Insertion Routes to Tetrasubstituted Guanidinate Complexes of Ta(V) and Nb(V)

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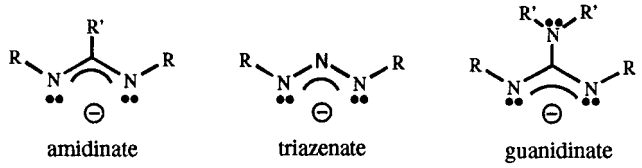
The preparation and characterization of guanidinate-containing complexes of Nb and Ta is described. The direct reactions of $M(NMe_2)_5$ with either dicyclohexylcarbodiimide (CyN═C═NCy) and diisopropylcarbodiimide (^{i}PrN═C═N^{i}Pr) proceeded smoothly at room temperature under nitrogen to yield $[RNC(NMe_2)NR]M(NMe_2)_4$ (M = Ta, Nb; R = Cy, ^{i}Pr). The spectroscopic characterization of these materials is consistent with a symmetrical chelating bidentate guanidinate anion bonded to a pseudo-octahedral metal center. Confirmation of these details was provided by a single-crystal X-ray diffraction study in the case of $[CyNC(NMe_2)NCy]Ta(NMe_2)_4$ (**1**). Delocalization of the lone pair of electrons on the guanidinate NMe_2 group into the ligand N−C−N π system does not appear to be significant in these species.

Introduction

Amidinates and triazinates are well established as versatile and flexible ligand systems for a variety of transition metal and main group metal centers (Chart 1).[1] Among the important features of these species are the donor ability of the nitrogen centers and the potential to explore both the steric and electronic effects induced by the variation of organic substituents on the ligand framework. This is particularly true and has been heavily exploited in the amidinate ligand system, for which a wide variety of organic substituents on both nitrogen and the central carbon atoms have been reported.[2]

Guanidinate anions also fall into this general class of ligands and, in contrast to the aforementioned species, have received limited attention in coordination and organometallic chemistry.[3,4]

Chart 1



A key difference between these ligands is the presence of an additional nitrogen center for the guanidinate. The resonance contributors for *N*,*N*,*N*′,*N*″-tetrasubstituted guanidinate anions are summarized in Scheme 1. The lone pair of electrons on the NR'_2 function allows the zwitterionic resonance structure **A**. In order for this particular contribution to be important, the N center must be planar, sp^2 hybridized and there must be a small dihedral angle between the planes defined by the CNR'_2 group and that defined by the conjugated NCN moiety. Although the ability to stabilize the positive charge on nitrogen is likely to be superior for the disubstituted NR'_2 group, the attendant steric congestion caused by the two organic substituents would probably encourage a larger dihedral angle thus hindering the appropriate orientation for π conjugation. Clearly, the role of substituents from both an electronic and a steric standpoint will be important in analyzing the bonding in guanidinate anions.

We were attracted to N-substituted guanidinate anions, $[RNC(NR'_2)NR]^-$, as bulky supporting ligands for transition metal complexes, and herein we report the synthesis and characterization of a series of guanidinate complexes of Nb and Ta. These species were derived by the insertion of carbodiimides into the metal−amido linkage of $M(NMe_2)_5$ to yield $[RNC(NMe_2)NR]M(NMe_2)_4$ (M = Nb, Ta; R = cyclohexyl, isopropyl). These materials represent the first report of the use of guanidinate ligands for the metals of group 5.

Experimental Section

General Considerations. All manipulations were carried out either in a nitrogen-filled drybox or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuterated benzene and deuterated pyridine were dried by vacuum transfer from potassium. Diisopropylcarbodiimide, dicyclohexylcarbodiimide, and bis(trimethylsilyl)carbodiimide were purchased from

(1) (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Moore, D. S.; Robinson, S. D. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 1.

(2) Littke, A.; Sleiman, N.; Bensimon, C.; Richeson, D.; Yap, G. P. A.; Brown, S. *Organometallics* **1998**, *17*, 446 and references therein. Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359 and references therein. Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. *Organometallics* **1997**, *16*, 5183. Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417 and references therein.

(3) For examples of transition metal complexes of guanidinate monoanions, see: (a) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1970**, 2550. (b) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood-John Wiley: Chichester, U.K., 1980; Chapter 10 and references therein. (c) Yip, H.-K.; Che, C.-M.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369. (d) Bailey, P. J.; Mitchell, L. A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2839. (e) da S. Maia, J. R.; Gazard, P. A.; Kilner, M.; Batsanova, A. S.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1997**, 4625. (f) Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1997**, 3349. (g) Bailey, P. J.; Bone, S. F.; Mitchell, L. A.; Parsons, S.; Taylor, K. J.; Yellowless, L. J. *Inorg. Chem.* **1997**, *36*, 867.

(4) For examples of main group metal complexes of guanidinate monoanions, see: (a) Snaith, R.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. A* **1970**, 380. (b) Clegg, W.; Snaith, R.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1309. (c) Pattison, I.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. A* **1968**, 837. (d) Bailey, P. J.; Gould, R. O.; Harmer, C. N.; Pace, S.; Steiner, A.; Wright, D. S. *Chem. Commun.* **1997**, 1161. (e) Chivers, T.; Parvez, M.; Schatte, G. *J. Organomet. Chem.* **1998**, *550*, 213.

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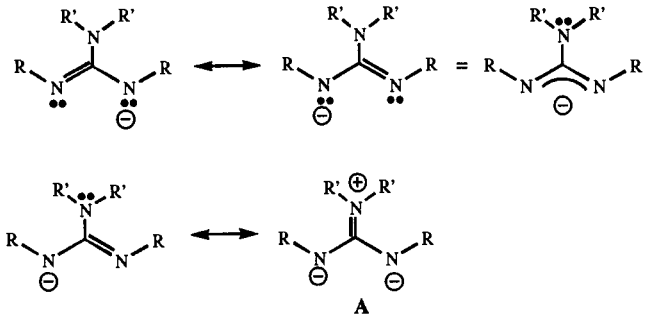
Scheme 1



Aldrich and used without further purification. Preparation of $Ta(NMe_2)_5$ and $Nb(NMe_2)_5$ was carried out according to literature procedures.[5] ^1H NMR spectra were run on a Gemini 200 MHz spectrometer with deuterated benzene or pyridine as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

$Ta(NMe_2)_4[CyNC(NMe_2)NCy]$ (1). A Schlenk flask was charged with CyNCNCy (0.103 g, 0.498 mmol) in 20 mL of hexane. $Ta(NMe_2)_5$ (0.200 g, 0.498 mmol) was added slowly to this solution. The reaction mixture was stirred for 24 h at room temperature followed by removal of solvent under oil pump vacuum. The product was subsequently recrystallized from toluene at −30 °C to yield 0.245 g (80%) of **1**: ^1H NMR (C_6D_6, ppm): 3.52, (s, 12H, NMe_2), 3.39 (s, 12H, NMe_2), 3.10 (br, 2H, C_6H_{11}), 2.48 (s, 6H, NMe_2), 1.1−1.9 (m, 20H, C_6H_{11}). ^{13}C NMR (C_6D_6, ppm): 167.7 (N*C*(NMe_2)N), 56.9 (N*C*H), 48.7 (TaN*C*H_3), 48.2 (TaN*C*H_3), 40.84 (CN*C*H_3), 35.4, 27.2, 26.4 (3s, C_6H_{11}). Anal. Calcd for $C_{23}H_{52}N_7Ta$: C, 45.46; H, 8.63; N, 16.14. Found: C, 45.77; H, 9.05; N, 16.64.

$Nb(NMe_2)_4[CyNC(NMe_2)NCy]$ (2). A Schlenk flask was charged with CyNCNCy (0.264 g, 1.28 mmol) in 20 mL of hexane. To this solution was added 0.400 g of $Nb(NMe_2)_5$ (1.28 mmol) to produce a blood red solution mixture, which was stirred overnight at room temperature. The solvent was removed under oil pump vacuum, and the 0.458 g of residue was extracted with diethyl ether, concentrated to 30 mL, and cooled to −30 °C to give 0.240 g of pale orange **2** (70% yield). ^1H NMR (C_6D_6, ppm): 3.38 (s, 12H, $NbNMe_2$), 3.22 (s, 12H, $NbNMe_2$), 3.20 (br, 2H, C_6H_{11}), 2.53 (s, 6H, $CNMe_2$), 1.15−1.90 (m, 20H, C_6H_{11}). ^{13}C NMR (C_6D_6, ppm): 167.23 (N*C*(NMe_2)N), 57.18 (NCH), 50.13 ($NbNCH_3$), 49.57 ($NbNCH_3$), 40.95 ($CNCH_3$), 35.67, 27.19, 26.50 (3s, C_6H_{11}). Anal. Calcd for $C_{23}H_{52}N_7Nb$: C, 53.16; H, 10.09; N, 18.87. Found: C, 53.51; H, 10.46; N, 18.48.

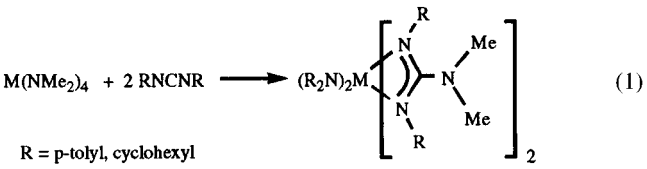
$Ta(NMe_2)_4[(CH_3)_2CHNC(NMe_2)NCH(CH_3)_2]$ (3). The procedure was similar to the synthesis of **1** using 0.200 g of $Ta(NMe_2)_5$ (0.498 mmol) and 0.062 g of $(CH_3)_2CHNCNCH(CH_3)_2$ (0.49 mmol) in hexane followed by recrystallization from toluene at −30 °C. Complex **3** was isolated in 94% yield (0.25 g): ^1H NMR (C_6D_6, ppm): 3.75 (br, 2H, $CHMe_2$), 3.52 (s, 12H, $TaNMe_2$), 3.39 (s, 12H, $TaNMe_2$), 2.47 (s, 6H, NMe_2), 1.19 (d, 12H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6, ppm): 163.80 (N*C*(NMe_2)N), 48.51 (TaN(*C*$H_3)_2$), 48.10 (TaN(*C*$H_3)_2$), 47.54 (N*C*HMe_2), 40.65 (CN(*C*$H_3)_2$), 25.00 (CH(*C*$H_3)_2$). Anal. Calcd for $C_{17}H_{44}N_7Ta$: C, 38.71; H, 8.41; N, 18.59. Found: C, 39.02; H, 8.81; N, 18.20.

$Nb(NMe_2)_4[(CH_3)_2CHNC(NMe_2)NCH(CH_3)_2]$ (4). Following a procedure similar to the synthesis of **2** using 0.40 g of $Nb(NMe_2)_5$ (1.28 mmol) and 0.162 g of $(CH_3)_2CHNCNCH(CH_3)_2$ (1.28 mmol) in hexane produced a blood red solution. After stirring for 24 h at room temperature followed by workup and recrystallization from toluene at −30 °C, complex **4** was isolated in 71% yield (0.40 g) as light yellow crystals. ^1H NMR (C_6D_6, ppm): 3.75 (br, 2H, $CHMe_2$), 3.40 (s, 12H, $NbNMe_2$), 3.24 (s, 12H, $NbNMe_2$), 2.52 (s, 6H, NMe_2), 1.19 (d, 12H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6, ppm): 167.10 (N*C*(NMe_2)N), 49.90 ($NbN(CH_3)_2$), 49.41 ($NbN(CH_3)_2$), 47.80 (N*C*HMe_2), 40.81 (CN(*C*$H_3)_2$), 25.31 (CH(*C*$H_3)_2$). Anal. Calcd for $C_{23}H_{52}N_7Nb$: C, 46.46; H, 10.09; N, 22.31. Found: C, 46.10; H, 10.16; N, 22.04.

(5) Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 1355. Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 449.

Results and Discussion

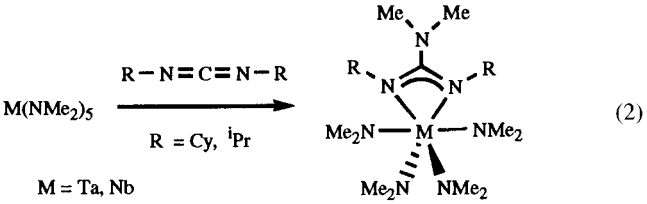
While the insertion reactions of carbodiimides is rather well-known for a variety of M−H[6] and M−R[7,8] species where M is either a main group or transition metal, the analogous reactions with M−Cl[9] and M−N[3,10,11] are less well developed especially for the transition metals. The only reported examples of carbodiimide insertion into transition metal amido functions is the reaction between $M(NMe_2)_4$ (M = Ti, Zr, Hf) and di(*p*-tolyl)carbodiimide or dicyclohexylcarbodiimide to yield a bis-(dimethylamido)bis(guanidinate)M series (eq 1).[3a,b] In the case of zirconium, this reaction has been generalized to include insertion of carbodiimides into Zr−P and Zr−As bonds.[12]



$M(NMe_2)_4 + 2\ RNCNR \longrightarrow (R_2N)_2M[\ldots]_2$ (1)

R = p-tolyl, cyclohexyl

The direct reactions of pentakis(dimethylamido)M (M = Ta, Nb) complexes with both dicyclohexylcarbodiimide and diisopropylcarbodiimide proceeded smoothly at room temperature under nitrogen to provide good yields of complexes **1**−**4** (eq 2). Only in the case of the Nb reactions was a dramatic color change noted during reaction. The origin of this phenomenon is not clear, but given the fact that all of the products are pale in color, this red material is likely a minor product or impurity. These new guanidinate-containing complexes were characterized by spectroscopic methods and in the case of **1** by a single-crystal X-ray diffraction study.



$M(NMe_2)_5 \xrightarrow[R = Cy,\ ^iPr]{R-N=C=N-R} Me_2N-M(NMe_2)_3$ (2)

M = Ta, Nb

(6) For some examples, see: (a) Dionne, M.; Hao, S.; Gambarotta, S. *Can. J. Chem.* **1995**, *73*, 1126 and references therein. (b) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastitin, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278 and references therein. (c) Harris, A. D.; Robinson, S. D.; Sahajpal, A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 1327 and references therein.

(7) (a) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastitin, C. *Inorg. Chem.* **1985**, *24*, 654. (b) Wilkins, J. D. *J. Organomet. Chem.* **1974**, *80*, 349. (c) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1974**, 1579. (d) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2611.

(8) For examples of the insertion reaction into main group metal−carbon bonds, see: (a) Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1997**, 957. (b) Li, M.-D.; Chang, C.-C.; Wang, Y.; Lee, G.-H. *Organometallics* **1996**, *15*, 2571. (c) Lechler, R.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1989**, *359*, 1. (d) Kottmair-Maieron, D.; Lechler, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1991**, *593*, 111.

(9) (a) Kennepohl, D. K.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 5081 and references therein. (b) Schwarz, W.; Rajca, G.; Weidlein, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *525*, 143.

(10) For examples with M = Mg, see: Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1997**, 957.

(11) For examples with M = Si, Ge, Sn, see: (a) Matsuda, I.; Itoh, K.; Ishii, Y. *J. Organomet. Chem.* **1974**, *69*, 353. (b) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. A* **1970**, 2550. (c) George, T. A.; Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 2157.

(12) (a) Lindenberg, F.; Sieler, J.; Hey-Hawkins, E. *Polyhedron* **1996**, *15*, 1459. (b) Hey-Hawkins, E.; Lindenberg, F. *Z. Naturforsch.* **1993**, *48b*, 951.

Table 1. Summary of Crystal Data and Structure Refinement for $Ta(NMe_2)_4[CyNC(NMe_2)NCy]$ (**1**)

empirical formula	$C_{23}H_{57}N_7Ta$
fw	607.67
temp	153(2) K
wavelength	0.710 73 (Å)
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 10.3664(6)$ Å $b = 14.6400(9)$ Å $c = 18.549(1)$ Å $\alpha = 81.304(1)°$ $\beta = 88.894(1)°$ $\gamma = 89.103(1)°$
volume, Z	2782.0(3) Å^3, 2
density (calcd)	1.451 Mg/m^3
abs coeff	3.973 mm^{-1}
$F(000)$	1248
cryst size	0.10 × 0.10 × 0.10 mm
θ range for data collection	1.11−28.68°
limiting indices	$-13 \le h \le 7$, $-19 \le k \le 19$, $-24 \le l \le 24$
reflns collected	17 104
indep reflns	12 070 [R(int) = 0.0260]
abs correction	none
refinement meth	full-matrix least-squares on F^2
data/restraints/params	12066/0/559
goodness-of-fit on F^2	1.050
final R indices [$I > 2\sigma(I)$]	R1 = 0.0357, wR2 = 0.0747
R indices (all data)	R1 = 0.0502, wR2 = 0.0865
largest diff peak and hole	1.288 and −1.124 e·Å^{-3}

Table 2. Selected Bond Lengths (Å) for $Ta(NMe_2)_4[CyNC(NMe_2)NCy]$ (**1**)

Ta(1)−N(5)	2.011(4)	N(5)−C(18)	1.454(7)
Ta(1)−N(4)	2.013(4)	N(5)−C(19)	1.464(6)
Ta(1)−N(6)	2.025(4)	N(6)−C(21)	1.455(7)
Ta(1)−N(7)	2.038(4)	N(6)−C(20)	1.465(7)
Ta(1)−N(1)	2.246(4)	N(7)−C(23)	1.455(6)
Ta(1)−N(2)	2.280(4)	N(7)−C(22)	1.465(6)
Ta(1)−C(13)	2.695(5)	N(8)−C(36)	1.328(6)
Ta(2)−N(12)	2.015(4)	N(8)−C(29)	1.479(6)
Ta(2)−N(11)	2.019(4)	N(9)−C(36)	1.334(6)
Ta(2)−N(14)	2.041(4)	N(9)−C(35)	1.464(6)
Ta(2)−N(13)	2.045(4)	N(10)−C(36)	1.415(6)
Ta(2)−N(9)	2.258(4)	N(10)−C(37)	1.426(8)
Ta(2)−N(8)	2.263(4)	N(10)−C(38)	1.459(8)
N(1)−C(13)	1.331(6)	N(11)−C(40)	1.460(7)
N(1)−C(6)	1.469(6)	N(11)−C(39)	1.458(7)
N(2)−C(13)	1.318(6)	N(12)−C(42)	1.454(6)
N(2)−C(12)	1.466(5)	N(12)−C(41)	1.459(7)
N(3)−C(13)	1.427(6)	N(13)−C(46)	1.449(6)
N(3)−C(14)	1.442(6)	N(13)−C(45)	1.462(6)
N(3)−C(15)	1.442(7)	N(14)−C(44)	1.455(7)
N(4)−C(16)	1.460(7)	N(14)−C(43)	1.451(7)
N(4)−C(17)	1.461 (7)		

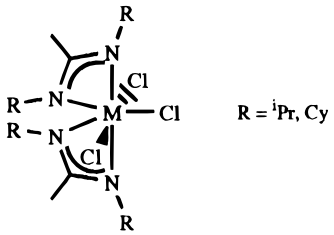
Both the ^{1}H and ^{13}C NMR spectra were consistent with the single insertion product. The most obvious changes from the starting materials were a shift in signals for the alkyl groups originating on the carbodiimides and the division of the dimethylamino protons signal (singlets at 3.25 and 3.12 ppm for the Ta and Nb staring materials, respectively) into three singlets. The integrated ratios of the signals assigned to the NMe_2 groups (1:2:2) as well as their chemical shifts provided the first direct evidence for the number of guanidinate and amido ligands within the compounds. The observation of a single resonance for the cyclohexyl and isopropyl protons on the α carbon indicated a structure with either a symmetric arrangement of the ligands or one that was fluxional. ^{13}C NMR was consistent with the proton spectrum in all cases and revealed that the central, sp^2 C of the guanidine ligands had undergone a substantial downfield shift from the starting carbodiimides (142.1 and 140.2 ppm for Cy and ^{i}Pr, respectively). Despite attempts to provoke the incorporation of a second equivalent of carbodiimide through prolonged reaction time and increased temperature, only the monoinsertion products were observed. Multiple insertion products have been observed in the analogous reactions of Me_xMCl_{5-x} (M = Ta, Nb; x = 1, 2, 3) with carbodiimides RNCNR (R = isopropyl, cyclohexyl, *p*-tolyl) to give acetamidinate complexes $MCl_4[RNC(Me)=NR]$, $MeMCl_3[RN-C(Me)=NR]$, and $MCl_3[RN-C(Me)=NR]_2$.[7b−d] Furthermore, a double insertion product is reported for the reaction of $M(NMe_2)_5$ (M = Ti, Zr, Hf) with carbodiimides to yield bis(guanidinate) complexes $[(p\text{-tolylN})_2CNMe_2]_2M(NMe_2)_2$ and $[(CyN)_2CNMe_2]_2M(NMe_2)_2$.[3a,b]

These observations might be attributed to two possible factors. The first is the increased steric congestion of complexes **1**−**4** compared to the monoinsertion products $MCl_4[RN-C(Me)=NR]$ and $[(RN)_2CNMe_2]M(NMe_2)_3$ compounds. A second possibility for the decreased reactivity of **1**−**4** toward further insertion may arise from the increased π-donating ability of amido versus chloro and the consequent reduction in the acidity of the Ta or Nb center. Further support for the idea that steric constraints may play a role in these reactions is provided by the fact that attempts to get a similar insertion reaction with bis(trimethylsilyl)carbodiimide have been completely unsuccessful.

Table 3. Selected Bond Angles (deg) for $Ta(NMe_2)_4[CyNC(NMe_2)NCy]$ (**1**)

N(5)−Ta(1)−N(4)	105.3(2)	C(14)−N(3)−C(15)	116.7(4)
N(5)−Ta(1)−N(6)	91.6(2)	C(16)−N(4)−C(17)	108.0(5)
N(4)−Ta(1)−N(6)	89.7(2)	C(16)−N(4)−Ta(1)	126.2(4)
N(5)−Ta(1)−N(7)	91.0(2)	C(17)−N(4)−Ta(1)	125.7(4)
N(4)−Ta(1)−N(7)	90.4(2)	C(18)−N(5)−C(19)	108.2(4)
N(6)−Ta(1)−N(7)	177.3(2)	C(18)−N(5)−Ta(1)	125.3(4)
N(5)−Ta(1)−N(1)	98.4(2)	C(19)−N(5)−Ta(1)	126.3(3)
N(4)−Ta(1)−N(1)	156.2(2)	C(21)−N(6)−C(20)	107.1(4)
N(6)−Ta(1)−N(1)	87.9(2)	C(21)−N(6)−Ta(1)	129.2(4)
N(7)−Ta(1)−N(1)	90.9(2)	C(20)−N(6)−Ta(1)	122.5(4)
N(5)−Ta(1)−N(2)	157.0(2)	C(23)−N(7)−C(22)	108.8(4)
N(4)−Ta(1)−N(2)	97.7(2)	C(23)−N(7)−Ta(1)	130.6(3)
N(6)−Ta(1)−N(2)	89.9(2)	C(22)−N(7)−Ta(1)	120.5(3)
N(7)−Ta(1)−N(2)	87.5(2)	C(36)−N(8)−C(29)	119.4(4)
N(1)−Ta(1)−N(2)	58.66(14)	C(36)−N(8)−Ta(2)	94.3(3)
N(5)−Ta(1)−C(13)	127.9(2)	C(29)−N(8)−Ta(2)	146.2(3)
N(4)−Ta(1)−C(13)	126.7(2)	C(36)−N(9)−C(35)	121.6(4)
N(6)−Ta(1)−C(13)	87.2(2)	C(36)−N(9)−Ta(2)	94.4(3)
N(7)−Ta(1)−C(13)	90.6(2)	C(35)−N(9)−Ta(2)	144.1(3)
N(1)−Ta(1)−C(13)	29.50(13)	C(36)−N(10)−C(37)	116.6(5)
N(2)−Ta(1)−C(13)	29.24(13)	C(36)−N(10)−C(38)	119.5(5)
N(12)−Ta(2)−N(11)	104.7(2)	C(37)−N(10)−C(38)	116.4(5)
N(12)−Ta(2)−N(14)	89.9(2)	C(40)−N(11)−C(39)	108.6(4)
N(11)−Ta(2)−N(14)	91.4(2)	C(40)−N(11)−Ta(2)	125.5(4)
N(12)−Ta(2)−N(13)	89.8(2)	C(39)−N(11)−Ta(2)	125.8(3)
N(11)−Ta(2)−N(13)	91.7(2)	C(42)−N(12)−C(14)	109.0(4)
N(14)−Ta(2)−N(13)	176.9(2)	C(42)−N(12)−Ta(2)	126.2(3)
N(12)−Ta(2)−N(9)	158.4(2)	C(41)−N(12)−Ta(2)	124.5(3)
N(11)−Ta(2)−N(9)	96.9(2)	C(46)−N(13)−C(45)	108.4(4)
N(14)−Ta(2)−N(9)	90.3(2)	C(46)−N(13)−Ta(2)	131.2(3)
N(13)−Ta(2)−N(9)	88.9(2)	C(45)−N(13)−Ta(2)	120.4(3)
N(12)−Ta(2)−N(8)	99.8(2)	C(44)−N(14)−C(43)	108.7(4)
N(11)−Ta(2)−N(8)	155.5(2)	C(44)−N(14)−Ta(2)	124.6(3)
N(14)−Ta(2)−N(8)	87.6(2)	C(43)−N(14)−Ta(2)	125.7(3)
N(13)−Ta(2)−N(8)	89.4(2)	N(2)−C(13)−N(1)	113.6(4)
N(9)−Ta(2)−N(8)	58.61(14)	N(2)−C(13)−N(3)	125.9(4)
C(13)−N(1)−C(6)	119.3(4)	N(1)−C(13)−N(3)	120.5(4)
C(13)−N(1)−Ta(1)	94.3(3)	N(2)−C(13)−Ta(1)	57.6(2)
C(6)−N(1)−Ta(1)	145.4(3)	N(1)−C(13)−Ta(1)	56.2(2)
C(13)−N(2)−C(12)	121.6(4)	N(3)−C(13)−Ta(1)	174.1(3)
C(13)−N(2)−Ta(1)	93.1(3)	N(8)−C(36)−N(9)	112.5(4)
C(12)−N(2)−Ta(1)	144.7(3)	N(8)−C(36)−N(10)	121.6(4)
C(13)−N(3)−C(14)	120.2(4)	N(9)−C(36)−N(10)	125.8(4)
C(13)−N(3)−C(15)	114.1(4)		

In order to confirm the structural details of complexes **1**−**4** a single-crystal X-ray analysis of one of these compounds was undertaken. Complex **1** crystallized in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit. Selected bond distances and angles are provided in Tables 1−3 for both molecules. Figure 1 provides an ORTEP of one of these molecules and reveals the Ta(V) center in a distorted octahedral-based coordination geometry. The coordination environment of Ta contains a tetrasubstituted, bidentate guanidinate ligand derived from the insertion of a dicyclohexylcarbodiimide into one of the Ta−NMe_2 ligands of the starting material along with four remaining NMe_2 ligands. Completing the equatorial plane defined by the coordinated N−C−N function are two dimethylamido ligands (N(4) and N(5) or N(12) and N(13)). Two axial dimethylamido functions (N(6) and N(7) or N(14) and N(15)) complete the Ta coordination sphere (average N−Ta−N angle of 177.1°). The guanidinate ligand binds to Ta through two nitrogen atoms to yield a planar four-membered ring of sp^2-hybridized N and C centers with an average bite angle of 58.6°. The delocalized π interaction within the NCN moieties (N(1)−C(13)−N(2) and N(8)−C(36)−N(9)) leads to partial double bonded C−N distances which average 1.33 Å. The distances and angles within this cyclic arrangement are reminiscent of those in the structurally characterized seven-coordinate bis(diisopropylacetamidinato) and bis(dicyclohexylacetamidinato) complexes $Cl_3Ta(RNC(CH_3)NR)_2$ (R = ^{i}Pr, Cy) (**B**).[7c,d]



R = ^{i}Pr, Cy

B

The third guanidinate nitrogen (N(3) and N(10)) was derived from a dimethylamido function and lies just slightly out of the ligand plane. For example, the N(3)−C(13)−Ta(1) angle is 174.1(3)°. Although this exocyclic nitrogen appears to be distorted toward planar, sp^2 hybridization (Table 3), the angles of the mean planes defined by the C−NMe_2 and the bidentate NCN fragments average 80.7°. This feature militates against conjugation of the N−C−N π system and the lone pair on these NMe_2 groups. In accord with this are the N(3)−C(13) and N(10)−C(36) distances (average = 1.42 Å) which are consistent with an N−C single bond. Rather than being conjugated with the ligand π system, it appears that, in fact, this orientation of the dimethylamino group effectively adds a third dimension to the guanidinate ligand.

The four amido groups in each molecule are planar, a feature consistent with π donation of the nitrogen lone pair into a metal d orbital. Furthermore the values for the Ta−NMe_2 distances

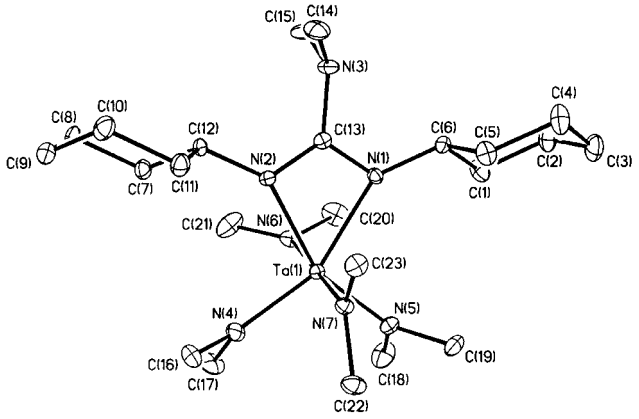


Figure 1. ORTEP diagram and atom-numbering scheme for Ta(NMe_2)$_4$[CyNC(NMe_2)NCy] (**1**) (Cy = cyclohexyl) showing one of the two independent molecules in the asymmetric unit. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

average 2.03 Å, which is compatible with a π interaction,[13] and the orientation of the amido groups is consistent with d−p interactions between the nitrogen p orbitals and metal d_{xy}, d_{xz}, d_{yz} orbitals of the distorted octahedral geometry described above. The angles between the mean planes of the axial amides are nearly orthogonal (84.4° and 88.4°), an alignment appropriate for these two amides to interact with two orthogonal tantalum d orbitals (i.e. d_{xz} and d_{yz}). The two equatorial amido ligands also exhibit a preferred orientation with the mean Me−N−Me planes at an average of 64° with respect to the plane defined by the Ta and NCN of the guanidine anion. It would appear that the maximum π overlap with the remaining tantalum d orbital (d_{xy}) would be achieved for these ligands if this angle were 90°. Opposing this orientation are the steric interactions between the axial and equatorial amido ligands and the fact that the two amido ligands are competing for donation to a single orbital.

In conclusion, we have shown that guanidinate ligands can be generated by the insertion reaction of carbodiimides into Ta and Nb amido functions. The structure of complex **1** indicates some of the steric and electronic features of these tetrasubstituted guanidinate ligands by providing initial details on the role of the bulk of the organic substituents and π delocalization in the ligand. Our current efforts and future reports will be directed at clarifying these issues through changes to the guanidinate framework, variation of the metal centers, and manipulation of ancillary ligands.

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Supporting Information Available: Listing providing a description of the structural solution and ORTEP drawings for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.