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

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## **General Experimental Conditions**

All manipulations were carried out under dry nitrogen using standard Schlenk and glovebox techniques. Solvents were purified by passage through a column of activated alumina (Innovative Technologies) 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 for NOESY-1D, COSY, g-HSQC, and g-HMBC. The compounds  $[Nb(NMe_2)_3(N-2,6-i^2Pr_2C_6H_3)]$  (1),<sup>1</sup> 1,2,3-trisisopropylguanidine<sup>2</sup> and 2-butyl-1,3-diisopropylguanidine<sup>2</sup> were prepared according to published procedures.

Synthesis of  $[Nb(NMe_2)_2\{N(2,6-{}^{i}Pr_2C_6H_3)\}\{(N^{i}Pr)_2C(NH^{i}Pr)\}]$  (2).

1,2,3-Trisisopropylguanidine (0.09 g, 0.50 mmol) in toluene (10 mL) was added to a solution of  $[Nb(NMe_2)_3(N-2,6^{-i}Pr_2C_6H_3)]$  (1) (0.20 g, 0.50 mmol) in toluene (10 mL). The reaction mixture was stirred for 10 min at room temperature. The resulting yellow solution was evaporated to dryness in vacuo. The yellow solid was redissolved in pentane and cooled to -20 °C for crystallization, to afford yellow crystals of **2**. Yield: 0.22 g (83%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.87 (d, 6H, J = 6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) 1.11(d, 12H, J = 6.4 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) 1.44 (d,12H, J = 5.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) 3.31(s, 12H, N(CH<sub>3</sub>)<sub>2</sub>) 3.49 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub> and NH); 4.41 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>) 7.02 (t, 1H, J = 7.7 Hz, C<sub>6</sub>H<sub>3</sub>); 7.18 (d, 2H, J = 7.7 Hz, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>) 122.7, 143.3, 152.3 (C<sub>6</sub>H<sub>3</sub>) 164.9 (CN<sub>3</sub>). Anal. Calcd. for C<sub>26</sub>H<sub>51</sub>N<sub>6</sub>Nb: C, 57.76; H, 9.51. Found: C, 57.68; H, 9.54.





<sup>1</sup>H NMR spectrum of  $[Nb(NMe_2)_2{N(2,6^{-i}Pr_2C_6H_3)}(N^iPr)_2C(NH^iPr)]$  (2) in C<sub>6</sub>D<sub>6</sub>. Synthesis of  $[Nb(NMe_2)_2{(NMe_2)C=N^tBu}{N(2,6^{-i}Pr_2C_6H_3)}]$  (3).

<sup>t</sup>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%).<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.28 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) 1.36 (d, 12H, J = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) 2.78 (s, 6H, CN(CH<sub>3</sub>)<sub>2</sub>) 3.27 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>) 4.20 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>) 6.98-7.16 (m, 3H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  24.3 (CH(CH<sub>3</sub>)<sub>2</sub>) 28.0 (CH(CH<sub>3</sub>)<sub>2</sub>) 30.3 (C(CH<sub>3</sub>)<sub>3</sub>) 44.3 (CN(CH<sub>3</sub>)<sub>2</sub>) 47.7 (N(CH<sub>3</sub>)<sub>2</sub>) 55.1 (C(CH<sub>3</sub>)<sub>3</sub>) 121.2, 122.4, 141.6, 152.9 (C<sub>6</sub>H<sub>3</sub>) 201.5 (C=N<sup>t</sup>Bu). Anal. Calcd. for C<sub>23</sub>H<sub>44</sub>N<sub>5</sub>Nb: C, 57.13; H, 9.17. Found: C, 57.27; H, 9.30.





<sup>1</sup>H NMR spectrum of  $[Nb(NMe_2)_2\{(NMe_2)C=N^tBu\}\{N(2,6-Pr_2C_6H_3)\}]$  (3) in C<sub>6</sub>D<sub>6</sub>.

Experimental details for the reaction of **3** and 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<sub>6</sub>D<sub>6</sub> and then 0.05 mmol of 1,2,3-trisisopropylguanidine dissolved in C<sub>6</sub>D<sub>6</sub> were added. The evolution of the reaction was followed by <sup>1</sup>H NMR spectroscopy at room temperature. Similar experiment was carried out using 2-butyl-1,3-diisopropylguanidine. The presence of free <sup>t</sup>BuNC was observed both in the <sup>1</sup>H ( $\delta$  0.89 ppm) and <sup>13</sup>C{<sup>1</sup>H} ( $\delta$  30.2 ppm) NMR spectra.



Final <sup>1</sup>H NMR spectrum for the reaction of 1,2,3-trisisopropylguanidine and  $[Nb(NMe_2)_2\{(NMe_2)C=N^tBu\}\{N(2,6^{-i}Pr_2C_6H_3)\}]$  (3) after 24 h at room temperature in C<sub>6</sub>D<sub>6</sub>. The spectrum is a combination of that of compound 2 and free <sup>t</sup>BuNC.

Synthesis of  $\{Nb(NMe_2)_2[N(2,6^{-i}Pr_2C_6H_3)][(N^iPr)_2C(NH^nBu)]\}$  (4).

Compound **4** was prepared by the procedure described for **2** using the following quantities: **1** (0.20 g, 0.50 mmol), 2-butyl-1,3-diisopropylguanidine (0.06 g, 0.50 mmol), resulting in a bright yellow oil. Yield 0.25 g (92%).<sup>1</sup>H NMR data for the mixture of isomers (symmetric and asymmetric, the latter as a racemic mixture of enantiomers) (400 MHz,  $C_6D_6$ , the mixture of isomers and signals overlapping prevent a clear integration of the peaks):  $\delta$  0.87 (m,  $(CH_2)_3CH_3$ ) 1.09-1.14, 1.52-1.60, 3.18-3.55 (m,  $(CH_2)_3CH_3$ ) 1.11, 1.26, 1.44 (d,  $CH(CH_3)_2$ ) 3.18-3.55 (m,  $CH(CH_3)_2$ ) 4.38 (m,  $CH(CH_3)_2$ ) 3.18-3.55 (m, NH) 3.31 (s,  $N(CH_3)_2$ ) 3.33 (s,  $N(CH_3)_2$ ) 7.00-7.20 ( $C_6H_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  14.4-35.2 ( $(CH_2)_3CH_3$ ) 24.3-24.8 ( $CH(CH_3)_2$ ) 28.0, 28.2, 45.1, 45.5, 46.3 ( $CH(CH_3)_2$ ) 46.8 ( $N(CH_3)_2$ ) 47.0 ( $N(CH_3)_2$ ) 122.4-152.4 ( $C_6H_3$ ) 164.9, 165.4 ( $CN_3$ ). Anal. Calcd. for  $C_{27}H_{53}N_6Nb$ : C, 58.47; H, 9.63. Found: C, 58.10; H, 9.41.



<sup>1</sup>H NMR spectrum of {Nb(NMe<sub>2</sub>)<sub>2</sub>[N(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)][(N<sup>i</sup>Pr)<sub>2</sub>C(NH<sup>n</sup>Bu)]} (4) in C<sub>6</sub>D<sub>6</sub>.

X-ray structure determination for complex 3

Crystals of compound **3** were mounted at low temperature in inert oil on a glass fiber on a Bruker X8 APPEX II CCD-based equipped with a graphite monochromated MoK $\alpha$  (radiation source)  $\lambda = 0.71073$  Å).

The crystal data, data collection, structural solution, and refinement parameters for the complexes are summarized below. Data were integrated using SAINT<sup>3</sup> and an absorption correction was performed with the program SADABS.<sup>4</sup> The structures were solved by patterson using SHELXTL,<sup>5</sup> 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 and then were refined with an overall isotropic temperature factor using a riding model.

Empirical formula	$C_{23} H_{44} N_5 Nb$
Temperature (K)	260(2)
Wavelength (Å)	0.71073
Cryst. Syst.	Monoclinic
Space group	C2/c
a (Å)	35.179(2)
b (Å)	9.443(1)
<i>c</i> (Å)	16935(1)
lpha (deg)	90
$\beta$ (deg)	107.282(1)
γ(deg)	90
Volume (Å <sup>3</sup> )	5371.7(6)
Z	8
Density (calcd) (g/cm <sup>3</sup> )	1.196
Abs. coeff (mm <sup>-1</sup> )	0.465
<i>F</i> (000)	2064
Crystal size (mm <sup>3</sup> )	0.45 x 0.20 x 0.10
Index ranges	-29 ≤ h ≤ 49 -13 ≤ k ≤ 12 -24 ≤ /≤ 22
Reflections collected	21659
Independent reflections	8144 [ <i>R</i> (int) = 0.0858]
Observed reflections	4844
Data/restraints/params.	8144 / 0 / 275
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.954
Final <i>R</i> indices	R1 = 0.0465 wR2 = 0.0852
Largest diff peak hole (eÅ <sup>-3</sup> )	0.380 and -0.578

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