Group 5 transition metal imido complexes with dianionic guanidinate ligands displaying extended interactions

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N,N′,N″–tri(isopropyl)guanidinate complexes of M(v) (M = Nb, Ta) bearing imido ligands represent unique examples of monoanionic and dianionic guanidinate complexes of these metals; single crystal X-ray analyses for two of the latter species, $\{[\mu\text{-}(NPr^i)_3C]_2TaMe(NPr^i)\}(Mg_2Cl_2)\cdot4C_6D_6$ and $\{(\mu\text{-}\eta^2\text{:}\eta^2 (Pr^iN)_3C)Ta(NPr^i)Cl\}_2$, exhibit unusual bonding modes involving all of the nitrogen centers of the ligand.

Guanidinate anions have received surprisingly limited attention as supporting ligands for metal complexes in comparison with isoelectronic amidinate species.[1] This omission is particularly conspicuous with electrophilic main group and early transition metals where amidinate complexes have displayed an exceptionally rich and varied organometallic and inorganic chemistry.[2,3] Guanidinates should certainly possess the same versatility and flexibility in coordination properties that have been exhibited by amidinates. Moreover, the presence of a third nitrogen center, which can bear either one or two organic substituents provides an additional coordination site within the ligand and the added capability of yielding dianionic species. This aspect offers bonding motifs that are not possible for the related amidinate systems.

Employing *N,N′,N″*-trialkylguanidines as ligands requires the development of fundamental ideas regarding the introduction of guanidinate anions and dianions into a metal coordination sphere, the definition of features that favor different binding modes of the ligand, and investigation of the general reactivity characteristics of these complexes. Reported preparative routes to trialkylguanidiante complexes include the elimination of HX (X = Cl, Br) from halo metal complexes,[4] elimination of H_2 from metal hydrides,[5] elimination of alkane from a metal alkyl,[6] and elimination of amine from a metal amido complex.[7,8] Examples of a dianionic guanidinate complexes include $[(OC)_3Fe\{\mu\text{-}\eta^2(RN)_2CNR\}Fe(CO)_3]$ (R = Pr^i or Cy),[9] $(cod)Pt[C(NPh)_3]$[10] and the main group species, $Li_2[C(NPh)_3]$,[11] $Li_2[C(NBu^t)_3]$,[12] and $Sb[(Pr^iN)_2CNHPr^i][(Pr^iN)_3C]$.[8] We wish to expand upon the procedures for introducing guanidinate ligands and to find general methods for the generation of dianionic guanidinate ligands.

The room temp. reaction of MCl_5 (M = Ta, Nb) with *N,N′,N″*-tri(isopropyl)guanidine lead to direct formation of $MCl(NPr^i)[(NPr^i)_2C(NHPr^i)]_2$ (M = Ta **1**; M = Nb **2**) after separation of guanidinium hydrochloride from the reaction mixture [eqn. (1)].† Reproducible yields in the range 30–40%

$$MCl_5 \xrightarrow[\text{(Pr}^i\text{NH)}_3\text{CCl}]{\text{(Pr}^i\text{NH)}_2\text{CNPr}^i} \qquad (1)$$
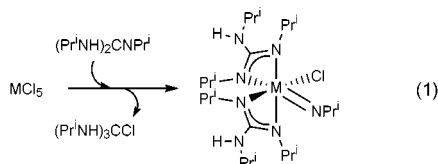
can be obtained from this procedure using spectroscopically (¹H, ¹³C NMR) and analytically pure tri(isopropyl)guanidine. On the basis of these observations it seems clear that the imido function must arise from cleavage of the parent guanidine, the mechanism of this transformation is currently under investiga-
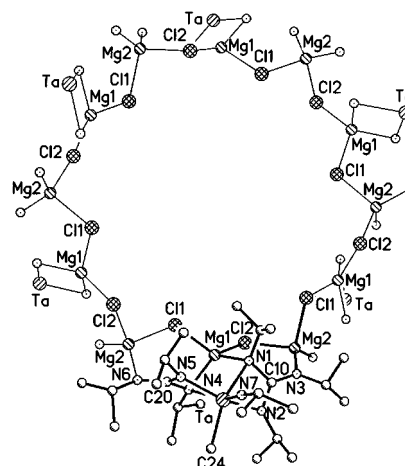

Fig. 1 Molecular structure of **3** showing a labeled asymmetric unit and the aggregation described in the text. Within the asymmetric unit, hydrogen atoms and benzene molecules of crystallization have been omitted for clarity. All atoms atoms have been refined anisotropically.

tion.[13,14] In contrast, reaction of $M(NMe_2)_5$ with guanidine yields only $[(Pr^iN)_3C]M(NMe_2)_3$ a species which possessed a single dianionic guanidinate ligand.[8]

With only one equivalent of MeMgX (X = Cl, Br), complex **1** only undergoes halogen exchange. However, employing two equivalents or more readily generated alkyl complex **3**.[15] Owing to the likelihood that our synthetic procedure had generated a dianionic guanidinate ligand we performed an X-ray analysis of **3** with the results shown in Fig. 1.‡ Complex **3** exhibits a Ta center in a pseudo-octahedral environment with two dianionic chelating bidentate guanidinate ligands, one Me group and an imido function. The two guanidinate ligands span axial/equatorial sites and the bonding features within the $\{[(NPr^i)_3 C]_2TaMe(NPr^i)\}^{2-}$ fragment are reminiscent of the reported bis(amidinate)Nb(O)Cl and the bis(guanidinate) complexes **1** and **2**.†[16] Charge balance for this fragment and completion of the asymmetric unit is provided by an $(Mg_2Cl_2)^{2+}$ cation which is coordinated to the guanidinate ligands.

Both guanidinate ligands form planar cycles with the Ta(v) center and exhibit similar bonding parameters. Within the guanidinate CN_3 cores the central C is planar as are the N atoms [N(2), N(5)] that coordinate exclusively to Ta. The C=N bond appears to be localized between these three coordinate N atoms with the longest C–N bonds observed for the four coordinate N centers [N(1), N(4)] which interact with one of the Mg^{2+} cations. The isopropyl imido linkage is similar to that observed in **1** and **2** and in **4** reported below. The *trans* influence of the imido ligand is manifest in the elongation of Ta–N(4) bond relative to Ta–N(1) [2.486(7) *cf.* 2.365(7) Å].

The two Mg centers within the asymmetric unit possess different coordination environments with Mg(1) being co-ordinated to the two *cis*-oriented N atoms [N(1), N(4)], and to Cl(1) and Cl(2) to give a pseudo-tetrahedral coordination sphere while Mg(2) is coordinated only to N(6) and Cl(1) within the asymmetric unit. Bridging interactions of Mg(2) to N(3) and
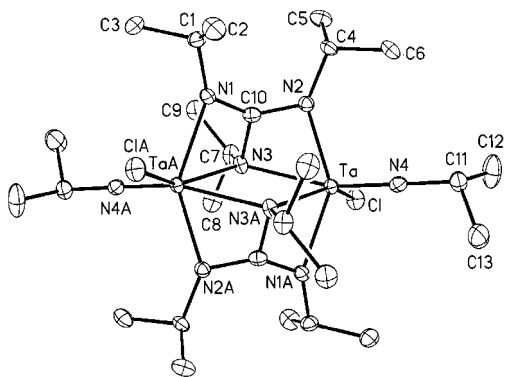
Fig. 2 Molecular structure of **4**. Hydrogen atoms have been omitted for clarity.

Cl(2) of an adjacent unit complete the coordination sphere of this center and result in a supramolecular aggregation of these subunits. This assemblage of complexes propagated through the bridging interactions of Mg(2) generates a macrocyclic ring of six subunits with a diameter of 12.1 Å which is colinear with a crystallographic $\bar{6}$ axis as shown in Fig. 1. The void space left in the center of this cyclic arrangement is occupied in this case with four benzene molecules of crystallization.

The ^{1}H and ^{13}C NMR spectra of **3** provide a probe of the solution behavior of this species. Based on the similarity of these spectra to those of complexes **1** and **2**, it appears that the intermolecular interactions exhibited by the observed static structure of **3** are not maintained in solution.

Reaction of metal halides with a lithium guanidinate, Li{(Pr^{i}N)$_2$CN(H)Pr^i}, offers an alternative metathetical route for introduction of guanidinate anions. From the reaction between *in situ* generated monolithium guanidinate and TaCl$_5$, complex **4** was isolated.† The complexity of the NMR spectra for this reproducibly obtained product prompted us to investigate **4** by X-ray crystallography. The results are summarized in Fig. 2.‡

Complex **4** is a dinuclear species possessing two bridging dianionic tri(isopropyl)guanidinate ligands each exhibiting a previously unknown chelating bridging coordination mode in which two of the nitrogen atoms [N(1), N(2)] bond to one Ta center and the third [N(3)] bridges the two metal centers. The coordination geometry of each Ta center can be described as distorted octahedral with the overall geometry of **4** being an edge-sharing bioctahedral polyhedron. An inversion center relates the two halves of the molecule. The individual Ta centers are in geometries reminiscent of the other bis(guanidinate) complexes reported herein. For example, within the asymmetric unit the metrical parameters of the guanidinate ligand are similar to those observed in **3**, *i.e.* the ligand spans axial equatorial sites with a bite angle [N(2)–Ta–N(3)] of 60.83(16)°. The central C atom of the guanidinate CN$_3$ core is planar. Furthermore N(1) and N(2) exhibit very similar geometric parameters and are nearly planar [Σ N(1) = Σ N(2) = 357°]. In contrast, the bridging N atom [N(3)] is distorted tetrahedral with the six defining angles ranging from 81.7(3) to 125.5(3)° (av. = 107°). The C=N double bond of the dianionic ligand appears to be delocalized between C(10)–N(1) and C(10)–N(2) as reflected by bond distances. As in **1**–**3**, the Ta coordination sphere is completed by an isopropyl imido function and a chloride ligand [Cl(1)] remaining from the starting material.

The mechanism of formation for **4** is still under scrutiny. Attempts to employ the dianionic form of tri(isopropyl)guanidinate, in what would appear to be a more direct pathway to **4**, also yield **4** but in a lower yield.

In the case of **4**, both ^{1}H and ^{13}C NMR data confirm that the observed structure remains intact upon dissolution in organic solvents. For example each of the isopropyl CH$_3$ signals appears as a distinct doublet. While the isopropyl(imido) function appears to exhibit equivalent methyl groups in the ^{1}H NMR, these CH$_3$ groups are distinguishable in the ^{13}C NMR spectra.

Our continuing efforts are directed toward the further development of these complexes and of guanidinate ligands with the specific goals of understanding the details that dictate the formation of mono- *vs.* dianionic ligands. Furthermore, we are interested in understanding the features that govern the intra- and inter-molecular interactions exhibited by these ligands.

Notes and references

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