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

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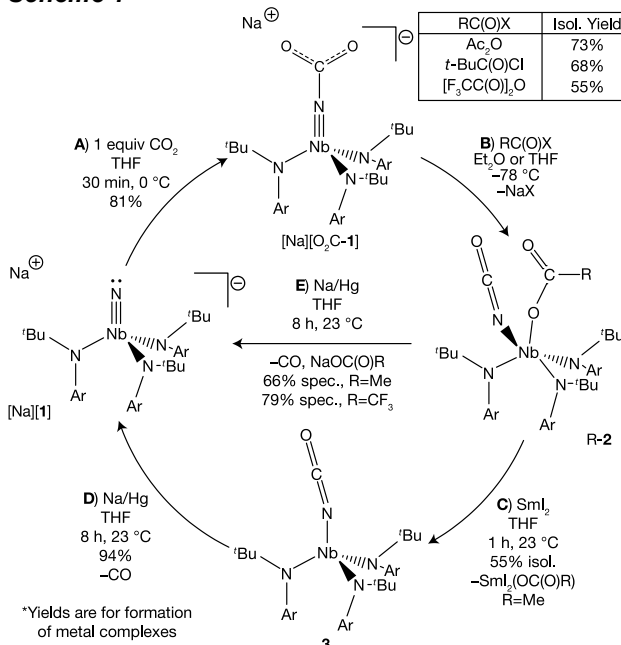
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There are several motivations for producing chemicals from CO₂ whenever possible, and in particular, CO is a promising target being both a versatile chemical precursor and a fuel.¹ Reducing metal complexes capable of O-atom abstraction from CO₂ typically 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 CO₂ 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 CO₂ reduction to CO in systems that likely involve a direct interaction between CO₂ and the metal center at some point in the catalytic cycle.⁴ Another commonly observed trend in metal-mediated CO₂ reduction is disproportionation reactivity leading to the formation of CO and CO₃^{2–}, highlighted by the reaction of Li₂[W(CO)₆] with CO₂ to give W(CO)₆ and Li₂CO₃.⁵ With regard to organic systems, conversion of CO₂ to CO has recently been achieved with an *N*-heterocyclic carbene serving as the catalyst, activating the CO₂ 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} CO₂ 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 CO₂ 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 CO₂ reduction to CO, using a terminal niobium nitride anion complex as a stable platform that is maintained throughout.

Complex [Na][NNb(N^tBuAr)₃] ([Na][1], Ar = 3,5-C₆H₃Me₂) reacts with 1 equiv of CO₂ at 0 °C to give the carbamate complex [Na][O₂CNNb(N^tBuAr)₃] ([Na][O₂C-1]) in 81% isolated yield (A, Scheme 1). Complex [Na][O₂C-1] is isolated solvate free and has limited solubility in hydrocarbon solvents. Complex [Na][O₂C-1] has been characterized using ¹H and ¹³C NMR and IR (ν_{OCO} = 1598 cm^{–1}) spectroscopies. When ¹³CO₂ was used in the reaction, the ¹³C 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][O₂C-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)₂Na][O₂C-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 CO₂ (1.17 Å),¹² but are slightly shorter than those found for organic carbamate functional groups.¹³

Although we refer to the N–CO₂ functionality as an *N*-bound carbamate, it may be thought of as an imido ligand bearing a CO₂ 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][O₂C-1] is stable indefinitely as a solid or in solution under high vacuum and at 23 °C. At higher temperatures, [Na][O₂C-1] gives rise to the oxo complex ONb(N^tBuAr)₃ (80 h, 70 °C, THF) and sodium cyanate as the co-product (confirmed by ¹³C NMR spectroscopy).²² An analogous intramolecular metathesis has been observed in the reaction of CS₂ with [Na][NV(N^tBuAr)₃] to give sodium thiocyanate and the terminal sulfide complex SV(N^tBuAr)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][O₂C-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

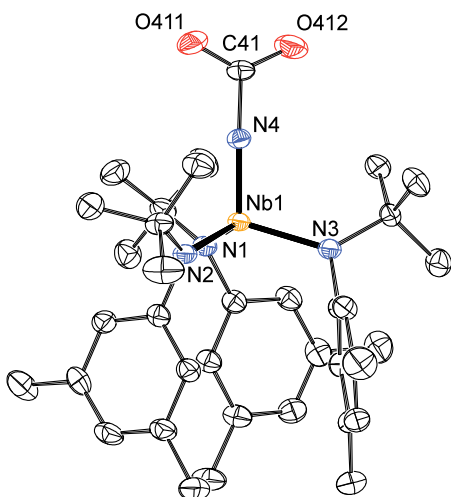


Figure 1. Solid-state structure of $[(12\text{-crown-4})_2\text{Na}][\text{O}_2\text{C-1}]\cdot\text{C}_7\text{H}_8$ ($[(12\text{-crown-4})_2\text{Na}]^+$ and C_7H_8 omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.²⁶ Selected distances (Å) and angles (deg): 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 $[\text{Na}][\text{O}_2\text{C-1}]$ 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 ($\nu_{\text{NCO}} = 2208\text{ cm}^{-1}$, $\nu_{\text{OCO}} = 1698\text{ cm}^{-1}$, Fig. 3A) the reaction product was formulated as isocyanate-acetate $(\text{AcO})(\text{OCN})\text{Nb}(\text{N}^t\text{BuAr})_3$ (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 $[\text{Na}][\text{O}_2\text{C-1}]$ and trifluoroacetic anhydride or pivaloyl chloride were found to produce $\text{F}_3\text{C-2}$ and $^t\text{Bu-2}$, 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 ^1H 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 $(\text{OCN})\text{Nb}(\text{N}^t\text{BuAr})_3$ (3), the precursor to $[\text{Na}][\text{I}]$, 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^+ ($\text{Fc} = (\text{C}_5\text{H}_5)_2\text{Fe}$), assigned as the $\text{Nb}^{5+/4+}$ 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

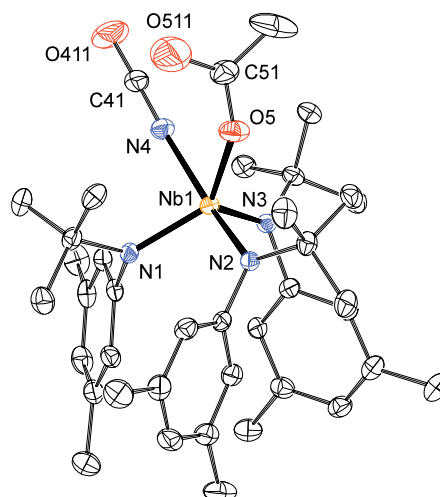


Figure 2. Solid-state structure of Me-2· $\text{C}_4\text{H}_8\text{O}$ ($\text{C}_4\text{H}_8\text{O}$ omitted) with thermal ellipsoids at 50% probability and hydrogen atoms omitted for clarity.²⁶ Selected distances (Å) and angles (deg): Nb1–N4 2.156(2), Nb1–O511 1.991(1), N4–C41 1.180(4), C41–O411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

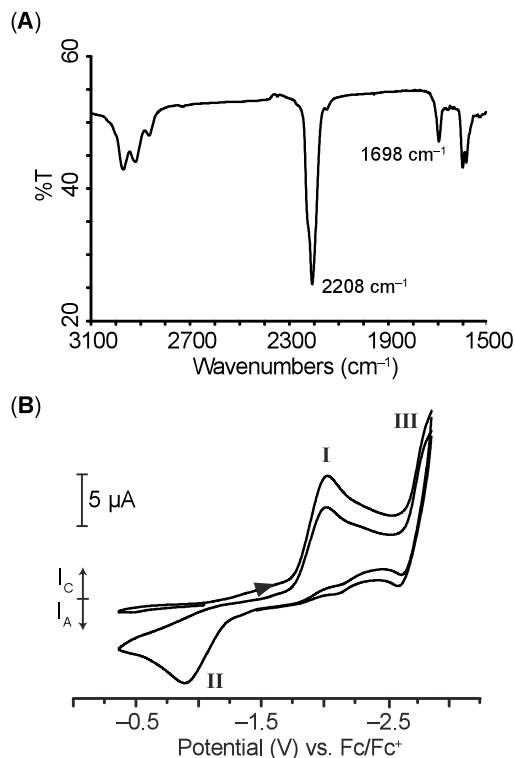
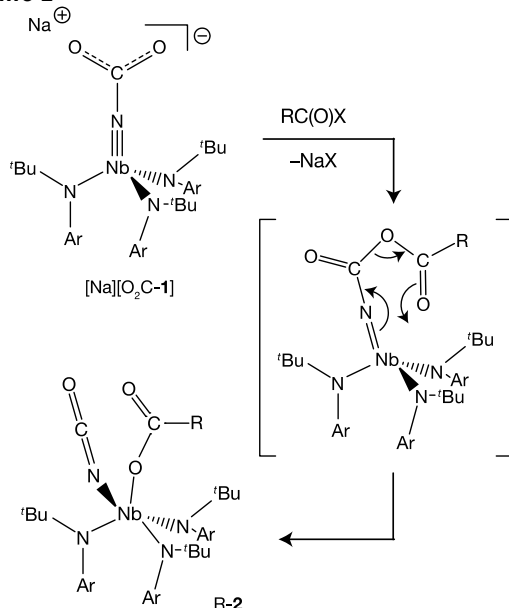


Figure 3. (A) IR spectrum of Me-2, thin film (KBr). (B) CV of Me-2, 0.2 M $[(^t\text{Bu})_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ in THF, 300 mV/s. Event I = -2.0 V , II = -0.9 V , III = -2.8 V vs Fc/Fc^+ .

$\text{Nb}^{5+/4+}$ 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 $\text{Nb}^{4+/3+}$ 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 niobium metal center that results in rapid dissociation of the acetate ligand to generate 3. In comparison, the CVs of $\text{F}_3\text{C-2}$ and $^t\text{Bu-2}$ contain three similar features.²² For $\text{F}_3\text{C-2}$, 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



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_2 was chosen as a reducing agent given its reported selectivity for 1e reductions of niobium(V) complexes.²⁸ Treatment of **Me-2** with SmI_2 in THF at 23 °C produced a deep purple reaction mixture. After stirring for 1 h followed by removal of $\text{SmI}_2(\text{OAc})$, **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 $[\text{Na}][\mathbf{1}]$ 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 $[\text{Na}][\mathbf{1}]$ 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 $[\text{Na}][\mathbf{1}]$ 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 $\text{Cp}^*\text{RuCl}(\text{PCy}_3)$ is indicated by a dramatic color change from blue to yellow as well as by clear ^{31}P NMR signatures.^{22,29} 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%).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:



Although the overall process represented in Eq. 1 is two-electron reduction of 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.

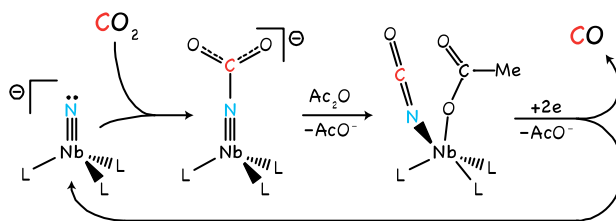
In conclusion, we have developed a synthetic cycle for CO_2 to CO conversion where the transformation is mediated by an anionic niobium nitride complex. These findings expand the field of CO_2 reduction chemistry and illustrate the promise of ligand-based approaches.^{7,8} Furthermore, this work, in 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 CO_2 and the oxide ion acceptor electrophiles.

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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>.

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The terminal nitride anion complex $[\text{Na}][\text{N}\equiv\text{Nb}(\text{N}[\text{t-Bu}]\text{Ar})_3]$ ($[\text{Na}][\mathbf{1}]$, $\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$) reacts quantitatively with CO_2 to give the carbamate complex $[\text{Na}][\text{O}_2\text{CN}\equiv\text{Nb}(\text{N}[\text{t-Bu}]\text{Ar})_3]$ ($[\text{Na}][\text{O}_2\text{C-}\mathbf{1}]$). The structure of $[\text{Na}][\text{O}_2\text{C-}\mathbf{1}]$ 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 $[\text{Na}][\text{O}_2\text{C-}\mathbf{1}]$ reacts via salt-elimination to give the five-coordinate complexes $(\text{RC}(\text{O})\text{O})(\text{OCN})\text{Nb}(\text{N}[\text{t-Bu}]\text{Ar})_3$ (**R-2**, $\text{R} = \text{Me}$, t-Bu , F_3C). We show that complexes **R-2** yield the starting complex $[\text{Na}][\mathbf{1}]$ 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.