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Generation of a Doubly Bridging CO_2 Ligand and Deoxygenation of CO_2 by an (NHC)Ni(0) Complex

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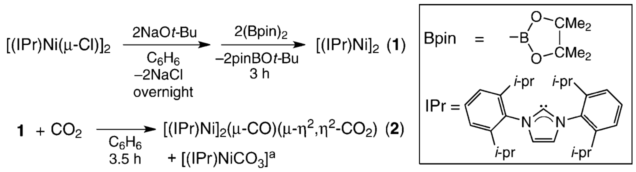
Carbon dioxide is a useful carbon source for the synthesis of organic molecules,[1] and it is a small molecule that figures prominently in global energy scenarios.[2,3] Transition metal complexes offer a wide range of strategies for CO_2 fixation and activation.[1,4,5] Often CO_2 is reduced to CO at a metal center with the concomitant formation of strong metal−oxygen bonds to compensate for overcoming the high enthalpy of the O═CO bond. Such reactivity is observed at the metal center of U^{III} to produce free CO and U^{IV}-(μ-O)U^{IV} [6] and at Fe^{I} to produce CO bound within a $Fe^{II}(\mu\text{-O})(\mu\text{-CO})Fe^{II}$ core.[7] We have recently shown that oxygen can catalytically be abstracted from CO_2 at the metal center of a carbene-supported Cu^{I} center at turnovers exceeding 10^3.[8] In nature, catalytic CO_2 reduction is performed by the enzyme acetyl-CoA synthase/CO dehydrogenase (ACS-CODH)[9,10] with the Ni site of the C-cluster in the CODH subunit believed to play a crucial role in CO_2 reduction.[11,12] The anticipation of the importance of Ni in fixing CO_2 at synthetic active sites is borne out in Kubiak et al.'s resourceful use of dinuclear and trinuclear nickel complexes to reduce CO_2[13−15] and Louie et al.'s catalytic fixation of CO_2 in organic substrates by $(NHC)_2Ni(0)$ (N-heterocyclic carbene) precatalysts that were generated in situ.[16,17] We now report the reduction of CO_2 by a (NHC)Ni(0) complex gives rise to a heretofore unknown coordination mode for CO_2, μ-η^2,η^2-CO_2, at a dinickel core.

The reaction of $[(IPr)Ni(\mu\text{-Cl})]_2$[18] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with NaO*t*-Bu in benzene followed by the addition of an excess of bis(pinacolato)diboron caused the solution to change from yellow to brown to reddish brown. A ^{1}H NMR spectrum of the reacted solution indicated the clean formation of the new nickel complex **1** (Scheme 1). When a crystalline solid of **1** is dissolved in C_6D_6, the ^{1}H NMR spectrum of the NHC backbone protons is distinct. However, over the course of a week, the ^{1}H NMR changes and a single resonance appears for the backbone protons (see Figure S1). We propose that dimer **1** slowly dissociates in benzene solution, likely forming the monomer, (IPr)Ni(η^6-C_6D_6). We note that this symmetric pattern for the backbone protons is observed in reacted solution, suggesting that a monomer is produced as the initial reaction product, which then dimerizes upon isolation of the product as a solid.

Reaction of $[(IPr)Ni(\mu\text{-Cl})]_2$ with $Li(HBEt_3)$ or with NaO*t*-Bu followed by $HSi(OEt)_3$ also formed the same product. No deuterium resonance is observed in the ^{2}H NMR spectrum of the product when $Li(DBEt_3)$ was used. Single crystals of **1** that were subject to X-ray analysis were grown by slow diffusion of 2,2-dimethylbutane into the THF solution of the reaction mixture. The dimeric nature of **1** is confirmed by the crystal structure shown in Figure 1. Each nickel center of the bimetallic core interacts in an η^6 fashion with a 2,6-diisopropyl phenyl group of the NHC ligand. The reaction of $Li(HBEt_3)$ with $[(IPr)Ni(\mu\text{-Cl})]_2$ to form **1** is unexpected inasmuch as phosphine complexes of Ni(II) furnish dihydride complexes suchas $[(dippe)NiH]_2$ (dippe = $(i\text{-}Pr_2PCH_2)_2$) using similar reaction conditions.[19]

Scheme 1



[a] The putative byproduct was not isolated.

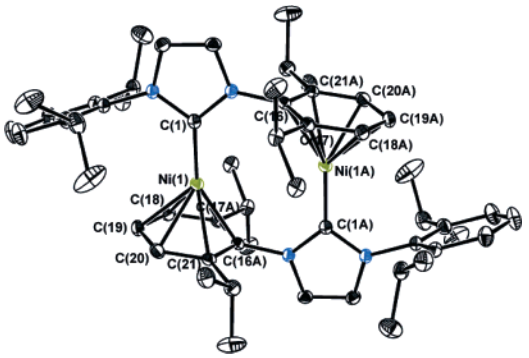


Figure 1. The molecular structure of **1** showing thermal ellipsoids at 50% probability. The solvent molecules are omitted for clarity. Selected bond lengths (Å): Ni(1)−C(1), 1.856(2); Ni(1)−C(16), 2.101(2); Ni(1)−C(17), 2.1404(19); Ni(1)−C(18), 2.1525(18); Ni(1)−C(19), 2.174(2); Ni(1)−C(20), 2.1521(19); Ni(1)−C(21), 2.1351(19).

Complex **1** is an ideal synthon for the coordinatively unsaturated (IPr)Ni moiety since the relatively weakly coordinated arene rings are readily displaced. CO_2 (1 atm) reacts readily with **1** to form a single product as judged by ^{1}H NMR spectroscopy (48% isolated yield) (Scheme 1). Single crystals of the product, suitable for X-ray crystallography, were grown from a solution of the crude reaction product in hexanes. The X-ray structure of the product, $[(IPr)Ni]_2(\mu\text{-CO})(\mu\text{-}\eta^2,\eta^2\text{-}CO_2)$ (**2**), is shown in Figure 2. The most remarkable feature of the crystal structure is a CO_2 bridging two Ni atoms. The CO_2 ligand is bent at 133.43(15)° and the C−O bond lengths are 1.2552(19) Å and 1.257(2) Å, which are longer than the C−O bond length (1.16 Å) of free CO_2. A similar binding mode has been observed for other heterocumulenes such as isocyanates and carbodiimides, but a symmetric double-bridging binding mode for CO_2 appears to be unprecedented as determined from a search of the Cambridge Crystallographic Database. All other known dinuclear CO_2 complexes coordinate the CO_2 carbon atom to only one metal center.[4,5,20−22]

Two signals are isotopically enriched in the ^{13}C NMR spectrum of **2** prepared using $^{13}CO_2$ (see Figure S2). These resonances are weakly coupled to each other (J = 3.5 Hz) and they are assigned to μ-η^2,η^2-CO_2 (δ 172.6) and μ-CO (δ 246.4 ppm). When complex **2**, prepared using CO_2 with natural isotopic abundance, is treated with $^{13}CO_2$ (1 atm), the signal at δ 172.6 ppm increases in intensity.

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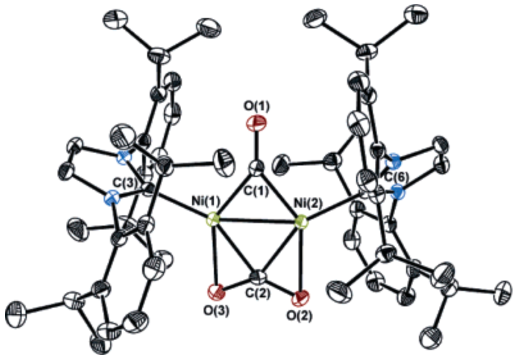


Figure 2. The molecular structure of **2** showing thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): Ni(1)−Ni(2), 2.3374(4); Ni(1)−C(3), 1.8940(15); Ni(2)−C(6), 1.8877(16); C(1)−O(1), 1.184(2); C(2)−O(2), 1.2552(19); C(2)−O(3), 1.257(2); O(2)−C(2)−O(3), 133.43(15); Ni(1)−C(1)−Ni(2), 79.08(6).

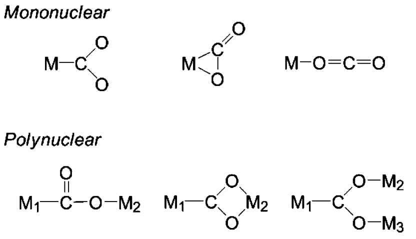
This is consistent with exchange of the CO_2 ligand of **2** with free CO_2. Complex **2** exhibits intense CO stretching bands at 1773, 1630, and 1205 cm^{-1}; these absorptions shift to 1731, 1586, and 1183 cm^{-1} upon $^{13}CO_2$ isotopic substitution.

CO_2 reduction is evident from the presence of the bridging CO in **2**. Notwithstanding, the crystal structure of **2** does not account for the fate of the oxygen atom delivered from CO_2 on its reduction. Though **2** was the only product observed by NMR spectroscopy and no free, oxidized, or carboxylated carbene ligands were formed, the yield of the product was 66% by ^1H NMR relative to an internal standard. Thus, the formation of an NMR-silent paramagnetic nickel complex accounting for the missing oxygen is assumed, though such a complex could not be cleanly isolated from the solid residue of recrystallized samples of **2**. An IR spectrum of the residue showed strong peaks at 1618, 1595, and 1561 cm^{-1}. These peaks shift to 1576, 1560, and 1515 cm^{-1} upon isotopic substitution using $^{13}CO_2$. We propose that complex **1** effectively disproportionates CO_2 to form **2** and a nickel(II) carbonate complex, which is consistent with the well-known metal-mediated disproportionation of CO_2 to CO and CO_3^{2-}.[24−29]

The outcome for CO_2 activation reported here may be extended to other nickel(0) complexes. We find that the biscarbene complex $(IMes)_2Ni(0)$,[30] also reacts with CO_2 to form an analogous complex, $[(IMes)Ni]_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}CO_2)$ (**3**) (IMes = 1,3-dimesitylimidazol-2-ylidene) (see Figure S3).

CO_2 has been observed to bind to a mononuclear metal site in the three different modes shown in Chart 1.[24,25,31−37] Since the report of the first structurally characterized CO_2 complex in a η^2-CO_2 binding mode in $Ni(PCy_3)_2(\eta^2\text{-}CO_2)$[24] (Cy = cyclohexyl), CO_2 has been observed to assume η^1-CO_2 and η^1-OCO coordination geometries as well.[34−37] At polynuclear metal centers, the three additional binding modes,[4,5,20−23] shown in Chart 1 have been observed. We now report a new mode for CO_2 binding to a metal, the $\mu\text{-}\eta^2,\eta^2\text{-}CO_2$ coordination geometry shown in Figure 2. Noting that the activation of small molecules is predisposed by the nature of its mode of binding to the metal center, the new binding mode reported here for CO_2 may present new strategies for the CO_2 activation.

Chart 1



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Supporting Information Available: Complete ref 1; all experimental procedures and characterization data for **1**, **2**, and **3**; structural parameters for **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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