

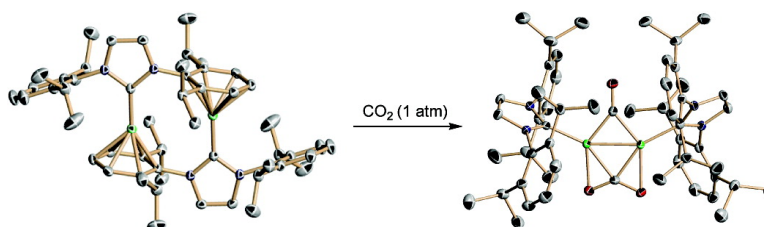
Communication

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Chang Hoon Lee, David S. Laitar, Peter Mueller, and Joseph P. Sadighi

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Generation of a Doubly Bridging CO₂ Ligand and Deoxygenation of CO₂ by an (NHC)Ni(0) Complex

Chang Hoon Lee, David S. Laitar, Peter Mueller, and Joseph P. Sadighi*

Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

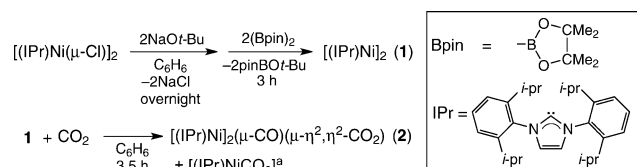
Received July 27, 2007; E-mail: jsadighi@mit.edu

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 CO₂ fixation and activation.^{1,4,5} Often CO₂ 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}(μ-O)(μ-CO)Fe^{II} core.⁷ We have recently shown that oxygen can catalytically be abstracted from CO₂ at the metal center of a carbene-supported Cu^I center at turnovers exceeding 10³.⁸ In nature, catalytic CO₂ 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 CO₂ reduction.^{11,12} The anticipation of the importance of Ni in fixing CO₂ at synthetic active sites is borne out in Kubiak et al.'s resourceful use of dinuclear and trinuclear nickel complexes to reduce CO₂^{13–15} and Louie et al.'s catalytic fixation of CO₂ in organic substrates by (NHC)₂Ni(0) (N-heterocyclic carbene) precatalysts that were generated in situ.^{16,17} We now report the reduction of CO₂ by a (NHC)Ni(0) complex gives rise to a heretofore unknown coordination mode for CO₂, μ-η²,η²-CO₂, at a dinickel core.

The reaction of [(IPr)Ni(μ-Cl)]₂¹⁸ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with NaOt-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 ¹H 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 C₆D₆, the ¹H NMR spectrum of the NHC backbone protons is distinct. However, over the course of a week, the ¹H 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(η⁶-C₆D₆). 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(μ-Cl)]₂ with Li(HBEt₃) or with NaOt-Bu followed by HSi(OEt)₃ also formed the same product. No deuterium resonance is observed in the ²H NMR spectrum of the product when Li(DBEt₃) was used. Single crystals of **1** that were subject to X-ray

Scheme 1



^a The putative byproduct was not isolated.

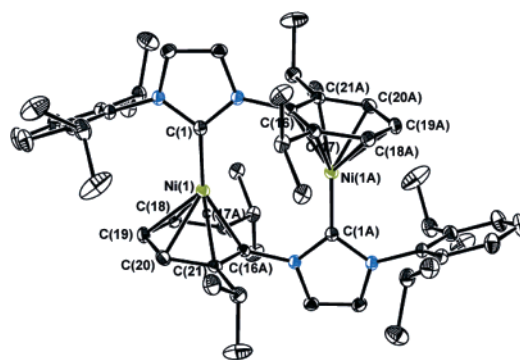


Figure 1. The molecular structure of **1** showing thermal ellipsoids at 50% probability. The solvent molecules are omitted for clarity. Selected bond lengths (Å): Ni(1)–C(1), 1.856(2); Ni(1)–C(16), 2.101(2); Ni(1)–C(17), 2.1404(19); Ni(1)–C(18), 2.1525(18); Ni(1)–C(19), 2.174(2); Ni(1)–C(20), 2.1521(19);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

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 η⁶ fashion with a 2,6-diisopropyl phenyl group of the NHC ligand. The reaction of Li(HBEt₃) with [(IPr)Ni(μ-Cl)]₂ to form **1** is unexpected inasmuch as phosphine complexes of Ni(II) furnish dihydride complexes such as [(dippe)NiH]₂ (dippe = (*i*-Pr₂PCH₂)₂) using similar reaction conditions.¹⁹

Complex **1** is an ideal synthon for the coordinatively unsaturated (IPr)Ni moiety since the relatively weakly coordinated arene rings are readily displaced. CO₂ (1 atm) reacts readily with **1** to form a single product as judged by ¹H 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(μ-CO)(μ-η²,η²-CO₂) (**2**), is shown in Figure 2. The most remarkable feature of the crystal structure is a CO₂ bridging two Ni atoms. The CO₂ 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 CO₂. A similar binding mode has been observed for other heterocumulenes such as isocyanates and carbodiimides, but a symmetric double-bridging binding mode for CO₂ appears to be unprecedented as determined from a search of the Cambridge Crystallographic Database. All other known dinuclear CO₂ complexes coordinate the CO₂ carbon atom to only one metal center.^{4,5,20–22}

Two signals are isotopically enriched in the ¹³C NMR spectrum of **2** prepared using ¹³CO₂ (see Figure S2). These resonances are weakly coupled to each other (*J* = 3.5 Hz) and they are assigned to μ-η²,η²-CO₂ (δ 172.6) and μ-CO (δ 246.4 ppm). When complex **2**, prepared using CO₂ with natural isotopic abundance, is treated with ¹³CO₂ (1 atm), the signal at δ 172.6 ppm increases in intensity.

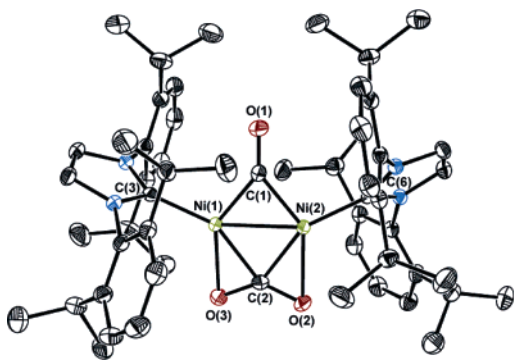


Figure 2. The molecular structure of **2** showing thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): Ni(1)–Ni(2), 2.3374(4); Ni(1)–C(3), 1.8940(15); Ni(2)–C(6), 1.8877(16); C(1)–O(1), 1.184(2); C(2)–O(2), 1.2552(19); C(2)–O(3), 1.257(2); O(2)–C(2)–O(3), 133.43(15); Ni(1)–C(1)–Ni(2),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

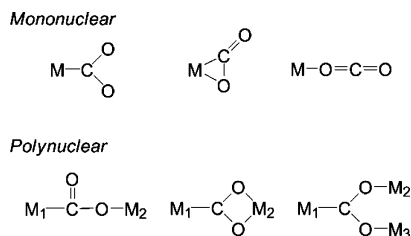
This is consistent with exchange of the CO₂ ligand of **2** with free CO₂. Complex **2** exhibits intense CO stretching bands at 1773, 1630, and 1205 cm⁻¹; these absorptions shift to 1731, 1586, and 1183 cm⁻¹ upon ¹³CO₂ isotopic substitution.

CO₂ 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 CO₂ 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 ¹³CO₂. We propose that complex **1** effectively disproportionates CO₂ to form **2** and a nickel(II) carbonate complex, which is consistent with the well-known metal-mediated disproportionation of CO₂ to CO and CO₃²⁻.^{24–29}

The outcome for CO₂ activation reported here may be extended to other nickel(0) complexes. We find that the biscarbene complex (IMes)₂Ni(0),³⁰ also reacts with CO₂ to form an analogous complex, [(IMes)Ni]₂(μ-CO)(μ-η²,η²-CO₂) (**3**) (IMes = 1,3-dimesitylimidazol-2-ylidene) (see Figure S3).

CO₂ 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 CO₂ complex in a η²-CO₂ binding mode in Ni(PCy₃)₂(η²-CO₂)²⁴ (Cy = cyclohexyl), CO₂ has been observed to assume η¹-CO₂ and η¹-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 CO₂ binding to a metal, the μ-η²,η²-CO₂ coordination geometry shown in Figure 2. Noting that the activation of small molecules is predisposed by the nature

Chart 1



of its mode of binding to the metal center, the new binding mode reported here for CO₂ may present new strategies for the CO₂ activation.

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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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