MIT Open Access Articles

Ligand-Based Reduction of CO2 to CO Mediated by an Anionic Niobium Nitride Complex

Ligand-Based Reduction of CO$_2$ to CO Mediated by an Anionic Niobium Nitride Complex

Jared S. Silvia and Christopher C. Cummins

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139

RECEIVED DATE (automatically inserted by publisher); E-mail: ccummins@mit.edu

There are several motivations for producing chemicals from CO$_2$ whenever possible, and in particular, CO is a promising target being both a versatile chemical precursor and a fuel.[1] Reducing metal complexes capable of O-atom abstraction from CO$_2$ typically lead to the formation of strong metal-oxygen bonds that represent a challenge to catalytic turnover.[2] In a special case for which the binding of CO$_2$ evidently involves insertion into a Cu–B linkage, catalytic turnover producing CO was accomplished by taking advantage of the ultimate delivery of oxygen into a stable B–O–B reservoir.[3] This is to be compared with electrocatalytic methods for CO$_2$ reduction to CO in systems that likely involve a direct interaction between CO$_2$ and the metal center at some point in the catalytic cycle.[4] Another commonly observed trend in metal-mediated CO$_2$ reduction is disproportionation reactivity leading to the formation of CO and CO$_3^{2-}$, highlighted by the reaction of Li$_2$[W(CO)$_5$] with CO$_2$ to give W(CO)$_6$ and Li$_2$CO$_3$.[5] With regard to organic systems, conversion of CO$_2$ to CO has recently been achieved with an *N*-heterocyclic carbene serving as the catalyst, activating the CO$_2$ through nucleophilic attack, and a variety of aldehydes serving as the oxygen acceptors to form carboxylic acids.[6] Taking a different approach, we have sought to develop a ligand-based[7,8] CO$_2$ reduction protocol in which the initial binding event is to a terminal nitrido nitrogen atom, rather than directly to the redox-active metal itself; this approach avoids the formation of strong oxometal bonds while ultimately making possible oxide ion transfer to *variable* externally added acceptors. This paradigm suggested itself through the twin discoveries of facile CO$_2$ uptake by a terminal vanadium nitride anion complex and corresponding niobium nitride anion synthesis via isocyanate decarbonylation.[9,10] Accordingly, herein we present a sequence of reactions constituting a cycle for CO$_2$ reduction to CO, using a terminal niobium nitride anion complex as a stable platform that is maintained throughout.

Complex [Na][NNb(N[^{t}Bu]Ar)$_3$] ([Na][**1**], Ar = 3,5-C$_6$H$_3$Me$_2$) reacts with 1 equiv of CO$_2$ at 0 °C to give the carbamate complex [Na][O$_2$CNNb(N[^{t}Bu]Ar)$_3$] ([Na][O$_2$C-**1**]) in 81% isolated yield (A, Scheme 1). Complex [Na][O$_2$C-**1**] is isolated solvate free and has limited solubility in hydrocarbon solvents. Complex [Na][O$_2$C-**1**] has been characterized using ^{1}H and ^{13}C NMR and IR (ν_{OCO} = 1598 cm^{-1}) spectroscopies. When ^{13}CO$_2$ was used in the reaction, the ^{13}C chemical shift of the carbamate group was definitively identified at 161 ppm, and the ν_{OCO} stretch shifts to 1537 cm^{-1}. Although a closely related vanadium complex has been reported,[9] structural data have not been disclosed previously for an *N*-bound carbamate complex. Crystals of [Na][O$_2$C-**1**] suitable for single-crystal X-ray diffraction studies were grown by encapsulating the sodium cation with 2 equiv of 12-crown-4 and cooling a saturated solution of [(12-crown-4)$_2$Na][O$_2$C-**1**] in 1:1 toluene:diethyl ether to –35 °C. The solid-state structure of the

Scheme 1
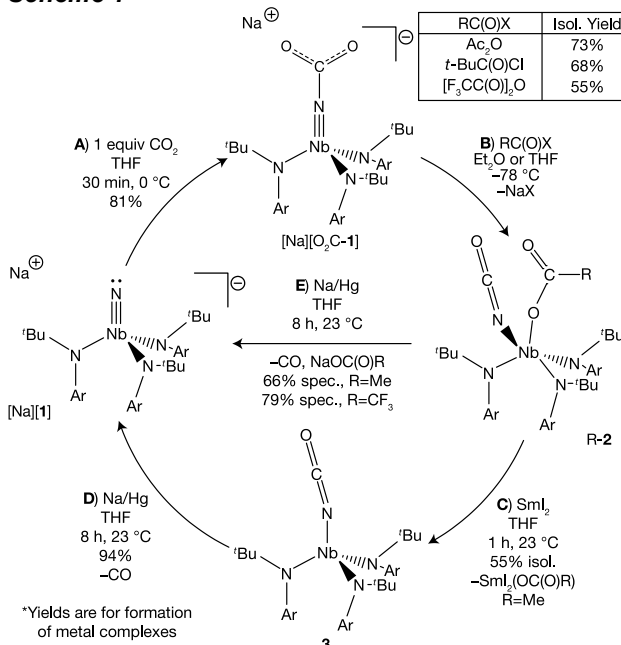
complex anion reveals a terminal *N*-bound carbamate functional group with the oxygen atoms extended away from the niobium metal center (Fig. 1). The short Nb–N$_{imido}$ distance (1.764(2) Å) is comparable to other structurally characterized niobium imido groups and is characteristic of a niobium nitrogen triple-bond.[11] The C–O distances (avg. 1.236(4) Å) show significant elongation when compared to free CO$_2$ (1.17 Å),[12] but are slightly shorter than those found for organic carbamate functional groups.[13]

Although we refer to the N–CO$_2$ functionality as an *N*-bound carbamate, it may be thought of as an imido ligand bearing a CO$_2$ substituent and is closely related to the acylimido functional group, for which a number of examples have been synthesized and structurally characterized.[14-21] Complex [Na][O$_2$C-**1**] is stable indefinitely as a solid or in solution under high vacuum and at 23 °C. At higher temperatures, [Na][O$_2$C-**1**] gives rise to the oxo complex ONb(N[^{t}Bu]Ar)$_3$ (80 h, 70 °C, THF) and sodium cyanate as the co-product (confirmed by ^{13}C NMR spectroscopy).[22] An analogous intramolecular metathesis has been observed in the reaction of CS$_2$ with [Na][NV(N[^{t}Bu]Ar)$_3$] to give sodium thiocyanate and the terminal sulfide complex SV(N[^{t}Bu]Ar)$_3$.[9] This reactivity is also consistent with previous observations that acylimido complexes can extrude organic nitriles.[14,15,20,23,24]

The reactivity of [Na][O$_2$C-**1**] has been studied with the goal of deoxygenating the carbamate carbon. The adopted strategy was derivatization with an electrophile to incorporate a carbamate oxygen into a good leaving group, thus rendering a C–O bond susceptible to reductive cleavage.[25] Treatment of
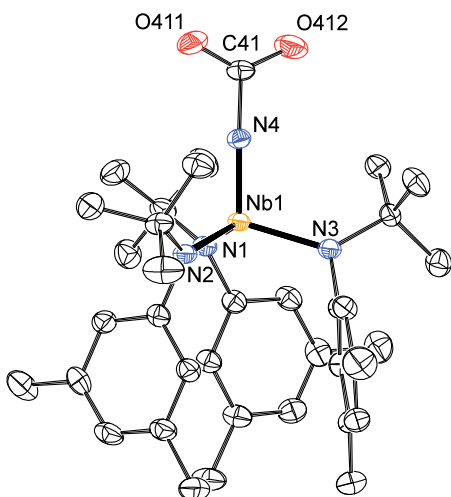
Figure 1. Solid-state structure of [(12-crown-4)$_2$Na][O$_2$C-**1**]•C$_7$H$_8$ ([(12-crown-4)$_2$Na]$^+$ and C$_7$H$_8$ omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.[26] Selected distances (Å) and angles (deg): Nb1–N4 1.764(2), N4–C41 1.449(3), C41–O411 1.226(4), C41–O412 1.246(4), Nb1–N4–C41 175.8(2), O411–C41–C412 127.3(3).

a solution of [Na][O$_2$C-**1**] in THF with acetic anhydride at −78 °C produced a color change from pale brown to bright orange along with a colorless precipitate. After removal of sodium acetate, the product was isolated as a bright orange powder by drying the reaction mixture and washing the residue with *n*-pentane (B, Scheme 1). Using a combination of spectroscopic methods (ν_{NCO} = 2208 cm^{-1}, ν_{OCO} = 1698 cm^{-1}, Fig. 3A) the reaction product was formulated as isocyanate-acetate (AcO)(OCN)Nb(N[^{t}Bu]Ar)$_3$ (Me-**2**). This assignment was further confirmed by determining the solid-state structure of Me-**2** using single-crystal X-ray diffraction methods (Fig. 2). In Me-**2**, the niobium center is in a pseudo-trigonal bipyramidal coordination environment with two anilide ligands and the acetate in the equatorial plane. The Nb–N$_{NCO}$ distance has elongated to 2.156(2) Å, and the Nb–N–C angle is 165.2(2)°. Similarly, reactions between [Na][O$_2$C-**1**] and trifluoroacetic anhydride or pivaloyl chloride were found to produce F$_3$C-**2** and ^{t}Bu-**2**, respectively.[22] We propose that these reactions proceed through a carbamate acetyl ester intermediate that undergoes a rapid intramolecular rearrangement to form the five-coordinate complexes (Scheme 2). However, in the case of the formation of Me-**2**, said intermediate could not be observed by ^{1}H or ^{13}C NMR spectroscopy at −80 °C, indicating that the rate of rearrangement is on par with the rate of the initial salt-elimination reaction.[22] The proposed mechanism also implies that the carbamate carbon becomes incorporated into the isocyanate ligand, and this was confirmed by performing a ^{13}C labeling study. The ^{13}C chemical shift of labeled Me-**2** is observed at 132 ppm, a shift characteristic of isocyanate, not carboxylate, moieties, and the IR spectrum further confirms this conclusion with the ν_{OCN} shifting from 2208 cm^{-1} to 2149 cm^{-1} and the ν_{OCO} remaining unchanged.

In order to generate the isocyanate complex (OCN)Nb(N[^{t}Bu]Ar)$_3$ (**3**), the precursor to [Na][**1**], from Me-**2**, the one-electron reduction of Me-**2** would have to result in selective dissociation of acetate ion over isocyanate ion. The cyclic voltammogram (CV) of Me-**2** contains three observable features (Fig. 3). When scanning cathodically, the first redox event (**I**) is an irreversible reduction that occurs at −2.0 V vs. Fc/Fc$^+$ (Fc = (C$_5$H$_5$)$_2$Fe), assigned as the Nb$^{5+/4+}$ couple. If the cathodic scan is reversed after this event, a new irreversible anodic event (**II**) is observed at −0.9 V and is assigned to a
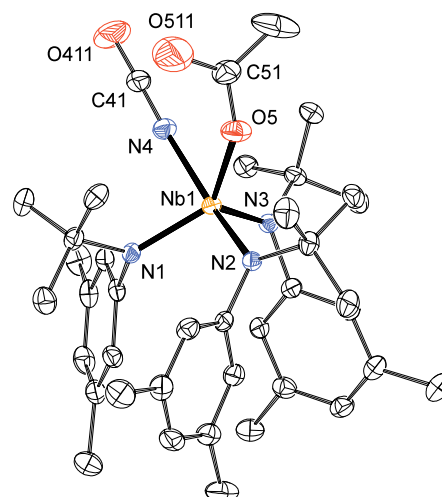

Figure 2. Solid-state structure of Me-**2**•C$_4$H$_8$O (C$_4$H$_8$O omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.[26] Selected distances (Å) and angles (deg): Nb1–N4 2.156(2), Nb1–O511 1.991(1), N4–C41 1.180(4), C41–O411 1.184(4), Nb1–N4–C41 165.2(2).
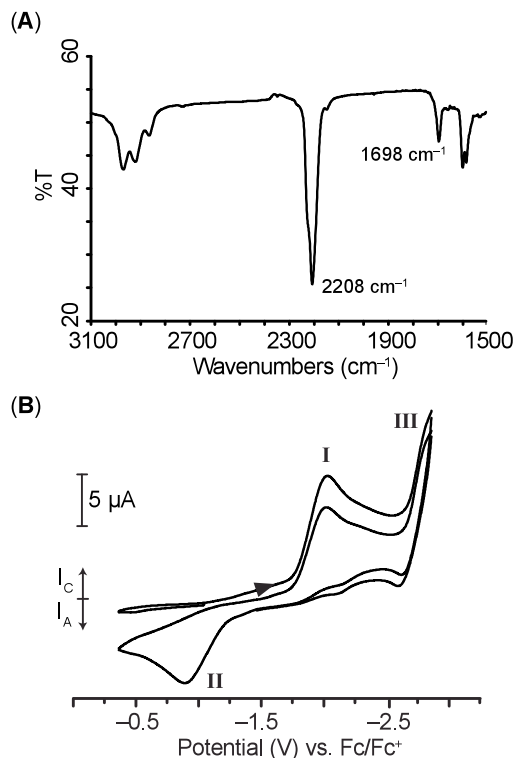

Figure 3. (**A**) IR spectrum of Me-**2**, thin film (KBr). (**B**) CV of Me-**2**, 0.2 M [(^{n}Bu)$_4$N][B(C$_6$F$_5$)$_4$] in THF, 300 mV/s. Event **I** = −2.0 V, **II** = −0.9 V, **III** = −2.8 V vs Fc/Fc$^+$.

Nb$^{5+/4+}$ couple. If the cathodic scan is allowed to continue beyond −2.0 V, a third redox event (**III**) is observed at −2.8 V and is assigned to the Nb$^{4+/3+}$ couple. The potentials of **II** and **III** agree with the previously reported CV of complex **3**.[27] We take this observation as support for the hypothesis that the cathodic event **I** is a 1e reduction of the niobum metal center that results in rapid dissociation of the acetate ligand to generate **3**. In comparison, the CVs of F$_3$C-**2** and ^{t}Bu-**2** contain three similar features.[22] For F$_3$C-**2**, event **I** is shifted to −1.7 V, this shift representing the most pronounced difference between the three CVs. Events **II** and **III** are nearly identical for all three complexes, again consistent with the idea that carboxylate dissociation occurs rapidly upon one-electron

Scheme 2

[Na][O₂C-**1**]
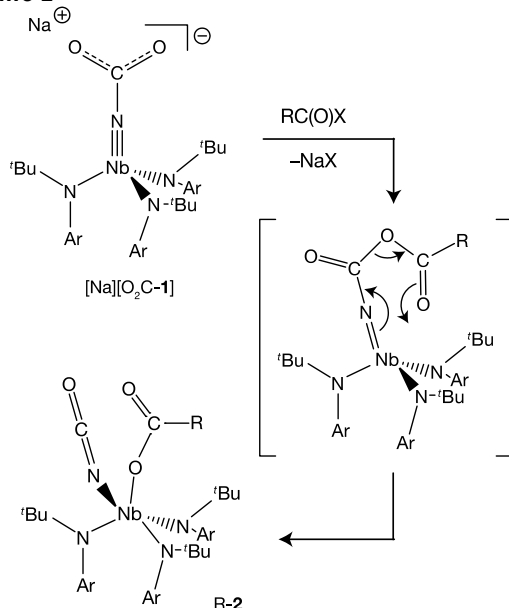
reduction of the complexes to generate **3** in each case.

Following electrochemical measurements, the chemical reduction of Me-**2** was studied. To carry out a 1e reduction of Me-**2**, SmI₂ was chosen as a reducing agent given its reported selectivity for 1e reductions of niobium(V) complexes.[28] Treatment of Me-**2** with SmI₂ in THF at 23 °C produced a deep purple reaction mixture. After stirring for 1 h followed by removal of SmI₂(OAc), **3** was isolated as purple crystalline material in 55% yield by storing saturated solutions in *n*-pentane at −35 °C (C, Scheme 1). Alternatively, reduction of Me-**2** with Na/Hg gave [Na][**1**] directly in 63% isolated yield (E, Scheme 1), agreeing well with the 66% yield determined by ¹H NMR spectroscopy. One hypothesis for the incomplete conversion of Me-**2** to [Na][**1**] is that under the reaction conditions, isocyanate dissociation competes with acetate dissociation upon reduction. Corroborating this idea is the observation that reduction of F₃C-**2** with Na/Hg under similar conditions results in formation of [Na][**1**] in 79% yield as determined by ¹H NMR spectroscopy, presumably due to an enhanced proclivity of trifluoroacetate to undergo dissociation.

To verify formation of CO during the reduction of R-**2**, a two-pot, three-phase chemical trapping experiment was performed wherein volatile materials are transported in the vapor phase and facile CO binding by Cp*RuCl(PCy₃) is indicated by a dramatic color change from blue to yellow as well as by clear ³¹P NMR signatures.[22,29] These experiments confirm formation of gaseous CO with Cp*RuCl(PCy₃)(CO) production assessed at 27% for Me-**2** and 56% for F₃C-**2**. Partially accounting for the incomplete carbonylation of Cp*RuCl(PCy₃) is the observed formation of the hexacarbonyl niobate complex [Na(THF)₆][Nb(CO)₆], in small but reproducible yields (1-5%).[22] Given the highly reducing conditions employed in this reaction as well as the aggressive nature of CO as a ligand, the formation of such a byproduct is not surprising and underscores the importance of developing carbonylation-resistant ancillary ligand combinations.

In the case of acetic anhydride as the oxide acceptor, the net reaction accomplished with the simple three-step (A, B, E) cycle of Scheme 1 is summarized in Eq. 1:

$$CO_2 + Ac_2O + 2e^- \rightarrow CO + 2\,AcO^- \qquad (1)$$

Although the overall process represented in Eq. 1 is two-electron reduction of CO₂ to CO with an anhydride serving as

the oxide ion acceptor, an essential component of the system is the coupling of sequential metal-based one-electron steps (Scheme 1C, D) to bond-making and -breaking processes taking place at the nitrido ligand.

In conclusion, we have developed a synthetic cycle for CO₂ to CO conversion where the transformation is mediated by an anionic niobium nitride complex. These findings expand the field of CO₂ reduction chemistry and illustrate the promise of ligand-based approaches.[7,8] Furthermore, this work, in conjunction with previously reported nitride transfer cycles,[14,30] demonstrates the versatile chemistry available to terminal nitride ligands. To make feasible a catalytic version of the Scheme 1 chemistry, means must be developed such that the nitride nucleophile is able to discriminate between the CO₂ and the oxide ion acceptor electrophiles.

Supporting Information Available: Complete experimental, spectroscopic, electrochemical, and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

References
(1) Marks, T. J. *et al. Chem. Rev.* **2001**, *101*, 953-996.
(2) Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2005**, *127*, 11242-11243.
(3) Laitar, D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196-17197.
(4) Simón-Manso, E.; Kubiak, C. P. *Organometallics* **2005**, *24*, 96-102.
(5) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604-7606.
(6) Gu, L.; Zhang, Y. *J. Am. Chem. Soc.* **2009**. **DOI:** 10.1021/ja909038t
(7) Kerr, M. J.; Harrison, D. J.; Lough, A. J.; Fekl, U. *Inorg. Chem.* **2009**, *48*, 9043-9045.
(8) Harrison, D. J.; Lough, A. J.; Nguyen, N.; Fekl, U. *Angew. Chem., Int. Ed.* **2007**, *46*, 7644-7647.
(9) Brask, J. K.; Durá-Vilá, V.; Diaconescu, P. L.; Cummins, C. C. *Chem. Commun.* **2002**, 902-903.
(10) Fickes, M. G.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1993-1994.
(11) A search of the Cambridge Structural Database for niobium imidos revealed an average Nb–N distance of 1.779 Å.
(12) *CRC Handbook of Chemistry and Physics*; 88th ed.; Lide, D. R., Ed.; CRC Press Inc.: Boca Raton, FL, USA, 2007.
(13) A search of the Cambridge Structural Database of carbamate fragments revealed an average C–O distance of 1.275 Å.
(14) Figueroa, J. S.; Piro, N. A.; Clough, C. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 940-950.
(15) Clough, C. R.; Greco, J. B.; Figueroa, J. S.; Diaconescu, P. L.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 7742-7743.
(16) Sceats, E. L.; Figueroa, J. S.; Cummins, C. C.; Loening, N. M.; Van der Wel, P.; Griffin, R. G. *Polyhedron* **2004**, *23*, 2751-2768.
(17) Cross, J. L.; Garrett, A. D.; Crane, T. W.; White, P. S.; Templeton, J. L. *Polyhedron* **2004**, *23*, 2831-2840.
(18) Thomas, S.; Lim, P. J.; Gable, R. W.; Young, C. G. *Inorg. Chem.* **1998**, *37*, 590-593.
(19) Nielson, A. J.; Hunt, P. A.; Rickard, C. E. F.; Schwerdtfeger, P. *J. Chem. Soc., Dalton Trans.* **1997**, 3311-3317.
(20) Sarkar, S.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 16128-16129.
(21) Watanabe, D.; Gondo, S.; Seino, H.; Mizobe, Y. *Organometallics* **2007**, *26*, 4909-4920.
(22) See Supporting Information.
(23) Van Tamelen, E. E.; Rudler, H. *J. Am. Chem. Soc.* **2002**, *92*, 5253-5254.
(24) Bindl, M.; Stade, R.; Heilmann, E. K.; Picot, A.; Goddard, R.; Fürstner, A. *J. Am. Chem. Soc.* **2009**, *131*, 9468-9470.
(25) Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995-1996.
(26) Spek, A. *J. Appl. Crystallogr.* **2003**, *36*, 7-13.
(27) Silvia, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 446-447.
(28) Cossairt, B. M.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 169-172.
(29) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278-280.
(30) Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036-14037.
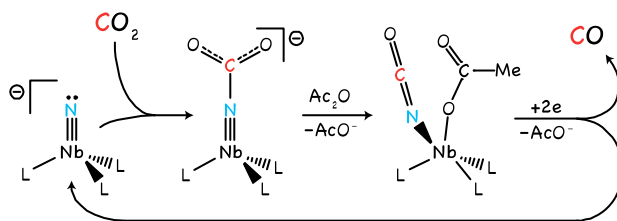
The terminal nitride anion complex [Na][N≡Nb(N[^{t}Bu]Ar)$_3$] ([Na][**1**], Ar = 3,5-Me$_2$C$_6$H$_3$) reacts quantitatively with CO_2 to give the carbamate complex [Na][O$_2$CN≡Nb(N[^{t}Bu]Ar)$_3$] ([Na][O$_2$C-**1**]). The structure of [Na][O$_2$C-**1**] as the *bis*-12-crown-4 solvate, as determined by X-ray crystallography, displays a unique *N*-bound carbamate ligand without any metal-oxygen interactions. When treated with organic acid anhydrides or acid chlorides, complex [Na][O$_2$C-**1**] reacts via salt-elimination to give the five-coordinate complexes (RC(O)O)(OCN)Nb(N[^{t}Bu]Ar)$_3$ (R-**2**, R = Me, ^{t}Bu, F$_3$C). We show that complexes R-**2** yield the starting complex [Na][**1**] with concomitant release of CO upon two-electron reduction. This series of reactions constitutes a closed cycle for the conversion of CO_2 to CO mediated by a terminal nitride anion complex.