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An uncommon nickel dinitrogen adduction and its tendency toward CO₂ binding are investigated with a (PPMe₃)Ni scaffold. (PPMe₃)Ni(N₂) (1) and [(PPMe₃)Ni]₂(μ-N₂) (2) were prepared and their treatment with CO₂ revealed the formation of (PPMe₃)Ni(μ₂-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 (PPMe₃)Ni[COOB(C₆F₅)₂] (4) possessing a Ni-μ-κ²C,κ-O-B moiety.

Carbon dioxide adducts of transition metals are drawing much attention due to their importance in developing synthetic catalysts. 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. In 1975, Aresta and coworkers firstly reported the structurally characterized nickel CO₂ adduct (PCy₃)Ni(μ₂-CO₂) generated from the reaction of (PCy₃)NiCl₂ with CO₂. A closely related example, (dbpe)Ni(μ₂-CO₂) (dbpe = 1,2-bis(di-tert-butylphosphino)ethane) was recently reported by Hillhouse and coworkers. Both nickel complexes possessing a 4-coordinate nickel center supported by two phosphorus donor atoms and μ₂-CO₂ are the only examples of the structurally characterized mononuclear nickel-CO₂ species reported in the literature. 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. 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.

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. To attain reactivity for a zero-valent nickel species in a tetracoordinate environment, we have employed a neutral PPMe₃ ligand (PPMe₃P = PMe₂PPPh₂(C₆H₃)) modified from the anionic PPP ligand previously reported in the literature. Herein, we report the synthesis and characterization of a dinuclear nickel dinitrogen complex [(PPMe₃)Ni]₂(μ₂-N₂) (2) and a mononuclear nickel carbon dioxide species (PPMe₃)Ni(μ₂-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 [(PPMe₃)Ni]₂(μ₂-N₂) (2). Hydrogen atoms of PPMe₃ 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), Ni1-N1 1.124(3), Ni1-N1 1.178.6(2). See SI for details.

The desired PPMe₃P 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 PPMe₃P ligand with Ni(CO₃)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 (Δv(N₂) = 70) in the solution IR spectrum (benzene, N₂), one of the species was assigned as a mononuclear nickel-dinitrogen species, (PPMe₃P)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 
I-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$_6$D$_6$) of (a) a 6 mM solution of 
(PPh$_4$)Ni(N$_2$)$_2$ (1) with (PPh$_4$)Ni(μ-μ-N$_2$) (2) under 1 atm N$_2$, (b) 
1 in lower concentration (0.5 mM), (c) 2 under vacuum and (d) 
(PPh$_4$)Ni(η$_2$-CO$_2$) (3) generated from the addition of CO$_2$ (g) to the 
solution of 2.

X-ray crystal structure of [(PPh$_4$)Ni]$^2$(μ-μ-N$_2$) (2) (Figure 1) 
reveals a dinuclear nickel adduct in which a N$_2$ molecule is 
briding through end-on binding mode. Two crystallo-
graphically equivalent nickel centers possess a pseudo 
tetrahedral geometry supported by a PPh$_4$ 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 
transformation of 2045 (near) and 2042 (in benzene, Δ(15N$_2$) = 68) 
cm$^{-1}$, respectively (Supporting Information), similar to 
previously reported dinuclear Ni$_2$ species, vide infra. 
Due to the weak binding of N$_2$, 1 and 2 are in equilibrium under 1 atm 
of N$_2$ (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$_6$D$_6$ 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$_6$. Under 1 atm of $^{15}$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 $^{15}$N$_2$ signal at –70.4 ppm 
(Supporting Information). By applying vacuum, a signal 
corresponding to 2 only remains. A few examples of nickel-
diinertogen species were previously reported. 
Compound 2 
features the first structurally characterized 4-coordinate dinickel 
N$_2$ species. 

The addition of CO$_2$ (1 atm) to a brown C$_6$D$_6$ solution of 2 
resulted in a rapid conversion (~10 min at room temperature) to an 
orange species characterized as (PPh$_4$)Ni(η$_2$-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). The O-C-O bond angle of 135.1(1)$^\circ$ 
suggests that the central carbon atom is perturbed from sp 
hybridization by interaction with nickel, similar to the 
previous example of (dtbpe)Ni(η$_2$-CO$_2$) where O-C-O bond 
angle is 138.0(2)$^\circ$. The C(1)-O(1) bond distance in 3 is 
1.218(2) Å, slightly elongated compared to those of 
(dtbpe)Ni(η$^2$-CO$_2$) and (PCy$_3$)$_2$Ni(η$^2$-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$^{-1}$ (Δ($^1$CO$_2$) = 44) lower 
than for other two known species, 1724–1740 cm$^{-1}$, 
supporting C=O bond elongation.$^{2,3,4}$

Figure 3. Displacement ellipsoid (50%) representation of (a) 
(PPh$_4$)Ni(η$^2$-CO$_2$) (3) and (b) (PPh$_4$)Ni(COOB(C$_3$)$_3$Me) (4). 
A co-crystallized toluene molecule and hydrogen atoms of 
PPh$_4$ are omitted for clarity. See Table 1 and SI for details.

Table 1. Selected bond distances and angles of (dtbpe)Ni(η$_2$-
CO$_2$), 3 and 4.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle ($^\circ$)</th>
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<tr>
<td>C-O</td>
<td>1.200(3)</td>
<td>128.6(3)</td>
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<tr>
<td>O-C-O</td>
<td>1.218(2)</td>
<td>135.1(1)</td>
</tr>
<tr>
<td>Ni-C(O)</td>
<td>1.868(2)</td>
<td>138.0(1)</td>
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<tr>
<td>Ni-O</td>
<td>1.904(2)</td>
<td>119.0(1)</td>
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<tr>
<td>C=O</td>
<td>1.210(3)</td>
<td>128.6(3)</td>
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<tr>
<td>O-C-O</td>
<td>1.223(4)</td>
<td>138.0(1)</td>
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<tr>
<td>Ni-C(O)</td>
<td>1.868(2)</td>
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</tr>
<tr>
<td>Ni-O</td>
<td>1.904(2)</td>
<td>119.0(1)</td>
</tr>
</tbody>
</table>

Figure 4. Comparison of the selected bond distance (Å) and 
angle ($^\circ$) in the core structures of (a) (dtbpe)NiCO$_2$ and 
(c) 3. DFT calculated HOMOs of (b) (dtbpe)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 (dtbpe)Ni(η$_2$-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 (PPh$_4$)Ni 
plane) with a Ni-C(1) bond (1.904(2) Å) (Figure 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 (dtbpe)Ni(η$_2$-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 S$^2$) 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 

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may serve as the precursor to the structurally characterized Ni(CO)Fe 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 consider that it is more available for electrophilic attack. To a THF solution of 3 tris(pentafluorophenyl)borane was added under argon atmosphere to give a yellow product (PP3P)Ni{COOB(CF3)3};\(4\) in moderate yield, 64% (Scheme 1 and Supporting Information). A new set of \(^{13}C\) NMR peaks at 64.07 ppm (d, J = 16.8 Hz) and 63.56 ppm (d, J = 14.0 Hz) were observed for the corresponding borane adducts to the Ni−η\(^2\)-COO−Fe structure, illustrating the same bonding mode reminiscent to that of the Ni−η\(^2\)-COO−Fe adduct in CODH. Further experiments will be necessary to evaluate the relative reactivity and stability of 4 regarding CO2 activation in this system.

In order to compare the relative stability of the corresponding borane adducts to (dtbpe)Ni(η\(^2\)-CO2) and 3, we conducted theoretical calculations on both (PP3P)Ni{COOB(CF3)3} and the hypothetical borane adduct, (dtbpe)Ni{CO2-B(CF3)3} (Supporting Information). While the geometry optimization of (PP3P)Ni{COOB(CF3)3} was successfully obtained using the X-ray crystallographic data of 4, the structural calculation failed to stabilize a borane adduct of (dtbpe)Ni(η\(^2\)-CO2)\(12\) indicating that the nickel-CO2 adduct supported by two phosphorus donor atoms and the 14-electron nickel(II) 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(η\(^2\)-CO2)\(12\) 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 (PP3P)Ni{COOB(CF3)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(η\(^2\)-CO2)\(12\), 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 PP3P phosphorus donor ligand. The dinickel-dinitrogen species \{(PP3P)Ni]2(η\(^2\)-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 practicability of the (PP3P)Ni scaffolds for accommodating a CO2 binding and in studying this activated molecule. The structure of a nickel-carbon dioxide species (PP3P)Ni[η\(^2\)-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 (PP3P)Ni{COOB(CF3)3};\(4\) adduct which bears resemblance to the [Ni-η\(^2\)-COO−Fe] structure in CODH.