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Carbon dioxide binding at a Ni/Fe center: synthesis and characterization of Ni(η^1-CO_2-κC) and Ni-μ-CO_2-κC:$\kappa^2 O,O'$-Fe†

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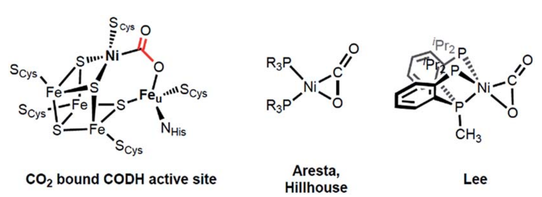
The degree of CO_2 activation can be tuned by incorporating a distinct electronic coordination environment at the nickel center. A mononuclear nickel carboxylate species (Ni–CO_2, **3**) and a dinuclear nickel–iron carboxylate species (Ni–CO_2–Fe, **5**) were prepared. The structure of **3** reveals a rare η^1-κC binding mode of CO_2, while that of **5** shows bridging CO_2 binding (μ_2-κC:$\kappa^2 O,O'$) between the nickel and iron, presented as the first example of a nickel-μ-CO_2-iron species. The structural analyses of **3** and **5** based on XRD and DFT data reveal a higher degree of CO_2 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.[1] In the area of transition metal catalyzed reactions, one of the main challenges is selective reduction of CO_2 to a product such as formate, carbon monoxide, methanol or methane.[2] In a 2-electron process, the binding mode of the CO_2 may determine the eventual product formation, *e.g.* formate *vs.* carbon monoxide.[3] When the initial metal–oxygen interaction occurs to form a metal CO_2 adduct M-η^1-CO_2-κO, subsequent hydride transfer *via* CO_2 addition to a M–H bond generates a metal-formate species. Alternatively, the metal–carbon bond formation can produce a metallacarboxylate species (M-η^1-CO_2-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 CO_2.[4,5] Therefore, CO_2 activation with a bimetallic system can be one way to guide the selectivity of the CO_2 catalyst and is receiving much attention.[5,6] In fact, an excellent example of a bimetallic center utilized in an efficient catalytic conversion of CO_2 can be found in the active site of carbon monoxide dehydrogenase (CODH).[7] According to recent studies, CO_2 coordination at a heterobimetallic nickel–iron active site can be found in CODH's intermediate species, which possesses a Ni-μ-CO_2-Fe moiety, Scheme 1.[8] Although X-ray analysis provides a structural snapshot of the CO_2 reduction sequence, the role of the unique iron ion is currently not well-understood.[7] Thus, acquiring an understanding of iron assisted CO_2-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-CO_2 adducts possessing both M–C and M–O bonds.[9] In 1975, Aresta and co-workers reported the first structurally characterized nickel–CO_2 adduct $(PCy_3)_2Ni(\eta^2$-$CO_2)$, Scheme 1.[9a] An analogous complex, (dtbpe)Ni(η^2-CO_2) (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–CO_2 adduct $(PP^{Me}P)Ni(\eta^2$-$CO_2)$ ($PP^{Me}P$ = $PMe(2$-P^iPr_2-$C_6H_4)_2$).[9f] According to its structural analysis, the five coordinate nickel CO_2 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^- = $N[2$-P^iPr_2-4-Me-$C_6H_3]_2^-$), our group reported the nickel hydroxycarbonyl species (PNP)NiCOOH (**1**), (PNP)NiCOONa (**2**) and $\{(PNP)Ni\}_2$-μ-CO_2-$\kappa^2 C,O$ (**4**), the first examples of Ni–CO_2 complexes that reveal a Ni–CO_2-κC 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–



Scheme 1 The active site of carbon monoxide dehydrogenase (CODH, left), and 4- and 5-coordinate nickel CO_2 adducts (right).

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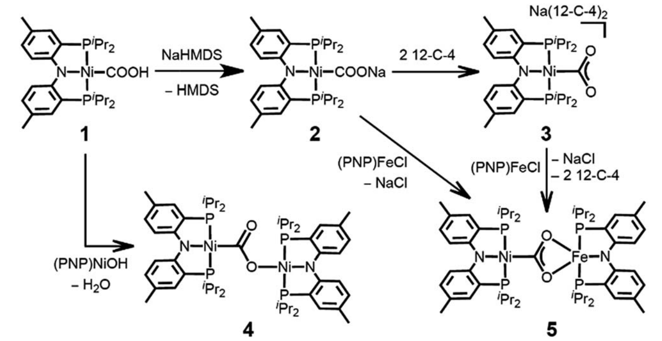

Scheme 2 Preparation of mononuclear- and dinuclear-CO_2 adducts.

CO_2 and (PNP)Ni–CO_2 to evaluate their fundamental differences in CO_2 activation. The different geometries favored with a PP^{Me}P or PNP ligand affect the identity of the nickel–CO_2 moiety, which can be Ni(II)–CO_2^{2-} or Ni(0)–CO_2 or an open-shell Ni(I)–$CO_2^{\bullet-}$, *vide 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-η^1-CO_2-κ*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-κ*C*:κ^2*O*,*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-η^1-CO_2-κ*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.[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 CO_2 ligand coordinates to the nickel center in a μ$_3$-κ^1*C*:κ^2*O*,*O*′:κ^1*O*′ 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-η^1-CO_2-κ*C*} (**3**). The crystal structure of **3** revealed the successful generation of a mononuclear nickel adduct possessing an η^1-κ*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

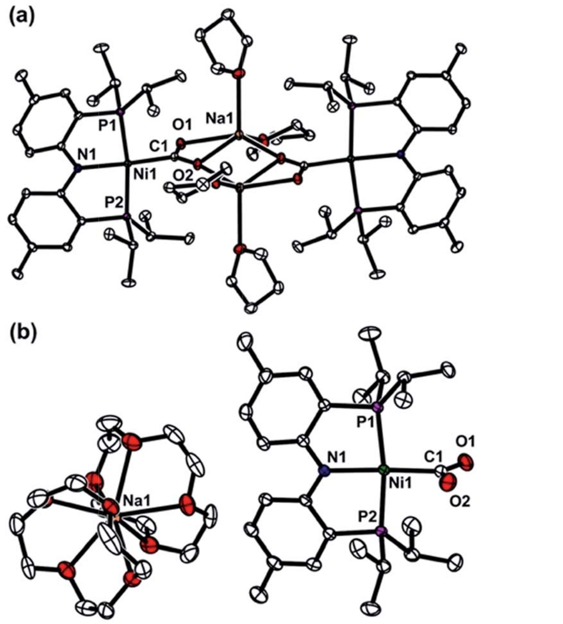

Fig. 1 Displacement ellipsoid (50%) representations for (a) (PNP)NiCOONa (**2**) in a dimeric assembly with co-crystallized THF molecules,[11] and (b) {Na(12-C-4)$_2$}{(PNP)Ni-η^1-CO_2-κ*C*} (**3**). A co-crystallized 12-crown-4 molecule and hydrogen atoms are omitted for clarity.

previously known nickel(II) species such as (PNP)NiCOOH (**1**) and {(PNP)Ni}$_2$-μ-CO_2-κ^2*C*,*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 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, ^{n}Pr) (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 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 ($d_{\text{Ni1–O2}}$ = 2.614(1) Å) is slightly closer to the nickel center than the other ($d_{\text{Ni1–O1}}$ = 2.776(1) Å), Table 2. These Ni–O distances are much longer than those for other known Ni-η^2-CO_2 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 ($d_{\text{C1–O1}}$ = 1.247(2) Å, $d_{\text{C1–O2}}$ = 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

Table 1 Selected bond distances and angles for the nickel carboxylate species **1**, **2**, **3**, **4** and **5**, and CO_2-bound CODH

	1[10]	**2**[11]	**3**	**4**[10]	**5**	CODH[8b]
$d_{Ni–C}$ (Å)	1.866(2)	1.882(1)	1.911(2)	1.888(2)	1.858(1)	1.805(31)
$d_{M–O}$ (Å)	—	2.352(1)^a	—	1.897(2)^b	2.204(1)^c	2.030(18)^c
		2.217(1)^a			2.066(1)^c	
		2.459(1)^a				
$d_{C–O}$ (Å)	1.269(3)	1.260(1)	1.247(2)	1.240(3)	1.269(2)	1.298(30)
	1.313(3)	1.271(1)	1.248(2)	1.296(3)	1.289(2)	1.316(30)
$\Delta d_{C–O}$ (Å)	0.044	0.011	0.001	0.056	0.020	0.018
∠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.

CO_2^{2-} being shifted to the nickel, the CO_2 moiety is slightly oxidized compared to the sp^2 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 η^1-κ*C* CO_2 coordination mode has been proposed for many CO_2 reduction strategies,[2,3] the only example of a crystallographically identified metal η^1-κ*C* CO_2 complex is a rhodium CO_2 adduct, Rh(CO_2)(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 CO_2 moiety in **3** shares similar structural and electronic features. Thus, compound **3** is a unique example possessing η^1-κ*C* CO_2 binding, since such a binding mode is unknown for 1st row transition metals and is rare in structurally characterized metal–CO_2 adducts.

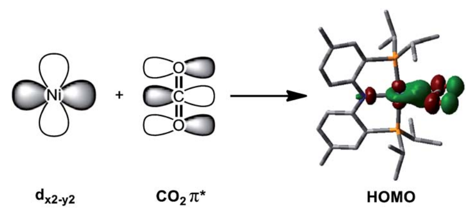

Fig. 2 Combination of the Ni $d_{x^2-y^2}$ and CO_2 π* orbitals provides the DFT calculated HOMO of {Na(12-C-4)$_2$}{(PNP)Ni-η^1-CO_2-κ*C*} (**3**).

Synthesis and characterization of the heterobimetallic nickel–iron CO_2 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–CO_2–Fe fragment by addition of $\{(PNP)Fe\}^+$ to a Ni-η^1-CO_2-κ*C* species. To a yellow solution of {Na(12-C-4)$_2$}{(PNP)Ni-η^1-CO_2-κ*C*} (**3**) in toluene, a purple solution of (PNP)FeCl was added. The immediate formation of a new orange species (PNP)Ni-μ-CO_2-κ*C*:κ^2*O*,*O′*-Fe(PNP) (**5**) was confirmed, using the ^{1}H 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 CO_2 ligand in the μ_2-κ*C*:κ^2*O*,*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					
$d_{Ni–C}$ (Å)	1.84(2)	1.868(2)	1.904(1)	1.911(2)	1.858(1)
$d_{Ni–O}$ (Å)	1.99(2)	1.904(2)	2.191(1)	2.614(1)	2.718(1)
				2.776(1)	2.792(1)
$d_{C–O}$ (Å)	1.17(2)	1.200(3)	1.218(2)	1.248(2)	1.269(2)
	1.22(2)	1.266(3)	1.252(2)	1.247(2)	1.289(2)
∠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	0.0798
				0.1358	0.0644
C–O	—	1.6927	1.6384	1.5112	1.3993
		1.4080	1.4701	1.4949	1.2933

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

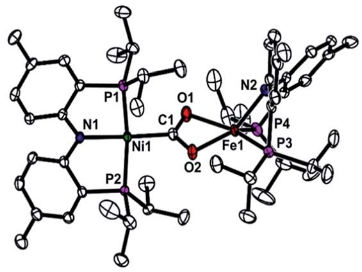

Fig. 3 Displacement ellipsoid (50%) representation for (PNP)Ni-μ-CO_2-κ*C*:κ^2*O*,*O*′-Fe(PNP) (**5**). Hydrogen atoms are omitted for clarity.

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 sp^2 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 CO_2 molecule (∠O–C–O = 117.2(26)°) is a carboxylate anion (CO_2^{2-}).[8b,8c] Regarding the similarity between these angles, the carboxylate moiety in **5** might be close to CO_2^{2-}. The asymmetric vibration for CO_2 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 CO_2. The effective magnetic moment of **5** was determined using the Evans' method ($\mu_{\text{eff}} = 4.95\ \mu_B$ in C_6D_6), 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 CO_2 into two types according to the difference between the two C–O distances.[19] Due to the two similar C–O distances of the CO_2 moiety, compound **5** ($\Delta d_{C-O} = 0.020$ Å) can be assigned as a class I complex.[20] In the dinickel CO_2 species (**4**), the CO_2 molecule is coordinated in a μ_2-κ*C*:κ*O* mode with the absence of a Ni2–O2 interaction ($d_{Ni2-O2} = 3.14(7)$) and two different C–O bond distances ($\Delta d_{C-O} = 0.056$ Å). In CODH, CO_2 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 ($\Delta d_{C-O} = 0.018$ 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 CO_2 oxygens are hydrogen bonded to His93 and Lys563, respectively.[8]

Compound **5** is the first example of a dinuclear nickel–iron–CO_2 complex. While dinuclear CO_2 complexes mostly employ 2nd and 3rd row transition metals,[19] several bimetallic iron carboxylates (Fe–CO_2–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 CO_2. 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-CO_2-Fe moiety closely related to CODH chemistry is not known. The Holm group constructed a series of [$NiFe_3S_4$] cubanes as structural model complexes for the [$NiFe_4S_4$] core in CODH.[23] However, the installation of an iron species corresponding to the Fe_u in CODH and reactions involving CO and CO_2 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 hydoroxo, cyanido and formato species have been generated, however, a Ni-μ-CO_2-Fe fragment had not yet been isolated.

Activation of CO_2 in 3 and 5

Previously known 4-coordinate Ni–CO_2 complexes possessing an η^2-CO_2 binding mode have a formally zero-valent nickel center, Scheme 1.[9] This suggests limited CO_2 activation in such species. Interestingly, the 5-coordinate nickel CO_2 adduct ($PP^{Me}P$)Ni(CO_2) also has a similar level of activation of CO_2 based on the C–O bond distances and the O–C–O angle, Table 2. Regarding CO_2 binding and activation, {Na(12-C-4)$_2$}{(PNP)Ni-η^1-CO_2-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^iPr_2-C_6H_4]$_2$) favors 5-coordinate η^2-CO_2 coordination at a single nickel center, while **3** remains as a 4-coordinate species with η^1-CO_2 coordination.[9f] Although the total number of Ni d-electrons and CO_2 π^*-electrons in both **3** and ($PP^{Me}P$)Ni(CO_2) is the same, ($PP^{Me}P$)Ni(CO_2) can be considered as formally Ni(0)–(CO_2) while **3** can be better described as a Ni(II)–(CO_2^{2-}) species. The asymmetric CO_2 stretching frequency for **3** is significantly shifted to a lower vibration, 1620 cm^{-1}, compared to those of the Ni-η^2-CO_2 complexes (Table 2), which is evidence of a reduced CO_2 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(CO_2) prefers Ni(0). However, the reduction state of the CO_2 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 sp^2 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 CO_2 radical anion ($CO_2^{\bullet-}$) is suggested to be 133°,[25] which is fairly similar to those of the previously reported Ni-η^2-CO_2 complexes, Table 2. Thus, the geometry of the CO_2 moiety in **3** may be thought of as being between a CO_2 radical anion and a carboxylate.

Upon addition of iron to compound **3**, the CO_2 is further reduced to carboxylate (CO_2^{2-}). The C–O bond distances and O–C–O angle in **5** clearly show a 2-electron reduced state of the CO_2 moiety, Table 2. This was also indicated by the asymmetric CO_2

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 $HBF_4\cdot Et_2O$, a nickel hydroxycarbonyl species (**1**) was produced and isolated with a 74% yield. A similar reaction of **3** with 2 equiv. of $HBF_4\cdot Et_2O$ resulted in the formation of a carbonyl species {(PNP)NiCO}{BF_4} in 75% yield, revealing that two sequential protonations can occur with compound **3** possessing a Ni-η^1-CO_2-κ*C* moiety, which are key steps in the transformation of CO_2 to CO. Although protonation of compound **5** seems to produce **1** and {(PNP)NiCO}{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 {Na(12-C-4)$_2$}{(PNP)Ni-η^1-CO_2-κ*C*} (**3**) and a dinuclear nickel–iron carboxylate species (PNP)Ni-μ-CO_2-κ*C*:κ^2*O*,*O*′-Fe(PNP) (**5**) were synthesized successfully. While the solid state structure of **3** revealed a rare η^1-κ*C* binding mode, compound **5** was structurally characterized to reveal a unique class I type μ_2-κ*C*:κ^2*O*,*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 Ni-μ-CO_2-Fe fragment found in the C-cluster of CODH. Comparison of the η^1-CO_2-κ*C* 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 carbonyl species {(PNP)NiCO}{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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