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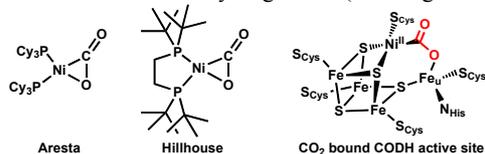
Formation of a Nickel Carbon Dioxide Adduct and its Transformation Mediated by a Lewis Acid

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An uncommon nickel dinitrogen adduction and its tendency toward CO₂ binding are investigated with a (PP^{Me}P)Ni scaffold. (PP^{Me}P)Ni(N₂) (**1**) and {(PP^{Me}P)Ni}₂(μ-N₂) (**2**) were prepared and its treatment with CO₂ revealed the formation of (PP^{Me}P)Ni(η²-CO₂) (**3**). This is a new type of CO₂ binding for a zero-valent nickel center supported by three donor ligands, reminiscent to the CODH active site environment. Clear unique structural differences in **3** are evident when comparing with previous 4-coordinate Ni-CO₂ adducts. Compound **3** when treated with B(C₆F₅)₃ gives the Lewis acid-base adduct (PP^{Me}P)Ni{COOB(C₆F₅)₃} (**4**) possessing a Ni-μ-CO₂-κ²C, O-B moiety.

Carbon dioxide adducts of transition metals are drawing much attention due to their importance in developing synthetic catalysts.¹ Several binding modes of CO₂ have been known for certain transition metals thus supplying crucial mechanistic snapshots for the activation of carbon dioxide at the metal center.¹ In 1975, Aresta and coworkers firstly reported the structurally characterized nickel CO₂ adduct (PCy₃)₂Ni(η²-CO₂) generated from the reaction of {(PCy₃)₂Ni}₂(N₂) with CO₂.^{2,3} A closely related example, (dtbpe)Ni(η²-CO₂) (dtbpe = 1,2-bis(di-tert-butylphosphino)ethane) was recently reported by Hillhouse and coworkers.⁴ Both nickel complexes possessing a 4-coordinate nickel center supported by two phosphorus donor atoms and η²-CO₂, are the only examples of the structurally characterized mononuclear nickel-CO₂ species reported in the literature (See diagram below). Although there are a series of metal complexes generated from the reaction of carbon dioxide, they are mostly employing transition metals such as Fe, Co, Ru, Ir and Os.⁵ Carbon dioxide adduct formation with nickel is of particular interest due to its relevance in biological CO₂ conversion, e.g., C-cluster of carbon monoxide dehydrogenases (See diagram below).⁶



In particular, further elucidating the chemistry of low-valent nickel supported by a tridentate ligand in which a pseudo-tetrahedral or square planar geometry can be accommodated, is essential in understanding how enzymatic conversion of CO₂ to CO occurs at the FeNi-binuclear active site of CODH. Since the N₂ ligand is sufficiently labile to be replaced by other small molecules such as H₂, CO and CO₂ at the desired metal center, the metal-N₂ species can be conveniently utilized as a precursor in the preparation of a nickel-

CO₂ adduct.⁷ To attain reactivity for a zero-valent nickel species in a tetracoordinate environment, we have employed a neutral PP^{Me}P ligand (PP^{Me}P = PMe[2-PⁱPr₂-C₆H₄]₂) modified from the anionic PPP ligand previously reported in the literature.⁸ Herein, we report the synthesis and characterization of a dinuclear nickel dinitrogen complex {(PP^{Me}P)Ni}₂(μ-N₂) (**2**) and a mononuclear nickel carbon dioxide species (PP^{Me}P)Ni(η²-CO₂) (**3**), both fairly uncommon species in organonickel chemistry. Interesting structural differences between previously reported Ni-CO₂ adducts and **3** exist.

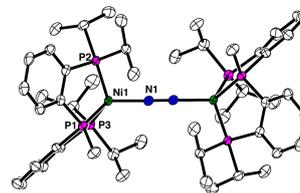
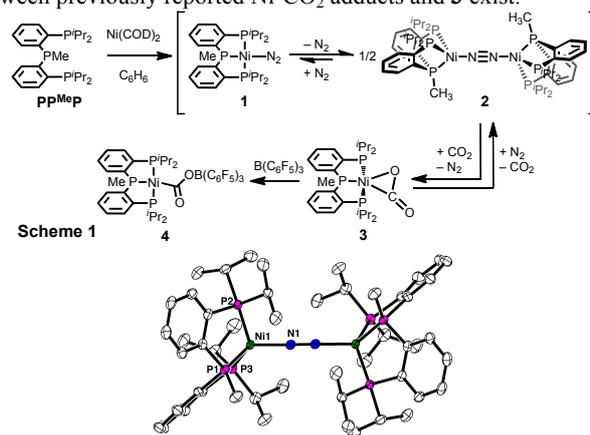


Figure 1. Displacement ellipsoid (50%) representation of {(PP^{Me}P)Ni}₂(μ-N₂) (**2**). Hydrogen atoms of PP^{Me}P are omitted for clarity. Selected bond distances (Å) and angles (°) for **2**: Ni1-N1 1.830(2), Ni1-P1 2.1168(5), Ni1-P2 2.1627(5), Ni1-P3 2.1544(5), N1-N1 1.124(3), Ni1-N1-N1 178.6(2). See SI for details.

The desired PP^{Me}P ligand was synthesized in good yield (>90%) via methylation of PPPCl with a methyl Grignard reagent in tetrahydrofuran. Metalation was accomplished by the reaction of a PP^{Me}P ligand with Ni(COD)₂ in benzene under N₂ atmosphere (Scheme 1). The product was isolated as a diamagnetic brown solid in moderate yield (70.9%) revealing two sets of phosphorus signals with a 1:1 ratio according to the integration of the corresponding peaks in ³¹P-NMR spectrum in C₆D₆ (Figure 2a). Due to the presence of a strong vibration at 2083 cm⁻¹ (Δ(¹⁵N₂) = 70) in the solution IR spectrum (benzene, N₂), one of the species was assigned as a mononuclear nickel-dinitrogen species, (PP^{Me}P)Ni(N₂) (**1**) (Supporting Information). At lower concentration (0.5 mM with respect to Ni in C₆D₆) of the brown solid, **1** was raised as a single species under 1 atm of N₂ (64.56 ppm (d, J = 54.3 Hz) and 19.02 ppm (t, J = 54.2 Hz) in the ³¹P-NMR spectrum, Figure 2b). After the

solution of the nickel complex was degassed in an NMR tube with a J-Young valve, the other species was formed solely revealing a doublet-like signal centered at 64.75 ppm ($J = 68.8$ Hz) and a triplet-like signal centered at 14.66 ppm ($J = 68.8$ Hz) (Figure 2c).

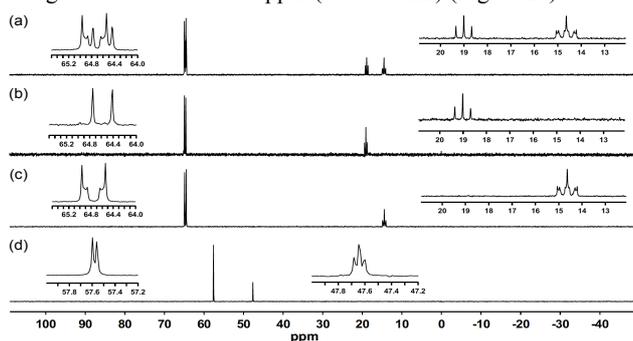


Figure 2. ^{31}P -NMR spectra (C_6D_6) of (a) a 6 mM solution of $(\text{PP}^{\text{MeP}}\text{Ni})(\text{N}_2)$ (**1**) with $\{(\text{PP}^{\text{MeP}}\text{Ni})_2(\mu\text{-N}_2)\}$ (**2**) under 1 atm N_2 , (b) **1** in lower concentration (0.5 mM), (c) **2** under vacuum and (d) $(\text{PP}^{\text{MeP}}\text{Ni})(\eta^2\text{-CO}_2)$ (**3**) generated from the addition of CO_2 (g) to the solution of **2**.

X-ray crystal structure of $\{(\text{PP}^{\text{MeP}}\text{Ni})_2(\mu\text{-N}_2)\}$ (**2**) (Figure 1) reveals a dinuclear nickel adduct in which a N_2 molecule is bridging through end-on binding mode. Two crystallographically equivalent nickel centers possess a pseudo tetrahedral geometry supported by a PP^{MeP} ligand (Figure 1). The triple bonding character of the bound N_2 ligand is ensured by its interatomic N-N distance of 1.124(3) Å, close to that of free N_2 (1.0976 Å), indicative of minimal π back-bonding. Raman data in both solid and solution states confirms a vibration of 2045 (neat) and 2042 (in benzene, $\Delta(^{15}\text{N}_2) = 68$) cm^{-1} , respectively (Supporting Information), similar to previously reported dinuclear Ni- N_2 species, *vide infra*.⁹ Due to the weak binding of N_2 , **1** and **2** are in equilibrium under 1 atm of N_2 (g) (Scheme 1 and Figure 1). Under 1 atm of N_2 and exploiting the ^1H -NMR signals of **1** and **2** at ~ 2 ppm, we estimated the equilibrium constant to be 8.6 ± 1.2 in favor of the dinuclear formation in C_6D_6 at room temperature (Supporting Information). This equilibrium was also supported by ^{15}N -NMR data involving a mixture of **1** and **2** measured at -60 °C in toluene- d_8 . Under 1 atm of $^{15}\text{N}_2$ (g), a sharp signal for **2** appears at -74.9 ppm and a set of two signals for **1** appear at -53.7 and -71.3 ppm with a free $^{15}\text{N}_2$ signal at -70.4 ppm (Supporting Information). By applying vacuum, a signal corresponding to **2** only remains. A few examples of nickel-dinitrogen species were previously reported.⁹ Compound **2** features the first structurally characterized 4-coordinate dinickel N_2 species.

The addition of CO_2 (1 atm) to a brown C_6D_6 solution of **2** resulted in a rapid conversion (<10 min at room temperature) to an orange species characterized as $(\text{PP}^{\text{MeP}}\text{Ni})(\eta^2\text{-CO}_2)$ (**3**), which was isolated as an orange powder in good yield (92%) (Scheme 1 and Supporting Information). The ^{31}P -NMR spectrum suggests a diamagnetic species with a doublet signal at 57.58 ppm ($J = 6.0$ Hz) and a triplet signal at 47.64 ppm ($J = 6.3$ Hz) (Figure 2d). X-ray quality single crystals were obtained from a cold saturated benzene solution of **3** at 18 °C. According to XRD data, the structure of **3** contains one η^2 -bound CO_2 molecule, reminiscent of the previously reported Ni- CO_2 adducts (Figure 3).^{2,3,4} The O-C-O bond angle of $135.1(1)^\circ$ suggests that the central carbon atom is perturbed from *sp* hybridization by the interaction with nickel, similar to the previous example of $(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)$ where O-C-O bond

angle is $138.0(2)^\circ$.⁴ The C(1)-O(1) bond distance in **3** is 1.218(2) Å, slightly elongated compared to those of $(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)$ and $(\text{PCy}_3)_2\text{Ni}(\eta^2\text{-CO}_2)$ (1.200(3) Å and 1.17 Å, respectively)^{2,3,4} (Table 1). IR data of **3** also reveal a C=O vibrational frequency at 1682 cm^{-1} ($\Delta(^{13}\text{CO}_2) = 44$) lower than those for other two known species, $1724\text{--}1740$ cm^{-1} , supporting C=O bond elongation.^{2,3,4}

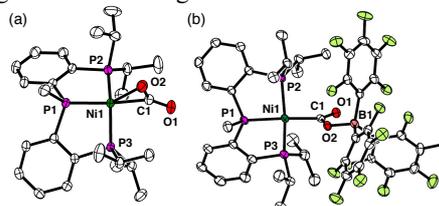


Figure 3. Displacement ellipsoid (50%) representation of (a) $(\text{PP}^{\text{MeP}}\text{Ni})(\eta^2\text{-CO}_2)$ (**3**) and (b) $(\text{PP}^{\text{MeP}}\text{Ni})(\text{COOB}(\text{C}_6\text{F}_5)_3)$ (**4**). A co-crystallized toluene molecule and hydrogen atoms of PP^{MeP} are omitted for clarity. See Table 1 and SI for details.

Table 1. Selected bond distances and angles of $(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)$, **3** and **4**.

	$(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)^4$	3	4
ν_{CO} (cm^{-1})	1724	1682	1639
C-O (Å)	1.200(3) 1.266(3)	1.218(2) 1.252(2)	1.223(4) 1.340(4)
Ni-C (Å)	1.868(2)	1.904(1)	1.923(3)
Ni-O (Å)	1.904(2)	2.191(1)	–
O-C-O ($^\circ$)	138.0(2)	135.1(1)	122.9(3)
Ni-C-O ($^\circ$)	149.3(2) 71.9(1)	139.5(1) 85.30(9)	129.7(3) 107.4(2)

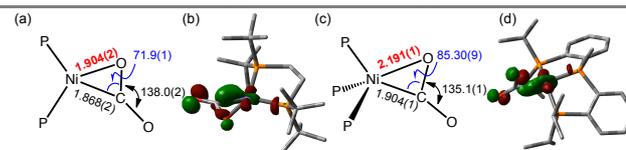


Figure 4. Comparison of the selected bond distance (Å) and angle ($^\circ$) in the core structures of (a) $(\text{dtbpe})\text{NiCO}_2$ and (c) **3**. DFT calculated HOMOs of (b) $(\text{dtbpe})\text{NiCO}_2$ and (d) **3**.

There are in fact, interesting differences when comparing **3** with previous 4-coordinate nickel CO_2 adducts. First, while the CO_2 moiety of $(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)$ accommodates the planar nickel geometry via a Ni-C(1) bond (1.868(2) Å), the moiety of **3** reveals orthogonal binding to the 5-coordinate nickel center (the plane of a CO_2 moiety is perpendicular to the $(\text{PP}^{\text{MeP}}\text{Ni})$ plane) with a Ni-C(1) bond (1.904(2) Å) (Figure 4).⁴ Secondly, the nickel oxygen bond distance is noticeably elongated in **3**, 2.191(1) vs. 1.904(2) Å (Figure 4 and Table 1). This might be due to the antibonding character between a oxygen atom and a nickel center in the HOMO of **3**, whereas $(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)$ reveals the partial bonding character according to DFT analyses (Figure 4 and Supporting Information). A bound CO_2 ligand in **3** can be replaced by N_2 to generate a nickel dinitrogen species as the mixture of **1** and **2**. However, a CO_2 molecule cannot be liberated by vacuum suggesting the reasonable stability of **3** in a solution state. Recent CODH structural studies have included the observation of substrate CO_2 bound species.⁶ Zero-valent nickel supported by three sulfur ligands (two μ_3 -sulfido and C526) is currently hypothesized to initially bind CO_2 (See diagram). Yet, no structural example in organonickel chemistry shows CO_2 coordination in a CODH-like environment. Thus, the structure of **3** reveals a binding mode of CO_2 (Figure 3) that

may serve as the precursor to the structurally characterized Ni(CO)₂Fe adduct, but yet has not been observed for any 5-coordinate Ni-adducts.

Since the oxygen atom of the bound CO₂ moiety in **3** is relatively weakly bound to a nickel center, we thus thought that it is more available for electrophilic attack. To a THF solution of **3** trispentafluorophenyl borane was added under argon atmosphere to give a yellow product (PP^{Me}P)Ni{COOB(C₆F₅)₃} (**4**) in moderate yield, 64% (Scheme 1 and Supporting Information). A new set of ³¹P-NMR peaks at 64.07 ppm (t, *J* = 20.6 Hz) and 63.56 ppm (d, *J* = 20.3 Hz) for **4** appear revealing a central phosphorus atom of a PP^{Me}P ligand has been dramatically affected by the strong boron-based Lewis acid (Supporting Information). Corresponding effect of the borane interaction in **4** also appears in the C=O vibration; 1631 cm⁻¹ shifted from 1682 cm⁻¹ of **3** and also in ¹³C NMR data; 185.47 ppm (dt, *J*_{PC} = 104.2, 14.0 Hz) shifted from 164.70 ppm (d, *J*_{PC} = 51.4 Hz) (Supporting Information). According to the X-ray structure of **4**, one of the oxygen atoms of the CO₂ moiety is coordinated to a B(C₆F₅)₃ group clearly resulting in a 4-coordinate nickel(II)-COOB₃ species (Table 1 and Figure 3). Analogous examples possessing Ni(II)-COO⁻κC moieties have been previously reported by our group.¹⁰ Both (PNP)Ni-COOH-κC and (PNP)Ni-μ-CO₂-κ²C, O-Ni(PNP) (PNP⁻ = N[2-P^{Pr}₂-4-Me-C₆H₃]₂⁻), along with **4** reveal the structural similarity in the binding mode reminiscent to that of the Ni-COO-Fe fragment found at the CODH active site.⁶

In order to compare the relative stability of the corresponding borane adducts to (dtbpe)Ni(η²-CO₂) and **3**, we conducted theoretical calculations on both (PP^{Me}P)Ni{COOB(CH₃)₃} and the hypothetical borane adduct, (dtbpe)Ni{CO₂-B(CH₃)₃} (Supporting Information).¹¹ While the geometry optimization of (PP^{Me}P)Ni{COOB(CH₃)₃} was successful and in agreement with the corresponding XRD data of **4**, the structural calculation failed to stabilize a borane adduct of (dtbpe)Ni(η²-CO₂)¹² indicating that the nickel-CO₂ adduct supported by two phosphorus donor atoms and the 14-electron nickel(II) product species might not favor attack on an exogenous Lewis acid in the absence of an additional donor ligand (Supporting Information). According to NBO analysis, a Wiberg Ni-O bond index of 0.31 in **3** is calculated, compared with a corresponding value of 0.43 for (dtbpe)Ni(η²-CO₂) revealing a relatively weak Ni-O interaction in **3** (Supporting Information). In fact, DFT optimization of both borane adducts revealed more dramatic differences. While a Wiberg Ni-O bond index was reduced to 0.16 in (PP^{Me}P)Ni{COOB(CH₃)₃} along with a B-O bond index of 0.44, a negligible effect on the corresponding Ni-O bond index was found for (dtbpe)Ni(η²-CO₂), suggesting a minimal interaction with a borane Lewis acid. Further experiments will be necessary to evaluate the relative reactivity and stability of 4- or 5-coordinate nickel species regarding CO₂ activation.

In summary, the current study reveals two uncommon small molecule species with zero-valent nickel, a dinickel-N₂ species (**2**) and a mononuclear-CO₂ adduct (**3**) supported by a neutral PP^{Me}P pincer ligand. The dinickel-dinitrogen species {(PP^{Me}P)Ni}₂(μ-N₂) (**2**) shows a weak binding of N₂ to the zero-valent nickel center, which enabled access to the Ni-CO₂ adduct. Reversible interconversion between Ni-N₂-Ni and Ni-CO₂ demonstrates the practicality of the (PP^{Me}P)Ni scaffold for accommodating a CO₂ binding and in studying this activated molecule. The structure of a nickel-carbon dioxide species (PP^{Me}P)Ni(η²-CO₂) (**3**), the first structurally characterized 5-coordinate mononuclear nickel carbon dioxide complex,

illustrates a new type of CO₂ intermediates which is an unique metal binding mode of CO₂ in organometallic chemistry and can be a potential novel intermediate present in the CODH enzymatic mechanism. Further studies particular to the reactivity of **3** regarding the CO₂ activation are currently under investigations. During this first phase, we were successful in obtaining the (PP^{Me}P)Ni{COOB(C₆F₅)₃} (**4**) adduct which bears resemblance to the {Ni-η¹-COO-Fe} structure in CODH.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and crystallographic details. CCDC-993623, CCDC-993624 and CCDC-994135. See DOI: 10.1039/c000000x/

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