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1. Experimental Details, Synthetic Procedures, Spectroscopic Characterization

General Considerations. Unless otherwise stated, all reactions and manipulations were carried out in a MBraun Lab Master DP glovebox or using standard Schlenk techniques under a nitrogen atmosphere. Pentane, hexanes, benzene, toluene, and 1,2-difluorobenzene were purchased from Sigma Aldrich. Diethyl ether was purchased from Honeywell and tetrahydrofuran was purchased from Macron Chemicals. Pentane, toluene, tetrahydrofuran, diethyl ether and 1,2-difluorobenzene were dried using a JC Meyers Phoenix SDS solvent purification system. Benzene and hexane were dried and degassed using a Vacuum Atmosphere solvent purifier system. Prior to drying, benzene was dethiophenated using standard techniques.[1] C_6D_6 was purchased from Cambridge Isotope Laboratories, dried over Na/K alloy and then degassed by four freeze-pump-thaw cycles. Potassium graphite[2] was prepared by standard literature procedure. Compounds $\mathbf{1}$[3], $\mathbf{2}$[4] and $\mathbf{4}$[3] were prepared by previously reported methods. All NMR spectra were collected at ambient temperature (ca. 22°C) on Bruker AVB-400, AV-500, AV-600 or AVQ-400 NMR spectrometers, each equipped with a 5 mm BB probe, and referenced to the residual proteo solvent signals. UV-Vis spectra were acquired in quartz cuvettes fitted with Chemglass Air-Free Teflon stoppered valves using a Varian Cary 50 UV-Vis spectrometer. Solution magnetic susceptibilities were determined by ^{1}H NMR spectroscopy using Evans' method.[5] Elemental analyses were performed by the UC Berkeley College of Chemistry Microanalytical facility. The abbreviation "DIPP" refers to a 2,6-diisopropylphenyl moiety.

Cyclic Voltammetry Experiments. Cyclic voltammetry experiments were conducted at ambient temperature in a Vacuum Atmospheres glovebox. Measurements employed a Bio-Logic SP-200 potentiostat with a standard three electrode configuration. The working electrode was a 3mm diameter glassy carbon electrode purchased from ALS. Silver wire was used as a quasi-reference electrode and sublimed ferrocene was used as an internal potential reference. The counter electrode was a 1/8 inch diameter graphite rod purchased from Electron Microscopy Sciences. The glassy carbon electrode was polished with 1 μm alumina prior to each use. The graphite rod was cleaned with acetone and dried prior to each use. Analyses of $\mathbf{1}$ were performed in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene with an analyte concentration of 1 mM at a scan rate of 100 mV/s. No solution resistance correction was applied. All potential values are reported as $E_{1/2}$ for reversible events and E_p for irreversible events.

DFT Calculations. Calculations on $\mathbf{1}$ and $\mathbf{2}$ were reported in a prior publication.[3] Calculations on $\mathbf{3}$ were performed using the Gaussian 09 program[6] using the revTPSS[7] functional. The basis set used for all atoms was 6-31+G(d), using polarization and diffuse orbitals for all atoms except

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[2] D. E. Bergbreiter, J. M. Killough, *J. Am. Chem. Soc.,* **1978**, *100*, 2126

[3] M. I. Lipschutz, X. Yang, R. Chatterjee, T. D. Tilley, *J. Am. Chem. Soc.* **2013**, *135*, 15298-15301

[4] M. I. Lipschutz, T. D. Tilley, *Chem. Commun.* **2012**, *48*, 7146-7148.

[5] D. F. Evans, *J. Chem. Soc.*, **1957**, 2003

[6] Frisch, M. J. *Gaussian 09, Revision C.01*, Gaussian, Inc.: Wallingford CT, 2009.

[7] Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. *Phys. Rev. Lett.,* **2011**, *106*, 179902

hydrogen. In all cases, frequency calculations confirm that the optimized structure resides at an energetic minimum. All geometries were optimized in the gas phase starting from the geometry indicated by X-ray diffraction.

X-ray Diffraction Experiments. Single crystal X-ray diffraction experiments were carried out at UC Berkeley CHEXRAY crystallographic facility. Measurements of compound **3** were performed on a Bruker APEX-II CCD area detector using Mo Kα radiation (λ = 0.71069 Å) monochromated using QUAZAR multilayer mirrors. Specific details of the experiment can be found below, in section S5 at the end of this document and in the included crystallographic information files.

Experimental Details:

	Detector Distance	Image Width	Exposure Time
Compound **3**	50mm	0.5°	30 seconds

Coupling Experiments. Coupling reactions were performed in dry and degassed solvent under an inert atmosphere, as described above. The progress of the reaction was monitored by GC/MS and yields were determined by ^{1}H NMR by integration against the hexamethylbenzene internal standard. Products were identified by GC/MS and by comparison of their NMR spectra to those previously reported in the literature: biphenyl[8], 1-phenylnaphthalene[9], 1-methylnaphthalene[10], 1-ethylnaphthalene[10], 8-phenylquinoline[11], 3-methoxy-1,1'-biphenyl[8], 3-methylanisole[12], 2-phenylpyridine[13], 2,6-diphenylpyridine[13], 4-phenyl-1-butene.[14]

General Procedure for C-C Coupling Reactions: To a 20 mL scintillation vial was added ArX (approx. 0.720 mmol), hexamethylbenzene (approx. 0.065 mmol), compound **2** (0.072 or 0.007 mmol for 5% and 0.5% loading, respectively) and 6 mL of diethyl ether. The vial was equipped with a Teflon coated magnetic stirbar and placed in a -35 ºC freezer for approx. 20 minutes. The vial was then removed, the solution was stirred vigorously, and 1.1 equiv. of 3.0 M RMgBr solution in diethyl ether was added via syringe. The solution was then allowed to warm to room temperature while stirring. Yields were determined by quenching an aliquot of the reaction mixture with water and using ^{1}H NMR to integrate the product signals against the hexamethylbenzene internal standard.

Modified C-C coupling procedure for (iodomethyl)cyclopropane: To a 20 mL scintillation vial was added **2** (0.016 g, 0.029 mmol), hexamethylbenzene (0.0108 g, 0.067 mmol) and 4 mL of THF, forming a dark purple solution. The vial was equipped with a Teflon-coated magnetic stirbar and the solution was stirred vigorously. To the stirring solution was added 0.22 mL of a 3.0 M solution of PhMgBr (0.66 mmol) in Et$_2$O, dropwise, via syringe, causing a color change

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[9] F. Zhou, M.-O. Simon, C.-J. Li, *Chem.—Eur. J.* **2013**, *19*, 7151-7155

[10] T. Krüger, K. Vorndran, T. Linker, *Chem.—Eur. J.* **2009**, *15*, 12082-12091

[11] Y. Zhang, J. Gao, W. Li, H. Lee, B. Z. Lu, C. H. Senanayake, *J. Org. Chem.* **2011**, *76*, 6394-6400

[12] J.-L. Huang, X.-J. Dai, C.-J. Li, *Eur. J. Org. Chem.* **2013**, *29*, 6496-6500

[13] M. Moreno-Mañas, R. Pleixats, A. Serra-Muns, *Synlett* **2006**, *18*, 3001-3004

[14] Maity, S. *et al.* Efficient and stereoselective nitration of mono- and disubstituted olefins with AgNO$_2$ and TEMPO. *J. Am. Chem. Soc.* **135**, 3355-3358 (2013).

from purple to blue. To this stirring solution was added a solution of (iodomethyl)cyclopropane (0.108 g, 0.593 mmol) dissolved in 2 mL of THF, dropwise, over a period of 5 minutes. After 40 minutes, the reaction was quenched with water and the volatile components of an aliquot of the reaction mixture were removed under reduced pressure. Yield was determined by using ^{1}H NMR to integrate the product signals against the hexamethylbenzene internal standard (79% yield relative to alkyl iodide).

Reaction of 2 with EtMgBr. To a solution of **2** (0.010 g, 0.018 mmol) and hexamethylbenzene (0.004 g, 0.025 mmol) in 0.7 mL d_8-THF in an NMR tube was added 1 drop of a solution of EtMgBr in Et_2O. The mixture was sealed and shaken, causing an immediate color change from dark purple to a turquoise color. The solution was then analyzed by ^{1}H NMR. Stoichiometric quantities of ethylene were detected. The yield determined from integration against the internal standard corresponded to approximately 55%, but this does not account for ethylene in the headspace of the NMR tube. Ethane was also detected along with **4**, probably formed due to the instability of the resulting anionic Ni(II) hydride.

Coupling of PhI and MeMgBr and Analysis of Post-Catalytic Reaction Mixture. The general procedure for catalytic coupling reactions described above was followed. After 1 hour of stirring, an aliquot was taken and the solvent and C-C coupling product were removed under vacuum. The Ni-containing components of the reaction mixture were then analyzed by ^{1}H NMR in d_8-THF whereupon both **3** and **4** were detected. Integration of the signals from **3** against the hexamethylbenzene standard indicated that 89% of the original catalytic loading was accounted for as **3**.

Mercury Drop Test. The effect of mercury on the rate of the reaction was analyzed by preparing a catalytic cross-coupling between MeMgBr and 1-iodonaphthalene under the standard conditions described above. After addition of the MeMgBr, the reaction mixture was immediately divided into two portions and 300 equiv. of mercury (relative to the catalyst) was added to one portion. The parallel reactions were monitored by GC/MS and found to reach completion at the time.

Methylation of 2 by MeMgBr and Analysis of Product. To a stirred, purple solution of **2** (0.100 g, 0.180 mmol) in 6 mL of THF chilled to -30 ºC was added 0.66 mL of a 0.30 M solution of MeMgBr (0.198 mmol), dropwise, via syringe over 30 seconds. Upon completion of the addition, the color had changed from dark purple to the characteristic blue color of **3**.

Spectroscopic Analysis and Yield Determination of the Product: An aliquot of the above solution was diluted to a concentration appropriate for analysis by UV-vis spectroscopy and its spectrum was compared to that of **3** prepared independently *via* reduction of **1** with KC_8 and found to match (see page S7 for overlaid spectra and page S5 for independent synthesis of **3**). The yield of the reaction was determined from the UV-vis spectra using the molar absorption coefficient determined from the spectrum of independently prepared **3**. The solvent from a second aliquot of the original reaction mixture was removed under vacuum and the resulting residue was analyzed by ^{1}H NMR spectroscopy d_8-THF and the spectrum was found to match that of independently prepared **3**. Addition of independently prepared **3** to the NMR sample did not result in additional shifts in the ^{1}H NMR spectrum, confirming that the product of the reaction of **2** and MeMgBr is **3**.

Stoichiometric Reactions Between 1, 3 and 1-iodonaphthalene.

1-iodonaphthalene and **3** (1 to 1): A solution of **3** (0.180 mmol) in 6 mL of THF was prepared from **2** (0.100 g, 0.180 mmol) and MeMgBr (0.198 mmol) in the manner described above. The solution was allowed to warm to room temperature. To this stirring solution was added a solution of 1-iodonaphthalene (0.046 g, 0.181 mmol) and hexamethylbenzene (0.011 g, 0.068 mmol) in 2 mL of THF. The reaction was stirred for 45 minutes, during which it was monitored by GC/MS and found to no longer be progressing. An aliquot of the reaction mixture was then taken, the solvent removed under vacuum, and the organic products were analyzed by ^{1}H NMR in CDCl$_3$. The yield of 1-methylnaphthalene (16%) was determined by integration of the product signal against those of hexamethylbenzene.

1-iodonaphthalene, **1** and **3** (1 to 1 to 1): A solution of **3** (0.180 mmol) in 6 mL of THF was prepared from **2** (0.100 g, 0.180 mmol) and MeMgBr (0.198 mmol) in the manner described above. To this solution was added **1** (0.103 g, 0.180 mmol), followed immediately by a solution of 1-iodonaphthalene (0.046 g, 0.181 mmol) and hexamethylbenzene (0.011 g, 0.068 mmol) in 2 mL of THF. The reaction was analyzed after 45 minutes in the same manner as described above and the yield of 1-methylnaphthalene was found to be 10%.

1-iodonaphthalene and **3** (1 to 2): A solution of **3** (0.360 mmol) in 6 mL of THF was prepared from **2** (0.100 g, 0.360 mmol) and MeMgBr (0.378 mmol) in a manner analogous to that described above. The solution was allowed to warm to room temperature. To this stirring solution was added a solution of 1-iodonaphthalene (0.046 g, 0.181 mmol) and hexamethylbenzene (0.011 g, 0.068 mmol) in 2 mL of THF. After 10 minutes, the solution became dark and an aliquot was analyzed in the same manner as described above. The yield of 1-methylnaphthalene was found to be 98%. A separate aliquot was taken, the solvent was removed under vacuum, and the resulting residue was washed with three aliquots of 2 mL of pentane, leaving behind a blue/green residue. The solvent from the pentane washings was removed under vacuum leaving behind a dark residue. The pentane-insoluble and pentane-soluble residues were analyzed by ^{1}H NMR in d_8-THF and d_6-benzene, respectively. The pentane-insoluble components were found to contain **3** and **4** and the pentane-soluble components were found to contain **1** and **2**. Quantification of **3** was not possible due to the solubility of hexamethylbenzene in pentane.

Redox Equilibrium Experiments

Determination of Conversion of **4a** and **1** to **2** and **3**: To a yellow solution of **4a** (0.0120 g, 0.015 mmol) in 1 mL of THF was added a dark green solution of **1** (0.0085 g, 0.015 mmol) in 1 mL of THF, resulting in an immediate color change to black. The volatile components were then removed under vacuum and the resulting residue was washed with three aliquots of 2 mL of pentane, leaving behind a blue residue. To this residue was added hexamethylbenzene (0.0036 g, 0.022 mmol) and *ca.* 0.5 mL d_8-THF. Integration against the hexamethylbenzene internal standard indicated a 29% yield of **3**.

Effect of MeMgBr on Redox Equilibrium: To a yellow solution of **4a** (0.120 g, 0.15 mmol) and hexamethylbenzene (0.0115 g, 0.07 mmol) in 3 mL of THF was added a dark green solution of **1** (0.085 g, 0.15 mmol) in 3 mL of THF, resulting in an immediate color change to black. The solution was stirred and 0.5 mL of a 0.30 M solution of MeMgBr in Et$_2$O (0.15 mmol) was added dropwise. Upon completion of the addition, the color had changed to characteristic blue

color of **3**. An aliquot was removed and the volatile components were removed under vacuum. The resulting residue was dissolved in *ca.* 0.7 mL d_8-THF. Integration against the hexamethylbenzene internal standard indicated complete conversion of all Ni-containing compounds to **3** (>98%).

Homocoupling of 1-iodonaphthalene to 1,1'-binaphthalene by 4. To a stirring, yellow solution of **4** (0.100 g, 0.168 mmol) in 4 mL of THF was added a solution of 1-iodonaphthalene (0.043 g, 0.169 mmol) and hexamethylbenzene (0.010 g, 0.062 mmol) in 2 mL of THF. The reaction mixture slowly darkened over the course of an hour, at which point the reaction mixture was dark purple. An aliquot was taken and analyzed by ^{1}H NMR in CDCl$_3$, which indicated that the yield of 1,1'-binaphthalene was 80%.

Investigation of Carbanion Transfer from [Ni(II)-R]⁻ to Ni(III)-R. To a stirring solution of **3** (0.090 mmol) in 2 mL of THF prepared from **2** and MeMgBr as described above, was added **1** (0.051 g, 0.090 mmol) dissolved in 2 mL of THF. The reaction mixture was stirred at ambient temperature for three hours and then analyzed by ^{1}H NMR spectroscopy. Large quantities of both **1** and **3** remained along with trace amounts of **2**, likely from the thermal decomposition of **1**. From these results, we conclude that a transfer of a hydrocarbyl group from an anionic nickel(II) alkyl species such as **3** to a neutral Ni(III) alkyl species such as **1** is too slow to be catalytically relevant.

(Me)Ni[N(SiMe₃)DIPP]₂ (1). Full preparation and characterization data for **1** is available in a prior publication.[3] Cyclic voltammetry (1,2-difluorobenzene, NBu$_4$PF$_6$, 100 mV/s): –1.30 V (ip_a/ip_c = 0.98).

Ni[N(SiMe₃)DIPP]₂ (2). Full preparation and characterization data for **1** is available in a prior publication.[4]

K{(Me)Ni[N(SiMe₃)DIPP]₂} (3). To a 20 mL scintillation vial was added **1** (0.100 g, 0.175 mmol) and 8 mL of toluene, forming a dark green solution. The mixture was stirred vigorously for approximately 5 minutes to ensure complete dissolution of **1**. The solution was then placed in a freezer at -30 °C where it was allowed to cool for 20 minutes. The vial containing the solution was then removed and the solution was stirred. To the stirring solution of **1** was added potassium graphite (0.026 g, 0.192 mmol) as a solid. The mixture was allowed to warm to room temperature and stirring was continued for 25 minutes at which point the color of the solution had changed from dark green to blue. The mixture was then filtered and the volatile components of the filtrate were removed under reduced pressure. The resulting residue was dissolved in 6 mL of toluene, forming a blue solution, upon which was layered 8 mL of pentane. The vial was placed in the freezer at -30 °C for two days, yielding 0.068 g (64%) of **3** as a blue powder which was isolated by decantation and dried in vacuo. ^{1}H NMR (600 MHz, C$_6$D$_6$, 22°C) δ 6.87 (d, 7.5Hz, 4H, Ar-meta-*H*), 6.74 (t, 7.4Hz, 2H, Ar-para-*H*), 3.36 (m, 4H, Me$_2$C-*H*), 1.12 (d, 6.7Hz, 12H, H(C*H₃*)$_2$), 1.08 (d, 6.8Hz, 12H, H(C*H₃*)$_2$), 0.67 (s, 9H, Si(C*H₃*)$_3$), -0.95 (s, 3H, Ni-C*H₃*). ^{13}C NMR (151 MHz, C$_6$D$_6$, 22 °C) δ 154.71, 148.44, 123.78, 118.61, 34.45, 27.43, 25.76, 24.89, 22.73, 14.27, 5.17, -46.5. The shift at -46.5 is not observable in the 1D ^{13}C NMR and is only visible in a 2D ^{1}H-^{13}C HSQC experiment. As such, its precise chemical shift is necessarily less accurate. Anal. Calcd. for C$_{31}$H$_{55}$KN$_2$NiSi$_2$: C, 61.06%; H, 9.09%; N, 4.59%. Found: C, 60.68%; H, 9.00%; N, 4.84%. UV-vis (THF) λ$_{max}$, ε (L mol^{-1} cm^{-1}) 630 nm, 456; 870 nm, 325. Crystals

suitable for single crystal X-ray diffraction studies were grown from a saturated solution of **3** in toluene cooled to -30 ºC for three days.

K{Ni[N(SiMe₃)DIPP]₂} (4). Full preparation and characterization data for **1** is available in a prior publication.[3]
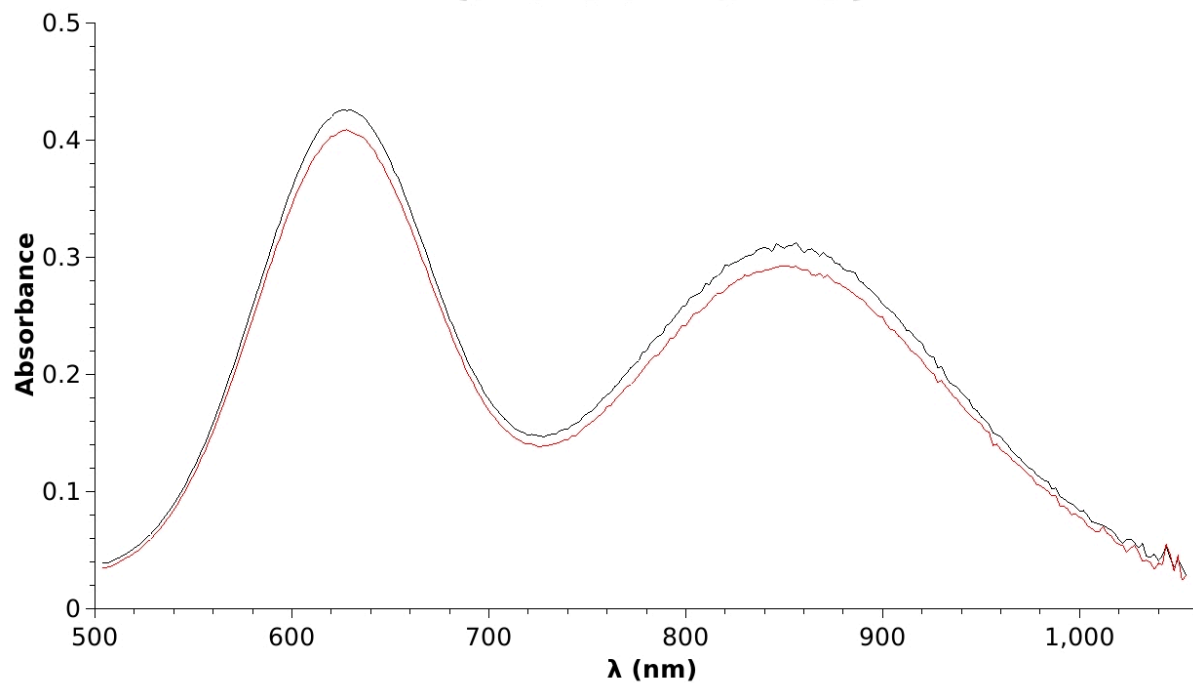
2. Enlarged ORTEP Diagrams
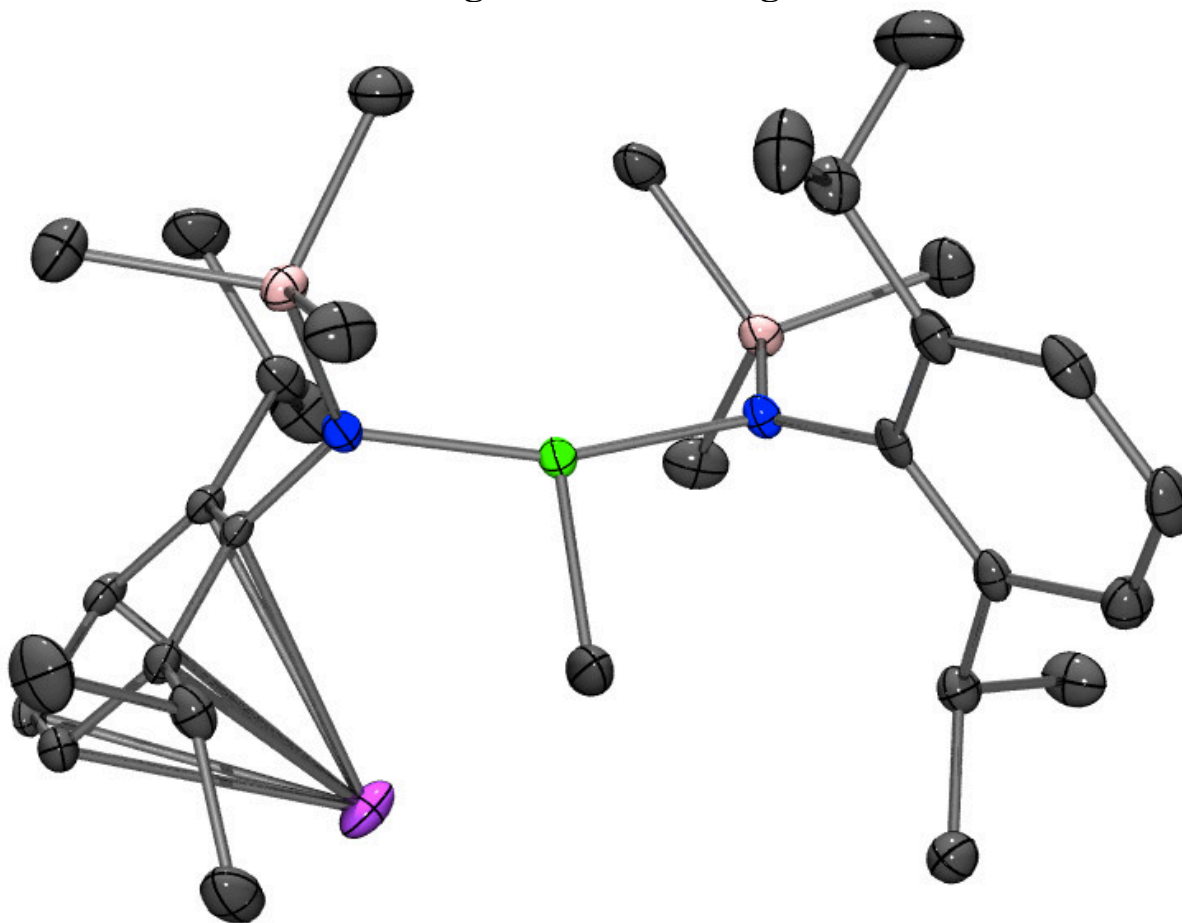
ORTEP diagram for compound **3** (thermal ellipsoids shown at 50% probability). Ni atom is shown in green, K atom in purple, N atoms in blue, Si atoms in pink and C atoms in dark grey.
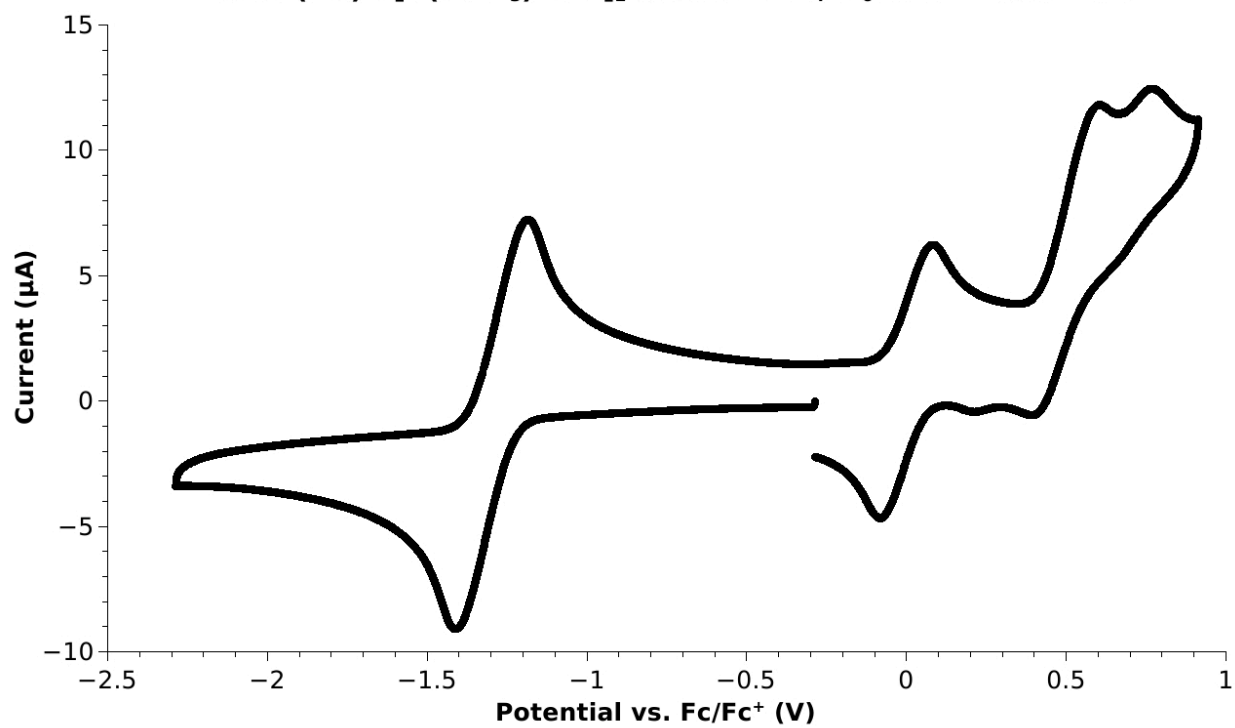
3. UV-Vis Spectra

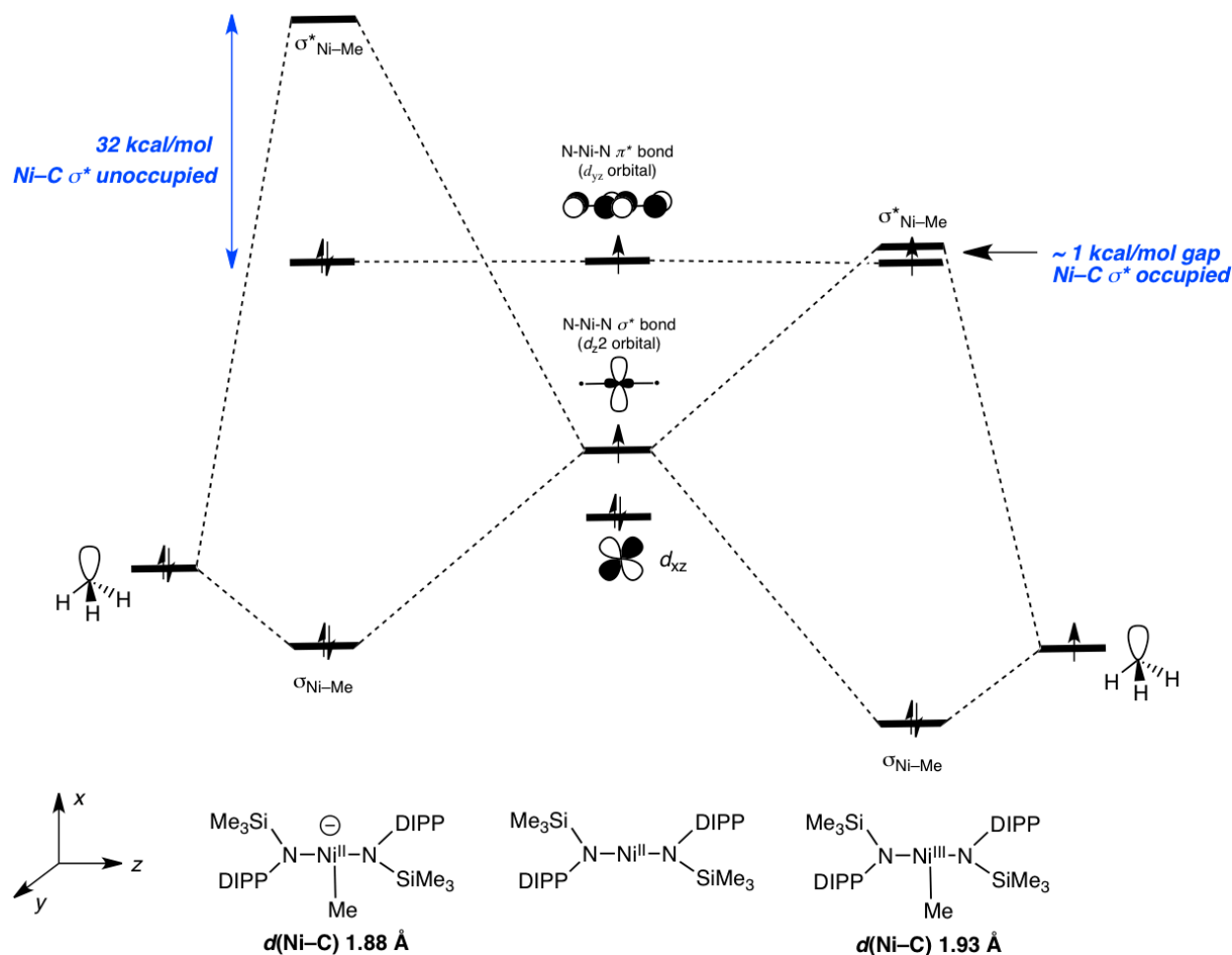**UV-Vis spectra of isolated (black) and in-situ (red) {(Me)Ni[N(SiMe₃)DIPP]₂}⁻**

4. Cyclic Voltammogram

CV of (Me)Ni[N(SiMe$_3$)DIPP]$_2$ in 0.1M NBu$_4$PF$_6$ with Fc Standard

5. Electronic Structure Comparison for [Ni(II)Me]⁻ (3) and Ni(III)Me (1)

d(Ni–C) 1.88 Å   **d(Ni–C) 1.93 Å**

The above figure is a partial MO diagram depicting the interaction of a CH_3^- fragment (left) and a $CH_3\bullet$ fragment (right) with the neutral, Ni(II) bis(amido) complex **2** to depict the Ni-CH_3 interactions for the [Ni(II)Me]⁻ species **3** and Ni(III)Me species **1**, respectively. The full computation treatment for **1** and **2** as well as the full MO diagram for **2** can be found in a prior publication.[3] The computations for **3** were performed according to the description found in section 1, page S2 of the Supporting Information (this document).

We attribute the unexpected shortening of the Ni-C bond upon reduction from a neutral Ni(III) complex to an anionic Ni(II) complex to partial occupancy of the Ni-C σ* orbital in the Ni(III) species, but not the Ni(II) species. As shown in the diagram above, the calculated frontier molecular orbitals of both species are the same, with a HOMO that has significant ,formal π* character for the N-Ni-N core and a LUMO corresponding to the Ni-C σ* orbital. In the Ni(III) species, the HOMO/LUMO gap is calculated to be very small (~1 kcal/mole) while in the Ni(II) species, it is substantially larger (~32 kcal/mole). The very small HOMO/LUMO gap in compound **1** suggests that the Ni-C σ* orbital may be thermally occupied, reducing the bond order of the Ni-C bond and resulting in a longer bond.

6. X-ray Data Tables

Compound 3:

Empirical formula	C31 H55 K N2 Ni Si2
Formula weight	609.76
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca

Unit cell dimensions
$a = 16.7953(4)$ Å $\quad a = 90º.$
$b = 17.1335(4)$ Å $\quad b = 90º.$
$c = 23.8238(6)$ Å $\quad g = 90º.$

Volume	6855.6(3) Å^3
Z	8
Density (calculated)	1.182 Mg/m^3
Absorption coefficient	0.778 mm^{-1}
F(000)	2640
Crystal size	0.13 x 0.04 x 0.01 mm^3
Theta range for data collection	1.71 to 25.37∞.
Index ranges	-17<=h<=20, -20<=k<=20, -28<=l<=28
Reflections collected	85599
Independent reflections	6295 [R(int) = 0.0628]
Completeness to theta = 25.00º	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9923 and 0.9056
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6295 / 0 / 349
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0650
R indices (all data)	R1 = 0.0518, wR2 = 0.0722
Largest diff. peak and hole	0.358 and -0.349 e. Å^{-3}