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Article

Volatile Imido–Hydrazido Compounds of the Refractory Metals Niobium, Tantalum, Molybdenum, and Tungsten

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Volatile 1,1-dimethyl-2-(trimethylsilyl)hydrazido(1–) complexes of niobium, tantalum, molybdenum, and tungsten have been synthesized and fully characterized for use as precursors in their chemical vapor deposition to metal nitrides. Different reaction patterns were observed in the hydrazinolysis of imido complexes of those four metals with (trimethylsilyl)dimethylhydrazine $HN(SiMe_3)NMe_2$ (H-TDMH). $[Ta(N^tBu)Cl_3Py_2]$ gave $[Ta(TDMH)_2Cl_3]$ (**1**) with loss of the imido functionality, and $[M(N^tBu)_2Cl_2Py_2]$ gave $[M(N^tBu)_2(TDMH)Cl]$ (M = W, **8a**; Mo, **8b**). Reactions of both types of metal imido complexes with magnesium hydrazides produced $[M(N^tBu)(TDMH)_2X]$ (M = Ta, X = Cl, **2a**; X = Br, **3a**; M = Nb, X = Cl, **2b**; X = Br, **3b**) and $[M(N^tBu)_2(TDMH)X]$ (M = W, X = Cl, **8a**; X = Br, **9a**; M = Mo, X = Cl, **8b**; X = Br, **9b**). Halogen substitution reactions at **2** and **3** by $–NMe_2$, $–NH^tBu$, and CH_2Ph groups as well as imido ligand replacement reactions have been investigated. The results of crystal structure determinations of **1**, **4a**, **5a**, **6a**, **7b**, and **9b** are presented.

Introduction

As structures in microelectronic devices become smaller, copper is replacing aluminum as the interconnection material because of its lower electrical resistivity and inclination toward electromigration. However, the use of copper generates the need for diffusion barriers between the conductor and the silicon substrate to prevent the formation of copper-doped silicon and copper silicides, which are formed at the interface at device fabrication temperatures.[1] One of the most promising materials for this application is TaN, which shows sufficient conductivity and diffusion barrier properties with respect to copper and silver migration.[2,3,11] Other promising diffusion barrier materials for copper and aluminum are the systems W/Si(C)/N[4−7,15] and Ta/Si/N.[8−11]

Because these barrier materials have to be deposited on targets with high aspect ratios, deposition techniques that provide high uniform coverage have to be applied. The state-of-the-art technique therefore is chemical vapor deposition (CVD), with the ultimate goal being atomic layer deposition. Apart from tantalum pentakisamides, the most promising class of volatile precursors for deposition of TaN via CVD is that of mixed tantalum imido−amido compounds.[11−17]

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Because volatile, highly covalent tantalum compounds usually contain the metal in the 5+ oxidation state, the films obtained from tantalum(V) precursors by CVD often consist of tantalum(V) nitride, $\mathrm{Ta_3N_5}$.[11] This is a significant problem in the deposition of TaN and is a minor one in CVD of films of NbN or WN_x. The incorporation of ligands with the potential to reduce the metal center at deposition temperatures is one possible strategy to avoid this problem for low-temperature thin film deposition of TaN. Hence, the replacement of amido groups $-\mathrm{NR_2}$ by hydrazido groups $-\mathrm{NR'NR_2}$ is a synthetic approach to this problem. Recently, Winter et al. stated that the hydrazinolysis product of $\mathrm{TaCl_5}$ and 1,1-dimethylhydrazine, which was claimed to be $[\mathrm{TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)}]$, can be used as a single source precursor for tantalum(III)-based films in CVD processes.[18] This indicated that hydrazine derivatives are promising ligands for volatile nitrogen-containing tantalum compounds.

The number of well-defined hydrazido complexes of group 5 is limited. Green et al. published a series of niobium compounds bearing a dimethylhydrazido(2−) ligand that were not described for tantalum.[19,20] There are very few tantalum compounds known that contain hydrazido ligands. Henderson et al. prepared $[\mathrm{Ta(NMeNMe_2)_2Cl_3}]$, which could not be crystallographically characterized.[21] Hursthouse et al. observed the reduction of $\mathrm{TaCl_5}$ during the reaction with 1-amino-2,2,6,6-tetramethylpiperidine, leading to the bis(isodiazene)tantalate(III) $(\mathrm{HNEt_3})[\mathrm{Ta(N{=}NC_9H_{18})_2Cl_4}]$.[22] Winter et al. recently presented cationic nonvolatile hydrazido(2−) complexes of formula $[\mathrm{M(NNMe_2)Cl_2(NH_2NMe_2)(TMEDA)}]\mathrm{Cl{\cdot}CH_2Cl_2}$ (M = Nb, Ta).[23]

In contrast, hydrazido compounds of molybdenum and tungsten are quite well investigated because there is a strong interest in group 6 complexes as model compounds for nitrogen fixation.[24−27] Hence, there are many compounds and a variety of coordination modes of unsubstituted and alkylated hydrazine, hydrazido(1−), and hydrazido(2−) ligands known such as in $[\mathrm{Cp^*WMe_3}(\eta^2\text{-}\mathrm{NH_2NH_2})][\mathrm{OTf}]$,[28] $[\mathrm{W(N\text{-}2,6\text{-}}i\mathrm{\text{-}Pr_2C_6H_3)(2,6\text{-}NC_5H_3(CH_2NTosyl)_2\text{-}}(\eta^2\text{-}\mathrm{NHNH_2})]$,[29] $[\mathrm{W(NNPhMe)Cl_3(PMe_3)_2}]$,[30] or $[\mathrm{(HIPTN_3N)Mo(NNH_2)}][\mathrm{Ar_4B}]$.[31] However, the synthesis of volatile molybdenum and tungsten hydrazido complexes for CVD is poorly investigated.

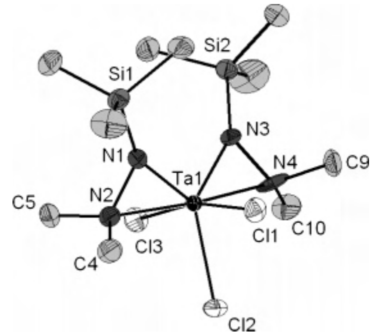

Figure 1. Molecular structure of **1** in the solid state. H atoms are omitted for clarity. Only one of two independent molecules in the elementary cell is presented. Ellipsoids are shown at 40% probability.

One particular hydrazido ligand that attracted attention is (trimethylsilyl)dimethylhydrazine $\mathrm{HN(SiMe_3)NMe_2}$ (H-TDMH). Gladfelter et al. prepared and investigated $[\mathrm{Ga(TDMH)_3}]$ and $[\mathrm{In(TDMH)_3}]$[32] as potential precursors for GaN and InN.

However, well-defined and volatile hydrazido compounds suitable for CVD remain scarce. Therefore, a quest for volatile hydrazido-containing tantalum and tungsten compounds is an attractive field of research. This led us to investigate the potential of the hydrazine $\mathrm{HN(SiMe_3)NMe_2}$ (H-TDMH) as a suitable ligand for refractory metal precursor compounds. Recently, Fischer et al. desribed monohydrazido complexes derived from hydrazinolysis of tantalum imido−amido complexes and a preliminary study of their deposition characteristics.[33] This report has prompted us to present our own work describing a number of volatile imido−bis(hydrazido) compounds of niobium and tantalum as well as their molybdenum and tungsten analogues.

Results and Discussion

We describe the reactivity of the imidotrichloroniobium and -tantalum cores and that of the bis(imido)dichloromolybdenum and -tungsten cores toward hydrazinolysis and ligand metathesis by hydrazido salts.

Hydrazinolysis of Imidoniobium and -tantalum Complexes. Hydrazinolysis of $[\mathrm{Ta(N^tBu)Cl_3Py_2}]$ with H-TDMH does not lead to the expected imido complex $[\mathrm{Ta(N^tBu)(TDMH)}_n\mathrm{Cl}_{3-n}]$ but quantitatively to $[\mathrm{Ta(TDMH)_2Cl_3}]$ (**1**) formed by protolytic replacement of the imido functionality (Figure 1). $[\mathrm{Ta(N(SiMe_3)NMe_2)_2Cl_3}]$ (**1**) is the silylated analogue of $[\mathrm{Ta(NMeNMe_2)_2Cl_3}]$ reported by Hughes et al.[21] The hydrazinolysis proceeds at room temperature in $\mathrm{CH_2Cl_2}$ under evolution of *tert*-butylamine and pyridine. The orange product **1** is

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Table 1. Selected Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of **1** in the Solid State

Ta1−N1	1.956(6)	Si1−N1−Ta1	151.8(4)
Ta1−N2	2.201(7)	Si2−N3−Ta1	151.8(4)
Ta1−N3	1.959(6)	N2−N1−Ta1	78.0(4)
Ta1−N4	2.092(8)	N4−N3−Ta1	74.7(4)
Ta1−Cl1	2.420(1)	Cl1−Ta1−Cl3	167.25(7)
Ta1−Cl2	2.440(1)	Cl2−Ta1−Cl3	84.04(7)
Ta1−Cl3	2.422(1)	N1−Ta1−N2	40.3(2)
N1−N2	1.451(9)	N3−Ta1−N4	40.7(3)
N3−N4	1.415(8)	E1(Ta1,N1, N2)−E2(Ta1,N3,N4)	33.5(5)
Si1−N1	1.787(6)	N1−Ta1−N3	98.3(2)
Si2−N3	1.768(6)		

perfectly soluble in toluene but hardly in hexane. ^{1}H and ^{13}C NMR spectra are consistent with a highly symmetric structure because only two singlets are observed for the NMe_2 and $NSiMe_3$ groups. Unlike $[Ta(NMeNMe_2)_2Cl_3]$, **1** is soluble in toluene and could be crystallographically characterized.

Crystallization by cooling a toluene solution of **1** gave crystals suitable for single-crystal X-ray diffraction analysis. The molecular structure of **1** is presented in Figure 1. Selected bond lengths and angles are given in Table 1.

Both hydrazido ligands are bonded in a side-on κ^2-(N,N′) mode. The Ta atom is surrounded in a pseudo-trigonal-bipyramidal manner by Cl1 and Cl3 in the apical positions and Cl2 and the centroids of the two hydrazido ligands forming the trigonal plane. In this view, the hydrazido ligands are assumed to occupy a single coordination site each. The distances between Ta1 and the anionic *N*-silyl groups N1 and N3 are about 1.96 Å, while the distances between Ta1 and the neutral donor centers N2 and N4 are 2.20 and 2.10 Å, respectively. The second independent molecule in the elementary cell does not show this deviation in distance between the neutral N atoms and the Ta atom. The sums of angles around N1 and N3 count to 357°, which confirms a close to planar configuration and sp^2 hybridization of the N atoms and π-bonding character to the metal center. This is in accordance with the structurally similar compound $[Ta(N(SiMe_3)_2)_2Cl_3]$,[34] where the Ta−N distances are 1.928(7) and 1.933(7) Å, respectively and the N−Ta−N angle is unexpectedly small with 115°. The slightly longer Ta−N distances in **1** may be explained by the more crowded coordination sphere and the higher number of donor atoms around the metal center. The bonds between the NMe_2 groups and Ta1 appear to be donor−acceptor interactions. The distances between the chloro ligands and the metal center are 2.42 Å for Cl1 and Cl3 and 2.44 Å for Cl2. The deviation of Ta1 from the plane defined by Cl2 and the centers of the hydrazine N−N bonds is 0.35 Å. This deviation, combined with 167° for the angle Cl1−Ta1−Cl3 and approximately 84° for the angles Cl3−Ta1−Cl2 and Cl1−Ta1−Cl2, suggests that the structure can be viewed as trigonal planar with Cl1 and Cl3 in the apical positions. The hydrazido ligands are not in the plane but twisted with respect to the equatorial plane. The interplanar angle of the two planes Ta1−N1−N2 and Ta1−N3−N4 is 33°.

Interestingly, $[Nb(N^tBu)Cl_3Py_2]$ does not react with H-TDMH under the same conditions. Only starting materials are observed after 16 h at room temperature. This may be attributed to the less polar character of the $[Nb{=}N^tBu]$ functionality compared to the corresponding tantalum analogue.

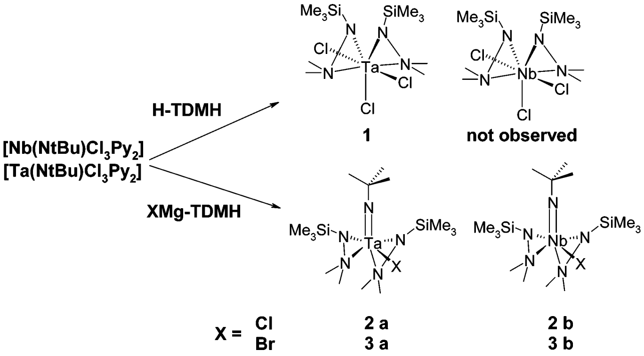

Figure 2. Reactions of tantalum and niobium imido complexes with H-TDMH and their magnesium salts.

Reactions of Imidoniobium and -tantalum Complexes with Hydrazido Salts. While lithium amides are strong bases and favored synthons for introducing anionic nitrogen ligands, magnesium amides are rarely used for these purposes. The lithium hydrazide formed in situ by reacting H-TDMH with *n*-BuLi failed to give a selective reaction with $[Ta(N^tBu)Cl_3Py_2]$. Fischer et al. spectroscopically observed a substitution of only one chloro ligand by Li-TDMH but reported neither a synthesis nor a full characterization of the product.[33] Recently, Sachdev prepared $[Mg(N(SiMe_3)NMe_2)_2]_2$ from dibutylmagnesium and H-TDMH.[35] This magnesium dihydrazide is capable of exchanging two chloro ligands of $[Ta(N^tBu)Cl_3Py_2]$, giving $[Ta(N^tBu)(TDMH)_2Cl]$ (**2a**) in very high yield (Figure 2). **2a** is a colorless, hexane-soluble, sublimable solid with a melting point of approximately 60 °C.

Because both hydrazido ligands of $[Mg(TDMH)_2]_2$ are transferred to the imidotantalum core, an intermediate such as ClMg(TDMH) should exist as a metathetically reactive species. As proof of this, H-TDMH was reacted with a Grignard reagent obtained from 2-bromobutane or 1-chlorobutane and magnesium in diethyl ether. The reaction is exothermic, and a white solid precipitates from the solution, giving a white dispersion from which the solid can be filtered off. This precipitate is not sufficiently soluble in benzene for NMR spectroscopy studies but shows two broad singlets in ^{1}H NMR spectra in THF-d_8 at +2.52 and −0.04 ppm, indicating that the composition should be BrMg(TDMH) and ClMg(TDMH), respectively, although no satisfactory elemental analysis could be obtained. This is supported by the fact that magnesium halides crystallize from tetrahydrofuran (THF) solutions of these salts and the NMR spectra of the nonsoluble parts of the mother liquor show that $[Mg(TDMH)_2]_2$ is formed simultaneously. To our surprise, the reaction of $[Ta(N^tBu)Cl_3Py_2]$ with a ClMg(TDMH) reagent leads to **2a** while the reaction with a BrMg(TDMH) reagent gives bromo complex $[Ta(N^tBu)(TDMH)_2Br]$ (**3a**) in good yield. Interestingly, an almost quantitative metathetical ligand

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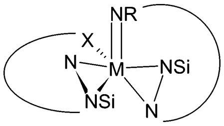

Figure 3. Coordination motif of the bis(hydrazido) compounds **2a/b**−**7a/b** (only one enantiomer is shown). The arcs show the two planes formed by one hydrazido ligand and the imido moiety or the ligand X in each case. NSi is the anionic silylated nitrogen, and N is the NMe$_2$ group of each TDMH ligand.

exchange between the [Mg−Br] and [Ta−Cl] functionalities is observed: bromo and chloro complexes differ slightly in their ^{1}H NMR shifts.

[Nb(N^{t}Bu)Cl$_3$Py$_2$] follows the same reaction pattern, giving [Nb(N^{t}Bu)(TDMH)$_2$Cl] (**2b**) and [Nb(N^{t}Bu)(TDMH)$_2$Br] (**3b**). In contrast to the tantalum hydrazides **2a** and **3a** being colorless and crystalline at room temperature, the niobium hydrazides **2b** and **3b** are orange liquids that can be distilled under reduced pressure.

NMR Studies of 2a and 2b. The presence of only two singlets for the four N−Me groups of **2a** and **2b** in their room-temperature ^{1}H NMR spectra indicates that there is a fast dynamic process in solution at room temperature. In order to get information on this dynamic behavior, low-temperature NMR spectra showing remarkable differences between the analogue niobium and tantalum compounds **2a** and **2b** were taken. As will be shown in the discussion of the crystal structures (see below), the TDMH ligands occupy two coordination sites of pseudotetrahedral complexes. The inner shell of this coordination motif is shown in Figure 3. Both enantiomers of this coordination motif are present in the solid state.

Low-temperature NMR spectra of **2b** (see Figure 4) show four singlets originating from the NMe groups, while one signal for the *tert*-butyl group and two signals for the silyl groups are found. This is in accordance with the crystal structures (see Figures 3 and 7−9), revealing that there are four different methyl groups present in the solid state. In addition to these expected signals, the presence of a minor species can be concluded from a second set of signals, suggesting a higher symmetry species. This shows two broad singlets in the NMe area: one next to the most downfield-shifted signal and one hidden in the two singlets that are shifted a bit highfield. The broad singlet originating from the *tert*-butyl group can be seen downfield of the signal of the major species, and the silyl group signal appears between the split silyl group signals of the major species. The conformation of the second species cannot be assigned because the signal set shows the same symmetry as the room-temperature signal set. It might be another diastereomer formed either by pseudorotation of one hydrazine N−N vector or via a dissociation/association mechanism. However, both species seem to be in equilibrium because the two signal sets are formed after coalescence of the room-temperature signal set while cooling down the sample. Thus, the configuration is metastable in solution. NMR data suggest that **2b** exists as a pair of diastereomers (80:20). The crystal structure displays one of these diastereomers. Both enantionmeric forms of it are present in the lattice. All isomers are in equilibrium at room temperature on the NMR time scale.

The low-temperature ^{1}H NMR spectra of **2a** (see Figure 5) draw a slightly different picture. Both signal sets seen in the spectra of **2b** are present but with an inverted ratio of integrals. The signal set of the major species shows the same symmetry as the room-temperature set consisting of two singlets for the NMe groups, one for the *tert*-butyl group, and one for the silyl groups. The signal set of the minor

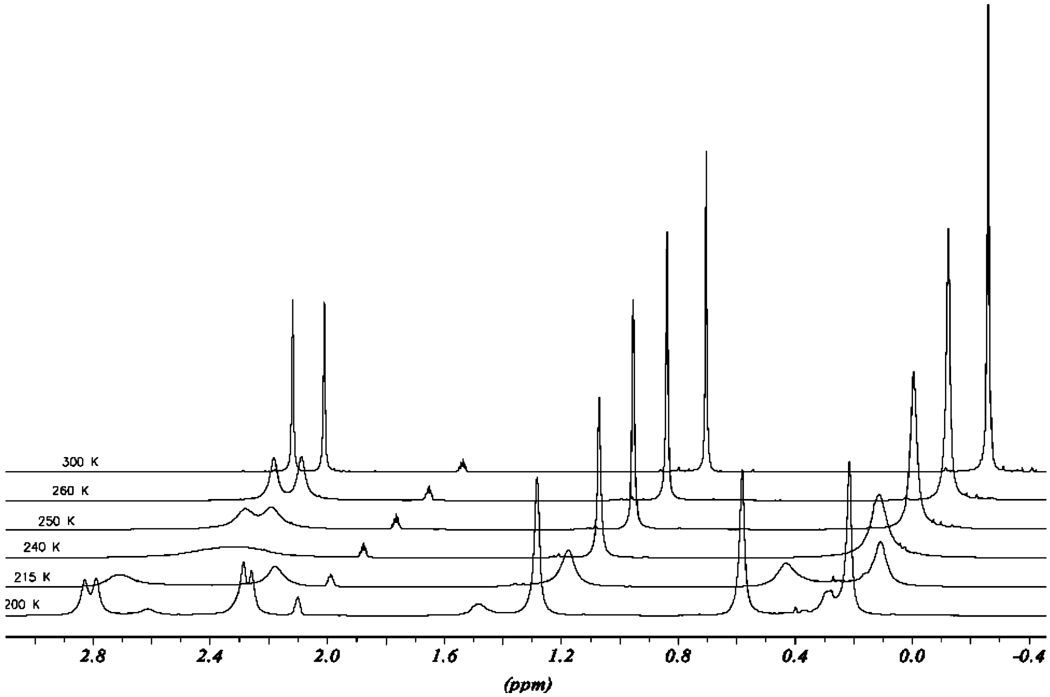

Figure 4. ^{1}H NMR spectra (400 MHz) of **2b** in toluene-d_8 at different temperatures.

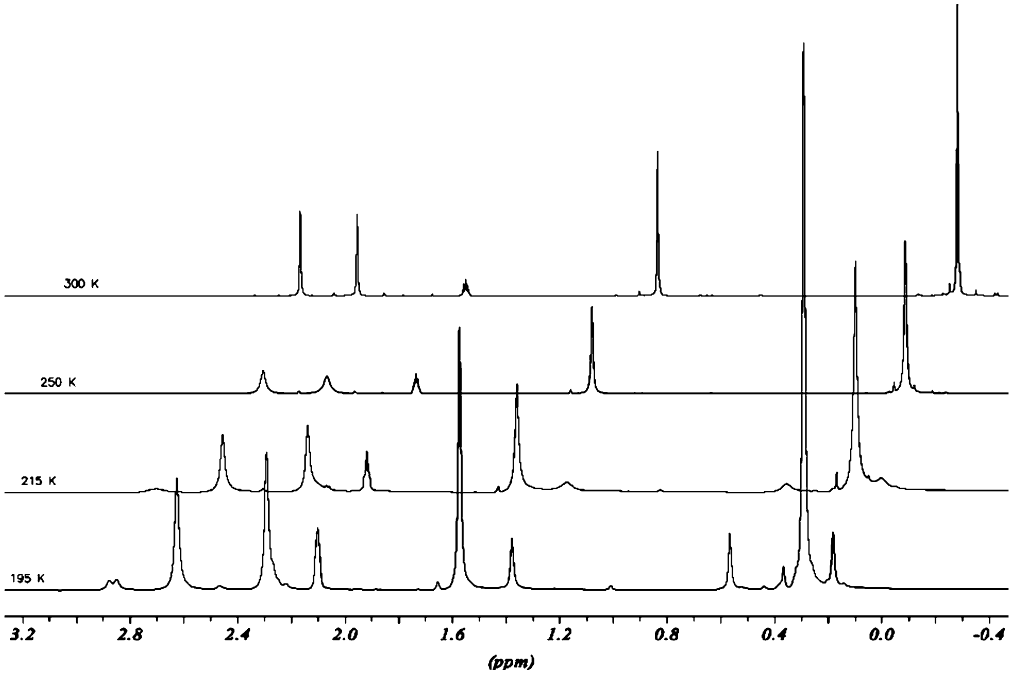

Figure 5. ^{1}H NMR spectra (400 MHz) of **2a** in toluene-d_8 at different temperatures.

diastereomer shows the same symmetry as that expected from the solid-state structure. Two broad singlets downfield of the major species' two singlets can be seen as well as the other two singlets hidden in the more upfield NMe group's signal. One singlet for the *tert*-butyl group and two singlets of the silyl groups make the minor species' set complete. The integrals show that about 80% of **2a** forms the second conformer while only 20% represents the solid-state conformation at 195 K in solution.

Once again, father and daughter, tantalum and niobium, differ in a subtle way. While niobium compound **2b** prefers the same most stable conformer in solution as in the solid state with one minor different species observable in solution at low temperature, the analogue tantalum compound **2a** forms the same species but in an inverted ratio under the same conditions.

Reactivity of 1−3. In order to get some information about the reactivity of the obtained compounds, several attempts have been made to exchange the halogeno ligands of **1**−**3** in nucleophilic substitution reactions using alkyl and amide synthons.

Several attempts were made to substitute the chloro ligands of **1** by treatment with alkaline-metal alkyls and amides like $LiNMe_2$ or NaCp. Usually, no reaction took place, or the reaction mixture showed several products that could not be separated.

Interestingly, **2** and **3** react more selectively in metathesis and substitution reactions compared to **1** (see Figure 6). One typical transformation of an imido group is the protolysis reaction with amines, which are more acidic than the amine originating from the imido group. To test the reactivity of the *tert*-butylimido groups of **2a** and **3a**, they were exposed to pentafluoroaniline. Both react slowly at room temperature over a period of several days to form $[M(NC_6F_5)(N(SiMe_3)NMe_2)_2Cl]$ **4a** (M = Ta) and **4b** (M = Nb). Aminolysis at 60 °C is complete after 18 h.

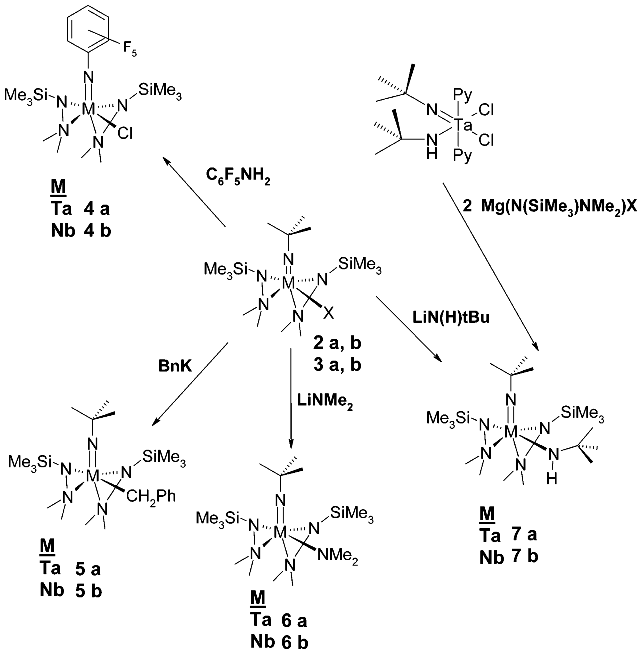

Figure 6. Reactions of **2** and **3** with salts and amines.

Single crystals of **4a** suitable for X-ray diffraction analysis were grown from hexane. The molecular structure of **4a** is presented in Figure 7, and selected distances and angles of **4a** are given in Table 2. Because the structures of the derivatives shown in Figure 6 show extraordinary similarities, they will be presented and discussed later.

The ^{1}H NMR spectra of **4a** and **4b** show two singlets for the four methyl groups and one singlet for the two silyl groups of the two hydrazido ligands at room temperature, which is the same behavior that has been observed for the parent halogeno derivatives **2a** and **2b**. However, the

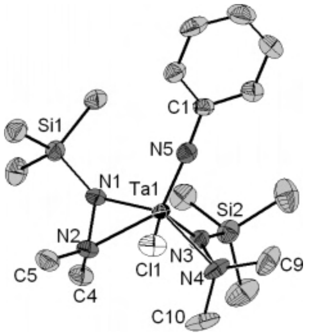

Figure 7. Molecular structure of **4a** in the solid state. H and F atoms are omitted for clarity. Ellipsoids are shown at 40% probability.

Table 2. Selected Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of **4a**, **5a**, **6a**, and **7b** in the Solid State

4a		5a	
Ta1−N1	1.960(4)	Ta1−N1	2.044(3)
Ta1−N2	2.318(4)	Ta1−N2	2.239(2)
Ta1−N3	2.012(4)	Ta1−N3	1.991(3)
Ta1−N4	2.216(4)	Ta1−N4	2.355(2)
Ta1−N5	1.792(4)	Ta1−N5	1.778(3)
Ta1−Cl1	2.4017(13)	Ta1−C1	2.234(3)
N5−Ta1−N1	104.53(16)	N5−Ta1−N1	105.99(10)
N5−Ta1−N3	107.03(18)	N5−Ta1−N3	108.25(11)
N5−Ta1−N2	142.05(15)	N5−Ta1−N2	142.05(15)
N5−Ta1−N4	113.71(18)	N5−Ta1−N4	146.17(11)
N5−Ta1−Cl1	101.52(14)	N5−Ta1−C1	101.31(12)
N1−Ta1−N2	38.58(13)	N1−Ta1−N2	39.25(9)
N3−Ta1−N4	39.91(16)	N3−Ta1−N4	37.93(1)
		C2−C1−Ta1	120.9(2)

6a		7b	
Ta1−N1	2.389(5)	Nb1−N1	2.0148(14)
Ta1−N2	2.007(5)	Nb1−N2	2.3875(16)
Ta1−N3	2.254(5)	Nb1−N3	2.0445(14)
Ta1−N4	2.050(5)	Nb1−N4	2.2499(15)
Ta1−N5	2.039(5)	Nb1−N5	1.7839(14)
Ta1−N6	1.787(5)	Nb1−N6	2.0249(17)
N6−Ta1−N1	143.7(2)	N5−Nb1−N1	108.01(6)
N6−Ta1−N3	117.6(2)	N5−Nb1−N3	104.80(6)
N6−Ta1−N2	107.1(2)	N5−Nb1−N2	145.12(6)
N6−Ta1−N4	105.4(2)	N5−Nb1−N4	116.00(6)
N6−Ta1−N5	100.6(2)	N5−Nb1−N6	104.76(8)
N1−Ta1−N2	37.03(17)	N1−Nb1−N2	37.12(6)
N3−Ta1−N4	38.63(19)	N3−Nb1−N4	38.69(6)

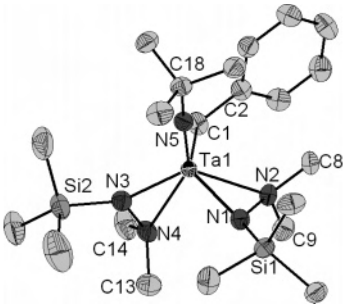

Figure 8. Molecular structure of **5a** in the solid state. H atoms are omitted for clarity. Ellipsoids are shown at 40% probability.

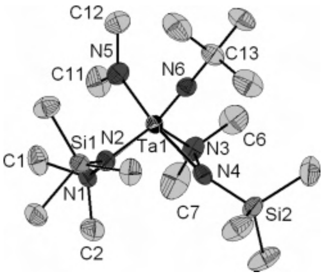

Figure 9. Molecular structure of **6a** in the solid state. H atoms are omitted for clarity. Ellipsoids are shown at 40% probability.

corresponding signals of **4a** do not show any tendency to decoalesce at temperatures down to 183 K (500 MHz, CD_2Cl_2).

A selective alkylation of **2a**,**b** and **3a**,**b** to the benzyl (Bn) complexes [M(N^{t}Bu)(N(SiMe$_3$)NMe$_2$)$_2$Bn] **5a** (M = Ta) and **5b** (M = Nb) is observed by reaction with BnK in toluene at room temperature. In the ^{1}H NMR spectrum of **5a** at room temperature, there is only one signal for the NMe$_2$ groups of the hydrazido ligands, while the ^{13}C NMR spectrum shows two signals differing by only 0.4 ppm. This indicates that the ligand replacing X has a strong influence on the dynamic processes in the ligand sphere. In contrast, the ^{1}H NMR spectrum of **5b** shows two signals for the NMe$_2$ groups of the hydrazido ligands differing by about 0.03 ppm, while the ^{13}C NMR spectrum shows two signals differing by only 0.15 ppm. Because of the unresolved coupling $^1J_{\mathrm{Nb-C}}$ of the quadrupole nucleus ^{93}Nb ($I = {}^9/_2$, 100% n.a.), the benzylic ^{13}C NMR signal of **5b** could only be located after more than 6000 scans as a broad signal at 44 ± 1 ppm. For the same reason, the tertiary carbon's signal of the *tert*-butylimido group is very weak in the ^{13}C NMR spectrum of **5b**.

5a and **5b** are colorless, low-melting, hexane-soluble, and sublimable solids. Single crystals of **5a** suitable for X-ray diffraction structure analysis were grown from hexane. The molecular structure of **5a** is presented in Figure 8, and selected bond lengths and angles are given in Table 2.

Reactions of **2** and **3** with 1 equiv of LiNMe$_2$ in toluene give [M(N^{t}Bu)(TDMH)$_2$(NMe$_2$)] **6a** (M = Ta) and **6b** (M = Nb) with almost quantitative yield. **6a** and **6b** are colorless, hexane-soluble, and sublimable compounds having an all-nitrogen ligand regime. Therefore, **6a** was selected as a single-source precursor for CVD experiments aimed at TaN-based thin films. First experiments have been made that proved that **6a** fulfills many requirements for CVD precursors. Preliminary results are presented later in this report. Single crystals of **6a** suitable for X-ray diffraction structure analysis were grown from hexane. The molecular structure of **6a** is presented in Figure 9, and selected bond lengths and angles are given in Table 2.

As alternative imido−amido−bis(hydrazido) compounds, [Ta(N^{t}Bu)(TDMH)$_2$(NH^{t}Bu)] (**7a**) and [Nb(N^{t}Bu)(TDMH)$_2$(NH^{t}Bu)] (**7b**) have been prepared. Both are accessible either by treatment of [M(N^{t}Bu)(TDMH)$_2$Cl] with 1 equiv of LiNH^{t}Bu in toluene or by reaction of [M(N^{t}Bu)(NH^{t}Bu)Cl$_2$Py$_2$] (M = Ta, Nb) with 2 equiv of the reagent BrMg(TDMH) or ClMg(TDMH) in THF. Both syntheses provide very good yields of **7a** and **7b** as colorless, hexane-soluble, and sublimable solids. Single crystals of **7b** suitable for X-ray diffraction structure analysis were grown from hexane. The molecular structure of **7b** is presented in Figure 10, and selected bond lengths and angles are given in Table 2.

The structures of the presented imido−bis(hydrazido) compounds **4a**, **5a**, **6a**, and **7b** show strong similarities. The

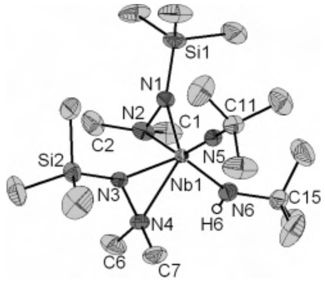

Figure 10. Molecular structure of **7b** in the solid state. H and C atoms of the disordered trimethylsilyl group at Si1 are omitted for clarity. Ellipsoids are shown at 40% probability.

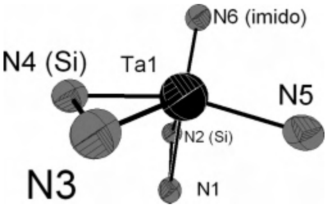

Figure 11. Perspective view of the inner core of **6a** showing the typical features of all imido−bis(hydrazido) complexes discussed in this text.

metal centers are pseudotetrahedrally surrounded if the hydrazido ligands are assumed to adopt a single coordination site despite their κ^2-bonding modi. The distances M−N$_{\mathrm{imido}}$ vary between 1.78 and 1.79 Å, which implies that the imido group is a six-electron donor. This is supported by the angle M−N$_{\mathrm{imido}}$−C of almost 180° in all compounds shown. In contrast to the room-temperature ^{1}H and ^{13}C NMR spectra, the κ^2-hydrazido ligands show inequivalent orientations and, as a consequence, different surroundings for all four NMe groups in the solid state.

Figure 11 shows the inner core of the ligand regime of **6a** with the two orientations of the hydrazido N−N vectors. It is evident that Ta1, N1, N2, and N6 lie in one plane while Ta1, N3, N4, and N5 define a second plane. The interplanar angle is close to 90° in all structures discussed here. This is probably the result of optimization of the molecule's σ- and π-bond frame in a pseudotetrahedral coordination sphere.

The distances between the metal and the silylated N atoms vary between 1.96 and 2.04 Å. The distances between the metal and the NMe$_2$ groups of the hydrazido ligands range from 2.21 to 2.38 Å. The silylated N atoms of the hydrazido ligands of **4a**, **5a**, **6a**, and **7b** coordinated perpendicular to the vector M−N$_{\mathrm{imido}}$ show slightly longer distances to the metal center than those coplanar with the M−N$_{\mathrm{imido}}$ bond. Looking at the Ta−NMe$_2$ interactions, this tendency is inverted. While in each compound the differences in the distance to the metal center differ by only 0.05 Å at the utmost for the silylated N atoms, the NMe$_2$ groups show deviations of 0.1 Å in their distances to the metal. The sums of angles around the silylated N atoms vary between 350° and 359°, indicating a sp^2 hybridization and a tendency toward pyramidalization as the dominant contribution. Because the silylated N atoms showing shorter M−N distances have sums of angles nearer to 360° than those showing slightly longer M−N distances, we can assume a higher M−N π interaction for those N atoms. A similar tendency is found in looking at the NMe$_2$ groups. The N atoms closer to the metal center show angles C−N−N of approximately 115°, while the other N atoms showing longer M−N distances show C−N−N angles of approximately 112°. **5a** is an electron-rich compound displaying a benzyl ligand that shows the absence of any π interaction between the metal center and the benzyl ligand known from very electron-deficient compounds of zirconium, molybdenum, or tungsten.[36,37] This is supported by the angle C2−C1−Ta1 of 120.9(2)° and a nonbonding distance Ta−C2 of 3.25 Å.

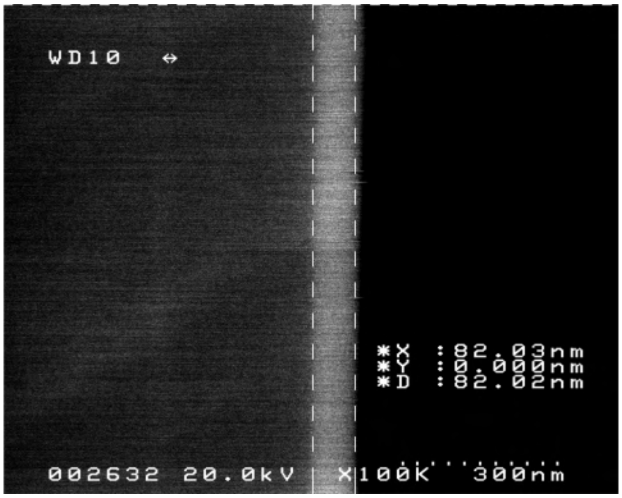

Figure 12. Cross-sectional back-scattered electron (BSE) micrograph of a layer deposited at 600 °C with **6a**.

Preliminary CVD Experiments. For a preliminary CVD study, we selected **6a** as the precursor. The experiments were carried out in a commercial Aixtron AIX-200 reactor system applying N$_2$ as the carrier gas. During the process, the reactor pressure was kept constant at 100 mbar with a total gas flow of 550 sccm. The temperature of the precursor container was kept constant at 80 °C, and the substrate temperature was varied between 500 and 700 °C. As the substrate, we used (100)-oriented p-doped silicon wafers coated with a native SiO$_x$ surface.

For determination of the thickness of the deposited layers, we used scanning electron microscopy investigations (see Figure 12). Under the chosen conditions, the highest deposition rates of 0.34 nm/min were obtained at a substrate temperature of 600 °C. Energy-dispersive X-ray analysis (EDX) showed that the deposited layers contained tantalum and nitrogen (approximately 3:1) with some amounts of carbon and oxygen.

Experiments with unsymmetric dimethylhydrazine (UDMHy) as an additional reactive gas were performed at a substrate temperature of 500 °C. These experiments showed a significant influence of the partial pressure ($P_{\mathrm{P(UDMHy)}}$) of UDMHy on the layer composition (see Figure 13). By an increase of the partial pressure of UDMHy, it was possible to change the Ta/N ratio from 3:1 ($P_{\mathrm{P(UDMHy)}} = 0$ mbar) to 1:1 ($P_{\mathrm{P(UDMHy)}} = 0.07$ mbar). However, the carbon content also shows a strong dependence on the partial pressure of

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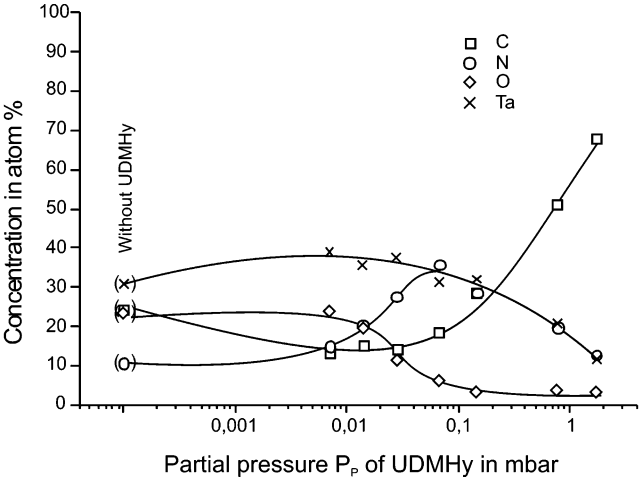

Figure 13. EDX analysis of layers deposited with **6a** and different partial pressures of UDMHy at 500 °C.

UDMHy. Experiments with hydrogen and other nitrogen sources such as ammonia will follow for a better understanding of the decomposition pathway of the tantalum precursor in the presence of different reactive secondary sources. Details of the layer composition as a function of the deposition conditions and the effects of different reactive gases on this and other precursors of interest will be reported elsewhere.

Hydrazinolysis of Bis(imido)molybdenum and -tungsten Complexes. In contrast to [Ta(N^{t}Bu)Cl$_3$Py$_2$], [W(N^{t}Bu)$_2$Cl$_2$Py$_2$] does not exchange its imido functionality for two hydrazido groups when reacted with an excess of H-TDMH. Instead, [W(N^{t}Bu)$_2$(TDMH)Cl] (**8a**) is formed under elimination of HCl and the loss of the two pyridine ligands.

8a is a low-melting, hexane-soluble, colorless to shiny orange solid that is sublimable at 70 °C and 10^{-3} mbar but slowly decomposes to a dark-red oil at 25 °C under inert conditions over a period of several weeks.

In the same manner, [Mo(N^{t}Bu)$_2$Cl$_2$] reacts to [Mo(N^{t}Bu)$_2$(TDMH)Cl] (**8b**). In contrast to **8a**, the molybdenum compound is a brownish, distillable oil.

Reactions of Bis(imido)molybdenum and -tungsten Complexes with Hydrazido Salts. [W(N^{t}Bu)$_2$Cl$_2$Py$_2$] reacts with BrMg(TDMH) in a manner similar to that of the tantalum and niobium compounds mentioned above, giving the bromo complex [W(N^{t}Bu)$_2$(TDMH)Br] (**9a**), and with ClMg(TDMH), giving the chloro complex **8a**. Again, a close to quantitative exchange of [W−Cl] and [Mg−Br] functionalities is observed. This surprising fact is consistent with the view that the refractory metals (Nb, Ta, Mo, and W) discussed here in a regime of strong N-donor ligands reveal a character of rather soft Lewis acids compared to magnesium(2+) even in THF. Additionally, the higher lattice energy of MgCl$_2$(s) compared to MgBr$_2$(s) as well as differences in the solvation energies of MgCl$_2$(THF)$_n$ compared to those of MgBr$_2$(THF)$_n$ probably plays a role in the shifting of the equilibrium of this halide metathesis. **9a** shows the same appearance and physical behavior as that of **8a**. Crystals of **9a** suitable for single-crystal X-ray diffraction analysis were grown in the oily substance itself.

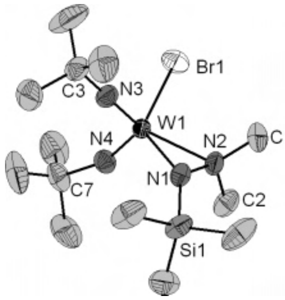

Figure 14. Molecular structure of **9a** in the solid state. H and C atoms of the disordered *tert*-butyl group at C7 are omitted for clarity. Ellipsoids are shown at 40% probability.

Table 3. Selected Distances (Å), Bond Angles (deg), and Torsion Angles (deg) of **9a** in the Solid State

W1−N1	1.986(3)	W1−N3−C3	178.0(3)
W1−N2	2.215(3)	W1−N4−C7	155.2(3)
W1−N3	1.737(3)	N3−W1−N4	111.11(15)
W1−N4	1.749(3)	N3−W1−Br1	101.72(10)
W1−Br1	2.5062(4)	N4−W1−Br1	104.03(10)
		N1−W1−N2	39.52(11)
		W1−N1−Si1	145.66(17)

The molecular structure of **9a** is presented in Figure 14, and selected bond lengths and angles are given in Table 3. W1 is coordinated in a pseudotetrahedral fashion if the hydrazido ligand is assumed to adopt a single coordination site. This is supported by the angles around W1, reaching from 101.7° (Br1−W1−N3) to 122.2° (N3−W1−N1/N2). The distances between W1 and N3 and N4 are 1.737(3) and 1.749(3) Å, respectively. The somewhat longer distance to the imido group containing N4 is accompanied by a considerable deviation of the imido angle W1−N4−C7 from 180°. It counts to only 155.2(3)°, while W1−N3−C3 is 178.0(3)°. This is a typical structural feature of π-bond-loaded bis(imido) complexes.[38] The distances between W1 and N1 and N2 are 1.986(3) and 2.215(3) Å, respectively. Comparison with the tungsten amido−nitrogen distances in [W(NPh)(N$_2$N$_{Py}$)Me$_2$][39] or [W{N(2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2${(NSiMe$_3$)C$_6$H$_3$-Me}$_2$][40] indicates a bonding situation in which N1 is bonded in an amido-like manner and N2 in a donor−acceptor manner. The sum of the angles around N1 is 352°, which implies a sp^2 hybridization of the N atom and the presence of a π character in bonding to the metal center.

N1 occupies a coordination site that lies close to the ideal tetrahedral site. This is indicated by the angles N1−W1−N3 and N1−W1−N4 of 105.6° and 108.1°, respectively. The two planes Br1−W1−N1 and N3−W1−N4 intersect each other at almost 90°. For steric reasons, N2 deviates by 0.65 Å from the plane Br1−W1−N1. Sutton et al. structurally characterized [Cp$_2$W(H$_2$NNPh)][BF$_4$].[41] The W atom in this compound is pseudotetrahedrally surrounded, with three corners being occupied by the two cyclopentadienyl's

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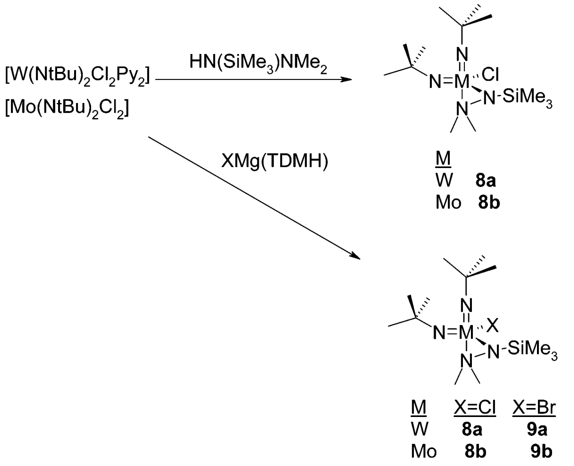

Figure 15. Reactions of molybdenum and tungsten imido complexes with H-TDMH and their magnesium salts, giving complexes **8** and **9**.

centroids and the anionic N atom of the hydrazido(1−) ligand.

Although the methyl groups of the hydrazido ligand are in inequivalent positions, according to the molecular structure in the solid state, there is no splitting of the corresponding signals in the ^1H NMR spectrum of **9a** observable down to 170 K (toluene-d_8, 500 MHz).

Using the same conditions, **8b** and $[Mo(N^tBu)_2(N(SiMe_3)NMe_2)Br]$ (**9b**) can be obtained (Figure 15). **9b** is also a red distillable oil.

Conclusion

The present work reveals highly selective and, in part, contrasting reaction pathways for tantalum, niobium, tungsten, and molybdenum imido complexes with the hydrazine $HN(SiMe_3)NMe_2$. Unexpectedly, hydrazinolysis of $[Ta(N^tBu)Cl_3Py_2]$ leads to displacement of the imido functionality by two κ^2-hydrazido(1−) ligands in **1**, whereas the corresponding niobium complex is unreactive under the same conditions. In contrast, hydrazinolysis of group 6 bis(imido) complexes leads to chlorine substitution products $[M(N^tBu)_2(TDMH)Cl]$ **8a** (M = W) and **8b** (M = Mo). In accordance with literature reports, Li-TDMH tends to be a nonselective reagent for introducing the hydrazido anion. We found that $[Mg(TDMH)_2]_2$ or even more convenient XMg(TDMH) prepared from the reaction of a Grignard reagent with H-TDMH are cheap and selective synthons in anion exchange of imido−chloro complexes of the refractory metals. To our surprise, chloro ligands were replaced not only by hydrazido but also in a close to quantitative manner by bromo ligands if the bromo-containing mixed salt [BrMg(TDMH)] is applied, giving $[M(N^tBu)(TDMH)_2Br]$ **3a** (M = Ta) and **3b** (M = Nb) and $[M(N^tBu)_2(TDMH)Br]$ **9a** (M = W) and **9b** (M = Mo).

This observation is in accordance with a relatively soft character of these highly N-donor-substituted d^0-metal centers niobium(V), tantalum(V), molybdenum(VI), and tungsten(VI) compared to $[Mg(THF)_4]^{2+}$.

From variable-temperature ^1H NMR spectroscopy, it is evident that compounds of the type $[M(N^tBu)(TDMH)_2X]$ (M = Nb, Ta) form different diastereomers in solution and only the most stable forms have been characterized in the solid-state structures of **4a**, **5a**, **6a**, and **7b**. In contrast, we have no indication that $[M(N^tBu)_2(TDMH)X]$ (M = Mo, W) shows any tendency to slow down dynamic exchange of the NMe_2 protons in the low-temperature ^1H NMR spectra.

Furthermore, a tantalum compound could be obtained that supplements a logical row of nitrogen-rich CVD precursors could be obtained: $[Ta(N^tBu)(NEt_2)_3]$ (TBTDET), $[Ta(N^tBu)(N(SiMe_3)NMe_2)(NMe_2)_2]$,[33] $[Ta(N^tBu)(N(SiMe_3)NMe_2)_2(NMe_2)]$ (**6a**, this work). These compounds show properties that justify the need for a comprehensive and comparative CVD study under standardized conditions.

Experimental Section

All experiments were carried out using standard Schlenk-tube or glovebox techniques under a dry dinitrogen or argon atmosphere. Solvents were purified with appropriate drying agents, distilled, and stored under dinitrogen. The compounds $[M(N^tBu)Cl_3Py_2]$ (M = Nb, Ta),[42] $[M(N^tBu)(NH^tBu)Cl_2Py_2]$ (M = Nb, Ta),[43] $[W(N^tBu)_2Cl_2Py_2]$,[44] $[Mo(N^tBu)_2Cl_2]$,[44] $[Mg(N(SiMe_3)NMe_2)_2]_2$[35], BnK,[45] and $LiNMe_2$[46] were prepared by literature methods. $HN(SiMe_3)NMe_2$ has been prepared by a modified literature[47] procedure. The procedure presented here avoids problems due to the sublimation of 1,1-dimethylhydrazine−hydrochloride during distillation of the desired product. Furthermore, unpublished ^{13}C and ^{29}Si NMR data are included. 1,1-Dimethylhydrazine (Aldrich) was dried over BaO and distilled before use. Me_3SiCl (Acros) was distilled prior to use. $TaCl_5$ (H.C. Starck) was stored under inert conditions and used as received.

NMR spectra were taken on Bruker ARX 200, AVANCE 300 A, and AVANCE 300 B spectrometers using deuterated benzene or deuterated chloroform as the solvent. The carbon signal (128.0 ppm/77.0 ppm) has been used for calibration of $^{13}C\{^1H\}$ NMR spectra and the residual proton signal (7.15 ppm/7.26 ppm) for calibration of ^1H NMR spectra. Tetramethylsilane was used as the external standard for calibration of ^{29}Si NMR spectra of highly concentrated solutions. Electron impact mass spectra (EI-MS) were taken on a Varian CH7A at 70 eV, and data are reported as *m*/*z* (assignment, highest peak of the isotopic pattern, % relative intensity). IR spectra were measured on a Nicolet 510M, and solid samples were prepared as Nujol mulls between KBr plates. Melting points were determined on a Büchi B-540, with the samples being in wax-sealed test tubes.

Elemental analysis samples of **2**−**9** were prepared from repeatedly sublimed or crystallized material. Nevertheless, the obtained data are poor and not reproducible. This is an annoying phenomenon due to the formation of refractory carbides and nitrides.

H-TDMH [$HN(SiMe_3)NMe_2$].[47] A total of 60 mL (47 g, 0.78 mmol) of 1,1-dimethylhydrazine was dissolved in 500 mL of pentane followed by the slow addition of 50 mL (43 g, 0.40 mmol) of chlorotrimethylsilane. After complete addition, the reaction mixture was refluxed for 3 h and afterward filtered off. The residue was washed with 60 mL of pentane, and the combined filtrates were distilled under argon (1 atm). The first fraction (38 °C) was

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discarded. The second fraction (99 °C) gave 42.12 g (0.32 mmol; 81%) of a colorless liquid.

^{1}H NMR (300 MHz, CDCl$_3$): δ 2.22 (6H, N(CH_3)$_2$), 1.78 (1H, NH), −0.09 (9H, Si(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 52.4 (N(CH$_3$)$_2$), −0.8 (Si(CH$_3$)$_3$). ^{29}Si NMR (79 MHz, CDCl$_3$): δ −5.59 (N-Si(CH$_3$)$_3$). IR (Nujol mull, cm^{-1}): 3284 m, 2985 s, 2950 s, 2895 s, 2849 s, 2811 s, 2763 s, 1462 m, 1450 s, 1434 m, 1399 m, 1247 s, 1153 m, 1062 s, 1009 m, 895 s, 838 s, 747 m, 720 m, 685 m, 614 m, 493 m, 445 w.

BrMg(TDMH) Reagent. To a solution of the Grignard reagent prepared from 4.21 g (173 mmol) of Mg and 24.8 mL (31.2 g, 228 mmol) of 2-bromobutane in 600 mL of diethyl ether was added dropwise 23.0 g (174 mmol) of HN(SiMe$_3$)NMe$_2$. After the addition of one-third of the hydrazine, a white solid started to precipitate. The mixture was stirred overnight and reduced to two-thirds of its volume before the colorless solid was filtered off and dried in vacuo.

Yield: 37.2 g (158 mmol; 91%). ^{1}H NMR (300 K, 200 MHz, THF-d_8): δ 2.52 (6H, N(CH_3)$_2$), −0.04 (9H, Si(CH_3)$_3$). IR (Nujol mull, cm^{-1}): 1249 m, 1242 m, 1012 m, 981 m, 871 m, 842 m, 771 m, 756 m, 673 m, 468 m.

ClMg(TDMH) Reagent. To a solution of the Grignard reagent prepared from 1.0 g (41.14 mmol) of Mg and 5.6 mL (4.9 g, 53.2 mmol) of 1-chlorobutane in 60 mL of diethyl ether was added dropwise through a septum 5.8 g (43.8 mmol) of HN(SiMe$_3$)NMe$_2$. After the addition of one-third of the hydrazine, a white solid started to precipitate. The mixture was stirred overnight before the colorless solid was filtered off and dried in vacuo.

Yield: 6.8 g (35.6 mmol; 87%). IR (Nujol mull, cm^{-1}): 1249 m, 1242 m, 1012 m, 981 m, 871 m, 842 m, 771 m, 756 m, 673 m, 468 m.

[Ta(TDMH)$_2$Cl$_3$] (1). A total of 5.2 g (9.94 mmol) of [Ta(N^{t}Bu)Cl$_3$Py$_2$] was dissolved in 30 mL of CH$_2$Cl$_2$, and 2.9 g (21.86 mmol) of HN(SiMe$_3$)NMe$_2$ was added to the clear yellow solution, which was stirred overnight. The orange dispersion was filtered, and the residue was washed with 4 mL of toluene, leaving a colorless solid and an orange filtrate. The solvent of the combined filtrates was removed in vacuo, yielding an orange solid, which was digested with 100 mL of hexane, filtered off, and dried in vacuo, giving an orange powder. The product can be purified by recrystallization from toluene upon cooling of a concentrated solution or upon the addition of hexane.

Yield: 5.34 g (9.72 mmol; 97%). ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 3.08 (6H, N(CH_3)$_2$), 0.17 (9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 52.9 (N(CH$_3$)$_2$), 0.17 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{10}$H$_{30}$N$_4$Cl$_3$Si$_2$Ta: C, 21.48; H, 5.50; N, 10.19. Found: C, 22.05; H, 5.40; N, 10.42. EI-MS: 550 [{M$^+$}, 0.1], 417 [{M − (N(SiMe$_3$)NMe$_2$)}$^+$, 25.5], 131 [{N(SiMe$_3$)NMe$_2$}$^+$, 49.9]. IR (Nujol mull, cm^{-1}): 1248 s, 1168 w, 1041 s, 1006 s, 910 s, 893 m, 844 s, 773 m, 734 m, 723 m, 696 m, 634 m, 501 s, 472 w.

[Ta(N^{t}Bu)(TDMH)$_2$Cl] (2a). Method A. A total of 4.0 g (7.7 mmol) of [Ta(N^{t}Bu)Cl$_3$Py$_2$] and 2.2 g (3.86 mmol) of [Mg(TDMH)$_2$]$_2$ were mixed and cooled to −78 °C before 40 mL of THF cooled to −78 °C was added. The mixture was stirred for 4 h at −78 °C before it was allowed to slowly warm up to room temperature. After 12 h of stirring, the volatile components were removed in vacuo and the residue was extracted twice with 40 mL of hexane each. The solvent of the combined extracts was evaporated and the residue sublimed (10^{-3} mbar, 70 °C). Yield: 3.53 g (6.42 mmol; 83%).

Method B. A total of 1.0 g (1.93 mmol) of [Ta(N^{t}Bu)Cl$_3$Py$_2$] and 740 mg (3.87 mmol) of the reagent with the idealized formula ClMg(TDMH) were mixed and cooled to −78 °C before 10 mL of THF (−78 °C) was added. The mixture was stirred for 4 h before it was allowed to warm to room temperature and stirred for a further 12 h. The beige suspension was dried in vacuo, and the residue was extracted with 30 mL of hexane. The suspension was filtered, and the residue was washed twice with 5 mL of hexane each. The solvent of the combined filtrates was removed in vacuo, and the orange residue was sublimed (10^{-3} mbar, 70 °C).

Yield: 670 mg (1.22 mmol; 63%). Mp (uncorrected): 59 °C. ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.69 (6H, N(CH_3)$_2$), 2.46 (6H, N(CH_3)$_2$), 1.40 (9H, NC(CH_3)$_3$), 0.25 (18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 63.9 (NC(CH$_3$)$_3$), 51.6 (N(CH$_3$)$_2$), 51.1 (N(CH$_3$)$_2$), 34.1 (NC(CH$_3$)$_3$), 2.8 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{14}$H$_{39}$N$_5$ClSi$_2$Ta: C, 30.59; H, 7.16; N, 12.75. Found: C, 29.70; H, 7.34; N, 12.23. EI-MS: 549 [{M}$^+$, 5.5], 534 [{M − CH$_3$}$^+$, 100], 492 [({M − C$_4$H$_9$}$^+$, 3.9], 131 [{(Me$_3$Si)NNMe$_2$}$^+$, 18.6], 73 [{SiMe$_3$}$^+$, 51.5], 58 [{NNMe$_2$}$^+$, 9.9], 44 [{NMe$_2$}$^+$, 2.4]. IR (Nujol mull, cm^{-1}): 1351 m, 1279 s, 1246 s, 1211 m, 1055 s, 1031 s, 902 s, 838 s, 785 m, 774 m, 715 m, 683 s, 634 m, 537 m, 480 s.

[Nb(N^{t}Bu)(TDMH)$_2$Cl] (2b). A total of 21.38 g (49.9 mmol) of [Nb(N^{t}Bu)Cl$_3$Py$_2$] and 19.18 g (100.4 mmol) of the reagent ClMg(TDMH) were mixed and cooled to −78 °C before 300 mL of THF (−78 °C) was added. The mixture was stirred for 4 h before the mixture was allowed to warm to room temperature and stirred for a further 12 h. The blue suspension was taken to dryness, and the residue was extracted with 250 mL of hexane. The suspension was filtered, and the residue was washed twice with 100 mL of hexane each. The solvent of the combined filtrates was removed in vacuo, and the orange residue was distilled (10^{-3} mbar, 130 °C).

Yield: 17.3 g (37.4 mmol; 76%). ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.65 (6H, N(CH_3)$_2$), 2.53 (6H, N(CH_3)$_2$), 1.30 (9H, NC(CH_3)$_3$), 0.30 (18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 65.8 (NC(CH$_3$)$_3$), 52.9 (N(CH$_3$)$_2$), 52.7 (N(CH$_3$)$_2$), 35.5 (NC(CH$_3$)$_3$), 2.9 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{14}$H$_{39}$N$_5$ClSi$_2$Nb: C, 36.39; H, 8.51; N, 15.16. Found: C, 36.05; H, 8.38; N, 15.15. EI-MS: 462 [{M}$^+$, 0.1], 446 [{M − CH$_3$}$^+$, 18.9], 132 [{H(Me$_3$Si)NNMe$_2$}$^+$, 9.6], 131 [{(Me$_3$Si)NNMe$_2$}$^+$, 14.6], 73 [{SiMe$_3$}$^+$, 76.8], 59 [{HNNMe$_2$}$^+$, 6.0], 58 [{NNMe$_2$}$^+$, 12.5], 44 [{NMe$_2$}$^+$, 29.8]. IR (Nujol mull, cm^{-1}): 1351 m, 1279 s, 1246 s, 1211 m, 1055 s, 1031 s, 902 s, 838 s, 785 m, 774 m, 715 m, 683 s, 634 m, 537 m, 480 s.

[Ta(N^{t}Bu)(TDMH)$_2$Br] (3a). A total of 33.5 g (64.8 mmol) of [Ta(N^{t}Bu)Cl$_3$Py$_2$] and 30.6 g (129.9 mmol) of the reagent BrMg(TDMH) were mixed and cooled to −50 °C before 300 mL of THF cooled to −50 °C was added. The mixture was allowed to warm to −20 °C and stirred for 4 h before the mixture was allowed to warm to room temperature and stirred for a further 12 h. The brown suspension was taken to dryness, and the residue was extracted with 300 mL of hexane. The suspension was filtered, and the residue was washed twice with 200 mL of hexane each. The volatile contents of the combined filtrates was removed in vacuo, and the orange residue was sublimed (10^{-3} mbar, 70 °C).

Yield: 26.04 g (43.8 mmol; 68%) contaminated with small amounts of **2a**. ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.70 (6H, N(CH_3)$_2$), 2.46 (6H, N(CH_3)$_2$), 1.41 (9H, NC(CH_3)$_3$), 0.25 (18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 63.9 (NC(CH$_3$)$_3$), 51.6 (N(CH$_3$)$_2$), 51.1 (N(CH$_3$)$_2$), 34.1 (NC(CH$_3$)$_3$), 2.8 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{14}$H$_{39}$N$_5$BrSi$_2$Ta: C, 28.32; H, 6.63; N, 11.80. Found: C, 28.72; H, 7.01; N, 12.03. EI-MS: 580 [{M − CH$_3$}$^+$, 19.3], 131 [{(Me$_3$Si)NNMe$_2$}$^+$, 18.6], 73 [{SiMe$_3$}$^+$, 51.5], 58 [{NNMe$_2$}$^+$, 12.6], 44 [{NMe$_2$}$^+$, 14.9]. IR (Nujol mull, cm^{-1}): 1351 m, 1279 s, 1246 s, 1211 m, 1055 s, 1031 s, 902 s, 838 s, 785 m, 774 m, 715 m, 683 s, 634 m, 537 m, 480 s.

[Nb(N^{t}Bu)(TDMH)$_2$Br] (3b). A total of 150 mg (0.35 mmol) of [Nb(N^{t}Bu)Cl$_3$Py$_2$] and 255 mg (1.08 mmol) of the reagent BrMg(TDMH) were mixed and cooled to −78 °C before 5 mL of THF cooled to −78 °C was added. The mixture was allowed to warm to −20 °C and stirred for 3 h before the mixture was allowed to warm to room temperature and stirred for a further 12 h. The orange solution was taken to dryness, and the residue was extracted with 15 mL of hexane. The suspension was filtered, and the residue was washed twice with 5 mL of hexane each. The volatile contents of the combined filtrates was removed in vacuo, and the resulting orange oil was distilled (10^{-3} mbar, 120 °C).

Yield: 104 mg (0.21 mmol; 60%). ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.65 (6H, N(CH_3)$_2$), 2.54 (6H, N(CH_3)$_2$), 1.27 (9H, NC(CH_3)$_3$), 0.30 (18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 66.3 (NC(CH$_3$)$_3$), 53.5 (N(CH$_3$)$_2$), 53.1 (N(CH$_3$)$_2$), 32.3 (NC(CH$_3$)$_3$), 2.9 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{14}$H$_{39}$N$_5$BrSi$_2$Nb: C, 33.20; H, 7.76; N, 13.83. Found: C, 32.88; H, 7.51; N, 13.78. EI-MS: 492 [{M − CH$_3$}$^+$, 10.4], 449 [{M − NNMe$_2$}$^+$, 3.3], 131 [{(Me$_3$Si)NNMe$_2$}$^+$, 30.9], 73 [{SiMe$_3$}$^+$, 100.0], 58 [{NNMe$_2$}$^+$, 17.7], 44 [{NMe$_2$}$^+$, 52.0]. IR (Nujol mull, cm^{-1}): 1351 m, 1279 s, 1246 s, 1211 m, 1055 s, 1031 s, 902 s, 838 s, 785 m, 774 m, 715 m, 683 s, 634 m, 537 m, 480 s.

[Ta(NC$_6$F$_5$)(TDMH)$_2$Cl] (4a). A total of 669 mg (1.21 mmol) of **3a** and 224 mg (1.22 mmol) of pentafluoroaniline were mixed and dissolved in 5 mL of hexane. The mixture was stirred at 60 °C for 18 h and stored at −20 °C while **4a** precipitated. Subsequent reduction of the volume and precipitation at −20 °C gave 620 mg (0.94 mmol; 77%) of the product.

^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.64 (6H, N(CH_3)$_2$), 2.40 (6H, N(CH_3)$_2$), 0.16 (9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 51.5 (N(CH$_3$)$_2$), 50.9 (N(CH$_3$)$_2$), 2.0 (Si(CH$_3$)$_3$). Because of unresolved higher order coupling between the aromatic C and F atoms, no resonances for the pentafluorophenyl C atoms are listed. ^{19}F NMR (300 K, 282 MHz, C$_6$D$_6$): δ −135.9 (*pseudo*-d, 2F, *o*-F), −167.0 (*pseudo*-t, 2F, *m*-F), −170.9 (*pseudo*-t, 1F, *p*-F). Anal. Calcd for C$_{16}$H$_{30}$N$_5$ClSi$_2$Ta: C, 29.12; H, 4.58; N, 10.16. Found: C, 28.23; H, 4.78; N, 9.81. EI-MS: 183 [{C$_6$F$_5$NH$_2$}$^+$, 22.0], 131 [{N(SiMe$_3$)NMe$_2$}$^+$, 1.0], 73 [{SiMe$_3$}$^+$, 36.7], 44 [{NMe$_2$}, 53.9]. IR (Nujol mull, cm^{-1}): 1460 s, 1332 m, 1251 s, 1224 m, 1045 s, 1026 s, 983 m, 900 s, 841 s, 777 w, 751 w, 721 w, 684 w, 634 w, 482 w.

[Nb(NC$_6$F$_5$)(TDMH)$_2$Cl] (4b). A total of 1.5 g (3.2 mmol) of **2b** was dissolved in 15 mL of toluene and added to 603 mg (3.2 mmol) of pentafluoroaniline. The mixture was stirred at 60 °C for 18 h and stored at −20 °C while **4b** precipitated. Subsequent reduction of the volume and precipitation at −20 °C gave 1.02 g (1.79 mmol; 55%) of the product.

^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 2.64 (6H, N(CH_3)$_2$), 2.45 (6H, N(CH_3)$_2$), 0.22 (9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 52.2 (N(CH$_3$)$_2$), 51.8 (N(CH$_3$)$_2$), 2.1 (Si(CH$_3$)$_3$). Because of unresolved higher order coupling between the aromatic C and F atoms, no resonances for the pentafluorophenyl C atoms are given. ^{19}F NMR (300 K, 282 MHz, C$_6$D$_6$): δ −152.8 (*pseudo*-d, 2F, *o*-F), −166.4 (*pseudo*-t, 2F, *m*-F), −168.7 (*pseudo*-t, 1F, *p*-F). Anal. Calcd for C$_{16}$H$_{30}$N$_5$ClF$_5$Si$_2$Nb: C, 33.60; H, 5.29; N, 12.24. Found: C, 33.23; H, 5.08; N, 11.82. EI-MS: 183 [{C$_6$F$_5$NH$_2$}$^+$, 2.74], 131 [{N(SiMe$_3$)NMe$_2$}$^+$, 6.15], 73 [{SiMe$_3$}$^+$, 92.4], 44 [{NMe$_2$}, 58.9]. IR (Nujol mull, cm^{-1}): 1500 s, 1458 s, 1327 m, 1248 s, 1217 s, 1168 m, 1047 s, 985 s, 898 s, 839 s, 769 m, 720 m, 713 m, 680 m, 542 m, 499 m.

[Ta(N^{t}Bu)(TDMH)$_2$Bn] (5a). To a mixture of 500 mg (0.84 mmol) of **3a** and 127 mg (0.97 mmol) of BnK was added at 0 °C 8 mL of toluene. After 1 h, the mixture was allowed to warm to room temperature and stirred for 17 h. The volatile components were removed in vacuo, and the residue was extracted with 20 mL of hexane. The solvent of the combined extracts was evaporated, and the residue was sublimed (70 °C, 10^{-3} mbar), yielding 465 mg (0.77 mmol; 91%) of the product.

^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 7.53 (d, 2H, *o*-H), 7.28 (t, 2H, *m*-H), 6.94 (t, 1H, *p*-H), 2.41 (s, 2H, PhCH_2Ta), 2.35 (s, 12H, N(CH_3)$_2$), 1.44 (s, 9H, NC(CH_3)$_3$), 0.24 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 153.5 (Bn), 128.9 (Bn), 121.2 (Bn), 63.6 (NC(CH$_3$)$_3$), 51.2 (N(CH$_3$)$_2$), 50.8 (N(CH$_3$)$_2$), 49.7 (PhCH$_2$Ta), 3.0 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{21}$H$_{46}$N$_5$Si$_2$Ta: C, 41.64; H, 7.65; N, 11.56. Found: C, 41.03; H, 7.34; N, 10.83. EI-MS: 514 [{M − C$_7$H$_7$}$^+$, 100.0], 471 [{M − C$_7$H$_7$ − NMe$_2$}$^+$, 6.6], 91 [{C$_7$H$_7$}$^+$, 23.3], 73 [{SiMe$_3$}$^+$, 26.1], 58 [{NNMe$_2$}, 7.8]. IR (Nujol mull, cm^{-1}): 3059 w, 1596 m, 1485 w, 1351 w, 1275 s, 1246 s, 1209 m, 1053 s, 1026 s, 898 s, 838 s, 743 m, 716 w, 697 m, 480 m.

[Nb(N^{t}Bu)(TDMH)$_2$Bn] (5b). To 1.57 g (3.3 mmol) of **2b** was added at 0 °C a solution of 512 mg (3.9 mmol) of BnK in 15 mL of toluene. After 1 h, the mixture was allowed to warm to room temperature and stirred for 17 h. The volatile components were removed in vacuo, and the residue was extracted with 20 mL of hexane. The filtrate was reduced and stored at −20 °C, yielding 1.43 g (2.77 mmol; 81%) of the product as light-yellow crystals. These can be sublimed at 90 °C (10^{-3} mbar) for further purification.

^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 7.50 (d, $^3J_{\mathrm{H,H}} = 7.2$ Hz, 2H, *o*-H), 7.25 (t, 2H, $^3J_{\mathrm{H,H}} = 7.5$ Hz, *m*-H), 6.94 (t, 1H, $^3J_{\mathrm{H,H}} = 7.2$ Hz, *p*-H), 2.71 (s, 2H, PhCH_2), 2.37 (s, 6H, N(CH_3)$_2$), 2.34 (s, 6H, N(CH_3)$_2$), 1.37 (s, 9H, NC(CH_3)$_3$), 0.26 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 126 MHz, C$_6$D$_6$): δ 154.3 (*i*-Bn), 128.4 (*o*-Bn), 127.8 (*m*-Bn), 120.6 (*p*-Bn), 64.3 (NC(CH$_3$)$_3$), 51.6 (N(CH$_3$)$_2$), 51.5 (N(CH$_3$)$_2$), 44.3 (−CH$_2$−, very broad), 33.3 (NC(CH$_3$)$_3$), 3.1 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{21}$H$_{46}$N$_5$Si$_2$Nb: C, 48.72; H, 8.96; N, 13.53. Found: C, 48.57; H, 8.87; N, 13.39. EI-MS: 514 [{M − C$_7$H$_7$}$^+$, 100.0], 471 [{M − C$_7$H$_7$ − NMe$_2$}$^+$, 6.6], 91 [{C$_7$H$_7$}$^+$, 23.3], 73 [{SiMe$_3$}$^+$, 26.1], 58 [{NNMe$_2$}, 7.8]. IR (Nujol mull, cm^{-1}): 2822 m, 2776 m, 1396 m, 1352 m, 1249 s, 1213 m, 1134 m, 1055 s, 1033 s, 964 s, 896 s, 839 s, 773 m, 748 m, 681 m, 634 w, 575 w, 527 m, 481 m.

[Ta(N^{t}Bu)(TDMH)$_2$(NMe$_2$)] (6a). To a mixture of 30.32 g (50.9 mmol) of **3a** and 2.86 g (56.1 mmol) of LiNMe$_2$ was added at 0 °C 300 mL of toluene. After 1 h, the mixture was allowed to warm to room temperature and stirred for 14 h. The reaction mixture was filtered, and the residue was washed with 150 mL of hexane. The solvent of the combined filtrates was evaporated, and the residue was sublimed (90 °C, 10^{-3} mbar), yielding 24.86 g (44.5 mmol; 87%) of **7**.

Mp (uncorrected): 103 °C. ^{1}H NMR (300 K, 300 MHz, C$_6$D$_6$): δ 3.43 (s, 6H, TaN(CH_3)$_2$), 2.53 (s, 6H, N(CH_3)$_2$), 2.40 (s, 6H, N(CH_3)$_2$), 1.50 (s, 9H, NC(CH_3)$_3$), 0.34 (s, 9H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C$_6$D$_6$): δ 63.2 (NC(CH$_3$)$_3$), 51.6 (TaN(CH$_3$)$_2$), 51.3 (N(CH$_3$)$_2$), 50.5 (N(CH$_3$)$_2$), 35.0 (NC(CH$_3$)$_3$), 3.5 (Si(CH$_3$)$_3$). Anal. Calcd for C$_{16}$H$_{45}$N$_6$Si$_2$Ta: C, 34.40; H, 8.12; N, 15.04. Found: C, 34.27; H, 7.92; N, 15.14. EI-MS: 558 [{M}$^+$, 5.5], 543 [{M − CH$_3$}$^+$, 50.5], 501 [{M − C$_4$H$_9$}$^+$, 33.3], 132 [{HN(SiMe$_3$)NMe$_2$}$^+$, 15.0], 131 [{N(SiMe$_3$)NMe$_2$}$^+$, 9.0], 73 [{SiMe$_3$}$^+$, 100.0], 58 [{NNMe$_2$}, 54.1], 44 [{NMe$_2$}, 20.5]. IR (Nujol mull, cm^{-1}): 2810 s, 2758 s, 1350 m, 1275 s, 1244 s, 1211 m, 1157 m, 1053 s, 1031 s, 964 s, 895 s, 837 s, 775 s, 717 m, 682 s, 634 m, 540 s, 474 m.

[Nb(N^{t}Bu)(TDMH)$_2$(NMe$_2$)] (6b). To 1.5 g (3.2 mmol) of **2b** was added at 0 °C a solution of 164 mg (3.3 mmol) of LiNMe$_2$ in 15 mL of toluene. After 1 h, the mixture was allowed to warm to room temperature and stirred for 14 h. The reaction mixture was filtered, and the filtrate was dried in vacuo. The residue was sublimed (100 °C, 10^{-3} mbar), yielding 1.12 g (2.4 mmol; 73%) of **6b**.

Mp (uncorrected): 76 °C. ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 3.40 (s, 6H, $TaN(CH_3)_2$), 2.51 (s, 6H, $N(CH_3)_2$), 2.41 (s, 6H, $N(CH_3)_2$), 1.46 (s, 9H, $NC(CH_3)_3$), 0.34 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (300 K, 75 MHz, C_6D_6): δ 52.0 ($TaN(CH_3)_2$), 51.2 ($N(CH_3)_2$), 50.57 ($N(CH_3)_2$), 33.7 ($NC(CH_3)_3$), 3.5 ($Si(CH_3)_3$). EI-MS: 470 [$\{M\}^+$, 1.7], 412 [$\{M - NN(CH_3)_2\}^+$, 5.7], 367 [$\{M - NN(CH_3)_2 - HN(CH_3)_2\}^+$, 33.3], 132 [$\{HN(SiMe_3)NMe_2\}^+$, 3.0], 131 [$\{N(SiMe_3)NMe_2\}^+$, 3.0], 73 [$\{SiMe_3\}^+$, 48.9], 58 [$\{NNMe_2\}$, 54.1], 44 [$\{NMe_2\}$, 20.5]. Anal. Calcd for $C_{16}H_{45}N_6Si_2Nb$: C, 40.83; H, 9.64; N, 17.86. Found: C, 40.37; H, 9.55; N, 17.74. IR (Nujol mull, cm^{-1}): 2754 s, 1352 w, 1247 s, 1210 w, 1155 w, 1131 w, 1053 s, 1032 s, 958 s, 892 s, 837 s, 777 m, 716 m, 681 m, 634 w, 552 w, 476 w.

[Ta(N^{t}Bu)(TDMH)$_2$(N(H)^{t}Bu)] (7a). Method A. To a mixture of 306 mg (0.54 mmol) of **3a** and 55 mg (0.69 mmol) of LiN(H)^{t}Bu was added at 0 °C 5 mL of toluene. After 30 min, the suspension was allowed to warm to room temperature and stirred for a further 10 h. The suspension was filtered, and the residue was washed with 5 mL of hexane. The combined filtrates were dried in vacuo, and the residue was sublimed (100 °C, 10^{-3} mbar), yielding 220 mg (0.36 mmol; 67%) of **7a**.

Method B. To a mixture of 4.0 g (7.23 mmol) of [Ta(N^{t}Bu)(N(H)^{t}Bu)Cl$_2$Py$_2$] and 3.4 g (14.44 mmol) of [BrMg(TDMH)] was added at −78 °C 20 mL of THF. After 1 h, the suspension was allowed to warm to room temperature and stirred for a further 12 h. The suspension was taken to dryness, and the residue was extracted with 40 mL of hexane. The washing was filtered, and the residue was washed twice with 10 mL of hexane each. The solvent of the combined filtrates was evaporated, and the residue was sublimed (100 °C, 10^{-3} mbar), yielding 2.77 g (4.72 mmol; 65%) of **7a**.

Mp (uncorrected): 78−98 °C. ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 3.00 (s, 1H, HN^tBu), 2.60 (s, 6H, $N(CH_3)_2$), 2.35 (s, 6H, $N(CH_3)_2$), 1.54 (s, 9H, $NC(CH_3)_3$), 1.52 (s, 9H, $NC(CH_3)_3$), 0.32 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (300 K, 75 MHz, C_6D_6): δ 63.4 ($NC(CH_3)_3$), 52.8 ($NC(CH_3)_3$), 50.4 ($TaN(CH_3)_2$), 49.7 ($N(CH_3)_2$), 35.8 ($NC(CH_3)_3$), 35.1 ($NC(CH_3)_3$), 3.4 ($Si(CH_3)_3$). EI-MS: 570 [$\{M - CH_4\}^+$, 3.4], 528 [$\{M - HN_2(CH_3)_2\}^+$, 2.7], 131 [$\{N(SiMe_3)NMe_2\}^+$, 14.9], 73 [$\{SiMe_3\}^+$, 64.2], 59 [$\{HN_2(CH_3)_2\}^+$, 3.8], 58 [$\{N_2(CH_3)_2\}^+$, 12.9], 57 [$\{C_4H_9\}^+$, 4.1], 44 [$\{NMe_2\}$, 10.0]. Anal. Calcd for $C_{18}H_{49}N_6Si_2Ta$: C, 36.85; H, 8.42; N, 14.32. Found: C, 36.29; H, 8.34; N, 14.31. IR (Nujol mull, cm^{-1}): 2724 w, 1351 w, 1271 s, 1245 s, 1211 m, 1052 s, 1029 s, 979 m, 896 s, 837 s, 774 m, 724 bm, 682 m, 530 w, 475 w.

[Nb(N^{t}Bu)(N(SiMe$_3$)NMe$_2$)$_2$(N(H)^{t}Bu)] (7b). Method A. To a mixture of 1.52 g (3.29 mmol) of **2b** and 256 mg (3.21 mmol) of LiN(H)^{t}Bu was added at 0 °C 15 mL of toluene. After 30 min, the suspension was allowed to warm to room temperature and stirred for a further 10 h. The suspension was filtered, and the residue was washed with 5 mL of hexane. The combined filtrates were dried in vacuo, and the residue was sublimed (100 °C, 10^{-3} mbar), yielding 1.08 g (2.16 mmol; 67%) of **7b**.

Method B. To a mixture of 10.0 g (21.6 mmol) of [Nb(N^{t}Bu)(N(H)^{t}Bu)Cl$_2$Py$_2$] and 10.1 g (43.0 mmol) of [BrMg(TDMH)] was added at −78 °C 200 mL of THF. After 1 h, the suspension was allowed to warm to room temperature and stirred for a further 12 h. The suspension was taken to dryness, and the residue was extracted with 200 mL of hexane. The washing was filtered, and the residue was washed twice with 50 mL of hexane each. The solvent of the combined filtrates was evaporated, and the residue was sublimed (100 °C, 10^{-3} mbar), yielding 7.56 g (15.1 mmol, 70%) of **7b**.

Mp (uncorrected): 68 °C. ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 3.67 (s, 1H, HN^tBu), 2.57 (s, 6H, $N(CH_3)_2$), 2.36 (s, 6H, $N(CH_3)_2$), 1.53 (s, 9H, $NC(CH_3)_3$), 1.48 (s, 9H, $NC(CH_3)_3$), 0.34 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (300 K, 75 MHz, C_6D_6): δ 50.4 ($NC(CH_3)_3$), 50.4 ($TaN(CH_3)_2$), 49.9 ($N(CH_3)_2$), 35.6 ($NC(CH_3)_3$), 33.8 ($NC(CH_3)_3$), 3.4 ($Si(CH_3)_3$); the signals of the tertiary C atoms cannot be sufficiently located because of extreme broadening at ca. 63.5 ppm. EI-MS: 498 [$\{M\}^+$, 1.3], 483 [$\{M - CH_3\}^+$, 0.1], 440 [$\{M - N_2C_2H_6\}^+$, 13.9], 426 [$\{M - CH_3 - C_4H_9\}^+$, 18.1], 367 [$\{M - N(SiMe_3)NMe_2\}^+$, 8.1], 351 [$\{M - HN(SiMe_3)NMe_2 - CH_3\}^+$, 3.7], 236 [$\{M - 2N(SiMe_3)NMe_2\}^+$, 3.2], 235 [$\{M - N(SiMe_3)NMe_2 - HN(SiMe_3)NMe_2\}^+$, 4.9], 132 [$\{HN(SiMe_3)NMe_2\}^+$, 4.4], 131 [$\{N(SiMe_3)NMe_2\}^+$, 6.7], 73 [$\{SiMe_3\}^+$, 65.4], 58 [$\{N_2Me_2\}^+$, 60.0], 45 [$\{HNMe_2\}^+$, 1.9]. Anal. Calcd for $C_{18}H_{49}N_6Si_2Nb$: C, 43.35; H, 9.90; N, 16.85. Found: C, 42.78; H, 9.99; N, 16.41. IR (Nujol mull, cm^{-1}): 2725 w, 1352 w, 1246 s, 1210 m, 1053 s, 1029 s, 975 w, 892 s, 837 s, 773 m, 717 m, 681 w, 533 w, 477 w.

[W(N^{t}Bu)$_2$(TDMH)Cl] (8a). Method A. A mixture of 1.0 g (1.81 mmol) of [W(N^{t}Bu)$_2$Cl$_2$Py$_2$] and 355 mg (1.86 mmol) of [ClMg(TDMH)] was cooled to −78 °C, and 20 mL of toluene of the same temperature was added. The reaction mixture was stirred overnight while it was allowed to warm to room temperature. All volatile components of the blue-green suspension were removed in vacuo, and the residue was extracted with 30 mL of hexane. The filtrate was dried in vacuo, and the oily residue was sublimed (80 °C, 10^{-3} mbar) to a cooled finger.

Yield: 656 mg (1.33 mmol; 73.5%).

Method B. A total of 502 mg (0.9 mmol) of [W(N^{t}Bu)$_2$Cl$_2$Py$_2$] was suspended in 6 mL of 5:1 hexane/diethyl ether and cooled to 0 °C before 380 mg (2.8 mmol) of HN(SiMe$_3$)NMe$_2$ was added. The green suspension turned orange-green with stirring overnight. The suspension was filtered, and the residue was washed with 4 mL of hexane. The solvent of the combined filtrates was evaporated, and the brown residue was sublimed to a cooled finger (10^{-3} mbar, 75 °C).

Yield: 90 mg (0.18 mmol; 20%). ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 2.60 (6H, $N(CH_3)_2$), 1.41 (18H, $NC(CH_3)_3$), 0.13 (9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (300 K, 75 MHz, C_6D_6): δ 65.8 ($NC(CH_3)_3$), 51.3 ($N(CH_3)_2$), 33.0 ($NC(CH_3)_3$), 1.5 ($Si(CH_3)_3$). Anal. Calcd for $C_{13}H_{33}N_4ClSiW$: C, 31.68; H, 6.75; N, 11.37. Found: C, 31.32; H, 6.94; N, 11.08. EI-MS: 477 [$\{M - Me\}^+$, 14.3], 73 [$\{SiMe_3\}^+$, 39.9], 44 [$\{NMe_2\}$, 47.7]. IR (Nujol mull, cm^{-1}): 1356 m, 1290 s, 1248 s, 1215 m, 1167 w, 1140 w, 1055 s, 900 s, 841 s, 777 m, 727 m, 686 m, 480 m.

[Mo(N^{t}Bu)$_2$(TDMH)Cl] (8b). A mixture of 1.0 g (3.3 mmol) of [Mo(N^{t}Bu)$_2$Cl$_2$] and 1.75 g (6.6 mmol) of [ClMg(TDMH)] was cooled to −78 °C, and 20 mL of THF of the same temperature was added. The reaction mixture was stirred overnight while it was allowed to warm to room temperature. All volatile components of the suspension were removed in vacuo, and the residue was extracted with 20 mL of hexane. The filtrate was concentrated, and the resulting oil was distilled under reduced pressure (75 °C, 10^{-3} mbar).

Yield: 483 mg (1.33 mmol; 36%). ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 2.61 (6H, $N(CH_3)_2$), 1.38 (18H, $NC(CH_3)_3$), 0.13 (9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (300 K, 75 MHz, C_6D_6): δ 67.6 ($NC(CH_3)_3$), 51.3 ($N(CH_3)_2$), 31.7 ($NC(CH_3)_3$), 1.4 ($Si(CH_3)_3$). Anal. Calcd for $C_{13}H_{33}N_4ClSiMo$: C, 38.56; H, 8.21; N, 13.84. Found: C, 38.10; H, 8.14; N, 13.89. EI-MS: 391 [$\{M - Me\}^+$, 5.3], 333-[$\{M - SiMe_3\}^+$, 5.8], 131 [$\{Me_3SiNNMe_2\}^+$, 12.3], 73 [$\{SiMe_3\}^+$, 100.0], 58 [$\{NNMe_2\}^+$, 52.3], 44 [$\{NMe_2\}$, 47.7]. IR (neat, cm^{-1}):

Table 4. Crystal Data and Structure Refinement for Compounds **1**, **4a**, **5a**, **6a**, **7b**, and **9a**

	1	**4a**	**5a**	**6a**	**7b**	**9a**
empirical formula	$C_{10}H_{30}Cl_3N_4Si_2Ta$	$C_{16}H_{30}ClF_5N_5Si_2Ta$	$C_{21}H_{46}N_5Si_2Ta$	$C_{16}H_{45}N_6Si_2Ta$	$C_{18}H_{49}N_6NbSi_2$	$C_{13}H_{33}BrN_4SiW$
formula mass [g/mol]	549.86	660.03	605.76	558.71	498.72	537.28
cryst size [mm]	0.18 × 0.07 × 0.05	0.24 × 0.18 × 0.03	0.45 × 0.18 × 0.12	0.36 × 0.3 × 0.12	0.42 × 0.28 × 0.19	0.36 × 0.24 × 0.05
cryst shape	needle	plate	prism	prism	plate	prism
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	20.6186(11)	15.848(2)	17.5882(12)	10.2499(17)	8.9516(12)	14.8943(12)
b [Å]	10.3248(5)	7.9382(9)	10.3497(4)	16.1415(18)	30.228(3)	10.2528(5)
c [Å]	20.6359(13)	20.989(4)	15.9474(10)	16.683(3)	10.9993(15)	14.6359(12)
β [deg]	106.432(4)	93.768(15)	94.528(5)	103.302(19)	105.645(15)	100.874(7)
V [Å^3]	4213.6(4)	2634.7(7)	2893.9(3)	2686.0(7)	2866.0(6)	2194.9(3)
Z	8	4	4	4	4	4
D_{calcd} [g/cm^3]	1.734	1.668	1.390	1.382	1.156	1.626
μ [mm^{-1}]	5.708	4.423	3.896	4.192	0.517	7.136
$\theta_{min}/\theta_{max}$ [deg]	1.65/26.15	1.29/25.95	2.29/25.97	2.14 /25.00	2.04 /25.95	1.39/25.95
T_{max}/T_{min}	0.7872/0.4931	0.8208/0.5111	0.7186/0.364	0.6008/0.2238	0.941/0.8902	0.6079/0.1577
reflcns collect	29 042	18 048	39 968	18 886	20 488	26 437
reflcns unique	8338	5108	5623	4711	5538	4269
reflcns obsd	6976	4157	4755	3409	4407	3618
param refined	382	281	276	241	295	224
extinction coeff			0.00066(8)			0.00091(9)
R1 [$I > 2\sigma(I)$]	0.0286	0.0218	0.0222	0.0375	0.0239	0.0208
wR2 (all data)	0.0596	0.0515	0.0534	0.0858	0.0586	0.0472
S (GOF) on F^2	0.987	0.921	0.961	0.921	0.920	0.963
$\Delta\rho_{max}$ [e/Å^3] /$\Delta\rho_{min}$ [e/Å^3]	2.021/−1.269	0.740/−0.861	0.647/−0.749	1.441 /−0.593	0.329/−0.247	0.640/−0.475
CCDC no.	614299	614301	614302	626411	614303	614300

2968 s, 2922 s, 2897 s, 2864 s, 1452 s, 1356 m, 1248 s, 1209 s, 1109 m, 1058 s, 895 s, 839 s, 804 m, 775 m, 748 w, 723 m, 686 m, 478 m.

[W(N^{t}Bu)$_2$(TDMH)Br] (9a). A total of 3.247 g (5.29 mmol) of [W(N^{t}Bu)$_2$Cl$_2$Py$_2$] and 2.078 g (8.82 mmol) of [BrMg(TDMH)] were mixed and cooled to −78 °C before 20 mL of toluene of the same temperature was added. The reaction mixture was stirred overnight while it was allowed to warm to room temperature. All volatile components of the resulting suspension were removed, and the residue was extracted with 20 mL of hexane twice. The filtrate was concentrated, and the oily residue was sublimed (80 °C, 10^{-3} mbar) to a cooled finger.

Yield: 2.39 g (4.44 mmol, 75%). ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 2.61 (6H, N(C*H*$_3$)$_2$), 1.41 (18H, NC(C*H*$_3$)$_3$), 0.13 (9H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C_6D_6): δ 66.1 (N*C*(CH$_3$)$_3$), 52.2 (N(*C*H$_3$)$_2$), 32.8 (NC(*C*H$_3$)$_3$), 1.3 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{13}H_{33}N_4ClSiW$: C, 31.68; H, 6.75; N, 11.37. Found: C, 31.32; H, 6.94; N, 11.08. EI-MS: 477 [{M − Me}$^+$, 14.3], 73 [{SiMe$_3$}$^+$, 39.9], 44 [{NMe$_2$}, 47.7]. IR (Nujol mull, cm^{-1}): 1356 m, 1290 s, 1248 s, 1215 m, 1167 w, 1140 w, 1055 s, 900 s, 841 s, 777 m, 727 m, 686 m, 480 m.

[Mo(N^{t}Bu)$_2$(TDMH)Br] (9b). A mixture of 1.22 g (3.9 mmol) of [Mo(N^{t}Bu)$_2$Cl$_2$] and 1.22 g (5.8 mmol) of [BrMg(TDMH)] was cooled to −78 °C, and 20 mL of THF of the same temperature was added. The reaction mixture was stirred for 2 h before it was allowed to warm to 0 °C. After further stirring for 1 h, it was warmed to room temperature. After 2 h, all volatile components of the suspension were removed in vacuo and the residue was extracted with 20 mL of hexane. The residue was washed four times with 5 mL of hexane each. The combined filtrates were concentrated, and the resulting oil was distilled under reduced pressure (80 °C, 10^{-3} mbar).

Yield: 793 mg (1.76 mmol; 45%). ^{1}H NMR (300 K, 300 MHz, C_6D_6): δ 2.62 (6H, N(C*H*$_3$)$_2$), 1.38 (18H, NC(C*H*$_3$)$_3$), 0.13 (9H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (300 K, 75 MHz, C_6D_6): δ 67.9 (N*C*(CH$_3$)$_3$), 52.1 (N(*C*H$_3$)$_2$), 31.5 (NC(*C*H$_3$)$_3$), 1.3 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{13}H_{33}N_4BrSiMo$: C, 34.75; H, 7.40; N, 12.42. Found: C, 34.58; H, 7.21; N, 13.43. EI-MS: 435 [{M − Me}$^+$, 6.0], 377 [{M − SiMe$_3$}$^+$, 6.0], 131 [{Me$_3$SiNNMe$_2$}$^+$, 7.0], 73 [{SiMe$_3$}$^+$, 73.8], 44 [{NMe$_2$}, 27.6]. IR (neat, cm^{-1}): 2970 s, 2922 s, 1452 s, 1356 m, 1250 s, 1213 s, 1107 m, 1061 s, 894 s, 844 s, 804 m, 774 m, 748 w, 722 m, 686 m, 478 m.

X-ray Crystallographic Data Collection and Refinement of the Structures. Colorless single crystals were coated with inert oil, picked up with a loop, and mounted in the nitrogen cold stream of the STOE IPDS 2 diffractometer (**7b** STOE IPDS1 diffractometer). Intensity data were collected at 193 K (**1**, **4a**, and **7b**) or 173 K (**6a** and **9a**) using graphite-monochromated Mo Kα radiation (λ = 0.17073 Å). Data collection was performed by hemisphere runs taking frames at 1.0° in ω. Final cell constants were obtained from a least-squares fit of a subset of several thousand strong reflections. Absorption corrections were performed using indexed faces (**1**−**6** and dgrs 16)[48] or semiempirical from equivalents (**8a**).[48] The structures have been solved by direct methods in *SIR92*[49] (**1**, **4a**, and **7b**) or *SIR2004*[50] (**5a**, **6a**, and **9a**) and refined using the full-matrix least-squares refinement procedure of *SHELXL97*;[51] all non-H atoms have been refined anisotropically, and H atoms have been placed at calculated positions and refined with $U_{iso}(H) = 1.2U_{eq}(C)$ (methyl groups: $U_{iso}(H) = 1.5U_{eq}(C)$). The N-bonded H atom in **7b** has been located and isotropically refined with a

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restraint for the N−H distance. The crystal of **1** happened to be a twin. The refinement has been performed using the twin matrix (0 0 1 0 1 0 1 0); the refined twin ratio was 0.48:0.52. The N−N distances and anisotropic displacement factors for the N atoms have been restrained to be approximately equal. In **9a**, the *tert*-butyl group bonded to N4 was disorderd; in **7b**, the $SiMe_3$ group bonded to N1 was disordered. Crystallographic data of the compounds are listed in Table 4. CCDC 614299−614303 and 626411 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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