

Mixed Amido/Imido/Guanidinato Complexes of Tantalum: Effects of Ligand Substitution on Thermal Properties

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Mixed amido/imido/guanidinato tantalum complexes $[\text{Ta}(\text{NR}^1\text{R}^2)\{\text{C}(\text{NR}^3\text{R}^2)(\text{NR}^3)_2(\text{NR}^4)\}]$ [R^1, R^2 = methyl, ethyl; R^3 = cyclohexyl (cy), isopropyl; R^4 = *tert*-butyl, *n*-propyl] have been synthesized by the insertion of carbodiimides into tantalum–amide bonds. All compounds have been characterized by means of NMR spectroscopy, mass spectrometry, and CHN analysis. Additionally, single crystal structures of five compounds (**4**: R^1 = Me, R^2 = Et, R^3 = *i*Pr, R^4 = *t*Bu; **5**: R^1 , R^2 = Et, R^3 = *i*Pr, R^4 = *t*Bu; **6**: R^1 , R^2 = Me, R^3 = cy, R^4 = *t*Bu; **8**: R^1 , R^2 = Et, R^3 = cy, R^4 = *t*Bu; **9**: R^1 , R^2 = Et, R^3 = *i*Pr, R^4 = *n*Pr) have been determined and relevant structural issues are

discussed. The thermal properties of all complexes have been investigated by TGA/DTA measurements. Thus, complexes originating from diisopropylcarbodiimide (*i*Pr-cdi) are significantly more volatile than complexes derived from dicyclohexylcarbodiimide (cy-cdi). In contrast, variations of R^1 , R^2 , and R^4 have only a small impact on the thermal behavior of the complexes. Finally, selected compounds have been pyrolyzed at 600 °C, and the decomposition products studied by GC-MS and ^1H NMR spectroscopy.

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Introduction

Thin films of tantalum nitride (TaN) play an important role in the ongoing process of device optimization in microelectronics. Conducting TaN films serve as gate electrode materials in metal oxide semiconductor field-effect transistors as well as diffusion barriers for the inhibition of copper or silver diffusion into the silicon substrates.^[1] A rough literature survey shows that 492 patents on the production, processing, and use of TaN films were filed in 2005 alone. TaN thin films can be deposited by various methods, including sputtering processes and gas-phase deposition techniques such as MOCVD (metal organic chemical vapor deposition), plasma-enhanced CVD (PECVD), or atomic layer deposition (ALD). These gas-phase-based techniques make use of binary metal halides, although more recently metal-organic tantalum coordination complexes have also been used. Key parameters for precursors in MOCVD or ALD processes include volatility, thermal decomposition behavior, chemical reactivity, accessibility, and safety issues. Several tantalum–ligand systems have been tested for the deposition of TaN films, amongst which mixed amido/

imido tantalum complexes are the most prominent.^[2] While most compounds in this class are liquid and have a sufficiently high vapor pressure, they tend to be chemically and thermally rather fragile and show problems in terms of long-term stability at vaporization temperatures as well as a high sensitivity towards moisture or reactive gases. Thus, the use of didentate ligands such as hydrazines has been suggested.^[3] In this paper we wish to report on an extension of this approach by introducing guanidinates as suitable chelating ligands for mixed amido/imido tantalum complexes. The use of guanidinates has already shown promising results for the deposition of Ti(C)N or HfO₂ thin films in CVD processes.^[4,5] Moreover, we recently published a communication on the synthesis and characterization of mixed amido/imido/guanidinato complexes **3–5** and showed the successful deposition of conductive, almost carbon-free TaN (C content < 1%) thin films using compound **4** as a single source precursor.^[6] This is a rather surprising result considering the fact that less complex amido/imido compounds of tantalum with a considerably lower relative carbon content produce films with much higher carbon contents of around 10%.^[7] These results encouraged us to carry out a more detailed examination of the tantalum guanidinato/amido/imido complex system and the impact of substituent variations at different ligand sites on the chemical and thermal properties of the resulting complexes. Table 1 gives a summary of all complexes synthesized and characterized in this paper.

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Table 1. Overview of compounds **3–10** in this publication.

Compound	R ¹	R ²	R ³	R ⁴	M.p. [°C]
3 ^[a]	Me	Me	<i>i</i> Pr	<i>t</i> Bu	232
4 ^[b]	Me	Et	<i>i</i> Pr	<i>t</i> Bu	217
5 ^[b]	Et	Et	<i>i</i> Pr	<i>t</i> Bu	210
6	Me	Me	cy	<i>t</i> Bu	210
7	Me	Et	cy	<i>t</i> Bu	218
8	Et	Et	cy	<i>t</i> Bu	204
9	Et	Et	<i>i</i> Pr	<i>n</i> Pr	195
10	Et	Et	cy	<i>n</i> Pr	205

[a] Included for reasons of comparison. [b] Crystal structure has not been published so far.

Results and Discussion

Two basic pathways are known in the literature for the synthesis of metal guanidinate complexes: (i) salt metathesis reactions in which sodium or lithium guanidates are treated with the metal halides^[4,8] and (ii) the insertion of carbodiimides into metal–amido bonds, which is a more convenient pathway that does not involve the formation of LiX or NaX byproducts.^[6,9] In the case of tantalum guanidates, previous work from Tin et al. includes the synthesis of [Ta(NMe₂)₄{C(NMe₂)(NR')₂}] (R' = cy, *i*Pr) as well as the preparation of tantalum complexes of the neutral, protonated guanidine ligand.^[10] The large variety of compounds published before 2001 have been summarized in a recent review.^[11]

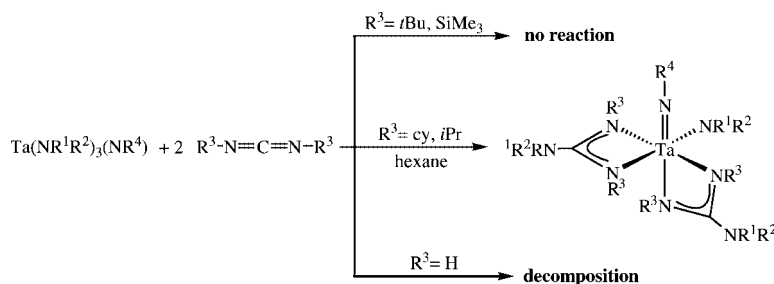
The synthesis of the starting compounds [Ta(NR¹R²)₃(NR⁴)] followed published procedures.^[12] At first the intermediate compound [TaCl₃(N-*n*Pr)(py)₂] (**1**) was formed by reaction of TaCl₅ with *n*-propylamine, chlorotrimethylsilane, and pyridine. It should be noted that on scaling up the literature procedure it is possible to keep the amount of solvent almost constant by increasing the amount of pyridine, which significantly increases the solubility of **1** in toluene and thus allows the separation of the product from the precipitated ammonium salts (see Experimental Section). In a second step, this pyridine-stabilized salt was treated with LiNEt₂ in order to form [Ta(NEt₂)₃(N-*n*Pr)] (**2**). Higher yields of **2** can be obtained when stoichiometric amounts of lithium amide are added to **1** at –60 °C instead of an excess at room temperature. The mixed amido/imido tantalum complexes were then treated with the respective carbodiimides in hexane to give the guanidinato/amido/imido complexes **3–10** (Scheme 1).

The synthesis of **3–5** has already been described in a previous communication.^[6a] It is noteworthy that no insertion products could be isolated when sterically encumbering carbodiimides such as (*t*Bu)₂C₂N or (SiMe₃)₂C₂N were used, even after refluxing the reaction mixtures for 24 h in the presence of a large excess of the carbodiimides. On the other hand, reaction with the unsubstituted carbodiimide (which exists as its tautomer H₂NC≡N) did not lead to isolable products but instead gave an orange solid which is insoluble in organic solvents. It is likely that transamination reactions lead to the formation of insoluble, oligomeric tantalum amides.

Compounds **3–10** can be prepared in high yields (>80%) and are white solids with rather high melting points of 195–230 °C. All compounds are highly soluble in hexane, benzene, or toluene and their elemental analyses are in good agreement with their suggested molecular formulae. The mass spectra of **3–10** show differences between the bis(cyclohexyl)carbodiimide (cy-cdi) containing compounds and their (*i*Pr-cdi) based congeners. Thus, the intensities of the [M⁺] peaks of **6**, **7**, **8**, and **10** (cy-cdi) are below 1% of the base peak (if visible at all), while they are above 10% for **3**, **4**, **5**, and **9** (*i*Pr-cdi). As will be shown below, this is consistent with the thermal properties of these compounds, since cy-cdi based compounds generally show significant decomposition during evaporation. The most intense peaks for **6**, **7**, **8**, and **10** are observed at *m/z* 41, 43 and 55 and are due to the cyclohexyl fragments C₃H₅⁺, C₃H₇⁺, and C₄H₇⁺.

NMR Analysis

All NMR assignments are based on two-dimensional NMR spectra of the previously published compounds **3–5**.^[6a] The ¹H NMR spectra of **3–10** show rather large differences in the exact chemical shifts of the diastereotopic alkyl substituents of the Ta-amido groups, which also show a hindered rotation due to the partial π character of the Ta–N bond. In the case of the dimethyl-substituted amido group (**6**), the two singlets are separated by 0.5 ppm and in the case of the diethyl-substituted amido group (**8**, **9**, and **10**), the four doublets of quartets (ABX₃ spin system) are found in a range of 1.5 ppm. Of these four multiplets, three are close to each other while the other is strongly high-field shifted, probably because of the anisotropic magnetic field of the guanidinate π systems. The ¹H and ¹³C NMR spectra

Scheme 1. Synthesis of compounds **3–10**.

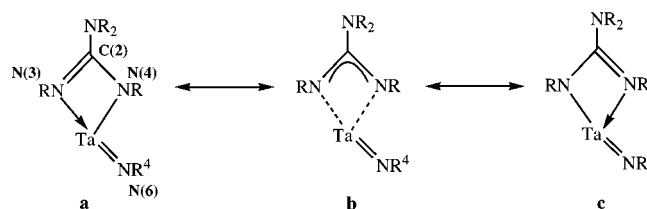
of **7** (MeEtN substitution) could not be fully assigned due to the formation of rotational isomers, which leads to a mixture of several interconvertible isomers and thus highly complex solution spectra. The ^1H NMR spectra of the cycdi based complexes **6**, **7**, **8**, and **10** show broad signals for the cyclohexyl groups, with only the C_α proton being slightly low-field shifted. The assignment of all ^{13}C NMR spectra, with the exception of **7**, was straightforward and is therefore not discussed here in detail.

X-ray Analysis

Single crystals of **4**, **5**, **6**, **8**, and **9** were obtained by recrystallization of the compounds from toluene at -30°C . Several attempts to obtain crystals of **7** or **10** suitable for single-crystal X-ray analysis failed. Compounds **4** and **5** crystallize in an orthorhombic crystal system while the crystal systems of **6**, **8**, and **9** are of lower symmetry, i.e. monoclinic for **6** and **8** and triclinic for **9**. The molecular structures of **6** and **9** are displayed in Figure 1 as representatives of all solid-state structures.^[13] Table 2 contains bond lengths, angles, and dihedral angles for all the above complexes.

The molecular structures of all compounds are very similar to each other and to that of compound **3**, which has already been discussed in an earlier publication.^[6a] Thus, only the solid-state structure of **6** will be discussed here in more detail. The tantalum(V) center in **6** is sixfold coordinated by two didentate guanidinato ligands, one amido, and one imido group, resulting in a highly distorted octahedron. The Ta–N(6)–C(18) unit of the imido ligand is almost linear [$170.6(4)^\circ$] and the Ta–N(6) bond is relatively short ($1.79\text{ \AA}$), which indicates an almost sp-hybridized imido ligand. Due to the strong π -donating effect of this imido ligand,^[14] the Ta(1)–N(3) bond of the guanidinato ligand opposite to the imido group is lengthened [$2.437(5)\text{ \AA}$], while the second Ta–N bond in the same guanidinato ligand [Ta(1)–N(4) = $2.123(5)\text{ \AA}$] is considerably shorter. Obviously, the π -donating effect of the imido group results in an

unsymmetrical charge distribution within the delocalized π system of the guanidinato ligand, which is also well reflected in a rather large difference in the N–C bond lengths [N(3)–C(2) = $1.308(9)$, N(4)–C(2) = $1.363(9)\text{ \AA}$]. Scheme 2 illustrates the mesomeric structures for the metal–guanidinato interactions, with structure **a** describing best the observed bond lengths in the solid-state structure.



Scheme 2. Mesomeric structures for metal–guanidinato interactions.

The second guanidinato ligand [N(1)–C(1)–N(2)] is more symmetric – the two Ta–N bond lengths are $2.168(6)\text{ \AA}$ [Ta–N(1)] and $2.279(5)\text{ \AA}$ [Ta(1)–N(2)]. Again, the longer Ta–N bond is found *trans* to the more basic ligand, i.e. the amido group. The noncoordinated NR_2 groups of the guanidinato ligands are almost planar, with angular sums around the nitrogen atoms of 355.1° and 359° , respectively. A rather weak π -donating effect of the NR_2 groups to the guanidinato π -systems is suggested by a relatively large tilt angle of the C–N–C planes of 45.3° and 40.6° , respectively, which is obviously an effect of the steric repulsions of the alkyl substituents. However, an even weaker interaction is found in $[\text{Ta}(\text{NMe}_2)_4\{\text{C}(\text{NMe}_2)(\text{N-cy})_2\}]$,^[10a] which shows a tilt angle of the two CNC planes of more than 80° . Indeed, the C–N bond length of the exocyclic nitrogen ligand to the guanidinato core is elongated by $0.03\text{ \AA}$ compared to **6**.

Analysis of Thermal Properties

The thermal properties of compounds **6–10** were analyzed by classic melting point determinations, standard TG/DTA measurements, isothermal analyses, and sublimation

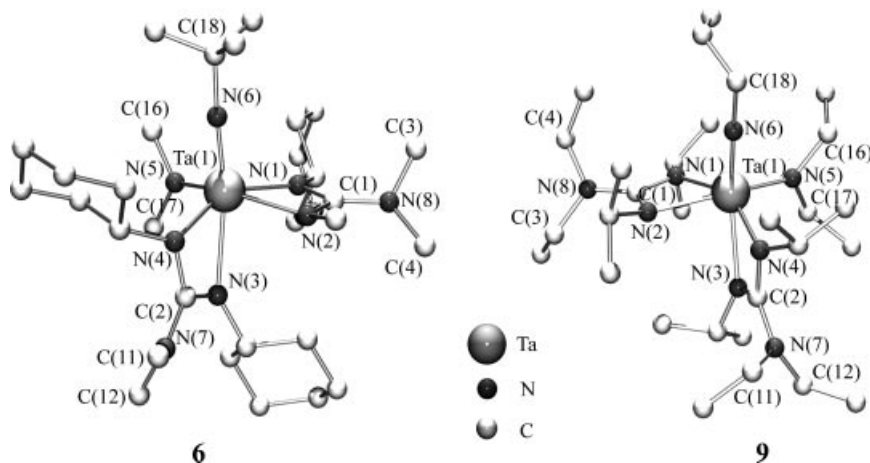


Figure 1. Povray/Ortep drawings of the molecular structures of **6** and **9** in the solid state. All hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths [Å] and bond and torsion angles [°] for **3**,^[a] **4**, **5**, **6**, **8**, and **9**.

	3	4	5-Et	6	8-Et	9-Et
Ta(1)–N(1)	2.174(4)	2.185(7)	2.198(8)	2.168(6)	2.198(4)	2.192(4)
Ta(1)–N(2) (opp. amido)	2.254(4)	2.251(7)	2.275(8)	2.279(5)	2.269(4)	2.250(4)
Ta(1)–N(3) (opp. imido)	2.396(5)	2.409(7)	2.408(8)	2.437(5)	2.408(4)	2.433(4)
Ta(1)–N(4)	2.129(4)	2.127(7)	2.126(8)	2.123(5)	2.136(4)	2.122(4)
Ta(1)–N(5) (Ta-amido)	2.014(5)	2.002(8)	2.023(8)	2.005(5)	2.008(4)	2.013(4)
Ta(1)–N(6) (Ta-imido)	1.785(5)	1.791(8)	1.790(10)	1.786(6)	1.797(4)	1.780(4)
N(1)–C(1)	1.345(7)	1.352(11)	1.327(13)	1.389(8)	1.342(6)	1.329(6)
N(2)–C(1)	1.309(7)	1.318(11)	1.327(14)	1.318(9)	1.319(6)	1.325(6)
N(3)–C(2)	1.320(7)	1.319(11)	1.323(13)	1.308(9)	1.320(6)	1.308(6)
N(4)–C(2)	1.361(7)	1.356(11)	1.359(13)	1.363(9)	1.363(6)	1.359(6)
N(5)–C(16)	1.456(7)	1.453(12)	1.464(13)	1.451(8)	1.457(7)	1.471(6)
N(5)–C(17)	1.463(7)	1.468(13)	1.465(12)	1.453(8)	1.464(6)	1.454(7)
N(6)–C(18)	1.444(7)	1.453(12)	1.449(14)	1.457(9)	1.440(7)	1.439(7)
N(7)–C(2)	1.390(7)	1.382(11)	1.400(13)	1.388(9)	1.400(6)	1.388(6)
N(7)–C(11)	1.442(7)	1.454(12)	1.464(14)	1.465(9)	1.456(7)	1.467(6)
N(7)–C(12)	1.440(8)	1.447(12)	1.467(16)	1.443(9)	1.446(7)	1.457(6)
N(8)–C(1)	1.393(7)	1.391(11)	1.393(13)	1.397(8)	1.393(7)	1.393(6)
N(8)–C(3)	1.444(8)	1.437(13)	1.444(14)	1.455(8)	1.456(8)	1.451(7)
N(8)–C(4)	1.450(7)	1.447(12)	1.461(14)	1.459(9)	1.483(10)	1.463(7)
N(1)–Ta(1)–N(2)	59.56(18)	59.4(3)	58.8(3)	60.3(2)	59.14(15)	59.38(14)
N(2)–Ta(1)–N(5)	155.36(19)	154.8(3)	158.7(3)	153.7(2)	156.64(17)	155.50(16)
N(3)–Ta(1)–N(4)	58.92(16)	58.1(3)	58.5(3)	58.0(2)	58.62(14)	58.05(14)
N(3)–Ta(1)–N(6)	162.19(19)	161.1(3)	160.6(4)	161.4(2)	161.69(16)	156.78(16)
N(1)–C(1)–N(2)	112.0(5)	111.0(7)	111.6(9)	111.3(6)	111.9(4)	112.1(4)
N(3)–C(2)–N(4)	113.2(5)	112.0(8)	112.5(8)	113.0(6)	112.9(4)	113.2(4)
C(1)–N(8)–C(3)	122.7(5)	120.6(8)	120.6(9)	121.0(6)	120.3(5)	120.0(4)
C(1)–N(8)–C(4)	121.9(5)	121.4(8)	120.1(8)	119.0(5)	118.4(5)	121.8(4)
C(3)–N(8)–C(4)	115.3(5)	117.2(8)	118.5(9)	115.1(5)	120.9(5)	116.9(4)
C(2)–N(7)–C(11)	120.7(5)	122.9(8)	121.4(8)	123.0(6)	121.1(4)	120.6(4)
C(2)–N(7)–C(12)	122.8(5)	120.7(8)	121.4(8)	120.9(6)	121.1(4)	119.1(4)
C(11)–N(7)–C(12)	116.5(5)	116.1(8)	117.2(8)	115.1(6)	116.0(4)	118.2(4)
Ta(1)–N(6)–C(18)	170.6(4)	175.7(7)	174.9(8)	175.7(5)	172.3(4)	176.2(4)
Ta(1)–N(5)–C(16)–C(17)	178.5(7)	179.4(12)	178.4(14)	175.7(10)	180.0(7)	178.0(5)
C(2)–N(7)–C(11)–C(12)	179.8(9)	174.6(11)	179.0(14)	169.0(10)	166.2(6)	163.6(4)
C(1)–N(8)–C(3)–C(4)	176.3(9)	169.9 (12)	169.9(14)	155.5(10)	172.4(5)	166.8(5)
C(3)–N(8)–C(4) plane vs. N(1)–C(1)–N(2)–plane	45.5(13)	50.4(18)	53.7(14)	45.3(10)	58.6(6)	48.7(8)
C(11)–N(7)–C(12) plane vs. N(3)–C(2)–N(4)–plane	44.2(13)	45.0(18)	42.2(14)	40.6(10)	46.2(7)	45.9(6)

[a] The data of **3** have already been published and are only given here for comparison.

experiments under vacuum conditions. The melting points of all compounds are relatively high (195–232 °C, see Table 1) and cannot be rationalized by the type of ligand substitution (R^1 – R^4). It can be concluded from the DTA spectra that the melting process is accompanied by the initiation of decomposition reactions. The compounds do not melt fully at the documented temperatures but undergo some sort of waxy transition phase over a temperature range of approximately 5 °C (vide infra).

The nature of the carbodiimide substituents (cy vs. *i*Pr) has a big influence on the volatility of the compounds. Thus, **3**, **4**, **5**, and **9** (*i*Pr-cdi) can be sublimed without any residues at 120 °C in vacuo (10^{-4} mbar) whereas **6**, **7**, **8**, and **10** (cy-cdi) do not sublime at all under these conditions. Isothermal studies at 120 °C underline these results. After 240 min at ambient pressure the weight loss of **3**, **4**, **5**, and **9** is approximately 10% in all cases, while compounds **6** and **7**, for example, show a weight loss of only 2.5% (Figure 2). The mass transport of these complexes is highest for **9** ($4.9 \mu\text{g min}^{-1}$) and significantly lower for **6** and **7** (0.93 and $0.59 \mu\text{g min}^{-1}$, respectively). The simplest explanation for this observation is the higher molecular masses of the cy-

cdi based compounds. However, by changing R^1 and R^2 from methyl to ethyl (e.g. **3** to **5**) no significant effect on the volatility is observed. Obviously, the variation of R^3 has a significant effect on the interactions between the molecules in the solid state, for example by a different packing of the moieties.

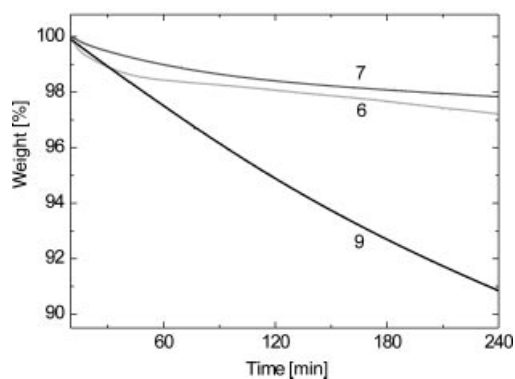


Figure 2. Isothermal analysis of **6**, **7**, and **9**. The spectra were recorded at a temperature of 120 °C, 300 sccm nitrogen flow for 4 h. Heating from 25 °C to 120 °C at a rate of 10 °C min^{-1} .

The residual masses after TG/DTA measurements from cy-cdi based complexes are higher than the theoretical masses (residual masses for **6–8**, **10**: 29–35%, theoretical content of TaN: 22–24%). This indicates the incorporation of significant amounts of carbon during the decomposition. In contrast, the *i*Pr-cdi based complexes **4**, **5**, and **9** show considerably lower residual masses and thus cleaner decomposition processes (residual masses: 10–12%, theoretical content of TaN: 27–28%).

With the exception of **7**, all compounds show one or two endothermic peaks at temperatures below their melting/decomposition points (Figure 3). Due to the fact that no weight loss can be observed in any case, a phase change of the solids is possibly responsible for this behavior. This phase change is not reversible, which means that running a program in which the sample is heated, cooled down, and heated again shows endothermic peaks only in the first period of heating. The position of the peaks is strongly dependent on the nature of the alkyl substituents R^1 , R^2 , and R^3 . Going from methyl to ethyl for the amido substituents R^1 and R^2 results in a shift of these peaks to higher temperatures (**3**→**4**→**5**: 52 °C→70 °C→110 °C; **6**→**8**: 112 °C→139 °C). The same is true for the variation of R^3 from *i*Pr to cy (**3**→**6**: 52 °C→112 °C; **5**→**8**: 110 °C→139 °C; **9**→**10**: 82 °C→140 °C). It can be concluded, that the onset of the temperature for phase changes depends on the mobility of the molecules in the solid state, which supposedly increases with higher chain lengths and/or size of the substituents.

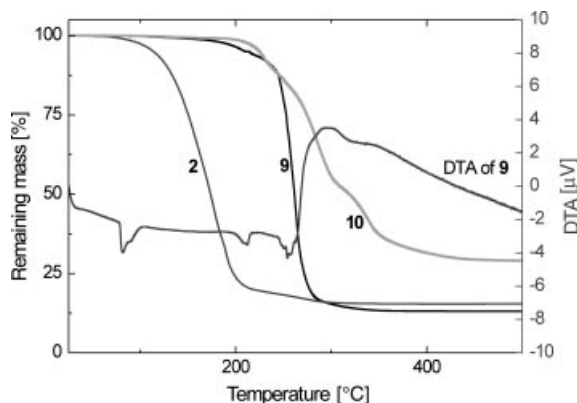


Figure 3. TG/DTA spectrum of **9** and TG curves of **2** and **10**. Heating rate: 5 °C min⁻¹.

Decomposition Experiments of 3–5

The nature of the thermal decomposition of potential MOCVD precursors into the desired materials is crucial. Thus, compounds **3–5** were evaporated at 120 °C in vacuo, with a constant flow of argon providing a continuous transport of the precursor through a decomposition tube at 600 °C (Figure 4). The decomposition products were subsequently trapped at –196 °C (liquid nitrogen) in a slightly modified cooling trap. After full evaporation of the precursor

(300 mg), deuterated benzene was injected into the cooling trap, and the resulting C₆D₆ solutions analyzed by ¹H NMR spectroscopy and GC-MS measurements. The ¹H NMR spectra revealed the formation of the corresponding free amines for **3–5** (HNMe₂, HNMeEt and HNEt₂), small amounts of *t*BuNH₂ (resulting from the former imido ligand), as well as free carbodiimide. At these very high temperatures (600 °C) carbodiimide could be released from the guanidinato ligand by deinsertion analogous to the behavior of amidinate complexes.^[15] It should be noted that although these compounds represent the major part of decomposition products, smaller peaks were also present which could not be unequivocally assigned. GC-MS measurements confirm these ¹H NMR results and additionally show the presence of small amounts of isopropylamine as well as several unidentified species containing the carbodiimide group. Although the relatively large variety of decomposition products suggests rather complex decomposition mechanisms, preliminary MOCVD experiments of compound **4** as a single-source precursor showed the possibility of carbon-free (atomic concentration < 1 %)^[6] TaN deposition, which requires clean thermal decomposition processes.



Figure 4. Setup for the decomposition experiments of **3–5**.

Conclusions

We have presented the synthesis and characterization of several new guanidinato/amido/imido complexes of the type [Ta(NR¹R²){C(NR³R²)(NR³)₂]₂(NR⁴)] {R¹, R² = methyl, ethyl; R³ = cyclohexyl (cy), isopropyl; R⁴ = *tert*-butyl, *n*-propyl}. All complexes are structurally very similar, the bond lengths and angles of the solid-state structures showing only minor variations. TG/DTA measurements and isothermal studies reveal the low volatility of the cy-cdi based complexes. This is rather unexpected considering the fact that the structural and chemical behaviors of compounds **3–10** are very similar. Thus, cy-cdi based complexes are, in general, not suitable for MOCVD purposes due to a supposedly weak precursor transport. However, application of the compounds derived from cy-cdi in liquid injection MOCVD is feasible. The choice of substituents of the amido or imido groups does not seem to have a significant impact on the thermal behavior of the resulting complexes. Finally, thermal decomposition experiments of **3–5** clearly show that highly complex pyrolysis reactions are taking place, although they lead to a clean decomposition of the selected precursors in all cases.

Experimental Section

All manipulations of air- and moisture-sensitive compounds were performed on a conventional vacuum/argon line using standard

Schlenk techniques. Preparations of samples for further analysis were carried out in argon-filled glove boxes. All solvents were purified by an MBraun solvent purification system (SPS) and stored over activated molecular sieves (4 Å). C_6D_6 was degassed and dried with activated molecular sieves. Elemental analysis was performed by the analytical service of our Chemistry Department (CHNSO Vario EL 1998). 1H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX-250 spectrometer. EI mass spectra were recorded with a Varian MAT spectrometer. Simultaneous TG/DTA analysis was carried out using a Seiko TG/DTA 6300S11 at ambient pressure (sample weight ≈ 10 mg). GC-MS measurements were carried out on a Shimadzu QP2010 instrument at a column temperature of 290 °C. The tantalum-containing starting compounds, namely $[Ta(NMe_2)_3(N-tBu)]$, $[Ta(NMeEt)_3(N-tBu)]$, $[Ta(NEt_2)_3(N-tBu)]$, and $[Ta(NEt_2)_3(N-nPr)]$ were synthesized in batches of 15–40 g following modified literature procedures.^[12] Reagents were purchased from the following companies and used without further purification: butyllithium (1.6 M solution in hexane, Merck), diethylamine (>99% purity, Merck), methylethylamine (>97% purity, Fluka), pyridine (Normapur grade, VWR), chlorotrimethylsilane (98%, Acros), lithium dimethylamide (95%, Aldrich), diisopropylcarbodiimide (99%, careful: very toxic, Acros), and dicyclohexylcarbodiimide (99%, Aldrich). The synthesis and characterization of **3–5** was described in a previous publication.^[6a] For a brief summary of the crystallographic data see Table 3. CCDC-611058 to -611062 (**4–6**, **8**, and **9**, respectively) 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.

[TaCl₃(N-*n*Pr)(py)₂] (1): *N*-Propylamine (20.2 mL, 14.52 g, 246 mmol) and chlorotrimethylsilane (15 mL, 118 mmol) were added to a cooled suspension of TaCl₅ (20 g, 55.8 mmol) in toluene (150 mL). The color of the suspension changed to slight yellow-greenish. After stirring the reaction mixture at room temperature for 25 min, pyridine was added (25 mL, 24.5 g, 310 mmol). After 24 h, the clear, yellow-green solution was filtered, and the solvents removed in vacuo. The crude product was recrystallized from hot toluene (100 °C, ca. 120 mL). Yield: 22.2 g (44.2 mmol, 79% based on TaCl₅). C₁₃H₁₇Cl₃N₃Ta (502.63): calcd. C 31.13, H 3.39, N 8.38; found C 31.14, H 3.67, N 8.67. All other analyses (NMR, MS) were in accordance with the previously published results.

[Ta(NEt₂)₃(N-*n*Pr)] (2): A suspension of lithium diethylamide (62 mmol) was prepared in situ by adding 40 mL of a 1.6 M BuLi solution (hexane) to diethylamine (7.5 mL, 62 mmol) at –60 °C. After stirring the reaction mixture for 24 h at room temperature, the resulting suspension was added to a suspension of **1** (10 g, 20.8 mmol) in hexane at –60 °C. The reaction mixture slowly turned yellow/orange and was filtered after stirring for an additional 24 h. The yellow/orange filtrate was concentrated in order to obtain the dark orange product **2**. Yield: 8.38 g (18.4 mmol, 92% based on **1**). C₁₅H₃₇N₄Ta (454.43): calcd. C 39.65, H 8.20, N 12.33; found C 39.87, H 7.80, N 12.49. All other analyses (NMR, MS) were in accordance with the previously published results.

[Ta(NMe₂)₂{(N-cy)₂C(NMe₂)₂(N-*n*Bu)}] (6): A solution of dicyclohexylcarbodiimide (1.52 g, 7.83 mmol) in hexane (20 mL) was added to a solution of $[Ta(NMe_2)_3(N-tBu)]$ (1.55 g, 4.03 mmol) in hexane (40 mL). The temperature of the solution increased to about 45 °C

Table 3. Crystallographic data and structure refinement details for **4**, **5**, **6**, **8**, and **9**.

	4 (CVD82)	5 (CVD72)	6 (CVD101)	8 (CVD76)	9 (CVD99)
Empirical formula	C ₂₇ H ₆₁ N ₈ Ta	C ₃₀ H ₆₇ N ₈ Ta	C ₃₆ H ₇₁ N ₈ Ta	C ₄₂ H ₈₃ N ₈ Ta	C ₂₉ H ₆₅ N ₈ Ta
Formula mass	678.79	720.87	796.96	881.11	706.84
<i>T</i> [K]	108(2)	105(2)	113(2)	108(2)	111(2)
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	10.7124(7)	11.4691(11)	10.1139(9)	14.4945(9)	11.0993(12)
<i>b</i> [Å]	18.2835(10)	18.1889(18)	16.8089(14)	17.4746(8)	19–395(4)
<i>c</i> [Å]	34.0026(18)	34.854(3)	23.796(2)	21.6152(14)	15.960(2)
α [°]	90	90	80.815(7)	90	90
β [°]	90	90	88.860(7)	98.182(5)	91.702(9)
γ [°]	90	90	78.771(7)	90	90
<i>V</i> [Å ³]	6659.8(7)	7270.8(12)	3916.8(6)	5045.2(5)	3434.2(9)
<i>Z</i>	8	8	4	4	4
Density (calcd.) [g cm ^{–3}]	1.354	1.317	1.351	1.160	1.367
μ (Mo- <i>K</i> α) [mm ^{–1}]	3.328	3.053	2.841	2.211	3.230
<i>T</i> _{max} / <i>T</i> _{min}	0.967/0.787	0.643/0.589	0.833/0.465	0.733/0.556	0.529/0.298
<i>R</i> (000)	2816	3008	1664	1856	1472
Crystal size [mm]	0.21 × 0.06 × 0.01	0.16 × 0.10 × 0.07	0.18 × 0.08 × 0.03	0.16 × 0.11 × 0.07	0.25 × 0.17 × 0.11
θ range [°]	2.99–25.00	2.92–25.00	2.60–25.00	3.01–27.56	2.76–25.00
Completeness to θ [%]	99.8	98.2	99.7	99.9	99.8
Index ranges	–12 ≤ <i>h</i> ≤ 12 –21 ≤ <i>k</i> ≤ 19 –40 ≤ <i>l</i> ≤ 40	–13 ≤ <i>h</i> ≤ 13 –21 ≤ <i>k</i> ≤ 21 –39 ≤ <i>l</i> ≤ 40	–12 ≤ <i>h</i> ≤ 12 –19 ≤ <i>k</i> ≤ 19 –28 ≤ <i>l</i> ≤ 27	–17 ≤ <i>h</i> ≤ 15 –22 ≤ <i>k</i> ≤ 19 –28 ≤ <i>l</i> ≤ 28	–13 ≤ <i>h</i> ≤ 13 –23 ≤ <i>k</i> ≤ 23 –18 ≤ <i>l</i> ≤ 18
Reflections collected	48057	48479	53636	50240	42514
Independent reflections	5852	6292	13711	11646	6019
Data/restraints/parameters	5852/0/325	6292/0/369	13711/6/811	11646/0/460	6019/0/358
Goodness-of-fit on <i>F</i> ²	1.393	1.058	1.229	1.113	1.097
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁	0.0869	0.0707	0.0662	0.0562	0.0406
<i>wR</i> ₂	0.1086	0.1447	0.0960	0.1119	0.0977
<i>R</i> indices (all data) <i>R</i> ₁	0.1041	0.1197	0.0861	0.0797	0.0440
<i>wR</i> ₂	0.1138	0.1663	0.1016	0.1221	0.1000
Largest diff. peak/hole [e Å ^{–3}]	2.699/–1.589	4.998/–1.103	1.771/–0.725	3.882/–1.493	2.954/–1.558

during addition; no color change was observed. After stirring the mixture for 24 h, the solvent was removed in vacuo. Small, white crystallites suitable for X-ray analysis were obtained by recrystallizing the crude product from toluene. M.p. 210 °C (uncorrected). Yield: 2.73 g (3.43 mmol, 85% based on $[\text{Ta}(\text{NMe}_2)_3(\text{N-}i\text{Bu})]$). $\text{C}_{36}\text{H}_{71}\text{N}_8\text{Ta}$ (796.96): calcd. C 45.27, H 8.71, N 17.60; found C 45.22, H 9.00, N 17.83. ^1H NMR (25 °C, 250 MHz, C_6D_6): δ = 1.30–2.10 (m, cyclohexyl), 1.58 [s, 9 H, $\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 2.58, 2.62 [2 × s, 2 × 6 H, $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_3)_2]\}$], 3.2–3.7 (m, 4 H, cyclohexyl, N–C–H), 3.59 [s, 3 H, $\text{Ta-N}(\text{CH}_3)_2$], 4.20 [s, 3 H, $\text{Ta-N}(\text{CH}_3)_2$] ppm. ^{13}C NMR (25 °C, 62.5 MHz, C_6D_6): δ = 26.2, 26.5, 26.6 (2×), 26.7 (3×), 27.1 (2×), 27.2, 27.4 (2×) (cyclohexyl, 3,4-position), 35.2 [$\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 34.3, 34.5, 35.2, 36.3, 36.6, 37.0, 37.1, 37.5 (cyclohexyl, 2-position), 40.3 [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_3)_2]\}$], 49.1, 59.3 [$\text{Ta}\{\text{N}(\text{CH}_3)_2\}$], 55.1, 56.0, 57.3, 57.5 (cyclohexyl, N–C), 63.6 [$\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 164.8, 169.3 [$\text{Ta}\{(\text{N-cy})_2\text{C}(\text{NMe}_2)\}$] ppm. EI-MS (70 eV): m/z (%) = 796 (0.5) [M^+], 590 (15) [$\text{M}^+ - \text{cy-cdi}$], 206 (25) [cy-cdi^+], 124 (45) [$\text{cy-N}=\text{C}=\text{N-H}^+$], 83 (80) [cy^+], 55 (100) [C_4H_7^+], 43 (70) [C_3H_7^+], 41 (75) [C_3H_5^+].

[Ta(NEtMe){(N-cy)₂C(NEtMe)₂(N-*i*Bu)}] (7): The synthesis of **7** followed the same procedure as for **6** but with $[\text{Ta}(\text{NEtMe})_3(\text{N-}i\text{Bu})]$ (1.72 g, 4.03 mmol) and dicyclohexylcarbodiimide (1.52 g, 7.83 mmol). M.p. 218 °C (uncorrected). Yield: 2.77 g (3.30 mmol, 82% based on $[\text{Ta}(\text{NEtMe})_3(\text{N-}i\text{Bu})]$). $\text{C}_{39}\text{H}_{77}\text{N}_8\text{Ta}$ (839.03): calcd. C 53.98, H 9.25, N 13.36; found C 53.62, H 9.34, N 13.48. ^1H NMR (25 °C, 250 MHz, C_6D_6): δ = 0.9–1.1 [3 × q, 3 × 3 H, 2 × $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)\text{Me}]\}$ and $\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)\text{Me}\}$], 1.10–2.10 (m, cyclohexyl), 1.57 [s, 9 H, $\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 2.62, 2.63, 2.64 [no assignment possible, most probably $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_3)\text{Et}]\}$], 2.9–3.7 [m, cyclohexyl, N–C–H, $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)\text{Me}]\}$ and $\text{Ta}\{\text{N}[\text{CH}_2\text{CH}_3]\text{Me}\}$], 4.25 [s, 3 H, $\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)_2\}$] ppm. ^{13}C NMR (25 °C, 62.5 MHz, C_6D_6): δ = 14.0 [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)\text{Me}]\}$], 15.2 [$\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)\text{Me}\}$], 35.4 [$\text{Ta}\{\text{N}[\text{C}(\text{CH}_3)_3]\}$], 54.5, 54.6 [$\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)\text{Me}\}$ and $\text{Ta}\{\text{NEt}(\text{CH}_3)\}$], 63.8 [$\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 166.1 [$\text{Ta}\{(\text{N-cy})_2\text{C}(\text{NMeEt})\}$] ppm; peaks that cannot be clearly assigned: δ = 26.0, 26.7, 27.1, 27.3, 27.5, 24.4, 35.1, 36.6, 37.0, 56.5, 57.4 ppm. EI-MS (70 eV): m/z (%) = 576 (3) [$\text{M}^+ - \text{guanidinate}$], 265 (10) [guanidinate^+], 206 (10) [cy-cdi^+], 163 (37) [$\text{cy-cdi}^+ - \text{C}_3\text{H}_7$], 124 (35) [$\text{cy-N}=\text{C}=\text{N-H}^+$], 83 (67) [cy^+], 55 (97) [C_4H_7^+], 43 (100) [C_3H_7^+], 41 (97) [C_3H_5^+].

[Ta(NEt₂){(N-cy)₂C(NEt₂)₂(N-*i*Bu)}] (8): The synthesis of **8** followed the same procedure as for **6** but with $[\text{Ta}(\text{NEt}_2)_3(\text{N-}i\text{Bu})]$ (1.89 g, 4.03 mmol) and dicyclohexylcarbodiimide (1.52 g, 7.83 mmol). M.p. 204 °C (uncorrected). Yield: 3.09 g (3.50 mmol, 87% based on $[\text{Ta}(\text{NEt}_2)_3(\text{N-}i\text{Bu})]$). $\text{C}_{42}\text{H}_{83}\text{N}_8\text{Ta}$ (881.11): calcd. C 57.25, H 9.49, N 12.72; found C 57.41, H 10.18, N 11.96. ^1H NMR (25 °C, 250 MHz, C_6D_6): δ = 0.9–1.1 [m, 12 H, 4 of 6 CH_3 groups of $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and $\text{Ta}\{\text{N}[\text{CH}_2\text{CH}_3)_2]\}$, 1.40, 1.46 [m, 2 of 6 CH_3 groups of $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and $\text{Ta}\{\text{N}[\text{CH}_2\text{CH}_3)_2]\}$, 1.20–2.20 (m, cyclohexyl), 1.58 [s, 9 H, $\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 2.9–3.2 [m, 8 H, $\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 3.30–3.70 [m, 4 H, cyclohexyl, N–C–H, and 1 H, $\text{Ta-N}(\text{CH}_2\text{CH}_3)$], 4.44, 4.66, 5.00 [3 × d of q, 1J = 6.5, 6.2, 6.3 Hz, 3 × 1 H, $\text{Ta-N}(\text{CH}_2\text{CH}_3)$] ppm. ^{13}C NMR (25 °C, 62.5 MHz, C_6D_6): δ = 13.5, 14.3, 15.7, 15.9 [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and $\text{TaN}(\text{CH}_2\text{CH}_3)$], 26.0, 26.5, 26.6 (2×), 26.7, 26.8 (2×), 26.9, 27.2, 27.3, 27.5, 27.6 (cyclohexyl, 3,4-position), 34.0, 34.5, 34.6, 35.9, 36.4, 37.1, 37.6, 38.7 (cyclohexyl, 2-position), 35.2 [$\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 41.5, 43.0, 43.1 (br), 44.6 (br) [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 47.5, 58.1 [$\text{TaN}(\text{CH}_2\text{CH}_3)$], 55.6, 56.2, 57.5, 58.8 (cyclohexyl, N–C), 64.1 [$\text{Ta}\{\text{NC}(\text{CH}_3)_3\}$], 166.2, 170.2 [$\text{Ta}\{(\text{N-cy})_2\text{C}(\text{NEt}_2)\}$] ppm. EI-MS (70 eV): m/z (%) = 810 (3) [$\text{M}^+ - \text{NEt}_2$], 604 (calcd. 605) (3) [$\text{M}^+ - \text{cy-cdi}$], 206 (27) [cy-cdi^+], 163 (48) [$\text{cy-cdi}^+ - \text{C}_3\text{H}_7$], 124 (44) [$\text{cy-N}=\text{C}=\text{N-H}^+$], 83 (81) [cy^+], 55 (100) [C_4H_7^+], 43 (70) [C_3H_7^+], 41 (71) [C_3H_5^+].

$\text{N}=\text{C}=\text{N-H}^+$, 83 (81) [cy^+], 55 (100) [C_4H_7^+], 43 (70) [C_3H_7^+], 41 (71) [C_3H_5^+].

[Ta(NEt₂){(N-*i*Pr)₂C(NEt₂)₂(N-*n*Pr)}] (9): The synthesis of **9** followed, in general, the same procedure as for **6** but with $[\text{Ta}(\text{NEt}_2)_3(\text{N-}i\text{Pr})]$ (1.83 g, 4.03 mmol) and diisopropylcarbodiimide (1.01 g, 8.06 mmol). The diimide was used without dissolving it in hexane. M.p. 195 °C (uncorrected). Yield: 2.39 g (3.38 mmol, 84% based on $[\text{Ta}(\text{NEt}_2)_3(\text{N-}i\text{Pr})]$). $\text{C}_{29}\text{H}_{65}\text{N}_8\text{Ta}$ (706.84): calcd. C 49.28, H 9.27, N 15.85; found C 49.28, H 9.17, N 16.10. ^1H NMR (25 °C, 250 MHz, C_6D_6): δ = 0.89 [t, 1J = 6.9 Hz, 3 H, $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 0.91, 2 × 0.96, 1.06, 1.07, 1.47 [6 × t, 1J = 6.7, 2 × 7.0, 7.4, 6.8, 7.0 Hz, 6 × 3 H, 4 × $\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and 2 × $\text{TaN}[\text{CH}_2\text{CH}_3]$], 1.16, 1.23, 1.35, 1.38, 2 × 1.40, 1.47, 1.58 [8 × d, 1J = 6.4, 6.4, 6.5, 6.0, 2 × 6.0, 6.4, 6.5 Hz, 24 H, $\text{Ta}\{[\text{N}[\text{CH}(\text{CH}_3)_2]_2\text{C}(\text{NEt}_2)]\}$, 1.72 [sextet, 1J = 7.3 Hz, 2 H, $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 2.80–3.15 [m, 8 H, $\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 3.41, 4.25, 4.59, 4.73 [4 × d of q, 1J = 6.3, 6.0, 6.0, 5.9 Hz, 4 H, $\text{TaN}(\text{CH}_2\text{CH}_3)$], 3.76, 3.87, 3.94, 4.10 [4 × septet, 1J = 6.5, 6.4, 6.4, 6.5 Hz, 4 H, $\text{Ta}\{[\text{N}[\text{CH}(\text{CH}_3)_2]_2\text{C}(\text{NEt}_2)]\}$, 4.31, 4.37 [2 × d of t, 1J = 6.8, 6.7 Hz, 2 H, $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$] ppm. ^{13}C NMR (25 °C, 62.5 MHz, C_6D_6): δ = 12.40 [$\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 13.6, 14.0, 14.8, 15.7, 17.0 [$\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and $\text{TaN}(\text{CH}_2\text{CH}_3)$], 23.5, 24.5, 25.0, 25.2, 25.9, 26.1, 26.5, 28.0 [$\text{Ta}\{[\text{N}[\text{CH}(\text{CH}_3)_2]_2\text{C}(\text{NEt}_2)]\}$, 28.5 [$\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 41.4, 42.3, 43.7 (br) [$\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 46.8, 56.7 [$\text{TaN}(\text{CH}_2\text{CH}_3)$], 47.2, 47.5, 48.4, 48.8 [$\text{Ta}\{[\text{N}[\text{CH}(\text{CH}_3)_2]_2\text{C}(\text{NEt}_2)]\}$, 61.9 [$\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 166.5, 170.3 [$\text{Ta}\{(\text{N-}i\text{Pr})_2\text{C}(\text{NEt}_2)]\}$ ppm. EI-MS (70 eV): m/z (%) = 706 (12) [M^+], 635 (79) [$\text{M}^+ - \text{NEt}_2$], 509 (100) [$\text{M}^+ - \text{guanidinate}$], 466 (29) [$\text{M}^+ - \text{guanidinate} - i\text{Pr}$], 407 (calcd. 409) (10) [$\text{M}^+ - i\text{Pr} - \text{N-Pr}$ (*i* or *n*)], [$\text{M}^+ - \text{guanidinate}$], 198 (4) [guanidinate^+], 141 (15) [$\text{N}(i\text{Pr})_2\text{C}(\text{NH})^+$], 126 (5) [$i\text{Pr-N}=\text{C}=\text{N-}i\text{Pr}^+$], 69 (34) [$i\text{Pr-N-C}^+$], 58 (10) [HN-Pr^+], 43 (10) [$i\text{Pr}$].

[Ta(NEt₂){(N-cy)₂C(NEt₂)₂(N-*n*Pr)}] (10): The synthesis of **10** followed the same procedure as for **6** but with $[\text{Ta}(\text{NEt}_2)_3(\text{N-}n\text{Pr})]$ (1.83 g, 4.03 mmol) and dicyclohexylcarbodiimide (1.52 g, 7.83 mmol). M.p. 205 °C (uncorrected). Yield: 2.27 g (2.62 mmol, 65% based on $[\text{Ta}(\text{NEt}_2)_3(\text{N-}n\text{Pr})]$). $\text{C}_{41}\text{H}_{81}\text{N}_8\text{Ta}$ (866.61): calcd. C 56.80, H 9.41, N 12.92; found C 56.13, H 10.04, N 13.20. ^1H NMR (25 °C, 250 MHz, C_6D_6): δ = 0.97, 0.98, 2 × 1.02, 1.08, 1.09 [6 × t, coupling constants could not be determined, 18 H, $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 3 × $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and 2 × $\text{Ta}\{\text{N}[\text{CH}_2\text{CH}_3)_2]\}$, 1.49 [t, 1J = 7.1 Hz, 3 H, $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$, 1.73 [m, $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 1.2–2.3 (m, cyclohexyl), 2.90–3.20 [m, 8 H, $\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 3.30–3.80 [m, 5 H, 4 × cyclohexyl (N–C–H) and 1 × $\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)_2\}$], 4.25–4.50 [m, 3 H, 2 × $\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$ + 1 × $\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)_2\}$], 4.62, 4.76 [2 × sextet, 1J = 5.8, 6.0 Hz, 2 H, $\text{Ta}\{\text{N}(\text{CH}_2\text{CH}_3)_2\}$] ppm. ^{13}C NMR (25 °C, 62.5 MHz, C_6D_6): δ = 12.56 [$\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 13.6, 13.9, 14.90 (br), 15.9, 16.8 [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$ and $\text{TaN}(\text{CH}_2\text{CH}_3)$], 26.5, 2 × 26.6, 26.7, 26.8, 26.9, 2 × 27.0, 2 × 27.1, 27.5, 27.6, 28.5 [12 × cyclohexyl (3,4-position), 1 × $\text{Ta}\{(\text{NCH}_2\text{CH}_2\text{CH}_3)\}$], 33.5, 34.8, 35.7, 35.8, 36.6, 2 × 36.7 (cyclohexyl, 2-position), 39.1, 41.5, 42.5, 44.0 (br) [$\text{Ta}\{(\text{N-cy})_2\text{C}[\text{N}(\text{CH}_2\text{CH}_3)_2]\}$], 47.5 [1 × $\text{TaN}(\text{CH}_2\text{CH}_3)_2$], 55.7, 55.9, 56.2, 56.9, 58.0, 58.3 [1 × $\text{TaN}(\text{CH}_2\text{CH}_3)_2$, 4 × cyclohexyl (N–C)], 62.0 [$\text{Ta}(\text{NCH}_2\text{CH}_2\text{CH}_3)$], 166.6, 170.3 [$\text{Ta}\{(\text{N-cy})_2\text{C}(\text{NEt}_2)]\}$ ppm. Small amounts of free cy-cdi were detected in the ^{13}C NMR spectrum of this compound. EI-MS (70 eV): m/z (%) = 795 (calcd. 794) (0.5) [$\text{M}^+ - \text{NEt}_2$], 589 (calcd. 588) (0.5) [$\text{M}^+ - \text{guanidinate}$], 206 (20) [$\text{cy-N}=\text{C}=\text{N-cy}^+$], 82 (61) [cy^+], 56 (100), 55 (C_4H_7^+), 43 (60) [C_3H_7^+], 41 (67) [C_3H_5^+].

Supporting Information (see footnote on the first page of this article): Ortep/Povray drawings of the molecular structures of **4**, **5**, and **8** in the solid state.

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