# Insertion of Isocyanides into Tantalum−Methyl and Tantalum−Amido Bonds

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The imido−amido complex [TaCp*(N$^t$Bu)Cl(NH$^t$Bu)], **1**, was isolated from the reaction of [TaCp*Cl$_4$] with 3 equiv of LiNH$^t$Bu. The dimethyl [TaCp*(N$^t$Bu)Me$_2$], **2**, and chloro−methyl [TaCp*(N$^t$Bu)ClMe], **3**, complexes were obtained by methylation of [TaCp*(N$^t$Bu)Cl$_2$] with 2 equiv of LiMe and 1 equiv of ZnMe$_2$, respectively. Metathetical reactions of complex **3** with alkali metal salts MX (M = Na, X = OMe; M = Li, X = O$^t$Bu, NH$^t$Bu) afforded the new imido−methyl compounds [TaCp*(N$^t$Bu)MeX] (X = OMe **4**, O$^t$Bu **5**, NH$^t$Bu **6**). Insertion of CNR (R = 2,6-Me$_2$C$_6$H$_3$) into the Ta−NH$^t$Bu and Ta−Me bonds of the imido−pentamethylcyclopentadienyl complexes **1**−**6** gave the $\eta^2$-iminocarbamoyl compound [TaCp*(N$^t$Bu)Cl{$\eta^2$-C(NH$^t$Bu)═NR}], **7**, and the $\eta^2$-iminoacyl compounds [TaCp*(N$^t$Bu)X{$\eta^2$-C(Me)═NR}] (X = Me **8**, Cl **9**, OMe **10**, O$^t$Bu **11**, NH$^t$Bu **12**), which under appropriate thermal conditions react with a second equivalent of CNR (R = 2,6-Me$_2$C$_6$H$_3$) to give the double insertion imine−$\eta^2$-iminoacyl products [TaCp*(N$^t$Bu)X{$\eta^2$-C[C(Me)═NR]═NR}] (X = Me **13**, Cl **14**, OMe **15**, O$^t$Bu **16**, NH$^t$Bu **17**). When compound **17** was heated at 140 °C for 3 days, an intramolecular proton migration occurred to give the $\eta^2$-diamidoalkene complex [TaCp*(N$^t$Bu){$\eta$-N$^t$Bu-C(NHR)═C(Me)-$\eta$-NR}], **18**. All of the new compounds were characterized by IR, $^1$H NMR, and $^{13}$C NMR spectroscopy, and the molecular structures of **14** and **18** were studied by X-ray diffraction methods.



## Introduction

Migratory insertion of carbon monoxide or isocyanides into M−X bonds (X = alkyl, hydrido, silyl, amido, phosphido) is one of the most exciting fields of research in organometallic chemistry because of the reactivity of the resulting products and their involvement in many stoichiometric and catalytic applications.[1] The insertion of isocyanides into early transition metal−alkyl bonds has been extensively studied in recent years because the resulting $\eta^2$-iminoacyl compounds are much more accessible and less reactive than the related $\eta^2$-acyl derivatives. Moreover, while further insertion of CO into the metal−carbon bond of $\eta^2$-acyl compounds is less known, insertion of isocyanides into metal−iminoacyl bonds has been observed, and many examples of the double insertion of isocyanides into the metal−carbon bond of $\eta^2$-iminoacyl ligands have been reported.[1−5] However, very few examples of this type of reaction have been reported for tantalum. An important study[5b] by Rothwell et al. describes the isolation of adducts containing two coupled isocyanides to give diazametallacycles with exocyclic ketene−imine or phosphine ligands bound to the electrophilic isocyanide carbon atom.

The insertion of CO and CNR into early transition metal−amido bonds has been less intensively studied, although participation of the analogous $\eta^2$-carbamoyl complexes in intramolecular alkylations and inter- and intramolecular coupling reactions, to give the amino counterparts of the dialkyl-$\eta^2$-imino and enediamido ligands, respectively, are important and potentially useful reactions that open new horizons in synthetic applications based on C−N bond formation processes.[1,6]

We reported the insertion of isocyanides into the tantalum−methyl bonds of various $\eta^5$-pentamethylcyclopentadienyl chloro methyl tantalum complexes[7] to

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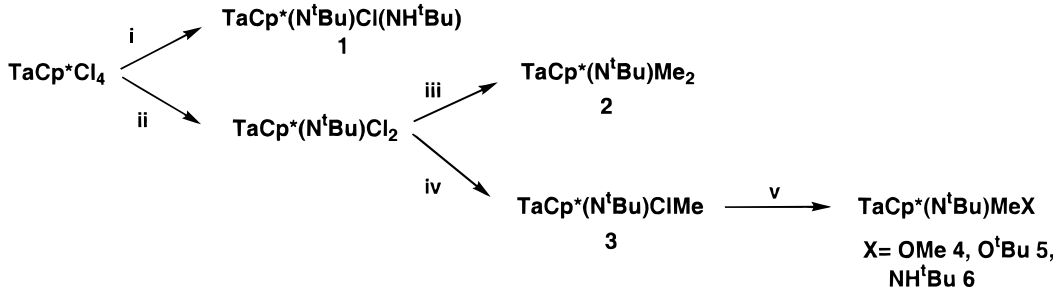
**Scheme 1**[a]




[a] Legend: (i) 3 LiNH$^t$Bu, $Et_2O$, 12 h; (ii) LiNH$^t$Bu, $Et_2O$; (iii) 2 LiMe, $Et_2O$, 4 h; (iv) $ZnMe_2$, toluene, 12 h; (v) MX (M = Li, X = O$^t$Bu, NH$^t$Bu; M = Na, X = OMe), $Et_2O$.

give azatantalacyclopropane derivatives, which were then converted into their imido and vinylamido compounds by further reactions with isocyanide. More recently we also reported the reactivity of related imido methyl−tantalum[8] and benzyl−niobium[9] compounds in similar carbon monoxide and isocyanide insertion reactions.

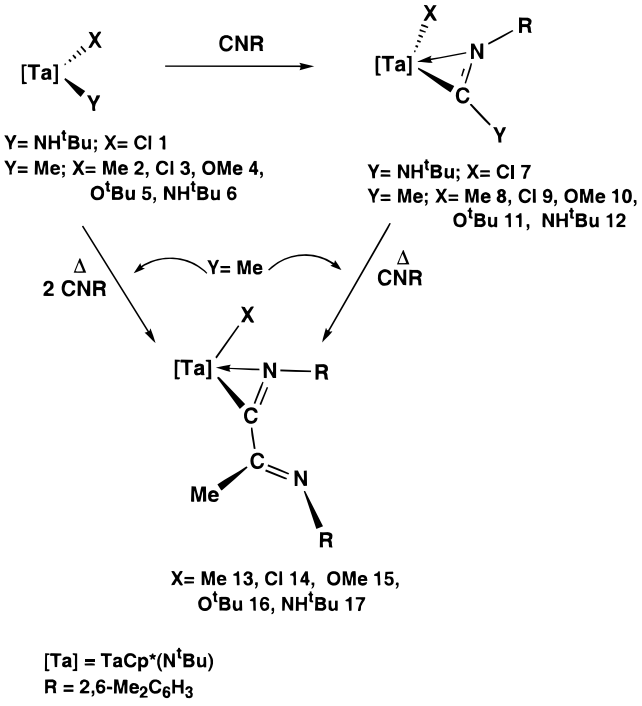
In this paper we report the synthesis of new methyl− and amido−tantalum complexes containing the imido $\eta^5$-pentamethylcyclopentadienyl tantalum moiety and the insertion of 2,6-dimethylphenylisocyanide into their tantalum−alkyl and tantalum−amido bonds to give new products resulting from single and double insertion reactions.

## Results and Discussion

The reactivity of a metal−alkyl bond to migratory insertion of CO or isocyanides and the stability of the resulting $\eta^2$-acyl and $\eta^2$-iminoacyl products are greatly influenced by the nature of the other substituents on the metal. We reported[8] that insertion of CO into the Ta−Me bond of complexes of the type [Ta]MeX, where [Ta] = [TaCp*{N(2,6-$Me_2C_6H_3$)}], gave enediolate derivatives when X = Me, whereas it resulted in exchange of the imido group by the oxo group with formation of the oxo-$\eta^2$-iminoacyl derivative when X = Cl. This moved us to study related reactions with isocyanide using different X substituents in order to compare their behavior. The migratory insertion in all of these formally 16-electron compounds proceeds by coordination of the isocyanide and further migration of methyl to the electrophilic isocyanide carbon atom to give the iminoacyl derivative, which is then $\eta^2$-coordinated to complete the 18-electron configuration. The reactivity should thus be influenced by the acidity of the metal center, which can be modified by the electron-releasing and $\pi$-bond-donating capacity of the X substituent as well as by its steric demand. To study the influence of different X substituents, we isolated some new [TaCp*(N$^t$Bu)MeX] complexes to complete a series together with the already reported[10] dimethyl complex [TaCp*(N$^t$Bu)$Me_2$].

The new imido−amido derivative [TaCp*(N$^t$Bu)Cl(NH$^t$Bu)], **1**, obtained from the reaction of [TaCp*$Cl_4$] with 3 equiv of LiNH$^t$Bu in ethyl ether was used as a starting material. Methylation[10] of the dichloro compound [TaCp*(N$^t$Bu)$Cl_2$] with 2 equiv of LiMe gave the dimethyl derivative [TaCp*(N$^t$Bu)$Me_2$], **2**, whereas selective monoalkylation to give [TaCp*(N$^t$Bu)ClMe], **3**, resulted when 1 equiv of $ZnMe_2$ was used as the alkylating agent (Scheme 1). Metathetical replacement of the chloro group by different substituents was achieved by reaction of complex **3** with 1 equiv of lithium (O$^t$Bu, NH$^t$Bu) or sodium (OMe) MX salts to give the new compounds [TaCp*(N$^t$Bu)MeX] (X = OMe **4**, O$^t$Bu **5**, NH$^t$Bu **6**).

**Scheme 2**




The amido compound **1** and all of the new methyl complexes **3**−**6** were isolated as air-sensitive yellow-brown oils, thermally stable for long periods under a dry inert atmosphere ($N_2$, Ar) at room temperature. They were identified as pure compounds by $^1$H and $^{13}$C NMR spectroscopy, although not entirely satisfactory analytical data were obtained for compounds **1** and **4**−**6** (see Experimental Section).

Reaction of the amido complex **1** with 1 equiv of the isocyanide CNR (R = 2,6-$Me_2C_6H_3$) in hexane afforded the $\eta^2$-iminocarbamoyl compound [TaCp*(N$^t$Bu)Cl{$\eta^2$-C(NH$^t$Bu)═NR}], **7**, and similar reactions of the methyl derivatives gave the $\eta^2$-iminoacyl compounds [TaCp*-

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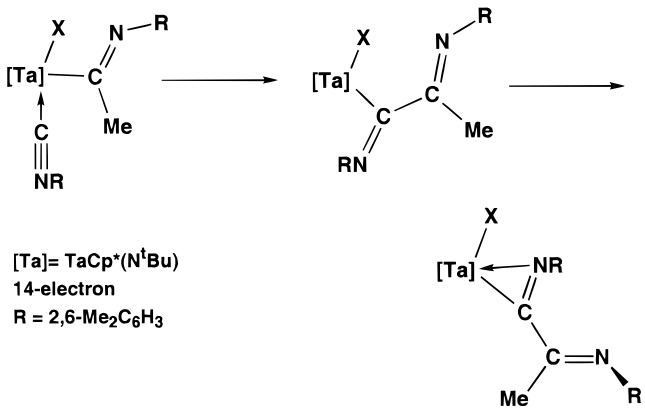
(N$^t$Bu)X{$\eta^2$-C(Me)═NR}] (X = Me **8**, Cl **9**, OMe **10**, O$^t$Bu **11**, NH$^t$Bu **12**) (see Scheme 2).

Insertion into the Ta−Me bond is almost immediate at room temperature for methyl **2**, chloro **3**, and methoxo **4** derivatives, although complex **10** could not be obtained free of a small amount of **4** and **15** (see below). Clearly, the presence of potential $\pi$-donor ligands such as Cl or OMe, which have the capacity to block the empty metal orbital required to allow the isocyanide to coordinate, does not significantly influence the insertion reaction. However, the insertion reaction using the *tert*-butyloxo complex **5** was significantly slower and **11** was obtained after stirring for 7 h at room temperature. Heating the amido complex **6** with 1 equiv of CNR for 3 days at 75 °C in $C_6D_6$ resulted in only partial formation of **12**, which could not be isolated, as evidenced by $^1$H and $^{13}$C NMR. This behavior indicates that the higher steric demand of the more bulky $^t$Bu substituent in the alkoxo **5** and amido **6** ligands hinders coordination of the isocyanide and slows down the insertion process. Insertion into the Ta−NH$^t$Bu bond of **1** was slower than insertion into the Ta−Me bond of **3**, and the quantitative transformation required 7 h stirring at room temperature. Furthermore, in complex **6**, which has both Ta−Me and Ta−NH$^t$Bu bonds, the insertion reaction occurred preferentially at the Ta−Me bond, indicating a higher activation energy for insertion into the Ta−N bond.

NMR evidence suggests that the iminoacyl ligand in all of these compounds is coordinated in an $\eta^2$ fashion, probably with the nitrogen atom occupying the central position in the equatorial plane.[11] The $^{13}$C resonance observed between $\delta$ 243 and $\delta$ 253 is consistent with an iminoacyl sp$^2$ carbon atom, while the $^1$H resonance of the inserted methyl group observed between $\delta$ 2.40 and $\delta$ 2.56 is displaced to low field. The $^{13}$C resonance of the $\eta^2$-iminocarbamoyl sp$^2$ carbon atom in complex **7** at $\delta$ 203.1 indicated an even more significant effect attributable to the presence of the more nucleophilic amino substituent. The $\nu$(CN) IR stretching vibration is lower for the $\eta^2$-iminocarbamoyl complex **7** (1540 cm$^{-1}$) than for the $\eta^2$-iminoacyl compounds (1616−1597 cm$^{-1}$), indicating that the different electron distribution in **7** modifies the C═N bond order.

The $\eta^2$-iminoacyl compounds **8**−**11** are air stable, whereas the $\eta^2$-iminocarbamoyl derivative **7** is air sensitive and must be manipulated under an inert atmosphere. Complexes **7**−**11** are all very soluble in the usual organic solvents and most are thermally stable, with the exception of **7**, which decomposes when heated above 120 °C. Complex **12** also decomposes by heating at 90 °C. We reported that when the related methyl−iminoacyl complexes were heated, a double migration of the methyl group occurred to give $\eta^2$-imino derivatives;[7] a similar transformation did not occur when **8** was heated. However a further double insertion into the Ta−iminoacyl bond was observed (see Scheme 2) when complexes **8**−**11** were treated with an additional 1 equiv of the isocyanide CNR (R = 2,6-Me$_2$C$_6$H$_3$) or when 2 equiv of CNR was added to compounds **2**−**6** under identical conditions, giving white to yellow solids identified as the double insertion imine−$\eta^2$-iminoacyl products [TaCp*(N$^t$Bu)X{$\eta^2$-C[C(Me)═NR]═NR}] (X = Me **13**, Cl **14**, OMe **15**, O$^t$Bu **16**, NH$^t$Bu **17**) by elemental analyses, $^1$H and $^{13}$C NMR spectroscopy, and a molecular structure determination of **14**. This reaction is rapid for complex **10**, which was easily and completely converted into **15** at room temperature. This rapid transformation explains how small amounts of **15** are formed even when a 1:1 molar ratio of the isocyanide was used. However the same reaction is much slower and was not observed at room temperature for any of the other complexes, their solutions required heating in sealed tubes under various conditions to effect the transformation. Compound **8** was the most reactive species and was quantitatively transformed into **13** after 14 h at 120 °C, whereas **9** and **11** required 3 days at 150 °C and 2 days at 120 °C, respectively. **17** was obtained after heating **6** with 2 equiv of CNR for 3 days at 75 °C.

**Scheme 3**




These results cannot be explained by the coordination of the isocyanide at the electrophilic carbon of the $\eta^2$-iminoacyl ligand observed by Rothwell et al.,[5b] which would lead to an amido keteneimine compound. The alternative pathway proposed for this reaction is shown in Scheme 3.

The initial transformation of the $\eta^2$-iminoacyl complex into the 16-electron $\eta^1$-iminoacyl species with coordination of the isocyanide to the metal center, followed by migration of the $\eta^1$-iminoacyl ligand, would give an imine−$\eta^1$-iminoacyl derivative. The results observed indicate that this reaction is favored by the presence of $\pi$-donor ligands such as OMe, which enhance the transformation of $\eta^2$- into $\eta^1$-iminoacyl and favor coordination of the isocyanide. However the steric demands of bulky substituents also have an important influence and would justify the lower reactivity observed for the O$^t$Bu derivative. Further $\eta^2$-coordination of the imine−$\eta^1$-iminoacyl ligand takes place through the $\beta$-nitrogen to give the imine−$\eta^2$-iminoacyl compound. Under our experimental conditions we have never observed the incorporation of a third isocyanide when excess isocyanide was used, as evidenced by the elemental analyses of the isolated compounds. This can probably be attributed to both the steric demands of the ligand and the fact that the temperatures the reaction would require would cause decomposition, which occurs at 130 °C for **13**, 160 °C for **14**, 130 °C for **15**, 170 °C for **16**, and 90 °C for **17**. We did not study reactions with less

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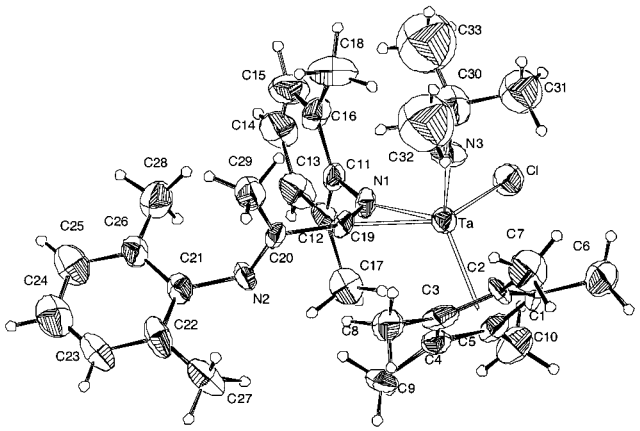


**Figure 1.** ORTEP view of the molecular structure of the complex **14** with the atom-numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

bulky or more electrophilic isocyanides, which could lead to further insertions,[4] coupling,[5,12] or polymerization[13] processes.

The $^{13}C$ NMR spectra observed for compounds **13**−**17** are consistent with their formulation as compounds containing the imine−$\eta^2$-iminoacyl ligand. They showed one resonance between $\delta$ 238.2 and $\delta$ 247.2 due to the metal-coordinated iminoacyl carbon, which is sensitive to the nature of the other metal substituents, and one resonance between $\delta$ 168.6 and $\delta$ 173.2 due to the noncoordinated imino carbon, which is much less sensitive to the metal substituents. Higher field resonances with less diverse chemical shifts would be expected for cyclic imino−$\eta$-alkyl−$\eta$-imine compounds,[2,3] and very different chemical shifts should be observed if the second isocyanide were not inserted but simply coordinated to the metal.[14]

No second migration of the remaining methyl group of **13** or the amido group of **17** was observed under these conditions. This proposal was confirmed by an X-ray study of complex **14**.

A view of the molecular structure of complex **14** is shown in Figure 1 together with the atomic labeling system. Selected bond distances and angles are given in Table 1.

The tantalum atom is bound to a pentamethylcyclopentadienyl ring [Ta−CE(1) = 2.15(2) Å, CE(1) being the centroid of the ring], to a chlorine atom [Ta−Cl = 2.405(5) Å], to an imido ligand [Ta−N(3) = 1.790(15) Å], and to the carbon and nitrogen atoms from the imine−$\eta^2$-*C,N*-iminoacyl ligand [Ta−C(l9) = 2.14(2) and Ta−N(1) = 2.161(14) Å]. The coordination geometry around the Ta atom can be described as pseudotetrahedral if the centroid of the Cp* ring and the midpoint M(1) of the imine C(19)−N(1) double bond

**Table 1. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for Compound 14[a]**

| | | | |
|---|---|---|---|
| Ta−Cl | 2.405(5) | Ta−C(4) | 2.52(2) |
| Ta−N(3) | 1.790(15) | Ta−C(5) | 2.53(2) |
| Ta−N(1) | 2.161(14) | N(3)−C(30) | 1.43(3) |
| Ta−C(19) | 2.14(2) | N(1)−C(19) | 1.25(2) |
| Ta−CE(1) | 2.15(2) | N(1)−C(11) | 1.44(2) |
| Ta−M(1) | 2.060(14) | C(19)−C(20) | 1.47(2) |
| Ta−C(1) | 2.44(2) | N(2)−C(20) | 1.24(2) |
| Ta−C(2) | 2.38(2) | N(2)−C(21) | 1.41(2) |
| Ta−C(3) | 2.41(2) | C(20)−C(29) | 1.51(3) |
| CE(1)−Ta−Cl | 107.2(5) | N(3)−Ta−C(19) | 99.5(7) |
| CE(1)−Ta−N(3) | 122.2(8) | Ta−N(1)−C(19) | 72.4(11) |
| CE(1)−Ta−M(1) | 118.6(7) | Ta−N(1)−C(11) | 156.4(12) |
| Cl−Ta−N(3) | 100.2(6) | C(11)−N(1)−C(19) | 130.2(15) |
| Cl−Ta−M(1) | 100.8(5) | Ta−C(19)−N(1) | 73.9(10) |
| N(3)−Ta−M(1) | 104.3(7) | Ta−C(19)−C(20) | 159.6(15) |
| CE(1)−Ta−N(1) | 124.6(6) | N(1)−C(19)−C(20) | 126.5(17) |
| CE(1)−Ta−C(19) | 110.4(7) | C(19)−C(20)−N(2) | 120.1(16) |
| N(1)−Ta−C(19) | 33.6(6) | C(19)−C(20)−C(29) | 113.6(16) |
| Cl−Ta−N(1) | 84.1(4) | N(2)−C(20)−C(29) | 126.3(17) |
| Cl−Ta−C(19) | 117.7(5) | C(20)−N(2)−C(21) | 123.4(16) |
| N(3)−Ta−N(1) | 107.8(7) | Ta−N(3)−C(30) | 174.7(17) |

[a] CE(1) is the centroid of the C(1)···C(5) cyclopentadienyl ring and M(1) the midpoint of the N(1)−C(19) double bond.

[Ta−M(1) = 2.060(14) Å] are considered as coordination sites. The complex is chiral, and both enantiomers are present in the crystals (in Figure 1 the T-4(*R*) enantiomer is shown). The *inside* coordination of the iminoacyl N(1) located between C(19) and Cl is similar to that found[8] for the related iminoacyl derivative [TaCp*Me(NR)($\eta^2$-CMe=NR)] (R = 2,6-$Me_2C_6H_3$). The Cp* ring is not coordinated in a symmetric $\eta^5$-fashion; a slight trend toward the $\eta^3$-coordination is observed, as indicated by three short and two long Ta-to-$C_{Cp^*}$ ring carbon distances [Ta−C(l) = 2.44(2), Ta−C(2) = 2.38(2), Ta−C(3) = 2.41(2), Ta−C(4) = 2.52(2), and Ta−C(5) = 2.53(2) Å] involving the two carbon atoms trans to the imido ligand. In the complex the imido N(3) atom eclipses the C(2) atom of the Cp* ($\tau$[C(2)−CE(1)−Ta−N(3)]= −5(2)°), and this conformation leads to a greater bending of the eclipsed ring substituent away from the imido group, as observed in the half-sandwhich imido complexes of niobium and tantalum [M($\eta^5$-$C_5R_5$)(NR′)$Cl_2$] (M = Nb, Ta; R = H, Me; R′ = Me, $^t$Bu, $C_6H_3Pr^i_2$-2,6).[15] In fact the maximum deviation of the methyl carbon atoms from the cyclopentadienyl ring is observed for the C(7) atom [0.28(2) Å]. The value of the Ta−N(3) bond length, 1.790(15) Å, consistent with a triple bond character, and the nearly linear Ta−N(3)−C(3) angle of 174.7(17)° are those expected for an imido ligand and are strictly comparable with those found for the same ligand in complex **18** (see below). The 1,4-diaza-1,3-butadiene fragment exibits the $\eta^2$-*C,N*-imine mode D[16] as found in [Cp*Ta($^t$Bu$_2$-dad)(S$^t$Bu)$_2$] (dad = 1,4-diaza-1,3-butadiene).[17] The Ta−C(19) bond distance, 2.14(2) Å, is comparable to that found, 2.188(9) Å, in the imido iminoacyl complex [TaCp*Me(NAr)($\eta^2$-NAr=CCMe$_2$-CMe=NAr)][7c] (Ar = 2,6-$Me_2C_6H_3$) and in the azatantalacyclopropane ligand in [TaCp*Me$_2$($\eta^2$-Me$_2$CNAr)], 2.209(6) Å.[7b] The value of the Ta−N(1) bond length, 2.161(14)

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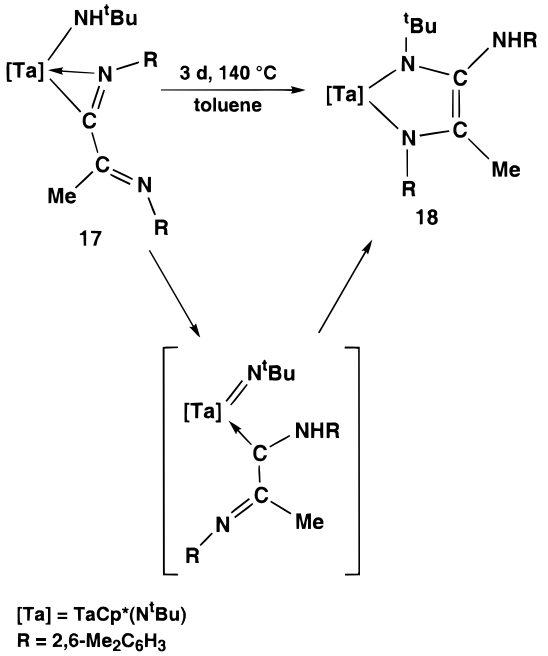
**Scheme 4**




Å, is in agreement with that found in the above-mentioned imido imino iminoacyl tantalum complex, 2.148(7) Å.[7c] The values of the N(1)−C(19) and N(2)−C(20) bond lengths, 1.25(2) and 1.24(2) Å, respectively, are consistent with a double bond character, and the two double bonds are not conjugated ($\tau$[N(1)−C(19)−C(20)−N(2)] = 65(3)°). The C(11)N(1)C(19)C(20) moiety forms dihedral angles of 4.7(8)° and 86.1(6)° with the TaN(1)C(19) and the aryl groups, respectively, and the C(29)C(19)C(20)N(2)C(21) fragment forms an angle of 87.1(8)° with the phenyl ring C(21)···C(26). The phenyl rings C(11)···C(16) and C(21)···C(26) are almost perpendicular one to another (dihedral angle 81.3(6)°).

When compound **17** was heated at 140 °C for 3 days, the iminoacyl ligand rearranged to give a new cyclic alkenediamido product [TaCp*(N$^t$Bu){$\eta$-N$^t$Bu-C(NHR)═C(Me)-$\eta$-NR}] (R = 2,6-Me$_2$C$_6$H$_3$), **18**, isolated as yellow crystals, which were characterized by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction methods (see Scheme 4). The most significant features of this diazabutadiene derivative are the $^{13}$C resonance due to the amino-substituted carbon, which was greatly displaced to high field ($\delta$ 104.9), and the IR absorption band observed at 1594 cm$^{-1}$ due to the $\nu$(C═C) stretching vibration.

This rearrangement could be explained by assuming the intermediate formation of a diimido amino−carbene species whose formation would result from proton transfer from the amido to the imino group, followed by attack of the imido ligand at the electrophilic carbene carbon, as shown in Scheme 4. However we have no experimental data for this proposal because no intermediate was observed when the reaction was monitored by NMR spectroscopy.

The molecular structure of complex **18** is shown in Figure 2 together with the atomic labeling system. Selected bond distances and angles are given in Table 2.

The tantalum atom is bound to a pentamethylcyclopentadienyl ring [Ta−CE(1) = 2.222(6) Å, CE(1) being

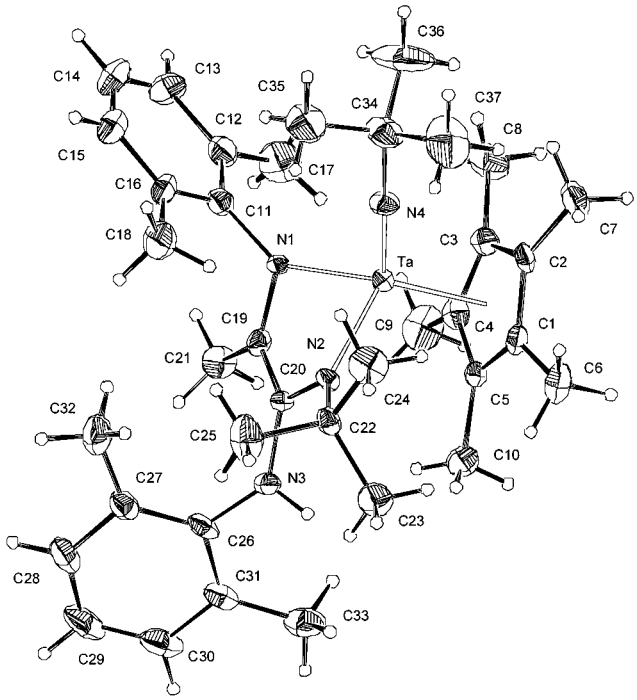



**Figure 2.** ORTEP view of the molecular structure of the complex **18** with the atom-numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for Compound 18[a]**

| | | | |
|---|---|---|---|
| Ta−N(1) | 1.997(4) | N(4)−C(34) | 1.463(7) |
| Ta−N(2) | 2.072(4) | N(1)−C(19) | 1.386(7) |
| Ta−N(4) | 1.772(5) | C(19)−C(20) | 1.397(7) |
| Ta−CE(1) | 2.222(6) | N(2)−C(20) | 1.374(6) |
| Ta−C(1) | 2.490(6) | N(3)−C(20) | 1.429(7) |
| Ta−C(2) | 2.488(6) | N(1)−C(11) | 1.442(7) |
| Ta−C(3) | 2.486(6) | N(2)−C(22) | 1.510(7) |
| Ta−C(4) | 2.586(6) | N(3)−C(26) | 1.423(7) |
| Ta−C(5) | 2.571(6) | C(19)−C(21) | 1.535(7) |
| CE(1)−Ta−N(1) | 123.5(2) | Ta−N(2)−C(22) | 136.2(3) |
| CE(1)−Ta−N(2) | 115.9(2) | C(20)−N(2)−C(22) | 124.4(4) |
| CE(1)−Ta−N(4) | 118.8(2) | N(1)−C(19)−C(20) | 116.9(5) |
| N(1)−Ta−N(2) | 82.5(2) | N(1)−C(19)−C(21) | 120.3(5) |
| N(1)−Ta−N(4) | 101.4(2) | C(20)−C(19)−C(21) | 122.7(6) |
| N(2)−Ta−N(4) | 108.6(2) | N(2)−C(20)−C(19) | 118.6(5) |
| Ta−N(1)−C(19) | 100.0(3) | N(2)−C(20)−N(3) | 118.1(5) |
| Ta−N(1)−C11) | 139.4(4) | C(19)−C(20)−N(3) | 122.9(5) |
| C(11)−N(1)−C(19) | 120.2(4) | C(20)−N(3)−C(26) | 133.0(5) |
| Ta−N(2)−C(20) | 99.4(4) | Ta−N(4)−C(34) | 173.3(5) |

the centroid of the ring] and to three nitrogen atoms: N(4) from the imido ligand and N(1) and N(2) from the enediamido ligand. The complex can be described as pseudo-tetrahedral if the centroid of the Cp* ring CE(1) is considered as occupying a coordination site and is chiral. In the crystals both enantiomers are present (in Figure 2 the T-4(*R*) enantiomer is shown) due to the centrosymmetric space group. The Cp* ring is again not coordinated in an ideal $\eta^5$-fashion; a slight trend toward the $\eta^3$-coordination is still observed, leading to three short and two long Ta−C$_{Cp*}$ ring carbon distances [Ta−C(l) = 2.490(6), Ta−C(2) = 2.488(6), Ta−C(3) = 2.486(6), Ta−C(4) = 2.586(6), and Ta−C(5) = 2.571(6) Å]. In the complex the imido N(4) atom again eclipses the C(2) atom of the Cp* ($\tau$[C(2)−CE(1)−Ta−N(4)] = 6.3(5)°), and a greater bending of the eclipsed ring substituent away from the imido group is observed. In fact the largest deviations of the methyl carbon atoms from the cyclo-

pentadienyl ring are 0.236(6) Å for C(7) and 0.237(6) Å for C(9). This last bending is due to the nearly eclipsed conformation of C(4) (from Cp*) and the amido N(1) atoms ($\tau$[C(4)−CE(1)−Ta−N(1)] = −8.5(5)°). The longest Ta−$C_{Cp^*}$ bonds involve again the two carbon atoms trans to the imido ligand. The Ta−N(4) bond length, 1.772(5) Å, lies within the range expected for a triple bond and is comparable with the values of the Ta−imido nitrogen values found in **14**, 1.790(15) Å, in [TaCp*(*N*-$C_6H_3{}^iPr_2$-2,6)$Cl_2$],[15] 1.780(5) Å, in [TaCp*$Cl_2$(NAr)],[7a] 1.774(5) Å, in [TaCp*Me(NAr){N(Ar)C(Me)=$CMe_2$}],[7c] 1.784(4) Å, in [TaCp*Me(NAr)($\eta^2$-NAr=$CCMe_2$CMe=NAr)],[7c] 1.812(8) Å, and in [TaCp*(NAr)($CH_2$=$CH_2$)($PMe_3$)],[18] 1.833(4) Å (Ar = 2,6-$Me_2C_6H_3$). The Ta−N(4)−C(34) angle is almost linear, 173.3(5)°.

The slightly asymmetric Ta−N(1) and Ta−N(2) bond lengths, 1.997(4) and 2.072(4) Å, present a certain degree of double bond character and are comparable to those found in other tantalum amido derivatives such as [TaCp*$Me_2$($\eta^2$-$Me_2$CNAr)],[7b] 1.930(4) Å, [TaCp*$Cl_3$-{$\eta^2$-N(Ar)($CMe_2$CNHAr)}],[7c] 2.029(3) Å, and [TaCp*Me-(NAr){N(Ar)(CMe=$CMe_2$)}],[7c] 2.050(5) Å. The tantalum−amido nitrogen bond lengths agree well with those found in the substituted 1,4-diaza-1,3-butadiene (dad) chloro, methyl, alkynyl, and benzyl CpTa and Cp*Ta complexes, in the range 2.000(4)−2.046(3) Å[17] and 2.004(5)−2.064(4) Å,[16] respectively.

These Ta−N amido distances are shorter than those found in the dad butadiene tantalum complexes [TaCp*($\eta^2$-*N,N′-p*-$MeOC_6H_4$-dad)($\eta^4$-*s-cis*-1,3-butadiene)],[16] 2.128(4) and 2.128(4) Å, and in [TaCp*($\eta^2$-*N,N′*-Cy-dad)-($\eta^4$-*s-cis*-1,3-butadiene)],[16] 2.118(8) and 2.116(9) Å. The three N(1)−C(19), C(19)−C(20), and N(2)−C(20) bond distances, 1.386(7), 1.397(7), and 1.374(6) Å, are shorter, longer, and shorter than those expected for a single C−N, double C−C, and single C−N bond, respectively. The TaN(1)C(19)C(20)N(2) five-membered ring adopts an envelope conformation and is folded by 136.0(2)° along the N−N vector, with the Ta atom displaced by 1.062(1) Å from the mean plane through NCCN. This fold $\theta$ angle is larger than those found in the $\eta^4$-supine (in the range 118.4−121.1°) and $\eta^4$-prone (in the range 121.2−127.3°) conformations in the dad Ta complexes[16,17] and narrower than those found in the $\eta^2$-*N,N′*-enediamido dad Ta complexes,[16] in the range 154.9(3)−155.9-(3)°. The distances Ta−C(19) and Ta−C(20), 2.621(5) and 2.667(5) Å, are longer than those found in the $\eta^4$-dad complexes, in the range 2.430(5)−2.555(6) Å. The N−C−C−N fragment assumes a slightly prone conformation ($\tau$[CE(1)−Ta−N(1)−C(19)] = 76.0(4)°, ($\tau$[CE(1)−Ta−N(2)−C(20] = −86.7(4)°).

The dihedral angle between the planes TaC(19)C(20) and N(1)C(19)C(20)N(2)C(21)N(3) is only 27.0(2)°. All these structural features prevent some $\pi$-donation of the C=C bond, which was found weaker in the prone than in the supine conformation. All the above-mentioned arguments indicate that the new $\eta^2$-enediamido ligand exibits a coordination mode A,[16] with some contribution of the structure C.[16] The sums of the three angles around the N(1) and N(2) atoms are 359.6° and 360.0°, indicating a planar geometry as in the prone conformation, and this trigonal planar geometry is preferred to make the p$\pi$−d$\pi$ interaction with the metal center.

## Conclusions

Insertion of 2,6-dimethylphenylisocyanide into the Ta−Me bond of complexes [TaCp*($N^tBu$)MeX] is dependent on the nature of the substituent X and yields $\eta^2$-iminoacyl [TaCp*($N^tBu$)X{$\eta^2$-[C(Me)=NR]}] derivatives.

The influence of $\pi$-donor ligands on the insertion process is less significant than their steric requirement, which hinders the coordination of the isocyanide to the metal center. Under appropriate thermal conditions a second insertion into the Ta−iminoacyl bond also takes place through the coordination of the isocyanide to the metal after a preliminary transformation of the $\eta^2$- into $\eta^1$-iminoacyl ligand. This step is also dominated by the steric demands of the remaining ligand.

The presence of the imido ligand is also significant because the double insertion does not take place for the weaker $\pi$-donor [N(2,6-$Me_2C_6H_3$)] ligand,[8] probably due to a stronger interaction of the $\eta^2$-iminoacyl ligand in the resulting product.

## Experimental Section

**General Comments.** All operations were carried out under a dry argon atmosphere either in a Vacuum Atmosphere Drilab or by standard Schlenck techniques. Hydrocarbon solvents were dried and freshly distilled: *n*-hexane from sodium potassium alloy and toluene from sodium. Reagent grade CN-(2,6-$Me_2C_6H_3$) (Fluka) and NaOMe (Fluka) were purchased form commercial sources and used without further purification. The starting complexes [TaCp*$Cl_4$],[19] [TaCp*($N^tBu$)$Cl_2$],[20] and [TaCp*($N^tBu$)$Me_2$][10] were synthesized by reported methods and LiX (X = $O^tBu$, $NH^tBu$) were obtained by deprotonating the alcohol or amine with LiBu in *n*-hexane. Infrared spectra were recorded on a Perkin-Elmer 583 spectrophotometer (4000−200 $cm^{-1}$). $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity VXR 300 MHz instrument, and chemical shifts were measured relative to residual $^1H$ and $^{13}C$ resonances in the deuterated solvents $C_6D_6$ ($\delta$ 7.15), $CDCl_3$ ($\delta$ 7.24) and $C_6D_6$ ($\delta$ 128), $CDCl_3$ ($\delta$ 77). C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer.

**[TaCp*($N^tBu$)Cl($NH^tBu$)] (1).** A solution of [TaCp*$Cl_4$] (1.00 g, 2.18 mmol) and 3 equiv of Li$NH^tBu$ (0.51 g, 6.55 mmol) in $Et_2O$ (20 mL) was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the oily residue was extracted into pentane (20 mL). Removal of the solvent gave **1** as a yellow oil (yield: 0.78 g, 72%).

Data for **1**: IR (KBr, $\nu$, $cm^{-1}$): 3330 (w), 1356 (s). $^1H$ NMR ($CDCl_3$; $\delta$, ppm): 5.64 (s, 1H, N*H*), 2.07 (s, 15H, $C_5Me_5$), 1.29 (s, 9H, C$Me_3$), 1.22 (s, 9H, C$Me_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; $\delta$, ppm): 116.8 ($C_5Me_5$), 65.0 (Ta=N$CMe_3$), 55.7 (Ta=NH$CMe_3$), 34.3 (C$Me_3$), 33.3 (C$Me_3$), 11.6 ($C_5Me_5$). Anal. Calcd for $C_{18}H_{34}$-$ClN_2Ta$: C, 43.68; H, 6.94; N, 5.66. Found: C, 42.40; H, 6.11; N, 5.23.

**[TaCp*($N^tBu$)ClMe] (3).** A 2.0 M toluene solution of $ZnMe_2$ (2.50 mL, 5.00 mmol) was added to a solution of [TaCp*($N^t$-Bu)$Cl_2$] (2.00 g, 4.36 mmol) in toluene (15 mL). The solution, which turned immediately cloudy, was stirred overnight at room temperature. The volatiles were removed in vacuo, and *n*-hexane (15 mL) was added to give a solution, which after

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filtration and removal of solvent in vacuo rendered compound **3** as a yellow oil (yield: 1.43 g, 75%).

Data for **3**: IR (CsI, $\nu$, cm$^{-1}$): 1275 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 2.07 (s, 15H, $C_5Me_5$), 1.19 (s, 9H, C$Me_3$), 0.40 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 117.2 ($C_5Me_5$), 64.8 ($C$Me$_3$), 37.6 (Ta−*Me*), 33.0 (C$Me_3$), 11.5 ($C_5Me_5$). Anal. Calcd for $C_{15}H_{27}ClNTa$: C, 41.15; H, 6.23; N, 3.20. Found: C, 41.19; H, 6.11; N, 3.53.

**[TaCp*(N$^t$Bu)Me(OMe)] (4).** A mixture of **3** (2.00 g, 4.57 mmol) and NaOMe (0.24 g, 4.57 mmol) was stirred in $Et_2O$ (40 mL) for 16 h at room temperature. The solvent was removed in vacuo, and the residue was extracted into *n*-hexane (20 mL) to give a solution, which gave **4** as a dark oil after removal of the solvent in vacuo (yield: 1.76 g, 89%).

Data for **4**: IR (CsI, $\nu$, cm$^{-1}$): 1279 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 4.34 (s, 3H, O*Me*), 1.99 (s, 15H, $C_5Me_5$), 1.22 (s, 9H, C$Me_3$), 0.10 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 115.5 ($C_5$Me$_5$), 65.6 (O*Me*), 63.8 ($C$Me$_3$), 33.8 (C$Me_3$), 22.5 (Ta−*Me*), 11.0 ($C_5Me_5$). Anal. Calcd for $C_{16}H_{30}NOTa$: C, 44.34; H, 6.98; N, 3.23. Found: C, 43.79; H, 6.71; N, 3.00.

**[TaCp*(N$^t$Bu)Me(O$^t$Bu)] (5).** A mixture of **3** (2.00 g, 4.57 mmol) and LiO$^t$Bu (0.37 g, 4.57 mmol) was stirred in $Et_2O$ (40 mL) for 4 h at room temperature. The solvent was removed in vacuo, and the residue was extracted into *n*-hexane (20 mL). Compound **5** was isolated as a brown oil after removal of the solvent in vacuo (yield: 1.87 g, 86%).

Data for **5**: IR (CsI, $\nu$, cm$^{-1}$): 1350 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 1.99 (s, 15H, $C_5Me_5$), 1.24 (s, 9H, C$Me_3$), 1.12 (s, 9H, C$Me_3$), 0.04 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 115.3 ($C_5$Me$_5$), 77.0 (O$C$Me$_3$), 63.5 (N$C$Me$_3$), 33.7 (C$Me_3$), 32.6 (C$Me_3$), 21.1 (Ta−*Me*), 11.2 ($C_5Me_5$). Anal. Calcd for $C_{19}H_{36}NOTa$: C, 47.99; H, 7.65; N, 2.94. Found: C, 47.00; H, 7.43; N, 2.71.

**[TaCp*(N$^t$Bu)Me(NH$^t$Bu)] (6).** A mixture of **2** (2.00 g, 4.57 mmol) and LiNH$^t$Bu (0.36 g, 4.57 mmol) was stirred in $Et_2O$ (40 mL) for 4 h at room temperature. The solvent was removed in vacuo, and the residue was extracted into *n*-hexane (20 mL) to give **6** as a brown oil after removal of the solvent in vacuo (yield: 1.80 g, 84%).

Data for **6**: IR (CsI, $\nu$, cm$^{-1}$): 3250 (w), 1280 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 5.06 (s, 1H, N*H*), 1.98 (s, 15H, $C_5Me_5$), 1.22 (s, 9H, C$Me_3$), 1.16 (s, 9H, C$Me_3$), −0.21 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 113.9 ($C_5$Me$_5$), 64.0 (Ta=N$C$Me$_3$), 54.6 (NH$C$Me$_3$), 34.6 (C$Me_3$), 33.6 (C$Me_3$), 19.2 (Ta−*Me*), 11.3 ($C_5Me_5$). Anal. Calcd for $C_{19}H_{37}NOTa$: C, 48.09; H, 7.88; N, 5.90. Found: C, 47.29; H, 7.71; N, 5.78.

**[TaCp*(N$^t$Bu)Cl{$\eta^2$-C(NH$^t$Bu)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (7).** A solution of [TaCp*(N$^t$Bu)Cl(NH$^t$Bu)] **1** (1.00 g, 2.02 mmol) in *n*-hexane (20 mL) was treated with CNR (0.28 g, 2.13 mmol), and the mixture was stirred for 7 h at room temperature. Formation of a dark precipitate was observed. The solution was filtered off, and the solid residue was extracted into *n*-hexane (2 × 25 mL). The solution was concentrated to ca. 10 mL and cooled to −30 °C to give **7** as white crystals (yield: 1.09 g, 86%).

Data for **7**: IR (KBr pellets, $\nu$, cm$^{-1}$): 3200 (w), 1540 (s), 1260 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 6.99 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$), 5.75 (s, 1H, N*H*), 2.19 (s, 15H, $C_5Me_5$), 2.15 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 2.00 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.46 (s, 9H, C$Me_3$), 1.13 (s, 9H, C$Me_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 203.1 ($C$[NH$^t$Bu]NR), 139.8, 133.4, 132.4, 128.6, 127.8, 125.4 (2,6-Me$_2$*C*$_6$H$_3$), 116.6 ($C_5$Me$_5$), 65.7 (N$C$Me$_3$), 52.8 (NH$C$Me$_3$), 32.9 (C$Me_3$), 31.3 (C$Me_3$), 19.7 (2,6-*Me*$_2$C$_6$H$_3$), 19.0 (2,6-*Me*$_2$C$_6$H$_3$), 12.4 ($C_5Me_5$). Anal. Calcd for $C_{27}H_{43}ClN_3Ta$: C, 51.79; H, 6.94; N, 6.71. Found: C, 51.57; H, 6.91; N, 6.64.

**[TaCp*(N$^t$Bu)Me{$\eta^2$-C(Me)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (8).** *n*-Hexane (15 mL) was added to a mixture of [TaCp*(N$^t$Bu)-Me$_2$], **2** (1.00 g, 2.40 mmol), and CNR (0.31 g, 2.40 mmol), and the solution was stirred for 1 h at room temperature. The solution was filtered, and the solvent was removed in vacuo to yield **8** as a pale orange oil (yield: 1.21 g, 92%).

Data for **8**: IR (CsI, $\nu$, cm$^{-1}$): 1612 (s), 1268 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 6.97 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$), 2.46 (s, 3H, C(*Me*)-NR), 2.03 (s, 15H, $C_5Me_5$), 1.99 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.80 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 0.99 (s, 9H, C$Me_3$), −0.07 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 244.5 ($C$(Me)NR), 142.2, 130.3, 129.5, 128.1, 127.6, 125.2 (2,6-Me$_2$*C*$_6$H$_3$), 112.5 ($C_5$Me$_5$), 64.1 ($C$Me$_3$), 33.6 (C$Me_3$), 21.8 (C(*Me*)NR), 18.9 (2,6-*Me*$_2$C$_6$H$_3$), 18.7 (2,6-*Me*$_2$C$_6$H$_3$), 13.2 (Ta−*Me*), 11.6 ($C_5Me_5$). Anal. Calcd for $C_{25}H_{39}N_2Ta$: C, 54.73; H, 7.18; N, 5.11. Found: C, 54.12; H, 7.15; N, 5.17.

**[TaCp*(N$^t$Bu)Cl{$\eta^2$-C(Me)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (9).** *n*-Hexane (15 mL) was added to a mixture of [TaCp*(N$^t$Bu)-ClMe], **3** (1.00 g, 2.28 mmol), and CNR (0.32 g, 2.44 mmol), and the solution was stirred for 1 h at room temperature. Formation of a dark precipitate was observed. The solution was filtered off, and the solid residue was recrystallized from *n*-hexane (50 mL) by cooling at −30 °C to give **9** as a yellow solid (yield: 1.17 g, 90%).

Data for **9**: IR (KBr, $\nu$, cm$^{-1}$): 1616 (s), 1256 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 6.95 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$), 2.56 (s, 3H, C(*Me*)-NR), 2.12 (s, 15H, $C_5Me_5$), 2.08 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.92 (s, 3H, 2,6-Me$_2$C$_6$H$_3$), 1.06 (s, 9H, CMe$_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 243.7 ($C$(Me)NR), 140.4, 130.4, 130.0, 128.4, 127.8, 125.9 (2,6-Me$_2$*C*$_6$H$_3$), 115.4 ($C_5$Me$_5$), 65.4 ($C$Me$_3$), 33.8 (C$Me_3$), 22.4 (C(*Me*)NR), 19.1 (2,6-*Me*$_2$C$_6$H$_3$), 19.0 (2,6-*Me*$_2$C$_6$H$_3$), 11.9 ($C_5Me_5$). Anal. Calcd for $C_{24}H_{36}N_2ClTa$: C, 50.65; H, 6.39; N, 4.92. Found: C, 50.44; H, 6.26; N, 4.78.

**[TaCp*(N$^t$Bu)(OMe){$\eta^2$-C(Me)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (10).** *n*-Hexane (10 mL) was added to a mixture of [TaCp*(N$^t$-Bu)Me(OMe)], **4** (1.00 g, 2.31 mmol), and CNR (0.30 g, 2.31 mmol), and the solution was stirred for 1 h at room temperature. The solution was filtered and the volatiles were removed in vacuo to yield a residue that could not be purified by recrystallization. This residue contained **10** as the major component (>90% by $^1$H NMR).

Data for **10**: $^1$H NMR ($CDCl_3$; $\delta$, ppm): 6.97 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$), 3.98 (s, 3H, O*Me*), 2.43 (s, 3H, C(*Me*)NR), 2.13 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 2.09 (s, 15H, $C_5Me_5$), 1.98 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.08 (s, 9H, C$Me_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 252.6 ($C$(Me)NR), 143.6, 130.1, 129.3, 128.2, 127.7, 125.1 (2,6-Me$_2$*C*$_6$H$_3$), 114.8 ($C_5$Me$_5$), 65.5 (N$C$Me$_3$), 62.1 (O*Me*), 34.3 (C$Me_3$), 23.1 (C(*Me*)NR), 19.0 (2,6-*Me*$_2$C$_6$H$_3$), 18.8 (2,6-*Me*$_2$C$_6$H$_3$), 11.5 ($C_5Me_5$).

**[TaCp*(N$^t$Bu)(O$^t$Bu){$\eta^2$-C(Me)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (11).** *n*-Hexane (10 mL) was added to a mixture of [TaCp*(N$^t$-Bu)Me(O$^t$Bu)], **5** (1.00 g, 2.10 mmol), and CNR (0.29 g, 2.21 mmol), and the solution was stirred for 7 h at room temperature. Formation of a white precipitate was observed. The solvent was filtered off, and the solid residue was washed with *n*-pentane (15 mL) to yield **11** as yellow solid (yield: 1.06 g, 83%).

Data for **11**: IR (KBr, $\nu$, cm$^{-1}$): 1597 (s), 1263 (s). $^1$H NMR ($CDCl_3$; $\delta$, ppm): 6.97 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$), 2.40 (s, 3H, C(*Me*)-NR), 2.06 (s, 15H, $C_5Me_5$), 1.98 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.97 (s, 3H, 2,6-*Me*$_2$C$_6$H$_3$), 1.11 (s, 9H, C$Me_3$), 1.02 (s, 9H, C$Me_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$; $\delta$, ppm): 252.2 ($C$(Me)NR), 143.9, 130.7, 129.2, 127.6, 124.8 (2,6-Me$_2$*C*$_6$H$_3$), 114.5 ($C_5$Me$_5$), 73.1 (O$C$Me$_3$), 64.2 (N$C$Me$_3$), 34.4 (C$Me_3$), 32.8 (C$Me_3$), 23.8 (C(*Me*)NR), 19.1 (2,6-*Me*$_2$C$_6$H$_3$), 18.7 (2,6-*Me*$_2$C$_6$H$_3$), 11.7 ($C_5Me_5$). Anal. Calcd for $C_{28}H_{45}N_2OTa$: C, 55.43; H, 7.49; N, 4.62. Found: C, 55.35; H, 7.49; N, 4.48.

**[TaCp*(N$^t$Bu)(NH$^t$Bu){$\eta^2$-C(Me)=NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (12).** A $C_6D_6$ solution of [TaCp*(N$^t$Bu)Me(NH$^t$Bu)], **6** (0.20 g, 0.04 mmol), and CNR (0.005 g, 0.04 mmol) was prepared into a sealed NMR tube, and the reaction was monitored by $^1$H NMR. After 3 days at 75 °C the CNR signals disappeared, leaving a solution that contained **6**, **12**, and **17** (see below) in a 1:3:2 molar ratio.

Data for **12**: $^1$H NMR ($C_6D_6$; $\delta$, ppm): 4.15 (s, 1H, N*H*), 1.99 (s, 15H, $C_5Me_5$), 1.87 (s, 18H, C$Me_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$; $\delta$,

ppm): 240.9 (*C*(Me)NR), 115.0 ($C_5Me_5$), 64.9 (N*C*Me$_3$), 55.2 (NH*C*Me$_3$), 35.1 (C*Me$_3$*), 34.3 (C*Me$_3$*), 19.8 (*Me*), 19.5 (*Me*), 11.9 ($C_5$*Me$_5$*).

**[TaCp*(N$^t$Bu)Me{$\eta^2$-C[C(Me)═NR]═NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (13).** Toluene (15 mL) was added to a mixture of [TaCp*(N$^t$Bu)Me{$\eta^2$-C(Me)═NR}], **8** (1.00 g, 1.82 mmol), and CNR (0.25 g, 1.88 mmol) in an ampule with a Teflon cap, and the solution was heated at 120 °C for 14 h. After cooling at room temperature the solvent was removed in vacuo and the dark oily residue was recrystallized from *n*-hexane by cooling the solution at −30 °C to yield **13** as dark yellow crystals (0.90 g, 73%).

Data for **13**: IR (KBr, $\nu$, cm$^{-1}$): 1636 (s), 1580 (s), 1262 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.94 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 2.16 (s, 18H, C$_5$*Me$_5$* and 2,6-*Me$_2$*C$_6$H$_3$), 2.12, 1.97, 1.86 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.18 (s, 3H, C(*Me*)NR), 1.09 (s, 9H, C*Me$_3$*), 0.08 (s, 3H, Ta−*Me*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 239.6 (*C*[C(Me)NR]NR}), 170.0 (*C*(Me)NR), 148.0, 145.2, 130.5, 128.6, 128.0, 127.9, 127.4, 126.2, 125.4, 125.1, 123.1 (2,6-Me$_2$*C$_6$*H$_3$), 113.4 (*C*$_5$Me$_5$), 64.6 (*C*Me$_3$), 33.7 (C*Me$_3$*), 19.4, 19.1, 18.6, 17.6, 16.8 (2,6-*Me$_2$*C$_6$H$_3$ and C(*Me*)NR), 14.0 (Ta−*Me*), 11.8 (C$_5$*Me$_5$*). Anal. Calcd for C$_{34}$H$_{48}$N$_3$Ta: C, 60.07; H, 7.13; N, 6.18. Found: C, 59.76; H, 7.07; N, 6.13.

**[TaCp*(N$^t$Bu)Cl{$\eta^2$-C[C(Me)═NR]═NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (14).** Toluene (15 mL) was added to a mixture of [TaCp*(N$^t$Bu)Cl{$\eta^2$-C(Me)═NR}], **9** (1.00 g, 1.75 mmol), and CNR (0.27 g, 2.06 mmol) in a Carius tube, which was then sealed under vacuum. The Carius tube was heated in an autoclave at 145 °C for 3 days. After cooling at room temperature the solvent was removed in vacuo and the dark oily residue was recrystallized from *n*-hexane by cooling at −30 °C to yield **14** as yellow crystals (yield: 0.95 g, 77%).

Data for **14**: IR (KBr, $\nu$, cm$^{-1}$): 1638 (s), 1580 (s), 1256 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.80−7.00 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 2.22 (s, 15H, C$_5$*Me$_5$*), 2.17, 2.16, 2.04, 1.84 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.25 (s, 3H, C(*Me*)NR), 1.15 (s, 9H, C*Me$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 238.2 (*C*[C(Me)NR]NR}), 168.6 (*C*(Me)NR), 147.6, 142.2, 130.5, 128.9, 128.2, 128.0, 127.9, 127.7, 126.1, 125.0, 124.9, 123.4 (2,6-Me$_2$*C$_6$*H$_3$), 116.4 (*C*$_5$Me$_5$), 65.7 (*C*Me$_3$), 33.4 (C*Me$_3$*), 19.6, 19.5, 18.7, 18.0 (2,6-*Me$_2$*C$_6$H$_3$), 16.8 (C(*Me*)NR), 12.1 (C$_5$*Me$_5$*). Anal. Calcd for C$_{33}$H$_{45}$ClN$_3$Ta: C, 56.60; H, 6.49; N, 6.00. Found: C, 56.56; H, 6.43; N, 6.18.

**[TaCp*(N$^t$Bu)(OMe){$\eta^2$-C[C(Me)═NR]═NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (15).** *n*-Hexane (30 mL) was added to a mixture of [TaCp*(N$^t$Bu)Me(OMe)], **4** (1.00 g, 2.31 mmol), and CNR (0.60 g, 4.62 mmol), and the solution was stirred for 16 h at room temperature. The solution was filtered and concentrated in vacuo to ca. 10 mL to render **15** as yellow crystals by cooling the solution at −30 °C (yield: 1.37 g, 85%).

Data for **15**: IR (KBr, $\nu$, cm$^{-1}$): 1631 (m), 1588 (m), 1263 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.92 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 4.08 (s, 3H, O*Me*), 2.21 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 2.18 (s, 15H, C$_5$*Me$_5$*), 2.16, 2.13, 1.79 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.23 (s, 3H, C(*Me*)NR), 1.18 (s, 9H, C*Me$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 247.4 (*C*[C(Me)NR]NR}), 169.9 (*C*(Me)NR), 147.9, 145.0, 130.5, 128.2, 128.0, 127.9, 127.8, 127.7, 126.2, 125.2, 123.1 (2,6-Me$_2$*C$_6$*H$_3$), 115.7 (*C*$_5$Me$_5$), 64.9 (N*C*Me$_3$), 63.2 (O*Me*), 34.5 (C*Me$_3$*), 19.7, 19.0, 18.7, 17.8 (2,6-*Me$_2$*C$_6$H$_3$), 16.9 (C(*Me*)NR), 11.7 (C$_5$*Me$_5$*). Anal. Calcd for C$_{34}$H$_{48}$N$_3$OTa: C, 58.70; H, 6.95; N, 6.04. Found: C, 58.23; H, 6.99; N, 5.87.

**[TaCp*(N$^t$Bu)(O$^t$Bu){$\eta^2$-C[C(Me)═NR]═NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (16).** Toluene (30 mL) was added to a mixture of [TaCp*(N$^t$Bu)(O$^t$Bu){$\eta^2$-C(Me)═NR}], **11** (1.50 g, 2.47 mmol), and CNR (0.42 g, 3.20 mmol) in an ampule with Teflon cap, and the solution was heated at 130 °C for 48 h. After cooling at room temperature the solution was filtered and concentrated to ca. 10 mL in vacuo. Cooling the solution at −30 °C rendered 16 as white crystals (yield: 1.48 g, 81%).

Data for **16**: IR (KBr, $\nu$, cm-1): 1627 (s), 1588 (s), 1255 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.86 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 2.18 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 2.15 (s, 15H, C$_5$*Me$_5$*), 2.06, 2.03, 1.90 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.21 (s, 9H, C*Me$_3$*), 1.13 (s, 3H, C(*Me*)NR), 1.04 (s, 9H, C*Me$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 247.3 (*C*[C(Me)NR]NR}), 170.4 (*C*(Me)NR), 147.9, 145.4, 131.2, 128.1, 127.9, 127.8, 127.6, 127.2, 126.6, 125.3, 125.0, 123.0 (2,6-Me$_2$*C$_6$*H$_3$), 115.3 (*C*$_5$Me$_5$), 73.6 (O*C*Me$_3$), 64.6 (N*C*Me$_3$), 34.5 (C*Me$_3$*), 32.9 (C*Me$_3$*), 19.3, 19.1, 18.9, 18.1 (2,6-*Me$_2$*C$_6$H$_3$), 16.8 (C(*Me*)NR), 12.1 (C$_5$*Me$_5$*). Anal. Calcd for C$_{37}$H$_{54}$N$_3$OTa: C, 60.22; H, 7.39; N, 5.70. Found: C, 60.48; H, 7.23; N, 5.83.

**[TaCp*(N$^t$Bu)(NH$^t$Bu){$\eta^2$-C[C(Me)═NR]═NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (17).** Toluene (30 mL) was added to a mixture of [TaCp*(N$^t$Bu)(NH$^t$Bu)Me], **6** (2.00 g, 4.22 mmol), and CNR (1.33 g, 10.12 mmol) in an ampule with Teflon cap, and the solution was heated at 80 °C for 4 d. After cooling at room temperature the solution was filtered and concentrated to ca. 10 mL in vacuo. Cooling at −30 °C afforded **17** as yellow crystals (yield: 2.45 g, 79%).

Data for **17**: IR (KBr, $\nu$, cm$^{-1}$): 3298 (w), 1635 (s), 1590 (s), 1250 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.90 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 3.62 (s, 1H, N*H*), 2.19 (s, 15H, C$_5$*Me$_5$*), 2.17, 2.09, 2.04, 1.78 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.25 (s, 9H, C*Me$_3$*), 1.19 (s, 3H, C(*Me*)NR), 1.18 (s, 9H, C*Me$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 240.5 (*C*[C(Me)NR]NR}), 173.2 (*C*(Me)NR), 149.0, 148.4, 128.9, 127.9, 127.7, 127.6, 126.7, 126.1, 123.6, 122.6 (2,6-Me$_2$*C$_6$*H$_3$), 115.4 (*C*$_5$Me$_5$), 64.6 (N*C*Me$_3$), 54.8 (NH*C*Me$_3$), 35.1 (C*Me$_3$*), 34.3 (C*Me$_3$*), 20.2, 20.1, 18.8, 18.1, 17.1 (2,6-*Me$_2$*C$_6$H$_3$ and C(*Me*)NR), 12.6 (C$_5$*Me$_5$*). Anal. Calcd for C$_{37}$H$_{55}$N$_4$Ta: C, 60.30; H, 7.54; N, 7.60. Found: C, 60.10; H, 7.25; N, 7.51.

**[TaCp*(N$^t$Bu){$\eta$-N($^t$Bu)C(NHR)═C(Me)-$\eta$-NR}] (R = 2,6-Me$_2$C$_6$H$_3$) (18).** Toluene (30 mL) was added to [TaCp*(N$^t$Bu)(NH$^t$Bu){$\eta^2$-C[C(Me)═NR]═NR}], **17** (1.20 g, 1.63 mmol), in an ampule with a Teflon cap, and the solution was heated at 140 °C for 3 days. After cooling at room temperature the solution was filtered and concentrated to ca. 10 mL. Cooling at −30 °C afforded **18** as yellow crystals (yield 0.95 g, 79%).

Data for **18**: IR (KBr, $\nu$, cm$^{-1}$): 3450 (w), 1554 (m), 1256 (s). $^1$H NMR (CDCl$_3$; $\delta$, ppm): 6.90 (m, 6H, 2,6-Me$_2$C$_6$*H$_3$*), 4.74 (s, 1H, N*H*), 2.49 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 2.33 (s, 6H, 2,6-*Me$_2$*C$_6$H$_3$), 2.15 (s, 15H, C$_5$*Me$_5$*), 1.98 (s, 3H, 2,6-*Me$_2$*C$_6$H$_3$), 1.50 (s, 9H, C*Me$_3$*), 1.28 (s, 3H, C(*Me*)═C(NHR)), 0.87 (s, 9H, C*Me$_3$*). $^{13}$C{$^1$H} NMR (CDCl$_3$; $\delta$, ppm): 151.9, 141.1, 135.7, 133.1, 130.6, 128.4, 128.1, 127.5, 126.9, 126.1, 125.6, 123.9, 119.9 (2,6-

**Table 3. Summary of Crystallographic Data for the Compounds 14 and 18**

| | 14 | 18 |
|---|---|---|
| formula | C$_{33}$H$_{45}$ClN$_3$Ta | C$_{37}$H$_{55}$N$_4$Ta |
| mol wt | 700.12 | 736.80 |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/a$ |
| radiation ($\lambda$, Å) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| *a*, Å | 8.767(4) | 10.317(4) |
| *b*, Å | 10.956(5) | 32.891(9) |
| *c*, Å | 17.316(6) | 10.561(6) |
| α, deg | 98.15(2) | |
| $\beta$, deg | 95.94(2) | 92.45(2) |
| $\gamma$, deg | 97.70(2) | |
| *V*, Å$^3$ | 1619(1) | 3580(3) |
| Z | 2 | 4 |
| $D_{calcd}$, Mg m$^{-3}$ | 1.436 | 1.367 |
| *F*(000) | 708 | 1512 |
| cryst size, mm | 0.25 × 0.28 × 0.30 | 0.24 × 0.26 × 0.28 |
| $\mu$(Mo Kα), mm$^{-1}$ | 3.502 | 3.099 |
| diffractometer | Siemens AED | Philips PW 1100 |
| scan type | $\theta/2\theta$ | $\theta/2\theta$ |
| $\theta$ range, deg | 3−22 | 3−24 |
| no. of reflectns measd | 3966 | 5918 |
| no. of unique total data | 3966 | 5597 |
| no. of unique obsd data | 2682 [$I > 2\sigma(I)$] | 3553 [$I > 2\sigma(I)$] |
| R1[a] [$I > 2\sigma(I)$] | 0.0695 | 0.0291 |
| wR2[b] [$I > 2\sigma(I)$] | 0.1763 | 0.0476 |
| R1 (all data) | 0.1185 | 0.0795 |
| wR2 (all data) | 0.2027 | 0.0590 |

[a] $R1 = \sum|F_o - F_c|/|\sum(F_o)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

$Me_2C_6H_3$ and *C*(Me)═C(NHR)), 113.4 ($C_5Me_5$), 104.9 (C(Me)═*C*(NHR), 64.2 (Ta═N*C*$Me_3$), 55.3 (*C*$Me_3$), 34.6 (C*Me*$_3$), 33.5 (C*Me*$_3$), 21.3, 20.4, 20.1 (2,6-*Me*$_2C_6H_3$), 16.6 (C(*Me*)═C(NHR)), 12.5 ($C_5$*Me*$_5$). Anal. Calcd for $C_{37}H_{55}N_4Ta$: C, 60.30; H, 7.54; N, 7.60. Found: C, 60.12; H, 7.58; N, 7.40.

**Crystal Structure Determinations.** All crystals of compound **14**, obtained by crystallization from *n*-hexane, were of very poor quality, and a suitably sized crystal in a Lindemann tube was mounted on an Siemens AED diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). Crystals of **18** were obtained by crystallization from *n*-hexane, and a suitably sized crystal in a Lindemann tube was mounted in a Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). Crystallographic and experimental details for both structures are summarized in Table 3. An empirical correction for absorption was applied to both compounds [maximum and minimum values for the transmission coefficient was 1.000 and 0.440 for **14** and 1.000 and 0.765 for **18**].[21] Both structures were solved by direct methods and refined by least squares against $F_o^2$ (SHELXL-97).[22] All non hydrogen atoms were refined anisotropically excepting the C(31), C(32), and C(33) carbon atoms of **14**. All the hydrogen atoms were introduced from geometrical calculations and refined using a riding model with fixed thermal parameters, excepting that bound to N(3), which was found in the final $\Delta F$ map and refined isotropically. The final cycles of refinement were carried out on the basis of 338 variables for **14** and 393 for **18.** The biggest remaining peak in the final difference map was equivalent to about 1.70 e/Å$^3$ for **14** and 1.06 e/Å$^3$ for **18**. A weighting scheme $w = 1/[\sigma^2(F_o)^2 + (0.1224P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the last cycles of refinement for **14** and $w = 1/[\sigma^2(F_o)^2 + (0.0149P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. All calculations were carried out on DIGITAL AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R., Parma.

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**Supporting Information Available:** The details of the crystal structure investigations are deposited in the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-140106 (**14**) and CCDC-140107 (**18**). This material is also available free of charge via the Internet at http://pubs.acs.org.

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