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Imido Complexes Derived from the Reactions of Niobium and Tantalum Pentachlorides with Primary Amines: Relevance to the Chemical Vapor Deposition of Metal Nitride Films

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Reactions of niobium and tantalum pentachlorides with *tert*-butylamine ($\geq$6 equiv) in benzene afford the dimeric imido complexes $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (90%) and $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (79%). The niobium complex exists as two isomers in solution, while the tantalum complex is composed of three major isomers and at least two minor isomers. Analogous treatments with isopropylamine ($\geq$7 equiv) give the monomeric complexes $NbCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$ (84%) and $TaCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$ (84%). The monomeric complexes are unaffected by treatment with excess isopropylamine, while the dimeric complexes are cleaved to the monomers $MCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)_2$ upon addition of excess *tert*-butylamine in chloroform solution. Treatment of niobium and tantalum pentachlorides with 2,6-diisopropylaniline affords insoluble precipitates of $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (100%) and $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (100%), which react with 4-*tert*-butylpyridine to afford the soluble complexes $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (45%) and $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (44%). Sublimation of $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$, $MCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$, and $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[MCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ leads to decomposition to give $[MCl_3(NR)(NH_2R)]_2$ as sublimates (32−49%), leaving complexes of the proposed formulation $MCl(NR)_2$ as nonvolatile residues. By contrast, $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ sublimes without chemical reaction. Analysis of the organic products obtained from thermal decomposition of $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ showed isobutylene and *tert*-butylamine in a 2.2:1 ratio. Mass spectra of $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$, $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$, and $[NbCl_3(N^iPr)(NH_2{}^iPr)]_2$ showed the presence of dimeric imido complexes, monomeric imido complexes, and nitrido complexes, implying that such species are important gas phase species in CVD processes utilizing these molecular precursors. The crystal structures of $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$, $[NbCl_3(N^iPr)(NH_2{}^iPr)]_2$, $[NbCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$, and $[TaCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$ were determined. $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ crystallizes in the space group $P2_1/c$ with $a = 12.448(3)$ Å, $b = 10.363(3)$ Å, $c = 28.228(3)$ Å, $\beta = 94.92(1)°$, $V = 3628(5)$ Å^3, and $Z = 4$. $[NbCl_3(N^iPr)(NH_2{}^iPr)]_2$ crystallizes in the space group $P2_1/c$ with $a = 9.586(4)$ Å, $b = 12.385(4)$ Å, $c = 11.695(4)$ Å, $\beta = 112.89(2)°$, $V = 1279.0(6)$ Å^3, and $Z = 2$. $[NbCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$ crystallizes in the space group $P2_1/n$ with $a = 10.285(3)$ Å, $b = 11.208(3)$ Å, $c = 23.867(6)$ Å, $\beta = 97.53°$, $V = 2727(1)$ Å^3, and $Z = 2$. $[TaCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$ crystallizes in the space group $P2_1/n$ with $a = 10.273(1)$ Å, $b = 11.241(2)$ Å, $c = 23.929(7)$ Å, $\beta = 97.69(2)°$, $V = 2695(2)$ Å^3, and $Z = 2$. These findings are discussed in the context of niobium and tantalum nitride film depositions from molecular precursors.

Introduction

Niobium nitride (NbN) is a hard, silver-colored, metallic, refractory material and has been studied extensively both in bulk form and as films due to its superconducting properties ($T_c = 17.3$ K).[2,3] Tantalum nitride occurs both as tantalum(V) nitride (Ta_3N_5) and as tantalum(III) nitride (TaN). TaN is the more important of the two tantalum nitrides and is a hard, silver-colored, metallic, refractory material. TaN films have been suggested as diffusion barriers and gates in very large scale integrated circuits.[4] Several chemical vapor deposition (CVD) processes are available for the preparation of niobium nitride and tantalum nitride films. The CVD reaction of niobium pentachloride with ammonia and hydrogen at 950−1000 °C affords NbN films.[2] Recently, Gordon and Hoffman reported that treatment of $Nb(NR_2)_5$ with ammonia at 200−450 °C, and atmospheric pressure gives Nb_3N_4 films.[5] Analogous treatment of $Ta(NMe_2)_5$ with ammonia affords Ta_3N_5 films.[5] Ta_3N_5 films have also been prepared by gas-phase reaction of tantalum pentachloride with ammonia at 600−1000 °C.[6] Preparation of TaN films was achieved through the CVD reaction of tantalum pentachloride, nitrogen, and hydrogen in the temperature range 700−1000 °C.[7] NbN and TaN films can be prepared by sputtering of the metals in a nitrogen atmosphere.[8] Chiu recently reported that the complex $(Et_2N)_3Ta(\eta^2\text{-}EtN{=}CMeH)$ serves as a single-source precursor to TaN films between 500 and 650 °C.[9] Sugiyama described the deposition of tantalum nitride films (phase not identified) from the single-source precursor

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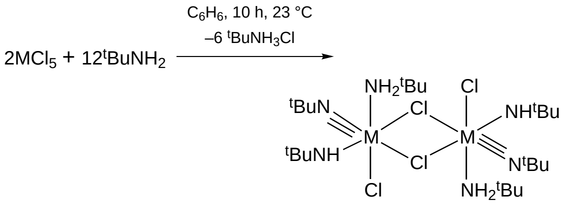
$Ta(NEt_2)_5$.[10] We recently disclosed that complexes of the formula $[MCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (M = Nb, Ta) serve as single-source precursors to NbN and Ta_3N_5 films, respectively.[11]

In the course of preparing molecular precursors to niobium and tantalum nitride films, it was necessary to prepare a range of complexes with niobium−nitrogen and tantalum−nitrogen bonds. Since the structures of complexes derived from the metal pentachlorides and organoamines are relevant to the mechanism of film depositions, we sought to explore this chemistry. Herein we report a study of the reaction of niobium and tantalum pentachlorides with *tert*-butylamine, isopropylamine, and 2,6-diisopropylaniline, which affords the diverse structures $[MCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$, $MCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$, and $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[MCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$. Sublimation of these materials affords dimers of the formula $[MCl_3(NR)(NH_2R)]_2$. The crystal structures of four imido complexes are presented. Finally, the mass spectra of several complexes are described. The relevance of these observations to the deposition of metal nitride films from molecular precursors is discussed.

Results

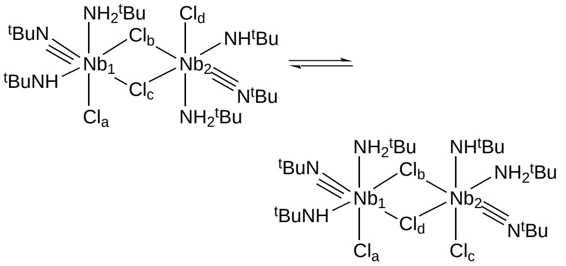
Reactions of Niobium and Tantalum Pentachlorides with *tert*-Butylamine. Treatment of niobium and tantalum pentachloride with ≥6 equiv of *tert*-butylamine in benzene at ambient temperature afforded yellow and white solids of $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (**1**, 90%) and $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (**2**, 79%), respectively (eq 1). Compounds **1** and **2** have been previously described by Nielson,[12] and while the conditions used herein are basically the same as those reported by Nielson, we made no efforts to reproduce the reported conditions exactly. The crystal structure of **2** was also reported.[12a]



(1)

1, M = Nb, 90%
2, M = Ta, 79%

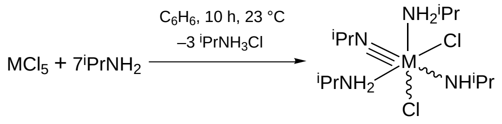
Nielson was able to establish the solid state structure of **2** and suggested that it was a mixture of two isomers in solution on the basis of the ^{13}C NMR spectrum. The present study suggests that **1** consists of two isomers in solution, while **2** exists as three major and at least two minor isomers. The ^1H and $^{13}C\{^1H\}$ NMR data for **1** revealed isomers that were static on the NMR time scale at ambient temperature with an equilibrium constant of about 1 at ambient temperature. The isomers were evident from AB patterns that were observed for the N−H hydrogens of the *tert*-butylamine ligand in the ^1H NMR spectrum and from the observation of doubled peaks in the $^{13}C\{^1H\}$ NMR spectrum. We propose that the observed isomers result from cleavage of a bridging niobium−chlorine bond, followed by rotation of one niobium unit and coordination to the other chlorine of a metal unit. One isomerization step is illustrated in eq 2. Cleavage of the Nb_1-Cl_c bond, followed by rotation along the $Cl_b-Nb_2-N^tBu$ vector and coordination of Cl_d, is an example of the proposed pathway. A full analysis yields six possible isomers (see Supporting Information). Several of the six possible compounds are of similar energies, since two isomers were observed for **1**.



(2)

Unlike **1**, **2** showed three major isomers in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum revealed three AB patterns for the amine ligand N−H hydrogens, in an approximate ratio of 1:1:1 at ambient temperature. The chemical shifts and coupling constants for **2a** and **2b** are nearly identical to those of **1** and suggest isomers analogous to **1a** and **1b**. The $^{13}C\{^1H\}$ spectrum of **2** showed three closely spaced resonances for each chemically distinct carbon, consistent with the three isomers observed in the ^1H NMR spectrum. In addition, five additional weak resonances (ca. 10% intensity versus major isomers) were detected for the *tert*-butyl methyl groups, suggesting the presence of at least two additional minor isomers.

Reactions of Niobium and Tantalum Pentachlorides with Isopropylamine. Treatment of niobium and tantalum pentachloride with ≥7 equiv of isopropylamine in benzene at ambient temperature afforded yellow and white solids of $NbCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$ (**3**, 84%) and $TaCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2$ (**4**, 84%), respectively (eq 3). Compound **4** was previously described by Nielson and was proposed to have the structure $[TaCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2]_2$, in analogy with **2**.[12] However, the present data suggest that **3** and **4** are monomeric, rather than dimeric. The spectroscopic data for **3** and **4** are consistent with four isopropyl groups per metal, rather than the three that are present in **1** and **2**. For **3**, the ^1H NMR spectrum revealed isopropyl methyl resonances at δ 1.26 (d, $J = 6.3$ Hz), 1.23 (d, $J = 6.3$ Hz), and 1.13 (d, $J = 6.3$ Hz) in a 1:2:1 ratio, while the $^{13}C\{^1H\}$ spectrum showed singlets at 26.40 ($NbCH(\mathbf{C}H_3)_2$), 24.58 ($NbCH(\mathbf{C}H_3)_2$), and 24.50 (2 $NbNH_2CH(\mathbf{C}H_3)_2$) ppm. By contrast, the ^1H NMR spectrum of **4** showed four isopropyl methyl doublets at δ 1.31, 1.27, 1.18, and 1.12, while the $^{13}C\{^1H\}$ spectrum showed equal-intensity singlets at 27.49, 26.22, 24.57, and 24.52 ppm.



(3)

3, M = Nb, 84%
4, M = Ta, 84%

In order to probe the proposed monomeric formulations of **3** and **4**, their reactions with excess isopropylamine were investigated by ^1H and ^{13}C NMR spectroscopy. It was envisioned that monomeric **3** and **4** should be essentially unaffected by excess isopropylamine, since the coordination spheres are already saturated. By contrast, a dimeric structure would be cleaved by excess amine ligand, giving very different NMR

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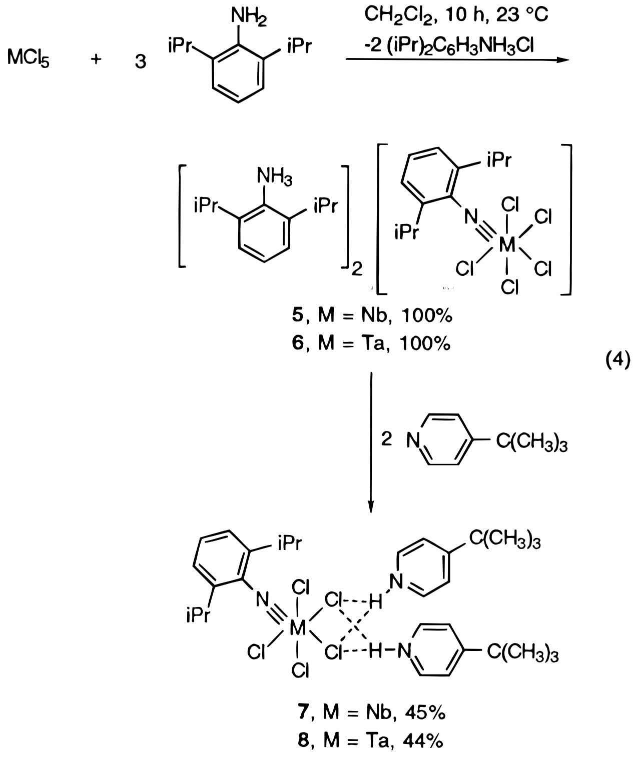
spectra. Accordingly, treatment of **3** with isopropylamine (5 equiv) in chloroform-*d* at ambient temperature did not give any changes in the ^{1}H and ^{13}C NMR spectra. Analogous treatment of **4** gave similar behavior.

For comparison, **1** and **2** were reacted with *tert*-butylamine (2 equiv) in chloroform-*d* and the reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy. Treatment of **1** with *tert*-butylamine in chloroform-*d* at ambient temperature in an NMR tube, followed by immediate analysis ($\leq$5 min) by ^{1}H and ^{13}C{^{1}H} NMR, showed that complete conversion to a new compound had occurred. Resonances were observed in the ^{1}H NMR at δ 10.51 (s, $\mathrm{N}\boldsymbol{H}{}^t\mathrm{Bu}$), 3.56 (d, $J = 12.3$ Hz, $\mathrm{N}\boldsymbol{H}\mathrm{H}'{}^t\mathrm{Bu}$), 3.42 (d, $J = 12.3$ Hz, $\mathrm{NH}\boldsymbol{H}'{}^t\mathrm{Bu}$), 1.28 (s, $\mathrm{C(C}\boldsymbol{H}_3)_3$), 1.23 (s, $\mathrm{C(C}\boldsymbol{H}_3)_3$), and 1.16 (s, 2 $\mathrm{C(C}\boldsymbol{H}_3)_3$). In the ^{13}C{^{1}H} NMR spectrum, the two isomers associated with **1** disappeared and were replaced by resonances at δ 67.57 ($\mathrm{NbN}\boldsymbol{C}\mathrm{(CH_3)_3}$), 58.93 (s, $\mathrm{NbNH}\boldsymbol{C}\mathrm{(CH_3)_3}$), 51.40 (s, $\mathrm{NbNH_2}\boldsymbol{C}\mathrm{(CH_3)_3}$), 32.75 (s, $\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$), 30.91 (s, $\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$), and 30.48 (s, 2 $\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$). These data are consistent with a monomeric complex of the formulation $\mathrm{NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)_2}$. Addition of more than 2 equiv of *tert*-butylamine did not change the ^{1}H and ^{13}C{^{1}H} NMR spectra any further. Analogous treatment of **2** afforded a similar monomeric adduct of the formula $\mathrm{TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)_2}$. Resonances were observed in the ^{1}H NMR at δ 8.15 (s, $\mathrm{N}\boldsymbol{H}{}^t\mathrm{Bu}$), 3.46 (d, $J = 12.6$ Hz, $\mathrm{N}\boldsymbol{H}\mathrm{H}'{}^t\mathrm{Bu}$), 3.31 (d, $J = 12.6$ Hz, $\mathrm{NH}\boldsymbol{H}'{}^t\mathrm{Bu}$), 1.19 (s, $\mathrm{C(C}\boldsymbol{H}_3)_3$), 1.16 (s, 2 $\mathrm{C(C}\boldsymbol{H}_3)_3$), and 1.11 (s, $\mathrm{C(C}\boldsymbol{H}_3)_3$). In the ^{13}C{^{1}H} NMR spectrum, signals for the isomers associated with **2** disappeared and were replaced by resonances at δ 64.71 ($\mathrm{TaN}\boldsymbol{C}\mathrm{(CH_3)_3}$), 56.88 (s, $\mathrm{TaNH}\boldsymbol{C}\mathrm{(CH_3)_3}$), 52.09 (s, 2 $\mathrm{TaNH_2}\boldsymbol{C}\mathrm{(CH_3)_3}$), 33.53 (s, $\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$), 32.46 (s, $\mathrm{C(}\boldsymbol{C}\mathrm{H_3)_3}$), and 30.43 (s, 2 $\boldsymbol{C}\mathrm{(CH_3)_3}$).

Reactions of Niobium and Tantalum Pentachlorides with 2,6-Diisopropylaniline. Treatment of niobium pentachloride and tantalum pentachloride with 2,6-diisopropylaniline in dichloromethane at ambient temperature led to a gray precipitate of $\mathrm{[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]}$ (**5**, 100%) and a pink precipitate of $\mathrm{[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]}$ (**6**, 100%), respectively (eq 4). Neither **5** nor **6** was soluble in any common organic solvent, which precluded analysis by solution NMR methods. The compounds were characterized by infrared spectroscopy, by microanalyses, and by reaction with 4-*tert*-butylpyridine. Carbon, hydrogen, and nitrogen microanalyses were consistent with the proposed formulations. In order to obtain further insight into the structures of **5** and **6**, their reactions with 4-*tert*-butylpyridine were examined. Treatment of **5** with 4-*tert*-butylpyridine (2 equiv) in dichloromethane at ambient temperature for 3 h led to the slow dissolution of **5** to give a brown solution, from which pink crystals of $\mathrm{[4\text{-}}t\mathrm{\text{-}C_4H_9C_5H_4NH]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]}$ (**7**, 45%) were grown by layering the reaction solution with hexane. Analogous treatment of **6** with 4-*tert*-butylpyridine afforded orange crystals of $\mathrm{[4\text{-}}t\mathrm{\text{-}C_4H_9C_5H_4NH]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]}$ (**8**, 44%). The structures of **7** and **8** were established by a combination of ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, by microanalyses, and from a crystal structure determination of **8** (vide infra).



5, M = Nb, 100%

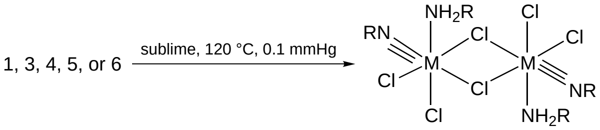
6, M = Ta, 100%

7, M = Nb, 45%

8, M = Ta, 44%

(4)

Sublimation Studies. Since the critical first step in the deposition of films from molecular precursors is transport into the gas phase, the sublimations of **1**−**6** were carefully investigated. Sublimations were carried out in a horizontal 1-in. quartz tube at 120 °C (0.1 mmHg) using a Buchi Kugelrohr furnace as the heat source. With **1**, **3**, **4**, **5**, and **6**, this procedure gave a reaction to afford sublimates of the general formula $\mathrm{[MCl_3(NR)(NH_2R)]_2}$ (eq 5). Thus obtained were $\mathrm{[NbCl_3(N^tBu)(NH_2{}^tBu)]_2}$ (**9**, 44% from **1**), $\mathrm{[NbCl_3(N^iPr)(NH_2{}^iPr)]_2}$ (**10**, 43% from **3**), $\mathrm{[TaCl_3(N^iPr)(NH_2{}^iPr)]_2}$ (**11**, 32% from **4**), $\mathrm{[NbCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2}$ (**12**, 49% from **5**), and $\mathrm{[TaCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2}$ (**13**, 45% from **6**). The structures of **9**−**13** were deduced from spectral and analytical data and from X-ray crystal structure determinations of **10**, **12**, and **13** (vide infra).



(5)

9, M = Nb, R = ^{t}Bu, 44%

10, M = Ta, R = ^{i}Pr, 43%

11, M = Ta, R = ^{i}Pr, 32%

12, M = Nb, R = 2,6-^{i}Pr$_2$-C$_6$H$_3$, 49%

13, M = Ta, R = 2,6-^{i}Pr$_2$-C$_6$H$_3$, 45%

The formation of **9**−**13** in reproducible yields approaching 50%, coupled with nonvolatile residues always left in the sublimation tubes, suggested that **9**−**13** might be formed from **1**, **3**, **4**, **5**, and **6** by a decomposition reaction. In order to probe for such a possibility, the residue left in the tube after sublimation of **3** was examined in detail. The residue was a black solid that was insoluble in all common deuterated solvents, thus precluding analysis by NMR methods. Treatment with several Lewis bases (e.g., triphenylphosphine oxide, substituted pyridines) gave no reactions, apparently due to the extreme insolubility of the black solid. The infrared spectrum was superimposable with that of **3**, implying that **3** and the black solid contain similar functionality. A C, H, N microanalysis of the black solid gave results close to those calculated for $\mathrm{NbCl(N^iPr)_2}$, although the values were not within the ±0.4% limit generally accepted for pure compounds. However, the insolubility and nonvolatility of the black solid did not allow any further purification. Assuming a $\mathrm{NbCl(N^iPr)_2}$ formulation, a yield of 46% was obtained for the black solid. On the basis of these analyses, we *tentatively* propose that **1**, **3**, **4**, **5**, and **6** decompose in the solid state upon thermolysis to afford **9**−**13** as sublimates, leaving the nonvolatile solids $\mathrm{[MCl(NR)_2]}_n$.

Table 1. Mass Spectral Data for Imido Complexes[a]

fragment	**1**	**2**	**9**
$[MCl_3(N^tBu)]_2^{\bullet-}$		1.7	3.0
$[(MCl_3(N^tBu))(MCl_3(NH))]^{\bullet-}$		3.9	3.1
$[MCl_2(N^tBu)(NH^tBu)]^{\bullet-}$	100	58.9	
$[MCl_3(N^tBu)]^{\bullet-}$ or $[M(N^tBu)_2Cl]^{\bullet-}$	17.8	100	100
$[MCl_2(N^tBu)]^{\bullet-}$	3.0		
$[MCl_3(NH)]^{\bullet-}$	1.5		30.9
$[MCl_2N]_2^{\bullet-}$		11.8	
$[MCl_2N]^{\bullet-}$		3.0	

[a] Mass spectra were determined using negative chemical ionization conditions with butane as the bath gas. Data are presented as percent intensity versus the base peak. The elemental compositions of all mass envelopes were verified by computer simulation.

Surprisingly, sublimation of **2** did not give rise to decomposition but rather led to the sublimation of **2** (70%) as an intact molecule. Analysis of sublimed **2** by ^1H NMR revealed isomers **2a** and **2b** (1:1 ratio), as described above, but isomer **2c** was not detectable. Obtention of a 70% isolated yield of sublimed **2** suggests that isomer **2c** transforms to **2a** and/or **2b** upon heating.

Organic Products from Precursor Decomposition. In order to understand better the decomposition process, the organic products derived from thermolysis of **1** were analyzed. The volatile products of a deposition carried out at 500 °C were collected in an NMR tube. The deposition setup has been described previously.[11] A 10/30 ground-glass joint was affixed to an NMR tube, and the tube (cooled to −196 °C; containing 0.8 mL of chloroform-*d*) was placed in an adapter situated at the end of the deposition tube.[13] The deposition system was evacuated to ca. 0.1 mmHg, and then the pyrolysis was conducted with the system isolated from the vacuum to allow efficient collection of the volatiles in the cold NMR tube. After collection, the tube was flame-sealed and the sample was analyzed by a combination of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR spectra revealed isobutylene and *tert*-butylamine as the sole volatile products, in a ratio of 2.2:1 as determined by integration of the methyl resonances in the ^1H NMR spectrum.

Mass Spectral Data. We have previously reported that complexes **1** and **2** constitute single-source precursors to niobium(III) nitride (NbN) and tantalum(V) nitride (Ta_3N_5) films, respectively.[11] The deposition of disparate phases (NbN versus Ta_3N_5) from isostructural precursors raises the possibility that there are major differences in the film-forming processes with **1** and **2**. Furthermore, **1** is transformed to **9** upon sublimation, while **2** sublimes intact. Mass spectral data have been used to provide information about decomposition pathways of precursors under CVD conditions.[14a−c] Therefore, the fragmentation patterns of complexes **1**, **2**, and **9** were carefully analyzed by mass spectrometry. Table 1 lists the mass fragments generated from these complexes under negative chemical ionization conditions.[14d] The use of the negative chemical ionization mode was important, since positive chemical ionization or electron impact mass spectra gave considerably more fragmentation (with concomitant loss of information), apparently due to the low stability of the positively charged ions containing high-valent niobium or tantalum. We have previously discussed the caveats that are inherent with relating mass spectral data of molecular precursors to CVD mechanisms.[15]

The mass spectra of **2** and **9** showed weak mass envelopes corresponding to structures of the formula $[MCl_3(N^tBu)]_2^{\bullet-}$. This fragment indicates that **2** and **9** sublime as dimeric species, but **2** obviously reacts to afford a trichloro imido complex, in analogy with the syntheses of **9**−**13** described above. The *tert*-butylamine ligands of **9** are not observed, indicating that they are loosely coordinated. Complexes **2** and **9** both show weak mass envelopes corresponding to loss of isobutylene from $[MCl_3(N^tBu)]_2^{\bullet-}$. This fragmentation mode results from expulsion of isobutylene from the imido nitrogen to form the hydrogen-substituted imido complex $[(MCl_2(N^tBu))(\mu\text{-}Cl)_2(MCl_2(NH))]^{\bullet-}$. This is an important pattern, since nitrogen−carbon bond cleavage is required to form the metal nitride films. Furthermore, the mass spectra suggest that dealkylation of nitrogen occurs by expulsion of isobutylene rather than by radical fragmentation of carbon−carbon bonds in the *tert*-butyl group. Major mass envelopes observed for **1** (100%) and **2** (58.9%) have a molecular composition consistent with $[MCl_2(N^tBu)(NH^tBu)]^{\bullet-}$. A similar pattern is absent from the mass spectrum of **9**. Another intense fragment observed for **1** (17.8%), **2** (100%), and **9** (100%) corresponds to the formula $[MCl_3(N^tBu)]^{\bullet-}$. This pattern corresponds to symmetrical cleavage of the dimeric unit in $[MCl_3(N^tBu)(NH_2{}^tBu)]_2^{\bullet-}$, followed by loss of coordinated *tert*-butylamine. Again, observation of $[MCl_3(N^tBu)]^{\bullet-}$ implies that conversion of **1** and **2** to trichloro imido complexes is rapid. Such behavior is expected on the basis of the formation of **9**−**13** during sublimation of the precursor complexes. A minor mass envelope for **1** (1.5%) and a major mass envelope for **9** (30.9%) correspond to $[NbCl_3(NH)]^{\bullet-}$, which is likely formed from $[MCl_3(N^tBu)]^{\bullet-}$ by expulsion of isobutylene. Finally, mass envelopes corresponding to fragments of formulas $[TaCl_2N]^{\bullet-}$ and $[Ta_2Cl_3N_2]^{\bullet-}$ were observed for **2** but not for **1** and **9**. These ions apparently correspond to monomeric and dimeric tantalum(V) chloride nitrides.

Crystal Structures of 8, 10, 12, and 13. The X-ray crystal structures of **8**, **10**, **12**, and **13** were determined, since the molecular structures could not be assigned on the basis of analytical and spectroscopic data. Experimental crystallographic data are summarized in Table 2, selected bond lengths and angles are given in Tables 3−6, and perspective views are presented in Figures 1−4. Further data are available in the Supporting Information.

Complex **8** crystallizes as an ionic tantalate with two 4-*tert*-butylpyridinium ions to balance the charge. The tantalum center possesses approximate octahedral geometry, with five chlorine ligands and a (2,6-diisopropylphenyl)imido ligand. The cis angles about the tantalum range from about 81 to 100°, while the trans angles span about 165−175°. The tantalum−nitrogen distance is 1.773(8) Å, and the Ta−N(1)−C(6) angle is 176.2(7)°. The short tantalum−nitrogen bond, coupled with the nearly linear imido linkage, is consistent with a tantalum−nitrogen triple bond. The tantalum−chlorine bond lengths for the chlorines that are cis to the imido ligand range between 2.391(3) and 2.444(3) Å, with an average bond length of 2.419 Å. By contrast, the chlorine that is trans to the imido ligand, Cl(5), shows a tantalum−chlorine bond length of 2.695(3) Å. This bond length is substantially longer than those for the other chlorines. The origin of this lengthening can be partially attributed to the strong trans influence of the imido ligand.

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Table 2. Experimental Crystallographic Data for **8**, **10**, **12**, and **13**

	8	**10**	**12**	**13**
empirical formula	$C_{30}H_{45}Cl_5N_3Ta$	$C_{12}H_{32}Cl_6N_4Nb_2$	$C_{48}H_{70}Cl_6N_4Nb_2$	$C_{48}H_{70}Cl_6N_4Ta_2$
fw	805.89	630.9	1101.6	1268.0
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	12.448(3)	9.586(4)	10.285(3)	10.273(1)
b (Å)	10.363(3)	12.385(4)	11.208(3)	11.241(2)
c (Å)	28.228(3)	11.695(4)	23.867(6)	23.929(7)
β (deg)	94.92(1)	112.89(2)	97.53(3)	97.69(2)
V (Å^3)	3628(5)	1279.0(6)	2727(1)	2695(2)
Z	4	2	2	2
T (K)	296	228	296	296
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.475	1.638	1.340	1.550
μ (cm^{-1})	34.20	15.27	7.47	43.88
T(max)/T(min)	1.50	2.04	1.98	5.43
$R(F)$ (%)	5.28[a]	5.32[b]	4.94[b]	10.45[b]
$R_w(F)$ (%)	9.30[a]	5.88[b]	6.07[b]	14.96[b]

[a] Quantity minimized $= \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$; $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$; $\Delta = |(F_o - F_c)|$. [b] Quantity minimized $= \sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R_w = \sum\Delta w^{1/2}/\sum(F_o w^{1/2})$; $\Delta = |(F_o - F_c)|$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8**

Ta−N(1)	1.773(8)	Ta−Cl(1)	2.391(3)
Ta−Cl(2)	2.444(3)	Ta−Cl(3)	2.427(3)
Ta−Cl(4)	2.413(3)	Ta−Cl(5)	2.695(3)
N(15)−Cl(2)	3.40	N(15)−Cl(5)	3.13
N(25)−Cl(2)	3.42	N(25)−Cl(5)	3.20
N(1)−Ta−Cl(1)	99.6(3)	N(1)−Ta−Cl(4)	96.6(3)
Cl(1)−Ta−Cl(4)	90.77(11)	N(1)−Ta−Cl(3)	98.6(3)
Cl(1)−Ta−Cl(3)	88.83(12)	Cl(4)−Ta−Cl(3)	164.62(10)
N(1)−Ta−Cl(2)	95.2(3)	Cl(1)−Ta−Cl(2)	165.00(10)
Cl(4)−Ta−Cl(2)	90.03(10)	Cl(3)−Ta−Cl(2)	86.46(10)
N(1)−Ta−Cl(5)	175.5(2)	Cl(1)−Ta−Cl(5)	84.43(10)
Cl(4)−Ta−Cl(5)	81.20(9)	Cl(3)−Ta−Cl(5)	83.46(9)
Cl(2)−Ta−Cl(5)	80.89(8)	C(6)−N(1)−Ta	176.2(7)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **10**

Nb−N(1)	2.271(8)	Nb−N(2)	1.731(6)
Nb−Cl(1)	2.380(3)	Nb−Cl(2)	2.492(2)
Nb−Cl(2A)	2.802(2)	Nb−Cl(3)	2.369(3)
Cl(2)−Nb(A)	2.802(2)		
Cl(2)−Nb−Cl(3)	160.2(1)	Cl(2)−Nb−Cl(1)	90.0(1)
Cl(3)−Nb−Cl(1)	96.9(1)	Cl(2)−Nb−N(1)	78.9(2)
Cl(3)−Nb−N(1)	89.8(2)	Cl(1)−Nb−N(1)	163.0(2)
Cl(2)−Nb−N(2)	96.0(2)	Cl(3)−Nb−N(2)	101.0(3)
Cl(1)−Nb−N(2)	100.5(3)	N(1)−Nb−N(2)	93.5(3)
Cl(2)−Nb−Cl(2A)	77.6(1)	Cl(3)−Nb−Cl(2A)	84.4(1)
Cl(1)−Nb−Cl(2A)	85.8(1)	N(1)−Nb−Cl(2A)	79.4(2)
N(2)−Nb−Cl(2A)	171.1(2)	Nb−Cl(2)−Nb(A)	102.4(1)
Nb−N(1)−C(1)	125.4(5)	Nb−N(2)−C(4)	176.1(6)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **12**

Nb(1)−Cl(1)	2.518(1)	Nb(1)−Cl(2)	2.372(2)
Nb(1)−Cl(3)	2.332(2)	Nb(1)−N(1)	1.757(4)
Nb(1)−N(2)	2.305(4)	Nb(1)−Cl(1A)	2.816(2)
Cl(1)−Nb(1A)	2.816(2)		
Cl(1)−Nb(1)−Cl(2)	88.9(1)	Cl(1)−Nb(1)−Cl(3)	158.3(1)
Cl(2)−Nb(1)−Cl(3)	98.0(1)	Cl(1)−Nb(1)−N(1)	98.3(1)
Cl(2)−Nb(1)−N(1)	99.5(2)	Cl(3)−Nb(1)−N(1)	100.8(1)
Cl(1)−Nb(1)−N(2)	77.3(1)	Cl(2)−Nb(1)−N(2)	159.9(1)
Cl(3)−Nb(1)−N(2)	90.2(1)	N(1)−Nb(1)−N(2)	96.9(2)
Cl(1)−Nb(1)−Cl(2A)	76.9(1)	Cl(2)−Nb(1)−Cl(1A)	87.0(1)
Cl(3)−Nb(1)−Cl(1A)	82.9(1)	N(1)−Nb(1)−Cl(1A)	171.9(1)
N(2)−Nb(1)−Cl(1A)	75.8(1)	Nb(1)−Cl(1)−Nb(1A)	103.1(1)
Nb(1)−N(1)−C(6)	179.1(4)	Nb(1)−N(2)−C(18)	126.2(3)

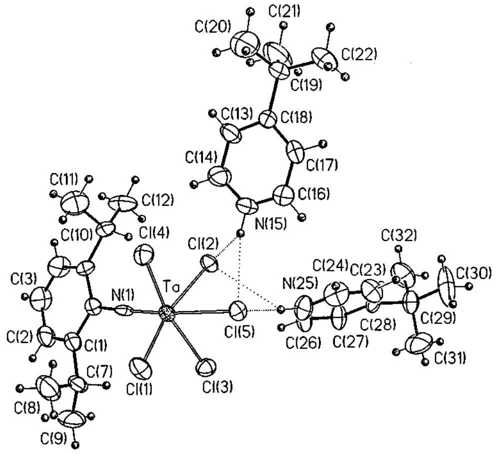

Figure 1. Perspective view of $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (**8**) with thermal ellipsoids at the 35% probability level.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **13**

Ta−Cl(1)	2.268(19)	Ta−Cl(2)	2.350(11)
Ta−Cl(3)	2.552(10)	Ta−N(1)	2.281(30)
Ta−N(2)	1.763(39)	Ta−Cl(3A)	2.808(10)
Cl(3)−Ta(A)	2.808(10)		
Cl(1)−Ta−Cl(2)	96.5(5)	Cl(1)−Ta−Cl(3)	155.8(5)
Cl(2)−Ta−Cl(3)	89.1(4)	Cl(1)−Ta−N(1)	87.5(10)
Cl(2)−Ta−N(1)	161.2(8)	Cl(3)−Ta−N(1)	80.2(9)
Cl(1)−Ta−N(2)	98.2(15)	Cl(2)−Ta−N(2)	101.0(13)
Cl(3)−Ta−N(2)	103.9(14)	N(1)−Ta−N(2)	96.6(15)
Cl(1)−Ta−Cl(3A)	79.7(5)	Cl(2)−Ta−Cl(3A)	85.1(4)
Cl(3)−Ta−Cl(3A)	77.4(4)	N(1)−Ta−Cl(3A)	77.5(8)
N(2)−Ta−Cl(3A)	173.7(13)	Ta−Cl(3)−Ta(A)	102.6(4)
Ta−N(1)−C(16)	132.6(23)	Ta−N(2)−C(26)	168.2(33)

Closer inspection of the crystal structure reveals that the pyridinium N−H hydrogens are hydrogen-bonded to Cl(5) (N(15)−Cl(5) 3.13 Å; N(25)−Cl(5) 3.20 Å) and Cl(2) (N(15)−Cl(2) 3.40 Å; N(25)−Cl(2) 3.42 Å). It is possible that the hydrogen bonding occurs because of the more basic lone pairs on Cl(5) afforded by the weaker, longer Ta−Cl(5) bond. Alternatively, the presence of hydrogen bonding may be stabilizing enough to permit lengthening of the Ta−Cl(5) bond. The Ta−Cl(2) bond length sheds some light on this matter. The N(15)−Cl(2) and N(25)−Cl(2) distances are short enough to require some hydrogen bonding with Cl(2), although these interactions are weaker than those involving Cl(5). The Ta−Cl(2) distance (2.443(3) Å) is slightly longer than those of Ta−Cl(1) (2.391(3) Å), Ta−Cl(3) (2.427(3) Å), and Ta−Cl(4) (2.413(3) Å), although the difference is at the edge of experimental uncertainty. However, the lengthening of Ta−Cl(2) is accompanied by a shortening of the trans bond, Ta−Cl(1). These data suggest that hydrogen bonding to Cl(2) leads to a slight increase in the bond length, relative to Cl(3), Cl(4), and especially Cl(1). Thus, it is likely that the hydrogen bonding

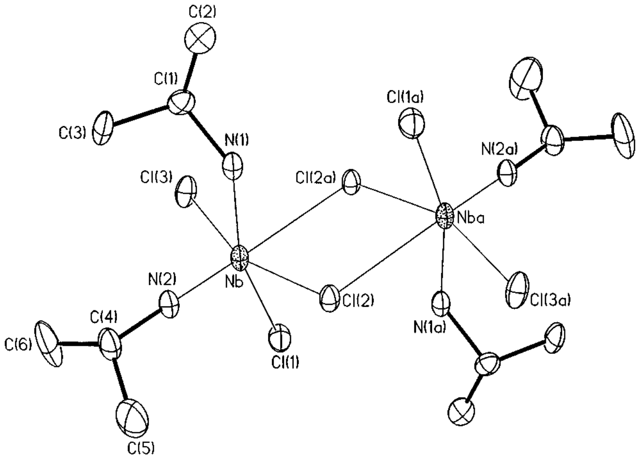

Figure 2. Perspective view of [NbCl$_3$(N^{i}Pr)(NH$_2$^{i}Pr)]$_2$ (**10**) with thermal ellipsoids at the 35% probability level.

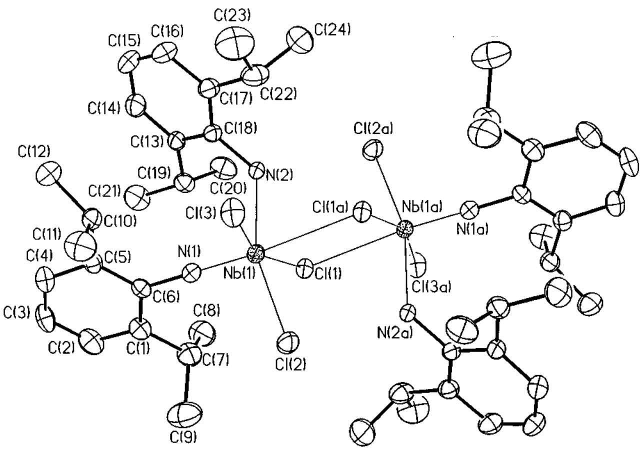

Figure 3. Perspective view of [NbCl$_3$(N(2,6-(CH(CH$_3$)$_2$)$_2$C$_6$H$_3$))(NH$_2$-(2,6-(CH(CH$_3$)$_2$)$_2$C$_6$H$_3$))]$_2$ (**12**) with thermal ellipsoids at the 35% probability level.

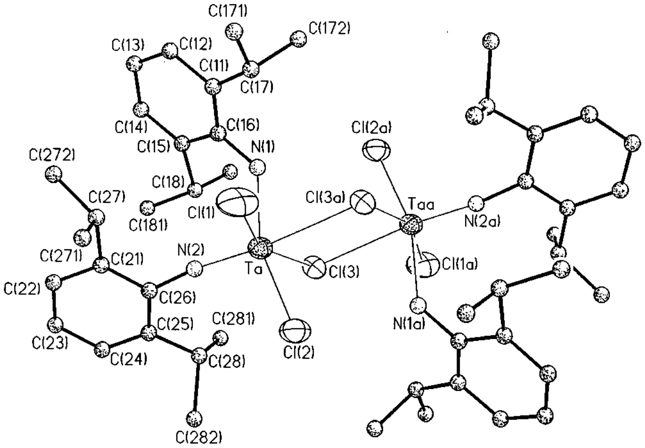

Figure 4. Perspective view of and [TaCl$_3$(N(2,6-(CH(CH$_3$)$_2$)$_2$C$_6$H$_3$))-(NH$_2$(2,6-(CH(CH$_3$)$_2$)$_2$C$_6$H$_3$))]$_2$ (**13**) with thermal ellipsoids at the 35% probability level.

associated with Cl(5) contributes to the lengthening of the Ta−Cl(5) bond, although the magnitude of the increase is probably small.

Complex **10** crystallizes as a dimer with two bridging chloride ligands. The molecule occupies a crystallographic center of inversion. The geometry about each niobium center exhibits substantial deviations from ideal octahedral geometry, with the cis angles for the terminal ligands ranging from 78.9 to 101.0°. The chlorine−niobium−chlorine angle of the bridging chlorines is 77.6°. The trans angles range between 160.2 and 171.1°. The niobium−nitrogen bond distance of the imido fragment is 1.731(6) Å, with a Nb−N(2)−C(4) angle of 176.1(6)°. These data are consistent with a niobium−nitrogen triple bond. The Nb−N(1) bond length (2.271(8) Å) and Nb−N(1)−C(1) angle (125.4(5)°) are appropriate for a niobium−nitrogen singly-bonded isopropylamine ligand. The Nb$_2$Cl$_2$ ring is asymmetric (Nb−Cl(2) 2.492(2) Å; Nb−Cl(2A) 2.802(2) Å) due to the trans influence of the imido ligands that are trans to the bridging chlorines. As expected, the terminal niobium−chlorine bond lengths (Nb−Cl(1) 2.380(3) Å; Nb−Cl(3) 2.369(3) Å) are substantially shorter than those associated with the bridging chlorines.

Complex **12** also crystallizes as a dimer with two bridging chloride ligands. The molecule occupies a crystallographic center of inversion. The geometry about each niobium center exhibits substantial deviations from ideal octahedral geometry, with the cis angles for the terminal ligands ranging from 75.8 to 100.8°. The chlorine−niobium−chlorine angle of the bridging chlorines is 76.9(1)°. The trans angles range between 158.3 and 171.9°. The niobium−nitrogen bond distance of the imido fragment is 1.757(4) Å, with a Nb−N(1)−C(6) angle of 179.1(4)°. These data are consistent with a niobium−nitrogen triple bond. The Nb−N(2) bond length (2.305(4) Å) and Nb−N(2)−C(18) angle (126.2(3)°) are appropriate for a singly-bonded 2,6-diisopropylphenyl ligand. The Nb$_2$Cl$_2$ ring is asymmetric (Nb−Cl(1) 2.518(1) Å; Nb−Cl(1A) 2.816(2) Å). The terminal niobium−chlorine bond lengths (Nb−Cl(2) 2.372(2) Å; Nb−Cl(3) 2.332(2) Å) are substantially shorter than the analogous values associated with the bridging chlorines. Thus, the gross structural features about the coordination sphere of **12** are similar to those of **10**, despite the large differences in steric profile between isopropyl and 2,6-diisopropylphenyl moieties.

Complex **13** is isostructural with **12** and has nearly identical structural features. The data quality is not as good for **13** as for the other structures, resulting in larger uncertainties. The geometry about each tantalum center exhibits substantial deviations from ideal octahedral geometry, with the cis angles for the terminal ligands ranging from 77.5 to 103.9°. The chlorine−tantalum−chlorine angle of the bridging chlorines is 77.4(4)°. The trans angles range between 155.8 and 173.7°. The tantalum−nitrogen bond distance of the imido fragment is 1.763(39) Å, with a Ta−N(2)−C(26) angle of 168.2(33)°. These data are consistent with a tantalum−nitrogen triple bond. The Ta−N(1) bond length (2.281(30) Å) and Ta−N(1)−C(16) angle (132.6(23)°) are appropriate for a singly-bonded 2,6-diisopropylaniline ligand. The Ta$_2$Cl$_2$ ring is asymmetric (Ta−Cl(3) 2.552(10) Å; Nb−Cl(3A) 2.808(10) Å). The terminal tantalum−chlorine bond lengths (Ta−Cl(1) 2.268(14) Å; Ta−Cl(2) 2.350(11) Å) are substantially shorter than the analogous values associated with the bridging chlorines.

The structural data associated with **8**, **10**, **12**, and **13** can be compared with those of the related complexes [NbCl$_4$(NPPh$_3$)]$_2$,[16] [PhCH$_2$PPh$_3$][NbCl$_4$(N^{t}Bu)(py)],[17] [TaCl$_3$(NPh)(Me$_2$S)]$_2$,[18] [TaCl$_2$(N^{t}Bu)(NH^{t}Bu)(NH$_2$^{t}Bu)]$_2$,[12a] and TaCl(N(2,6-^{i}Pr$_2$-C$_6$H$_3$))$_2$-(py)$_2$.[19] Since the sizes of niobium and tantalum are nearly identical,[20] bond lengths in their complexes can be directly

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Table 7. Structural Data for Niobium and Tantalum Imido Complexes

complex	imido M−N (Å)	imido M−N−X (deg)	M−Cl (Å)
8	1.773(8)	176.2(7)	2.391(3), 2.444(3), 2.427(3), 2.413(3), 2.695(3)
10	1.731(6)	176.1(6)	terminal: 2.380(3), 2.369(3) bridging: 2.492(2), 2.802(2)
12	1.757(4)	179.1(4)	terminal: 2.332(2), 2.372(2) bridging: 2.518(1), 2.816(2)
13	1.763(39)	168.2(33)	terminal: 2.268(19), 2.350(11) bridging: 2.552(10), 2.808(10)
$[NbCl_4(NPPh_3)]_2$	1.776(8)	171.6(6)	terminal: 2.349(3), 2.367(3), 2.337(3) bridging: 2.462(3), 2.796(3)
$[PhCH_2PPh_3][NbCl_4(N^tBu)(py)]$	1.731(3)	176.4(4)	2.446(2), 2.429(2), 2.425(2), 2.434(2)
$[TaCl_3(NPh)(Me_2S)]_2$	1.747(8)	176.4(8)	terminal: 2.344(3), 2.316(3) bridging: 2.454(2), 2.751(3)
$[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$	1.61(3)	169(2)	terminal: 2.410(9) bridging: 2.66(1), 2.687(9)
$TaCl(N(2,6\text{-}^iPr_2\text{-}C_6H_3))_2(py)_2$	1.812(6), 1.809(6)	170.9(5), 165.4(5)	2.466(2)

compared. Table 7 lists the imido metal−nitrogen bond lengths, the imido metal−nitrogen−X angles, and metal−chlorine bond lengths of the structures described herein along with the above selected imido complexes. Complex **8** possesses a structure distinctly different from those of **10**, **12**, and **13**. The doubly negative charge of **8** is scarcely evident in the structural parameters associated with the imido linkage. The tantalum−nitrogen imido distance is one of the longer of the selected complexes (range 1.61−1.812 Å) but certainly falls within a normal range. The negative charge on the tantalum center is more clearly reflected in the metal−chlorine distances. The average terminal metal−chlorine distance in the neutral complexes listed below is 2.358 Å, while the average value for **8** (excluding Ta−Cl(5)) is 2.419 Å. The long Ta−Cl(5) distance, 2.695(3) Å, results from the strong trans influence of the imido ligand and hydrogen bonding with the pyridinium counterions. This value is more similar to the *bridging* metal−chlorine bond lengths given below (average = 2.650 Å) and is certainly a very long bond. The N−H···Cl hydrogen bonding observed in **8** should not be viewed as unusual, since there are many examples of related E−H···Cl hydrogen bonding in metal chloride complexes.[21] Comparison of the structures of **10**, **12**, and **13** with those of the selected complexes in Table 7 shows that their structural features are typical of neutral imido complexes. The formation of dimers with unsymmetrical M_2Cl_2 rings appears to be favored over the formation of symmetrical M_2Cl_2 rings, since only $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ showed a symmetrical core and it was a very low precision structure.

Discussion

The present study was motivated by the desire to explore the hypothetical gas phase reaction of niobium pentachloride or tantalum pentachloride with primary organoamines as a route to metal nitride films. Such processes are hypothetical, since the metal pentachlorides possess extremely low vapor pressures and a two-component CVD process requiring their volatilization would give unacceptably low deposition rates. The use of organoamines, rather than more traditional approaches using ammonia,[2,6,22,23] has several advantages. First, Proscia[24] has demonstrated that the atmospheric-pressure CVD reaction of titanium tetrachloride with primary alkylamines gives excellent-quality titanium nitride films without detectable levels of carbon or chlorine contaminants. Organoamines can thus be expected to add a powerful new parameter to nitride film depositions. Second, titanium nitride depositions using alkylamines proceed at slightly lower temperatures (≥475 °C) than the process based upon titanium tetrachloride and ammonia (Kurtz−Gordon process[22]; ≥550 °C). Third, the Kurtz−Gordon process is notorious for giving powders that clog the deposition apparatus;[25] elaborate engineering is required to obtain useful depositions. Fourth, the low vapor pressures of the metal pentachlorides require that volatile molecular precursors be used. Ammonia adducts of high-valent early transition metal halides (e.g., $TiCl_4(NH_3)_n$[26]) are often insoluble, polymeric solids that either are not volatile or possess very low vapor pressures. By contrast, addition of hydrocarbon groups to the nitrogen atoms attenuates intermolecular interactions, giving more volatile complexes. Finally, the presence of hydrocarbon groups generally makes the precursor complexes soluble in organic solvents. Hence, the techniques of solution chemistry can be easily applied, resulting in well-characterized complexes that can be obtained in high purity by crystallization or other techniques. The following section discusses the results in light of their use as molecular precursors to metal nitride films.

The first critical step in the formation of metal nitride films is reaction between the metal pentachlorides and primary alkylamines. In solution reactions with *tert*-butylamine and isopropylamine, three metal−chlorine bonds undergo aminolysis to afford complexes of formulas $[MCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ and $[MCl_2(N^iPr)(NH^iPr)(NH_2{}^iPr)_2]$, along with 3 equiv of the RNH_3Cl. The remaining metal−chlorine bonds are resistant to further aminolysis. The reaction of niobium and tantalum pentachloride with alkylamines was studied by Fowles[27] and more recently by Nielson.[12] With the slightly less sterically demanding isopropylamine, monomeric complexes **3** and **4** can be isolated. A completely different type of complex is obtained with 2,6-diisopropylaniline. Insoluble products **5** and **6** were isolated, which have the formula $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2$-

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$[MCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ as determined by microanalyses. The insolubility of **5** and **6** probably arises from intermolecular N−H···Cl hydrogen bonding between the anilinium hydrogens and metal−chlorine bonds. Only intramolecular hydrogen bonds are present in **7** and **8**, giving pseudomolecular, soluble complexes. The formation of **5** and **6**, as opposed to structures similar to **1**−**4**, can be attributed the extreme insolubility of **5** and **6** and possibly to the steric bulk of the 2,6-diisopropylphenyl moiety, which would not allow approach of another aniline ligand to each metal center. Surprisingly, complexes similar to **5** and **6** have not been described previously. Imido complexes of the formula $TaCl_3(NAr)L_2$ (Ar = 2,6-diisopropylphenyl) have been previously prepared by treatment of tantalum(V) chloride with $Me_3SiNHAr$.[28]

The first step in the CVD reaction using the molecular precursors **1**−**8** is their sublimation to provide gas-phase species. Despite the diverse structures obtained upon reaction of the metal pentachlorides with the three amines studied herein, sublimation of **1** and **3**−**8** gave structurally similar dimeric imido complexes of the formula $[MCl_3(NR)(NH_2R)]_2$. In preparative sublimations, the yields of **9**−**13** ranged from 32 to 49%. We tentatively suggest that **9**−**13** are formed upon decomposition of the starting materials, leaving impure residues of $MCl(NR)_2$. This proposal is backed up by a microanalysis of the residue from sublimation of **3**. Complexes $TaCl(NAr)_2L_2$ have been reported by Wigley,[19] although base-free complexes $MCl(NR)_2$ (R = alkyl or aryl) have not been described previously. Our results suggest either that $NbCl(N^iPr)_2$ is a highly insoluble polymer or that it decomposes after formation under the sublimation conditions. The fact that **2** sublimes without decomposition while the structurally similar **4** decomposes to $[TaCl_3(N^iPr)(NH_2{}^iPr)]_2$ is puzzling. The steric bulk of the *tert*-butyl moieties in **2** must keep the complex from being able to achieve the transition state required for the disproportionation. A very clear implication from the sublimation study of **1** and **3**−**8** is that 50% of the metal is wasted if these compounds are used as molecular precursors. It is well-known that $[MCl_3(NR)(NH_2R)]_2$ can be directly prepared by treatment of the metal pentachloride with 2 equiv of $(Me_3Si)_2NR$ or Me_3SiNHR.[12,28] The trichlorides should be superior molecular precursors, compared to the dichlorides.

Results of the mass spectrometry studies, coupled with the volatile organic product analysis, give unique insight into path(s) by which the molecular precursors are converted to metal nitride films. With **1**, the highest mass envelope and the base peak corresponded to an ion of the formula $NbCl_2(N^tBu)(NH^tBu)$. While this fragment could be formed by symmetrical cleavage of **1**, the model chemistry suggests that an indirect path is taken. We have proposed herein that **1** decomposes in the solid state to give $[NbCl_3(N^tBu)(NH_2{}^tBu)]_2$ as the first gas-phase species. The dimer should be in equilibrium with the monomer $NbCl_3(N^tBu)(NH_2{}^tBu)$ and could evolve coordinated *tert*-butylamine to afford $NbCl_3(N^tBu)$. The $NbCl_3(N^tBu)$ ion could then react directly with free *tert*-butylamine to afford the $[NbCl_2(N^tBu)(NH^tBu)]^{\bullet -}$. As precedent for this possible path, Nielson has reported that $[NbCl_3(N^tBu)(NH_2{}^tBu)]_2$ readily reacts with *tert*-butylamine to afford **1**.[12b] It is reasonable to expect that a similar reaction would occur in the gas phase. Alternatively, loss of hydrogen chloride (2 equiv) from $NbCl_3(N^tBu)(NH_2{}^tBu)$ would also give the ion $NbCl(N^tBu)_2$, which has a nearly identical mass due to the fortuitously similar masses of the *tert*-butylimido fragment and two chlorine-35 atoms. The intermediacy of $NbCl(N^tBu)_2$ and derived fragments can be ruled out, since the calculated mass envelopes match closely with $NbCl_3(N^tBu)$ and its fragmentation ions and are not good matches for $NbCl(N^tBu)_2$ and derived fragments. Additionally, the mass spectrum of **11**, wherein the isopropylimido moiety and two chlorine-35 atoms differ by 13 mass units, showed a single mass envelope corresponding to $[TaCl_3(N^iPr)]^{\bullet -}$ and nothing for $[TaCl(N^iPr)_2]^{\bullet -}$. The next highest molecular weight ion for **1** corresponded to loss of chlorine from $[NbCl_3(N^tBu)]^{\bullet -}$ or loss of amide from $[NbCl_2(N^tBu)(NH^tBu)]^{\bullet -}$. This ion, albeit of weak intensity, is the result of reduction of niobium(V) to niobium(IV). Another weak-intensity ion is consistent with the formula $[NbCl_3(NH)]^{\bullet -}$ and results from loss of isobutylene from $[NbCl_3(N^tBu)]^{\bullet -}$. This observation is consistent with the volatile products trapped from **1**, which showed only isobutylene and *tert*-butylamine.

The mass spectrum of **2** showed several important differences from that of **1**. First, weak-intensity ions corresponding to the dimeric fragments $[TaCl_3(N^tBu)]_2{}^{\bullet -}$ and its dealkylation product $[(TaCl_3(N^tBu))(TaCl_3(NH))]^{\bullet -}$ were observed. These ions suggest that **2** undergoes the type of disproportionation reaction described above for **1** and **3**−**6**. Since **2** sublimes with only a minor change in the ratio of isomers, the decomposition must occur in the gas phase upon thermal excitation or electron capture. An intense mass envelope was observed for $[TaCl_2(N^tBu)(NH^tBu)]^{\bullet -}$, but the base peak was $[TaCl_3(N^tBu)]^{\bullet -}$. Finally, ionizations possibly consistent with $[TaCl_2N]^-$ and $[Ta_2Cl_3N_2]_2{}^-$ were observed for **2**. These ions are important, since they suggest that complete removal of the hydrocarbon groups occurs in the gas phase. Moreover, their presence signifies that nitrido complexes are likely to be important gas-phase intermediates in the film depositions.

The mass spectrum of **9** was very similar to that of **1** except that it showed weak-intensity ions corresponding to the dimeric fragments $[NbCl_3(N^tBu)]_2{}^{\bullet -}$ and its dealkylation product $[(NbCl_3(N^tBu))(NbCl_3(NH))]^{\bullet -}$. The ion $[NbCl_2(N^tBu)(NH^tBu)]^{\bullet -}$ was not observed. The base peak was $[NbCl_3(N^tBu)]^{\bullet -}$, consistent with the lower concentration of *tert*-butylamine. An intense mass envelope of $[NbCl_3(NH)]^{\bullet -}$ was the only other feature in the mass spectrum.

The results of the solution chemistry, the mass spectrometry, and volatile product trapping allow us to make some generalizations and predictions regarding the deposition of metal nitride films from the reactions of niobium and tantalum halides with organoamines. In the hypothetical gas phase, two-component CVD reactions between the metal pentachlorides and primary alkylamines, complexes bearing imido linkages will be formed and should be the major gas-phase species present. In traditional two-component CVD reactions leading to the deposition of metal nitride films, there is always a large excess (often ≥30:1) of the nitrogen source over the metal halide.[22−24] Thus, the already thermodynamically favorable aminolysis of three metal−chlorine bonds will be further aided kinetically. The mass spectral data support the idea that the last two metal−chlorine bonds are inert toward aminolysis in the gas phase, since no ions consistent with such pathways were observed. The mass spectra of **1**, **2**, and **9**, coupled with the organic product trapped from **1**, show that the imido *tert*-butyl group departs as isobutylene, leaving a hydrogen-substituted imido complex. Hydrogen-substituted imido complexes of niobium and tantalum are exceedingly rare.[29] Their likely involvement in the CVD process makes them extremely attractive synthetic targets. The

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[28] Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860.

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further observation of $[TaCl_2N]^-$ and $[Ta_2Cl_3N_2]_2^-$ fragments in the mass spectrum of **9** makes nitrido chlorides of niobium and tantalum strong candidates for advanced CVD precursors. Finally, a major puzzle is why the isostructural complexes **1** and **2** lead to films of different nitride phases, i.e. niobium(III) nitride and tantalum(V) nitride. While the exact rationale for this behavior will have to await further experimentation, we offer a possible explanation based upon what has been reported about the chemistry of MCl_2N. $NbCl_2N$ is a known compound and is reported to decompose to NbN and chlorine at ≥450 °C in the solid state.[30] Any $NbCl_2N$ that forms from **1** probably would decompose instantly under the thermal conditions of the CVD experiment. Furthermore, the large energies associated with electron capture would make the observation of ions derived from $NbCl_2N$ unlikely in the mass spectrometer. There is less known about the thermal decomposition of $TaCl_2N$.[31] However, we propose that $TaCl_2N$ does not undergo reduction to tantalum(III) nitride under the thermal conditions of our CVD reactor but rather decomposes to give tantalum(V) nitride and tantalum(V) chloride (eq 6). Such a reaction is consistent with

$$5TaNCl_2 \xrightarrow{\Delta} 2TaCl_5 + Ta_3N_5 \qquad (6)$$

the more negative reduction potential of tantalum(V) compared to niobium(V) ($M_2O_5 + 10H^+ + 10e^- \rightarrow 2M + 5H_2O$; $E°(Ta) = -0.750$ V, $E°(Nb) = -0.644$ V[32]). Moreover, $TaOCl_3$ is well-known to decompose upon thermolysis to afford tantalum(V) oxide and tantalum(V) chloride.[33]

Experimental Section

General Considerations. Reactions were performed under an atmosphere of nitrogen or argon using Schlenk techniques. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Benzene was distilled from sodium benzophenone ketyl. Chloroform-*d* was dried over 4-Å molecular sieves. The starting materials were used as received from Strem Chemicals and Aldrich Chemical Co.

^1H NMR and $^{13}C\{^1H\}$ NMR spectra were obtained at 500, 300, 121, or 75 MHz in chloroform-*d*, unless otherwise noted. Infrared spectra were obtained using Nujol as the medium. Mass spectra were obtained using the negative chemical ionization mode with butane bath gas. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Preparation of $[NbCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (1). A 250-mL Schlenk flask was charged with niobium pentachloride (5.00 g, 18.5 mmol), benzene (70 mL), and a stir bar and was fitted with a rubber septum. *tert*-Butylamine (15.6 mL, 148 mmol) was added via a syringe to give a yellow turbid solution. The solution was allowed to reach ambient temperature and was stirred for 10 h. The volatile components were pumped off, the resultant yellow solid was extracted with a minimum amount of benzene, and the suspension was filtered through a 2-cm pad of Celite on a coarse glass frit to give a clear, yellow solution. The solvent was pumped off, and the resultant material was vacuum-dried overnight to afford **1** as a yellow powder (6.30 g, 90% based upon niobium pentachloride): mp 220 °C dec; IR (Nujol, cm^{-1}) 3291 (m), 3235 (m), 3178 (m), 3100 (s), 2733 (m), 2699 (m), 2587 (m), 2491 (w), 1601 (w), 1567 (m), 1499 (w), 1398 (m), 1353 (m), 1279 (m), 1234 (s), 1212 (s), 1155 (m), 1133 (m), 1093 (w), 1020 (w), 975 (w), 919 (w), 891 (w), 862 (w), 789 (m), 772 (m); ^1H NMR ($CDCl_3$, 21 °C, δ) 9.53 (s, $N\boldsymbol{H}$), 4.26 (d, $J = 12.6$ Hz, $(N\boldsymbol{H}H')_a$), 4.06 (d, $J = 12.6$ Hz, $(N\boldsymbol{H}H')_b$), 3.98 (d, $J = 12.6$ Hz, $(NH\boldsymbol{H'})_b$), 3.85 (d, $J = 12.0$ Hz, $(NH\boldsymbol{H'})_a$), 1.31 (s, 2 $C(C\boldsymbol{H}_3)_3$), 1.27 (s, $C(C\boldsymbol{H}_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 69.68, 69.50 (s, $NbN\boldsymbol{C}(CH_3)_3$), 59.44, 59.39 (s, $NbNH\boldsymbol{C}(CH_3)_3$), 52.25 (s, $NbNH_2\boldsymbol{C}(CH_3)_3$), 32.35, 32.28 (s, $C(\boldsymbol{C}H_3)_3$), 30.73 (s, $C(\boldsymbol{C}H_3)_3$), 30.47 (s, $C(\boldsymbol{C}H_3)_3$). Anal. Calcd for $C_{24}H_{60}Cl_4N_6Nb_2$: C, 37.91; H, 7.95; N, 11.05. Found: C, 37.60; H, 7.80; N, 10.96.

Preparation of $[TaCl_2(N^tBu)(NH^tBu)(NH_2{}^tBu)]_2$ (2). In a procedure similar to the preparation of **1**, tantalum pentachloride (5.00 g, 14.0 mmol) and *tert*-butylamine (14.9 mL, 141 mmol) were reacted to afford **2** as a white powder (5.14 g, 79% based upon tantalum pentachloride): mp 270 °C dec; IR (Nujol, cm^{-1}) 3278 (m), 3240 (w), 3202 (m), 3171 (s), 3096 (m), 2701 (w), 2594 (w), 2500 (w), 1559 (w), 1396 (w), 1346 (m), 1264 (s), 1208 (s), 1164 (m), 1133 (w), 1020 (w), 982 (w), 926 (w), 888 (w), 782 (w), 738 (w); ^1H NMR ($CDCl_3$, 21 °C, δ) 8.40 (s, $N\boldsymbol{H}$), 7.31 (s, $N\boldsymbol{H}$), 4.33 (d, $J = 12.9$ Hz, $(N\boldsymbol{H}H')_a$), 4.22 (d, $J = 12.9$ Hz, $(N\boldsymbol{H}H')_b$), 4.13 (d, $J = 12.9$ Hz, $(NH\boldsymbol{H'})_b$), 3.97 (d, $J = 12.9$ Hz, $(NH\boldsymbol{H'})_a$), 3.73 (d, $J = 11.4$ Hz, $(N\boldsymbol{H}H')_c$), 3.64 (d, $J = 11.4$ Hz, $(NH\boldsymbol{H'})_c$), 1.38 (s, 2 $C(C\boldsymbol{H}_3)_3$), 1.34 (s, $C(C\boldsymbol{H}_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 66.50, 66.40, 65.30 (s, $TaN\boldsymbol{C}(CH_3)_3$), 57.88, 57.51, 57.45 (s, $TaNH\boldsymbol{C}(CH_3)_3$), 53.74, 53.17, 52.64 (s, $TaNH_2\boldsymbol{C}(CH_3)_3$), 33.92, 33.21, 33.17, 32.90, 32.31, 32.04, 30.89, 30.45, 30.00 (s, $C(\boldsymbol{C}H_3)_3$)). Anal. Calcd for $C_{24}H_{60}Cl_4N_6Ta_2$: C, 30.78; H, 6.49; N, 8.93. Found: C, 30.47; H, 6.49; N, 8.93.

Preparation of $NbCl_2(NCH(CH_3)_2)(NHCH(CH_3)_2)(NH_2CH(CH_3)_2)_2$ (3). In a procedure similar to the preparation of **1**, niobium pentachloride (2.50 g, 9.25 mmol) and isopropylamine (6.30 mL, 74.0 mmol) were reacted to afford **3** as a bright yellow solid (3.10 g, 84% based upon niobium pentachloride): mp 76−77 °C dec; IR (Nujol, cm^{-1}) 3273 (w), 3238 (w), 3203 (w), 3167 m), 3090 (m), 2801 (s), 2703 (w), 2590 (w), 2498 (w), 1604 (m), 1562 (w), 1506 (m), 1477 (m), 1301 (m), 1259 (m), 1210 (s), 1168 (w), 1132 (w), 1020 (w), 985 (w), 886 (w), 787 (w); ^1H NMR ($CDCl_3$, 21 °C, δ) 9.76 (d, $J = 10.2$ Hz, $N\boldsymbol{H}$), 4.78 (septet, $J = 6.3$ Hz, $C\boldsymbol{H}(CH_3)_2$), 3.97 (septet, $J = 6.3$ Hz, $C\boldsymbol{H}(CH_3)_2$), 3.33 (m, 7H, 2 $N\boldsymbol{H}_2CH(CH_3)_2$), 2 $C\boldsymbol{H}(CH_3)_2$), 1.26 (d, $J = 6.3$ Hz, $CH(C\boldsymbol{H}_3)_2$), 1.23 (d, $J = 6.3$ Hz, 2 $CH(C\boldsymbol{H}_3)_2$), 1.13 (d, $J = 6.3$ Hz, $CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 62.37 (s, $NbN\boldsymbol{C}H(CH_3)_2$), 61.78 (s, $NbNH\boldsymbol{C}H(CH_3)_2$), 48.71 (s, $NbNH_2\boldsymbol{C}H(CH_3)_2$), 26.40 (s, $NbNCH(\boldsymbol{C}H_3)_2$), 24.58 (s, $NbNHCH(\boldsymbol{C}H_3)_2$), 24.50 (s, 2 $NbNH_2CH(\boldsymbol{C}H_3)_2$). Anal. Calcd for $C_{12}H_{33}Cl_2N_4Nb$: C, 36.28; H, 8.37; Cl, 17.85; N, 14.10. Found: C, 35.22; H, 8.21; Cl, 19.47; N, 14.02 (not obtained analytically pure).

Preparation of $TaCl_2(NCH(CH_3)_2)(NHCH(CH_3)_2)(NH_2CH(CH_3)_2)_2$ (4). In a procedure similar to the preparation of **1**, tantalum pentachloride (2.00 g, 5.58 mmol) and isopropylamine (3.80 mL, 44.6 mmol) were reacted to afford **4** as a white solid (2.00 g, 74% based upon tantalum pentachloride): mp 193 °C dec; IR (Nujol, cm^{-1}) 3285 (m), 3205 (s), 3135 (s), 3103 (m), 1575 (s), 1559 (s), 1350 (m), 1307 (m), 1269 (s), 1205 (s), 1157 (s), 1114 (m), 1082 (s), 985 (w), 937 (m), 840 (w), 808 (m); ^1H NMR ($CDCl_3$, 21 °C, δ) 7.64 (d, $J = 10.2$ Hz, $N\boldsymbol{H}CH(CH_3)_2$), 4.72 (septet, $J = 6.3$ Hz, $C\boldsymbol{H}(CH_3)_2$), 4.51 (septet, $J = 6.3$ Hz, $C\boldsymbol{H}(CH_3)_2$), 3.50 (septet, $J = 6.3$ Hz, 2 $C\boldsymbol{H}(CH_3)_2$), 3.40 (broad s, 2 $N\boldsymbol{H}_2CH(CH_3)_2$), 1.31, 1.27, 1.18, 1.12 (d, $J = 6.3$ Hz, $CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 59.95 (s, $TaN\boldsymbol{C}H(CH_3)_2$), 59.74 (s, $TaNH\boldsymbol{C}H(CH_3)_2$), 49.16 (s, $TaNH_2\boldsymbol{C}H(CH_3)_2$), 27.49, 26.22, 24.57, 24.52 (s, $CH(\boldsymbol{C}H_3)_2$). Anal. Calcd for $C_{12}H_{33}Cl_2N_4Ta$: C, 29.70; H, 6.85; Cl, 14.61; N, 11.55. Found: C, 28.15; H, 6.49; Cl, 16.23; N, 10.58 (not obtained analytically pure).

Preparation of $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (5). A 250-mL Schlenk flask was charged with niobium pentachloride (1.00 g, 3.70 mmol), dichloromethane (45 mL), and a stir bar and was fitted with a rubber septum. 2,6-Diisopropylaniline (2.09 mL, 11.1 mmol) was added via a syringe, and the resultant turbid gray mixture was stirred for 10 h. Removal of the solvent under reduced pressure, followed by vacuum-drying, afforded **5** as an insoluble gray powder (2.97 g, 100% based upon niobium pentachloride): mp 253 °C dec; IR (Nujol, cm^{-1}) 3062 (s), 2554 (m), 1614 (m), 1572 (s), 1496 (s), 1478 (s), 1360 (m), 1342 (m), 1330 (m), 1283 (m), 1247 (m), 1224 (w), 1164 (w), 1099 (m), 1058 (w), 1040 (m), 1023 (m), 981 (w), 928 (w), 792 (s), 751 (s), 721 (s). Anal. Calcd for $C_{36}H_{57}Cl_5N_3Nb$: C, 53.91; H, 7.16; N, 5.24. Found: C, 54.23; H, 7.39; N, 5.57.

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Preparation of $[NH_3(2,6\text{-}(CH(CH_3)_2)_2C_6H_3)]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (6). In a procedure to the preparation of **5**, tantalum pentachloride (1.01 g, 2.81 mmol) and 2,6-diisopropylaniline (1.58 mL, 8.37 mmol) were reacted to afford **6** as an insoluble pink solid (2.50 g, 100% based upon tantalum pentachloride): mp 259 °C dec; IR (Nujol, cm^{-1}) 3063 (s), 2553 (m), 1616 (m), 1569 (s), 1517 (m), 1487 (s), 1476 (s), 1435 (s), 1347 (s), 1294 (m), 1253 (m), 1165 (w), 1101 (w), 1060 (w), 1042 (m), 1025 (m), 990 (w), 919 (w), 785 (s), 750 (s), 738 (s), 726 (s). Anal. Calcd for $C_{36}H_{57}Cl_5N_3Ta$: C, 48.58; H, 6.45; N, 4.72. Found: C, 48.81; H, 6.76; N, 4.23.

Preparation of $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[NbCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (7). A 150-mL Schlenk flask was charged with niobium pentachloride (0.500 g, 1.85 mmol), dichloromethane (30 mL), and a stir bar and was fitted with a rubber septum. To this mixture was added 2,6-diisopropylaniline (1.40 mL, 7.40 mmol). The resultant turbid gray mixture was stirred for 10 h. Next, 4-*tert*-butylpyridine (0.55 mL, 3.7 mmol) was added and the resultant red-brown solution was stirred for 3 h. The volatile components were pumped off to afford a brown powder. This powder was dissolved in dichloromethane (20 mL), and the resultant solution was filtered through a 2-cm pad of Celite to give a clear brown solution. Hexane (70 mL) was carefully layered on top of the dichloromethane layer, and the system was allowed to equilibrate for 24 h. The solvent was decanted by a cannula, and flask contents were vacuum-dried to afford **7** as pink crystals (0.60 g, 45% based upon niobium pentachloride): mp 157 °C dec; IR (Nujol, cm^{-1}) 3199 (m), 3112 (m), 3057 (s), 1629 (s), 1596 (s), 1492 (s), 1333 (s), 1301 (m), 1279 (s), 1262 (m), 1202 (s), 1115 (w), 1098 (m), 1060 (w), 983 (m), 945 (m), 929 (m), 836 (m), 797 (s), 753 (s), 732 (s); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 9.24 (d, $J = 6.6$ Hz, 2,6-$\boldsymbol{H}$ of C_5H_4N), 7.99 (d, $J = 6.3$ Hz, 3,5-$\boldsymbol{H}$ of C_5H_4N), 7.07 (d, $J = 7.8$ Hz, 3,5-$\boldsymbol{H}$ of $(^iPr)_2C_6H_3$), 6.90 (t, $J = 7.5$ Hz, 4-$\boldsymbol{H}$ of $(^iPr)_2C_6H_3$) 4.78 (septet, $J = 6.9$ Hz, $C\boldsymbol{H}(CH_3)_2$), 3.40 (broad s, pyridinium N$-\boldsymbol{H}$), 1.34 (s, $C(C\boldsymbol{H}_3)_3$), 1.31 (d, $J = 6.9$ Hz, $CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 171.82 (s, py $\boldsymbol{C}$), 151.12, 148.72 (s, aromatic $\boldsymbol{C}$ of $(^iPr)_2C_6H_3$), 141.63 (s, py $\boldsymbol{C}$), 125.65 (s, $\boldsymbol{C}$ of $(^iPr)_2C_6H_3$), 124.47 (s, py $\boldsymbol{C}$), 122.28 (s, py $\boldsymbol{C}$), 36.68 (s, $\boldsymbol{C}(CH_3)_3$), 30.07 (s, $C(\boldsymbol{C}H_3)_3$), 27.51 (s, $\boldsymbol{C}H(CH_3)_2$), 25.28 (s, $CH(\boldsymbol{C}H_3)_2$). Anal. Calcd for $C_{30}H_{45}Cl_5N_3Nb$: C, 50.19; H, 6.32; N, 5.85. Found: C, 45.68; H, 6.15; N, 5.63 (not obtained analytically pure).

Preparation of $[4\text{-}t\text{-}C_4H_9C_5H_4NH]_2[TaCl_5(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]$ (8). In a procedure similar to the preparation of **7**, tantalum pentachloride (0.500 g, 1.40 mmol), 2,6-diisopropylaniline (1.06 mL, 5.60 mmol), and 4-*tert*-butylpyridine (0.41 mL, 2.8 mmol) were reacted to afford **8** as orange crystals (0.50 g, 44% based upon tantalum pentachloride): mp 200 °C dec; IR (Nujol, cm^{-1}) 3198 (m), 3136 (m), 3113 (m), 3061 (m), 3051 (m), 1635 (s), 1598 (s), 1497 (s), 1427(s), 1357 (s), 1353 (s), 1304 (m), 1294 (m), 1269 (m), 1248 (w), 1206 (s), 1118 (w), 1107 (w), 1099 (m), 1062 (w), 989 (w), 930 (w), 838 (w), 805 (m), 795 (m), 751 (s), 735 (m), 718 (m); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 9.14 (d, $J = 5.4$ Hz, 2,6-$\boldsymbol{H}$ of C_5H_4N), 7.91 (d, $J = 5.4$ Hz, 3,5-$\boldsymbol{H}$ of $(^iPr)_2C_6H_3$), 7.13 (d, $J = 7.8$ Hz, 3,5-$\boldsymbol{H}$ of $(^iPr)_2C_6H_3$), 6.70 (t, $J = 7.5$ Hz, 4-$\boldsymbol{H}$ of $(^iPr)_2C_6H_3$), 4.66 (septet, $J = 6.6$ Hz, $C\boldsymbol{H}(CH_3)_2$), 3.40 (broad s, pyridinium N$-\boldsymbol{H}$), 1.34 (s, $C(C\boldsymbol{H}_3)_3$), 1.27 (d, $J = 6.6$ Hz, $CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 172.03, 171.98 (s, py $\boldsymbol{C}$), 149.29, 148.78 (s, aromatic $\boldsymbol{C}$ of $(^iPr)_2C_6H_3$), 141.47 (s, py $\boldsymbol{C}$), 124.28 (s, py $\boldsymbol{C}$), 124.15 (s, aromatic $\boldsymbol{C}$ of $(^iPr)_2C_6H_3$), 121.46 (s, aromatic $\boldsymbol{C}$ of $(^iPr)_2C_6H_3$), 36.74 (s, $\boldsymbol{C}(CH_3)_3$), 30.04 (s, $C(\boldsymbol{C}H_3)_3$), 26.99 (s, $\boldsymbol{C}H(CH_3)_2$), 25.28 (s, $CH(\boldsymbol{C}H_3)_2$). Anal. Calcd for $C_{30}H_{45}Cl_5N_3Ta$: C, 44.71; H, 5.63; N, 5.21. Found: C, 43.76; H, 5.55; N, 5.23 (not obtained analytically pure).

Preparation of $[NbCl_3(N^tBu)(NH_2{}^tBu)]_2$ (9). Complex **1** (0.500 g, 1.32 mmol) was placed in a vial (0.5 in diameter), and a plug of glass wool was placed above the compound. This vial was placed in a sublimation tube (1-in. diameter), and the tube was connected to the vacuum line. The tube was evacuated and placed in a sublimation furnace. The complex was sublimed (110 °C, 0.1 mmHg) to afford **9** as yellow crystals (0.200 g, 44% based upon complex **1**): mp 200 °C dec; IR (Nujol, cm^{-1}) 3255 (s), 3195 (s), 3088 (s), 1552 (s), 1392 (m), 1352 (s), 1279 (m), 1239 (s), 1219 (s), 1206 (s), 1159 (s), 1133 (m), 1026 (w), 1006 (w), 920 (w), 880 (w), 827 (w), 794 (w); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 4.57 (broad s, $N\boldsymbol{H}H'C(CH_3)_3$), 3.39 (broad s, $NH\boldsymbol{H'}C(CH_3)_3$), 1.47, 1.42 (s, $NbNC(C\boldsymbol{H}_3)_3$ and $NbNH_2C(C\boldsymbol{H}_3)_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 68.47 (s, $NbN\boldsymbol{C}(CH_3)_3$), 53.78 (s, $NbNH_2\boldsymbol{C}(CH_3)_3$), 30.40 (s, $NbNC(\boldsymbol{C}H_3)_3$), 29.61 (s, $NbNH_2C(\boldsymbol{C}H_3)_3$). Anal. Calcd for $C_{16}H_{40}Cl_6N_4Nb_2$: C, 27.97; H, 5.87; N, 8.15. Found: C, 28.17; H, 5.97; N, 8.63.

Preparation of $[NbCl_3(NCH(CH_3)_2)(NH_2CH(CH_3)_2)]_2$ (10). In a procedure similar to the preparation of **9**, complex **3** (0.500 g, 1.48 mmol) was sublimed (120 °C, 0.1 mmHg) to afford **10** as yellow crystals (0.200 g, 43%): mp 190 °C dec; IR (Nujol, cm^{-1}) 3256 (s), 3218 (s), 3108 (w), 1562 (s), 1392 (m), 1353 (m), 1337 (w), 1309 (m), 1287 (w), 1232 (s), 1150 (m), 1111 (m), 1089 (s), 1056 (s), 930 (m), 919 (m), 864 (w), 814 (m); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 4.27 (septet, $J = 6.3$ Hz, $NbNC\boldsymbol{H}(CH_3)_2$), 4.00 (broad s, $N\boldsymbol{H}H'CH(CH_3)_2$), 3.52 (septet, $J = 6.3$ Hz, $NbNH_2C\boldsymbol{H}(CH_3)_2$), 3.40 (broad s, $NH\boldsymbol{H'}CH(CH_3)_2$), 1.37 (d, $J = 6.3$ Hz, $NbNCH(C\boldsymbol{H}_3)_2$), 1.35 (d, $J = 6.3$ Hz, $NbNH_2CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 68.58 (s, $NbN\boldsymbol{C}H(CH_3)_2$), 50.37 (s, $NbNH_2\boldsymbol{C}H(CH_3)_2$), 24.27 (s, $NbNCH(\boldsymbol{C}H_3)_2$), 22.75 (s, $NbNH_2CH(\boldsymbol{C}H_3)_2$). Anal. Calcd for $C_{12}H_{32}Cl_6N_4Nb_2$: C, 22.84; H, 5.11; N, 8.88. Found: C, 22.78; H, 5.09; N, 8.84.

Preparation of $[TaCl_3(NCH(CH_3)_2)(NH_2CH(CH_3)_2)]_2$ (11). In a procedure similar to the preparation of **9**, **4** (0.300 g, 0.70 mmol) was sublimed (110 °C, 0.1 mmHg) to afford **11** as colorless crystals (0.090 g, 32%): mp 140 °C dec; IR (Nujol, cm^{-1}) 3255 (s), 3210 (s), 3199 (m), 3104 (w), 3087 (w), 1558 (s), 1390 (m), 1351 (m), 1334 (m), 1301 (m), 1279 (s), 1251 (m), 1228 (s), 1156 (m), 1111 (m), 1089 (s), 1055 (s), 938 (m), 921 (w), 860 (w), 810 (m), 715 (w), 648 (s); ^{1}H NMR ($CDCl_3$, 21 °C, δ) 5.04 (septet, $J = 6.3$ Hz, $NC\boldsymbol{H}(CH_3)_2$), 4.0 (broad s, $N\boldsymbol{H}H'CH(CH_3)_2$), 3.65 (septet, $J = 6.3$ Hz, $NH_2C\boldsymbol{H}(CH_3)_2$), 3.4 (broad s, $NH\boldsymbol{H'}CH(CH_3)_2$), 1.38 (d, $J = 6.3$ Hz, $NbNCH(C\boldsymbol{H}_3)_2$), 1.29 (d, $J = 6.3$ Hz, $NbNH_2CH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 21 °C, ppm) 63.58 (s, $TaN\boldsymbol{C}H(CH_3)_2$), 50.94 (s, $TaNH_2\boldsymbol{C}H(CH_3)_2$), 25.10 (s, $TaNCH(\boldsymbol{C}H_3)_2$), 24.33 (s, $TaNH_2CH(\boldsymbol{C}H_3)_2$); MS (negative CI, butane bath gas) m/z 343 ($[TaCl_3(N^iPr)]^{\bullet -}$, 100%). Anal. Calcd for $C_{12}H_{32}Cl_6N_4Ta_2$: C, 17.86; H, 4.00; Cl, 26.36; N, 6.94. Found: C, 18.17; H, 4.11; Cl, 25.27; N, 5.80.

Preparation of $[NbCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$ (12). A 150-mL Schlenk flask was charged with niobium pentachloride (0.500 g, 1.85 mmol), dichloromethane (30 mL), and a stir bar and was fitted with a rubber septum. 2,6-Diisopropylaniline (1.40 mL, 7.40 mmol) was added via a syringe, and the resultant turbid gray mixture was stirred for 10 h. The volatile components were pumped off to afford an insoluble gray solid. The solid was placed in a vial (0.5-in. diameter), and a plug of glass wool was placed above the compound. This vial was placed in a sublimation tube (1-in. diameter) and was connected to the vacuum line. The tube was placed in a Kugelrohr furnace, and the complex was sublimed (160 °C, 0.1 mmHg) to afford **12** as insoluble purple-black crystals (0.50 g, 49% based upon niobium pentachloride): mp 220 °C dec; IR (Nujol, cm^{-1}) 3304 (m), 3261 (m), 3051 (w), 1554 (s), 1536 (w), 1360 (m), 1339 (w), 1280 (w), 1253 (w), 1220 (w), 1172 (w), 1124 (s), 1108 (m), 1088 (m), 775 (w), 783 (m), 795 (s), 757 (s), 741 (s). Anal. Calcd for $C_{48}H_{72}Cl_6N_4Nb_2$: C, 52.24; H, 6.58; N, 5.08. Found: C, 52.79; H, 6.57; N, 5.00.

Preparation of $[TaCl_3(N(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))(NH_2(2,6\text{-}(CH(CH_3)_2)_2C_6H_3))]_2$ (13). In a procedure similar to the preparation of **12**, tantalum pentachloride (0.50 g, 1.40 mmol) and 2,6-diisopropylaniline (1.06 mL, 5.60 mmol) were reacted to afford **13** as insoluble orange crystals (0.40 g, 44% based upon tantalum pentachloride): mp 278 °C dec; IR (Nujol, cm^{-1}) 3336 (w), 3298 (m), 3254 (m), 3245 (m), 3057 (w), 1548 (s), 1362 (s), 1335 (s), 1307 (m), 1296 (m), 1286 (m), 1253 (w), 1187 (w), 1171 (w), 1138 (s), 1116 (m), 1099 (m), 1083 (m), 1056 (w), 1039 (m), 1028 (m), 990 (w), 925 (w), 881 (w), 810 (w), 788 (s), 750 (s), 733 (s). Anal. Calcd for $C_{48}H_{72}Cl_6N_4Ta_2$: C, 45.05; H, 5.67; N, 4.38. Found: C, 44.65; H, 5.55; N, 4.41.

Analysis of Residue Left from Sublimation of 3. Complex **3** (0.60 g, 1.8 mmol) was placed in a vial (0.75 cm diameter), and a loosely-packed plug of glass wool was placed above the compound. The vial was placed in a 2.5-cm-diameter quartz tube, and the quartz tube was evacuated to 0.1 mmHg. The tube was heated to 120 °C, whereupon sublimation of **9** commenced. After sublimation was complete (ca. 1.0 h), the residue left in the vial was isolated to afford a black powder (0.200 g, 46% assuming a $[NbCl(N^iPr)_2]_n$ formulation): IR (Nujol, cm^{-1}) 3260 (s), 3198 (s), 3102 (m), 1563 (s), 1389 (m), 1355 (m), 1332 (m), 1298 (m), 1236 (s), 1158 (s), 1129 (m), 1112 (m), 1084 (s), 1062 (m), 814 (m), 774 (s), 718 (m), 645 (s). Anal. Calcd for $C_8H_{18}ClN_2Nb$: C, 29.71; H, 5.82. Found: C, 26.45; H, 5.53.

Trapping of Volatile Organic Products Derived from Thermolysis of 1. The CVD equipment used for the product-trapping experiment has been previously described,[11] as has the adapter for trapping the volatile products in the NMR tube. Complex **1** (0.30 g, 0.54 mmol) was placed in a 0.5 cm × 3.0 cm glass vial, and the vial was transferred to the CVD apparatus. The deposition system was evacuated to ca. 0.1 mmHg, and then the pyrolysis was conducted with the system isolated from the vacuum to allow efficient collection of the volatiles in the cold NMR tube. Precursor **1** was slowly sublimed at about 100 °C (using heat tape) into the CVD chamber, which was held at 500 °C. The precursor was sublimed into the chamber over about 5 min, resulting in decomposition, although some of the precursor sublimed through the hot zone intact. As a result, no quantification of the organic products could be made. After collection, the tube was flame-sealed and the sample was analyzed by a combination of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. A 2.2:1 ratio of isobutylene (^1H NMR δ 4.62 (s, $C\boldsymbol{H}_2C(CH_3)_2$), 1.68 (s, $CH_2C(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR 142.22 (s, $CH_2\boldsymbol{C}(CH_3)_2$), 110.39 (s, $\boldsymbol{C}H_2C(CH_3)_2$), 23.98 (s, $CH_2C(\boldsymbol{C}H_3)_2$)) and *tert*-butylamine (^1H NMR δ 1.11 (s, $(C\boldsymbol{H}_3)_3CNH_2$), 0.82 (s, $(CH_3)_3CN\boldsymbol{H}_2$); $^{13}C\{^1H\}$ NMR 47.27 (s, $(CH_3)_3\boldsymbol{C}NH_2$), 32.43 (s, $(\boldsymbol{C}H_3)_3CNH_2$) ppm) was observed. No other products were identified within the detection limits of ^1H NMR spectroscopy.

Crystal Structure of 8. A suitable crystal was selected and mounted in a nitrogen-flushed glass capillary. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 24°$). The systematic absences in the diffraction data were uniquely consistent with the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and was refined by full-matrix least-squares methods. Semiempirical absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The largest remaining peak in the difference map (0.97 e $Å^{-3}$) occurred at a chemically unreasonable position and was considered as noise. All software and sources of the scattering factors were contained in the SHEXTL (5.1) library (G. Sheldrick, Siemens XRD, Madison, WI).

Crystal Structures of 10, 12, and 13. Suitable crystals were selected and mounted in nitrogen-flushed glass capillaries. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 24°$). The systematic absences in the diffraction data were uniquely consistent with the reported space groups. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and were refined by full-matrix least-squares methods. Semiempirical absorption corrections were applied. Compounds **12** and **13** were crystallographically isomorphous. All three compounds had similar core structures, with inversion centers located at each M_2Cl_2 rhombus. Phenyl rings in **13** were refined as rigid bodies. Tantalum and chlorine atoms in **13** and all other non-hydrogen atoms in **10** and **12** were refined with anisotropic displacement coefficients. Hydrogen atoms were ignored in **13** and were treated as idealized contributions in **10** and **12**. Approximately 10% of the data for **13** were rejected by the learned-profile routine as spurious diffraction contributions from a minor satellite or twin crystal. Several large remaining peaks in the difference map (maximum = 4.35 e $Å^{-3}$) occurred at chemically unreasonable positions and were considered as heavy-atom noise arising from the less than satisfactory application of the absorption corrections.

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Supporting Information Available: Tables listing full experimental details for data collection and refinement, atomic coordinates, bond distances and angles, and thermal parameters for **8**, **10**, **12**, and **13**, mass spectra and listings of mass spectrometry data for **1**, **2**, and **9**, and a scheme showing the isomer analysis for **1** (37 pages). Ordering information is given on any current masthead page.

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