Carbon dioxide is a useful carbon source for the synthesis of organic molecules, and it is a small molecule that figures prominently in global energy scenarios. Transition metal complexes offer a wide range of strategies for CO₂ fixation and activation. 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 U₃⁺ to produce free CO and UIV, (μ-O)₂UUV₆, and at Fe to produce CO bound within a Fe³⁺(μ-O)(μ-CO)Fe⁴⁺ core. We have recently shown that oxygen can catalytically be abstracted from CO₂ at the metal center of a carbene-supported Cu¹ center at turnovers exceeding 10⁶. In nature, catalytic CO₂ reduction is performed by the enzyme acetyl-CoA synthase/CO dehydrogenase (ACS-CODH), with the Ni site of the C-cluster backbone protons (see Figure S1). We propose that dimer dissociates in benzene solution, likely forming the monomer, (IPr)-Ni moiety since the relatively weakly coordinated arene rings of [N(HBEt3)] with [(IPr)Ni(Cl)]₂ to form [(IPr)Ni]₂-(μ-η²:η²-CO₂), at a dinickel core.

The reaction of [(IPr)Ni(μ-Cl)]₁₈ (IPr = 1,3-bis(2,6-dipropylphenyl)imidazol-2-ylidene) with NaO₂ produced as the initial reaction product, which then dimerizes upon isolation of the product as a solid. Isolated crystals of 1 were subjected to X-ray diffraction analysis. 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), 1.186(2); Ni(1)–C(16), 1.701(2); Ni(1)–C(17), 1.240(4); Ni(1)–C(18), 1.525(18); Ni(1)–C(19), 1.274(2); Ni(1)–C(20), 1.251(19); Ni(1)–C(21), 2.135(19).

**Scheme 1**

\[
\begin{align*}
\text{[(IPr)Ni(μ-Cl)]} & \quad \text{[Ni(OEt)₂]} \\
\text{Cp}_2 & \quad \text{2HBEt₃} \\
\text{3.5 h} & \quad \text{3 h}
\end{align*}
\]

1 + CO₂

**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), 1.186(2); Ni(1)–C(16), 1.701(2); Ni(1)–C(17), 1.240(4); Ni(1)–C(18), 1.525(18); Ni(1)–C(19), 1.274(2); Ni(1)–C(20), 1.251(19); Ni(1)–C(21), 2.135(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° 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 isocyanoates 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.

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

CO\textsubscript{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\textsubscript{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 \textsuperscript{1}H NMR relative to an internal standard. Thus, the formation of an NMR-silent paramagnetic nickel standard. Thus, the formation of an NMR-silent paramagnetic nickel complex could not be cleanly isolated from the solid residue showing thermal ellipsoids at 50\% probability. Selected bond lengths (\AA) 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).

of its mode of binding to the metal center, the new binding mode reported here for CO\textsubscript{2} may present new strategies for the CO\textsubscript{2} activation.

Acknowledgment. We thank Daniel Nocera for his help in preparing the manuscript for publication and for helpful discussions. We thank the NSF (Grant No. CHE-0349204), Corning Inc., and the MIT Department of Chemistry for the generous support. MIT NMR facilities are supported in part by NSF Awards CHE-9808061 and DBI-9729592.

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.

References