

Supporting Information for

**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*

Experimental

General Considerations. All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere, or in an Innovative Technologies glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven- or flame-dried glassware cooled under vacuum. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Anhydrous tetrahydrofuran and hexane were purchased from Aldrich in 18-L Pure-Pac™ solvent delivery kegs and sparged vigorously with argon for 40 minutes prior to first use. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and for tetrahydrofuran, a third column packed with activated 4 Å molecular sieves. Benzene, pentane, 2,2-dimethylbutane and hexamethyldisiloxane were purchased from Aldrich and stored in a glovebox over 4 Å molecular sieves. 2,2-dimethylbutane and hexamethyldisiloxane were degassed by three freeze-pump-thaw cycles prior to being stored in a glovebox.

IR spectra were recorded on a Nicolet Impact 410 spectrometer as CsI pellets. NMR solvents were obtained from Cambridge Isotope Laboratories. C₆D₆ was dried over sodium benzophenone ketyl. The solvent was degassed by three freeze-pump-thaw cycles, and vacuum-transferred prior to use. ¹H NMR and ¹³C NMR spectra were recorded on a Varian 500 MHz instrument, with shifts reported relative to the residual solvent peak.

[(IPr)Ni(μ-Cl)]₂¹ and (IMes)₂Ni² were synthesized as described in the published procedure. 1.0 M lithium triethylborohydride in THF (Aldrich), bis(pinacolato)diboron (Frontier Scientific) and sodium *tert*-butoxide (Aldrich) were used as received.

Preparation of [(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)Ni]₂ (**1**).

Method A. In a glovebox, [(IPr)Ni(μ-Cl)]₂ (0.200 g, 0.207 mmol) and sodium *tert*-butoxide (0.040 g, 0.416 mmol) were added to a vial equipped with a Teflon-coated magnetic stirbar. Benzene (10 mL) was added and the mixture was stirred overnight. Bis(pinacolato)diboron (0.100 g, 0.395 mmol) was added to the resulting greenish brown solution, and the mixture was stirred for 3 hours. The resulting reddish brown solution was filtered through Celite on a fritted glass funnel and dried *in vacuo*. The resulting brown solid was dispersed in hexamethyldisiloxane (2 mL) and transferred into a vial. The resulting suspension in the vial was cooled at –40 °C for 3 days. If substantial amount of crystals or precipitation is not seen, the mixture has to be dried and re-dispersed in hexamethyldisiloxane. The brown solid was collected on a fritted glass funnel and washed with cold hexamethyldisiloxane 5 times. The product was dried *in vacuo* giving 0.052 g (28 %) of **1**.

Method B. In a glovebox, [(IPr)Ni(μ-Cl)]₂ (0.200 g, 0.207 mmol) was added to a vial equipped with a Teflon-coated magnetic stirbar. Benzene (10 mL) was added and lithium triethylborohydride in THF solution (0.410 mL, 0.410 mmol) was added via syringe. The

¹ Dible, B. R.; Sigman, M. S.; Arif, A. M. *Inorg. Chem.* **2005**, *44*, 3772-3776

² Arduengo, A. J.; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391-4394.

mixture was stirred for 3 hours. The resulting reddish brown solution was filtered through Celite on a fritted glass funnel and dried *in vacuo*. A reddish brown solid was collected, dispersed in pentane (3 mL) and transferred into a vial. The suspension was cooled at $-40\text{ }^{\circ}\text{C}$ for 2 days. The brown solid was collected on a fritted glass funnel and washed with cold pentane 5 times. The product was dried *in vacuo* giving 0.095 g (51 %) of **1**. ^1H NMR (C_6D_6)³: δ 7.36 (t, $J = 7.7$ Hz, 2 H, *para*-CH), 7.26 (d, $J = 7.5$ Hz, 4 H, *meta*-CH), 6.65 (d, $J = 1.8$ Hz, 2 H, NCH), 6.38 (d, $J = 1.8$ Hz, 2 H, NCH), 5.71 (d, $J = 6.4$ Hz, 4 H, *meta*-CH), 5.22 (t, $J = 6.3$ Hz, 2 H, *para*-CH), 3.11 (sept., $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 2.72 (sept., $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.44 (m, 24 H, $\text{CH}(\text{CH}_3)_2$), 1.10 (m, 24 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 198.0, 147.2, 140.2, 128.9, 123.8, 121.9, 120.4, 108.8, 106.0, 93.1, 86.8, 28.9, 28.1, 25.6, 25.2, 23.9, 23.8. IR (CsI, cm^{-1}): 3069, 2960, 2868, 1467, 1423, 1384, 1363, 1327, 1280, 1234, 1182, 1121, 1087, 1062, 955, 928, 800, 782, 760, 715, 669. Anal. Calcd. $\text{C}_{54}\text{H}_{72}\text{N}_4\text{Ni}_2$: C, 72.50; H, 8.11; N, 6.26. Found: C, 72.39; H, 8.04; N, 6.17.

Complex **1** is obtained from monomer in the reaction mixture. Solids of **1** convert to monomer by dissolving in benzene (Figure S1). ^1H NMR (C_6D_6): δ 7.30 (t, $J = 7.7$ Hz, 2 H, *para*-CH), 7.19 (d, $J = 7.6$ Hz, 4 H, *meta*-CH), 6.37 (s, 2 H, NCH), 2.90 (sept., $J = 6.9$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 1.40 (d, $J = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.12 (d, $J = 7.0$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 195.5 (NCNi), 147.0 (*ortho*-C), 139.5 (*ipso*-C), 129.1 (*para*-C), 123.8 (*meta*-C), 119.8 (NCH), 29.0 ($\text{CH}(\text{CH}_3)_2$), 24.9 ($\text{CH}(\text{CH}_3)_2$), 23.9 ($\text{CH}(\text{CH}_3)_2$).

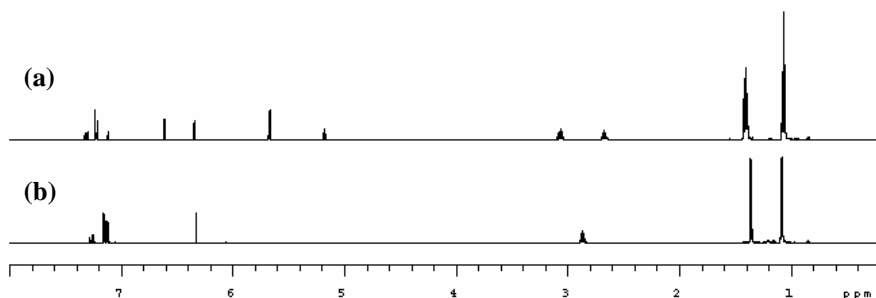


Figure S1. (a) ^1H NMR spectrum of **1** in C_6D_6 . (b) ^1H NMR spectrum of **1** after one week at $45\text{ }^{\circ}\text{C}$.

Preparation of [(1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) Ni] $_2(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^2\text{-CO}_2)$ (**2**).

Method A. In a glovebox, $[(\text{IPr})\text{Ni}(\mu\text{-Cl})]_2$ (0.200 g, 0.207 mmol) and sodium *tert*-butoxide (0.040 g, 0.416 mmol) were added to a vial equipped with a Teflon-coated magnetic stirbar. Benzene (10 mL) was added and the mixture was stirred overnight. Bis(pinacolato)diboron (0.100 g, 0.395 mmol) was added to the resulting greenish brown solution, and the mixture was stirred for 3 hours. The resulting reddish brown solution was filtered through Celite on a fritted glass funnel and dried *in vacuo*. The resulting brown solid was re-dissolved in benzene (5 mL) and transferred into a sealable Schlenk flask. The solution was degassed by one freeze-pump-thaw cycle and backfilled with CO_2 (1 atm). The flask was sealed after 30

³ The splitting of resonances at δ 6.65, 6.38, 5.71, 5.22, 3.11 and 2.72 ppm is not obvious sometimes, even though the samples with those broad signals are converted to monomer cleanly.

minutes stirring, and the solution was stirred for 3 hours. The solution was dried *in vacuo* and the resulting solid was recrystallized in benzene (1 mL) / hexane (10 mL) at $-40\text{ }^{\circ}\text{C}$ for 3 days. The supernatant was decanted to remove small particles and the resulting orange red crystals were washed with cold pentane. This process was repeated until the supernatant became a clear orange solution. The resulting crystals were dried *in vacuo* giving 0.097 g (48 %) of **2**.

Method B. In a glovebox, $[(\text{IPr})\text{Ni}(\mu\text{-Cl})]_2$ (0.200 g, 0.207 mmol) was added to a vial equipped with a Teflon-coated magnetic stirbar. Benzene (10 mL) was added and lithium triethylborohydride in THF solution (0.410 mL, 0.410 mmol) was added via syringe. The mixture was stirred for 3 hours. The resulting reddish brown solution was filtered through Celite on a fritted glass funnel and dried *in vacuo*. The reddish brown solid that was collected was re-dissolved in benzene (10 mL) and transferred into a sealable Schlenk flask. The solution was degassed by one freeze-pump-thaw cycle and backfilled with CO_2 (1 atm). The flask was sealed after 30 minutes stirring, and the solution was stirred for 3 hours. The solution was dried *in vacuo* and the resulting solid was recrystallized in benzene (1 mL) / hexane (10 mL) at $-40\text{ }^{\circ}\text{C}$ for 3 days. The supernatant was decanted to remove small particles and the resulting orange red crystals were washed with cold pentane. This process was repeated until the supernatant became a clear orange solution. The resulting crystals were dried *in vacuo* giving 0.064 g (32 %) of **2**. ^1H NMR (C_6D_6): δ 7.24 (t, $J = 7.7$ Hz, 4 H, *para*-CH), 7.13 (d, $J = 7.8$ Hz, 8 H, *meta*-CH), 6.46 (s, 4 H, NCH), 2.87 (sept., $J = 6.9$ Hz, 8 H, $\text{CH}(\text{CH}_3)_2$), 1.32 (d, $J = 6.7$ Hz, 24 H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $J = 7.0$ Hz, 24 H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (C_6D_6): δ 246.4 ($\mu\text{-CO}$), 195.0 (NCNi), 172.6 ($\mu\text{-}\eta^2, \eta^2\text{-CO}_2$), 146.6 (*ortho*-C), 136.6 (*ipso*-C), 129.9 (*para*-C), 124.2 (*meta*-C), 123.3 (NCH), 29.1 ($\text{CH}(\text{CH}_3)_2$), 26.0 ($\text{CH}(\text{CH}_3)_2$), 24.0 ($\text{CH}(\text{CH}_3)_2$). IR (CsI, cm^{-1}): 2963, 2869, 1773, 1702, 1630, 1468, 1401, 1385, 1364, 1327, 1269, 1205, 1115, 1060, 966, 943, 802, 756, 748, 696, 602. Anal. Calcd. $\text{C}_{56}\text{H}_{72}\text{N}_4\text{O}_3\text{Ni}_2$: C, 69.58; H, 7.51; N, 5.80. Found: C, 69.57; H, 7.32; N, 5.62

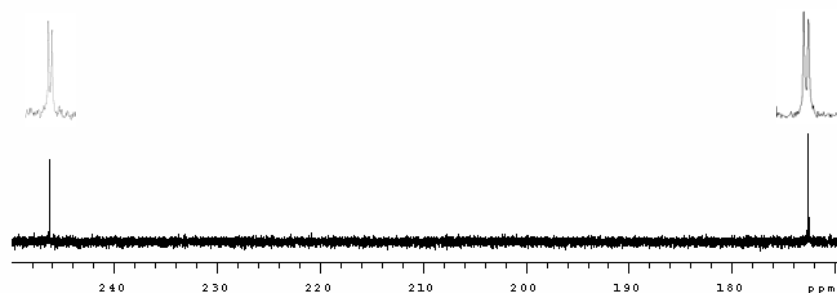


Figure S2. ^{13}C NMR spectrum of **2** prepared using $^{13}\text{CO}_2$ showing resonances of $\mu\text{-CO}$ and $\mu\text{-}\eta^2, \eta^2\text{-CO}_2$. Insets show the splitting of each resonance.

Preparation of $[(1,3\text{-dimesitylimidazol-2-ylidene})\text{Ni}]_2(\mu\text{-CO})(\mu\text{-}\eta^2, \eta^2\text{-CO}_2)$ (**3**).

In a glovebox, $(\text{IMes})_2\text{Ni}$ (0.200 g, 0.300 mmol) was added to a sealable Schlenk flask equipped with a Teflon-coated magnetic stirbar and dissolved in benzene (10 mL). The

solution was degassed by one freeze-pump-thaw cycle and backfilled with CO₂ (1 atm). The solution turned red immediately. The solution was stirred for 3 days. The mixture turned orange slowly forming precipitation. The resulting solution was filtered on a fritted glass funnel and dried *in vacuo*. The resulting solid was recrystallized in benzene (2 mL) / hexane (6 mL) at −40 °C for 3 days. The supernatant was decanted to remove small particles and the resulting orange red crystals were washed with cold pentane. This process was repeated until the supernatant became a clear orange solution. The resulting crystals were dried *in vacuo* giving 0.047 g (39 %) of **3**. ¹H NMR (C₆D₆): δ 6.71 (s, 8H, *meta*-CH), 6.11 (s, 4 H, NCH), 2.22 (s, 12H, *para*-CCH₃), 2.05 (s, 24 H, *ortho*-CCH₃). ¹³C NMR (C₆D₆): δ 249.2 (μ-CO), 194.0 (NCNi), 175.5 (μ-η², η²-CO₂), 138.0 (*ipso*-C), 137.0 (*para*-C), 136.2 (*ortho*-C), 129.4 (*meta*-C), 121.8 (NCH), 21.7 (*para*-CCH₃), 18.2 (*ortho*-CCH₃). IR (CsI, cm^{−1}): 2922, 1767, 1702, 1610, 1489, 1400, 1327, 1267, 1202, 1035, 928, 850, 750, 702, 609, 575. Anal. Calcd. C₄₄H₄₈N₄O₃Ni₂: C, 66.20; H, 6.06; N, 7.02. Found: C, 66.02; H, 6.37; N, 6.95

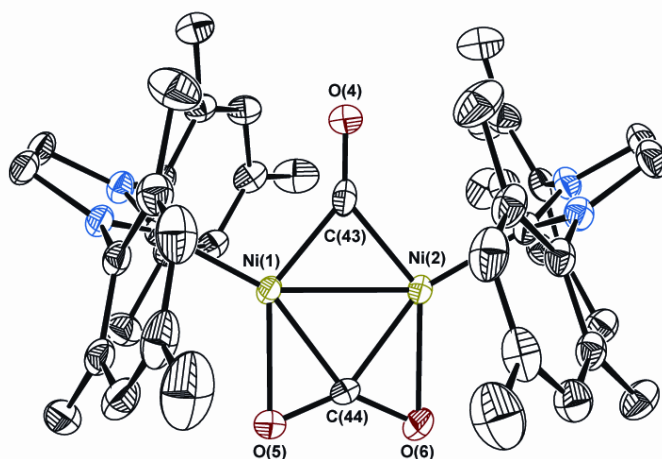


Figure S3. The molecular structure of **3** showing thermal ellipsoids at 50% probability.

X-ray Diffraction Studies: Experiments were performed on single crystals of **1**, **2** and **3**. The single crystals of **1** were grown at −40 °C by slow diffusion of 2,2-dimethylbutane into a THF solution of the reaction mixture prepared through method **B**. The target molecule co-crystallizes with one molecule of THF and 2,2-dimethylbutane. The single crystals of **2** were grown at −40 °C from hexane solution of the reaction mixture prepared through method **A**. The single crystals of **3** were grown at −40 °C from benzene / hexane solution of the reaction mixture. The crystals were removed from the supernatant and transferred onto a microscope slide coated with Paratone N oil. Crystals were affixed to a glass fiber or a cryoloop using the oil, frozen in a nitrogen stream, and optically centered. The data were collected on a Siemens three-circle platform goniometer equipped with a Bruker Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), using both phi and omega scans at −173 °C. The structures were solved by direct methods (SHELXS)⁴ and refined against *F*²

⁴ Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, 46, 467.

on all data by full matrix least squares with SHELXL-97.⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The ratio between the two components of the disordered 2,2-dimethylbutane in a single crystal of **1** was refined freely and converged at 0.687(6). The disorder was refined with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Full listing for text reference (1):

Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953-996.

⁵ Sheldrick, G. M. *SHELXL 97*; Universität Göttingen: Göttingen, Germany, 1997