Competitive Insertion of Isocyanide into Tantalum−Amido and Tantalum−Methyl Bonds

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The (amido)methyl complexes [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NR_2)] [R = Ph (**3**), $SiMe_3$ (**4**)] were prepared by reaction of [Ta(η^5-C_5Me_5)(N*t*Bu)ClMe] (**1**) with the appropriate lithium amides. Attempts to isolate the analogous NHMe derivative afforded a mixture of complexes [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NHMe)] (**5**) and [Ta(η^5-C_5Me_5)(NMe)Me(NH*t*Bu)] (**6**), resulting from hydrogen exchange between the amido and imido ligands. Insertion of CN(2,6-$Me_2C_6H_3$) into the Ta–Me bond of complexes **3** and **4** gave the η^1-iminoacyl derivatives [Ta(η^5-C_5Me_5)(N*t*Bu)(NR_2){η^1-C(Me)=N(2,6-$Me_2C_6H_3$)}] [R = Ph (**7**), $SiMe_3$ (**8**)], while insertion into the Ta–NRMe (R = H, Me) bond of the complexes [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NRMe)] [R = H (**5**), Me (**2**)] gave the η^2-iminocarbamoyl compounds [Ta(η^5-C_5Me_5)(N*t*Bu)Me{η^2-C(NRMe)=N(2,6-$Me_2C_6H_3$)}] [R = H (**10**), Me (**9**)]. All of the new compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy. The X-ray crystal structure of **9** is reported. DFT calculations were carried out to justify the preference of the insertion either into the Ta–C or the Ta–N bond.

Introduction

It is well known that isocyanides can be inserted into early transition metal−alkyl[1−5] and metal−amido[1,6−10] bonds to give η^2-iminoacyl and η^2-iminocarbamoyl compounds, respectively. These are versatile and potentially useful reagents in many synthetic applications.[1]

We reported[11] the insertion of isocyanide into the tantalum−methyl bond of various (η^5-pentamethylcyclopentadienyl)(imido) complexes of the type [Ta(η^5-C_5Me_5)(NR)MeX] to verify that this insertion takes place into the tantalum−methyl bond[12] not only for X = Cl, OR (R = Me, *t*Bu), noncompetitive ligands, but also for X = NH*t*Bu, which could behave as a competitive ligand to give η^2-iminocarbamoyl derivatives. We concluded that the steric demands of the X substituent influence these reactions more significantly than its π-donor capacity, the reaction being easier for X = Cl, Me, OMe (immediate at room temperature) than for X = O*t*Bu (7 h at room temperature) and X = NH*t*Bu (3 d at 75 °C). We also observed that the double insertion of isocyanide into the tantalum−iminoacyl bond is preferred over the insertion into the Ta−NH*t*Bu bond, allowing for the isolation of [Ta(η^5-C_5Me_5)(N*t*Bu)(NH*t*Bu){η^2-C(CMe=NR)=NR}] (R = 2,6-$Me_2C_6H_3$) complexes. Consequently, formation of η^2-iminocarbamoyl derivatives by insertion into tantalum−amido bonds would only be possible if no alkyl substituent were present, as observed for [Ta(η^5-C_5Me_5)(N*t*Bu)Cl{NH*t*Bu)][12] and related (amido)niobium compounds.[13]

However, an unexpected behaviour was observed when [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NMe_2)], which contains a less bulky dimethylamido ligand, was used. This reaction was immediate at room temperature affording the η^2-iminocarbamoyl derivative with preferential insertion into the tantalum−amido rather than the tantalum−methyl bond. For this reason we decided to thoroughly investigate these insertion reactions using different amido ligands. Meanwhile, a similar preferential insertion into a metal−dimethylamido bond was reported for related [Nb(η^5-$C_5H_4SiMe_3$){N(2,6-$Me_2C_6H_3$)}Me(NMe_2)] and [Ta(η^5-C_5Me_5){N(2,6-$Me_2C_6H_3$)}Me(NMe_2)] complexes.[14]

Here we report the synthesis of new (amido)methyltantalum complexes [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NR_2)] [R_2 = HMe, Ph_2, $(SiMe_3)_2$] and the competitive insertion of

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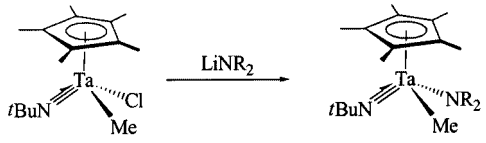
$CN(2,6\text{-}Me_2C_6H_3)$ into their Ta−Me and Ta−NR_2 bonds. The X-ray molecular structure of the η^2-iminocarbamoyl complex $[Ta(\eta^5\text{-}C_5(CH_3)_5](NtBu)Me\{\eta^2\text{-}C(NMe_2)=N(2,6\text{-}Me_2C_6H_3)\}]$ is also reported, as well as DFT calculations carried out to justify the notion of preferential insertion into Ta−dimethylamido bonds.

Results and Discussion

As previously reported[15] the dimethylamido complex $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me(NMe_2)]$ (**2**) was isolated in high yield as a dark yellow oil by addition of $LiNMe_2$ to an ethereal solution of the (chloro)(methyl) derivative $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)ClMe]$ (**1**). As shown in Equation (1), the same procedure afforded complex $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me(NPh_2)]$ (**3**) as a yellow oil in 90% yield. It is an air-sensitive compound that can be stored for long periods under an inert gas. The complex $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me\{N(SiMe_3)_2\}]$ (**4**), which was not isolated as a solid, was prepared in quantitative yield by the same reaction in a sealed NMR tube, and is stable in C_6D_6 solution for long periods.

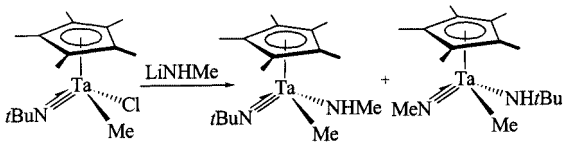


(1)

1 R = Ph, **3**; $SiMe_3$, **4**

It was found[15] that **2** shows dynamic NMR spectroscopic behaviour, indicating free rotation of the amido ligand and making the two methyl groups equivalent, to give a unique broad signal in both ^1H and ^{13}C NMR spectra at room temperature. Dynamic NMR spectroscopy experiments showed a coalescence temperature of ca. 302 K and a Gibbs activation energy $\Delta G^{\neq}$ of 58.15 kJ/mol for this process, in agreement with reported values for analogous complexes.[16] However, the ^1H NMR spectra of complexes **3** and **4** show the presence of two nonequivalent phenyl- and silylamido substituents, respectively, every aryl ring proton of **3** appearing as a sharp signal (δ = 6.7−7.2 ppm) while two sharp signals for the $SiMe_3$ groups of **4** were observed at δ = 0.18 and 0.50 ppm. Resonances for the methyl, *tert*-butyl and pentamethylcyclopentadienyl groups in complexes **3** and **4** appear in the usual region (see Exp. Sect.).

In an attempt to complete the series of (amido)(imido) complexes analogous to **2**, we tried the reaction of **1** with LiNHMe in THF. This reaction was not so simple and gave a mixture of $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me(NHMe)]$ (**5**) and $[Ta(\eta^5\text{-}C_5Me_5)(NMe)Me(NHtBu)]$ (**6**) in ca. 1:1 ratio [Equation (2)], as a pale yellow oil from which they could not be separated. No interconversion between **5** and **6** was observed when the mixture was heated up to 80 °C in the NMR tube, indicating that the temperature does not substantially modify the equilibrium.



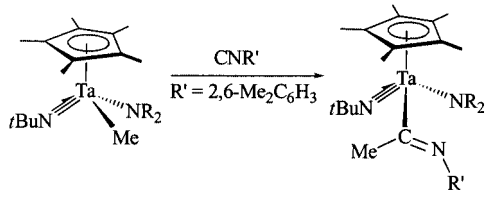
(2)

1 **5** **6**

Complexes **5** and **6** were easily distinguished by their ^1H NMR spectrum, which shows the methyl resonance of the amido ligand as a doublet (δ = 3.63 ppm, $^3J_{H,H}$ = 7 Hz) whereas that of the imido ligand appears as a singlet (δ = 3.77 ppm). Two sets of signals for the methyl, *tert*-butyl and pentamethylcyclopentadienyl groups were observed for the mixture of complexes **5** and **6**. The amido proton of the corresponding NHMe and NH*t*Bu appears as a broad signal at δ = 4.62 and 4.88 ppm, respectively. The values of $\Delta\delta$ ($\Delta\delta = \delta_{quat} - \delta_{Me}$) observed in the ^{13}C NMR spectra of **5** (30.2 ppm) and **6** (21.6 ppm) are consistent with the presence of the *tert*-butylimido and *tert*-butylamido ligands, respectively.[17]

Therefore, formation of **5**, followed by proton transfer from the methylamido to the more basic *tert*-butylimido ligand,[16,18−25] affords complex **6**, and the kinetic barrier for interconversion between **5** and **6** must be high.

Treatment of complexes **3** and **4** with $CN(2,6\text{-}Me_2C_6H_3)$ resulted in insertion into the Ta−Me bond, to give the η^1-iminoacyl compounds $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)(NPh_2)\{\eta^1\text{-}C(Me)=N(2,6\text{-}Me_2C_6H_3)\}]$ (**7**) and $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)[N(SiMe_3)_2]\{\eta^1\text{-}C(Me)=N(2,6\text{-}Me_2C_6H_3)\}]$ (**8**), after heating at 80 °C for 8 h and 20 h, respectively [Equation (3)]. This is the same behaviour previously observed for $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me(NHtBu)]$.[12]

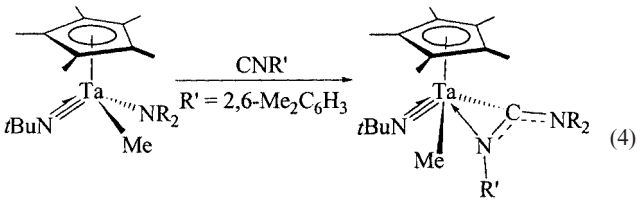


(3)

R_2 = Ph_2, **3**; $(SiMe_3)_2$, **4** R_2 = Ph_2, **7**; $(SiMe_3)_2$, **8**

Formation of the iminoacyl compounds **7** and **8** was confirmed by the low-field shift ($\delta > 1$ ppm) of the ^1H NMR signal of the migrated methyl group and the ^{13}C resonance of the iminoacyl sp^2-carbon atom observed at δ = 249.3 (**7**) and 251.9 ppm (**8**), as expected for complexes of this type.

In contrast, an almost immediate and complete reaction of the dimethylamido complex **2** with 1 equiv. of $CN(2,6\text{-}Me_2C_6H_3)$ took place at room temperature in hexane to afford the η^2-iminocarbamoyl compound $[Ta(\eta^5\text{-}C_5Me_5)(NtBu)Me\{\eta^2\text{-}C(NMe_2)=N(2,6\text{-}Me_2C_6H_3)\}]$ (**9**) [Equation (4)], which was recrystallized from pentane and isolated as colourless air-stable crystals soluble in all the usual organic solvents. Its crystal structure was determined by X-ray diffraction methods.



(4)

$R_2 = Me_2$, **2**; HMe, **5** $R_2 = Me_2$, **9**; HMe, **10**

Addition of 2 equiv. of CN(2,6-$Me_2C_6H_3$) to a C_6D_6 solution of a ca. 1:1 mixture of **5** and **6** proceeded with darkening of the solution and isocyanide insertion into the Ta−NHMe bond of complex **5** to give [Ta(η^5-C_5Me_5)(N*t*Bu)Me{η^2-C(NHMe)=N(2,6-$Me_2C_6H_3$)}] (**10**) after 24 h at room temperature [Equation (4)]. Under these conditions complex **6** remained unaltered. No insertion into the Ta−Me bond was observed even after heating to 80 °C, which caused complex **6** to decompose, while **10** remained unchanged.

Formation of the η^2-iminocarbamoyl compounds **9** and **10** was confirmed by the high-field shift ($\delta \approx 1$ ppm) of the methylamido signal, the very slight displacement of the Ta-Me resonance and the presence in the ^{13}C NMR spectra of a low-field signal ($\delta > 200$ ppm) due to the iminocarbamoyl sp^2-carbon atom.[26] Three ν(C=N) IR stretching vibrations were observed[6] for the η^2-iminocarbamoyl complex **9**.

The transformation of the (benzyl)(η^2-iminocarbamoyl) species into the corresponding (amido)(η^2-iminoacyl) derivative, typical in related (amido)niobium compounds,[13] was not observed for complex **9**, which decomposed on heating to over 100 °C. It can therefore be concluded that insertion occurred directly into the Ta−NMe_2 rather than the Ta−Me bond.

An X-ray diffraction study of complex **9** confirms that the isocyanide was inserted into the tantalum−amido bond. A view of the molecular structure of complex **9**, together with the atomic labeling system, is shown in Figure 1. Selected bond lengths and angles are given in Table 1.

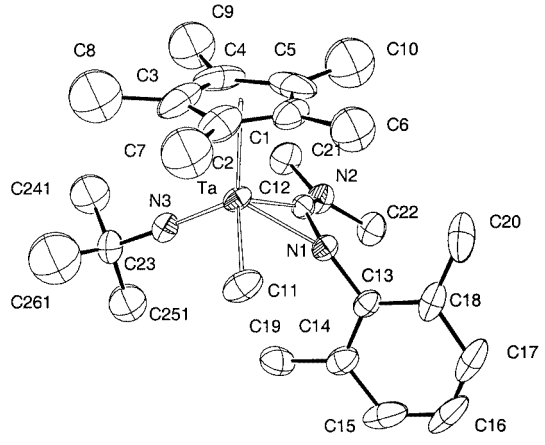


Figure 1. ORTEP view of the molecular structure of **9**; thermal ellipsoids are drawn at 30% probability level; hydrogen atoms are omitted for the sake of clarity

Table 1. Selected bond lengths [Å] and angles [°] with e.s.d.s in parentheses for compound **9** [CE(1) is the centroid of the C(1)···C(5) cyclopentadienyl ring and M(1) the midpoint of the N(1)−C(12) double bond]

Ta−N(3)	1.785(4)	Ta−C(4)	2.406(6)
Ta−C(11)	2.230(5)	Ta−C(5)	2.503(6)
Ta−N(1)	2.164(4)	N(1)−C(12)	1.303(5)
Ta−C(12)	2.146(5)	N(1)−C(13)	1.418(6)
Ta−CE(1)	2.182(6)	C(12)−N(2)	1.339(6)
Ta−M(1)	2.054(5)	N(2)−C(21)	1.444(6)
Ta−C(1)	2.567(5)	N(2)−C(22)	1.464(7)
Ta−C(2)	2.485(6)	N(3)−C(23)	1.441(7)
Ta−C(3)	2.441(6)		
CE(1)−Ta−C(11)	106.8(3)	N(1)−Ta−C(12)	35.2(1)
CE(1)−Ta−N(3)	122.6(2)	Ta−N(1)−C(12)	71.7(3)
CE(1)−Ta−M(1)	120.7(2)	Ta−N(1)−C(13)	150.0(3)
CE(1)−Ta−N(1)	122.6(2)	C(12)−N(1)−C(13)	133.6(4)
CE(1)−Ta−C(12)	115.7(2)	Ta−C(12)−N(1)	73.1(3)
C(11)−Ta−N(3)	97.0(2)	Ta−C(12)−N(2)	155.5(3)
C(11)−Ta−M(1)	98.4(2)	N(1)−C(12)−N(2)	130.3(4)
C(11)−Ta−N(1)	81.4(2)	C(12)−N(2)−C(21)	119.1(5)
C(11)−Ta−C(12)	115.5(2)	C(12)−N(2)−C(22)	124.6(4)
N(3)−Ta−M(1)	105.7(2)	C(21)−N(2)−C(22)	116.3(5)
N(3)−Ta−N(1)	111.9(2)	Ta−N(3)−C(23)	176.8(4)
N(3)−Ta−C(12)	98.2(2)		

The tantalum atom shows a four-legged piano stool arrangement involving the pentamethylcyclopentadienyl ring [Ta−CE(1) = 2.182(6) Å], [CE(1) being the centroid of the ring], the methyl carbon atom [Ta−C(11) = 2.230(5) Å], the nitrogen atom of the *tert*-butylimido ligand [Ta−N(3) = 1.785(4) Å], and the carbon and nitrogen atoms of the η^2-iminocarbamoyl ligand [Ta−C(12) = 2.146(5) and Ta−N(1) = 2.164(4) Å]. The dihedral angle between the cyclopentadienyl ring and the N(3)C(11)N(1)C(12) mean plane is 5.2(2)°. This arrangement can also be viewed as a three-legged piano-stool if the midpoint [M(1)] of the N(1)−C(12) bond is taken into consideration [Ta−M(1) = 2.054(5) Å]. The coordination geometry around the Ta atom can be described also as pseudotetrahedral if the centroid CE(1) and the midpoint M(1) are considered as coordination sites. The complex is chiral, and both enantiomers are present in the crystals. The insertion of CN(2,6-$Me_2C_6H_3$) into the coordinated dimethylamido group is stereoselective; in fact the η^2-iminocarbamoyl shows the N atom in a *cis* position with respect to the coordinated methyl group. Only one of the two possible stereoisomers is so formed. This stereoselectivity is probably mainly due to steric factors.

The *inside* coordination of the N(1) iminocarbamoyl nitrogen atom located between C(12) and C(11) is similar to that found for similar (chloro)(iminoacyl)(imido)(pentamethylcyclopentadienyl)- or (iminoacyl)(imido)(methyl)(pentamethylcyclopentadienyl)tantalum complexes[11,12,14,27] in which the N(1) iminoacyl nitrogen atom is located between the iminoacyl carbon atom and the chlorine atom or the methyl carbon atom. The values of the Ta−N(3) bond length, consistent with triple bond character, and of the nearly linear Ta−N(3)−C(23) bond angle of 176.8(4)° are as expected for an imido ligand and compare well with

those found in other (imido)(pentamethylcyclopentadienyl)-tantalum complexes.[11,12,14,27−30] The Ta−C(11) bond length presents the normal value for a $Ta-CH_3$ bond. The Cp* (C_5Me_5) ring is bound to the Ta atom in a nearly symmetric η^5-fashion; a slight trend towards η^3-coordination is observed, as indicated by three short [Ta−C(2) = 2.485(6), Ta−C(3) = 2.441(6), Ta−C(4) = 2.406(6) Å] and two long $Ta-C_{Cp^*}$ ring carbon distances [Ta−C(1) = 2.567(5) and Ta−C(5) = 2.503(6) Å], involving the C(1)−C(5) bond nearly *trans* to the imido group[30] {τ[N(3)−Ta−CE(1)−C(1)] = 159.7(4), τ[N(3)−Ta−CE(1)−C(5)] = −128.6(6), τ[N(3)−Ta−CE(1)−C(3)] = 17.3(7)°}. The midpoint of the N(1)−C(12) bond nearly eclipses the C(5) atom of Cp* {τ[M(1)−Ta−CE(1)−C(5)] = 10.3(7)°}. The Ta−N(1) and Ta−C(12) bond lengths are similar to those found in (η^2-*C*,*N*-iminoacyl)Ta complexes.[11,12,14,27] The N(1)−C(12) [1.303(5) Å], and the C(12)−N(2) [1.339(6) Å] bond lengths reveal π delocalizaton in the η^2-*C*,*N*-iminocarbamoyl moiety. The N(1)C(12)N(2)C(21)C(22) fragment is quite planar {max. dev. 0.050(7) Å for C(21), τ[N(1)−C(12)−N(2)−C(21)] = 173.4(5), τ[N(1)−C(12)−N(2)−C(22)] = −6.8(8)°} and forms dihedral angles of 4.5(2) and 81.7(2)° with the TaN(1)C(12) and the aryl groups, respectively.

The close similarity between the symmetry properties of the frontier orbitals of (cyclopentadienyl)(imido)metal [Ta(η^5-C_5Me_5)(N*t*Bu)] and the metallocene [Ti(η^5-C_5Me_5)$_2$] fragments[30] suggests that the $1a_1$ metal orbital is used for π-bonding by the NMe_2 ligand. The dynamic behaviour observed for **2** at room temperature indicates that this $1a_1$ orbital is energetically accessible for ligand binding, allowing the isocyanide to be located at any of the two positions appropriate for insertion into either the Ta−Me or $Ta-NMe_2$ bonds. Insertion into the Ta−NRMe (R = H, Me) bonds is the most favorable, being followed by rotation around the Ta−C bond to give the η^2-iminocarbamoyl compound, and similar behaviour should be expected for the NH*t*Bu derivatives **6** and [Ta(η^5-C_5Me_5)(N*t*Bu)-Me(NH*t*Bu)].[12] However steric effects from the presence of the bulky *tert*-butyl substituent are more important than the electronic effects and probably prevent this reaction, leaving the energetically less favorable insertion into the Ta−Me bond as the only possible pathway, which requires heating at 75 °C for 3 d in the case of [Ta(η^5-C_5Me_5)-(N*t*Bu)Me(NH*t*Bu)].[12] Complexes **3** and **4** favor preferential insertion into the Ta−Me bond when heated at 80 °C for 8 and 20 h, respectively, probably due to electronic effects of the amido substituents.

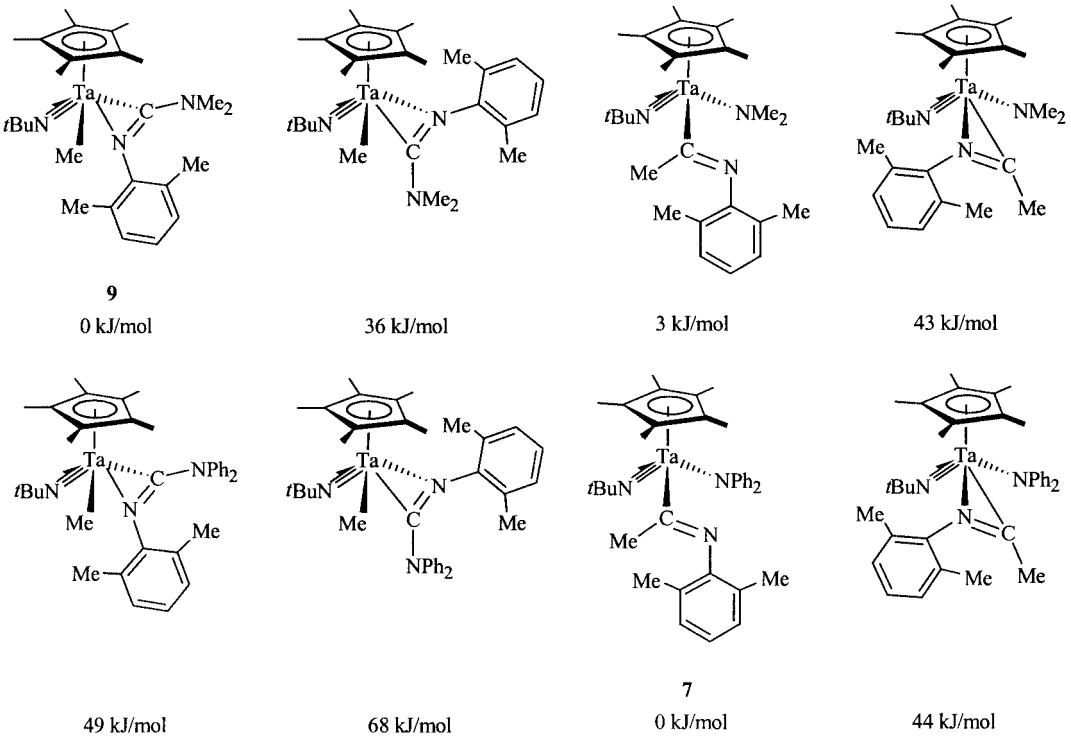
To help answer the question why compound **3** shows a preference for insertion into the tantalum−methyl bond, rather than insertion into the tantalum−amido bond, as observed for compound **2**, we performed density functional calculations on possible insertion products of the reaction of **2** and **3** with CN(2,6-$Me_2C_6H_3$). The relative energies and coordination geometries are collected in Scheme 1.

According to our calculations, the most stable insertion product for compound **2** is the η^2-iminocarbamoyl complex **9** based on the approach of the isocyanide between the alkyl and the amido ligands. However, the corresponding iminoacyl derivative is only 3 kJ/mol higher in energy. Furthermore, the optimized geometry shows that the iminoacyl ligand is bound in an η^1-fashion, with the two N groups in a *cis* position with respect to the Ta−C bond. A rotation around the latter bond leads to a complex with an η^2-iminoacyl ligand. This compound, however, is 40 kJ/mol higher in energy than the one bearing an η^1-iminoacyl ligand. The possibility of an attack of the isocyanide from the other "side" of the amido ligand (between the amido and imido ligands) has also been investigated but the η^2-iminocarbamoyl insertion product is about 36 kJ/mol higher in energy.

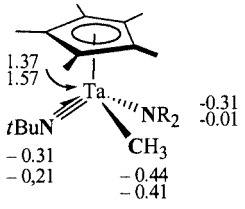
Turning to the insertion products for compound **3**, the calculations show that the iminoacyl complex **7** is the energetically favored insertion product. Again, the iminoacyl group acts as an η^1-ligand, and the corresponding η^2 complex is 44 kJ/mol higher in energy. Also, the η^2-iminocarbamoyl complexes are energetically disfavored by 49 and 68 kJ/mol.

An analysis of the charge distributions in complexes **2** and **3** holds an answer for the observed preferences in coordination geometry. Charges (in a.u.) at the atoms forming the Ta−C and Ta−N bonds of **2** and **3** are displayed in Scheme 2.

For both compounds, the imido N atom as well as the methyl C atom carry a negative charge, whereas the metal center is positively charged. However, whereas for compound **2** the electron-rich dimethylamido ligand carries a sizeable amount of negative charge at the N atom, the N atom of the diphenlyamido group of compound **3** carries almost no charge at all. Also, in this compound, the central metal atom as well as the imido N atom are more positively charged by 0.2 and 0.1 a.u., when compared with **2**. This suggests that the diphenylamido ligand possesses some electron-withdrawing properties, since charge can be effectively delocalized over the two aromatic phenyl groups. This assumption is supported when the total charge on the NMe_2 and NPh_2 in compounds **2** and **3** is analyzed. Summing up the individual contributions of all atoms of the NMe_2 group, we find a charge value of +0.10 a.u., indicating that the dimethylamido group is acting as an electron-donating group. On the other hand, the total charge of the NPh_2 group amounts to −0.61 a.u. This indicates that electron delocalization over the phenyl groups indeed induces some electron-withdrawing properties. The same behaviour should be expected for compound **4** by electron delocalization onto the silicon d orbitals. Thus, the isocyanide ligand will insert into that Ta−R (R = C, N) bond, in which R carries a sizeable amount of negative charge. In this case, the attack of R at the LUMO of the CN(2,6-$Me_2C_6H_3$) molecule, which is the first step in the formation of the new R−CN(2,6-$Me_2C_6H_3$) bond, is facilitated. We also note that when steric bulk is provided by alkyl groups, the sterically most hindered M−C bond can also be expected to contain the C atom with the largest amount of negative charge.



Scheme 1



R = Me, **2**
R = Ph, **3**

Scheme 2

Comparing the small energy difference between **9** and the corresponding η^1-iminoacyl complex, it becomes clear that thermodynamic considerations do not explain the preference for insertion into the Ta−NMe_2 bond. In order to gain further insight into the nature of the frontier orbitals, we carried out an orbital analysis of the (amido)(imido) compound **2**. As expected, the lone pair of the amido ligand interacts in a π-fashion with the empty $1a_1$ metal orbital. The π-bonding interaction takes place in the highest occupied molecular orbital of the complex (Figure 2), while the corresponding π-antibonding interaction is mainly localized in the LUMO.

The resulting metal−nitrogen π-bonding interaction leads to a more stable orientation with one of the amido substituents pointing towards the Cp* ring. For the real insertion process of the $CN(2,6\text{-}Me_2C_6H_3)$ molecule into the Ta−amido bond, we may then take the attack of the lone pair of the amido group in the HOMO (π-bonding orbital) on the π* LUMO of the isocyanide molecule as the major orbital transformation of this process (Scheme 3). The preference of Ta−N over Ta−C insertion is therefore governed by frontier orbital arguments, and is preferred on kinetic, rather than thermodynamic, grounds.

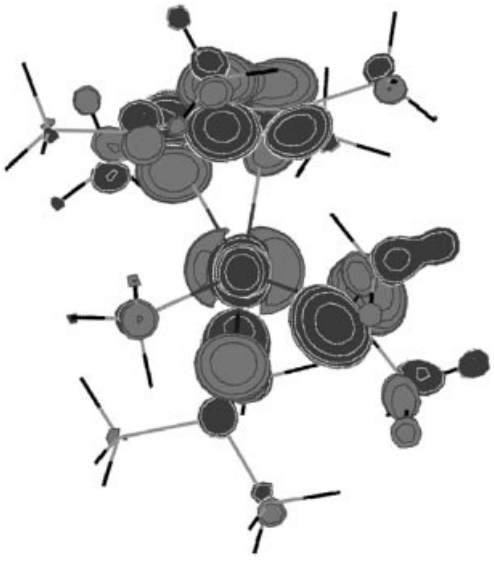
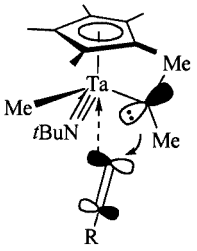


Figure 2. Calculated HOMO of the amido imido complex **2** showing the π-bonding interaction between the metal orbital and the amido lone pair



Scheme 3

Conclusions

Various (amido)methyltantalum complexes [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NR_2)] [R_2 = HMe, Ph_2, $(SiMe_3)_2$] were prepared by reaction of the (chloro)(methyl) derivative with appropriate lithium amides Li(NR_2). Easy hydrogen exchange between methylamido (NHMe) and the more basic *tert*-butylimido (N*t*Bu) groups was observed.

According to density functional calculations, coordination of isocyanide CN(2,6-$Me_2C_6H_3$) followed by nucleophilic attack initiates the insertion, either into Ta−amido or Ta−methyl bonds, that is governed by kinetic factors. Insertion into Ta−methyl bonds is preferred for amido NR_2 [R_2 = Ph_2, $(SiMe_3)_2$] complexes to give the η^1-iminoacyl [Ta(η^5-C_5Me_5)(N*t*Bu)(NR_2){η^1-C(Me)=N(2,6-$Me_2C_6H_3$)}] derivatives, whereas stereoselective insertion into the Ta−amido bonds is preferred for NRMe (R = H, Me) yielding *inside-N*-coordinated η^2-iminocarbamoyl [Ta(η^5-C_5Me_5)(N*t*Bu)Me{η^2-C(NRMe)=N(2,6-$Me_2C_6H_3$)}] complexes.

Experimental Section

General: All operations were performed under argon using standard Schlenk-line or glovebox techniques. Hexane and pentane were distilled from a sodium/potassium alloy and diethyl ether from sodium benzophenone ketyl. H_2NMe (Aldrich), $HNPh_2$ (Aldrich), $HN(SiMe_3)_2$ (Aldrich), CN(2,6-$Me_2C_6H_3$) (Fluka) were used as received. LiBu (Aldrich) was titrated prior to use.[31] Complexes [Ta(η^5-C_5Me_5)(N*t*Bu)ClMe] (**1**)[12] and [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NMe_2)] (**2**)[15] were prepared by known procedures. IR: Perkin−Elmer 583 spectrophotometer (4000−200 cm^{-1}). ^{1}H and ^{13}C NMR: Varian Unity 300 MHz spectrometer (^{1}H, 299.95 MHz; ^{13}C, 75.43 MHz). Chemical shifts (in ppm) were referenced internally using the residual solvent resonances and were reported relative to tetramethylsilane. Elemental analyses: Perkin−Elmer 2400 CHNO.

Preparation of [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NPh_2)] (3): Cooled THF (30 mL) was added to a solid mixture of **1** (1.36 g, 3.11 mmol) and $LiNPh_2$ (0.59 g, 3.42 mmol) at 0 °C. The mixture was allowed to warm slowly to room temperature. All volatiles were removed and pentane (2 × 15 mL) was added to give a brown-yellow solution. The solution was filtered and the solvent was completely removed to give **3** as a yellow oil. Yield 1.60 g (90%). IR (Nujol, CsI): $\tilde{\nu}$ = 1273 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ = 0.39 (s, 3 H, Ta*Me*), 0.79 (s, 9 H, NC*Me*$_3$), 1.89 (s, 15 H, C_5Me_5), 6.7−7.2 (s, 10 H, N*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 11.2 (C_5Me_5), 28.0 (Ta*Me*), 32.0 (NC*Me*$_3$), 64.5 (N*C*Me$_3$), 115.4 (C_5Me_5), 122.8, 125.3, 128.1, 129.3 (N*Ph*$_2$) ppm. $C_{27}H_{37}N_2Ta$ (570.55): calcd. C 56.84, H 6.49, N 4.91; found C 56.59, H 6.25, N 4.52.

NMR Tube Scale Preparation of [Ta(η^5-C_5Me_5)(N*t*Bu)Me{N($SiMe_3$)$_2$}] (4): C_6D_6 was added to a solid mixture of **1** (0.034 g, 0.077 mmol) and $LiN(SiMe_3)_2$ (0.013 g, 0.077 mmol) in a sealed NMR tube and the mixture was monitored by ^{1}H NMR spectroscopy. After 24 h at 90 °C, the signals of complex **1** disappeared leaving a solution that contained **4** in quantitative yield. ^{1}H NMR (C_6D_6, 298 K): δ = 0.18 [s, 9 H, N(Si*Me*$_3$)$_2$], 0.47 (s, 3 H, Ta*Me*), 0.5 [s, 9 H, N(Si*Me*$_3$)$_2$], 1.32 (s, 9 H, NC*Me*$_3$), 1.91 (s, 15 H, C_5Me_5) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 6.6, 7.7 [N(Si*Me*$_3$)$_2$], 12.2 (C_5Me_5), 20.3 (Ta*Me*), 33.5 (NC*Me*$_3$), 65.5 (N*C*Me$_3$), 116.4 (C_5Me_5) ppm.

Preparation of [Ta(η^5-C_5Me_5)(N*t*Bu)Me(NHMe)] (5) and [Ta(η^5-C_5Me_5)(NMe)Me(NH*t*Bu)] (6): According to a similar procedure to that used for **3**, compound **1** (1.06 g, 2.42 mmol) was treated with LiNHMe (0.11 g, 2.91 mmol) in hexane (30 mL) at −78 °C, to give a ca. 1:1 mixture of **5** and **6** as a pale yellow oil. Yield 0.76 g (72%). **5:** ^{1}H NMR (C_6D_6, 298 K): δ = 0.33 (s, 3 H, Ta*Me*), 1.37 (s, 9 H, NC*Me*$_3$), 1.84 (s, 15 H, C_5Me_5), 3.63 (d, $^3J_{H,H}$ = 7 Hz, 3 H, NH*Me*), 4.62 (br, 1 H, N*H*Me) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 11.1 (C_5Me_5), 20.4 (Ta*Me*), 33.9 (NC*Me*$_3$), 45.5 (NH*Me*), 64.1 (N*C*Me$_3$), 114.0 (C_5Me_5) ppm. **6:** ^{1}H NMR (C_6D_6, 298 K): δ = 0.29 (s, 3 H, Ta*Me*), 1.35 (s, 9 H, NHC*Me*$_3$), 1.82 (s, 15 H, C_5Me_5), 3.77 (s, 3 H, N*Me*), 4.88 (br, 1 H, N*H*CMe$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 10.6 (C_5Me_5), 20.4 (Ta*Me*), 34.7 (NHC*Me*$_3$), 45.9 (N*Me*), 56.3 (NH*C*Me$_3$), 113.3 (C_5Me_5) ppm.

Preparation of [Ta(η^5-C_5Me_5)(N*t*Bu)(NPh_2){η^1-C(Me)=N(2,6-$Me_2C_6H_3$)}] (7): A solution of **3** (1.79 g, 3.14 mmol) in toluene (20 mL) was treated with CN(2,6-$Me_2C_6H_3$) (0.42 g, 3.20 mmol) and the mixture was heated (80 °C) and stirred for 8 h. The solution was filtered and the solvent completely removed. The residue was washed with hexane (2 × 15 mL) to give **7** as a brown oil. Yield 1.65 g (75%). IR (Nujol CsI): $\tilde{\nu}$ = 1594 (s), 1260 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K): δ = 1.0 (s, 9 H, NC*Me*$_3$), 1.91 [s, 3 H, C(*Me*)=N], 1.98 (s, 3 H, 2,6-*Me*$_2$C$_6$H$_3$), 2.12 (s, 15 H, C_5Me_5), 2.46 (s, 3 H, 2,6-*Me*$_2$C$_6$H$_3$), 6.5−7.3 (m, 13 H, 2,6-Me$_2$C$_6$*H*$_3$, N*Ph*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 12.3 (C_5Me_5), 18.9, 19.3 (2,6-*Me*$_2$C$_6$H$_3$), 22.5 [C(*Me*)=N], 33.2 [NC*Me*$_3$], 65.8 [N*C*Me$_3$], 115.7 (C_5Me_5), 117.7, 120.9, 124.9, 125.0, 127.5, 127.9, 128.1, 129.3, 130.9, 142.0 (2,6-Me$_2$*C*$_6$H$_3$, N*Ph*$_2$), 249.3 [*C*(Me)=N] ppm. $C_{36}H_{46}N_3Ta$ (701.73): calcd. C 61.63, H 6.61, N 5.99; found C 61.33, H 6.39, N 5.66.

NMR Tube Scale Preparation of [Ta(η^5-C_5Me_5)(N*t*Bu){N($SiMe_3$)$_2$}{η^1-C(Me)=N(2,6-$Me_2C_6H_3$)}] (8): CN(2,6-$Me_2C_6H_3$) (0.015 g, 0.114 mmol) was added to an NMR tube containing a C_6D_6 solution of **4** (0.114 mmol) and the mixture was monitored by ^{1}H NMR spectroscopy. After ca. 20 h at 80 °C, the signals of complex **4** disappeared leaving a solution that contained **8** in quantitative yield. ^{1}H NMR (C_6D_6, 298 K): δ = 0.17, 0.63 [s, 9 H, N(Si*Me*$_3$)$_2$], 1.19 (s, 9 H, NC*Me*$_3$), 2.01 (s, 15 H, C_5Me_5), 2.04 [s, 3 H, C(*Me*)=N], 2.22, 2.38 (s, 3 H, 2,6-*Me*$_2$C$_6$H$_3$), 6.92 (m, 3 H, 2,6-Me$_2$C$_6$*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 8.3, 8.9 [N(Si*Me*$_3$)$_2$], 12.8 (C_5Me_5), 18.6, 19.9 (2,6-*Me*$_2$C$_6$H$_3$), 24.0 [C(*Me*)=N], 34.4 (NC*Me*$_3$), 66.3 (N*C*Me$_3$), 116.0 (C_5Me_5), 125.8, 128.5, 128.9, 132.2, 134.9, 144.0 (2,6-Me$_2$*C*$_6$H$_3$), 251.9 [*C*(Me)=N] ppm.

Preparation of [Ta(η^5-C$_5$Me$_5$)(N*t*Bu)Me{η^2-C(NMe$_2$)=N(2,6-Me$_2$C$_6$H$_3$)}] (9): A solution of **2** (1.0 g, 2.24 mmol) in hexane (20 mL) was added to CN(2,6-Me$_2$C$_6$H$_3$) (0.30 g, 2.26 mmol) and the mixture was stirred for 1 h at room temperature. The solution was filtered and the solvent was removed to give **9** as a white solid. Recrystallization from pentane gave **9** as colourless crystals. Yield 1.14 g (88%). IR (KBr pellets): $\tilde{\nu}$ = 1606 (s), 1586 (s), 1267 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 298 K): δ = −0.29 (s, 3 H, Ta*Me*), 1.03 (s, 9 H, NC*Me*$_3$), 1.96, 2.0 (s, 3 H, 2,6-*Me*$_2$C$_6$H$_3$), 2.04 (s, 15 H, C$_5$*Me*$_5$), 2.59, 3.39 [s, 3 H, C(N*Me*$_2$)=N], 6.87 (m, 3 H, 2,6-Me$_2$C$_6$*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ = 11.8 (C$_5$*Me*$_5$), 14.2 (Ta*Me*), 19.7 (2,6-*Me*$_2$C$_6$H$_3$), 33.7 (NC*Me*$_3$), 36.8, 45.3 [C(N*Me*$_2$)=N], 64.1 (N*C*Me$_3$), 112.4 (*C*$_5$Me$_5$), 123.7, 127.0, 127.4, 132.0, 132.5, 143.8 (2,6-Me$_2$*C*$_6$H$_3$), 206.6 [*C*(NMe$_2$)=N] ppm. C$_{26}$H$_{42}$N$_3$Ta (577.59): calcd. C 54.07, H 7.33, N 7.28; found C 54.26, H 7.46, N 7.48.

NMR Tube Scale Preparation of Ta(η^5-C$_5$Me$_5$)(N*t*Bu)Me{η^2-C(NHMe)=N(2,6-Me$_2$C$_6$H$_3$)} (10): C$_6$D$_6$ was added to a mixture of **5** and **6** (0.054 g, 0.125 mmol) and CN(2,6-Me$_2$C$_6$H$_3$) (0.016 g, 0.125 mmol) in a sealed NMR tube and the mixture was monitored by ^{1}H NMR spectroscopy. After ca. 24 h at room temperature, the signals of complex **5** disappeared leaving a solution that contained **10**, **6** and excess isocyanide. **10:** ^{1}H NMR (C$_6$D$_6$, 298 K): δ = 0.44 (s, 3 H, Ta*Me*), 1.29 (s, 9 H, NC*Me*$_3$), 2.04 (s, 15 H, C$_5$*Me*$_5$), 2.14, 2.21 (s, 3 H, 2,6-*Me*$_2$C$_6$H$_3$), 2.66 [d, $^3J_{H,H}$ = 7 Hz, 3 H, C(NH*Me*)=N], 4.68 [br, 1 H, C(N*H*Me)=N], 6.95 (m, 3 H, 2,6-Me$_2$C$_6$*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 298 K): δ = 12.0 (C$_5$*Me*$_5$), 16.6 (Ta*Me*), 19.3, 19.5 (2,6-*Me*$_2$C$_6$H$_3$], 34.1 (NC*Me*$_3$), 64.3 (N*C*Me$_3$), 67.8 [C(NH*Me*)=N], 112.8 (*C*$_5$Me$_5$), 125.0, 128.8, 132.5, 132.9, 141.8, 143.6 (2,6-Me$_2$*C*$_6$H$_3$), 208.4 [*C*(NHMe)=N] ppm.

Crystal Structure Determination of 9: Crystals of compound **9** were obtained by crystallization from pentane. A suitably sized crystal in a Lindemann tube was mounted on a Philips PW 1100 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystallographic and experimental details are summarized in Table 2. A semi-empirical method of absorption correction was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.582).[32] A decay of 15% was observed during the data collection. The structure was solved by direct methods (SIR92)[33] and refined by least squares against F_o^2 (SHELXL-97).[34] All non-hydrogen atoms were refined anisotropically except for the methyl carbon atoms of the Cp* ring and of the *t*Bu group. These last methyl groups were found to be disordered in two positions and refined with s.o.f. of 0.5. All hydrogen atoms were introduced from geometrical calculations and refined using a riding model. All calculations were carried out with the DIGITAL AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.", Parma. The programs PARST[35] and ORTEP[36] were also used. CCDC-187149 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: Gradient-corrected density functional calculations were carried out with corrections for exchange and correlation according to Becke[37] and Perdew,[38] respectively (BP86). Geometries were optimized using the program system TURBOMOLE[39] within the framework of the RI-*J* approximation.[40] The geometry was pre-optimized using a triple-ζ valence basis plus polarization TZVP[41] for Ta, and a split-valence basis set with one set of polarization functions for the non-H atoms SV(P)[42] for the remaining elements. In the final steps of the geometry optimization, all elements were treated with the TZVP basis. Atomic charges were obtained from a population analysis based on occupation numbers, and include multicenter corrections.[43] Optimized geometries and final energies are presented in the Supporting Information (see also footnote on the first page of this article).

Table 2. Summary of crystallographic data for compound **9**

Empirical formula	C$_{26}$H$_{42}$N$_3$Ta
Formula mass	577.58
Crystal system	triclinic
Space group	$P\bar{1}$
Radiation (λ [Å])	Mo-K_α (0.71073)
a [Å]	8.592(5)
b [Å]	9.874(4)
c [Å]	16.940(9)
α [°]	101.55(2)
β [°]	93.04(2)
γ [°]	102.50(2)
V [Å^3]	1367.7(12)
Z	2
$D_{calcd.}$ [Mg m^{-3}]	1.403
μ(Mo-K_α) [mm^{-1}]	4.034
F(000)	584
Crystal size [mm]	0.49 × 0.30 × 0.15
Diffractometer	Philips PW 1100
θ range [°]	3.20−30.01
Scan type	θ/2θ
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $0 \le l \le 23$
No. of reflections measured	7954
No. of unique total data	7954
No. of unique observed data	6016 [$I > 2\sigma(I)$]
Data/restraints/parameters	7954/0/253
Goodness-of-fit on F^2	0.955
*R*1 [$I > 2\sigma(I)$]	0.0385
*wR*2 [$I > 2\sigma(I)$]	0.0947
*R*1 (all data)	0.0572
*wR*2 (all data)	0.1023

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