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Carbon dioxide binding at a Ni/Fe center: synthesis and characterization of Ni(η^1 -CO₂- κ C) and Ni- μ -CO₂- κ C: κ^2 O,O'-Fe[†]

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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 η^1 - κ C binding mode of CO₂, while that of **5** shows bridging CO₂ binding (μ_2 - κ C: κ^2 O,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.

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Introduction

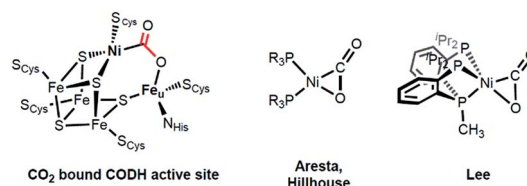
Activation of carbon dioxide is currently receiving much attention due to its relevance to environmental and energy related issues.¹ In the area of transition metal catalyzed reactions, one of the main challenges is selective reduction of CO₂ to a product such as formate, carbon monoxide, methanol or methane.² In a 2-electron process, the binding mode of the CO₂ may determine the eventual product formation, *e.g.* formate *vs.* carbon monoxide.³ When the initial metal-oxygen interaction occurs to form a metal CO₂ adduct M- η^1 -CO₂- κ O, 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 metallocarboxylate species (M- η^1 -CO₂- κ C), 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.^{4,5} Therefore, CO₂ activation with a bimetallic system can be one way to guide the selectivity of the CO₂ catalyst and is receiving much attention.^{5,6} 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).⁷ 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 1.⁸ 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.⁷ 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- η^2 -CO₂ adducts possessing both M-C and M-O bonds.⁹ In 1975, Aresta and co-workers reported the first structurally characterized nickel-CO₂ adduct (PCy₃)₂Ni(η^2 -CO₂), Scheme 1.^{9a} An analogous complex, (dtbpe)Ni(η^2 -CO₂) (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) was recently reported by Hillhouse and co-workers.^{9d} More recently, our group reported a similar but unique five-coordinate nickel-CO₂ adduct (PP^{Me}P)Ni(η^2 -CO₂) (PP^{Me}P = PMe(2-PⁱPr₂-C₆H₄)₂).^{9f} According to its structural analysis, the five coordinate nickel CO₂ species supported by three neutral P donors has a weak Ni-O bond available for electrophilic attack.^{9f} Additionally, by utilizing an anionic tridentate PNP ligand (PNP⁻ = N[2-PⁱPr₂-4-Me-C₆H₃]₂⁻), our group reported the nickel hydroxycarbonyl species (PNP)NiCOOH (**1**), (PNP)NiCOONa (**2**) and {(PNP)Ni}₂- μ -CO₂- κ^2 C,O (**4**), the first examples of Ni-CO₂ complexes that reveal a Ni-CO₂- κ C binding mode, Scheme 2.¹⁰ 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 (PP^{Me}P)Ni-

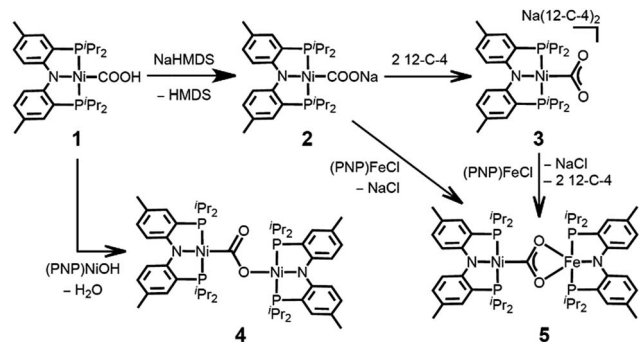
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Scheme 1 The active site of carbon monoxide dehydrogenase (CODH, left), and 4- and 5-coordinate nickel CO₂ adducts (right).



Scheme 2 Preparation of mononuclear- and dinuclear-CO₂ adducts.

CO₂ and (PNP)Ni-CO₂ to evaluate their fundamental differences in CO₂ activation. The different geometries favored with a PP^{Me}P or PNP ligand affect the identity of the nickel-CO₂ moiety, which can be Ni(II)-CO₂²⁻ or Ni(0)-CO₂ or an open-shell Ni(I)-CO₂⁻, *vide infra*. Furthermore, by isolating the native nickel-CO₂ 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-CO₂ moiety.

Here, we present a nickel carboxylate species {Na(12-C-4)₂}[(PNP)Ni-η¹-CO₂-κC] (3), in which the nickel-CO₂ moiety does not have any Lewis acid interactions. We also prepared a dinuclear nickel-iron carboxylate species (PNP)Ni-μ-CO₂-κC:κ²O,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 CO₂ ligand. The levels of CO₂ activation in compounds 3 and 5 are compared with other Ni-CO₂ adducts and the Ni-μ-CO₂-Fe moiety found in CODH.

Results and discussion

Synthesis and characterization of the Ni-η¹-CO₂-κC 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.¹⁰ Following deprotonation of (PNP)NiCOOH (1), its anionic congener (PNP)NiCOONa (2) was also prepared and recently reported by our group.¹⁰ 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 CO₂ ligand coordinates to the nickel center in a μ₃-κ¹C:κ²O,O':κ¹O' mode with a Ni-C1 bond distance of 1.882(1) Å. There are additional bonds of the CO₂ 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-η¹-CO₂-κC] (3). The crystal structure of 3 revealed the successful generation of a mononuclear nickel adduct possessing an η¹-κC 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

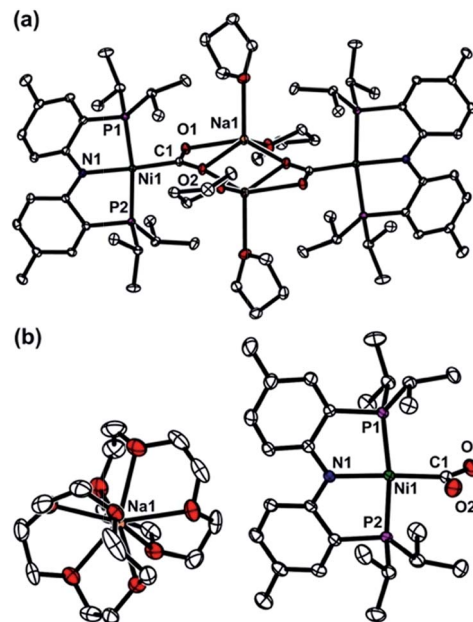


Fig. 1 Displacement ellipsoid (50%) representations for (a) (PNP)NiCOONa (2) in a dimeric assembly with co-crystallized THF molecules,¹¹ and (b) {Na(12-C-4)₂}[(PNP)Ni-η¹-CO₂-κC] (3). A co-crystallized 12-crown-4 molecule and hydrogen atoms are omitted for clarity.

previously known nickel(II) species such as (PNP)NiCOOH (1) and {(PNP)Ni}₂-μ-CO₂-κ²C,O (4), *vide infra*. The geometry of 3 is square planar ($\tau_4 = 0.12^{12}$) with a similar but slightly elongated Ni-C bond distance in comparison to those of 1 and 4 ($d_{\text{Ni-C}} = 1.866(2)$ and 1.888(2) Å, respectively, Table 1). This is probably due to a lower degree of π back-bonding between the nickel and CO₂. In fact, π back-donation from the nickel center to a CO₂ 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, ⁿPr) (1.963–2.004 Å).¹³ The molecular orbitals generated from DFT calculations also show the presence of π back-donation from the Ni d_{xz} to the CO₂ π^* orbital (see ESI†). Due to the absence of Lewis acid interactions in 3, a lower π -accepting ability of the CO₂ ligand is expected. Its structural data also revealed that the plane of the CO₂ ligand is perpendicular to that of the square planar (PNP)Ni moiety. One of the oxygen atoms ($d_{\text{Ni-O}_2} = 2.614(1)$ Å) is slightly closer to the nickel center than the other ($d_{\text{Ni-O}_1} = 2.776(1)$ Å), Table 2. These Ni-O distances are much longer than those for other known Ni-η²-CO₂ adducts (1.9–2.2 Å, Table 2), suggesting that neither of the oxygen atoms are bound.⁹ 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 ($d_{\text{C1-O}_1} = 1.247(2)$ Å, $d_{\text{C1-O}_2} = 1.248(2)$ 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 CO₂ π^* orbital, see Fig. 2. Due to additional electron density from



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

	1 ¹⁰	2 ¹¹	3	4 ¹⁰	5	CODH ^{8b}
$d_{\text{Ni-C}}$ (Å)	1.866(2)	1.882(1)	1.911(2)	1.888(2)	1.858(1)	1.805(31)
$d_{\text{M-O}}$ (Å)	—	2.352(1) ^a 2.217(1) ^a 2.459(1) ^a	—	1.897(2) ^b	2.204(1) ^c 2.066(1) ^c	2.030(18) ^c
$d_{\text{C-O}}$ (Å)	1.269(3) 1.313(3)	1.260(1) 1.271(1)	1.247(2) 1.248(2)	1.240(3) 1.296(3)	1.269(2) 1.289(2)	1.298(30) 1.316(30)
$\Delta d_{\text{C-O}}$ (Å)	0.044	0.011	0.001	0.056	0.020	0.018
$\angle \text{O-C-O}$ (°)	119.6(2)	124.0(1)	128.4(2)	123.7(2)	116.5(1)	117.2(26)

^a M = Na. ^b M = Ni. ^c M = Fe.

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-κC CO₂ coordination mode has been proposed for many CO₂ reduction strategies,^{2,3} the only example of a crystallographically identified metal η¹-κC CO₂ complex is a rhodium CO₂ adduct, Rh(CO₂)(Cl)(diars)₂ (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-κC 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

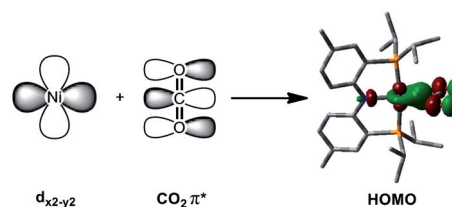


Fig. 2 Combination of the Ni $d_{x^2-y^2}$ and CO₂ π^* orbitals provides the DFT calculated HOMO of {Na(12-C-4)}₂{(PNP)Ni-η¹-CO₂-κC} (3).

fragment by addition of {(PNP)Fe}⁺ to a Ni-η¹-CO₂-κC species. To a yellow solution of {Na(12-C-4)}₂{(PNP)Ni-η¹-CO₂-κC} (3) in toluene, a purple solution of (PNP)FeCl was added. The immediate formation of a new orange species (PNP)Ni-μ-CO₂-κC:κ²O,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 μ₂-κC:κ²O,O' mode (Fig. 3). The Ni and Fe ions are separated by a distance of 4.3690(3) Å. The two C–O bond

Table 2 Selected physical parameters and bond indices from the natural bond orbital analysis

	Ni(PCy ₃) ₂ (η ² -CO ₂) ^{9a}	(dtbpe)Ni(η ² -CO ₂) ^{9d}	(PP ^{Me} P)Ni(η ² -CO ₂) ^{9f}	3	5
Structural parameters					
$d_{\text{Ni-C}}$ (Å)	1.84(2)	1.868(2)	1.904(1)	1.911(2)	1.858(1)
$d_{\text{Ni-O}}$ (Å)	1.99(2)	1.904(2)	2.191(1)	2.614(1) 2.776(1)	2.718(1) 2.792(1)
$d_{\text{C-O}}$ (Å)	1.17(2) 1.22(2)	1.200(3) 1.266(3)	1.218(2) 1.252(2)	1.248(2) 1.247(2)	1.269(2) 1.289(2)
$\angle \text{O-C-O}$ (°)	133	138.0(2)	135.1(1)	128.4(2)	116.5(1)
ν_{CO_2} (cm ⁻¹)	1740	1724	1682	1620	1510
Wiberg bond indices^a					
Ni–C	—	0.5766	0.5286	0.6143	0.6277
Ni–O	—	0.4300	0.3117	0.1679 0.1358	0.0798 0.0644
C–O	—	1.6927 1.4080	1.6384 1.4701	1.5112 1.4949	1.3993 1.2933

^a Wiberg bond indices were calculated using single-point calculations, for which geometries were obtained from the XRD data.



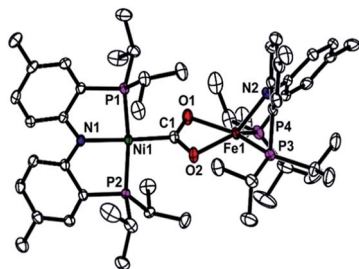


Fig. 3 Displacement ellipsoid (50%) representation for (PNP)Ni- μ -CO₂- κ C: κ^2 O, O' -Fe(PNP) (5). Hydrogen atoms are omitted for clarity.

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 ($\tau_4 = 0.10^{12}$). The geometry around the iron is distorted square pyramidal ($\tau = 0.13$,¹⁵ 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 ($d_{\min} = 1.03$ Å) revealed that the bound CO₂ molecule (\angle O–C–O = 117.2(26)°) is a carboxylate anion (CO₂²⁻).^{8b,8c} Regarding the similarity between these angles, the carboxylate moiety in **5** might be close to CO₂²⁻. The asymmetric vibration for CO₂ observed at 1510 cm⁻¹, which is similar to that observed for the dinickel carboxylate species (**4**) at 1518 cm⁻¹, also indicates a reduced state of CO₂. The effective magnetic moment of **5** was determined using the Evans' method ($\mu_{\text{eff}} = 4.95 \mu_{\text{B}}$ 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, Fe_u, was assigned as a high spin iron(II) (ferrous component II, FCII) using Mössbauer spectroscopy,¹⁷ 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 μ_2 - κ C: κ^2 O, O' binding modes of CO₂ into two types according to the difference between the two C–O distances.¹⁹ Due to the two similar C–O distances of the CO₂ moiety, compound **5** ($\Delta d_{\text{C-O}} = 0.020$ Å) can be assigned as a class I complex.²⁰ In the dinickel CO₂ species (**4**), the CO₂ molecule is coordinated in a μ_2 - κ C: κ O mode with the absence of a Ni2–O2 interaction ($d_{\text{Ni2-O2}} = 3.14(7)$) and two different C–O bond distances ($\Delta d_{\text{C-O}} = 0.056$ Å). In CODH, CO₂ is coordinated in a μ_2 - κ C: κ O fashion between the nickel and iron ions, but the two C–O bond distances are quite comparable ($\Delta d_{\text{C-O}} = 0.018$ Å), akin to the μ_2 - κ C: κ^2 O, O' mode. This might be due to hydrogen bonding with the protein matrix, since both the CO₂ oxygens are hydrogen bonded to His93 and Lys563, respectively.⁸

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,¹⁹ several bimetallic iron carboxylates (Fe–CO₂–M, M = Ti, Zr, Sn, Re) have been reported.^{5a,5c–e,21} 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 [NiFe₃S₄] cubanes as structural model complexes for the [NiFe₄S₄] core in CODH.²³ However, the installation of an iron species corresponding to the Fe_u 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.²⁴ With respect to CODH chemistry, bridging hydroxo, 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 η^2 -CO₂ binding mode have a formally zero-valent nickel center, Scheme 1.⁹ This suggests limited CO₂ activation in such species. Interestingly, the 5-coordinate nickel CO₂ adduct (PP^{Me}P)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)}{(PNP)Ni- η^1 -CO₂- κ C} (**3**) is a unique example. It is striking that a neutral pincer-type ligand PP^{Me}P (PP^{Me}P = PMe[2-P^{Pr}Pr₂-C₆H₄]₂) favors 5-coordinate η^2 -CO₂ coordination at a single nickel center, while **3** remains as a 4-coordinate species with η^1 -CO₂ coordination.^{9f} Although the total number of Ni d-electrons and CO₂ π^* -electrons in both **3** and (PP^{Me}P)Ni(CO₂) is the same, (PP^{Me}P)Ni(CO₂) can be considered as formally Ni(0)–(CO₂) while **3** can be better described as a Ni(II)–(CO₂²⁻) species. The asymmetric CO₂ stretching frequency for **3** is significantly shifted to a lower vibration, 1620 cm⁻¹, compared to those of the Ni- η^2 -CO₂ complexes (Table 2), which is evidence of a reduced CO₂ moiety in **3**.⁹ 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 PP^{Me}P ligand favors a Ni(0) center. In fact, the PNP ligand typically stabilizes a square planar geometry while the PP^{Me}P ligand favors a pseudo-tetrahedral geometry. Thus, **3** prefers to accommodate a divalent nickel center while (PP^{Me}P)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 sp² 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°,²⁵ which is fairly similar to those of the previously reported Ni- η^2 -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 (CO₂²⁻). 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 (**1**).¹⁰ From reaction of **3** with 1 equiv. of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$, a nickel hydroxycarbonyl species (**1**) was produced and isolated with a 74% yield. A similar reaction of **3** with 2 equiv. of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ resulted in the formation of a carbonyl species $\{(\text{PNP})\text{NiCO}\}\{\text{BF}_4\}$ in 75% yield, revealing that two sequential protonations can occur with compound **3** possessing a $\text{Ni}-\eta^1\text{-CO}_2\text{-}\kappa\text{C}$ 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 (PNP)Ni scaffold was accomplished. A mononuclear CO_2 adduct $\{\text{Na}(\text{12-C-4})_2\}\{(\text{PNP})\text{Ni}-\eta^1\text{-CO}_2\text{-}\kappa\text{C}\}$ (**3**) and a dinuclear nickel-iron carboxylate species $(\text{PNP})\text{Ni}-\mu\text{-CO}_2\text{-}\kappa\text{C}:\kappa^2\text{O},\text{O}'\text{-Fe}(\text{PNP})$ (**5**) were synthesized successfully. While the solid state structure of **3** revealed a rare $\eta^1\text{-}\kappa\text{C}$ binding mode, compound **5** was structurally characterized to reveal a unique class I type $\mu_2\text{-}\kappa\text{C}:\kappa^2\text{O},\text{O}'$ binding mode. This heterobimetallic 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 $\text{Ni}-\mu\text{-CO}_2\text{-Fe}$ fragment found in the C-cluster of CODH. Comparison of the $\eta^1\text{-CO}_2\text{-}\kappa\text{C}$ species **3** and dinuclear $\text{Ni}-\mu\text{-CO}_2\text{-Fe}$ species **5** with previously reported $\text{Ni}-\text{CO}_2$ adducts suggested that the CO_2 ligand can be stabilized and activated by interaction with the second metal. Protonation of **3** produces a nickel carbonyl 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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