DALTON
FULL PAPER

Guanidinate anions and dianions. Reactions involving alkylguanidines, $(RNH)_2CNR$ (R = *i*-Pr or Cy), and metal amido complexes $M(NMe_2)_5$ (M = Ta or Nb)

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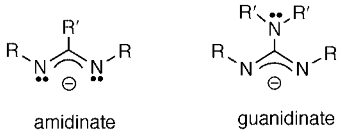
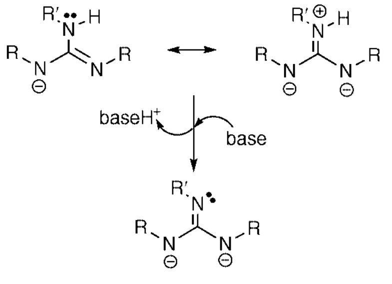
Protonation of the amido groups of $M(NMe_2)_5$ (M = Ta or Nb) with trialkylguanidines, $(RNH)_2CNR$ (R = *i*-Pr or Cy), directly produced a series of five-co-ordinated complexes, $M(NMe_2)_3[(RN)_2CNR]$ **1**–**4**. Single crystal X-ray analysis confirmed that **1** contained a dianionic *N*,*N*′,*N*″-triisopropylguanidinate ligand which was co-ordinated in a chelating bidentate mode. In contrast, protonation of the amido groups of $Ta(NMe_2)_4Cl$ with triisopropylguanidine gave the six-co-ordinated complex $Ta(NMe_2)_3Cl[(i\text{-}PrN)_2CNHi\text{-}Pr]$ **5** which possessed a bidentate monoanionic guanidinate ligand. Complex **5** can be converted into **1** by reaction with either $LiNMe_2$ or MeMgBr.

Introduction

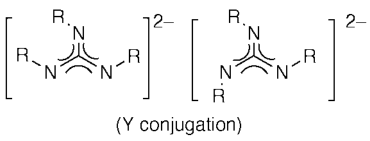
The ligating properties of monanionic guanidinates have received recent attention with a major focus being their resemblance to amidinates (Scheme 1).[1] This interest has been partly motivated by the rather limited application of guanidinates in transition metal chemistry.[2,3] We are particularly interested in the application of *N*,*N*′,*N*″-trialkylguanidines as ligands due to their ability to yield dianionic species by deprotonation of a second N–H function (Scheme 2). The resultant species could function as a diamido ligand and may exhibit π delocalization (Y conjugation) of the lone pairs on the sp^2 hybridized nitrogen centers (**I**) making it an analogue of the trimethylenemethane dianion.[4] In addition to possessing interesting electronic features, we felt that substituent modification of the guanidinate framework would allow investigation of deliberate variations to the steric and electronic parameters of the ligand and its metal complexes. Restriction of the R groups on the guanidinate ligand to alkyls should eliminate the possibility of unanticipated resonance contributions and, through inductive effects, further increase the donor ability of the ligands.



Scheme 1



Scheme 2

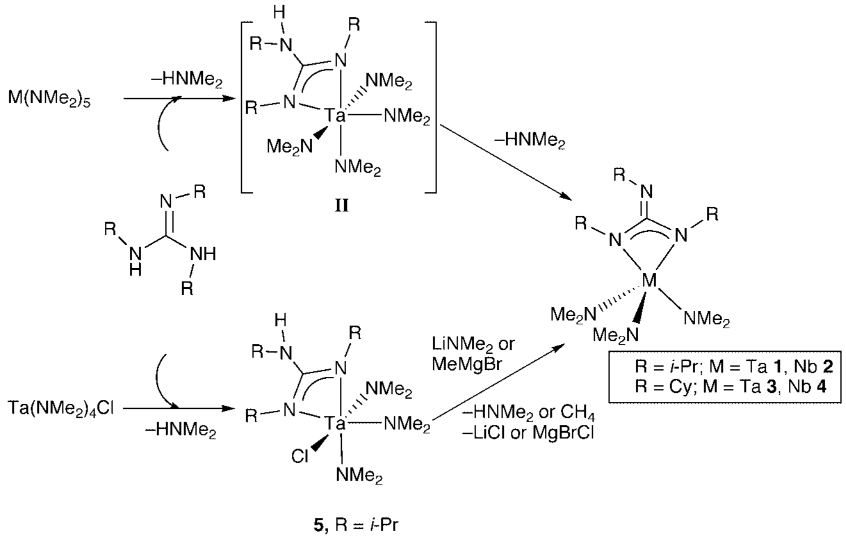


I

Employing trialkylguanidines as ligands requires the development of fundamental ideas regarding the introduction of guanidinate anions and dianions into a metal co-ordination sphere, the definition of features that favor different binding modes of the ligand, and investigation of the general reactivity characteristics of these complexes. Given the presence of two active N–H protons in an *N*,*N*′,*N*″-trialkylguanidine one introduction route which can be considered is the direct reaction of the parent guanidines with metal amido complexes. Such reactions would proceed through a protonation pathway to release amine with generation/introduction of the guanidinate anion. To this end we have been investigating the elimination of amido ligands from dimethylamido complexes of Ta^V and Nb^V. These materials are well known and easily synthesized in large quantities and the presence of more than one amido ligand in these compounds may provide the option either to introduce a second monoanionic guanidinate ligand or to remove a second proton from a co-ordinated guanidinate to yield a dianionic ligand.

Prior to our work, the sole reported example of a dianionic guanidinate bonded to a transition metal was represented by the dinuclear iron complex $[(OC)_3Fe\{\mu\text{-}\eta^2\text{-}(RN)_2CNR\}\text{-}Fe(CO)_3]$ (R = *i*-Pr or Cy), obtained as the unanticipated product of the reaction of $Fe(CO)_5$ and carbodiimides.[5] Recent reports of several main group complexes of guanidinate dianions include the crystallographically characterized species $Li_2(C(NPh)_3)$,[6] $Li_2(C(Nt\text{-}Bu)_3)$,[7] and $Sb[(i\text{-}PrN)_2CNHi\text{-}Pr][(iPrN)_3C]$.[8]

We recently reported the facile synthesis of $M(NMe_2)_3[(RN)_2CNR]$ **1**–**4** (M = Ta or Nb; R = *i*-Pr or Cy) from $M(NMe_2)_5$ and $(RNH)_2CNR$.[9] Herein, we now report the structural characterization of $Ta(NMe_2)_3[(i\text{-}PrN)_2CNi\text{-}Pr]$ **1** which possesses a dianionic guanidinate ligand. Furthermore we present the synthesis, structural characterization, and reactivity of $Ta(NMe_2)_3Cl[(i\text{-}PrN)_2CNHi\text{-}Pr]$ **5**, a complex possessing the monoanionic form of guanidinate ligand. The conversion of complex **5** into **1** by reaction with appropriate bases offers some insight on the formation of guanidinate complexes.

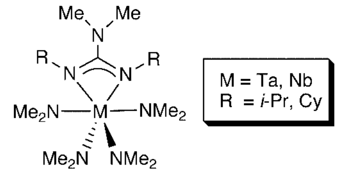


Scheme 3

Results and discussion

The reaction of triisopropylguanidine or tricyclohexylguanidine with homoleptic amido complexes, $M(NMe_2)_5$, in hexane proceeded smoothly at room temperature directly to provide complexes **1**–**4** in good yield.[9] Despite attempts to introduce a second equivalent of triisopropylguanidine through extended reaction time and increased temperature only these complexes can be isolated. The ^1H and ^{13}C NMR spectra of **1**–**4** exhibited similar general features. The proton signals for the alkyl groups shift and divide into three sets of resonances with equal intensity and the integrated intensity of the remaining amido groups and guanidinate alkyl groups is consistent with a product having a 3 : 1 ratio of amido to guanidinate. One of the most obvious changes in the guanidine upon deprotonation and co-ordination to the metal center is a shift in ^{13}C NMR signals for the central, sp^2 carbon (CN_3) nuclei to the δ 152–158 range. The corresponding ^{13}C resonances of the parent guanidines appear at δ 148.5 and 148.4 for tricyclohexylguanidine and triisopropylguanidine respectively. All of the spectroscopic evidence indicated that these reactions had proceeded directly to dianionic guanidinate-containing complexes that were likely co-ordinated in a chelating bidentate mode (Scheme 3). A structural study of **1** described below confirmed this proposal.

We anticipated that extension of this reaction scheme to include $Ta(NMe)_4Cl$ as starting material should offer an analogous product that would possess a Ta–Cl function that could be employed for subsequent reactions. However, the reaction of triisopropylguanidine with $Ta(NMe_2)_4Cl$ in hexane produced **5** in 71% yield (Scheme 3). All of the spectroscopic characterization of **5** indicated that this species contained a *monoanionic* triisopropylguanidinate co-ordinated to Ta. For example, the IR spectrum showed a sharp peak at 3336 cm^{-1} suggesting the presence of an N–H moiety and the NMR spectra indicated that the product possessed a 3 : 1 ratio of amido to guanidinate ligands with the NMe_2 ligands occupying two environments. Based on the presence of three amido groups, one guanidinate and one chloride ligand we proposed a six-co-ordinate pseudo-octahedral arrangement of ligands around a tantalum(V) center. The 2 : 1 intensity ratio for the amido functions appeared to be most consistent with the geometry of **5** provided in Scheme 3 (*i.e.* two NMe_2 groups *cis* to the Cl atom and one NMe_2 in *trans* position). This structural proposition is endorsed by our results with monoanionic tetrasubstituted guanidinates for which we observed species with structures represented by **III**[11] and the structural results presented below.



III

In contrast to the compounds with structure **III**, which displayed a single resonance for the R substituents, complex **5** exhibited three doublets of equal intensity for the CH_3 protons of *i*-Pr fragments. This observation suggests either a hindered rotation of the C–N(H)*i*-Pr bond or an asymmetry in the co-ordination of guanidinate nitrogen atoms to the Ta. The broadened ^1H NMR signals for two of the *i*-Pr signals, which we assign as corresponding to the groups on the nitrogen atoms bonded to Ta, indicates a fluxional process occurring within the ligand.

The ^{13}C NMR spectrum of complex **5** gave a signal at δ 164 for the central carbon (CN_3) nucleus of the guanidinate ligand. This value is substantially different from that observed for the central carbon nuclei in **1**–**4** but quite similar to that observed for **III** which, when M = Ta and R = *i*-Pr, exhibited a corresponding resonance at δ 163.8. This observation further reflects the monoanionic nature of the guanidinate function in **5** in comparison to the dianionic nature of the ligands in **1**–**4**.

Complex **5** is the chloride analogue of a likely intermediate (**II**) in the direct formation of **1** from $Ta(NMe_2)_5$. As such, reaction of **5** with an appropriate base should allow for transformation of the environment around the metal center and conversion of **5** into **1** (Scheme 3). Thus, reaction of **5** with $LiNMe_2$ in toluene gave **1** in 75% yield. Furthermore, reaction of **5** with MeMgBr in hexane gave **1** as determined by comparison of the product NMR signals with those of authentic material. Thermolysis of **5** at 80 °C gave a mixture of, as yet, unidentified products. At this stage, the reasons why reaction between guanidine and $Ta(NMe_2)_4Cl$ is arrested at the monoanion stage are not clear.

Crystallographic studies

In order to clarify the guanidinate ligand co-ordination modes and the geometry of the metal centers we undertook single crystal X-ray analyses of complexes **1** and **5**. Perspective views are shown in Figs. 1 and 2 respectively with corresponding values for selected bond distances and angles given in Tables 1 and 2.

From Fig. 1 it is clear that the co-ordination environment of the Ta^V in complex **1** is constituted of three dimethylamido

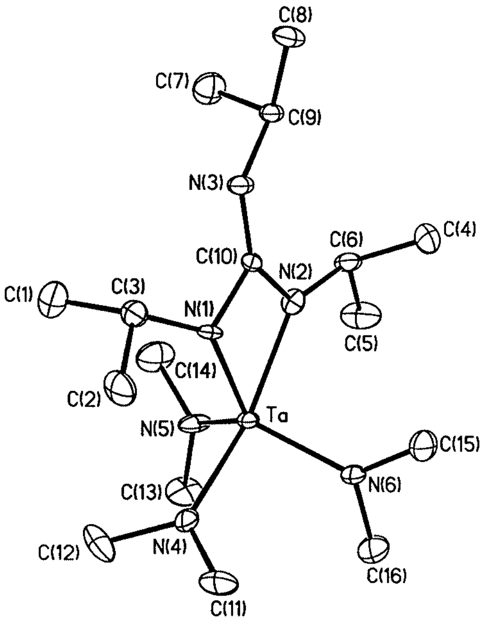


Fig. 1 An ORTEP[12] diagram for $Ta(NMe_2)_3\{[(CH_3)_2CHN]_2CHCN(CH_3)_2\}$ **1**. Thermal ellipsoids are drawn at 30% probability.

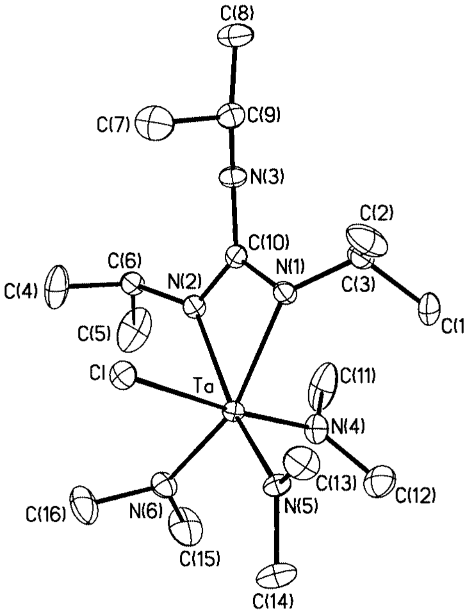


Fig. 2 An ORTEP diagram for $TaCl(NMe_2)_3\{[(CH_3)_2CHN]_2CN(H)CH(CH_3)_2\}$ **5**. Thermal ellipsoids are drawn at 30% probability.

Table 1 Selected bond lengths [Å] and angles [°] for complex **1**

Ta–N(5)	1.956(7)	N(6)–Ta–C(10)	112.6(2)
Ta–N(6)	1.961(6)	N(4)–Ta–C(10)	130.6(3)
Ta–N(4)	1.987(8)	N(1)–Ta–C(10)	32.2(2)
Ta–N(1)	2.004(6)	N(2)–Ta–C(10)	31.2(2)
Ta–N(2)	2.096(7)	C(10)–N(1)–C(3)	117.7(6)
Ta–C(10)	2.632(7)	C(10)–N(1)–Ta	99.0(4)
N(1)–C(10)	1.421(10)	C(4)–N(1)–Ta	139.4(5)
N(1)–C(3)	1.489(10)	C(10)–N(2)–C(6)	124.0(7)
N(2)–C(10)	1.372(10)	C(10)–N(2)–Ta	96.5(5)
N(2)–C(6)	1.468(11)	C(6)–N(2)–Ta	139.4(5)
N(3)–C(10)	1.276(10)	C(10)–N(3)–C(9)	124.6(7)
N(3)–C(9)	1.453(10)	C(12)–N(4)–C(11)	107.3(8)
N(4)–C(12)	1.477(11)	C(12)–N(4)–Ta	127.5(6)
N(4)–C(11)	1.502(12)	C(11)–N(4)–Ta	124.7(6)
N(5)–C(14)	1.469(12)	C(14)–N(5)–C(13)	110.9(8)
N(5)–C(13)	1.475(11)	C(14)–N(5)–Ta	122.4(6)
N(6)–C(16)	1.460(12)	C(13)–N(5)–Ta	126.5(6)
N(6)–C(15)	1.471(11)	C(16)–N(6)–C(15)	111.7(7)
C(1)–C(3)	1.526(12)	C(16)–N(6)–Ta	124.7(6)
C(2)–C(3)	1.513(13)	C(15)–N(6)–Ta	123.6(5)
C(4)–C(6)	1.530(12)	N(1)–C(3)–C(2)	111.9(6)
C(5)–C(6)	1.518(13)	N(1)–C(3)–C(1)	110.8(7)
C(7)–C(9)	1.522(12)	C(2)–C(3)–C(1)	111.4(8)
C(8)–C(9)	1.527(13)	N(2)–C(6)–C(5)	108.4(7)
N(5)–Ta–N(6)	118.9(3)	N(2)–C(6)–C(4)	113.0(7)
N(5)–Ta–N(4)	93.8(3)	C(5)–C(6)–C(4)	110.5(8)
N(6)–Ta–N(4)	92.8(3)	N(3)–C(9)–C(7)	109.8(7)
N(5)–Ta–N(1)	117.7(3)	N(3)–C(9)–C(8)	108.1(7)
N(6)–Ta–N(1)	121.1(3)	C(7)–C(9)–C(8)	110.0(8)
N(4)–Ta–N(1)	98.4(3)	N(3)–C(10)–N(2)	138.0(7)
N(5)–Ta–N(2)	95.8(3)	N(3)–C(10)–N(1)	121.1(7)
N(6)–Ta–N(2)	96.2(3)	N(2)–C(10)–N(1)	100.9(6)
N(4)–Ta–N(2)	161.7(3)	N(3)–C(10)–Ta	169.1(6)
N(1)–Ta–N(2)	63.4(2)	N(2)–C(10)–Ta	52.3(4)
N(5)–Ta–C(10)	107.9(2)	N(1)–C(10)–Ta	48.8(3)

functions and an *N*,*N*′,*N*″-triisopropylguanidinate dianion. The overall co-ordination number of the Ta atom is five but examination of the interatomic angles indicates that the geometry is better described as based on a distorted tetrahedral ligand array with the bisector of the bidentate guanidinate ligand, the Ta–C(10) vector, defining one of the vertices. The angles formed between the Ta–C(10) vector and the three Ta–N (amido) vectors are 107.9(2), 112.6(2), and 130.6(3)°. The angles between the three Ta–N (amido) vectors are 92.8(3), 93.8(3), and 118.9(3)°. The doubly deprotonated guanidine ligand binds to Ta through nitrogen atoms N(1) and N(2) to form a planar four-membered metallacycle.

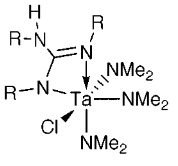
The third guanidinate nitrogen atom, N(3), lies outside of the metal co-ordination sphere and based on the short C(10)–N(3) distance of 1.27(1) Å and the C(9)–N(3)–C(10) angle of 124.6(7)° is best viewed as an sp^2 hybridized, imine function. These features are consistent with negative charges of the ligand localized on the two nitrogen centers bonded to Ta. In fact, the average Ta–N (guanidine) distance, 2.050(6) Å, is very close to the average Ta–N (amido) distance observed for $Ta(NMe_2)_4$(*t*-Bu) [2.03 Å], $Ta(NMe_2)_3(C_6H_4Me$-*p*)Br [1.95 Å] and $Ta(NMe_2)_4[(CyN)_2CNMe_2]$ [2.022 Å].[10,11] This interpretation is consistent with the observation of three different alkyl substituents in the ^1H and ^{13}C NMR spectra of complexes **1**–**4** due to the hindered rotation of the exocyclic C=N bond. The CN_3 core (N(1), N(2), N(3) and C(10)) is planar and C(9) is coplanar with these atoms within the error of measurement. The four p orbitals for the four sp^2 centers that describe the CN_3 core are in alignment for π conjugation of the CN_3 core of the guanidinate.

The results summarized in Fig. 2 confirm the proposed structure of complex **5** and reveal that the Ta^V indeed has a geometry that it is based on a distorted octahedron. The tantalum co-ordination environment is composed of a trisubstituted, bidentate, monoanionic guanidinate ligand, three NMe_2 ligands and a single chloride ligand. The pseudo-equatorial plane is defined by the planar co-ordinated N(1)–C(10)–N(2) function, the Ta atom and two dimethylamido nitrogen atoms N(5) and N(6). The sum of the angles of these ligands around Ta is 359° indicating that these groups are indeed planar. The Cl–Ta–N(4) angle of 174.6(1)° defines this as the pseudo-axial vector of this compound.

The guanidinate anion is bonded to Ta through the nitrogen atoms N(1) and N(2) to yield a planar four-membered ring of sp^2 hybridized N and C. The Ta–N(1) distance, 2.246(3) Å, is longer than the Ta–N(2) distance, 2.160(3) Å, indicating asymmetry in the co-ordination of this ligand to Ta. This asymmetry is further reflected in the ligand where the N(1)–C(10) distance of 1.326(5) Å is slightly shorter than the N(2)–C(10) distance, 1.347(5) Å. These two observations suggest a substantial contribution to the static structure of **5** from the localized bonding description provided by **IV**. Similar asymmetric bonding features have been observed for the triazenide complexes $[N_3(C_6H_4Me$-*p*$)_2]_2M(solv)_2$ (M = Mg; solv = THF, M = Ca; solv = DME) which possess two kinds of M–N bonds.[13]

Table 2 Selected bond lengths [Å] and angles [°] for complex **5**

Ta–N(4)	1.976(4)	N(2)–Ta–N(1)	60.26(13)
Ta–N(5)	1.984(3)	N(4)–Ta–Cl	174.65(11)
Ta–N(6)	1.997(4)	N(5)–Ta–Cl	83.82(11)
Ta–N(2)	2.160(3)	N(6)–Ta–Cl	92.01(12)
Ta–N(1)	2.246(3)	N(2)–Ta–Cl	83.32(10)
Ta–Cl	2.5729(10)	N(1)–Ta–Cl	82.93(10)
Ta–C(10)	2.652(4)	N(4)–Ta–C(10)	96.00(14)
N(1)–C(10)	1.326(5)	N(5)–Ta–C(10)	129.42(13)
N(1)–C(3)	1.458(6)	N(6)–Ta–C(10)	128.6(2)
N(2)–C(10)	1.347(5)	N(2)–Ta–C(10)	30.37(12)
N(2)–C(6)	1.468(5)	N(1)–Ta–C(10)	29.97(13)
N(3)–C(10)	1.379(5)	Cl–Ta–C(10)	80.34(9)
N(3)–C(9)	1.478(5)	C(10)–N(1)–C(3)	122.6(4)
N(4)–C(12)	1.449(7)	C(10)–N(1)–Ta	92.2(2)
N(4)–C(11)	1.467(7)	C(3)–N(1)–Ta	140.1(3)
N(5)–C(13)	1.456(5)	C(10)–N(2)–C(6)	123.2(3)
N(5)–C(14)	1.462(6)	C(10)–N(2)–Ta	95.4(2)
N(6)–C(15)	1.462(6)	C(6)–N(2)–Ta	138.4(3)
N(6)–C(16)	1.470(8)	C(10)–N(3)–C(9)	121.9(3)
C(1)–C(3)	1.514(8)	C(12)–N(4)–C(11)	108.7(4)
C(2)–C(3)	1.531(7)	C(12)–N(4)–Ta	127.4(4)
C(4)–C(6)	1.502(7)	C(11)–N(4)–Ta	123.8(4)
C(5)–C(6)	1.516(7)	C(13)–N(5)–C(14)	109.2(4)
C(7)–C(9)	1.508(7)	C(13)–N(5)–Ta	126.1(3)
C(8)–C(9)	1.523(6)	C(14)–N(5)–Ta	123.7(3)
N(4)–Ta–N(5)	95.7(2)	C(15)–N(6)–C(16)	108.2(4)
N(4)–Ta–N(6)	93.3(2)	C(15)–N(6)–Ta	125.1(4)
N(5)–Ta–N(6)	99.5(2)	C(16)–N(6)–Ta	126.7(3)
N(4)–Ta–N(2)	95.5(2)	N(1)–C(10)–N(2)	111.7(4)
N(5)–Ta–N(2)	158.17(13)	N(1)–C(10)–N(3)	124.9(4)
N(6)–Ta–N(2)	98.5(2)	N(2)–C(10)–N(3)	123.3(4)
N(4)–Ta–N(1)	91.9(2)	N(1)–C(10)–Ta	57.8(2)
N(5)–Ta–N(1)	100.66(13)	N(2)–C(10)–Ta	54.2(2)
N(6)–Ta–N(1)	158.5(2)	N(3)–C(10)–Ta	176.5(3)



IV

However, the tolyl groups in these species were shown to be equivalent in the ^{1}H NMR at room temperature.

The third guanidinate nitrogen, N(3), lies just slightly out of the ligand plane (Ta–C(10)–N(3) 176.5°). The only angle that can be used in the evaluation of N(3) hybridization is the C(10)–N(3)–C(9) angle of 121.9(3)°, which while consistent with sp^2 hybridization is by no means definitive. The question regarding the conjugation of the p orbital of an sp^2 N(3) with the π system of the N(1)–C(10)–N(2) group arises. For significant π interaction to occur between N(3) and C(10), the plane defined by C(9)–N(3)–C(10) should be coincident with the plane defined by N(1)–C(10)–N(2). Calculation of the angle between these two mean planes gave a value of 44.9°. This tends to discount a major degree of π bonding between N(3) and C(10). However, the rather short N(3)–C(10) distance of 1.379(5) Å compared with the average value for the single bond distances for N–C(H)Me$_2$ of 1.463(6) Å is consistent with some degree of multiple bonding between these atoms.

The three amido groups in complex **5** are planar, a feature compatible with π donation of the nitrogen lone pair into a metal d orbital. Furthermore, the average Ta–N (amido) distance, 1.99 Å compares favorably with those reported for Ta(NMe$_2$)$_4$(*t*-Bu),[10] Ta(NMe$_2$)$_3$(C$_6$H$_4$Me-*p*)Br,[10] and Ta(NMe$_2$)$_4$[(CyN)$_2$(CNMe$_2$)].[11]

Conclusion

These results show that protonation routes are a convenient and applicable methodology for the introduction of guanidinate mono- and di-anions into metal co-ordination spheres. Examples of products having both forms of the ligand are reported. Complexes **1**–**4** possessed dianionic ligands whereas **5** exhibited a monoanionic guanidinate ligand. These two types of complex were obtained by only slight variation of the starting materials. Among our current efforts is a desire to understand the origin of these variations in reactivity. Conversion of the monoanion into the dianionic ligand can rationally be induced as indicated by the reaction of **5** with either LiNMe$_2$ or MeMgBr to yield **1**. These observations indicated that **II** is a likely intermediate in the formation of **1**–**4**. We have shown that trialkylguanidines are versatile ligands in the co-ordination chemistry of Group V metals and are actively investigating the incorporation of these ligands into complexes with other transition and main group metals and the subsequent reactivity of these species.

Experimental

General

All manipulations were carried out in either a nitrogen filled dry-box or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuteriated benzene and toluene were dried by vacuum transfer from potassium. Diisopropylcarbodiimide, dicyclohexylcarbodiimide, cyclohexylamine and isopropylamine were purchased from Aldrich and used without further purification. Preparations of M(NMe$_2$)$_5$ [M = Ta or Nb],[14] Ta(NMe$_2$)$_4$Cl,[10] M(NMe$_2$)$_3$[(*i*-PrN)$_2$CN*i*-Pr][9] (M = Ta **1** or Nb **2**) and M(NMe$_2$)$_3$[(CyN)$_2$CNCy][9] (M = Ta **3** or Nb **4**) were carried out according to literature procedures. *N*,*N*′,*N*″-Tricyclohexylguanidine and *N*,*N*′,*N*″-triisopropylguanidine were prepared from the direct reaction of the appropriate carbodiimide and amine.[15] The NMR spectra were run on a Gemini 200 MHz spectrometer with deuteriated 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$_2$)$_3$Cl[(*i*-PrN)$_2$CNH*i*-Pr] 5

Triisopropylguanidine (0.175 g, 0.94 mmol) dissolved in hexane (10 mL) was added slowly to a stirred solution of Ta(NMe$_2$)$_4$Cl (0.370 g, 0.94 mmol) in hexane (30 mL) in a Schlenk flask. The reaction mixture was stirred for 12 h at room temperature. Solvent was removed under vacuum to yield crude complex **5** as a yellow solid. Crystallization from hexane at −30 °C gave yellow crystals (0.350 g, 71%). ν(NH) 3336 cm^{-1}. δ_H(C$_6$D$_6$) 0.98 (6 H, d, $^3J_{HH}$ 6.08, CH$_3$), 1.15 (6 H, br d, $^3J_{HH}$ 5.68, CH$_3$), 1.37 (6 H, br d, $^3J_{HH}$, 5.86 Hz, CH$_3$), 3.45 (6 H, s, NCH$_3$), 3.73 (12 H, s, NCH$_3$) and 3.85 (4 H, m, NH and NCH). δ_c(C$_6$D$_6$) 24.30 (4C, s, CH$_3$), 24.86 (2C, s, CH$_3$), 46.57 (3C, s, NCH$_3$), 47.88 (2C, s, NCH), 49.11 (1C, s, NCH) and 164.0 (1C, s, CN$_3$) (Found: C, 35.79; H, 7.52; N, 15.36. C$_{16}$H$_{40}$ClN$_6$Ta requires C, 36.06; H, 7.57; N, 15.77%).

Reaction of complex 5 with LiNMe$_2$

Complex **5** (0.400 g, 0.77 mmol) dissolved in toluene (20 mL) was added slowly to a Schlenk flask containing LiNMe$_2$ (0.043 g, 0.84 mmol). The reaction mixture was allowed to stir for 12 h at room temperature. Solvent was removed and hexane (20 mL) added to the resulting solid. The hexane insoluble materials were removed by filtration. Concentration of the filtrate gave **1** (0.280 g, 75%).

Structural determinations for complexes 1 and 5

Single crystals were mounted on thin glass fibers using viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are summarized in Table 3. Data were collected on a Bruker AX SMART 1k CCD

Table 3 Crystallographic data for $Ta(NMe_2)_3\{[(CH_3)_2CHN]_2CNCH(CH_3)_2\}$ **1** and $TaCl(NMe_2)_3\{[(CH_3)_2CHN]_2CN(H)CH(CH_3)_2\}$ **5**

	1	**5**
Empirical formula	$C_{16}H_{39}N_6Ta$	$C_{16}H_{40}ClN_6Ta$
Formula weight	496.48	532.94
T/K	203(2)	203(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.1317(6)	10.5747(6)
b/Å	10.3748(6)	13.4281(8)
c/Å	12.0067(7)	16.8615(9)
α/°	78.068(1)	107.5830(1)
β/°	65.405(1)	
γ/°	88.503(1)	
U/Å^3	1120.2(1)	2282.4(2)
Z	2	4
D_c/Mg m^{-3}	1.472	1.551
μ/mm^{-1}	4.914	4.943
Reflections collected	4653	11506
Independent reflections	2886 [R(int) = 0.0600]	4007 [R(int) = 0.0590]
Goodness of fit on F^2	1.038	1.021
$R1$, $wR2[I > 2\sigma(I)]$	0.0478, 0.1131	0.0036, 0.0796
(all data)	0.0514, 0.1146	0.0386, 0.0815

diffractometer using 0.3° ω scans at 0, 90, and 180° in φ. 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.[16]

The structures were solved by direct methods, completed with Fourier-difference 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 were from the SHELXTL 5.1 program library.[17]

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