*Organometallics* **2000,** *19,* 2573−2579 2573

# Mono- and Dianionic Guanidinate Ligands. Reactivity of $[^{i}PrN{=}C(N^{i}Pr)_2]Ta(NMe_2)_3$ and $[(^{i}PrNH)C(N^{i}Pr)_2]TaCl(NMe_2)_3$ with $Me_3SiCl$ and ArNC (Ar = 2,6-$Me_2C_6H_4$)

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*Received December 22, 1999*

Reactivities of the dianionic guanidinate complex of $[^{i}PrN{=}C(N^{i}Pr)_2]Ta(NMe_2)_3$ (**1**) and the monoanionic guanidinate complex $Ta(NMe_2)_3Cl[(^{i}PrN)_2CN(H)^{i}Pr]$ (**4**) have been investigated. Reaction of **1** with $Me_3SiCl$ produced compound **2**, $Ta(NMe_2)_3Cl[(^{i}PrN)_2CN(SiMe_3)^{i}Pr]$, which is proposed to arise from the addition of the Si−Cl bond across a Ta−N(guanidinate) bond of the starting material rather than one of the Ta−$NMe_2$ bonds. Complex **2** is the analogue of **4** in which H has been replaced by $SiMe_3$. Derivatization of **2** was achieved by reaction with $PhCH_2MgCl$ to produce $Ta(NMe_2)_3(CH_2Ph)[(^{i}PrN)_2CN(SiMe_3)^{i}Pr]$ (**3**). The single-crystal X-ray-determined structural features of **3** are reported and support the spectroscopic characterization of **3**, and indirectly that of **2**, by revealing a bidentate tetrasubstituted guanidinate monoanion and an $\eta^1$-benzyl group. Complexes **1** and **4** insert 2,6-dimethylphenyl isocyanide (ArNC) to yield the structurally characterized complex $Ta(NMe_2)[C(N^{i}Pr)_3][\eta^2\text{-}(Me_2N)C{=}N(2,6\text{-}Me_2C_6H_3)]_2$ (**5**), which possesses one dianionic bidentate guanidinate ligand and two $\eta^2$-iminocarbamoyl ligands derived from the insertion of ArNC into two of the Ta−$NMe_2$ bonds of the starting materials. The formally seven-coordinate Ta(V) center of **5** can be viewed as pseudo trigonal bipyramidal, with each of the $\eta^2$-C=N linkages occupying a single coordination site. In the case of **4**, the transformation of the guanidinate anion into its dianionic form was concomitant with insertion of ArNC. The sources of base for the deprotonation of the guanidinate ligand are likely the amido groups of a portion of the starting material.

## Introduction

The search for new ligands to support electron-deficient early-transition-metal complexes receives a major stimulus from the desire to mimic the flexibility and remarkable reactivity of metallocene-based systems.[1] Some efforts to prepare group 5 metal complexes that might emulate group 4 metallocenes have, for example, focused on employing dianionic ligands.[2] Nitrogen-based anionic ligands have also received recent attention as candidates for providing a supporting environment for group 5 metal chemistry.[3] Amidinate anions fall into this class of ligands and have been demonstrated to be versatile ligands for a variety of electron-deficient organometallic and inorganic complexes of the group 5 metals.[4−6] Related *N,N′,N″*-trialkylguanidinate-containing complexes are relatively scarce.[7−9] Guanidinates should certainly possess the same flexibility in coordination properties that have been exhibited by amidinates. Moreover, the presence of a third nitrogen center, which can bear either one or

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(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 429 and references therein.

(2) For some examples see: (a) Rodriguez, G.; Graham, J. P.; Cotter, W. D.; Sperty, C. K.; Bazan, G. C.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 12512. (b) Antonelli, D.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500. (c) Scheuer, S.; Fischer, J.; Kress, J. *Organometallics* **1995**, *14*, 2627. (d) Bazan, G. C.; Donnelly, S. J.; Rodriguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671.

(3) See for example: (a) Jaffart, J.; Nayral, C.; Choukroun, R.; Mathieu, R.; Etienne, M. *Eur. J. Inorg. Chem.* **1998**, 425. (b) Spannenberg, A.; Fuhrmann, H.; Arndt, P.; Baumann, W.; Kempe, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3363. (c) Desmangles, N.; Gambarotta, S.; Bensimon, C.; Davis, S.; Zahalka, H. *J. Organomet. Chem.* **1997**, *562*, 53.

(4) (a) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403 and references therein. (b) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219 and references therein.

(5) (a) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 4090. (b) Stewart, P. J.; Blake, A. J.; Mountford, P. J. *Inorg. Chem.* **1997**, *36*, 1982.

(6) Previously reported Ta amidinate complexes: (a) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4417. (b) Mullins, S. M.; Bergman, R. G..; Arnold, J. *Organometallics* **1999**, *18*, 4465. (c) Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111. (d) Cotton, F. A.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Bull. Soc. Chim. Fr.* **1996**, *133*, 711. (e) Schrumpf, F.; Roesky, H. W.; Subrahmanyan, T.; Noltemyer, M. *Z. Anorg. Allg. Chem.* **1990**, *583*, 124. (f) Merzweiler, K.; Fenske, D.; Harmann, E.; Dehnicke, K. *Z. Naturforsch.* **1989**, *44B*, 1003. (g) Dehnicke, K.; Ergezinger, C.; Harmann, E.; Zinn, A.; Hosler, K. *J. Organomet. Chem.* **1988**, *352*, C1. (h) Leboeuf, A.; Leblanc, J.-C.; Moise, C. *J. Organomet. Chem.* **1987**, *335*, 331. (i) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2611. (j) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *80*, 349. (k) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1974**, 1973. (l) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1974**, 1579.

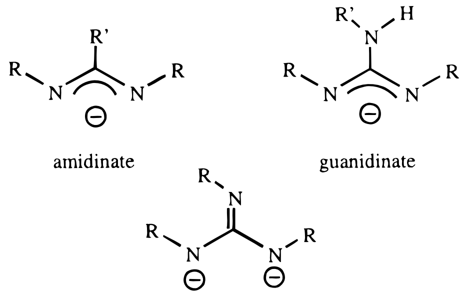
(7) (a) Tin, M. K. T.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **1999**, *38*, 998. (b) Tin, M. K. T.; Thirupathi, N.; Yap G. P. A.; Richeson, D. S. *J. Chem. Soc., Dalton Trans.* **1999**, 2947.

(8) Thirupathi, N.; Yap, G. P. A.; Richeson, D. S. *Chem. Commun.* **1999**, 2483.

(9) A triphenylguanidinate dianion complex of Ta(V) appears in: Rodriguez, G.; Sperry, C. K.; Bazan, G. C. *J. Mol. Catal. A* **1998**, *128*, 5.

10.1021/om991010f CCC: $19.00

**Chart 1**



**I**

two organic substituents ($NR'_2$ or N(H)R′), provides an additional coordination site within the ligand and the added capability of yielding dianionic species (**I**; Chart 1).

One of our research interests is the application of *N,N′,N″*-trialkylguanidines as ligands due to their ability to yield dianionic species which may have a conjugated $\pi$ system. The application of *N,N′,N″*-trialkylguanidines requires the development of fundamental ideas regarding the introduction of guanidinate anions and dianions into a metal coordination sphere and investigation of the general reactivity characteristics of these complexes. Reported preparative routes to trisubstituted guanidinate complexes include the elimination of HX (X = Cl, Br) from halometal complexes,[10] elimination of $H_2$ from metal hydrides,[11] elimination of alkane from a metal alkyl,[12] elimination of amine from metal amido complexes,[7,13] and the metathesis reaction between lithium guanidinate and metal halo complexes.[8,9]

Our efforts to employ guanidinate ligands in the preparation of early-transition-metal and lanthanide metal complexes led recently to the isolation of a series of group 5 complexes that possess trialkylguanidinate ligands in both the mono- and dianionic forms.[7,8,14] Complexes of the form $[(RN)_2C{=}NR]M(NMe_2)_3$ (M = Nb, Ta; R = $^i$Pr, Cy) and $[(^iPrN)_2CN(H)^iPr]Ta(NMe_2)_3Cl$ were prepared by reaction of tris(alkyl)guanidine with the metal−amido groups in $M(NMe_2)_5$ and $TaCl(NMe_2)_4$, respectively.[7] We now report further reactivity of some of these species. Specifically, reactions with $Me_3SiCl$ have been investigated in an effort to introduce a chloro ligand into the Ta coordination sphere. To our knowledge this approach has not been previously reported for group 5 amido species. Furthermore, we report the reactivity of these trialkylguanidinate Ta complexes with 2,6-dimethylphenyl isocyanide (ArNC) to yield a structurally characterized bis($\eta^2$-iminocarbamoyl) complex.[15] In the case of $[(^iPrN)_2CN(H)^iPr]Ta(NMe_2)_3Cl$, the transformation of the guanidinate anion into its dianionic form was concomitant with insertion of ArNC.

## Results and Discussion

The Ta(V) complex $Ta(NMe_2)_3[(^iPrN)_2C{=}N^iPr]$ (**1**) bears a dianionic *N,N′,N″*-triisopropylguanidinate ligand that is coordinated in a chelating bidentate mode. Structural parameters for this compound lead to the assignment of the localized resonance structure shown in Scheme 1.[7] To further develop the reactivity of **1**, we attempted to replace one or more of the dimethylamido ligands in this compound with chloride ligands. We anticipated that this would allow a straightforward avenue for future modifications. Reaction of **1** with excess $Me_3SiCl$ produced an oil that exhibited spectroscopic data indicating incorporation of a $Me_3Si$ group but without loss of dimethylamido ligands (Scheme 1). Although we have not been able to isolate a sample suitable for microanalysis, we feel confident in our assignment of the constitution of this complex as $Ta(NMe_2)_3Cl[(^iPrN)_2CN(SiMe_3)^iPr]$ (**2**) on the basis of spectroscopic characterization, subsequent reactivity, and reproducibility. Specifically, the appearance in the NMR spectra of a single $SiMe_3$ group and of a single guanidinate $CN_3$ site suggested formation of a single product. Furthermore, both $^1H$ and $^{13}C$ NMR provided a 2:1 ratio for the $^i$Pr groups of the guanidinate ligand at room temperature, consistent with formation of a monoanionic guanidinate group. Finally, the integrated intensity of the amido methyl signals corresponded to the presence of three dimethylamido groups in **2**. All of these spectroscopic features pointed to a formulation for **2** in which the Si−Cl bond of the $Me_3SiCl$ had added across one of the Ta−N(guanidinate) bonds rather than the anticipated Ta−N(amido) bond. This transformation would lead to the proposed intermediate **A**, which through rearrangement of the coordination mode of the guanidinate anion would generate **2** (Scheme 2). In hindsight this transformation is not so surprising, given our previous observation that the guanidinate was functioning essentially as a diamido ligand.[7] As proposed, complex **2** possesses a monoanionic tetrasubsubstitued guanidinate ligand and has incorporated a chloride ligand into the coordination sphere of the metal, making it the analogue of the reported compound $Ta(NMe_2)_3Cl[(^iPrN)_2CN(H)^iPr]$ (**4**), in which H has been replaced by $SiMe_3$.[7b] The room-temperature NMR spectra for **2** suggest that in solution this complex is fluxional (e.g., broadened $^i$Pr resonances and equivalent $NMe_2$ signals). Attempts to clarify this process by changing the NMR solvent and performing variable-temperature studies have not, so far, led to clarification of this process. As a result, the structural details of **2** remain a proposition. Additional support of our proposal is provided by subsequent derivatization of this species.

Reaction of **2** with benzyl Grignard produced a crystalline material in 53% overall isolated yield based on **1**. This product exhibited spectroscopic features consistent with the proposed structure **3** (Scheme 1).

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(10) da S. Maia, J. R.; Gazard, P. A.; Kilner, M. A.; Batsanova, S.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1997**, 4625. Bailey, P. J.; Mitchell, L. A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2839.

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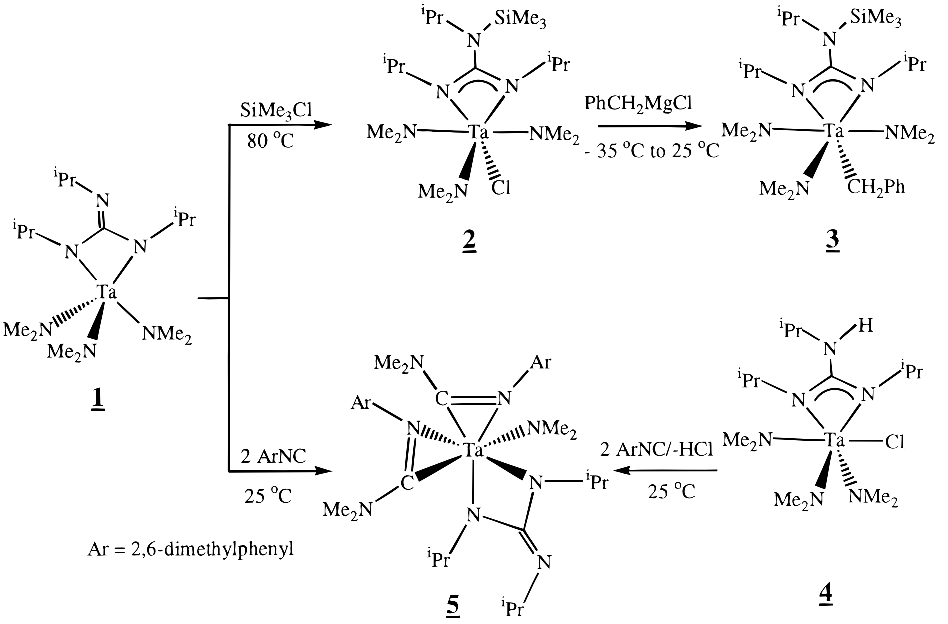
(12) Snaith, R.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. A* **1970**, 380.

(13) Bailey, P. J.; Gould, R. O.; Harmer, C. N.; Pace, S.; Steiner, A.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1997**, 1161.

(14) Additional examples of dianionic trialkyl- and triarylguanidinate complexes of transition and main-group elements can be found in: (a) Blake, A. J., McInnes, J. M.; Mountford, P.; Nikonov, G. I.; Swallow, D.; Watkin, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 379. (b) Chivers, T.; Parvez, M.; Schatte, G. *J. Organomet. Chem.* **1998**, *550*, 213. (c) Dinger, M. B.; Henderson, W. *J. Chem. Soc., Chem. Commun.* **1996**, 211. (d) Bailey, P. J.; Blake, A. J.; Kryszczuk, M.; Parsons, S.; Reed, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1647. (e) Bremer, N. J.; Cutcliffe, A. B.; Farona, M. F.; Kofron, W. G. *J. Chem. Soc. A* **1971**, 3264. (f) Bremer, N. J.; Cutcliffe, A. B.; Farona, M. F. *J. Chem. Soc. D* **1970**, 932.

(15) A search of the Cambridge Structural Data Base did not yield a structurally characterized Nb or Ta $\eta^2$-iminocarbamoyl complex.

**Scheme 1**



Ar = 2,6-dimethylphenyl

**Scheme 2**

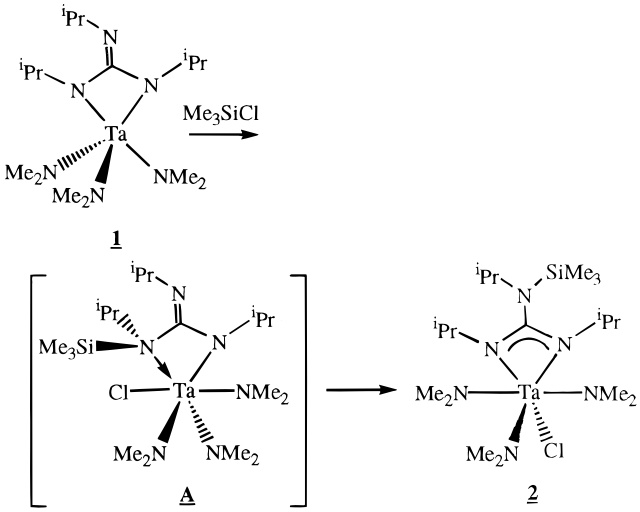


**Table 1. Crystal Data for $Ta(NMe_2)_3(CH_2Ph)[(^iPrN)_2CN(SiMe_3)^iPr]$ (3) and $Ta(NMe_2)[C(N^iPr)_3][(Me_2N)C{=}N(2,6\text{-}Me_2C_6H_3)]_2$ (5)**

| | 3 | 5 |
|---|---|---|
| empirical formula | $C_{26}H_{55}N_6SiTa$ | $C_{34}H_{57}N_8Ta$ |
| fw | 660.80 | 758.83 |
| temp (K) | 203(2) | 238(2) |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 |
| space group | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 9.494(4) | 10.803(2) |
| $b$ (Å) | 15.768(7) | 11.436(2) |
| $c$ (Å) | 21.247(9) | 16.729(2) |
| α (deg) | | 78.044(2) |
| $\beta$ (deg) | 97.457(8) | 81.238(2) |
| $\gamma$ (deg) | | 66.730(2) |
| $V$ (Å$^3$) | 3154(2) | 1851.8(5) |
| $Z$ | 4 | 2 |
| $d_{calcd}$ (g/cm$^3$) | 1.392 | 1.361 |
| abs coeff (mm$^{-1}$) | 3.546 | 3.001 |
| R1[a] | 0.0362 | 0.0486 |
| wR2[b] | 0.1066 | 0.1250 |

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

Replacement of the chloride ligand with a benzyl group appears to provide a more rigid coordination geometry about the Ta(V) center, as indicated by the appearance of four distinct doublets in the $^1$H NMR for the methyl groups of the guanidinate $^i$Pr substituents. The NMR spectrum also displayed three different multiplets for the CH signals for the $^i$Pr groups (3.23, 4.23, 4.28 ppm) and three unique $NMe_2$ moieties. The correlation between the isopropyl $CH_3$ and CH signals in the proton NMR (COESY) indicated that, at room temperature, the six possible signals for these $CH_3$ groups fall in a 1:1:1:1:2 pattern, with the last two of these signals overlapping.[16] The increased dispersion of the $^{13}$C NMR spectrum allowed for the resolution of all six of the isopropyl methyl carbons in **3**. The diastereotopic methylene protons of the benzyl substituent produce a clear AB pattern in the $^1$H NMR. Attempts to introduce a methyl group into the Ta coordination sphere by reaction of **2** with 1 equiv of MeLi produced a thermally unstable product, for which we have not yet been able to obtain clear results.

Direct confirmation of the structural features of **3** was obtained through a single-crystal X-ray study. The results are summarized in Tables 1 and 2 and Figure 1. Examination of Figure 1 shows that the pseudo-octahedral coordination geometry of the Ta(V) center is defined by a bidentate guanidinate anion and three $NMe_2$ ligands, with one coordination site occupied by a benzyl group. The guanidinate ligand is bonded to Ta through two nitrogen atoms to yield a planar four-membered cycle of sp$^2$-hybridized N and C centers with a bite angle of 58.38(19)°. The bond distances within the NCN moiety (N(1)−C(10) = 1.321(8) Å, N(2)−C(10) = 1.337(8) Å) are in agreement with a delocalized $\pi$ interaction. The third guanidinate nitrogen, N(3), has a planar geometry (sum of angles 360°) consistent with this being an sp$^2$-hybridized center. However, the potential for conjugation of the p orbital of N(3) with

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[16] Figures giving the 500 MHz $^1$H NMR spectrum and an expansion of the COESY spectrum of **3** are provided in the Supporting Information.

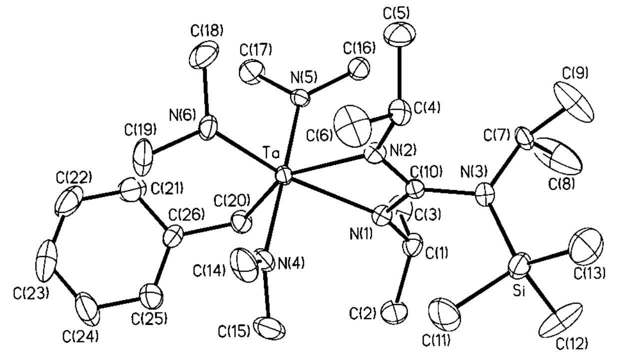

**Figure 1.** Molecular structure of $Ta(NMe_2)_3(CH_2Ph)[(^iPrN)_2CN(SiMe_3)^iPr]$ (**3**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for $Ta(NMe_2)_3(CH_2Ph)[(^iPrN)_2CN(SiMe_3)^iPr]$ (3)**

Distances

| | | | |
|---|---|---|---|
| Ta−N(6) | 1.992(5) | N(3)−C(7) | 1.509(8) |
| Ta−N(4) | 2.032(5) | N(4)−C(14) | 1.472(10) |
| Ta−N(5) | 2.043(5) | N(4)−C(15) | 1.474(10) |
| Ta−N(2) | 2.171(5) | N(5)−C(16) | 1.456(9) |
| Ta−C(20) | 2.275(7) | N(5)−C(17) | 1.458(9) |
| Ta−N(1) | 2.315(5) | N(6)−C(18) | 1.460(9) |
| Si−N(3) | 1.737(6) | N(6)−C(19) | 1.467(10) |
| Si−C(13) | 1.853(9) | C(1)−C(2) | 1.526(10) |
| Si−C(11) | 1.862(9) | C(1)−C(3) | 1.532(11) |
| Si−C(12) | 1.869(10) | C(4)−C(6) | 1.540(11) |
| N(1)−C(10) | 1.321(8) | C(4)−C(5) | 1.537(10) |
| N(1)−C(1) | 1.460(9) | C(7)−C(8) | 1.464(12) |
| N(2)−C(10) | 1.337(8) | C(7)−C(9) | 1.524(11) |
| N(2)−C(4) | 1.461(8) | C(20)−C(26) | 1.508(8) |
| N(3)−C(10) | 1.413(8) | | |

Angles

| | | | |
|---|---|---|---|
| N(6)−Ta−N(4) | 91.7(2) | C(4)−N(2)−Ta | 138.6(4) |
| N(6)−Ta−N(5) | 88.4(2) | C(10)−N(3)−C(7) | 115.3(5) |
| N(4)−Ta−N(5) | 177.6(2) | C(10)−N(3)−Si | 119.5(4) |
| N(6)−Ta−N(2) | 107.8(2) | C(7)−N(3)−Si | 125.2(4) |
| N(4)−Ta−N(2) | 93.2(2) | C(14)−N(4)−C(15) | 108.1(6) |
| N(5)−Ta−N(2) | 89.0(2) | C(14)−N(4)−Ta | 124.1(5) |
| N(6)−Ta−C(20) | 104.8(2) | C(15)−N(4)−Ta | 127.7(5) |
| N(4)−Ta−C(20) | 88.3(2) | C(16)−N(5)−C(17) | 108.0(5) |
| N(5)−Ta−C(20) | 89.4(2) | C(16)−N(5)−Ta | 129.4(4) |
| N(2)−Ta−C(20) | 147.3(2) | C(17)−N(5)−Ta | 121.9(4) |
| N(6)−Ta−N(1) | 166.1(2) | C(18)−N(6)−C(19) | 107.6(6) |
| N(4)−Ta−N(1) | 90.4(2) | C(18)−N(6)−Ta | 126.4(5) |
| N(5)−Ta−N(1) | 90.1(2) | C(19)−N(6)−Ta | 126.0(5) |
| N(2)−Ta−N(1) | 58.38(19) | N(1)−C(10)−N(2) | 111.0(5) |
| C(20)−Ta−N(1) | 89.0(2) | N(1)−C(10)−N(3) | 125.5(6) |
| C(10)−N(1)−C(1) | 122.3(6) | N(2)−C(10)−N(3) | 123.4(5) |
| C(10)−N(1)−Ta | 92.2(4) | C(26)−C(20)−Ta | 117.7(4) |
| C(1)−N(1)−Ta | 144.7(4) | C(25)−C(26)−C(20) | 120.5(4) |
| C(10)−N(2)−C(4) | 123.1(5) | C(21)−C(26)−C(20) | 119.4(4) |
| C(10)−N(2)−Ta | 98.3(4) | | |

the N(1)−C(10)−N(2) $\pi$-system can be eliminated, given the nearly perpendicular orientation (dihedral angle 97.9°) of the planes defined by C(7)−N(3)−Si and N(1)−C(10)−N(2). Consistent with this observation is a N(3)−C(10) single-bond distance of 1.413(8) Å. The Ta−N(1) distance is longer than Ta−N(2) (2.315(5) Å vs 2.171(5) Å), reflecting the asymmetry of the Ta coordination environment and the relative trans influence of $NMe_2$ and $CH_2Ph$. A similar structural feature was previously observed in $Ta(NMe_2)_3Cl[(^iPrN)_2CNH^iPr]$.[7b]

The two trans-disposed amido groups (N(4) and N(5)) can be conveniently chosen to define a pseudoaxial vector with an N(4)−Ta−N(5) angle of 177.6(2)°. The angles around the equatorial plane defined by the guanidinate ligand, the benzyl carbon (C(20)), and the third amido ligand (N(6)), although irregular, add up to 360°.

The three amido N centers (N(4)−N(6)) are planar, allowing them to function as four-electron donors to Ta. As a result, the Ta electron count can be accommodated without need of an $\eta^2$-benzyl interaction. In fact, the observed Ta−C(20)−C(26) angle of 117.7° is in agreement with an $\eta^1$ coordination mode for this group.

Insertion reactions represent one of the most fundamental reaction types in organometallic and inorganic chemistry, and isocyanides are among the more common substrates for investigation of such reactions.[17] Therefore, the reaction of **1** with 2,6-dimethylphenyl isocyanide (ArNC) was investigated. Complex **1** offers two potential sites for insertion and, given the relative reactivity of the $Ta-N_{guanidinate}$ vs the $Ta-NMe_2$ bond as observed with $Me_3SiCl$, this reaction offers the additional opportunity to compare the reactivities of these ligands. Addition of 2 equiv of isocyanide to a solution of **1** at room temperature led to a rapid reaction and isolation of the bis(iminocarbamoyl) product **5** (Scheme 1). Attempts to provoke the insertion of a third aryl isocyanide into the remaining $NMe_2$ ligand of **5** by adding excess isocyanide did not result in any further reaction. In addition, employing less than 2 equiv of arylisocyanide in this reaction did not lead to a single isolable product.

Complex **5** exhibited NMR data ($^1H$ and $^{13}C$) consistent with the formulation given in Scheme 1, in which the insertion of ArNC has proceeded for two of the $NMe_2$ ligands. In particular, the dianionic guanidinate ligand appears to remain intact and displayed three sets of resonances for the $^iPr$ substituents and a $^{13}C$ NMR shift for the $CN_3$ carbon (155.16 ppm) in line with those previously reported for dianions (152−158 ppm).[7,8] The two $NMe_2$ groups that have undergone insertion and are now part of the iminocarbamoyl moieties exhibited magnetically inequivalent methyl signals. This observation is consistent with diastereotopic groups and restricted rotation about the $C_{imine}-NMe_2$ bond. The remaining $NMe_2$ ligand in **5** produced a broadened signal in both $^1H$ and $^{13}C$ NMR, indicating fluxionality within this compound.

Further confirmation for the presence of the iminocarbamoyl groups is provided by a broad IR absorbance at 1588 $cm^{-1}$ with shoulders at 1600 and 1573 $cm^{-1}$. An assignment of this band as a C═N stretching mode is consistent with observed iminoacyl and iminocarbamoyl complexes.[17,18]

To define the metrical parameters of **5** and in light of the rather limited number of structurally characterized complexes possessing either iminocarbamoyl or guani-

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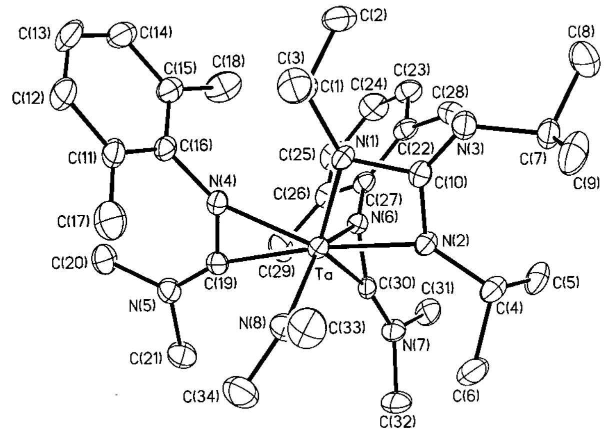

**Figure 2.** Molecular structure of Ta(NMe$_2$)[C(N$^i$Pr)$_3$][(Me$_2$N)C═N(2,6-Me$_2$C$_6$H$_3$)]$_2$ (**5**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

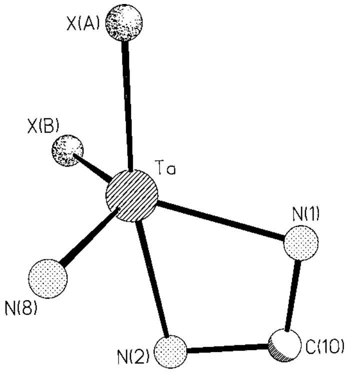

**Figure 3.** Simplified diagram of the coordination geometry of **5**. The spheres labeled X(A) and X(B) are defined as the centroids for N(4)═C(19) and N(6)═C(30). Selected angles (deg): X(B)−Ta−N(1) = 118.7, X(B)−Ta−N(8) = 130.1, X(B)−Ta−N(2) = 89.4, X(A)−Ta−X(B) = 95.4, X(A)−Ta−N(8) = 91.8, X(A)−Ta−N(1) = 106.2, X(A)−Ta−N(2) = 169.5.

**Table 3. Selected Bond Distances (Å) and Angles (deg) for Ta(NMe$_2$)[C(N$^i$Pr)$_3$][(Me$_2$N)C═N(2,6-Me$_2$C$_6$H$_3$)]$_2$ (5)**

| | Distances | | |
|---|---|---|---|
| Ta−X(A) | 2.063(5) | N(3)−C(10) | 1.278(8) |
| Ta−X(B) | 2.078(5) | N(3)−C(7) | 1.462(7) |
| Ta−N(8) | 2.009(5) | N(4)−C(19) | 1.310(8) |
| Ta−N(1) | 2.027(5) | N(4)−C(16) | 1.428(7) |
| Ta−N(2) | 2.122(5) | N(5)−C(19) | 1.326(8) |
| Ta−N(4) | 2.127(4) | N(5)−C(21) | 1.462(9) |
| Ta−N(6) | 2.171(5) | N(5)−C(20) | 1.469(8) |
| Ta−C(30) | 2.186(6) | N(6)−C(30) | 1.309(7) |
| Ta−C(19) | 2.201(6) | N(6)−C(27) | 1.422(8) |
| Ta−C(10) | 2.655(6) | N(7)−C(30) | 1.331(7) |
| N(1)−C(10) | 1.431(7) | N(7)−C(31) | 1.458(9) |
| N(1)−C(1) | 1.463(7) | N(7)−C(32) | 1.470(8) |
| N(2)−C(10) | 1.385(8) | N(8)−C(34) | 1.436(10) |
| N(2)−C(4) | 1.470(7) | N(8)−C(33) | 1.454(10) |
| | **Angles** | | |
| N(8)−Ta−N(1) | 106.1(2) | C(1)−N(1)−Ta | 138.2(4) |
| N(8)−Ta−N(2) | 92.0(2) | C(10)−N(2)−C(4) | 123.6(5) |
| N(1)−Ta−N(2) | 63.37(17) | C(10)−N(2)−Ta | 96.2(3) |
| N(8)−Ta−N(4) | 97.9(2) | C(4)−N(2)−Ta | 140.2(4) |
| N(1)−Ta−N(4) | 88.29(18) | C(10)−N(3)−C(7) | 124.9(5) |
| N(2)−Ta−N(4) | 151.6(2) | C(19)−N(4)−C(16) | 134.7(5) |
| N(8)−Ta−N(6) | 147.2(2) | C(19)−N(4)−Ta | 75.5(3) |
| N(1)−Ta−N(6) | 104.79(19) | C(16)−N(4)−Ta | 149.0(4) |
| N(2)−Ta−N(6) | 92.16(18) | C(19)−N(5)−C(21) | 119.3(6) |
| N(4)−Ta−N(6) | 93.67(18) | C(19)−N(5)−C(20) | 124.6(5) |
| N(8)−Ta−C(30) | 113.0(2) | C(21)−N(5)−C(20) | 116.1(6) |
| N(1)−Ta−C(30) | 131.22(19) | C(30)−N(6)−C(27) | 133.3(5) |
| N(2)−Ta−C(30) | 86.78(19) | C(30)−N(6)−Ta | 73.2(3) |
| N(4)−Ta−C(30) | 113.1(2) | C(27)−N(6)−Ta | 152.8(4) |
| N(6)−Ta−C(30) | 34.98(19) | C(30)−N(7)−C(31) | 125.3(5) |
| N(8)−Ta−C(19) | 85.7(2) | C(30)−N(7)−C(32) | 119.1(6) |
| N(1)−Ta−C(19) | 123.41(19) | C(31)−N(7)−C(32) | 114.9(5) |
| N(2)−Ta−C(19) | 173.22(18) | C(34)−N(8)−C(33) | 109.5(6) |
| N(4)−Ta−C(19) | 35.2(2) | C(34)−N(8)−Ta | 130.4(6) |
| N(6)−Ta−C(19) | 86.32(19) | C(33)−N(8)−Ta | 120.1(5) |
| C(30)−Ta−C(19) | 88.2(2) | N(3)−C(10)−N(2) | 137.9(5) |
| N(8)−Ta−C(10) | 101.8(2) | N(3)−C(10)−N(1) | 120.7(5) |
| N(1)−Ta−C(10) | 32.19(17) | N(2)−C(10)−N(1) | 101.5(5) |
| N(2)−Ta−C(10) | 31.23(17) | N(3)−C(10)−Ta | 169.2(4) |
| N(4)−Ta−C(10) | 120.38(18) | N(4)−C(19)−N(5) | 129.0(5) |
| N(6)−Ta−C(10) | 98.47(18) | N(4)−C(19)−Ta | 69.3(3) |
| C(30)−Ta−C(10) | 109.45(18) | N(5)−C(19)−Ta | 161.7(4) |
| C(19)−Ta−C(10) | 155.55(19) | N(6)−C(30)−N(7) | 129.2(6) |
| C(10)−N(1)−C(1) | 122.8(5) | N(6)−C(30)−Ta | 71.9(3) |
| C(10)−N(1)−Ta | 98.9(3) | N(7)−C(30)−Ta | 159.0(5) |

dinate dianion ligands, the single-crystal X-ray structure of **5** was obtained (Table 1). As seen in Figure 2 and consistent with our spectroscopic observations, complex **5** possesses one dianionic bidentate guanidinate ligand, one dimethylamido ligand, and two $\eta^2$-iminocarbamoyl ligands derived from the insertion of ArNC into two of the Ta−NMe$_2$ bonds of **1**. The geometry about the formally seven-coordinate Ta(V) center in **5** can be viewed as pseudo trigonal bipyramidal if each of the $\eta^2$-C═N linkages is considered to occupy a single coordination site that is defined by the midpoint of the C−N bond. Defining X(A) and X(B) as the centroids for N(4)═C(19) and N(6)═C(30), respectively, provides the simplified diagram for **5** shown in Figure 3.

This treatment and an examination of the observed distances and angles provided in Table 3 allows the assignment of the pseudoaxial ligands of **5** as one of the guanidinate nitrogen atoms (N(2)) and centroid X(A) (N(2)−Ta−X(A) = 169.5°). This requires the bidentate guanidinate dianion to span the axial and equatorial sites, which in turn leads to the largest distortion in the geometry of the metal since the bite angle of this ligand (N(1)−Ta−N(2) = 63.37(17)°) is substantially less than the ideal 90° axial/equatorial angle. The resultant equatorial sites X(B), N(1), and N(8) lie in an approximately planar arrangement (sum of angles 355°) with average interligand angles of 118.3°.

The dianionic guanidinate ligand in **5** exhibits bonding parameters similar to those observed in **1** and reported analogues.[7] The short N(3)−C(10) distance (1.278(8) Å) and the small dihedral angle between the N(1)−C(10)−N(2) and C(7)−N(3)−C(10) planes (5.5°) is consistent with a localized double bond between these two atoms. This formulation leaves the two anionic charges of the ligand to reside on the remaining two N centers of the ligand (N(1), N(2)) which are bonded to Ta.

The coordination of the iminocarbamoyl groups is clearly $\eta^2$ for both ligands, and the N−C bond lengths of 1.310(8) and 1.309(7) Å are consistent with double-bond formulation. The nitrogen atoms of the NMe$_2$ groups of these ligands (N(5), N(7)) are in planar, sp$^2$ environments. Both of the ligands exhibit N═C−NMe$_2$ groups that are planar within 1.7° (N(4)−C(19)−N(5)Me$_2$) and 10.4° (N6−C(30)−N(7)Me$_2$). In addition to having sp$^2$-hydridized centers and the correct orientation for $\pi$ conjugation, the C−NMe$_2$ bond distances (N(5)−C(19) = 1.326(8) Å and N(7)−C(30) = 1.331(7)

Å) are only slightly longer than the $\eta^2$-imido distance, thus supporting the importance of a resonance contribution with a partial C=NMe$_2$. The $\eta^2$-CN groups are symmetrically bonded to the Ta center, suggesting contribution from the amido−carbene resonance structure. Of course, the $\pi$ interaction of the imine carbon atoms (C(19), C(30)) with the NMe$_2$ substituents also contributes to the lengthening of the Ta−C$_{imine}$ distance.

Interestingly, compound **5** can also be obtained from the reaction of Ta(NMe$_2$)$_3$Cl[($^i$PrN)$_2$CN(H)$^i$Pr] (**4**) with excess 2,6-dimethylphenyl isocyanide. This transformation entails not only insertion of isocyanide into the Ta−amido bonds but also conversion of the guanidinate ligand into the dianion. Conclusive identification of this product is based on the equivalence of both spectroscopic and unit cell parameters, as determined by single-crystal X-ray diffraction, for this product and an authentic sample of **5** prepared from **1**. We have previously observed the conversion of **4** into **1** by addition of basic reagents such as LiNMe$_2$.[7b] In the reaction of **4** with ArNC an obvious source of strong base is the complex itself. In fact, a sacrifice of 25% of **4** provides one possible source of the required base as NMe$_2$ anions and allows for the isolated yield of **5** (70%) obtained from this route.

In conclusion, some reactivity features of mono- and dianionic guanidinate complexes of Ta(V) have been established. On the basis of the reaction with Me$_3$SiCl it would appear that, at least under some circumstances, the dianionic form of *N*,*N'*,*N''*-triisopropylguanidinate reacts as an amido ligand and is in fact more reactive than an NMe$_2$ ligand in the same complex. In contrast, insertion of 2,6-dimethylphenyl isocyanide occurs selectively into the Ta−NMe$_2$ bond, leaving the guanidinate ligand unaltered. The spontaneous transformation of the monoanionic guanidinate ligand in **4** into the dianionic ligand in **5** by reaction of **4** with isocyanide was an unanticipated result. The mechanism of this transformation is a current point of investigation. Other current efforts are directed to further developing this reaction chemistry of these guanidinate complexes and investigating possible subsequent reactions of the $\eta^2$-iminocarbamoyl compounds.

## Experimental Section

**General Considerations.** All manipulations were carried out in either a nitrogen filled drybox or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuterated benzene and toluene were dried by vacuum transfer from potassium. Trimethylsilyl chloride, PhCH$_2$MgCl, and 2,6-dimethylphenyl isocyanide were purchased from Aldrich and used without further purification. Preparation of Ta(NMe$_2$)$_3$[($^i$PrN)$_2$CN$^i$Pr] (**1**) and of Ta(NMe$_2$)$_3$Cl[($^i$PrN)$_2$CN(H)$^i$Pr] (**4**) was carried out according to literature procedures.[7,8] $^1$H NMR spectra were run on either a Gemini 200 MHz or a Bruker 500 MHz spectrometer with deuterated benzene or toluene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

**Preparation of Ta(NMe$_2$)$_3$(CH$_2$Ph)[(N$^i$Pr)$_2$CN($^i$Pr)SiMe$_3$] (3).** Chlorotrimethylsilane (1.10 g, 10.13 mmol) was added dropwise to Ta(NMe$_2$)$_3$[C(N$^i$Pr)$_3$] (**1**; 1.00 g, 2.01 mmol) dissolved in toluene (30 mL). The reaction mixture was heated to 80 °C for 12 h and then cooled. The reaction mixture turned dark orange. Volatile materials were removed under reduced pressure to give an orange oil (**2**). $^1$H NMR (C$_6$D$_6$, ppm): 0.13 (s, Si(C*H*$_3$)$_3$, 9 H), 1.02 (d, $^3J_{HH}$ = 6.40 Hz, (C*H*$_3$)$_2$CH, 6 H), 1.19−1.60 (br, (C*H*$_3$)$_2$CH, 12 H), 3.29 (sept, (CH$_3$)$_2$C*H*, 1 H), 4.24 (s, N(C*H*$_3$)$_2$, 18 H), 4.39 (br, (CH$_3$)$_2$C*H*, 2 H). $^{13}$C NMR (C$_6$D$_6$, ppm): 1.66 (s, Si(C*H*$_3$)$_3$), 23.18 (s, (*C*H$_3$)$_2$CH), 24.40 (s, (*C*H$_3$)$_2$CH), 49.11 (br, (CH$_3$)$_2$*C*H), 50.46 (s, N(*C*H$_3$)$_2$), 51.81 (s, (CH$_3$)$_2$*C*H), 172.80 (s, *C*N$_3$). The chloro tris(dimethylamido) complex **2** was dissolved in diethyl ether (30 mL). To this was added a 1.0 M diethyl ether solution of PhCH$_2$MgCl (10.0 mL, 10.0 mmol) dropwise at −35 °C. The temperature of the reaction mixture was slowly raised to 25 °C, and the mixture was stirred for another 4 h. It was then filtered to remove MgCl$_2$. Solvents were removed from the filtrate under reduced pressure, and the resulting oil was extracted with pentane (20 mL). Pentane was replaced with diethyl ether (10 mL), and this mixture was cooled to −35 °C. Yellow crystals of **3** were obtained in 53% yield (0.700 g, 1.06 mmol) based on **1**. Mp: 128.8 °C. Anal. Calcd for C$_{26}$H$_{55}$N$_6$SiTa: C, 47.26; H, 8.39; N, 12.72. Found: C, 46.98; H, 8.34; N, 12.56. $^1$H NMR (C$_6$D$_6$, ppm): 0.16 (s, Si(C*H*$_3$)$_3$, 9 H), 1.13 (overlapping d, $^3J_{HH}$ = 6.77 Hz, 9 H, (C*H*$_3$)$_2$CH), 1.18 (d, $^3J_{HH}$ = 6.47 Hz, 3 H, (C*H*$_3$)$_2$CH), 1.25 (d, $^3J_{HH}$ = 6.44 Hz, 3 H, (C*H*$_3$)$_2$CH), 1.35 (d, $^3J_{HH}$ = 6.60 Hz, 3 H, (C*H*$_3$)$_2$CH), 2.42, 2.61 (AB pattern, $J_{HH}$ = 11.72 Hz, 2H, C*H*$_2$Ph), 3.23 (s, 6 H, N(C*H*$_3$)$_2$), 3.24 (m, partially obscured by signal at 3.23, $^3J_{HH}$ = 6.77 Hz, 1 H, (CH$_3$)$_2$C*H*), 3.50 (s, 6 H, N(C*H*$_3$)$_2$), 3.58 (s, 6 H, N(C*H*$_3$)$_2$), 4.23, 4.28 (two overlapping m, 2 H, (CH$_3$)$_2$C*H*), 6.92 (t, $^2J_{HH}$ = 7.19 Hz, C$_6$*H*$_5$CH$_2$, *para* proton), 7.34 (t, $^2J_{HH}$ = 7.53 Hz, C$_6$*H*$_5$CH$_2$, *meta* protons), 7.40 (d, $^2J_{HH}$ = 7.55 Hz, C$_6$*H*$_5$CH$_2$, *ortho* protons). $^{13}$C NMR (C$_6$D$_6$, ppm): 2. 66 (s, Si(*C*H$_3$)$_3$), 24.87 (s, (*C*H$_3$)$_2$CH), 24.90 (s, (*C*H$_3$)$_2$CH), 25.09 (s, (*C*H$_3$)$_2$CH), 25.18 (s, (*C*H$_3$)$_2$CH), 25.23 (s, (*C*H$_3$)$_2$CH), 26.33 (s, (*C*H$_3$)$_2$CH), 47.07 (s, (CH$_3$)$_2$*C*H), 47.27 (s, (CH$_3$)$_2$*C*H), 48.04 (s, N(*C*H$_3$)$_2$), 49.00 (s, N(*C*H$_3$)$_2$), 49.88 (s, N(*C*H$_3$)$_2$), 51.55 (s, (CH$_3$)$_2$*C*H), 66.46 (s, *C*H$_2$C$_6$H$_5$), 121.64, 127.34, 127.81, 151.21 (s, CH$_2$*C*$_6$H$_5$), 168.40 (s, *C*N$_3$).

**Preparation of Ta(NMe$_2$)[C(N$^i$Pr)$_3$][(Me$_2$N)C=N(2,6-Me$_2$C$_6$H$_3$)]$_2$ (5).** Complex **1**, Ta(NMe$_2$)$_3$[C(N$^i$Pr)$_3$] (0.409 g, 0.82 mmol), was dissolved in diethyl ether (20 mL). To this solution was added 2,6-dimethylphenyl isocyanide (0.325 g, 2.47 mmol) dissolved in diethyl ether (20 mL), and the mixture was stirred. After 12 h, a pale yellow solid started depositing in the reaction flask. The reaction mixture was stirred for another 12 h. Solvents were removed under reduced pressure, and the resulting yellow powder was repeatedly washed with pentane to remove excess 2,6-dimethylphenyl isocyanide. Analytically pure samples of **5** were obtained by fractional crystallization of the crude product from toluene at −35 °C. Yield: 94%. Crystals suitable for X-ray diffraction were obtained from diethyl ether at −35 °C. Mp: 170−171 °C. Anal. Calcd for C$_{34}$H$_{57}$N$_8$Ta: C, 53.82; H, 7.57; N, 14.77. Found: C, 53.66; H, 7.45; N, 14.27. IR (Nujol): 1588 cm$^{-1}$ (br). $^1$H NMR (toluene-*d*$_8$, ppm): 1.26 (d, $^3J_{HH}$ = 7.00 Hz, (C*H*$_3$)$_2$CH, 3 H), 1.42 (s, C$_6$H$_3$(C*H*$_3$)$_2$, 3 H), 1.44 (d, $^3J_{HH}$ = 6.50 Hz, (C*H*$_3$)$_2$CH, 3 H), 1.47 (d, $^3J_{HH}$ = 5.96 Hz, (C*H*$_3$)$_2$CH, 3 H), 1.50 (d, $^3J_{HH}$ = 6.00 Hz, (C*H*$_3$)$_2$CH, 3 H), 1.55 (br, (C*H*$_3$)$_2$CH, 3 H), 1.61 (br, (C*H*$_3$)$_2$CH, 3 H), 1.68 (s, C$_6$H$_3$(C*H*$_3$)$_2$, 3 H), 2.06 (s, C$_6$H$_3$(C*H*$_3$)$_2$, 3 H), 2.15 (s, N(C*H*$_3$)$_2$, 3 H), 2.29 (s, N(C*H*$_3$)$_2$, 3 H), 2.51 (s, C$_6$H$_3$(C*H*$_3$)$_2$, 3 H), 2.83 (s, N(C*H*$_3$)$_2$, 3 H), 3.13 (s, N(C*H*$_3$)$_2$, 3 H), 3.29 (s, TaN(C*H*$_3$)$_2$, 6 H), 4.14 (br, (CH$_3$)$_2$C*H*, 1 H), 4.60 (br, (CH$_3$)$_2$C*H*, 1 H), 4.80 (sept, (CH$_3$)$_2$C*H*, 1 H), 6.71, 6.72, 6.74, 6.80, 6.81, 6.82, 6.83, 6.85, 6.86, 6.88, 6.90, 6.91, 6.93 (br, C$_6$*H*$_3$(CH$_3$)$_2$, aromatic protons). $^{13}$C NMR (toluene-*d*$_8$, ppm): 17.63 (s, C$_6$H$_3$(*C*H$_3$)$_2$), 17.99 (s, C$_6$H$_3$(*C*H$_3$)$_2$), 18.02 (s, C$_6$H$_3$(*C*H$_3$)$_2$), 19.88 (s, C$_6$H$_3$(*C*H$_3$)$_2$), 24.30 (br, (*C*H$_3$)$_2$CH), 25.20 (s, (*C*H$_3$)$_2$CH), 25.53 (s, (*C*H$_3$)CH), 26.71 (br, (*C*H$_3$)$_2$CH), 28.16 (s, (*C*H$_3$)$_2$CH), 28.33 (br, (*C*H$_3$)$_2$CH), 35.96 (s, N(*C*H$_3$)$_2$), 36.63 (s, N(*C*H$_3$)$_2$), 46.13 (s, N(*C*H$_3$)$_2$), 46.20 (s, N(*C*H$_3$)$_2$), 46.25 (s, (CH$_3$)$_2$*C*H), 47.91 (s, (CH$_3$)$_2$*C*H), 49.66 (br, TaN(*C*H$_3$)$_2$), 50.76 (br, (CH$_3$)$_2$*C*H), 124.24, 124.91, 127.04, 127.74, 127.81, 127.94, 129.16, 133.26, 145.79 (s, *C*$_6$H$_3$(CH$_3$)$_2$, aromatic carbon), 155.16 (s, *C*N$_3$), 214.23 (s, N=*C*−N(CH$_3$)$_2$).

**Reaction of 4 with 2,6-Dimethylphenyl Isocyanide.** Complex **4**, $Ta(NMe_2)_3Cl[(^iPrN)_2C(NH^iPr)]$ (0.772 g, 1.448 mmol) was dissolved in diethyl ether (30 mL). To this was added a solution of 2,6-dimethylphenyl isocyanide (0.570 g, 4.346 mmol) dissolved in diethyl ether (10 mL). The reaction mixture was stirred for 24 h. Solvent was emoved under reduced pressure to give an orange solid. Pentane (30 mL) was added to the solid, this solution was stirred for 1 h at room temperature, and the supernatant was decanted off. The pentane-insoluble solid was dried in vacuo to give **5** in 70% yield.

**Structural Determinations for 3 and 5.** Single crystals were mounted on thin glass fibers using a viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are summarized in Table 1. Data were collected on a Bruker AX SMART 1K CCD diffractometer using 0.3° $\omega$-scans at 0, 90, and 180° in $\phi$. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.

The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library.

**Acknowledgment.** This work was supported by the Natural Sciences and Engineering Research Council of Canada.

**Supporting Information Available:** Figures giving selected $^1H$ NMR spectra for **3** and X-ray diffraction data, including tables of atomic positions, thermal parameters, crystallographic data, and bond distances and angles and ORTEP drawings, for compounds **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM991010F