

Nickel(I)-mediated transformations of carbon dioxide in closed synthetic cycles: reductive cleavage and coupling of CO₂ generating Ni^ICO, Ni^{II}CO₃ and Ni^{II}C₂O₄Ni^{II} entities†‡

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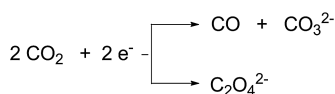
The β-diketiminato nickel(I) complex K₂[L^{tBu}Ni^I(N₂²⁻)Ni^IL^{tBu}] reacts with CO₂ via reductive disproportionation to form CO and CO₃²⁻ containing products, whereas after employment of the Ni^I precursor [L^{tBu}Ni^I(N₂)-Ni^IL^{tBu}] reductive coupling of CO₂ was observed giving an oxalate bridged dinickel(II) complex. The addition of K₂C₈ to the carbonate and oxalate compounds formed leads to the regeneration of the initial Ni^I complexes in an N₂ atmosphere, thus closing synthetic cycles.

Carbon dioxide is an abundant, cheap, nontoxic and also readily available gas, which acts as the planet's most important source of carbon. Although it is an environmentally friendly reagent only a few industrial processes utilize CO₂ as a raw material. Mostly, CO₂ is activated reductively and common products are formate, oxalate as well as carbon monoxide and carbonate (for the latter three see Scheme 1).^{1,2}

Often such conversions are hampered by the extreme thermodynamic stability of CO₂. Hence, its chemical transformation into useful products is a contemporary challenge,¹⁻⁵ and impressive progress has been made in recent years utilizing reduced transition metal² and f-block metal complexes,⁶ leading for instance to closed synthetic cycles for the reductive disproportionation of CO₂ to CO and carbonate as reported very recently by Meyer and co-workers for a uranium system.⁷ Narrowing the focus on late first row transition metals a number of interesting CO₂ transformations deserve mentioning: for example, Peters reported the reductive

cleavage of CO₂ mediated by a low coordinated Fe^I system to provide a Fe^{II}(μ-O)(μ-CO)Fe^{II} complex as the major product. Reductive CO₂ coupling was found to occur in a side path yielding a diiron(II) oxalate complex.⁸ A β-diketiminato diiron(I) precursor was found to react with CO₂ to form an iron(I) dicarbonyl compound as well as a diiron(II) carbonate complex by Holland and co-workers.⁹ Bouwman *et al.* reported the selective electrocatalytic conversion of atmospheric CO₂ into oxalate by a dicopper(I) complex.¹⁰ The catalytic deoxygenation of CO₂ using a copper(I) boryl complex, affording CO and a borate complex, was described by Sadighi,¹¹ who also reported a Ni⁰ N-heterocyclic carbene complex that binds and deoxygenates CO₂.¹² Caulton and co-workers showed that a Ni^I disilazide reacts with CO₂ via transposition of the amide N and one O atom of CO₂.¹³ With regard to nickel chemistry and the conversions depicted in Scheme 1 early work has demonstrated the potential of chemically¹⁴ or electrochemically¹⁵ reduced Ni complexes to mediate the transformation of CO₂ to CO, or to act as electrocatalysts¹⁶ for the reduction of CO₂ to oxalate. The former process is also relevant to natural systems, where it is realized at a nickel centre, too, within the active site of the carbon monoxide dehydrogenase.¹⁷

Based on the latest research progress regarding the reduction of carbon dioxide at synthetic transition metal active sites and the crucial role of Ni in enzymatic CO₂ reduction, we were interested in the reactivity of the reduced low coordinated nickel complexes [L^{tBu}Ni^I(N₂)Ni^IL^{tBu}], **IV**,¹⁸ and K₂[L^{tBu}Ni^I(N₂²⁻)Ni^IL^{tBu}], **I**,¹⁸ towards CO₂ (L^{tBu} = [HC(C(*t*Bu)NC₆H₃(*i*Pr)₂)₂]⁻). **IV** displays a weakly activated dinitrogen ligand spanned by two Ni^I centres, whereas in **I** the extent of N–N bond activation is more pronounced due to two additional electrons in the system.¹⁸ Previously, we reported that **IV** and **I** react with carbon monoxide to give the mononuclear Ni^I complex [L^{tBu}Ni^ICO], **II**, and the dinuclear Ni⁰ compound K₂[L^{tBu}Ni⁰CO]₂, respectively. That is, despite being moderately activated, the N₂ ligand within **I** can be readily displaced, with concomitant formation of a L^{tBu}Ni⁰ species.¹⁹ Therefore, **I** and **IV** appear to be ideal synthons for the activation of carbon dioxide, with **I** providing two reducing equivalents per Ni centre, while the Ni centres in **IV** are confined to one-electron transfer.

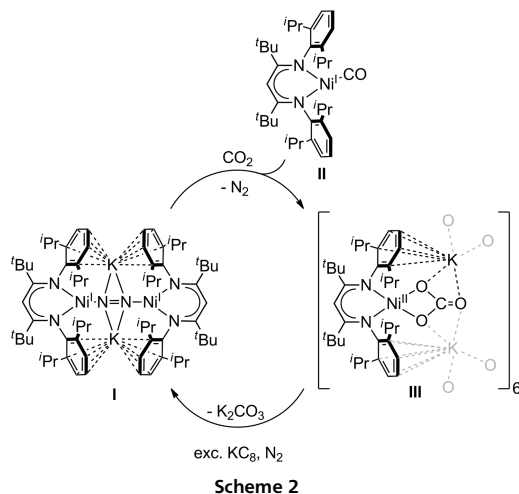


Scheme 1

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† Dedicated to Professor Dr Drs h.c. Helmut Schwarz on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Experimental section, details of density functional calculations and X-ray crystallographic data. CCDC 950231. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc45407j



Upon exposure of a suspension of $\text{K}_2[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{N}_2^{2-})\text{Ni}^{\text{I}}\text{L}^{\text{tBu}}]$, **I**, in hexane to an atmosphere of CO_2 at r.t. the initial dark violet suspension turned light yellow brown within some seconds. Without any purification steps evaporation of the solvent afforded a golden brown solid. The ^1H NMR spectrum recorded for a benzene- d_6 solution of this material (see ESI,† Fig. S3) shows two broad signals resulting from the nickel(I) carbonyl complex $[\text{L}^{\text{tBu}}\text{NiCO}]$, **II**,¹⁹ and a set of signals belonging to the hexanuclear nickel(II) carbonate compound $\text{K}_6[\text{L}^{\text{tBu}}\text{NiCO}_3]_6$, **III**,²⁰ as described earlier (see Scheme 2).

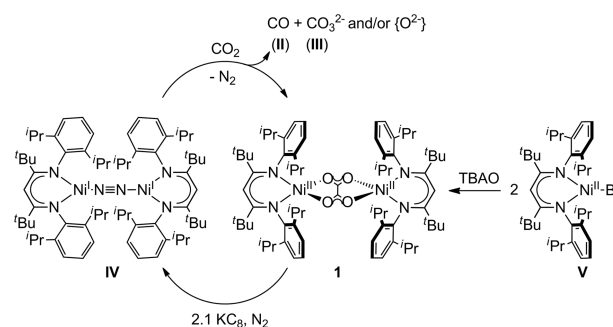
The presence of **II** and **III** in the crude product was further confirmed by IR spectroscopy through their characteristic bands (see ESI,† Fig. S2), and additional evidence for **II** was provided by an EPR spectrum recorded for a hexane solution, exhibiting the characteristic rhombic signal (see ESI,† Fig. S4). Therefore, **I** effectively mediates the reductive disproportionation of CO_2 to form the CO and CO_3^{2-} containing compounds **II** and **III**. **III** can be separated by cooling a hexane suspension of the product mixture to -30°C , which led to its precipitation in up to 36%²¹ yield expected, if both Ni centres in **I** would react exclusively to form **III**. However, partial consumption of **I** through formation of **II** does not permit such a clean reaction. **II** must be formed in a side path as CO is known to react with **I** to give a nickel(0) carbonyl complex $\text{K}_2[\text{L}^{\text{tBu}}\text{NiCO}]_2$, which in fact was found capable of reducing CO_2 , too.²² Employing KC_8 as the reducing reagent, the nickel(II) carbonate complex **III** can be transformed fully into the original Ni^{I} complex **I** in a dinitrogen atmosphere, and this process is accompanied by the elimination of K_2CO_3 as evidenced by ^{13}C NMR spectroscopy (Scheme 2).

It is reasonable to assume that in the first reaction step of **I** CO_2 replaces the N_2 ligand at the Ni centres. However, it is difficult to make substantiated mechanistic suggestions about this step and subsequent reaction sequences *via* theoretical considerations, as **I** is dinuclear (thus offering various pathways, including mononuclear ones) and contains K^+ ions that contribute to stabilization, while the end product **III** is hexanuclear. DFT calculations performed (see ESI†) allow for the following statements, though: (i) geometry optimizations setting out from $[\text{L}^{\text{tBu}}\text{Ni}(\text{O})(\text{CO})]^-$ or structures with CO_2 in various coordination modes always yielded $[\text{L}^{\text{tBu}}\text{Ni}(\text{CO}_2)]^-$ both on the singlet and on the triplet surface,²⁰ (ii) formation of $[\text{L}^{\text{tBu}}\text{Ni}(\text{O})]^-$ and free CO from $[\text{L}^{\text{tBu}}\text{Ni}(\text{CO}_2)]^-$ is thermodynamically

unfavourable, as is (iii) the approach of two $[\text{L}^{\text{tBu}}\text{Ni}(\text{CO}_2)]^-$ to give a $[\text{L}^{\text{tBu}}\text{Ni}(\text{OCOCO}_2)\text{NiL}^{\text{tBu}}]^{2-}$ moiety. (i) and (ii) exclude CO_2 dissociation exclusively at one Ni centre and suggest a dinuclear reactivity, perhaps involving a so far unknown $\text{Ni}^{\text{II}}\text{O}-\text{Ni}^{\text{II}}$ complex.

Having found that the $\text{Ni}^{\text{I}}(\text{N}=\text{N})^{2-}\text{Ni}^{\text{I}}$ core of **I**, which in course of the N_2 elimination provides two Ni^{0} centres, permits the conversion $[\text{Ni}^{\text{0}}] + 2\text{CO}_2 \rightarrow [\text{Ni}^{\text{II}}] + \text{CO}_3^{2-} + \text{CO}$ we got interested in the behaviour of a dinuclear nickel(I) core with only one reducing equivalent per Ni centre. Hence, a hexane suspension of **IV** was treated with carbon dioxide at r.t., which led to a slow colour change from red brown to dark brown over a period of 16 h. Analysis of the resulting crude product by IR spectroscopy revealed *inter alia* the formation of $[\text{L}^{\text{tBu}}\text{NiCO}]$, **II** (see ESI,† Fig. S9), whose terminal carbonyl ligand again is a result of a two-electron reduction of CO_2 .²³ Further investigations with the aid of ^1H NMR spectroscopy proved the formation of an additional reaction product, and the observed shifts hinted at a paramagnetic nickel(II) complex (see ESI,† Fig. S6). IR spectroscopy revealed the formation of a C_xO_y containing product through an absorption band in the region of $\text{C}=\text{O}$ vibrations at 1650 cm^{-1} . Through evaporation of the volatiles from a hexane solution of the crude mixture crystals could be obtained that contained the new product as part of a solid solution: X-ray diffraction analysis identified it as a dinuclear nickel(II) oxalate complex $[\text{L}^{\text{tBu}}\text{Ni}(\text{C}_2\text{O}_4)\text{NiL}^{\text{tBu}}]$, **1**,²⁴ indicating the coupling of two one-electron reduced molecules of CO_2 . Upon extension of the reaction time to 60 h at r.t. with vigorous stirring, cooling to -30°C led to the precipitation of violet **1** within one day in a yield up to 20%.²⁵ **1** can be synthesised alternatively by reaction of a diethyl ether suspension of $[\text{L}^{\text{tBu}}\text{NiBr}]$, **V**,¹⁸ and bis(tetrabutylammonium) oxalate (see Scheme 3), and subsequently it could be isolated in pure form (59% yield).

Violet crystals suitable for X-ray diffraction analysis were grown from a benzene- d_6 solution after slow evaporation of the solvent, and the molecular structure of $1\cdot 4\text{C}_6\text{D}_6$ is shown in Fig. 1.† The most remarkable feature of $[\text{L}^{\text{tBu}}\text{Ni}(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_2\text{O}_4)\text{NiL}^{\text{tBu}}]$ is the $\text{C}_2\text{O}_4^{2-}$ ligand bridging two slightly distorted tetrahedrally coordinated Ni^{II} atoms. The $\text{Ni}\cdots\text{Ni}$ separation of $5.2311(3)\text{ \AA}$ in $1\cdot 4\text{C}_6\text{D}_6$ is consistent with distances found in previously reported dinuclear complexes containing oxalate bridges. In the oxalate dianion, the length of the C–C bond ($1.527(3)\text{ \AA}$) is in the range of the values usually observed for coordinated $\text{C}_2\text{O}_4^{2-}$, and the C–O bond lengths of $1.2553(16)\text{ \AA}$ and $1.2534(16)\text{ \AA}$ are typical, too.²⁶ As other tetrahedrally coordinated β -diketiminato nickel(II) complexes exhibiting high-spin nickel centres²⁷ the ^1H NMR



Scheme 3 TBAO = bis(tetrabutylammonium) oxalate.

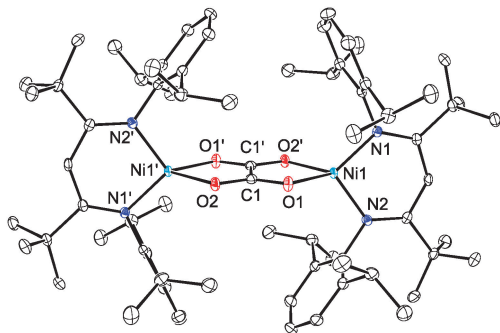


Fig. 1 Molecular structure of $1 \cdot 4\text{C}_6\text{D}_6$. Thermal ellipsoids are shown at 50% probability. Four co-crystallised benzene solvent molecules and carbon bound hydrogen atoms are omitted for clarity. The structure features a crystallographic inversion centre in the middle of the oxalate C–C bond.

spectrum of **1** dissolved in benzene- d_6 shows one set of signals corresponding to the protons of the β -diketiminato over a range of ± 150 ppm (see ESI,† Fig. S7). At r.t. in solution **1** exhibits a magnetic moment of $\mu_{\text{eff}} = 3.96 \mu_{\text{B}}$ (Evans' method,²⁸ thf- d_8), which is consistent with the expectations for two high spin Ni^{II} ions (two uncoupled spins of $S_1 = S_2 = 1$, $\mu_{\text{s.o.}} = 4 \mu_{\text{B}}$). Antiferromagnetic coupling should become visible only at low temperatures.²⁶ The IR spectrum of **1** shows a broad intense absorption band centred at 1650 cm^{-1} representing the oxalate dianion vibration. Also, the dinickel(II) oxalate complex, **1**, can be reduced by potassium graphite in the presence of dinitrogen regenerating the dinickel(I) precursor complex, **IV** (Scheme 3).

Again, in order to get some ideas on mechanistic possibilities orienting DFT calculations were performed (see ESI†). Surprisingly, an initial step consisting of the replacement of the N_2 ligand in **IV** by CO_2 with formation of a $[\text{L}^{\text{tBu}}\text{Ni}(\text{CO}_2)\text{NiL}^{\text{tBu}}]$ compound or the reaction with two CO_2 molecules to give $[\text{L}^{\text{tBu}}\text{Ni}(\text{CO}_2)_2]$ was found to be endothermic on all reasonable potential energy surfaces, so that the initiation of the reaction appears to be more complicated than should be expected. The overall reaction between **IV** and two CO_2 molecules to give **1** was found to be highly exothermic though ($-179.6 \text{ kJ mol}^{-1}$).

In conclusion, reaction of the dinuclear Ni^{I} complex $\text{K}_2[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{N}_2^{2-})\text{NiL}^{\text{tBu}}]$, **I**, with CO_2 results in the formation of the CO or CO_3^{2-} containing complexes **II** and **III**, respectively, whereas the dinickel(I) compound $[\text{L}^{\text{tBu}}\text{Ni}^{\text{I}}(\text{N}_2)\text{NiL}^{\text{tBu}}]$, **IV**, mediates the reductive coupling of CO_2 to give a nickel(II) oxalate complex **1**. In both cases reduction of the carbonate and oxalate products, respectively, with KC_8 in a dinitrogen atmosphere yielded back the corresponding starting materials, so that the synthetic cycles could be closed. While some nickel complexes mediating reductive cleavage of CO_2 exist in the literature,^{12,14,29} examples that are able to reductively couple CO_2 to generate $\text{C}_2\text{O}_4^{2-}$ are rather rare. These observations motivate continued studies on the activation of CO_2 by Ni^{I} compounds.

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- 21 Yields given here represent the average of at least 3 independent runs of an experiment.
- 22 In order to test the viability of an intermediate occurrence of the nickel(0) carbonyl complex $\text{K}_2[\text{L}^{\text{tBu}}\text{NiCO}]_2$, it was treated with CO_2 , and again **II** and **III** were obtained besides other intractable products. In contrast, $[\text{L}^{\text{tBu}}\text{NiCO}]$, **II**, does not react with CO_2 over a period of 18 h, and it thus represents the dead end of CO_2 activation.
- 23 $\text{K}_6[\text{L}^{\text{tBu}}\text{NiCO}_3]_6$, **III**, was detected as a byproduct accounting for the missing O^{2-} ion delivered from CO_2 reduction. We assume that the formation of **III** resulted from residual impurities of potassium bromide originating from the synthesis of the starting complex **IV**. Beyond that O^{2-} or CO_3^{2-} containing products could not be isolated.
- 24 X-ray diffraction analysis revealed a solid solution of **1** and $[\text{L}^{\text{tBu}}\text{NiBr}]$, **V** (unconsumed starting material from the synthesis of **IV**).
- 25 It is difficult to determine the relative yields of **II**, **III** and **1** within the crude product as there is no common spectroscopic tool for their detection and comparison at the same time. Small amounts of other unidentified products are formed, too.
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