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Unexpected mild C–N bond cleavage mediated by guanidine coordination to a niobium iminocarbamoyl complex†

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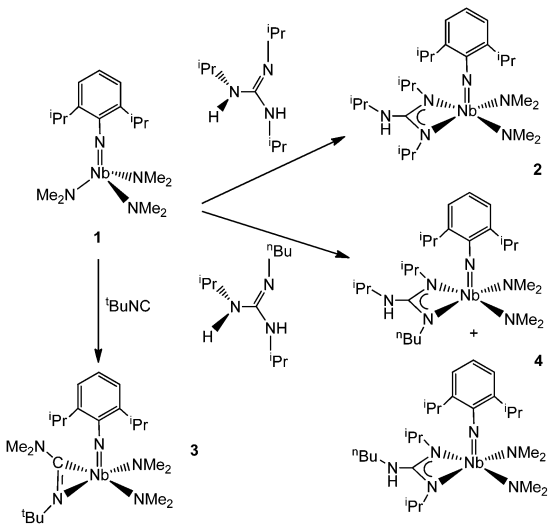
The complex $[Nb(NMe_2)_2\{(NMe_2)C{=}N^tBu\}\{N(2,6\text{-}^iPr_2C_6H_3)\}]$ reacts with trialkylguanidines and undergoes a room temperature C–N bond cleavage of the iminocarbamoyl moiety. This reaction affords the guanidinate complexes $[Nb(NMe_2)_2\{N(2,6\text{-}^iPr_2C_6H_3)\}\{(N^iPr)_2C(NH^iPr)\}]$ or $[Nb(NMe_2)_2\{N(2,6\text{-}^iPr_2C_6H_3)\}\{(N^iPr)_2C(NH^nBu)\}]$ and free isocyanide. The first crystal structure of a niobium iminocarbamoyl complex is reported.

Guanidines are an emerging class of nitrogen donor polydentate ligands and they are used to stabilize different metal centres in high oxidation states.[1] The presence of this kind of ligand has an interesting influence on the reactivity of the metal centre. It has been stated that the guanidinate ligands present in the coordination sphere of alkyl titanium, zirconium or niobium complexes influence the final product of the migratory insertion reaction of isocyanides. In fact, iminoacyl, enediamido, vinylamido or imido ligands can be obtained depending on the nature of the guanidinate ligand.[2] As part of our continuing study into the chemistry of imido and guanidinate niobium complexes,[3] we discovered that the reaction of the complex $[Nb(NMe_2)_3(N\text{-}2,6\text{-}^iPr_2C_6H_3)]$ (**1**)[4] with 1,2,3-trisisopropylguanidine yielded the guanidinate complex $[Nb(NMe_2)_2\{N(2,6\text{-}^iPr_2C_6H_3)\}\{(N^iPr)_2C(NH^iPr)\}]$ (**2**) (Scheme 1).

The NMR spectra of this new compound indicate a square pyramidal coordination around the metal centre. Insertion reactions of unsaturated substrates, such as CO or isocyanides, into metal–carbon bonds have been reported to give a wide variety of acyl and iminoacyl derivatives.[5] These studies have led to the expansion of the synthesis of transition metal–amido complexes with the aim of obtaining related products due to the insertion into metal–nitrogen bonds. Due to the lack of reactivity of many metal–amido compounds toward insertion few examples of metal-iminocarbamoyl derivatives, formed by insertion of isocyanides, have been reported.[6] In this context, attempts to obtain the migratory insertion products of **2** using *tert*-butylisocyanide resulted in the recovery of starting materials, even upon heating at 70 °C for 16 hours.‡ However, the reaction of **1** with *tert*-butylisocyanide results in the migratory insertion to give the corresponding iminocarbamoyl compound $[Nb(NMe_2)_2\{(NMe_2)C{=}N^tBu\}\{N(2,6\text{-}^iPr_2C_6H_3)\}]$ (**3**) in good yield. The molecular structure was determined using X-ray diffraction (Fig. 1). Selected bonds and angles are listed in the legend of Fig. 1.



Scheme 1 Guanidinate and iminocarbamoyl derivatives from **1**.

Very few examples of group 5 iminocarbamoyl derivatives have been structurally characterized[6f,i,7] and, to the best of our knowledge, this is the first example of an iminocarbamoyl niobium complex to be described. The complex is chiral and both enantiomers are present in the crystals. The imido ligand is quasi-linear with an Nb1–N1–C1 angle of 177.3(2)° and an Nb1–N1 bond distance of 1.783(2) Å.[3] The N2–C13 and the N3–C13 distances of 1.292(3) Å and 1.341(3) Å, respectively, reveal π delocalization in the iminocarbamoyl moiety supported by a partial donation of the lone pair on NMe_2 to the

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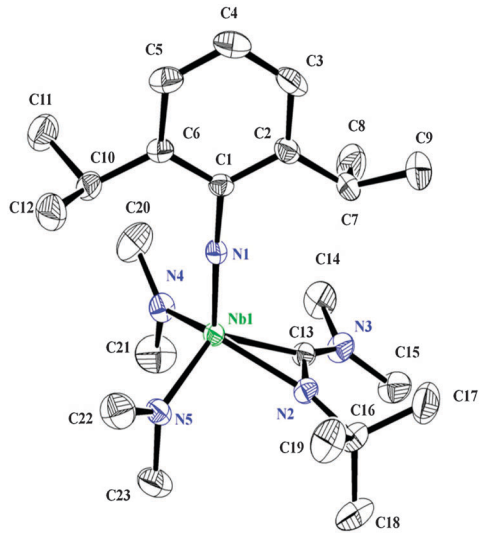


Fig. 1 Thermal ellipsoids plot of **3** at 30% probability. Selected bonds (Å) and angles (°): Nb1–N1 1.783(2); Nb1–N2 2.128(2); Nb1–N4 2.005(2); N2–C13 1.292(3); N3–C13 1.341(3); N1–Nb1–N4 104.4(1); N4–Nb1–N5 104.7(1); Nb1–N1–C1 177.3(2).

resonance contribution.[6f] If one considers that the iminocarbamoyl moiety occupies one coordination position, the niobium atom adopts a pseudotetrahedral coordination, making the two amido ligands inequivalent. In contrast, in solution, even at very low temperatures, both groups appear to be equivalent in the NMR spectra. This finding can be explained by a rapid formal rotation of the iminocarbamoyl ligand.[8]

Surprisingly, the reaction of **3** with 1,2,3-trisisopropylguanidine, at room temperature for 24 h, gave a mixture of the guanidinate complex **2** and free isocyanide. This represents an example of facile C–N single bond activation. Reactions that involve the metal-mediated rupture of C–N bonds are limited to activated substrates or the use of highly reactive metal complexes.[9] Recently, a room temperature C–N bond cleavage of an anionic guanidinate ligand promoted by rare-earth complexes has been reported.[9j] In the reaction of **3** and guanidine, as a result of the C–N bond cleavage, deinsertion of isocyanide takes place. Migratory insertion reactions have been extensively studied as fundamental mechanisms and as key steps in many important catalytic reactions.[10] According to the principle of microscopic reversibility, deinsertion of CO from acyl ligands is a widely reported process.[5a,11] The migratory insertion reaction of isocyanides is usually an irreversible process. Isocyanide deinsertion reactions of iminoacyl or iminocarbamoyl ligands are less well known and, in most cases, involve thermal treatments to give iminoacyl–iminocarbamoyl exchanges or mixtures of equilibrium products.[6g,12] In an effort to gain an insight into the reaction, the process was monitored by ^{1}H NMR in deuterated benzene (Fig. 2). It can be observed from Fig. 2 that dimethylamine (doublet close to 2.20 ppm) is present from the outset of the reaction and is produced by a protonolysis reaction by the acidic protons of guanidine.

We also observed the disappearance of the peaks corresponding to the starting complex **3** and the appearance, amongst others, of two peaks at 3.72 and 2.91 ppm, which were assigned

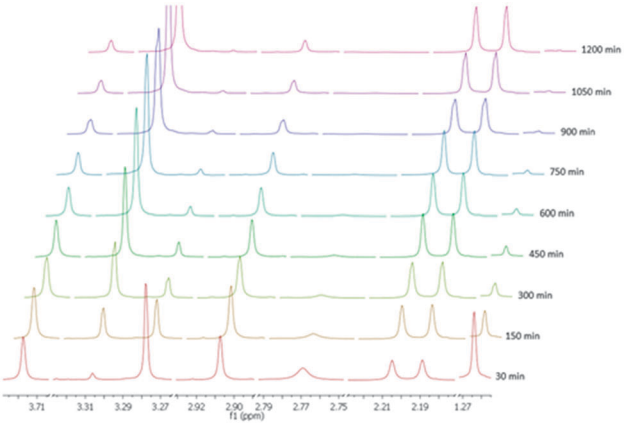
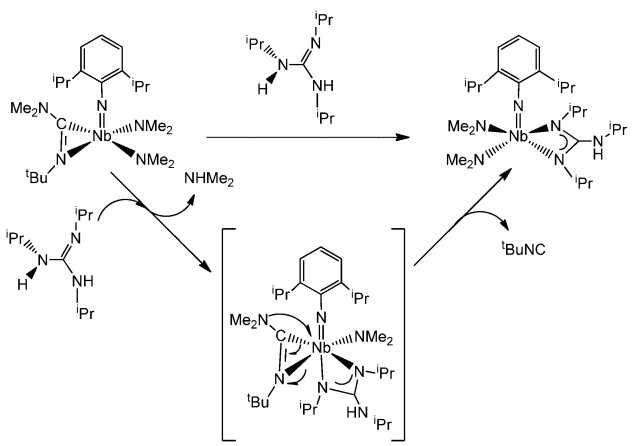


Fig. 2 Evolution of the reaction of **3** with trisisopropylguanidine monitored by ^{1}H NMR. Selected peaks are shown.

to methyl groups of an amido ligand bonded to metal and an amino group of an iminocarbamoyl moiety, respectively, in an intermediate complex. These peaks increase in intensity from the beginning of the reaction and start to disappear after approximately 5 hours with the simultaneous appearance of peaks corresponding to complex **2** and free isocyanide (Scheme 2). The long life time of this intermediate allows partial characterization by NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum shows the characteristic peak of a chelating guanidinate ligand at 164.9 ppm.[13] NOESY-1D experiments reveal a pseudooctahedral disposition around the niobium atom in this intermediate. The effect of the coordination of a strong donor guanidinate ligand was proven by the reaction of complex **3** with 2-butyl-1,3-diisopropylguanidine. In this case, the guanidinate complex $[Nb(NMe_2)_2\{N(2,6\text{-}^iPr_2C_6H_3)\}\{(N^iPr)_2C(NH^iPr)\}]$ (**4**), as a mixture of symmetrically and asymmetrically coordinated guanidinate isomers,[3c] and free isocyanide were obtained. Complex **4** can also be obtained by the direct reaction of **1** with 2-butyl-1,3-diisopropylguanidine (Scheme 1).

In summary, we report here the first example of a characterized niobium iminocarbamoyl complex that undergoes a facile C–N bond cleavage, presumably driven by the coordination of a



Scheme 2 Proposed mechanism for the deinsertion of isocyanide, mediated by guanidine coordination.

very stable guanidinate chelate ligand. The further reactivity of **1** towards other unsaturated substrates and deinsertion reactions mediated by guanidines are currently under investigation.

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Notes and references

‡ All manipulations were carried out under dry nitrogen using standard Schlenk and glovebox techniques. Solvents were purified by passing through a column of activated alumina (Innovative Technologies) and degassed under nitrogen before use. Microanalyses were carried out using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Varian FT-400 spectrometer using standard VARIAN-FT software for NOESY-1D, COSY, g-HSQC, and g-HMBC. The compounds $[Nb(NMe_2)_3(N\text{-}2,6\text{-}^iPr_2C_6H_3)]$ (**1**),[4] 1,2,3-trisisopropylguanidine[14] and 2-butyl-1,3-diisopropylguanidine[14] were prepared according to published procedures. Synthesis of $[Nb(NMe_2)_2\{(NMe_2)C{=}N^tBu\}\{N(2,6\text{-}^iPr_2C_6H_3)\}]$ (**3**): ^{t}BuNC (0.06 mL, 0.50 mmol) in toluene (10 mL) was added to a solution of **1** (0.20 g, 0.50 mmol) in toluene (10 mL). The reaction mixture was stirred for 16 h and evaporated to dryness *in vacuo*. The light brown oily material was redissolved in pentane and cooled to −20 °C for crystallization, to afford white crystals of **3**. Yield: 0.21 g (88%). ^{1}H NMR (400 MHz, C_6D_6): δ 1.28 (s, 9H, $C(CH_3)_3$) 1.36 (d, 12H, J = 6.9 Hz, $CH(CH_3)_2$) 2.78 (s, 6H, $CN(CH_3)_2$) 3.27 (s, 12H, $N(CH_3)_2$) 4.20 (m, 2H, $CH(CH_3)_2$) 6.98–7.16 (m, 3H, C_6H_3). $^{13}C\{^1H\}$ NMR: δ 24.3 ($CH(CH_3)_2$) 28.0 ($CH(CH_3)_2$) 30.3 ($C(CH_3)_3$) 44.3 ($CN(CH_3)_2$) 47.7 ($N(CH_3)_2$) 55.1 ($C(CH_3)_3$) 121.2, 122.4, 141.6, 152.9 (C_6H_3) 201.5 ($C{=}N^tBu$). Anal. calcd for $C_{23}H_{44}N_5Nb$: C, 57.13; H, 9.17%. Found: C, 57.27; H, 9.30%. Reaction of **3** with 1,2,3-trisisopropylguanidine: the reaction was performed under an inert atmosphere in a J. Young valve NMR tube. The tube was charged in the glovebox with 0.04 mmol of **3** dissolved in C_6D_6 and then 0.05 mmol of 1,2,3-trisisopropylguanidine dissolved in C_6D_6 were added. The evolution of the reaction was followed using ^{1}H NMR spectroscopy at room temperature. A similar experiment was carried out using 2-butyl-1,3-diisopropylguanidine. The presence of free ^{t}BuNC was observed both in the ^{1}H (δ 0.89 ppm) and $^{13}C\{^1H\}$ (δ 30.2 ppm) NMR spectra.

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