3$ in the carrier is predicted to result in increased nitrogen content in the resulting films. Use of NH$_3$ is more effective, as transamination results in formation of the parent (NH) imido ligand and loss of the isopropyl group as isopropylamine. In contrast, reaction with H$_2$ leaves the isopropyl ligand with its carbon-containing alkyl group that still must be cleaved. Note, however, that use of NH$_3$ can result in the deposition of higher resistivity films, due to the greater incorporation of nitrogen. It was observed that the film resistivity was significantly increased with the addition of NH$_3$ to depositions from **2** at low growth temperature (<550 °C).[14]

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Conclusions

In this study, computational chemistry was used for the investigation of gas phase decomposition of **2** and **3** in the presence of various gases that have been used as carrier gases in CVD from these precursors. Studies on unimolecular decompositions (inert gas conditions) were based on information from positive EI MS data and suggested that **2** and **3** decompose preferentially to generate WCl_4 by shift of the methine hydrogen and subsequent loss of the imido ligand as the imine $HN{=}C(CH_3)_2$ and azabutadiene $HN{=}CHCH{=}CH_2$, respectively. Loss of the nitrogen from the precursor in unimolecular reactions is consistent with the low N/W ratio in films deposited using **2** and **3**. The σ-bond metathesis of metal-chloride bonds with H_2 to generate metal hydrides was calculated to occur in the presence of hydrogen.[13] The W—N(imido) bond of the resulting hydrides (**2b** and **3b**) is calculated to become stronger as a result of σ-bond metathesis, resulting in less cleavage of the W—N bond during film deposition under H_2. For depositions with NH_3 in the carrier gas, addition of NH_3 to coordinatively unsaturated species followed by 1,2-elimination of HCl provided facile routes for loss of chloride and generation of additional N-bound ligands. In the presence of NH_3, addition to the coordinatively unsaturated intermediate **2a** also led to formation of $Cl_4W{=}NH$ via transamination of the isopropylimido ligand. The predominance of these pathways is consistent with the variation of nitrogen content in films deposited under the different carrier gases. The implication of these studies is that the properties of films deposited from the same precursor can be altered by changing the carrier gas from inert (Ar, N_2) to reducing (H_2) to nucleophilic (NH_3). Further computational studies on models for the relevant surface reactions are underway.

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