Pyridine C=N Bond Cleavage Mediated by (silox)₃Nb (silox = ᵗBu₃SiO)
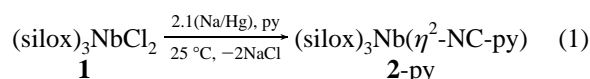
Troy S. Kleckley, Jordan L. Bennett,
Peter T. Wolczanski,* and Emil B. Lobkovsky

*Cornell University, Baker Laboratory
Department of Chemistry, Ithaca, New York 14853*

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During the hydrodenitrogenation (HDN) of crude oil, cleavage of the C−N bonds associated with 5- and 6-membered rings is critical to extrusion of nitrogen as ammonia.[1−8] Heterocycle hydrogenation is thought to precede C−N bond activation during catalysis;[2−5] however, the degradation of pyridine on metal surfaces has been demonstrated,[9] and limited, related homogeneous C−N bond cleavages have been observed.[6−8] Thus, both processes may be competitive. Reported herein is a ring-opening of pyridine[7] mediated by (silox)₃Nb (silox = ᵗBu₃SiO) fragments.

Treatment of (silox)₃NbCl₂ (**1**)[10] with 2.1 equiv of Na/Hg in pyridine afforded the brown η^2-py adduct, (silox)₃Nb(η^2-NC-py) (**2-py**), in 74% yield upon crystallization from hexanes (eq 1). Telltale ¹H NMR spectral features[11] observed at −80 °C

$$(silox)_3NbCl_2 \xrightarrow[25\,°C,\ -2NaCl]{2.1(Na/Hg),\ py} (silox)_3Nb(\eta^2\text{-NC-py}) \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}\text{-py}$$

revealed a structure analogous to the structurally characterized (silox)₃Ta(η^2-NC-py).[12] Unlike the latter, **2-py** exhibited a broadened set of resonances at temperatures >−10 °C, indicative of fluxionality derived from oscillation of the η^2-py ligand (T_c = 27 °C, $\Delta G^{\ddagger}$ = 13(1) kcal/mol) between the two equivalent η^2-N,C bonding sites. While addition of 1 equiv of pyridine
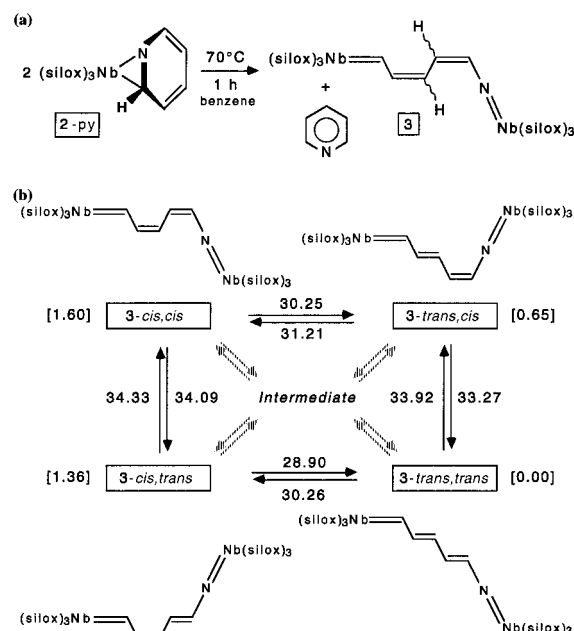

Figure 1. Generation (70 °C, a) of pyridine ring cleavage product (silox)₃Nb=CH(CH=CH)(CH=CH)N=Nb(silox)₃ (**3**) and equilibration (100 °C) of its four stereoisomers (b). Brackets indicate relative experimental ground state energies (±0.1 kcal/mol), and activation energies (±0.1 kcal/mol)[14] are given near appropriate arrows.

had no effect, subsequent reactivity hampered evaluation at higher temperatures.

Thermolysis of (silox)₃Nb(η^2-NC-py) (**2-py**) at 70 °C for 1 h in benzene generated 0.5 equiv of py and 0.5 equiv of the deep-red, ring-opened product (silox)₃Nb=CH(CH=CH)-(CH=CH)N=Nb(silox)₃ (**3**, Figure 1).[13] Initially, a mixture of ~55% **3-cis,cis** and ~45% (silox)₃Nb=CH(*trans*-CH=CH)(*cis*-CH=CH)N=Nb(silox)₃ (**3-trans,cis**) formed, but subsequent thermolysis at 100 °C revealed the rapid diminution of **3-cis,-cis**, a corresponding swift growth of **3-trans,cis**, and the later, slow growth of **3-trans,trans** and **3-cis,trans**. An equilibrium ratio (100 °C) for **3-cis,cis**/**3-trans,cis**/**3-trans,trans**/**3-cis,trans** of 6:26:59:9 was established over the course of ~1 mo. Once the relative standard free energies of the four stereoisomers were established, kinetics modeling of the approach to equilibrium yielded the activation energies given in Figure 1.[14] The data do not distinguish between a stepwise isomerization process and one that utilizes an intermediate(s). Regardless of mechanism, isomerization of the double bond adjacent to the imide (33−34 kcal/mol) is more difficult than the C=C next to the alkylidene (29−31 kcal/mol).

Stereoisomer assignments were based on ¹H and ¹³C{¹H} NMR spectroscopies (Table 1), including decoupling and heteronuclear multiple quantum coherence (HMQC)[15] experiments, which were needed for correlation of each CH and to enable reverse detection of alkylidene and imide-C_α carbon resonances broadened by nearby quadrupolar ⁹³Nb (I = ⁹/₂, 100%) and ¹⁴N (I = 1, 99.63%) nuclei.[16] Alkylidene resonances, readily identified by characteristic downfield chemical shifts (Nb=C*H*, δ 10.05−10.40; C*H*, δ 224−232), provided a

(1) (a) Gary, J. H.; Handwerk, G. E. *Petroleum Refining: Technology and Economics*, 3rd ed.; Marcel Dekker, Inc.: New York, 1993. (b) Speight, J. G. *The Chemistry and Technology of Petroleum*; Marcel Dekker: New York, 1983.

(2) (a) Ho, T. C. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 117−160. (b) Gates, B. C. *Catalytic Chemistry*; J. Wiley and Sons: New York, 1992.

(3) (a) Kätzer, J. R.; Sivasubramanian, R. C. *Catal. Rev.-Sci. Eng.* **1979**, *20*, 155−208. (b) Shah, Y. T.; Cronauer, D. C. *Catal. Rev.-Sci. Eng.* **1979**, *20*, 209−301.

(4) (a) Satterfield, C. N.; Smith, C. M.; Ingalls, M. *Ind. Eng. Chem., Process Des. Dev.* **1985**, *24*, 1000−1004. (b) Satterfield, C. N.; Ynag, S. H. *Ind. Eng. Chem., Process Des. Dev.* **1984**, *23*, 11−19. (c) Satterfield, C. N.; Cocchetto, J. F. *Ind. Eng. Chem., Process Des. Dev.* **1981**, *20*, 53−61. (d) Satterfield, C. N.; Cocchetto, J. F. *Ind. Eng. Chem., Process Des. Dev.* **1981**, *20*, 49−53.

(5) (a) Gioia, F.; Lee, V. *Ind. Eng. Chem., Process Des. Dev.* **1986**, *25*, 918−925. (b) Stern, E. W. *J. Catal.* **1979**, *57*, 390−396.

(6) (a) Laine, R. M. *Catal. Rev.-Sci. Eng.* **1983**, *25*, 459−474. (b) Fish, R. H. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academics: Dordrecht, The Netherlands, 1990. (c) Kabir, S. E.; Kolwaite, D. S.; Rosenberg, E.; Scott, L. G.; McPhillips, T.; Duque, R.; Day, M.; Hardcastle, K. I. *Organometallics* **1996**, *15*, 1979−1988 and references therein.

(7) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678−10693 and references therein.

(8) Bonanno, J. B.; Henry, T. P.; Neithamer, D. R.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1996**, *118*, 5132−5133.

(9) Serafin, J. G.; Friend, C. M. *J. Phys. Chem.* **1989**, *93*, 1998−2004.

(10) LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810−1818.

(11) For **2-py**: ¹H NMR (C₇D₈, −80 °C, δ, J(Hz)) 1.24 (s, ᵗBu), 4.16 (s, η^2-N,C²H), 5.35 (t, C⁵H, J = 6.0), 5.85 (dd, C⁴H, J = 9.4, 5.8), 6.56 (d, C³H, J = 9.4), 7.70 (d, C⁶H, J = 6.0); (C₇D₈, T_c = 27 °C, δ, J(Hz)) 1.24 (s, ᵗBu), 5.79 (t, C⁴H, J = 7.5), 5.9 (br s, C²H, C³H, C⁵H, C⁶H); ¹³C{¹H} (C₇D₈, −80 °C, δ) 23.46 (SiC), 30.44 (CH₃), 79.23 (η^2-N,C²), 107.22 (C⁵), 119.57 (C⁴), 129.1 (C³), 147.63 (C⁶). Anal. Calcd for NbSi₃O₃NC₄₁H₈₆: C, 60.18; H, 10.59; N, 1.71. Found: C, 58.48; H, 10.45; N, 1.29.

(12) (a) Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494−2508. (b) Neithamer, D. R.; Párkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421−4423.

(13) Anal. Calcd for Nb₂Si₆O₆NC₇₇H₁₆₇ (**3**): C, 59.38; H, 10.81; N, 0.90. Found: C, 59.41, 59.33; H, 11.17, 11.33; N, 0.69, 0.63.

(14) Kinetics modeling used experimental relative ground state energies, initial concentrations obtained from integration, and concentration vs time data for all stereoisomers of **4**. The program was written by Prof. Charles F. Wilcox of Cornell University.

(15) (a) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565−569. (b) Bax, A.; Griffey, R.; Hawkins, B. *J. Am. Chem. Soc.* **1983**, *105*, 7188−7190.

(16) Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591−1600.

Table 1. ¹H and ¹³C{¹H} NMR Spectral Data (δ, multiplicity (J in Hz)) for $(silox)_3Nb=C^1H(C^2H=C^3H)(C^4H=C^5H)N=Nb(silox)_3$ (**4**)[a]

isomer	silox	C¹H	C²H	C³H	C⁴H	C⁵H	SiC	C(CH₃)₃	C¹ [b]	C²	C³	C⁴	C⁵ [b]
4-*cis,cis*	1.197; 1.179	10.21, d (11.7)	7.38, dd (11.7, 10.6)	5.30, dd (11.7, 10.6)	5.06, dd (11.7, 8.1)	6.24, d (7.9)	24.03; 23.90	30.04	224	130.3	107.9	115.4	143.6
4-*trans,cis*	1.202; 1.173	10.24, d (12.5)	7.70, dd (14.2, 12.5)	5.41, dd (14.2, 11.5)	4.93, dd (11.5, 8.1)	6.34, d (8.1)	24.03; 23.89	30.02	232	133.7	110.5	119.7	144.7
4-*trans,trans*	1.193; 1.189	10.05, d (12.2)	7.57, dd (13.9, 12.2)	4.57, dd (13.9, 11.5)	5.75, dd (13.1, 11.5)	6.38, d (13.1)	24.00; 23.85	30.95	231	134.5	112.5	125.3	148.2
4-*cis,trans*	1.214; c	10.40, d (12.4)	7.51, dd (12.4, 10.8)	4.15, dd (11.6, 10.8)	5.58, dd (13.1, 11.6)	6.53, d (13.1)	24.17;c 23.86c	30.91c	228	131.0	109.3	118.1	c

[a] Benzene-d_6; C_6D_5H at δ 7.15 (¹H), C_6D_6 at δ 128.0. Assignments determined via decoupling and heteronuclear multiple quantum coherence (HMQC) experiments. [b] Due to quadrupolar broadening by Nb and N, signals detected via HMQC method. [c] Assignments tentative or could not be determined due to the low concentration.
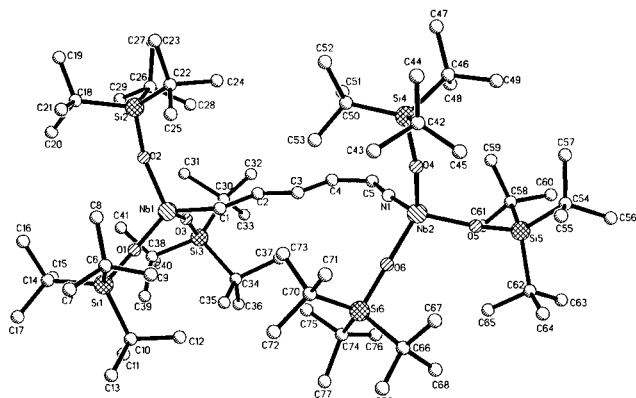

Figure 2. Molecular structure of $(silox)_3Nb=CH(trans\text{-}CH=CH)(cis\text{-}CH=CH)N=Nb(silox)_3$ (**3**-*trans,cis*). Selected interatomic distances (Å) and angles (deg): Nb1−O1, 1.875(6); Nb1−O2, 1.905(7); Nb1−O3, 1.915(7); Nb2−O4, 1.891(7); Nb2−O5, 1.904(6); Nb2−O6, 1.900(6); Si−O, 1.659(13) av; Si−C, 1.905(24) av; silox C−C, 1.54(6), restrained; O1−Nb1−O2, 110.4(3); O2−Nb1−O3, 109.0(3); C1−C2−C3, 128.9(11); C2−C3−C4, 123.6(11); C3−C4−C5, 127.6(11); C4−C5−N1, 125.3(10); O−Si−C, 106.5(13) av; C−Si−C, 112.3(16) av; Si−C−C, 111.8(24) av; silox C−C−C, 107.0(22) av.

clear indication of the cleavage reaction, while *cis*- vs *trans*-HC=CH stereochemistries were assigned primarily on 8.0−10.8 vs 13.1−14.2 Hz coupling constants, respectively.

Fractional crystallization of **3**-*trans,cis* from a ~4:1 mixture of **3**-*trans,cis*/**3**-*cis,cis*, obtained from an 13 h (100 °C) ring-opening reaction, enabled confirmation of its structure by X-ray crystallography.[17] The molecular view in Figure 2 reveals the flat conformation of alternating carbon−carbon single (d(C1−C2) = 1.426(14) Å, d(C3−C4) = 1.399(14) Å, d(C5−N1) = 1.358(12) Å) and double (d(C2−C3) = 1.366(13) Å, d(C4−C5) = 1.329(14) Å) bonds anchored by the bent alkylidene (125.8(8)°) and nearly linear C5−N1−Nb2 (174.9(8)°) fragments. Standard Nb=C (1.945(10) Å) and Nb=N (1.777(8) Å) bond lengths are observed,[18] the latter indicative of triple bond character due to additional π-donation. The pseudotetrahedral geometry about the imide-containing niobium is very regular ($\angle X_1NbX_2$ = 109.4(23)° av), but the remaining niobium is distorted, with $\angle O−Nb1−C1$ = 103.6(24)° av, and $\angle O1−$

Nb1−O3 = 124.5(3)°. No specific steric interaction can be identified; therefore, the deviations are attributed to subtle electronic factors intrinsic to the C_s niobium alkylidene core. Since the $\angle Nb1−C1−C2$ bond angle is 125.8(8)°, the more readily isomerized C2=C3 bond is closer to the Nb1 center than the C4=C5 bond is to Nb2, thus steric factors may influence isomerization rates. Alternatively, the niobium alkylidene center may be easier to reduce than the corresponding niobium imide, suggesting that a diradical intermediate such as $(silox)_3Nb^{IV}CH=CHC^\bullet(CH=CH)N=Nb(silox)_3$ may mediate C=C isomerization.

Electrophilic activation of the py in $(silox)_3Nb(\eta^2\text{-}NC\text{-}py)$ (**2**-py) promotes nucleophilic attack[19,20] by another $(silox)_3Nb$, generated upon py loss from **2**-py, consistent with the inhibition of ring-opening by added py. Similar dichotomous roles have been attributed to $(silox)_3Ta$, whose capability as both nucleophile/reductant and electrophile enable the activation of diverse substrates such as CO^{21} and anilines.[8] The initial preponderance of **3**-*cis,cis* suggests that py C=N cleavage occurs with retention of the remaining *cis*-double bonds. An intermediate or transition state comprised of two $(silox)_3Nb$ fragments *anti* with respect to the pyridine ring plane appears reasonable in view of related geometries in the crystallographically characterized $[(silox)_3Ta]_2\text{-}(\mu\text{-}\eta^2(1,2):\eta^2(4,5)\text{-}C_6H_6)$ and proposed $[(silox)_3Ta]_2(\mu\text{-}\eta^2(1,2):\eta^2(4,5)\text{-}1,4\text{-}C_6N_2H_4)$ dinuclear complexes.[13] Further substrate and mechanistic investigations are proceeding.

Supporting Information Available: X-ray structural data for **3**-*trans,cis* including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (14 pages). See any current masthead page for ordering and Internet access instructions.

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(17) Crystal data: monoclinic, $P2_1/n$, a = 13.239(2), b = 31.824(5), and c = 22.685(3) Å, β = 91.15(2)°, V = 9556(2) Å³, Z = 4, D_{calcd} = 1.083 g/cm³, T = 293(2) K, full matrix refinement on F^2 (Syntex P4, SHELX93, 12 498 independent reflections, 5577 with $I > 2\sigma(I)$), $R_1(F)$ = 8.28%, R_2-(wF^2) = 14.64%, GOF(F^2) = 1.016.

(18) (a) Wigley, D. E.; Gray, S. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 5, pp 57−153. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (c) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−482.
(19) Comins, D. L.; O'Connor, S. *Adv. Heterocycl. Chem.* **1988**, *44*, 199−267 and references therein.
(20) Molyneux, R. J.; Wong, R. Y. *Tetrahedron* **1977**, *33*, 1931−1934.
(21) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056−9072.