Carbon dioxide binding at a Ni/Fe center: synthesis and characterization of Ni(η¹-CO₂-κC) and Ni-μ-CO₂-κC:κ²O₂,O'-Fe†

Changho Yoo and Yunho Lee*

The degree of CO₂ activation can be tuned by incorporating a distinct electronic coordination environment at the nickel center. A mononuclear nickel carboxylate species (Ni-CO₂, 3) and a dinuclear nickel–iron carboxylate species (Ni-CO₂–Fe, 5) were prepared. The structure of 3 reveals a rare η¹-κC binding mode of CO₂, while that of 5 shows bridging CO₂ binding (μ₂-κC:κ²O₂,O') between the nickel and iron, presented as the first example of a nickel-μ-CO₂-iron species. The structural analyses of 3 and 5 based on XRD and DFT data reveal a higher degree of CO₂ activation in 5, imparted by the additional interaction with an iron ion.

Introduction

Activation of carbon dioxide is currently receiving much attention due to its relevance to environmental and energy related issues. In the area of transition metal catalyzed reactions, one of the main challenges is selective reduction of CO₂ to a product such as formate, carbon monoxide, methanol or methane. When the initial metal–oxygen interaction occurs to form a metal CO₂ adduct M-η²-CO₂:κO, subsequent hydride transfer via CO₂ addition to a M-H bond generates a metal-formate species. Alternatively, the metal–carbon bond formation can produce a metallacarboxylate species (M-η¹-CO₂-κC), followed by C-O bond cleavage to generate CO. In the latter case, an additional Lewis acid interaction can stabilize the negative charges at the oxygen atoms of the bound CO₂. Therefore, CO₂ activation with a bimetallic system can be one way to guide the selectivity of the CO₂ catalyst and is receiving much attention. In fact, an excellent example of a bimetallic center utilized in an efficient catalytic conversion of CO₂ can be found in the active site of carbon monoxide dehydrogenase (CODH). According to recent studies, CO₂ coordination at a heterobimetallic nickel–iron active site can be found in CODH’s intermediate species, which possesses a Ni-μ-CO₂-Fe moiety, Scheme 1. Although X-ray analysis provides a structural snapshot of the CO₂ reduction sequence, the role of the unique iron ion is currently not well-understood. Thus, acquiring an understanding of iron assisted CO₂-nickel coordination is of fundamental interest and is crucial for gaining mechanistic insight into this and other enzymatic reactions.

In organonickel chemistry, there are few mononuclear Ni-η¹-CO₂ adducts possessing both M-C and M-O bonds. In 1975, Aresta and co-workers reported the first structurally characterized nickel-CO₂ adduct (PCy₃)₂Ni(η¹-CO₂), Scheme 1. An analogous complex, (dtbpe)Ni(η¹-CO₂) (dtbpe = 1,2-bis(di-tert-butylphosphino)ethane) was recently reported by Hillhouse and co-workers. More recently, our group reported a similar but unique five-coordinate nickel-CO₂ adduct (PM(Me)P)Ni(η²-CO₂) (PM(Me)P = PMe₂P=CF₂=P=CF₂) and (PM(Me)P)Ni(NO₂) (2) and [(PM(Me)P)Ni(η²-CO₂-κ²C₂O)] (4), the first examples of Ni-CO₂ complexes that reveal a Ni-CO₂-κC binding mode, Scheme 2. The carboxylate group in these species is stabilized by a Lewis acid such as a proton, sodium or another nickel ion. Our interest then moved to comparing (PM(Me)P)Ni-
CO$_2$ and (PNP)Ni–CO$_2$ to evaluate their fundamental differences in CO$_2$ activation. The different geometries favored with a PP$_{Mg}P$ or PNP ligand affect the identity of the nickel–CO$_2$ moiety, which can be Ni(ni)–CO$_2$$^2- $ or Ni(ni)–CO$_2$ or an open-shell Ni(i)–CO$_2$$^-$, vidia infra. Furthermore, by isolating the native nickel–CO$_2$ species, we can further study the effect of the second iron ion. Although several nickel carboxylate species are already known, iron has never been introduced synthetically into a Ni–CO$_2$ moiety.

Here, we present a nickel carboxylate species (Na(12-C-4)$_2$) [(PNP)Ni$^{1-}$,CO$_2$–$\kappa^C$] (3), in which the nickel–CO$_2$ moiety does not have any Lewis acid interactions. We also prepared a dinuclear nickel–iron carboxylate species (PNP)Ni–µ-CO$_2$–$\kappa^C$C$_x$–$\kappa^O$–Fe(PNP) (5), reminiscent of the NiFe-binuclear active site of CODH. This is an unprecedented example of a nickel–iron hetero-bimetallic complex possessing a bridging CO$_2$ ligand. The levels of CO$_2$ activation in compounds 3 and 5 are compared with other Ni–CO$_2$ adducts and the Ni–µ-CO$_2$–Fe moiety found in CODH.

**Results and discussion**

**Synthesis and characterization of the Ni$^{1-}$,CO$_2$–$\kappa^C$ complex**

The coordination of a hydroxycarbonyl moiety via a Ni–C bond was previously realized at a divalent nickel center supported by a PNP ligand.$^{18}$ Following deprotonation of (PNP)NiCOOH (1), its anionic congener (PNP)NiCOO$^{\kappa^C}$ (2) was also prepared and recently reported by our group.$^{18}$ The X-ray structure reveals that two molecules of 2 are oriented to form a pair with ionic interactions with two sodium ions in the crystal lattice, Fig. 1.$^{11}$ The corresponding CO$_2$ ligand coordinates to the nickel center in a µ$_x$–x’–µ$_x$–x’ mode with a Ni–C1 bond distance of 1.882(1) Å. There are additional bonds of the CO$_2$ moiety to sodium ions with Na–O bond distances of 2.352(1), 2.217(1) and 2.459(1).$^{11}$ To obtain a sodium-free adduct, 2 equiv. of 12-crown-4 was added to a solution of 2, resulting in the formation of [Na(12-C-4)$_2$][(PNP)Ni$^{1-}$,CO$_2$–$\kappa^C$] (3). The crystal structure of 3 revealed the successful generation of a mononucular nickel adduct possessing an $^{1-}$,CO$_2$–$\kappa^C$ coordinated carbon dioxide species with a Ni–C bond distance of 1.911(2) Å, as shown in Fig. 1 and Table 1. The oxidation state of the nickel ion in 3 can be assigned as 2+ based on its similar structural features to the previously known nickel(ii) species such as (PNP)NiCOOH (1) and [(PNP)Ni$_{12}$,µ$_2$–CO$_2$–$\kappa^C$C$_x$–$\kappa^O$ (4), vidia infra]. The geometry of 3 is square planar ($\tau_4 = 0.12^{11}$) with a similar but slightly elongated Ni–C bond distance in comparison to those of 1 and 4 (d$_{Ni-C} = 1.866(2)$ and 1.888(2) Å, respectively, Table 1). This is probably due to a lower degree of π back-bonding between the nickel and CO$_2$. In fact, π back-donation from the nickel center to a CO$_2$ ligand in such nickel carboxylate species is indicated by shorter Ni–C distances (1.858–1.911 Å) than those of the nickel alkyl species (PNP)NiR (R = Me, Et, "Pr) (1.963–2.004 Å).$^{19}$ The molecular orbitals generated from DFT calculations also show the presence of π back-donation from the Ni d$_{ez}$ to the CO$_2$ π$^*$ orbital (see ESI†). Due to the absence of Lewis acid interactions in 3, a lower π-accepting ability of the CO$_2$ ligand is expected. Its structural data also revealed that the plane of the CO$_2$ ligand is perpendicular to that of the square planar (PNP)Ni moiety. One of the oxygen atoms (d$_{Ni-O2} = 2.614(1)$ Å) is slightly closer to the nickel center than the other (d$_{Ni-O1} = 2.776(1)$ Å), Table 2. These Ni–O distances are much longer than those for other known Ni$^{1-}$,CO$_2$ adducts (1.9–2.2 Å, Table 2), suggesting that neither of the oxygen atoms are bound. The DFT analysis also supports minimal interaction between the nickel and oxygen atoms (Wiberg index = 0.1358 for Ni1–O2 and 0.1679 for Ni1–O1, see Table 2). The two C–O bond distances are nearly identical (d$_{C1-O1} = 1.247(2)$ Å, d$_{C1-O2} = 1.248(2)$ Å, Table 1) and slightly shorter than in the analogous carboxylate complexes 2 and 4 (Table 1), due to the absence of a Lewis acid, Na or Ni. According to the DFT analysis, the HOMO of 3 possesses contributions from both a nickel d$_{x^2-y^2}$ orbital and a CO$_2$ π$^*$ orbital, see Fig. 2. Due to additional electron density from

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**Scheme 2** Preparation of mononuclear- and dinuclear-CO$_2$ adducts.

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**Fig. 1** Displacement ellipsoid (50%) representations for (a) (PNP)NiCOO$^{\kappa^C}$ (2) in a dimeric assembly with co-crystallized THF molecules, and (b) (Na(12-C-4)$_2$)(PNP)Ni$^{1-}$,CO$_2$–$\kappa^C$ (3). A co-crystallized 12-crown-4 molecule and hydrogen atoms are omitted for clarity.
CO₂²⁻ being shifted to the nickel, the CO₂ moiety is slightly oxidized compared to the sp² hybridized carboxylate ligands found in 2 and 4. The larger O–C–O angle (128.4(2)°) of 3 compared to others (124.0(1) and 123.7(2)°) also supports this electronic feature, vide infra. Although an η¹:C CO₂ coordination mode has been proposed for many CO₂ reduction strategies,¹⁰ the only example of a crystallographically identified metal η¹:C CO₂ complex is a rhodium CO₂ adduct, Rh(CO₂)₂[(Cl)₂(diars)] (diars = o-phenylene-bis(dimethylarsine)), reported by the Herskovitz group.¹⁴ According to their C–O bond distances (1.20(2) and 1.25(2) Å) and O–C–O angle (126(2)°), the CO₂ moiety in 3 shares similar structural and electronic features. Thus, compound 3 is a unique example possessing η¹:C CO₂ binding, since such a binding mode is unknown for 1st row transition metals and is rare in structurally characterized metal–CO₂ adducts.

Synthesis and characterization of the heterobimetallic nickel–iron CO₂ complex

To gain a better understanding of the role of the second metal ion in the CODH active site, we prepared a heterobimetallic nickel–iron carboxylate species possessing a Ni–CO₂–Fe fragment by addition of [(PNP)Fe]⁺ to a Ni–η¹:C–CO₂–kC species. To a yellow solution of [Na(12-C-4)]²⁺[(PNP)Ni–η¹:C–CO₂–kC] (3) in toluene, a purple solution of (PNP)FeCl was added. The immediate formation of a new orange species (PNP)Ni–μ–CO₂–kC:C=O,O’–Fe(PNP) (5) was confirmed, using the ¹H NMR spectrum, from the absence of peaks for 3 and (PNP)FeCl and the presence of new paramagnetically shifted signals. The same product was also prepared by substitution of the sodium ion of (PNP)NiCOONa (2) with (PNP)FeCl. The solid-state structure of 5 clearly revealed a dinuclear nickel–iron complex with a bridging CO₂ ligand in the μ–C=C=O,O’ mode (Fig. 3). The Ni and Fe ions are separated by a distance of 4.369(3) Å. The two C–O bond

Table 1  Selected bond distances and angles for the nickel carboxylate species 1, 2, 3, 4 and 5, and CO₂-bound CODH

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<th>1¹⁰</th>
<th>2¹¹</th>
<th>3</th>
<th>4¹⁰</th>
<th>5</th>
<th>CODH¹²</th>
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<td>d_{Ni–C} (Å)</td>
<td>1.866(2)</td>
<td>1.882(1)</td>
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<tr>
<td>d_{C–O} (Å)</td>
<td>1.17(2)</td>
<td>1.200(3)</td>
<td>1.218(2)</td>
<td>1.248(2)</td>
<td>1.269(2)</td>
<td></td>
</tr>
<tr>
<td>θ (O–C–O °)</td>
<td>133</td>
<td>138.0(2)</td>
<td>135.1(1)</td>
<td>128.4(2)</td>
<td>116.5(1)</td>
<td></td>
</tr>
<tr>
<td>ν_{CO₂} (cm⁻¹)</td>
<td>1740</td>
<td>1724</td>
<td>1682</td>
<td>1620</td>
<td>1510</td>
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Table 2  Selected physical parameters and bond indices from the natural bond orbital analysis

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<td>Structural parameters</td>
<td>1.84(2)</td>
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<td>d_{Ni–O} (Å)</td>
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<td>1620</td>
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Wiberg bond indices a

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<th>Ni–O</th>
<th>C–O</th>
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<td>Ni–C</td>
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<td>C–O</td>
<td>1.6927</td>
<td>1.6384</td>
<td>1.5112</td>
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a Wiberg bond indices were calculated using single-point calculations, for which geometries were obtained from the XRD data.
distances are 1.269(2) and 1.289(2) Å, revealing that a significant elongation has occurred due to the iron interaction compared to 3 (Table 1). The bond distances between the iron and both oxygen atoms are 2.204(1) and 2.066(1) Å. The nickel center possesses a square planar geometry ($\tau = 0.10^{12}$). The geometry around the iron is distorted square pyramidal ($\tau = 0.13$, Fig. 3). The O1–C1–O2 angle (116.5°) reflects the sp² hybridization of the carboxylate ligand in 5. In fact, recent crystallographic data of CODH at atomic resolution ($d_{\text{min}} = 1.03$ Å) revealed that the bound CO₂ molecule ($\angle O-C-O = 117.2(26)^\circ$) is a carboxylate anion (CO₂⁻). \(^{6,8,11}\) Regarding the similarity between these angles, the carboxylate moiety in 5 might be close to CO₂⁻. The asymmetric vibration for CO₂ observed at 1510 cm⁻¹, which is similar to that observed for the dinickel carboxylate species (5) at 1518 cm⁻¹, also indicates a reduced state of CO₂. The effective magnetic moment of 5 was determined using the Evans’ method ($\mu_{\text{eff}} = 4.95$ μₜ in C₆D₆), which indicated an S = 2 spin state. \(^{16}\) According to DFT calculations, most of the spin density is located on the iron center (see ESI). For CODH, the unique iron, Feₜ₁, was assigned as a high spin iron(II) (ferrous complex II, FCII) using Mössbauer spectroscopy, \(^{47}\) and a low-spin nickel(II) was demonstrated using X-ray absorption spectroscopy (XAS). \(^{18}\) The current structural and spectroscopic analyses suggest that 5 might share a similar electronic structure to that found in CODH. Gibson classified the μ₂-κₖC₅=C₅O mode with the absence of a Ni₂–O₂ interaction ($d_{\text{Ni2-O2}} = 3.14(7)$ Å) and two different C–O distances of the CO₂ moiety, compound 5 ($\Delta d_{C-O} = 0.020$ Å) can be assigned as a class I complex. \(^{19}\) In the dinickel CO₂ species (4), the CO₂ molecule is coordinated in a μ₂-κ₅C₅O mode with the absence of a Ni₂–O₂ interaction ($d_{\text{Ni2-O2}} = 3.14(7)$ Å) and two different C–O bonds ($\Delta d_{C-O} = 0.056$ Å). In CODH, CO₂ is coordinated in a μ₂-κ₅C₅O fashion between the nickel and iron ions, but the two C–O bond distances are quite comparable ($\Delta d_{C-O} = 0.018$ Å), akin to the μ₂-κ₅C₅O mode. This might be due to hydrogen bonding with the protein matrix, since both the CO₂ oxygen atoms are hydrogen bonded to His93 and Lys563, respectively. \(^{*}\)

Compound 5 is the first example of a dinuclear nickel–iron–CO₂ complex. While dinuclear CO₂ complexes mostly employ 2nd and 3rd row transition metals, \(^{59}\) several bimetallic iron carboxylates (Fe–CO₂–M, M = Ti, Zr, Sn, Re) have been reported. \(^{59-65}^{*}\) However, such complexes typically possess an Fe–C bond rather than an Fe–O bond with CO₂. There have been numerous examples of nickel–iron bimetallic complexes reported for synthetic model studies of NiFe hydrogenase, \(^{22}\) but a bimetallic complex possessing a Ni–μ–CO₂–Fe moiety closely related to CODH chemistry is not known. The Holm group constructed a series of [NiFe₅S₅] cubanes as structural model complexes for the [NiFe₅S₅] core in CODH. \(^{31}\) However, the installation of an iron species corresponding to the Feₜ in CODH and reactions involving CO and CO₂ have not yet been investigated. More recently, the Holm group also reported a bimetallic complex containing nickel and iron supported by a binucleating macrocycle. \(^{34}\) With respect to CODH chemistry, bridging hydroxyl, cyanido and formato species have been generated, however, a Ni–μ–CO₂–Fe fragment had not yet been isolated.

**Activation of CO₂ in 3 and 5**

Previously known 4-coordinate Ni–CO₂ complexes possessing an η¹-CO₂ binding mode have a formally zero-valent nickel center, Scheme 1. \(^{*}\) This suggests limited CO₂ activation in such species. Interestingly, the 5-coordinate nickel CO₂ adduct (PPMeP)Ni(CO₂) also has a similar level of activation of CO₂ based on the C–O bond distances and the O–C–O angle, Table 2. Regarding CO₂ binding and activation, [Na(12-C-4)₂][PPMeP]Ni(η¹-CO₂–C) \(^{3}(3)\) is a unique example. It is striking that a neutral pincer-type ligand PPMeP (PPMeP = P(2-P₂Pr₂-C₆H₄)₂) favors 5-coordinate η¹-CO₂ coordination at a single nickel center, while 3 remains as a 4-coordinate species with η¹-CO₂ coordination. \(^{7}\) Although the total number of Ni d-electrons and CO₂ π-electrons in both 3 and (PPMeP)Ni(CO₂) is the same, (PPMeP)Ni(CO₂) can be considered as formally Ni(0)–CO₂ while 3 can be better described as a Ni(–)(CO₂⁻) species. The asymmetric CO₂ stretching frequency for 3 is significantly shifted to a lower vibration, 1620 cm⁻¹, compared to those of the Ni–η¹-CO₂ complexes (Table 2), which is evidence of a reduced CO₂ moiety in 3. \(^{3}\) This may be due to the influence of the trans atom: an anionic amide nitrogen vs. a neutral phosphorus atom. The anionic nitrogen in 3 electrostatically favors a divalent nickel center, while the neutral π-acidic P atom in the PPMeP ligand favors a Ni(0) center. In fact, the PNP ligand typically stabilizes a square planar geometry while the PPMeP ligand favors a pseudo-tetrahedral geometry. Thus, 3 prefers to accommodate a divalent nickel center while (PPMeP)Ni(CO₂) prefers Ni(0). However, the reduction state of the CO₂ moiety in 3 is a little ambiguous according to the O–C–O angle. The O–C–O angle in 3 of 128.4(2)° is larger than those of an ideal sp³ hybridized carbon (120°) and the other nickel(II) carboxylate species 1, 2 and 4 (119.6(2)°, 124.0(1)° and 123.7(2)°, respectively, Table 1). The O–C–O angle of a CO₂ radical anion (CO₂⁻) is suggested to be 133°, \(^{35}\) which is fairly similar to those of the previously reported Ni–η¹-CO₂ complexes, Table 2. Thus, the geometry of the CO₂ moiety in 3 may be thought of as being between a CO₂ radical anion and a carboxylate.

Upon addition of iron to compound 3, the CO₂ is further reduced to carboxylate (CO₂⁻). The C–O bond distances and O–C–O angle in 5 clearly show a 2-electron reduced state of the CO₂ moiety, Table 2. This was also indicated by the asymmetric CO₂
vibration observed at 1510 cm\(^{-1}\), which is significantly lower than those of other CO\(_2\) species and 3. The Wiberg bond indices nicely agree with the bond distances, Table 2. These analyses of a series of nickel–CO\(_2\) compounds demonstrate how the degree of CO\(_2\) activation can be tuned by incorporating a distinct electronic coordination environment at the metal center, and may have parallels to the efficient CO\(_2\) conversion found in CODH.

In order to study further activation of the bound CO\(_2\) via C–O bond cleavage, protonation of 3 and 5 was attempted. Our group previously reported that reversible C–O bond cleavage/formation occurs with a nickel hydroxycarbonyl species \(\{\text{PNP}\}\text{Ni}-\text{CO}^{\text{2-}}\) in 75% yield. A similar reaction of 3 with 2 equiv. of HBF\(_4\)-Et\(_2\)O resulted in the formation of a carboxyl species \([\{\text{PNP}\}\text{NiCO}\] \(\{\text{BF}_4\}\) in 75% yield, revealing that two sequential protonations can occur with compound 3 possessing a Ni–η\(^1\)-CO\(_2\)-kC moiety, which are key steps in the transformation of CO\(_2\) to CO. Although protonation of compound 5 seems to produce 1 and \([\{\text{PNP}\}\text{NiCO}\] \(\{\text{BF}_4\}\), unfortunately, their yields were not clear due to thermal decomposition of 5 and the generation of multiple products. Demetallation of the iron seems to be one of the decomposition processes.

### Conclusions

In conclusion, the generation of unprecedented nickel–carbon dioxide adducts possessing a Ni–C bond accommodated by a \(\{\text{PNP}\}\text{Ni}\) scaffold was accomplished. A mononuclear CO\(_2\) adduct \([\text{Na}[\text{12-C}-4l]_2][\{\text{PNP}\}\text{Ni–η}\(^1\)-CO\(_2\)-kC}\) (3) and a dinuclear nickel–iron carboxylate species \([\text{PNP}]\text{Ni–μ–CO}_2\)-kC\(_2\)O\(_2\)-O\(_2\)-Fe(PNP) (5) were synthesized successfully. While the solid state structure of 3 revealed a rare η\(^1\)-kC binding mode, compound 5 was structurally characterized to reveal a unique class I type μ\(_2\)-kC\(_2\)-O\(_2\)-O\(_2\) binding mode. This heterometallic CO\(_2\) adduct is the first example of a nickel–iron carboxylate species, of which the structural and electronic features are reminiscent of those of the Ni–μ–CO\(_2\)-Fe fragment found in the C-cluster of CODH. Comparison of the η\(^1\)-CO\(_2\)-kC species 3 and dinuclear Ni–μ–CO\(_2\)-Fe species 5 with previously reported Ni–CO\(_2\) adducts suggested that the CO\(_2\) ligand can be stabilized and activated by interaction with the second metal. Protonation of 3 produces a nickel carboxyl species \([\{\text{PNP}\}\text{NiCO}\] \(\{\text{BF}_4\}\) via C–O bond cleavage, while the reactivity of 5 is limited. Further studies on incorporating a stable iron species and the subsequent reactivity toward protonation are currently underway.

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### Notes and references

The CO$_2$ ligand symmetrically bonded to M' and class II complexes possess two asymmetric M'–O bonds.


