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Asymmetric niobium guanidinates as intermediates in the catalytic guanylation of amines†

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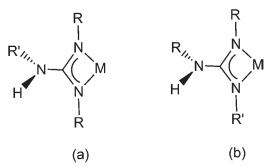
The molecular structure of the guanidinate complex {$NbBz_2(N^tBu)[(4\text{-}BrC_6H_4)N{=}C(N^iPr)(NH^iPr)]$}, previously obtained by reaction of [$NbBz_3(N^tBu)$] and the corresponding guanidine proligand, has been established by X-ray diffraction. The series of complexes {$NbBz_2(N^tBu)[(Ar)N{=}C(N^iPr)(NH^iPr)]$} (Ar = 4-$BrC_6H_4$, 4-^{t}Bu$C_6H_4$, 4-MeO$C_6H_4$) and {$[NbBz_2(N^tBu)]_2[(C_6H_4)(N{=}C(N^iPr)(NH^iPr))_2]$} show a preferred asymmetric coordination of the guanidinate ligand by means of one alkylamino nitrogen and the arylimino nitrogen atom. Computational studies confirm this preference and the results suggest that electronic factors prevail over steric factors. In addition, reaction of complex [$NbBz_3(N^tBu)$] with {2-(^{n}butyl)-1,3-diisopropylguanidine} did not give rise to the regioselective asymmetrical guanidinate. Instead, the complex {$NbBz_2(N^tBu)[(^nBu)N{=}C(N^iPr)(NH^iPr)]$} was obtained as a mixture of three isomers with symmetrical and asymmetrical coordination modes. Finally, the complex [$NbBz_3(N^tBu)$] was shown to be a suitable precatalyst for the guanylation reaction of a wide range of amines under mild conditions. Guanidinates are proposed as intermediates in the mechanism of this reaction. The molecular structure of the biguanidine {2,2′-(1,4-phenylene)bis(2′,3-diisopropylguanidine)} was also established by X-ray diffraction studies.

Introduction

N,*N*′,*N*″-Trisubstituted guanidinate ligands $(RNH)_2C{=}NR$ (R = alkyl or aryl) have proven to be an interesting alternative to classical ancillary ligands, such as cyclopentadienyl, as they have the advantages of tuneable electronic and steric effects by variation of the substituents on the nitrogen atoms.[1] The preparation of monoanionic guanidinate complexes usually involves: (a) the insertion of a carbodiimide into a metal–amido bond; (b) the reaction of a halide complex with a lithium guanidinate, formed by treatment of a lithium amide with a carbodiimide; or (c) the deprotonation of a neutral guanidine by means of an existent basic ligand.[2] In most cases, a symmetrical distribution of the guanidinate ligand is obtained (Scheme 1).

It is worth noting that, in the few reported cases where one of the nitrogen atoms is substituted by an aromatic group, a preferential asymmetric coordination was obtained, including the rearrangement of a plausible symmetric intermediate.[3] We recently extended the limited chemistry of niobium guanidinate complexes by reporting the synthesis of new dialkyl niobium complexes with aromatic-substituted guanidinate ligands {$NbBz_2(N^tBu)[(Ar)N{=}C(N^iPr)(NH^iPr)]$} (Ar = 4-$BrC_6H_4$ **1a**, 4-^{t}BuC_6H_4 **1b**, 4-MeOC_6H_4 **1c**) and {$[NbBz_2(N^tBu)]_2[(C_6H_4)\text{-}(N{=}C(N^iPr)(NH^iPr))_2]$} **1d** (Scheme 2), which are arranged in an asymmetrical manner.[4]



Scheme 1 Symmetrical (a) and asymmetrical (b) coordination of monoanionic guanidinate ligands.

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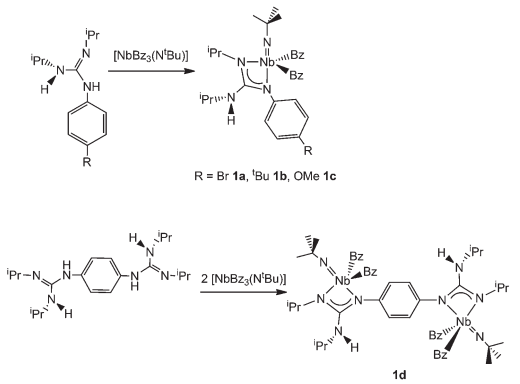
†Electronic supplementary information (ESI) available: Crystallographic data in CIF and refinement details (Table S1). Optimized geometries and Cartesian coordinates for **1a–d**, **1′a–d**, **3a–d**, **3′a–d**, **4a–c**, **5** and **5′**. Experimental details of the guanylation reactions. NMR spectra of the **4a–c** mixture. CCDC 924356 and 924357. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50477h



Scheme 2 Synthesis of dibenzyl niobium guanidinates.

As a continuation of our research in this field,[4,5] we describe here the structural characterization of the previously reported complex **1a** and comparative theoretical and reactivity studies concerning the preferred coordination of the guanidinate ligands in these dialkyl complexes. Catalytic guanylation of amines, as a waste-free process to obtain substituted guanidines, has been a topic of interest in recent years. Lanthanoid, main group and early transition metal complexes have been described as catalytic systems.[6] Despite the use of vanadium complexes as catalyst precursors,[6c,d,e] niobium complexes have not been reported in this context until now. As guanidinate complexes were widely proposed as intermediates in the catalytic guanylation of amines, we took the opportunity to study the use of the trialkyl parent compound $[NbBz_3(N^tBu)]$ **2**[7] as a new catalyst precursor.

Results and discussion

The direct reaction between the guanidine proligands and the trialkyl complex **2** gave rise, through a protonolysis pathway, to the corresponding guanidinate complexes $\{NbBz_2(N^tBu)[(Ar)N{=}C(N^iPr)(NH^iPr)]\}$ (Ar = 4-BrC_6H_4 **1a**, 4-$^tBuC_6H_4$ **1b**, 4-$MeOC_6H_4$ **1c**) and $\{[NbBz_2(N^tBu)]_2[(C_6H_4)(N{=}C(N^iPr)(NH^iPr))_2]\}$ **1d**. The molecular structures of complexes **1b–d** were reported previously.[4] Complex **1a** was crystallized and its molecular structure was determined by X-ray diffraction (Fig. 1). The crystal data are summarized in the Experimental section. Selected bond lengths and angles for **1a** are given in Table 1.

Complex **1a** crystallizes in the $P2_1/c$ space group. The distribution of the atoms around the niobium centre shows a distorted trigonal bipyramidal geometry, with an asymmetrical disposition of the guanidinate ligand, as observed for the analogous complexes **1b–d**. The imido group is quasilinear with an Nb1–N1–C1 angle of 178.1(2)° and an Nb1–N1 bond distance of 1.762(2) Å, both of which are close to those described for other imido complexes[7,8,2f] and are consistent with the existence of a metal–nitrogen fragment with a triple bond and an sp hybridized nitrogen atom. The Nb1–N4 bond *trans* to the imido group is elongated compared to the Nb1–N2 bond (ΔNb–N ~0.26 Å), as one would expect due to the *trans* influence of the imido group and the axial coordination of the N4 atom. The planarity of the 'CN$_3$' core is evidenced by the sum of the bond angles around C5 (360.0°).

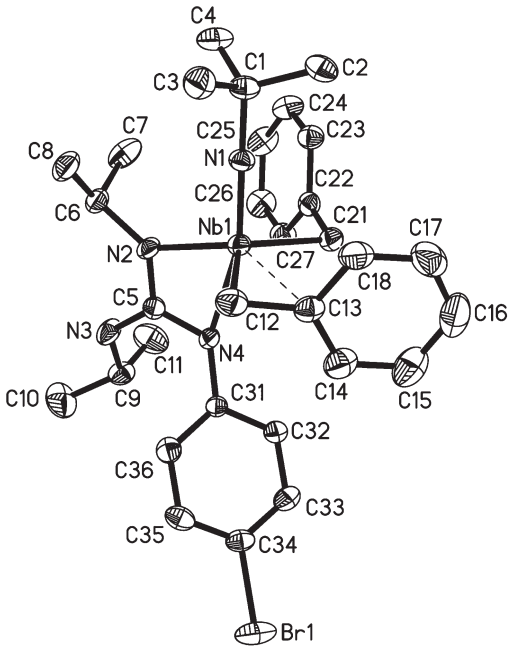


Fig. 1 ORTEP drawing of compound **1a**, with thermal ellipsoid at 30% probability.

Table 1 Selected bond lengths (Å) and angles (°) for **1a**

Bond lengths		Bond angles	
Nb1–N1	1.762(2)	N1–Nb1–N2	103.5(1)
Nb1–N2	2.102(2)	N1–Nb1–N4	162.4(1)
Nb1–N4	2.367(2)	N2–Nb1–N4	59.4(1)
Nb1–C12	2.211(3)	Nb1–N1–C1	178.1(2)
Nb1–C21	2.220(3)	N2–C5–N3	122.7(2)
N2–C5	1.350(3)	N2–C5–N4	112.3(2)
N3–C5	1.356(3)	N3–C5–N4	125.0(2)
N3–C9	1.478(3)	Nb1–C12–C13	87.8(2)
N4–C5	1.330(3)	Nb1–C21–C22	103.4(2)

Some charge delocalization within the guanidinate ligand is proposed from the C–N bond lengths, which average 1.34 Å and are intermediate between the values expected for C–N single and C=N double bonds. While the N2 atom is very close to being planar (the sum of angles 359.2°), N4 deviates significantly (351.2°) from planarity. The Nb1–C12–C13 angle of 87.8(2)° and the Nb1–C13 distance of 2.603(2) Å both indicate that one benzyl group shows η^2-hapticity. In contrast, the Nb1–C21–C22 angle of 103.4(2)° and the Nb1–C22 distance of 2.935(3) Å indicate that the second benzyl group shows η^1-hapticity. On considering the crystal packing, the hydrogen atom H33 on the aromatic group of the guanidinate ligand almost faces the π-electrons of the aromatic benzyl group of a neighbouring molecule, with a distance of 2.668 Å. This suggests an aromatic CH–π interaction,[9] which in turn leads to the formation of "dimeric" aggregates in the solid state (Fig. 2). Both aromatic rings are in an almost ideal orthogonal arrangement

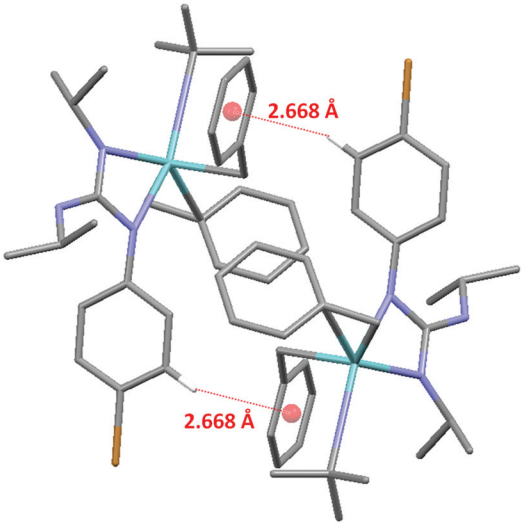


Fig. 2 The CH–π interaction scheme for complex **1a** in the solid state. Hydrogen atoms, except those on C33, have been omitted for clarity.

(92.5°), with a distance between centroids of 4.88 Å. This interaction could be the cause of the deviation of the N4 atom from planarity.

Guanidinate rearrangement from the asymmetrical (complexes **1a–d**) to the less sterically demanding symmetrical coordination (complexes **1′a–d**), through a formal 1,3-hydrogen shift, was not observed in solution, even on warming.

In order to account for the preferred asymmetric coordination of the guanidinate anions, the relative stability of complexes **1a–d** *vs.* **1′a–d** was studied by means of DFT calculations at the B3LYP/6-31G(d)+LANL2DZ level of theory. For comparative purposes, the free anions **3a–d** and **3′a–d** were also investigated.

As an example, optimized structures of **1a** and **1′a** are shown in Fig. 3. The optimized structures of **1b–d**, **1′b–d**, **3a–d** and **3′a–d**, along with their most relevant geometrical parameters, are given in the ESI.† All of these structures were characterized as minima on the potential energy surface and their absolute and relative energies are listed in Table 2. According to our calculations, the unsymmetrical complexes

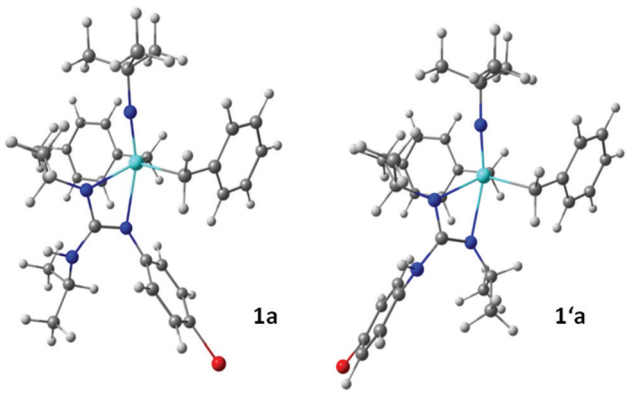


Fig. 3 Optimized structures of **1a** and **1′a**.

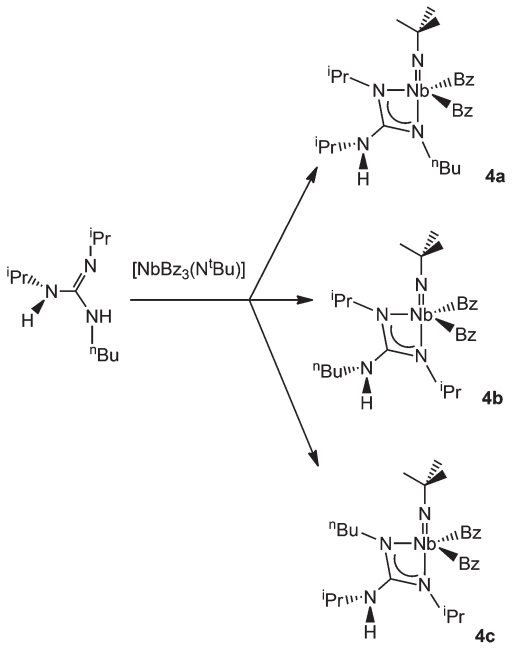
Table 2 Calculated total (Hartree) and relative (kcal mol^{-1}) energies for niobium complexes **1a–d** and **1′a–d** and the guanidinate anions[a]

Complex	Total (relative) energy (kcal mol^{-1})	Ligand	Total (relative) energy (kcal mol^{-1})
1a	−4053.39277511 (0.0)	**3a**	−3242.50051774 (0.0)
1′a	−4053.37407477 (11.7)	**3′a**	−3242.48091175 (12.3)
1b	−1639.84103061 (0.0)	**3b**	−828.939055043 (0.0)
1′b	−1639.82963265 (7.2)	**3′b**	−828.922596635 (10.3)
1c	−1597.10861888 (0.0)	**3c**	−786.216464799 (0.0)
1′c	−1597.09678503 (7.4)	**3′c**	−786.187257744 (18.3)
1d	−2732.93378629 (0.0)	**3d**	−1111.04289212 (0.0)
1′d	−2732.89762279 (22.7)	**3′d**	−1110.99855609 (27.8)
4a	−1408.78473948 (0.4)	**5**	−597.856972993 (0.0)
4b	−1408.77852231 (4.3)	**5′**	−597.857904302 (−0.6)
4c	−1408.78533689 (0.0)		

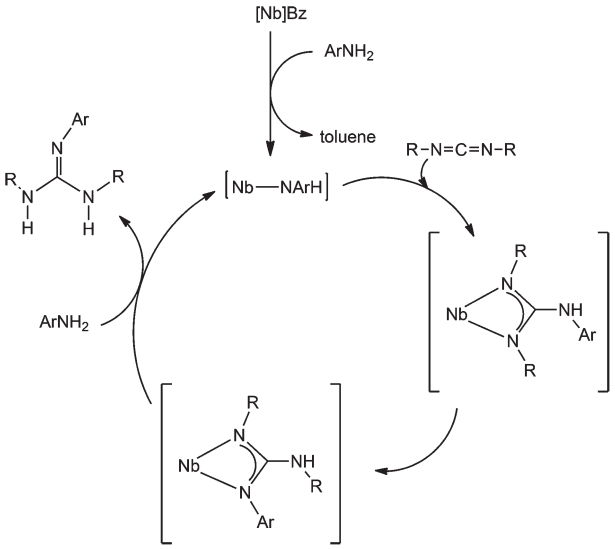
[a] B3LYP/6-31G(d)+LANL2DZ-optimized geometries.

1a–d are more stable than the symmetrical ones **1′a–d** by 7.2–22.7 kcal mol^{-1}. The largest energy difference was observed for the **1d/1′d** pair. This finding could be explained by some degree of electronic delocalization between the two metallic centres through the aromatic ring (the dihedral plane formed by the metal-guanidinate moiety and the central phenylene group is 61.6°). As far as the free guanidinate anions are concerned, the unsymmetrical anions proved to be much more stable than the symmetrical ones, with energy differences ranging from 10.3 to 27.8 kcal mol^{-1}. As for complex **1d**, the largest difference was found for ligand **3d**. All of these theoretical predictions suggest that electronic factors prevail over steric factors to rationalize the observed experimental asymmetric structures. The stabilization associated with the electronic conjugation of the delocalized π-electrons of the CN_3 core with the aromatic ring may be evoked to explain the higher thermodynamic stability of asymmetric compounds. With these results in mind, we proceeded to react the parent compound **2** with a trialkyl guanidine, {2-(^{n}butyl)-1,3-diisopropylguanidine} **5** (see the Experimental section). The same reaction with *N*-aromatic-substituted guanidines **3a–d** was 100% regioselective to the asymmetrical coordinated compounds **1a–d** with the NAr moiety *trans* to the imido group. However, in this case, three different isomers, **4a–c**, were obtained in a 1.3 : 1 : 0.4 ratio (Scheme 3).

Although the ^{1}H and ^{13}C NMR spectra of this mixture of isomers were quite complex and a complete peak assignment was not possible, three peaks were clearly assigned to ^{t}Bu groups. In addition, three pairs of coupled doublets ($^2J_{HH}$ values from 7.9 to 9.1 Hz) were observed in the ^{1}H NMR spectrum for the diastereotopic methylene protons of the two equivalent benzyl ligands in each isomer. Finally, three peaks were observed close to δ 166 ppm in the ^{13}C NMR spectrum due to the central carbon of the κ^2-monoanionic chelating guanidinates.[2a] NOESY-1D experiments provided evidence for the presence of three plausible relative orientations of the guanidinate ligand, giving rise to a mixture of symmetrical and asymmetrical coordination – the latter with the presence of the two possible orientations for the coordinated nitrogen atoms.



Scheme 3 Synthesis of the complexes **4a–c**.



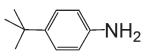
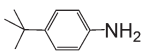
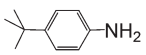
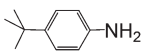
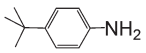
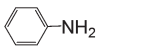
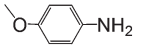
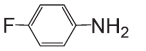
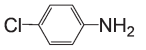
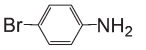
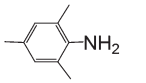
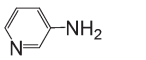
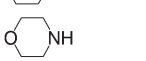
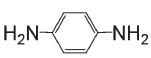
Scheme 4 Proposed mechanism for the catalytic guanylation of amines.

DFT calculations were extended in order to obtain information about the relative stability of isomers **4a–c** and the free asymmetric and symmetric anions **5** and **5′**. In this case, and in comparison with the NAr-substituted guanidinates, both asymmetrically coordinated complexes, **4a** and **4c**, had similar relative stabilities and were found to be more stable than the symmetric one, **4b**, by only 4.3 kcal mol^{-1}. Concerning the free guanidinate anions, it is worth noting that energy differences were not found between asymmetrical and symmetrical species. This finding provides further evidence of the influence of an aryl-substituent through an electronic effect.

As mentioned above, guanidinate complexes were proposed as clear intermediates in most processes for the guanylation of amines with carbodiimides.[6] In the mechanism of this reaction, an amido intermediate undergoes carbodiimide insertion, giving rise to the aforementioned guanidinate. Protonolysis by an amine molecule gives the final guanidine product (Scheme 4).

The catalytic activity of compound **2** was investigated (Scheme 4, Table 3). The conversion values were determined by ^{1}H NMR spectroscopy. We first used the reaction of *p-tert*-butylaniline with *N*,*N*′-diisopropylcarbodiimide as a model to establish the appropriate amount of precatalyst. In the absence of the complex, the reaction at 50 or 120 °C in deuterated toluene did not occur (Table 3, entries 1 and 2). In contrast, the addition of a small amount (1–3 mol% with respect to the carbodiimide) of **2** under mild conditions (50 °C) led to conversions of up to 99% to the *N*,*N*′,*N*″-trisubstituted guanidine in 24 h (Table 3, entries 3–5). As a descriptive example, the reaction was performed on a preparative scale, yielding 95% of the white crystalline guanidine.

Table 3 Catalytic addition of amines to *N*,*N*′-diisopropylcarbodiimide with **2**

Entry	Amine	Temperature (°C)	Conversion[e] (%)
1		50	0
2		120	0
3		50	80[a]
4		50	>99[b]
5		50	>99[c]
6		50	>99[b]
7		50	>99[b]
8		50	>99[b]
9		50	>99[b]
10		50	>99[b]
11		50	>99[b]
12		50	71[b]
13		50	70[b]
14		50	45[b]
15		50	>99[b,d]

Conditions: amine (1 mmol); *N*,*N*′-diisopropylcarbodiimide (1 mmol). Time: 24 h. [a] 1 mol% catalyst. [b] 2 mol% catalyst. [c] 3 mol% catalyst. [d] Conditions: amine (1 mmol); *N*,*N*′-diisopropylcarbodiimide (2 mmol). Time: 24 h. [e] Determined by ^{1}H NMR.

These results were in contrast to the high temperature needed for the imido vanadium complexes used in the same class of reaction (105 °C).[6c,d,e] We then proceeded to explore the scope of **2** in the catalytic addition of a variety of aromatic amines bearing electron-donating and electron-withdrawing substituents, heterocyclic and secondary cyclic amines to the *N*,*N*′-diisopropylcarbodiimide (Table 3, entries 6–14). As can be seen for the results in Table 3, the Nb-catalyzed guanylation displayed remarkable functional group tolerance. The functionalities present, such as halogens (F, Cl, Br), OMe, and Me, were unaffected under the reaction conditions used (Table 3, entries 7–11). 1,4-Phenylenediamine was also converted to the corresponding biguanidine (Table 3, entry 15). The conversion levels in these cases were found to be very high. The reaction also occurred with heterocyclic or secondary cyclic amines (Table 3, entries 12–14) in moderate yields. Finally, compound **1a** was tested as a catalyst for the guanylation reaction of *p*-*tert*-butylaniline under the same conditions. This compound showed very similar activity to the parent compound **2**, and this provides plausible evidence that this kind of species plays a principal role in the mechanism proposed for the guanylation reaction.

The molecular structure of the previously described {2,2′-(1,4-phenylene)bis(2′,3-diisopropylguanidine)} **3dH$_2$** [6o] was established by X-ray diffraction (Fig. 4).

This compound presents two 'CN_3' cores and there are two different types of distances for the carbon–nitrogen bonds. The distances C1–N1 and C1–N2 are 1.358(3) and 1.376(3) Å, respectively, and these are consistent with the distances of a single carbon–nitrogen bond, whereas the distance C1–N3 of 1.296(3) Å is closer to a double carbon–nitrogen bond. This information agrees with that found for other similar compounds described in the literature.[6g,h,n,s] The angles N(1)–C(1)–N(2), N1–C1–N3 and N2–C1–N3 are close to 120°, which indicates that the core CN_3 is practically planar. Looking at the crystal packing, H1 and H2 show intermolecular hydrogen bonding with the nitrogen atom N(3) of a neighbouring molecule, with distances of 2.322 and 2.529 Å, respectively, and angles of 173.3 and 156.6°, respectively. Selected bond distances and angles are shown in Table 4.

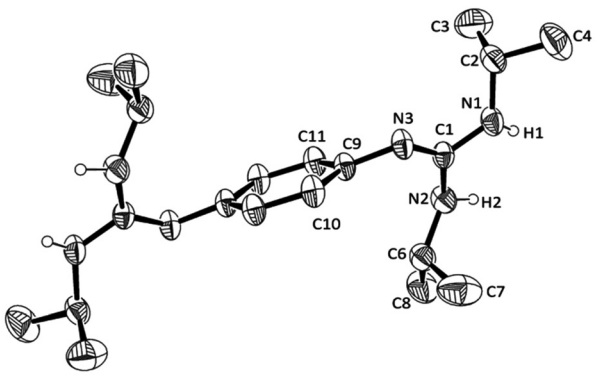


Fig. 4 ORTEP drawing of compound **3dH$_2$**, with thermal ellipsoids at 30% probability.

Table 4 Selected bond lengths (Å) and angles (°) for **3dH$_2$**

Bond lengths		Bond angles	
C1–N1	1.358(3)	N1–C1–N2	113.8(2)
C1–N2	1.376(3)	N1–C1–N3	119.6(2)
C1–N3	1.296(3)	N2–C1–N3	126.6(2)

Conclusions

In summary, a new example of the scarce niobium(v) guanidinate complexes, {$NbBz_2(N^tBu)[(4\text{-}BrC_6H_4)N{=}C(N^iPr)(NH^iPr)]$}, was structurally characterized by single-crystal X-ray diffraction techniques. Experimental and computational studies demonstrate that *N*-aromatic-substituted guanidinates feature a selective preference for an asymmetric coordination to the metal centre, and suggest that electronic factors prevail over steric factors. In addition, we demonstrated that the alkylimido complex [$NbBz_3(N^tBu)$] is an efficient catalyst for the guanylation reaction of a variety of amines under mild conditions, thus extending the limited catalytic applications of niobium compounds in homogeneous catalysis.

Experimental section

General procedures

All reactions were performed using standard Schlenk and glove-box techniques under an atmosphere of dry nitrogen. Solvents were purified by passage through a column of activated alumina (Innovative Tech.) and degassed under nitrogen before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Varian FT-400 spectrometer using standard VARIAN-FT software. {$NbBz_2(N^tBu)[(Ar)N{=}C(N^iPr)(NH^iPr)]$} (Ar = 4-$BrC_6H_4$ **1a**, 4-^{t}BuC_6H_4 **1b**, 4-$MeOC_6H_4$ **1c**), {$[NbBz_2(N^tBu)]_2[(C_6H_4)(N{=}C(N^iPr)(NH^iPr))_2]$} **1d**, [$NbBz_3(N^tBu)$] **2** and {2-(^{n}butyl)-1,3-diisopropylguanidine} **3e** were prepared according to literature procedures.[4,7,6s]

Synthesis of {$NbBz_2(N^tBu)[(^nBu)N{=}C(N^iPr)(NH^iPr)]$} 4

2-Butyl-1,3-diisopropylguanidine (0.06 g, 0.46 mmol) in toluene (20 mL) was added to a solution of [$NbBz_3(N^tBu)$] (0.20 g, 0.46 mmol) in toluene (10 mL). The reaction mixture was stirred for 1 h at room temperature. The resulting yellow solution was concentrated, cooled to −30 °C for 2 h, filtered and evaporated to dryness *in vacuo* to afford **4** as a yellow oily material. Yield: 0.22 g (89%). ^{1}H NMR (400 MHz, C_6D_6): δ = (mixture of three isomers) 0.79–0.85 (m, 3 × 6H, $CH(CH_3)_2$), 0.86–0.94 (m, 3 × 3H, CH_3), 1.13–1.20 (m, 3 × 6H, $CH(CH_3)_2$), 1.23–1.33 (m, 3 × 2H, CH_2), 1.35, 1.37. 1.38 (3 × s, 3 × 9H, ^{t}Bu), 1.44–1.53 (m, 3 × 2H, CH_2), 2.20 (d, 2H, J = 7.9 Hz, CH_2Ph), 2.35 (d, 2H, J = 8.2 Hz, CH_2Ph), 2.55 (d, 2H, J = 9.1 Hz, CH_2Ph), 2.76 (d, 2H, J = 7.9 Hz, CH_2Ph), 2.85 (d, 2H, J = 8.2 Hz, CH_2Ph), 2.99 (d, 2H, J = 9.1 Hz, CH_2Ph), 3.16–3.28 (m, 3 × 2H, CH_2), 3.26–3.56 (m, 3 × 2H, $CH(CH_3)_2$), 6.85–7.23 (m, 3 × 10H, C_6H_5).

$^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 166.22 166.63, 166.73 (CN_3). $C_{29}H_{48}N_4Nb$ (545.62): C, 63.84; H, 8.87. Found: C, 64.16; H, 8.98.

Computational details

All theoretical calculations were performed with the program package Gaussian03,[10] at density functional theory (DFT) level by means of the hybrid B3LYP functional.[11] The molecular geometries were optimized, without any molecular symmetry constraint, using Pople's 6-31G(d) split valence basis set for C, H, N, O, and Br elements,[12] and LANL2DZ for Nb, which combines quasi-relativistic effective core potentials with a valence double-basis set.[13] Frequency calculations were performed to determine whether the optimized geometries were minima on the potential energy surface. Optimized geometries and Cartesian coordinates for all the compounds studied can be found in the ESI.†

Procedure for the catalytic guanylation of amines at NMR tube scale

Catalytic reactions were performed under an inert atmosphere in a J. Young valve NMR tube. The tube was charged with 1 mmol of amine, 1 mmol of carbodiimide, and 1–3 mol% of the catalyst [$NbBz_3(N^tBu)$] in deuterated toluene. The tube was then heated at 50 °C for 24 h. The formation of guanidine was monitored by ^1H NMR spectroscopy, by comparing with the reported spectrum of the final compound. Conversion of the starting material to the product was determined by integration of the product resonances relative to the substrate peaks in the ^1H NMR spectrum.

X-ray structure determination for compounds 1a and $3dH_2$

Crystals of compound **1a** were mounted at low temperature in inert oil on a glass fiber and crystals of compound $\mathbf{3dH_2}$ were mounted at room temperature. Data for compound **1a** were collected on a Bruker X8 APPEX II CCD-based diffractometer, and for $\mathbf{3dH_2}$ on a Bruker X8 APPEX. Both diffractometers were equipped with a graphite monochromated MoKα (radiation source λ = 0.71073 Å).

The crystal data, data collection, structural solution, and refinement parameters for the complexes are summarized in Table S1.† Data were integrated using SAINT[14] and an absorption correction was performed with the program SADABS.[15] The structures were solved by direct methods using SHELXTL,[16] and refined by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were computed, except H3 in compound **1a** and H1 and H2 in compound $\mathbf{3dH_2}$, which were located in the electronic difference map, and then were refined with an overall isotropic temperature factor using a riding model.

One-half of a very disordered THF solvent molecule was found in the asymmetric unit of $\mathbf{3dH_2}$ which was removed using the program SQUEEZE implemented in Platon.[17]

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