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# Carbon dioxide binding at a Ni/Fe center: synthesis and characterization of Ni( $\eta^1$ -CO<sub>2</sub>- $\kappa$ C) and Ni- $\mu$ -CO<sub>2</sub>- $\kappa$ C: $\kappa^2$ O,O'-Fe<sup>+</sup>

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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 CO<sub>2</sub> to a product such as formate, carbon monoxide, methanol or methane.<sup>2</sup> In a 2-electron process, the binding mode of the CO<sub>2</sub> 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<sub>2</sub> adduct M- $\eta^1$ -CO<sub>2</sub>- $\kappa O$ , subsequent hydride transfer via CO2 addition to a M-H bond generates a metalformate species. Alternatively, the metal-carbon bond formation can produce a metallacarboxylate species (M- $\eta^1$ -CO<sub>2</sub>- $\kappa C$ ), 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, CO<sub>2</sub> activation with a bimetallic system can be one way to guide the selectivity of the CO<sub>2</sub> catalyst and is receiving much attention.<sup>5,6</sup> In fact, an excellent example of a bimetallic center utilized in an efficient catalytic conversion of CO<sub>2</sub> can be found in the active site of carbon monoxide dehydrogenase (CODH).<sup>7</sup> According to recent studies, CO<sub>2</sub> coordination at a heterobimetallic nickel-iron active site can be found in CODH's intermediate species, which possesses a Ni-µ-CO<sub>2</sub>-Fe moiety, Scheme 1.8 Although X-ray analysis provides a structural snapshot of the CO<sub>2</sub> reduction sequence, the role of the unique

The degree of CO<sub>2</sub> activation can be tuned by incorporating a distinct electronic coordination environment at the nickel center. A mononuclear nickel carboxylate species (Ni–CO<sub>2</sub>, **3**) and a dinuclear nickel–iron carboxylate species (Ni–CO<sub>2</sub>–Fe, **5**) were prepared. The structure of **3** reveals a rare  $\eta^1$ - $\kappa$ C binding mode of CO<sub>2</sub>, while that of **5** shows bridging CO<sub>2</sub> binding ( $\mu_2$ - $\kappa$ C: $\kappa^2$ O,O') between the nickel and iron, presented as the first example of a nickel- $\mu$ -CO<sub>2</sub>-iron species. The structural analyses of **3** and **5** based on XRD and DFT data reveal a higher degree of CO<sub>2</sub> activation in **5**, imparted by the additional interaction with an iron ion.

iron ion is currently not well-understood.<sup>7</sup> Thus, acquiring an understanding of iron assisted CO<sub>2</sub>-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- $\eta^2$ -CO<sub>2</sub> adducts possessing both M-C and M-O bonds.<sup>9</sup> In 1975, Aresta and co-workers reported the first structurally characterized nickel-CO<sub>2</sub> adduct (PCy<sub>3</sub>)<sub>2</sub>Ni( $\eta^2$ -CO<sub>2</sub>), Scheme 1.<sup>9a</sup> An analogous complex, (dtbpe)Ni( $\eta^2$ -CO<sub>2</sub>) (dtbpe = 1,2-bis(di-tertbutylphosphino)ethane) was recently reported by Hillhouse and co-workers.<sup>9d</sup> More recently, our group reported a similar but unique five-coordinate nickel-CO<sub>2</sub> adduct (PP<sup>Me</sup>P)Ni( $\eta^2$ -CO<sub>2</sub>)  $(PP^{Me}P = PMe(2-P^{i}Pr_{2}-C_{6}H_{4})_{2})$ .<sup>9</sup> 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.<sup>9</sup> Additionally, by utilizing an anionic tridentate PNP ligand (PNP<sup>-</sup> = N[2-P<sup>i</sup>Pr<sub>2</sub>-4-Me-C<sub>6</sub>H<sub>3</sub>]<sub>2</sub><sup>-</sup>), our group reported the nickel hydroxycarbonyl species (PNP)NiCOOH (1), (PNP)NiCOONa (2) and  $\{(PNP)Ni\}_2 + CO_2 + \kappa^2 C, O$  (4), the first examples of Ni-CO<sub>2</sub> complexes that reveal a Ni-CO<sub>2</sub>- $\kappa C$  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 (PPMeP)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<sub>2</sub> adducts.

 $CO_2$  and (PNP)Ni– $CO_2$  to evaluate their fundamental differences in  $CO_2$  activation. The different geometries favored with a PP<sup>Me</sup>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)– $CO_2^{--}$ , *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  $\{Na(12-C-4)_2\}$  $\{(PNP)Ni-\eta^1-CO_2-\kappa C\}$  (3), in which the nickel-CO<sub>2</sub> moiety does not have any Lewis acid interactions. We also prepared a dinuclear nickel-iron carboxylate species (PNP)Ni- $\mu$ -CO<sub>2</sub>- $\kappa C$ : $\kappa^2 O$ ,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<sub>2</sub> ligand. The levels of CO<sub>2</sub> activation in compounds 3 and 5 are compared with other Ni-CO<sub>2</sub> adducts and the Ni- $\mu$ -CO<sub>2</sub>-Fe moiety found in CODH.

#### Results and discussion

#### Synthesis and characterization of the Ni- $\eta^1$ -CO<sub>2</sub>- $\kappa C$ 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.<sup>10</sup> 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<sub>2</sub> ligand coordinates to the nickel center in a  $\mu_3$ - $\kappa^1 C$ : $\kappa^2 O$ ,O': $\kappa^1 O'$  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)<sub>2</sub>}{(PNP)Ni- $\eta^{1}$ -CO<sub>2</sub>- $\kappa C$ } (3). The crystal structure of 3 revealed the successful generation of a mononuclear nickel adduct possessing an  $\eta^1$ - $\kappa C$  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



Fig. 1 Displacement ellipsoid (50%) representations for (a) (PNP) NiCOONa (2) in a dimeric assembly with co-crystallized THF molecules,<sup>11</sup> and (b) {Na(12-C-4)<sub>2</sub>}{(PNP)Ni- $\eta^{1}$ -CO<sub>2</sub>- $\kappa$ 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}<sub>2</sub>- $\mu$ -CO<sub>2</sub>- $\kappa^2 C$ , 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  $\pi$  back-bonding between the nickel and  $CO_2$ . In fact,  $\pi$  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, <sup>*n*</sup>Pr) (1.963–2.004 Å).<sup>13</sup> The molecular orbitals generated from DFT calculations also show the presence of  $\pi$  back-donation from the Ni d<sub>xz</sub> to the CO<sub>2</sub>  $\pi^*$ orbital (see ESI<sup>†</sup>). Due to the absence of Lewis acid interactions in 3, a lower  $\pi$ -accepting ability of the CO<sub>2</sub> 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  $(d_{Ni1-O2} = 2.614(1) \text{ Å})$  is slightly closer to the nickel center than the other  $(d_{\text{Ni1-O1}} = 2.776(1) \text{ Å})$ , Table 2. These Ni-O distances are much longer than those for other known Ni- $\eta^2$ -CO<sub>2</sub> 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  $(d_{C1-O1} = 1.247(2) \text{ Å}, d_{C1-O2} = 1.248(2) \text{ Å}, \text{ Table 1})$  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<sub>2</sub>  $\pi^*$ 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
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	<b>1</b> <sup>10</sup>	2 <sup>11</sup>	3	<b>4</b> <sup>10</sup>	5	CODH <sup>8b</sup>
$d_{\rm Ni-C}$ (Å)	1.866(2)	1.882(1)	1.911(2)	1.888(2)	1.858(1)	1.805(31)
$d_{\rm M-O}$ (Å)	_ ()	$2.352(1)^{a}$	_	$1.897(2)^{b}$	$2.204(1)^{c}$	$2.030(18)^{c}$
		$2.217(1)^{a}$			$2.066(1)^{c}$	
		$2.459(1)^{a}$				
$d_{\rm C-O}$ (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)
$\Delta d_{\mathrm{C-O}}$ (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)
<sup><i>a</i></sup> $M = Na$ . <sup><i>b</i></sup> $M = N$	i. $^{c}$ M = Fe.					

 $CO_2^{2-}$  being shifted to the nickel, the  $CO_2$  moiety is slightly oxidized compared to the sp<sup>2</sup> hybridized carboxylate ligands found in 2 and 4. The larger O-C-O angle (128.4(2)°) of 3 compared to others  $(124.0(1) \text{ and } 123.7(2)^{\circ})$  also supports this electronic feature, vide infra. Although an  $\eta^1$ - $\kappa C$  CO<sub>2</sub> coordination mode has been proposed for many CO<sub>2</sub> reduction strategies,<sup>2,3</sup> the only example of a crystallographically identified metal  $\eta^{1}$ - $\kappa C$  CO<sub>2</sub> complex is a rhodium CO<sub>2</sub> adduct, Rh(CO<sub>2</sub>)- $(Cl)(diars)_2$  (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) $^{\circ}$ ), the CO<sub>2</sub> moiety in 3 shares similar structural and electronic features. Thus, compound 3 is a unique example possessing  $\eta^{1}$ - $\kappa C \operatorname{CO}_2$  binding, since such a binding mode is unknown for  $1^{st}$ row transition metals and is rare in structurally characterized metal-CO2 adducts.

#### Synthesis and characterization of the heterobimetallic nickeliron CO<sub>2</sub> 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 CO<sub>2</sub>  $\pi^*$  orbitals provides the DFT calculated HOMO of {Na(12-C-4)<sub>2</sub>}{(PNP)Ni-\eta^1-CO\_2-\kappa C} (3).

fragment by addition of  $\{(PNP)Fe\}^+$  to a Ni- $\eta^1$ -CO<sub>2</sub>- $\kappa C$  species. To a yellow solution of  $\{Na(12-C-4)_2\}\{(PNP)Ni-\eta^1-CO_2-\kappa C\}$  (3) in toluene, a purple solution of (PNP)FeCl was added. The immediate formation of a new orange species (PNP)Ni-µ-CO2- $\kappa C:\kappa^2 O, O'$ -Fe(PNP) (5) was confirmed, using the <sup>1</sup>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  $\mu_2$ - $\kappa C$ : $\kappa^2 O$ , 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 bo	ond indices from th	ne natural bond	orbital analysis
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	$Ni(PCy_3)_2(\eta^2-CO_2)^{9a}$	$(dtbpe)Ni(\eta^2-CO_2)^{9d}$	$(PP^{Me}P)Ni(\eta^2-CO_2)^{9f}$	3	5
Structural parameters					
$d_{\rm Ni-C}$ (Å)	1.84(2)	1.868(2)	1.904(1)	1.911(2)	1.858(1)
$d_{\rm Ni-O}$ (Å)	1.99(2)	1.904(2)	2.191(1)	2.614(1)	2.718(1)
				2.776(1)	2.792(1)
$d_{\text{C-O}}(\text{\AA})$	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)
$\nu_{\rm CO_2}  ({\rm cm}^{-1})$	1740	1724	1682	1620	1510
Wiberg bond indices <sup>a</sup>					
Ni-C		0.5766	0.5286	0.6143	0.6277
Ni-O		0.4300	0.3117	0.1679	0.0798
				0.1358	0.0644
С-О	_	1.6927	1.6384	1.5112	1.3993
		1.4080	1.4701	1.4949	1.2933

<sup>a</sup> 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- $\mu$ -CO<sub>2</sub>- $\kappa$ C: $\kappa$ <sup>2</sup>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 ( $\tau = 0.13$ ,<sup>15</sup> 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<sub>2</sub> molecule ( $\angle O$ -C-O = 117.2(26)°) is a carboxylate anion (CO2<sup>2-</sup>).<sup>8b,8c</sup> Regarding the similarity between these angles, the carboxylate moiety in 5 might be close to  $CO_2^{2-}$ . The asymmetric vibration for CO<sub>2</sub> observed at 1510 cm<sup>-1</sup>, which is similar to that observed for the dinickel carboxylate species (4) at 1518 cm<sup>-1</sup>, also indicates a reduced state of CO<sub>2</sub>. The effective magnetic moment of 5 was determined using the Evans' method ( $\mu_{eff} = 4.95 \ \mu_{B}$  in C<sub>6</sub>D<sub>6</sub>), 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<sup>†</sup>). For CODH, the unique iron, Fe<sub>u</sub>, was assigned as a high spin iron( $\pi$ ) (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  $\mu_2$ - $\kappa C$ : $\kappa^2 O, O'$  binding modes of CO2 into two types according to the difference between the two C-O distances.<sup>19</sup> Due to the two similar C-O distances of the CO<sub>2</sub> moiety, compound 5 ( $\Delta d_{C-O} = 0.020$  Å) can be assigned as a class I complex.<sup>20</sup> In the dinickel CO<sub>2</sub> species (4), the CO<sub>2</sub> molecule is coordinated in a  $\mu_2$ - $\kappa$ C: $\kappa$ 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, CO<sub>2</sub> is coordinated in a  $\mu_2$ - $\kappa C$ : $\kappa O$  fashion between the nickel and iron ions, but the two C-O bond distances are quite comparable  $(\Delta d_{\rm C-O} = 0.018 \text{ Å})$ , akin to the  $\mu_2$ - $\kappa C$ : $\kappa^2 O$ , O' mode. This might be due to hydrogen bonding with the protein matrix, since both the CO<sub>2</sub> oxygens are hydrogen bonded to His93 and Lys563, respectively.8

Compound 5 is the first example of a dinuclear nickel-iron-CO<sub>2</sub> complex. While dinuclear CO<sub>2</sub> complexes mostly employ  $2^{nd}$  and  $3^{rd}$  row transition metals,<sup>19</sup> several bimetallic iron carboxylates (Fe-CO<sub>2</sub>-M, M = Ti, Zr, Sn, Re) have been reported.<sup>5a,5c-e,21</sup> However, such complexes typically possess an Fe-C bond rather than an Fe-O bond with CO<sub>2</sub>. There have been numerous examples of nickel-iron bimetallic complexes reported for synthetic model studies of NiFe hydrogenase,<sup>22</sup> but a bimetallic complex possessing a Ni- $\mu$ -CO<sub>2</sub>-Fe moiety closely related to CODH chemistry is not known. The Holm group constructed a series of [NiFe<sub>3</sub>S<sub>4</sub>] cubanes as structural model complexes for the [NiFe<sub>4</sub>S<sub>4</sub>] core in CODH.<sup>23</sup> However, the installation of an iron species corresponding to the Fe<sub>u</sub> in CODH and reactions involving CO and CO<sub>2</sub> have not yet been investigated. More recently, the Holm group also reported a bimetallic complex containing nickel and iron supported by a binucleating macrocycle.<sup>24</sup> With respect to CODH chemistry, bridging hydoroxo, cyanido and formato species have been generated, however, a Ni- $\mu$ -CO<sub>2</sub>-Fe fragment had not yet been isolated.

#### Activation of CO<sub>2</sub> in 3 and 5

Previously known 4-coordinate Ni-CO<sub>2</sub> complexes possessing an  $\eta^2$ -CO<sub>2</sub> binding mode have a formally zero-valent nickel center, Scheme 1.9 This suggests limited CO<sub>2</sub> activation in such species. Interestingly, the 5-coordinate nickel CO2 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<sub>2</sub> binding and activation, {Na(12-C-4)<sub>2</sub>}{(PNP)Ni- $\eta^1$ -CO<sub>2</sub>- $\kappa C$  (3) is a unique example. It is striking that a neutral pincer-type ligand  $PP^{Me}P(PP^{Me}P = PMe[2 - P^{i}Pr_2 - C_6H_4]_2)$  favors 5coordinate  $\eta^2$ -CO<sub>2</sub> coordination at a single nickel center, while 3 remains as a 4-coordinate species with η<sup>1</sup>-CO<sub>2</sub> coordination.<sup>9</sup> Although the total number of Ni d-electrons and  $CO_2 \pi^*$ -electrons in both 3 and (PP<sup>Me</sup>P)Ni(CO<sub>2</sub>) is the same, (PP<sup>Me</sup>P)Ni(CO<sub>2</sub>) can be considered as formally Ni(0)-(CO<sub>2</sub>) 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<sup>-1</sup>, compared to those of the Ni- $\eta^2$ -CO<sub>2</sub> 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  $\pi$ -acidic P atom in the PP<sup>Me</sup>P 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  $(PP^{Me}P)Ni(CO_2)$  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  $128.4(2)^{\circ}$  is larger than those of an ideal sp<sup>2</sup> hybridized carbon  $(120^\circ)$  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<sub>2</sub> radical anion (CO<sub>2</sub><sup>•</sup>) is suggested to be 133°,25 which is fairly similar to those of the previously reported Ni- $\eta^2$ -CO<sub>2</sub> 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<sup>-1</sup>, 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<sub>2</sub> 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).<sup>10</sup> From reaction of 3 with 1 equiv. of HBF<sub>4</sub>·Et<sub>2</sub>O, a nickel hydroxycarbonyl species (1) was produced and isolated with a 74% vield. A similar reaction of 3 with 2 equiv. of HBF<sub>4</sub> · Et<sub>2</sub>O resulted in the formation of a carbonyl species  $\{(PNP)NiCO\}$  BF<sub>4</sub> $\}$  in 75% vield, revealing that two sequential protonations can occur with compound 3 possessing a Ni- $\eta^1$ -CO<sub>2</sub>- $\kappa C$  moiety, which are key steps in the transformation of CO<sub>2</sub> 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<sub>2</sub> adduct {Na(12-C-4)<sub>2</sub>}{(PNP)Ni- $\eta^1$ -CO<sub>2</sub>- $\kappa C$ } (3) and a dinuclear nickel-iron carboxylate species (PNP)Ni-μ-CO<sub>2</sub>-κC:κ<sup>2</sup>O,O'-Fe(PNP) (5) were synthesized successfully. While the solid state structure of 3 revealed a rare  $\eta^{1}$ - $\kappa C$  binding mode, compound 5 was structurally characterized to reveal a unique class I type  $\mu_2$ - $\kappa C: \kappa^2 O, O'$  binding mode. This heterobimetallic CO<sub>2</sub> 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<sub>2</sub>-Fe fragment found in the C-cluster of CODH. Comparison of the  $\eta^1$ -CO<sub>2</sub>- $\kappa C$  species 3 and dinuclear Ni- $\mu$ -CO<sub>2</sub>-Fe species 5 with previously reported Ni-CO<sub>2</sub> adducts suggested that the CO<sub>2</sub> ligand can be stabilized and activated by interaction with the second metal. Protonation of 3 produces a nickel carbonyl species {(PNP)NiCO}{BF<sub>4</sub>} 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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the  $CO_2$  ligand symmetrically bonded to M' and class II complexes possess two asymmetric M'–O bonds.

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