Selective Transformation of Nickel-Bound Formate to CO or C–C Coupling Products Triggered by Deprotonation and Steered by Alkali-Metal Ions

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Abstract: The complexes [L\textsubscript{6}\textsuperscript{2}\textit{Ni}(OCO-\textsubscript{2}\textit{O}C)\textit{M}\textsubscript{2}[\textit{N}(\textit{SiMe\textsubscript{3}})\textsubscript{3}]]\textsubscript{2} (\textit{M} = \textit{Li}, \textit{Na}, \textit{K}), synthesized by deprotonation of a nickel formate complex [L\textsubscript{6}\textsuperscript{2}\textit{Ni}OOCH\textsubscript{2}] with the corresponding anides \textit{M}[\textit{N}(\textit{SiMe\textsubscript{3}})\textsubscript{3}], feature a Ni\textsuperscript{2+}–CO\textsubscript{2}\textsuperscript{2−} core surrounded by Lewis-acidic cations (\textit{M}\textsuperscript{+}) and the influence of the latter on the behavior and reactivity was studied. The results point to a decrease of CO\textsubscript{2} activation within the series Li, Na, and K, which is also reflected in the reactivity with Me\textsubscript{3}SiOTf leading to the liberation of CO and formation of a Ni–OSiMe\textsubscript{3}\textsuperscript{2−} complex. Furthermore, in case of K\textsuperscript{+}, the \{\textit{K}[\textit{N}(\textit{SiMe\textsubscript{3}})\textsubscript{3}]\}\textsuperscript{+} shell around the Ni–CO\textsubscript{2}\textsuperscript{2−} entity was shown to have a large impact on its stabilization and behavior. If the number of \textit{K}[\textit{N}(\textit{SiMe\textsubscript{3}})\textsubscript{3}] equivalents used in the reaction with [L\textsubscript{6}\textsuperscript{2}\textit{Ni}OOCH\textsubscript{2}] is decreased from 3 to 0.5, the deprotonated part of the precursor enters a complex reaction sequence with formation of [L\textsubscript{6}\textsuperscript{2}\textit{Ni}(\textit{M}-OOCH)\textit{Ni}[L\textsubscript{6}\textsuperscript{2}\textit{K} and [L\textsubscript{6}\textsuperscript{2}\textit{Ni}(\textit{C}_\textsubscript{2}\textit{O}_\textsubscript{4})\textit{Ni}[L\textsubscript{6}\textsuperscript{2}]. The same reaction at higher concentrations additionally led to the formation of a unique hexanuclear Ni\textsuperscript{II} complex containing both oxalate and mesoxalate (\{\textit{O}_\textsubscript{2}C-CO\textsubscript{2}-CO\textsubscript{2}\}\textsuperscript{4+}) ligands.

Introduction

Producing chemicals and fuels from ubiquitous CO\textsubscript{2} is a central challenge aiming at changeover towards a sustainable resource.

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Results and Discussion

Our studies started with gathering insights concerning the behavior of complex I in contact with electrophiles. I had proven to react with CO to yield [L\textsubscript{6}Ni\textsuperscript{II}−CO], III, and CO\textsubscript{2}−,\textsuperscript{[13]} Contact with a mild acid led to [L\textsubscript{6}Ni\textsuperscript{II}−CO] (amongst others), thus resembling to some extent the conversion of CO\textsubscript{2}− to CO in NiFe-CODH,\textsuperscript{[8]} however, the stoichiometry and redox chemistry in this transformation had remained unclear. Consequently, the first goal was to achieve a cleaner conversion of CO\textsubscript{2}− to CO. To accomplish this we explored, whether—instead of providing protons in the form of acids, which partially also lead to protonation of the basic [L\textsubscript{6}−] ligand—silylium ions can be used as proton analogues in this conversion, i.e., we studied the silylation of the CO\textsubscript{2}− ligand in I.

Silylation of Ni−CO\textsubscript{2}−—Liberation of CO

Reaction of I with three equivalents of TMS-OTf (Scheme 1) instantly led to [L\textsubscript{6}NiOSiMe\textsubscript{3}] (I), which was isolated as a microcrystalline green solid in 99% yield. A single crystal X-ray analysis revealed, that the silylo ligand and the [L\textsubscript{6}−] co-ligand form a Y-shaped coordination sphere for the Ni center of I (Figure 1).

Concomitant liberation of CO has been verified (qualitatively) via GC-MS (21% yield from headspace). Surprisingly, unlike in case of the reactions of [L\textsubscript{6}Ni(OCO-κ\textsuperscript{2}O,C)][Li\textsubscript{2}Ni(SiMe\textsubscript{3})\textsubscript{3}], I, with H\textsuperscript{+} (or CO\textsubscript{2}),\textsuperscript{[14]} formation of [L\textsubscript{6}Ni\textsuperscript{II}−CO], III, was not observed to occur, although TMS-OTf likewise is an electrophilic reagent, that should react similarly. It thus may be inferred that III is formed in a secondary process, for example, through the reaction of unconsumed I with CO in the systems I/H\textsuperscript{+} or I/CO\textsubscript{2}, which is suppressed in case of TMS-OTf, as the latter reacts with I at sufficiently high rate (Scheme 2). Indeed, we were able to show that I reacts with CO to give III (ν\textsubscript{CO} = 2014 cm\textsuperscript{-1}, see S6). It is thus reasonable to assume that the principal reaction of I with electrophiles E\textsuperscript{+} consists of the formation of Ni-OE units with simultaneous generation of CO (Scheme 2).

Liberation of CO from Ni centers after reduction of CO\textsubscript{2} has been discussed quite controversially in the last years, especially with regards to the functioning of the Ni,Fe-CODH. It is still not clear, in which step of the mechanism CO is released and what the oxidation state of the Ni center is then. Scheme 3 shows two possible mechanisms, where mechanism E1 (Scheme 3, left) involves release of CO from a Ni\textsuperscript{II} state with subsequent reduction of Ni before CO\textsubscript{2} enters again and mechanism E2 (Scheme 3, right) first involves reduction to a Ni\textsuperscript{II}−CO state, followed by substitution of CO by CO\textsubscript{2}.

In recent model studies with Ni-PNP-pincer complexes it was found that subsequent to CO\textsubscript{2} reduction at a Ni\textsuperscript{II} center protonation of the resulting Ni\textsuperscript{II}−CO\textsubscript{2}− complexes led to Ni\textsuperscript{II}−CO complexes and only after consecutive reduction to Ni\textsuperscript{II} and addition of CO\textsubscript{2}, CO was released (Scheme 3, middle right circle).\textsuperscript{[21,22]} Recent DFT studies on the enzyme also support a mechanism where CO liberation takes place only when CO\textsubscript{2} enters the cycle (Scheme 3, E2), however, in this study Ni remained in the +1 oxidation state (not Ni\textsuperscript{II}) upon reduction and CO was generated from this Ni\textsuperscript{II}−CO state.\textsuperscript{[26]} Our findings contrast the abovementioned model studies in that CO is released directly from the Ni\textsuperscript{II} complex (Scheme 3, middle left) and thus supports the notion that in the NiFe-CODH reduction takes place after CO elimination or simultaneously. This matches the results of an X-ray diffraction analysis performed for crystals of the reduced active state of CODH grown in the absence of CO, which led to a structure that was suggested as an appropriate model for this state.\textsuperscript{[27]} Obviously, the ligand environment plays a crucial role in these transformations.

Bearing in mind that not many Ni\textsuperscript{II}−CO complexes are known to date,\textsuperscript{[20,26–29]} due to the limited ability of Ni\textsuperscript{II} to stabilize such entities via backbonding, we next tested whether a Ni\textsuperscript{II}−CO complex with the L\textsubscript{6}−ligand system would be stable at all and reacted the cationic complex

\begin{align*}
1) [L\textsubscript{6}Ni(OCO)]^+ &\rightarrow [L\textsubscript{6}Ni-OE]^{(\text{ex})} + CO \\
2) [L\textsubscript{6}Ni(OCO)] &+ CO \rightarrow [L\textsubscript{6}Ni(CO)] + CO_2 + \text{e}^-
\end{align*}

\[\text{E}^{\text{ex}} = \text{Me}_3\text{Si}^+, \text{H}^+, \text{CO}_2\]

\textbf{Scheme 2}. 1) Formation of CO in the reaction of [L\textsubscript{6}Ni(OCO)]\textsuperscript{+} with electrophiles (E\textsuperscript{+}). 2) Reaction of [L\textsubscript{6}Ni(OCO)]\textsuperscript{+} with in situ liberated CO.
The reaction between Ni and CO is initially observed to be stable, with CO binding to the Ni center to form a complex that can be derived from $\text{Ni}^2+\text{CO}$, as shown in Scheme 3. This complex is isolated and characterized by spectroscopic methods, including NMR spectroscopy and mass spectrometry. The CO ligand is readily replaced by other electrophiles, such as $\text{H}^+$, $\text{Me}_3\text{Si}^+$, and $\text{Li}^+$, indicating the coordination is flexible.

The activation of CO is influenced by the nature of the Lewis acidic centers. Using $\text{B}(\text{ArF})_3$ as a Lewis acid, the reaction is performed, which reveals a structure similar to the one of NiI$^2+\text{CO}$, indicating that CO can be easily replaced by other electrophiles. The reaction with electrophiles leads to the direct formation of CO, which is of interest also considering that the CO$_2^-$ ligand in I is derived from formate. Liberation of CO from HOOCH is known to occur in reactions with strong acids, however, there are only rather few examples, where formate coordinated to early transition metals (Ti, $\text{Ti}^{IV}$, and $\text{W}^{VI}$) releases CO upon deprotonation.

**Influence of Lewis Acids on CO$_2^-$ Activation**

Having learned that I readily generates CO in contact with electrophiles, the role of the Li$_3$ shell surrounding the CO$_2^-$ ligand in this conversion was explored. Initial in situ $^1$H NMR spectroscopic studies had indicated that the synthesis of $\text{L}^{\text{Ni}}\text{Ni}^2+\text{OCO}^-\text{C}_\text{O}$ could be possible as well as with $\text{M}^-\text{Na}^+$ or $\text{K}^+$, however, no structural information had been available then. We were now able to access the Na$^+$ derivative and crystallize it so that a single-crystal X-ray analysis could be performed, which revealed a structure that is similar to the one of I (Figure 3), but also shows some differences. The Ni–C bond lengths in I and 4 are almost identical (1.786(4) Å vs. 1.791(2) Å), but variations can be found for the different C–O bonds. While in 4 the bond of the C atom to the distal O atom is quite short (1.216(2) Å), the one to the coordinated O atom is long (1.298(3) Å), for I it converges (1.234(5) Å; 1.275(5) Å). The COC angles appear similar (127.3(2)° for 4; 128.0(4)° for I).

It thus emerges that the nature of Lewis acidic centers around the CO$_2^-$ unit influences its character and it was interesting to investigate how this reflects the spectroscopic properties. Hence, first of all the $^1$H NMR chemical shifts ($\delta^1$) were compared for the Li$_3$, Na$_3$, as well as the K$_3$ variants. A δ$^1$C of 177.6 ppm was determined for the CO$_2^-$.
The authors pointed out the importance of $\text{Li}^+$ ions in the reaction process, which shifted to 173.2 ppm upon replacement of the $\text{Li}^+$ ions by $\text{Na}^+$ ions, that is, in 4. A further shift to 169.5 ppm is observed for the $\text{K}^+$-adduct. As expected, an inverse trend was found for the $v_{\text{CO}}$ bands in the IR spectrum of the complexes, with frequencies of 1616 cm$^{-1}$ for $\text{Li}^+$, 1634 cm$^{-1}$ for $\text{Na}^+$, and 1637 cm$^{-1}$ for the $\text{K}^+$ adduct (1568, 1594 and 1594 cm$^{-1}$ for the $^{13}$C labelled derivatives). From these data it may be inferred that the activation of $\text{CO}_2$ is strongest in I, which is reasonable as the $\text{Li}^+$ ions are small and hard acids interacting strongly with the O atoms, while $\text{Na}^+$ and $\text{K}^+$ are softer and thus pull electron density to a smaller extent. Furthermore, in 4 the $\text{CO}_2$ appears to be somewhat more activated than in [L$^{\text{ds}}$$\text{Ni(OCO-)}_2$$\text{O}_2$$\text{C}$]$_2$Ni[N(SiMe$_3$)$_2$]$_2$, but the difference is not as pronounced as for the transition from I to 4.

This raised the question in how far the differences in activation translate into the reactivity of the Ni$\text{CO}_2$$_2$ moieties and thus also the $\text{Na}^-$ and $\text{K}^-$ derivatives were reacted with three equivalents of TMS-OTf. Again, 1 was formed in both cases as verified by means of $^1$H NMR. However, an ATR-IR spectrum of the solid crude product isolated after the K$^+$-adduct revealed that, unlike in cases of the $\text{Li}^+$ and $\text{Na}^+$ derivatives, additionally [L$^{\text{ds}}$$\text{Ni(CO)}_2$$_2$]$_2$ had been formed. This implicates a slower conversion in the case of K$^+$ counterions, leaving enough time for the secondary process 2 as depicted in Scheme 2, that leads to III. While this fits to the expectations, the difference between the $\text{Na}^-$ and $\text{K}^-$ derivatives in the grade of $\text{CO}_2$ activation according to IR spectroscopy is not so large, that it should lead to such a sharp contrast in reactivity. Hence, steric factors had to be considered as an origin and for this purpose the structure of [L$^{\text{ds}}$$\text{Ni(OCO-)}_2$$\text{C}$]$_2$Ni[N(SiMe$_3$)$_2$]$_2$ was calculated by DFT, using the structure of 4 as a basis for an optimization after replacement of all $\text{Na}^-$ ions by K$^+$ ions. Comparing the resulting structure to those of I and 4 a structural transformation becomes obvious that is most pronounced in the transition from $\text{Na}^-$ to K$^+$ (Figure 3 middle). The trend can be well illustrated, comparing the angles between the planes spanned by the (N)$_2$$\text{Ni(CO)}_2$$_2$ core and the plane defined by the three alkali metal cations, respectively. The small $\text{Li}^+$ ions integrate themselves almost perfectly into the (N)$_2$$\text{Ni(CO)}_2$$_2$ plane (3.0° deviation) and in fact even the amide $\text{N}$ atoms almost lie in the same plane, too (N to plane distances 0.35 Å and 0.08 Å). For $\text{Na}^+$, the twist angle between the two planes rises to 8.2°, and now the $\text{N}$ atoms deviate from the main plane by 1.10 Å and 0.28 Å. Finally, in case of the large K$^+$ ions the distortion becomes dramatic and the twist angle increases to 43.3°. This can clearly be seen in Figure 3, where it also becomes obvious, that in such a structure the $\text{CO}_2$$_2$ unit is shielded more strongly by the SiMe$_3$ groups of the [N(SiMe$_3$)$_2$]$_2$ ligands than in case of the two other derivatives, thus explaining the comparatively low reactivity.

As discussed, the contact with a Lewis acidic center can prepare a $\text{CO}_2$$_2$ ligand, formed via $\text{CO}_2$ activation at a reduced transition metal moiety, for the elimination of CO (Scheme 4). However, a $\text{M}^-$-$\text{CO}_2$$_2$ moiety generated by formate deprotonation has a further option if M is redox active: an intramolecular single electron transfer leading to $\text{CO}_2$$_2$-derived products and it seems likely that this process will also be influenced by LAs. While there is no report on a system where both pathways were accessible so far, notably, this is the case in the system described here, controlled by the
incorporated Lewis acidic center, as will be outlined in the next paragraph.

**Deprotonation with K[N(SiMe<sub>3</sub>)]—Nickel Formate to Oxalate**

Having shown that the nature of M<sup>+</sup> influences the degree of activation, we hypothesized that the number of ions M<sup>+</sup> will have an effect as well and started an investigation employing less than three equivalents of [M[N(SiMe<sub>3</sub>)]]. For M = Li<sup>+</sup> or Na<sup>+</sup> this led to incomplete conversions to the corresponding CO<sub>2</sub> adducts 1 and 4 only. While, as described above, it is possible to also generate the K<sub>2</sub>-analogue of 1 and 4, namely by slow addition of [L<sup>3</sup=Ni(OOCCH)]<sub>2</sub>, the deprotonation of II with just one equivalent of K[N(SiMe<sub>3</sub>)] in CD<sub>3</sub>C<sub>2</sub>H<sub>5</sub> leads to a mixture of paramagnetic and diamagnetic products, according to a <sup>1</sup>H NMR spectrum recorded subsequently. In order to accomplish a more uniform reaction, deprotonation was carried out then with only 0.5 equivalents of K[N(SiMe<sub>3</sub>)] in CD<sub>3</sub>C<sub>2</sub>H<sub>5</sub> which proved sufficient to convert all [L<sup>3</sup=Ni(OOCCH)]<sub>2</sub>, II, employed, as evidenced by the complete disappearance of all of its signals in the <sup>1</sup>H NMR spectrum. The latter revealed the concomitant formation of minor amounts of 1, as well as the signal sets for two paramagnetic complexes that formed as the main products. One of those was identified as the known Ni oxalate complex [L<sup>3</sup>Ni(C<sub>2</sub>H<sub>5</sub>O)Ni(L<sup>3</sup>Ni)]. IV<sup>[22]</sup> The second species shows paramagnetically broadened signals in the <sup>1</sup>H NMR spectrum, commonly observed for Ni<sup>III</sup> compounds and the presence of Ni<sup>II</sup> was indeed confirmed by EPR spectroscopy, showing a rhombic signal (best simulated for a 1:1 ratio of two very similar species, Figure 4, left). Hence, under these conditions deprotonation obviously triggers an electron transfer from the CO<sub>2</sub><sup>−</sup> ligand (generated by deprotonation of half of the [L<sup>3</sup>Ni(OOCCH)]<sub>2</sub>, present) to a Ni<sup>III</sup> center (which presumably belongs to the second equivalent of II, considering that all II is consumed). This would lead to a Ni<sup>II</sup> species and formally a CO<sub>3</sub><sup>2−</sup> radical anion that likely represents the origin of the oxalate found in the second product IV. The electron transfer mentioned could either occur directly from a Ni<sup>II</sup>CO<sub>3</sub><sup>2−</sup> unit, or, subsequent to an initial intramolecular electron transfer, from a Ni<sup>II</sup>CO<sub>3</sub><sup>2−</sup> unit. Two equivalents of the Ni<sup>II</sup>CO<sub>3</sub><sup>2−</sup> entities thus generated can then dimerize to give IV, leaving formally behind two equivalents of K[L<sup>3</sup>Ni(OOCCH)], the fate of which is investigated in the following.

**Electron Transfer—Nickel(I) Formate**

To simulate this situation, II, was reacted with KC<sub>6</sub>, which led to the formation of a vibrant red solution. Its <sup>1</sup>H NMR spectrum exhibited a set of paramagnetically broadened signals, which indeed matched the ones observed beside the signal set of IV after the reaction with K[N(SiMe<sub>3</sub>)]. Moreover, in the EPR spectrum a rhombic signal appeared, which was very similar to one observed before (Figure 4, right). After filtration and evaporation of the volatiles [L<sup>3</sup>Ni(OOCCH)]Ni[L<sup>3</sup>Ni]K (5) could be isolated as a vibrant red solid in 53% yield. X-ray analysis of single crystals revealed a structure where two L<sup>3</sup>Ni<sup>III</sup> moieties are bridged by a formate ligand and a K<sup>+</sup> ion (Figure 5). Thus, the decrease of the oxidation state from +1 to +2 has led to a change of the binding mode of the formate ligand from π to π and thus to a change of the coordination sphere from square planar to tetrahedral.

*Figure 4. X-band EPR spectrum (26 K, 9.39 GHz) of the reaction mixture resulting from the reaction between II and 0.5 equivalents K[N(SiMe<sub>3</sub>)] in CD<sub>3</sub>C<sub>2</sub>H<sub>5</sub> (black) and powder simulation for g = 2.47, 2.14, 2.07 and g = 2.48, 2.13, 2.08 (red). Right. EPR spectrum (26 K, 9.46 GHz) of 5 in CD<sub>3</sub>C<sub>2</sub>H<sub>5</sub> (black) and powder simulation for g = 2.47, 2.11, 2.09 and g = 2.46, 2.11, 2.06 (red).*

*Figure 5. Molecular structure of 5.[23] H atoms and Et<sub>2</sub>O molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-N1 1.861(2), Ni1-N2 1.886(2), Ni2-N5 1.866(2), Ni2-N4 1.896(2), Ni1-O2 1.894(3), Ni2-O1 1.905(3), C1-H1 1.03(3), K-O1 2.672(4), K-O2 2.588(2), C1-O1 1.245(5), C1-O2 1.237(6), O1-C1-O2 121.4(4), O1-C1-O2 121.4(4), Ni1-C1-Ni2 169.6(2).*
trigonal planar, which is plausible. The ATR-IR spectrum of pure 5 exhibits an asymmetric CO\(_2\) stretching vibration at 1565 cm\(^{-1}\) (Figure 6c), which shifts to 1525 cm\(^{-1}\) when the \(^{13}\)C labelled formate precursor is utilized. This absorption band can also be found in the ATR-IR spectrum of the product mixture isolated after the reaction between \([L^{6}\text{NiOOCH}]\) with 0.5 equiv. of KHMD\(_3\) in \(\text{C}_6\text{D}_6\) (Figure 6a) beside the characteristic CO stretching vibration of \([L^{6}\text{Ni}-(\text{C}_2\text{O}_4)\text{NiL}^{\text{Hd}}]\), IV (Figure 6b). Altogether the findings lead to a stoichiometry as shown in Scheme 5 for the reaction of II with 0.5 equiv of K[N(SiMe\(_3\))]\(_2\)].

Reaction of \([L^{6}\text{Ni}(\mu-\text{OOCH})\text{NiL}^{\text{Hd}}]\)K, 5, with one equivalent of K[N(SiMe\(_3\))]\(_2\)] in \(\text{C}_6\text{D}_6\) does not lead to a significant decrease of the signals of 5 in the \(^1\text{H}\) NMR spectrum. Accordingly, the \(^1\text{H}\) coordinate as in II appears to be a prerequisite for formate deprotonation. With this knowledge the reaction of II with more than half an equivalent of K[N(SiMe\(_3\))]\(_2\)] was revisited. Small amounts of K[N(SiMe\(_3\))]\(_2\)] were added stepwise to a solution of \(^{13}\)C-labelled II and the proceedings monitored by means of \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy (see S22). As outlined above, addition of 0.5 equiv. of K[N(SiMe\(_3\))]\(_2\)] led to the vanishing of all characteristic signals of II, while the signals for oxalate complex IV and Ni\(^{II}\) formate 5 reached a maximum intensity. Adding more K[N(SiMe\(_3\))]\(_2\)] led to the decrease of the signals of complex IV and the evolution of a new signal set that could be assigned to \([L^{6}\text{Ni}-(\text{N}(\text{SiMe}\(_3\)})_2]\) (6, see S7), until one equivalent of K[N(SiMe\(_3\))]\(_2\)] had been added in total. Accordingly, K[N(SiMe\(_3\))]\(_2\)] preferably deprotonates II, forming IV and 5, however, after completion of this conversion, K[N-(SiMe\(_3\))]\(_2\)] displaces the oxalate ligand, with concomitant precipitation of K\(_2\text{C}_2\text{O}_4\). The formation of I as a minor side product can also be observed and may be rationalized by a minor side reaction of in situ generated 6 with traces of CO\(_2\) (see S8).

**Intermediate of Oxalate Formation**

The formation of IV from complex II is remarkable, as the direct transformation of formate to oxalate so far has only been achieved via thermal decomposition, calcination or at elevated temperatures and high pressures from bulk CO\(_2\)\(^{\text{aq}}\) (via formate intermediates) but is unknown in coordination chemistry.\(^{[40–45]}\) There are only a few examples for oxalate formation directly from CO\(_2\)\(^{\text{aq}}\) and one precedent case, where the reaction of formate derived CO\(_2\)\(^{\text{aq}}\) with CO\(_2\) led to oxalate.\(^{[19]}\)

Thus, having clarified the stoichiometry of the reaction between \([L^{6}\text{NiOOCH}]\), II, and K[N(SiMe\(_3\))]\(_2\)]\(_2\), the mechanism of oxalate formation shifted into our focus. As discussed at the end of the last but one section a conceivable intermediate is, for instance, \([L^{6}\text{Ni}^{2+}(\text{OCO})^2\text{K, A}]\) namely the product of an intramolecular electron transfer within \([L^{6}\text{Ni}^{2+}(\text{CO})_2^2\text{K}\)] (see Figure 7). This does not occur within \([L^{6}\text{Ni}(\text{OCO}-\text{x}^\text{O},\text{C})]\)K[N(SiMe\(_3\))]\(_2\)], as there is no further K\(^+\)...

**Scheme 5.** Reaction scheme for the deprotonation of L\(^{6}\)NiOOCH with 0.5 equivalents of K[N(SiMe\(_3\))]\(_2\)].
Research Articles

Nickel Mesoxalate

In order to quantify the formation of the oxalate complex, crystallization attempts from benzene and hexane were conducted. In case of benzene (ca. 0.03 M) this gave solely purple crystals of the oxalate complex \([L^{\text{dis}}\text{Ni}\{\text{C}_2\text{O}_4\}]\text{Ni}L^{\text{dis}}\) (IV, 12% absolute yield, 48% relative yield). However, when working at high concentrations (ca. 0.15 M), from hexane solutions repeatedly and reproducibly also small orange crystals grew, that is, a further product was generated at high concentrations. Extraction with Et\(_2\)O and subsequent crystallization led to the enrichment of the orange crystals (see S10) and single-crystal X-ray crystallographic analysis revealed the structure of the unique multinuclear complex \([\{L^{\text{dis}}\text{Ni}\}_2(\text{C}_2\text{O}_4)_2(\text{C}_2\text{O}_4)_6\}\text{K}_6\) (9, Figure 8). The quality of the crystals did not allow an anisotropic refinement of all atoms during the solution of the structure, and hence the latter does not permit a discussion of metric parameters, but the molecular structure determined and the constitution are without doubt. 9, which was formed in up to 9% yield based on formate (6% based on \(L^{\text{dis}}\text{Ni}\)), contains, as IV, oxalate ligands, but also ligands with the configuration \(\text{C}_2\text{O}_4\)\(^{2-}\). Accordingly, three formate-derived CO\(_2\) units have been coupled, which to our knowledge has never been reported so far. However, while the formation of oxalate (\(\text{C}_2\text{O}_4\)\(^{2-}\)) from two CO\(_2\)\(^{2-}\) species (vide supra) is straightforward, a threefold coupling would give the unknown radical \(\text{C}_2\text{O}_4\)\(^{2-}\). Therefore, in a more realistic scenario two CO\(_2\)\(^{2-}\) equivalents and one CO\(_2\)\(^{2-}\) entity are combined yielding in the fourfold deprotonated form of dihydroxymalonic acid (\(\text{C}_3\text{O}_6\)\(^{3-}\)), which indeed is known as the hydrate of mesoxalic acid and represents as table compound; for its formation routes via reaction of oxalate with CO\(_2\)\(^{2-}\) or of a \(\text{C}_2\text{O}_4\)\(^{2-}\) intermediate with CO\(_2\)\(^{2-}\) are conceivable. 9 then contains two quadruply charged mesoxalate and two doubly negatively charged oxalate anions as well as six \([L^{\text{dis}}]^{-}\)ligands. This leads to 18 negative charges which are compensated by six K\(^+\) ions and six Ni\(^{II}\) ions, partly with tetrahedral and partly with square planar coordination.

![Figure 7](image1)

**Figure 7.** Left. Possible intermediate A leading to oxalate formation. Right. DFT-optimized structure for A. H atoms are omitted for clarity.

![Figure 8](image2)

**Figure 8.** Left: Molecular structure of \(9\cdot2\text{Et}_2\text{O}\)\(^{[58]}\). Atoms that could not be refined as ellipsoids are depicted as balls. Middle. Formate and CO\(_2\) and C–C coupling products. Right: Ball and Stick structure of the core of \(9\cdot2\text{Et}_2\text{O}\). H atoms, Et\(_2\)O molecules and \([L^{\text{dis}}]^{-}\) C atoms are omitted for clarity.
spheres, which is reasonable (note that the oxalate complex IV has tetrahedrally coordinated Ni centers, while II features a square planar coordination).

Separation of 9 from residual IV proved possible by extraction with MeCN that dissolves 9 to give a clear orange solution, from which an orange solid was isolated. However, storage of such solutions for crystallization leads to the precipitation of a white solid, indicating a certain instability of IV in MeCN. Thus, all analytical methods had to be applied within a short period of time after contact with MeCN.

The ATR-IR spectrum of 9 shows bands at 1666, 1617, 1391, 1312, 1255, and 1157 cm$^{-1}$ originating from the units.

Initiation of the CO coupling of three CO from the reaction of 2-hydroxy-2,3-dihydroxymalonic acid disodium salt with Ni(II) as a Ni complex is to our knowledge the first experimental example of a Ni formate complex, which explains why species at ametal-Pd d), with a coordinated diketone-derived enolate (an oxalate ester is 58.5 Hz). This consolidates the formation of meso-mesoxalate could be detected (the commercially available dihydroxymalonic acid disodium salt resonates at 171 and 91 ppm in D$_2$O), not even after $^{13}$C-labelling. This is not surprising as also the corresponding $^{13}$C NMR signal of the oxalate ligand in IV eluded detection due to its connection with the paramagnetic Ni$^{II}$ centers. However, trying to study the in situ formation of 9 through deprotonation of $^{13}$C in hexane-d$_6$, or C$_6$D$_6$, or D$_2$O, in an NMR tube scaled with a J. Young valve, after 4 days a characteristic set of signals at 177.7 ppm (dd, $^1$I$_{CC}$ = 57.8 Hz) and 103.9 ppm (t, $^1$I$_{CC}$ = 57.8 Hz) could be detected (see S10; compare; $^1$I$_{CC}$ of 1,2- and 1,3-C oxalic acid diethyl ester is 58.5 Hz). This consolidates the formation of mesoxalate, and its detection by $^{13}$C NMR spectroscopy in this experiment likely became possible, as 9 is not stable in solution over four days, so that the ligands get detached from the paramagnetic Ni centers.

Mesoxalate is found rather rarely in coordination chemistry. There are reports of Pd and Cu complexes with mesoxalate ligands, generated through decomposition (after heating/time) of D-erythulose (C$_5$H$_9$O$_5$; Pd) or D-glucuronate (C$_7$H$_9$O$_6$; Cu). Although it does not concern mesoxalate directly, a publication by Meyer and co-workers is noteworthy in this context, too, as it describes the reaction of CO$_2$ with a coordinated diketone-derived enolate (an oxalate equivalent) and based on this finding they envisioned that the coupling of three CO$_2$ building blocks should be possible. The formation of 9, which involves the reduced CO$_2$ species CO$_2^{-}$+ as to our knowledge the first experimental example of a direct threefold coupling of CO$_2$ entities, illustrating the feasibility of such transformations. This may even be relevant to the prebiotic synthesis of organic compounds and motivates further attempts to synthesize multi-carbon compounds directly from formate or CO$_2$.

Conclusion

In summary, we have shown that in complexes of the type [(L,C$_4$Ni(OCO,2,C)O)]M$_2$[N(SiMe$_3$)$_3$]$_2$ (M = Li, Na, K) formed via deprotonation of the formate complex with corresponding metal amides, the CO$_2^{-}$ ligand is prepared for facile CO elimination, which is triggered by a contact with electrophiles and influenced by the nature of the Lewis acidic alkali metal cations. Investigating the formate deprotonation with 0.5 equivalents of K[N(SiMe$_3$)$_3$] we could demonstrate for the first time the oxidative coupling of formate on defined Ni sites. This yields not only in 0.25 equivalents of oxalate, but also in 0.5 reducing equivalents, leading to the formation of a dinuclear Ni$^{III}$ formate complex, which explains why stoichoimetric amounts of K[N(SiMe$_3$)$_3$] proved sufficient to consume all formate precursor. A simple deprotonation reaction thus induces Ni reduction and the formation of a C–C coupling product.

Alltogether, formate deprotonation can give rise to reduced CO$_2$ species, just as the direct reduction of CO$_2$ does, and can thus lead to the same products (CO, oxalate). However, the simplicity of a deprotonation reaction with solid precursors (instead of using gaseous CO$_2$) and the easy variation of counter ions makes this route very convenient for systematic analysis of reduced CO$_2$ species. Additionally, we were able to show that the same deprotonation reaction conducted at higher concentrations can even lead to mesoxalate, formed in an unprecedented, direct threefold coupling of reduced CO$_2$ units.

Hence, in summary, the combination of a Ni formate with an amide base that deprotonates and at the same time introduces Lewis acidic centers generates a versatile system that bears a lot of potential, aiming at the further utilization of formate or CO$_2$ to generate more complex organic molecules. Both can be employed to generate a CO$_2^{-}$ species at a metal center and the interaction with a LA can decide upon the proceedings. If they are strong the entity is stabilized but activated for CO elimination in contact with an electrophile, if it is weak, the positioning of the electrons can be shifted towards the metal (this of course depends on the properties of the metal), which opens up CO$_2^{-}$ chemistry. Here, coupling reactions have been studied but a trapping by other substrates is conceivable. Hence, the development of CO$_2$ reduction catalysts (or such that utilize formate) in this direction requires a fine balancing and (for a given central metal) testing of a variety of LAs.

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Conflict of interest

The authors declare no conflict of interest.

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