

## Ligand-Based Reduction of CO<sub>2</sub> to CO Mediated by an Anionic Niobium Nitride Complex

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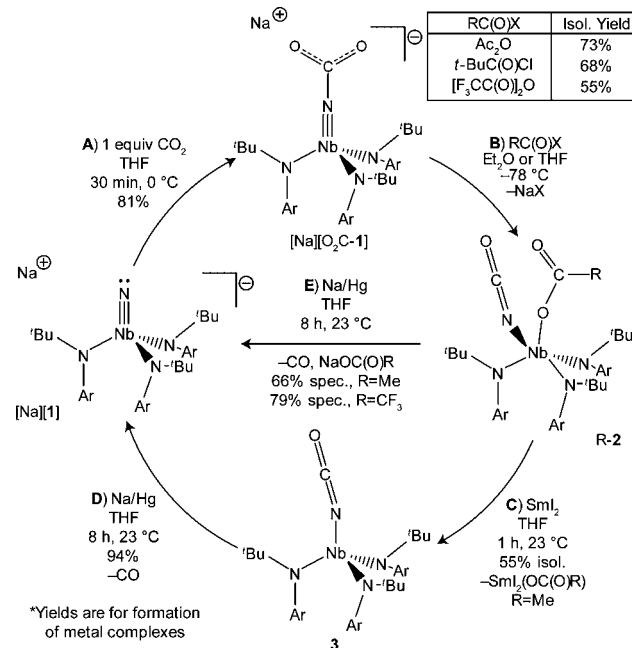
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There are several motivations for producing chemicals from CO<sub>2</sub> whenever possible, and in particular, CO is a promising target being both a versatile chemical precursor and a fuel.<sup>1</sup> Reducing metal complexes capable of O-atom abstraction from CO<sub>2</sub> typically lead to the formation of strong metal–oxygen bonds that represent a challenge to catalytic turnover.<sup>2</sup> In a special case for which the binding of CO<sub>2</sub> 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.<sup>3</sup> This is to be compared with electrocatalytic methods for CO<sub>2</sub> reduction to CO in systems that likely involve a direct interaction between CO<sub>2</sub> and the metal center at some point in the catalytic cycle.<sup>4</sup> Another commonly observed trend in metal-mediated CO<sub>2</sub> reduction is disproportionation reactivity leading to the formation of CO and CO<sub>3</sub><sup>2-</sup>, highlighted by the reaction of Li<sub>2</sub>[W(CO)<sub>5</sub>] with CO<sub>2</sub> to give W(CO)<sub>6</sub> and Li<sub>2</sub>CO<sub>3</sub>.<sup>5</sup> With regard to organic systems, conversion of CO<sub>2</sub> to CO has recently been achieved with an *N*-heterocyclic carbene serving as the catalyst, activating the CO<sub>2</sub> through nucleophilic attack, and a variety of aldehydes serving as the oxygen acceptors to form carboxylic acids.<sup>6</sup> Taking a different approach, we have sought to develop a ligand-based<sup>7,8</sup> CO<sub>2</sub> 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<sub>2</sub> uptake by a terminal vanadium nitride anion complex and corresponding niobium nitride anion synthesis via isocyanate decarbonylation.<sup>9,10</sup> Accordingly, herein we present a sequence of reactions constituting a cycle for CO<sub>2</sub> reduction to CO, using a terminal niobium nitride anion complex as a stable platform that is maintained throughout.

Complex [Na][NNb(N<sup>t</sup>Bu)Ar<sub>3</sub>] ([Na][1], Ar = 3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) reacts with 1 equiv of CO<sub>2</sub> at 0 °C to give the carbamate complex [Na][O<sub>2</sub>CNNb(N<sup>t</sup>Bu)Ar<sub>3</sub>] ([Na][O<sub>2</sub>C-1]) in 81% isolated yield (A, Scheme 1). Complex [Na][O<sub>2</sub>C-1] is isolated solvate free and has limited solubility in hydrocarbon solvents. Complex [Na][O<sub>2</sub>C-1] has been characterized using <sup>1</sup>H and <sup>13</sup>C NMR and IR (ν<sub>OCO</sub> = 1598 cm<sup>-1</sup>) spectroscopies. When <sup>13</sup>CO<sub>2</sub> was used in the reaction, the <sup>13</sup>C chemical shift of the carbamate group was definitively identified at 161 ppm, and the ν<sub>OCO</sub> stretch shifts to 1537 cm<sup>-1</sup>. Although a closely related vanadium complex has been reported,<sup>9</sup> structural data have not been disclosed previously for an *N*-bound carbamate complex. Crystals of [Na][O<sub>2</sub>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)<sub>2</sub>Na][O<sub>2</sub>C-1] in 1:1 toluene/diethyl ether to -35 °C. The solid-state structure of the complex anion reveals a terminal *N*-bound carbamate functional group with the oxygen atoms extended away from the niobium metal center (Figure 1). The short Nb–N<sub>imido</sub> distance (1.764(2) Å) is comparable to other

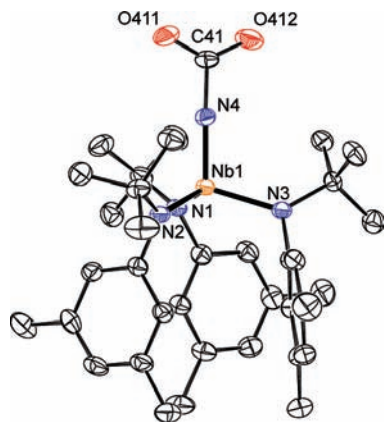
Scheme 1



structurally characterized niobium imido groups and is characteristic of a niobium nitrogen triple bond.<sup>11</sup> The C–O distances (avg 1.236(4) Å) show significant elongation when compared to free CO<sub>2</sub> (1.16 Å)<sup>12</sup> but are slightly shorter than those found for organic carbamate functional groups.<sup>13</sup>

Although we refer to the N–CO<sub>2</sub> functionality as an *N*-bound carbamate, it may be thought of as an imido ligand bearing a CO<sub>2</sub> substituent and is closely related to the acylimido functional group, for which a number of examples have been synthesized and structurally characterized.<sup>14–21</sup> Complex [Na][O<sub>2</sub>C-1] is stable indefinitely as a solid or in solution under high vacuum and at 23 °C. At higher temperatures, [Na][O<sub>2</sub>C-1] gives rise to the oxo complex ONb(N<sup>t</sup>Bu)Ar<sub>3</sub> (80 h, 70 °C, THF) and sodium cyanate as the coproduct (confirmed by <sup>13</sup>C NMR spectroscopy).<sup>22</sup> An analogous intramolecular metathesis has been observed in the reaction of CS<sub>2</sub> with [Na][NV(N<sup>t</sup>Bu)Ar<sub>3</sub>] to give sodium thiocyanate and the terminal sulfide complex SV(N<sup>t</sup>Bu)Ar<sub>3</sub>.<sup>9</sup> This reactivity is also consistent with previous observations that acylimido complexes can extrude organic nitriles.<sup>14,15,20,23,24</sup>

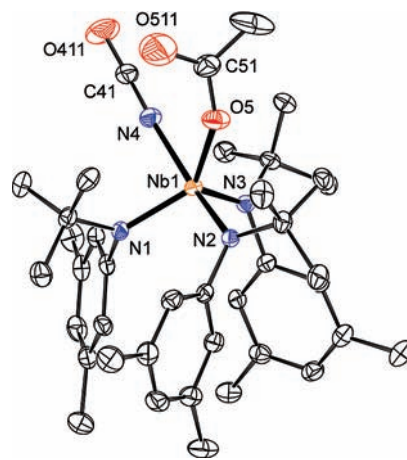
The reactivity of [Na][O<sub>2</sub>C-1] has been studied with the goal of deoxygenating the carbamate carbon. The adopted strategy was derivatization with an electrophile to incorporate a carbamate oxygen into a good leaving group, thus rendering a C–O bond susceptible to reductive cleavage.<sup>25</sup> Treatment of a solution of [Na][O<sub>2</sub>C-1] in THF with acetic anhydride at -78 °C produced a color change from pale brown to bright orange along with a



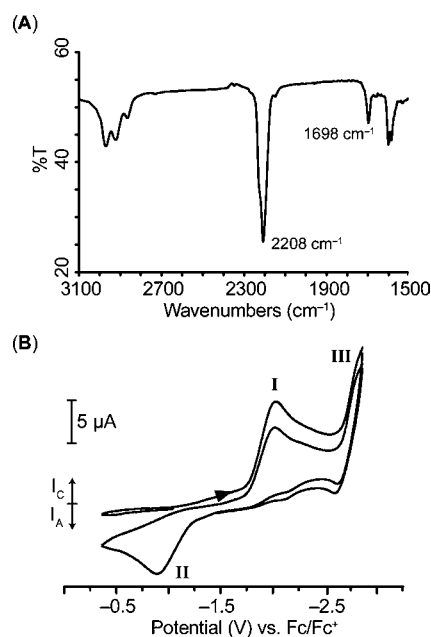
**Figure 1.** Solid-state structure of [(12-crown-4)<sub>2</sub>Na][O<sub>2</sub>C-1]•C<sub>7</sub>H<sub>8</sub> ([12-crown-4)<sub>2</sub>Na]<sup>+</sup> and C<sub>7</sub>H<sub>8</sub> omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.<sup>26</sup> Selected distances (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–O412 127.3(3).

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 ( $\nu_{\text{NCO}} = 2208 \text{ cm}^{-1}$ ,  $\nu_{\text{OCO}} = 1698 \text{ cm}^{-1}$ , Figure 3A) the reaction product was formulated as isocyanate-acetate (AcO)(OCN)Nb(N<sup>t</sup>Bu)Ar<sub>3</sub> (Me-2). This assignment was further confirmed by determining the solid-state structure of Me-2 using single-crystal X-ray diffraction methods (Figure 2). In Me-2, the niobium center is in a pseudotrigonal bipyramidal coordination environment with two anilide ligands and the acetate in the equatorial plane. The Nb–N<sub>NCO</sub> distance has elongated to 2.156(2) Å, and the Nb–N–C angle is 165.2(2)°. Similarly, reactions between [Na][O<sub>2</sub>C-1] and trifluoroacetic anhydride or pivaloyl chloride were found to produce F<sub>3</sub>C-2 and <sup>t</sup>Bu-2, respectively.<sup>22</sup> 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, the intermediate could not be observed by <sup>1</sup>H or <sup>13</sup>C NMR spectroscopy at –80 °C, indicating that the rate of rearrangement is approximately the same as the rate of the initial salt-elimination reaction.<sup>22</sup> The proposed mechanism also implies that the carbamate carbon becomes incorporated into the isocyanate ligand, and this was confirmed by performing a <sup>13</sup>C labeling study. The <sup>13</sup>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  $\nu_{\text{OCN}}$  shifting from 2208 cm<sup>–1</sup> to 2149 cm<sup>–1</sup> and the  $\nu_{\text{OCO}}$  remaining unchanged.

To generate the isocyanate complex (OCN)Nb(N<sup>t</sup>Bu)Ar<sub>3</sub> (**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 (Figure 3). When scanning cathodically, the first redox event (**I**) is an irreversible reduction that occurs at –2.0 V vs Fc/Fc<sup>+</sup> (Fc = (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe), assigned as the Nb<sup>5+/4+</sup> 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 Nb<sup>5+/4+</sup> 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<sup>4+/3+</sup> couple. The potentials of **II** and **III** agree with the previously reported CV of complex **3**.<sup>27</sup> We take this observation as support for the hypothesis that the cathodic event **I** is a 1e reduction of the niobium metal center that results in



**Figure 2.** Solid-state structure of Me-2•C<sub>4</sub>H<sub>8</sub>O (C<sub>4</sub>H<sub>8</sub>O omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.<sup>26</sup> Selected distances (Å) and angles (deg): Nb1–N4 2.156(2), Nb1–O5 1.991(1), N4–C41 1.180(4), C41–O411 1.184(4), Nb1–N4–C41 165.2(2).

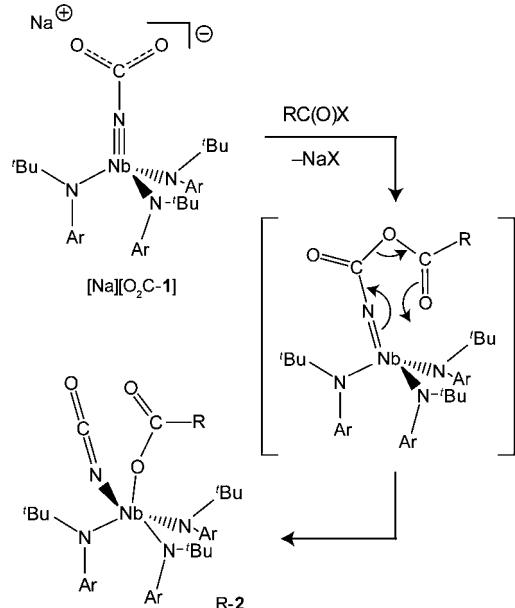


**Figure 3.** (A) IR spectrum of Me-2, thin film (KBr). (B) CV of Me-2, 0.2 M [(<sup>t</sup>Bu)<sub>4</sub>N][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in THF, 300 mV/s. Event **I** = –2.0 V, **II** = –0.9 V, **III** = –2.8 V vs Fc/Fc<sup>+</sup>.

rapid dissociation of the acetate ligand to generate **3**. In comparison, the CVs of F<sub>3</sub>C-2 and <sup>t</sup>Bu-2 contain three similar features.<sup>22</sup> For F<sub>3</sub>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 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, SmI<sub>2</sub> was chosen as a reducing agent given its reported selectivity for 1e reductions of niobium(V) complexes.<sup>28</sup> Treatment of Me-2 with SmI<sub>2</sub> in THF at 23 °C produced a deep purple reaction mixture. After stirring for 1 h followed by removal of SmI<sub>2</sub>(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

Scheme 2



in 63% isolated yield (E, Scheme 1), agreeing well with the 66% yield determined by  $^1\text{H}$  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  $\text{F}_3\text{C-2}$  with Na/Hg under similar conditions results in formation of [Na][1] in 79% yield as determined by  $^1\text{H}$  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  $\text{Cp}^*\text{RuCl}(\text{PCy}_3)$  is indicated by a dramatic color change from blue to yellow as well as by clear  $^{31}\text{P}$  NMR signatures.<sup>22,29</sup> These experiments confirm formation of gaseous CO with  $\text{Cp}^*\text{RuCl}(\text{PCy}_3)(\text{CO})$  production assessed at 27% for Me-2 and 56% for  $\text{F}_3\text{C-2}$ . Partially accounting for the incomplete carbonylation of  $\text{Cp}^*\text{RuCl}(\text{PCy}_3)$  is the observed formation of the hexacarbonyl niobate complex  $[\text{Na}(\text{THF})_6][\text{Nb}(\text{CO})_6]$ , in small but reproducible yields (1–5%).<sup>22</sup> 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:



Although the overall process represented in eq 1 is two-electron reduction of  $\text{CO}_2$  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  $\text{CO}_2$  to CO conversion where the transformation is mediated by an anionic niobium nitride complex. These findings expand the field of  $\text{CO}_2$  reduction chemistry and illustrate the promise of ligand-based approaches.<sup>7,8</sup> Furthermore, this work, in conjunction with previously reported nitride transfer cycles,<sup>14,30</sup> 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  $\text{CO}_2$  and the oxide ion acceptor electrophiles.

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**Supporting Information Available:** Complete experimental, spectroscopic, electrochemical, a complete author list for reference 1, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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