# Nickel *N*-Heterocyclic Carbene-Pyridine Complexes that Exhibit Selectivity for Electrocatalytic Reduction of Carbon Dioxide Over Water

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**General Synthetic and Physical Methods.** Unless noted otherwise, all manipulations were carried out at room temperature under a dinitrogen atmosphere in a VAC glovebox or using high-vacuum Schlenk techniques. Diethyl ether, tetrahydrofuran, and pentane were dried over activated 4 Å molecular sieves, passed through a column of activated alumina, and sparged with nitrogen prior to use. Acetonitrile, acetonitrile-$d_3$, propionitrile and butyronitrile were refluxed over $CaH_2$, distilled, and sparged with nitrogen. All other reagents and solvents were purchased from commercial sources and used without further purification. Literature methods were used to synthesize $Ni(DME)Cl_2$[1,2] and 2-(imidazolyl)pyridine.[3] NMR spectra were recorded on Bruker spectrometers operating at 300, 400, or 500 MHz as noted. Chemical shifts are reported in ppm relative to residual protiated solvent; coupling constants are reported in Hz. Mass spectra were determined at the University of California, Berkeley Mass Spectrometry Facility.

**Cyclic Voltammetry.** Non-aqueous electrochemical experiments were conducted under a $N_2$ or $CO_2$ atmosphere in 0.1 M $NBu_4PF_6$ in $CH_3CN$. Cyclic voltammetry and controlled-potential electrolysis experiments were carried out using BASI's Epsilon potentiostat and C-3 cell stand.

The working electrode was a glassy carbon disk (3.0 mm diameter) and the counter electrode was a platinum wire. A silver wire in porous Vycor tip glass tube filled with 0.1 M $NBu_4PF_6$ in $CH_3CN$ was used as a pseudo-reference electrode. The scan rate for all cyclic voltammograms was 100 mV/sec, unless otherwise noted. All potentials were referenced against ferrocene/ferrocenium as an external standard and converted to SCE by adding 0.40 V to the measured potentials.[4]

**Gas Chromatographic Analysis.** An Agilent 490-GC Micro-Gas Chromatograph with a Mol Sieve column and heated syringe injector was used for product detection. The column was heated to 80°C under Ar gas flow and the average sample volume of 200 nL was injected onto the column. Controlled-potential electrolysis was conducted using a custom-made glass cell fitted with a glassy carbon rod working electrode (5 mm diameter), $Ag/AgNO_3$ reference electrode, a Pt gauze auxiliary electrode in a glass frit, and a sparging needle. A glass adapter fused to Swagelok female miniature quick-connect with shut-off was also fitted to the cell and is used to attach to a male miniature quick-connect with shut-off on the injection line of the GC. Typically, a 10 mL solution of 0.3 M $NBu_4PF_6$/0.2 mM $H_2O$ in $CH_3CN$ was sparged for 10 minutes with $N_2$ or $CO_2$ and cyclic voltammograms were taken as controls. From a 3 mM solution of catalyst in 0.3 M $NBu_4PF_6$ in $CH_3CN$, 100 μL was injected into the cell and cyclic voltammograms were retaken under both $N_2$ and $CO_2$. The solutions are then electrolyzed at the second reductive wave (−1.5 V, −1.6 V, −1.7 V for **6**, **7**, and **8**, respectively) for 2 h under $CO_2$ and subjected to GC analysis. For calculating turnover frequencies (TOF), a control in the absence of catalyst was run and the charge was subtracted from the overall charge passed in the catalysis.

**General Methods for X-Ray Crystallography**. Single-crystal X-Ray diffraction was conducted at University of California, Berkeley, College of Chemistry, X-Ray Crystallography Facility. Crystals were mounted on nylon loops in Paratone-N hydrocarbon oil. Air-sensitive samples were transferred from the glove box to Paratone-N and mounted quickly to avoid decomposition. All data collections were performed on either a Bruker SMART, or Bruker APEX diffractometer equipped with a CCD area detector and a low temperature apparatus. Data integration was performed using SAINT. Preliminary data analysis and absorption correction were performed using XPREP and SADABS.[5] Structure solution and refinement was performed using SHELX software package.[6]

**Bis(*N*-pyridylimidazoliumyl)ethane hexafluorophosphate ($[H_2{}^{Et}bimpy](PF_6)_2$, 4).** A solution of 2-(imidazolyl)pyridine (1.6 g, 11 mmol) in 5 mL of 1,2-dibromoethane was refluxed overnight. The solution was filtered by vacuum filtration and washed with $CH_2Cl_2$ to remove excess 1,2-dibromoethane. A sticky brown tar was obtained as **1** and suspended in $CH_3CN$. A second equivalent of 2-(imidazolyl)pyridine was added and refluxed overnight. The solution was again filtered and washed with $CH_2Cl_2$ and the residue was dissolved in deionized $H_2O$. $NH_4PF_6$ (3.6 g, 0.011 mol) was added and the product was filtered by vacuum filtration as an off-white solid (2.6 g, 4 mmol, 38%). $^1H$ NMR (300 MHz, DMSO): δ 10.06 (2H, s), 8.63 (d, *J* = 4.5, 2H), 8.52 (2H, s), 8.21 (t, *J* = 8.1, 2H), 7.97 (d, *J* = 8.1, 2H), 7.866 (s, 2H), 7.63 (t, *J* = 5.1, 2H), 4.48 (s, 4H) $^{13}C$ NMR (125 MHz, DMSO): δ 149.70, 147.53, 141.13, 136.31, 125.84, 124.20, 119.81, 114.49, 49.52. Anal. Calcd for $C_{18}H_{18}N_6F_{12}P_2$: C, 35.54; H, 2.98; N, 13.82. Found: C, 35.40; H, 2.85; N, 13.50. ESI-HRMS ($[M]^+$) *m/z* calcd for $C_{18}H_{18}N_6$ 159.0791, found 159.0789.

**Bis(*N*-pyridylimidazoliumyl)propane hexafluorophosphate ([$H_2$$^{Et}$bimpy]($PF_6$)$_2$, 5).** The synthesis of **5** followed the procedure of **4**, starting with 468 mg (3.2 mmol) of imidazolylpyridine and 5 mL of dibromopropane (296 mg, 0.48 mmol, 15%). $^1$H NMR (500 MHz, $CD_3CN$) δ 9.38 (s, 1H), 8.64 (d, *J* = 4.0 Hz, 2H), 8.19 – 8.14 (m, 4H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 1.9 Hz, 2H), 7.64 (dd, *J* = 7.3, 5.0 Hz, 2H), 4.41 (t, *J* = 7.3 Hz, 4H), 2.65 – 2.57 (q, *J* = 7.3 Hz, 2H). $^{13}$C NMR (125 MHz, DMSO) ): δ 149.58, 146.34, 140.59, 134.27, 125.58, 123.57, 119.79, 114.10, 46.94, 29.53. Anal. Calcd for $C_{18}H_{18}N_6F_{12}P_2$: C, 36.17; H, 3.24; N, 13.50. Found: C, 36.17; H, 2.89; N, 13.17.

**[Ni($^{Et}$bimpy)]($PF_6$)$_2$ (7).** A solution of **4** (1.2 g, 1.9 mmol) and $Ag_2O$ (2.97 g, 12 mmol) in 5 mL of $CH_3CN$ was stirred overnight and the resulting solution was filtered by vacuum filtration to remove excess $Ag_2O$. To the colorless filtrate, Ni(DME)$Cl_2$ (0.425 g, 1.9 mmol) was added and stirred overnight. The resulting solution was filtered by vacuum filtration and precipitated from $Et_2O$. The precipitate was recrystallized in $CH_3CN$/$Et_2O$ diffusion and yellow-green crystals were obtained (0.505 g, 77 mmol, 40%). $^1$H NMR (500 MHz, $CD_3CN$): δ 8.43 (d, *J* = 5.5, 2H), 8.34 (t, *J* = 7.5, 2H), 7.90 (d, *J* = 2.5,2H), 7.85 (d, *J* = 8.5, 2H), 7.67 (t, *J* = 6.5, 2H), 7.39 (d, *J* = 2.5, 2H), 4.57 (s, 4H) $^{13}$C NMR (100 MHz, $CD_3CN$) ): δ 146.51, 150.51, 149.86, 143.85, 127.09, 124.50, 116.56, 112.23, 49.14 Anal. Calcd for $C_{18}H_{16}N_6NiP_2F_6$: C, 32.51; H, 2.43; N, 12.64. Found: C, 32.05; H, 2.40; N, 12.81. ESI-HRMS ($[M]^+$) *m/z* calcd for $C_{18}H_{16}N_6Ni$ 187.0389, found 187.0392.

**[Ni($^{Pr}$bimpy)]($PF_6$)$_2$ (8).** The synthesis of **8** followed the procedure of **7**, starting with 180 mg (0.3 mmol) of **5** and 64 mg (0.3 mmol) of Ni(DME)$Cl_2$. Structural characterization found that

[Ni($^{Pr}$bimpy)Cl]($PF_6$) was formed and 103 mg (0.3 mmol) of $TlPF_6$ was added to obtain **8** quantitatively. Single crystals were obtained by diffusing $Et_2O$ into a concentrated solution of **8** in $CH_3CN$. $^1$H NMR (500 MHz, $CD_3CN$) δ 8.47 (d, *J* = 5.4 Hz, 2H), 8.36 (t, *J* = 7.8 Hz, 2H), 7.98 (d, *J* = 1.8 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 1.9 Hz, 2H), 4.36 (s, br, 2H), 3.98 (s, br, 2H), 2.29 (s, br, 2H). $^{13}$C NMR (125 MHz, DMSO) ): δ 157.18, 150.37, 149.50, 143.26, 125.93, 124.40, 117.88, 112.25, 46.05, 29.64. Anal. Calcd for $C_{18}H_{18}N_6F_{12}P_2$: , 33.61; H, 2.67; N, 12.38. Found: C, 33.33; H, 2.35; N, 12.03.

**[$Ni_2$($^{Me}$bimpy)$_2$](OTf)$_2$ (9).** A suspension of $KC_8$ (21 mg, 0.15 mmol) in THF was added to a suspension of **6** (100 mg, 0.15 mmol) in THF slowly. The solution slowly turned dark and was stirred overnight. The solution was filtered to obtained a dark precipitate of the product and graphite. The precipitate was dissolved in $CH_3CN$ and the graphite was filtered. The filtrate was evaporated and a black residue was obtained (24 mg, 0.069 mmol, 92%). Single crystals were obtained by diffusing $Et_2O$ into a concentrated solution of **9** in $CH_3CN$ at -30°C. $^1$H NMR (500 MHz, $CD_3CN$) δ 7.84 (triplet, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 2.1 Hz, 2H), 7.59 (m, 4H), 7.54 (d, *J* = 2.1 Hz, 2H), 7.13 (dd, *J* = 6.8, 2H), 6.41 (s, 2H). $^{13}$C NMR (125 MHz, $CD_3CN$) ): δ 187.35, 148.53, 148.36, 138.38, 134.41, 123.76, 115.36, 110.69, 63.10 Anal. Calcd for $C_{36}H_{28}N_{12}F_6O_6S_2$ $Ni_2$: C, 42.53; H, 2.77; N, 16.48. Found: C, 33.33; H, 2.61; N, 16.55.

**[$Ni_2$($^{Et}$bimpy)$_2$]($PF_6$)$_2$ (10).** The synthesis of **10** followed the procedure of **9**, starting with 7.8 (0.057 mmol) of $KC_8$ and 37 mg of **7** (0.056 mmol) and obtaining a yield of 24 mg of **10** (0.023 mmol, 82%). Single crystals were obtained by diffusing $Et_2O$ into a concentrated solution of **9** in $CH_3CN$ at -30°C. $^1$H NMR (500 MHz, $CD_3CN$): δ 7.95, 7.84, 7.68, 7.62, 7.49, 7.7, 7.24, 7.12, 7.037, 6.27, 4.44, 4.23 $^{13}$C NMR (125 MHz, $CD_3CN$) ): δ 183.72, 148.81, 147.34, 138.02, 125.23, 122.54, 121.13, 110.61, 49.01, 14.57 ESI-HRMS ($[M]^+$) *m/z* calcd for $C_{18}H_{16}N_6Ni$ 374.0784, found 374.0776.

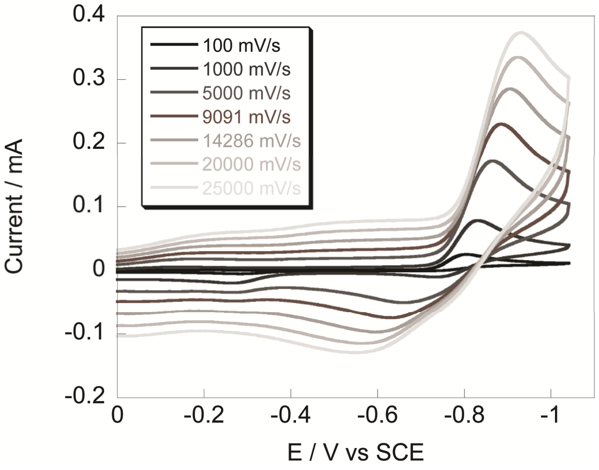

**Fig. S1** Cyclic voltammograms of **6** in the presence of $N_2$ at different scan rates, in 0.1 M $NBu_4PF_6$ in $CH_3CN$, using a glassy carbon disk electrode.

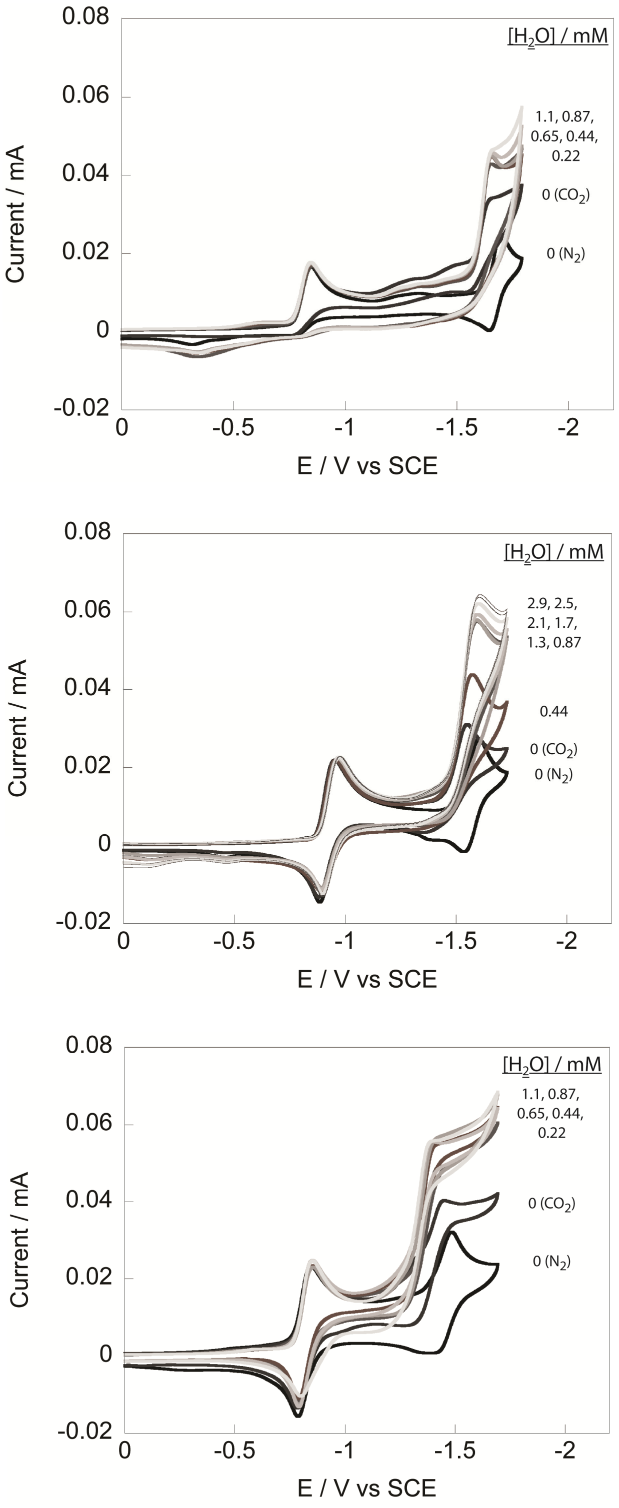

**Fig. S2** Cyclic voltammograms of **6** (top), **7** (middle), and **8** (bottom) in the presence of $N_2$, $CO_2$, and $H_2O$ under a $CO_2$ atmosphere in 0.1 M $NBu_4PF_6$ in $CH_3CN$. Scan rate: 100 mV/s; glassy carbon disk electrode.

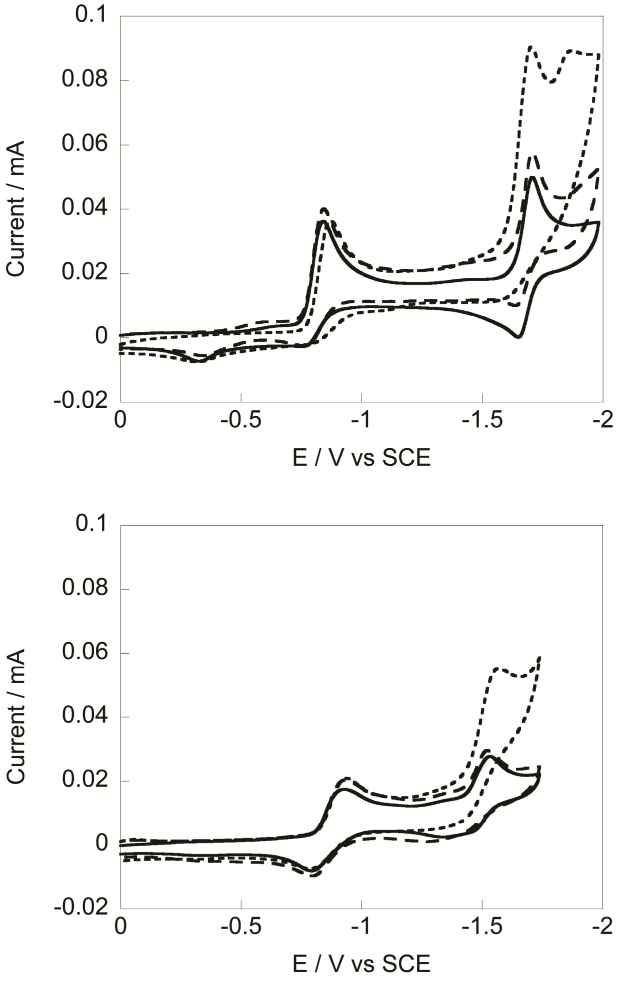

**Fig. S3** Cyclic voltammograms of **6** (top) and **7** (bottom) in the presence of $N_2$ (▬), 0.87 mM $H_2O$ under a $N_2$ atmosphere (▬ ▬), and subsequently, 0.87 mM $H_2O$ under a $CO_2$ atmosphere (▪▪▪) in 0.1 M $NBu_4PF_6$ in $CH_3CN$. Scan rate: 100 mV/s; glassy carbon disk electrode.

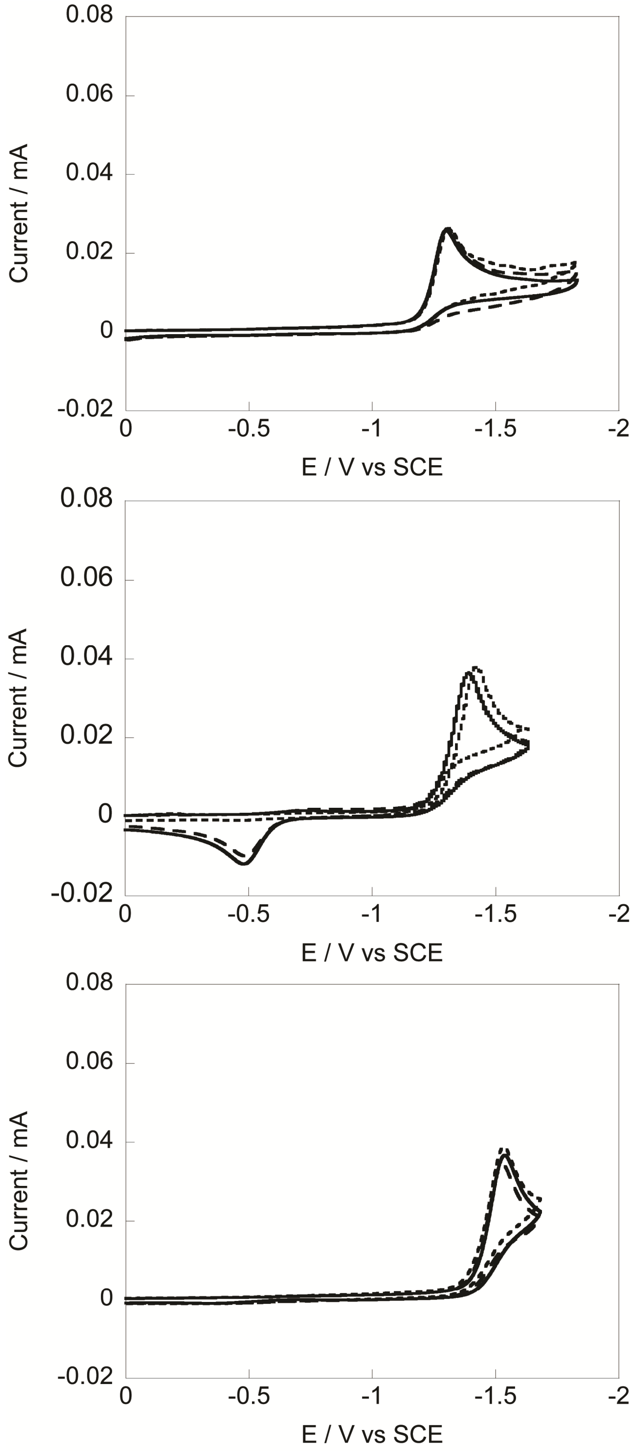

**Fig. S4** Cyclic voltammograms of **3** (top), **4** (middle), and **5** (bottom) in the presence of $N_2$ (▬), $CO_2$ (▬ ▬), and subsequently, 0.44 mM $H_2O$ under a $CO_2$ atmosphere (▪▪▪) in 0.1 M $NBu_4PF_6$ in $CH_3CN$. Scan rate: 100 mV/s; glassy carbon disk electrode.

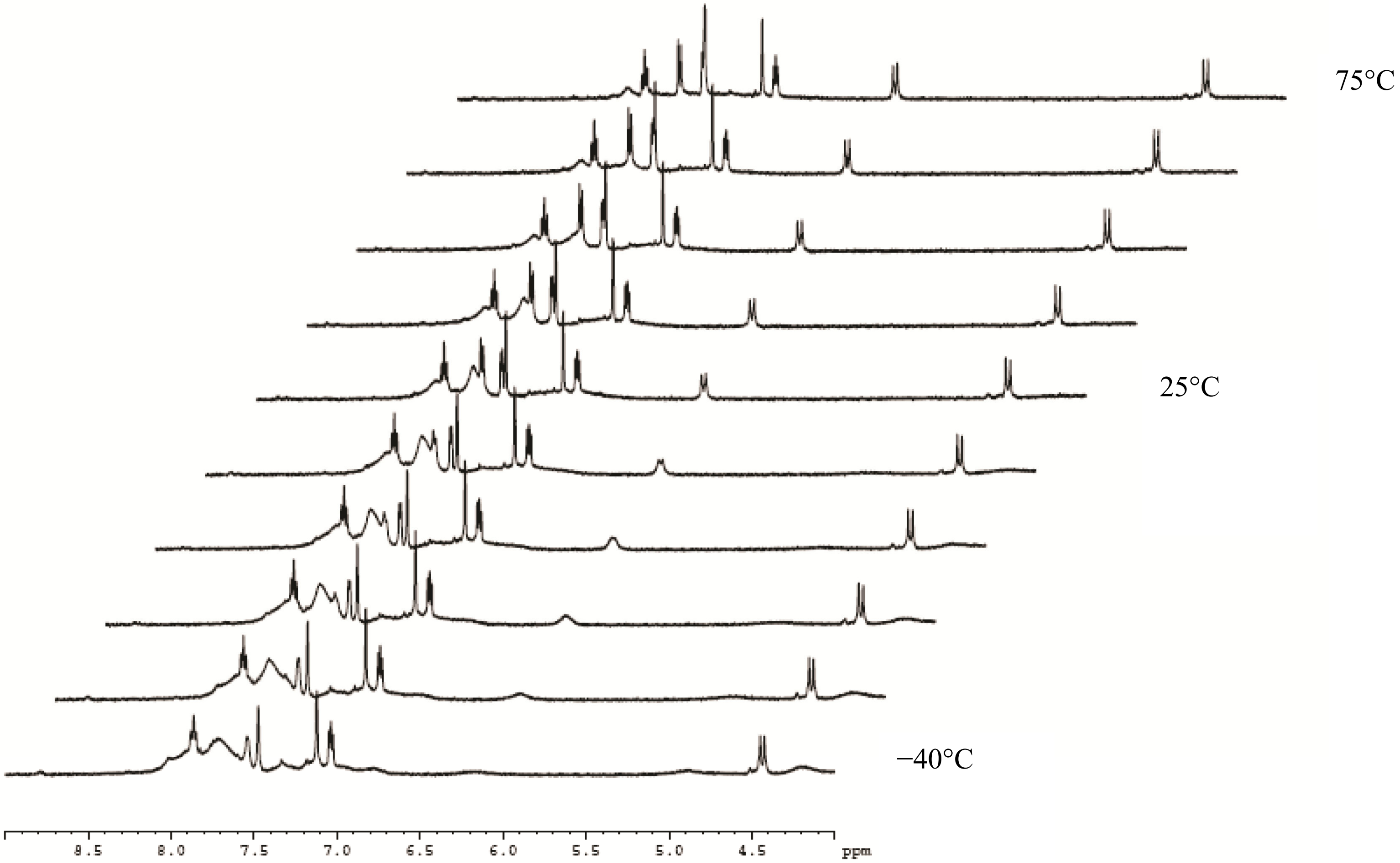

**Fig. S5** Variable-temperature $^1$H NMR of **10** from 75°C (top) to -40°C (bottom) in a gas-tight J. Young tube under a $N_2$ atmosphere. $CD_3CN$; 500 MHz.

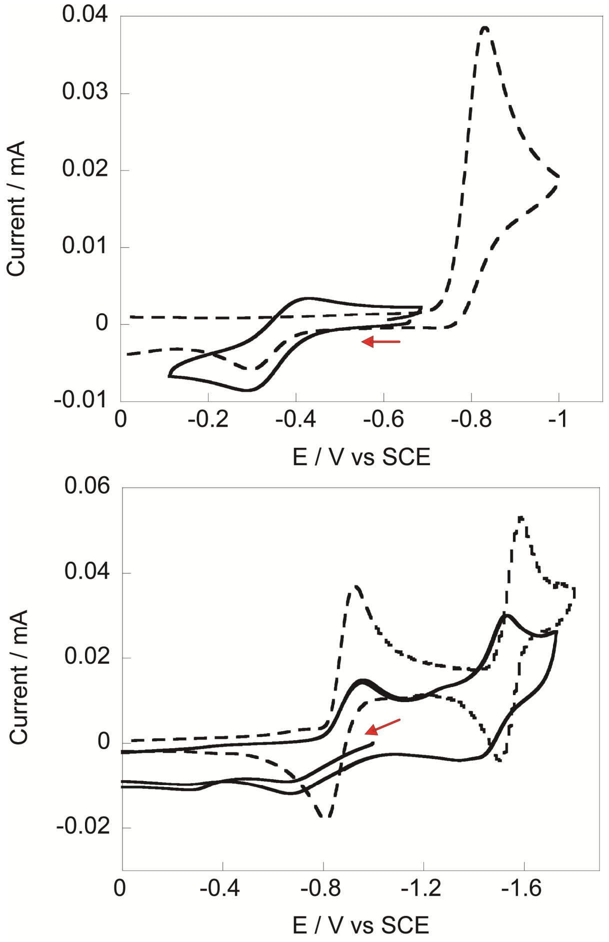

**Fig. S6** Cyclic voltammograms of **9** (top) and **10** (bottom) in the presence of $N_2$ (▬), and their Ni(II) congeners, **6** and **7**, respectively (▬ ▬) in 0.1 M $NBu_4PF_6$ in $CH_3CN$. The arrow refers to the direction of the potential scanned in **9** and **10**. Scan rate: 100 mV/s; glassy carbon disk electrode.

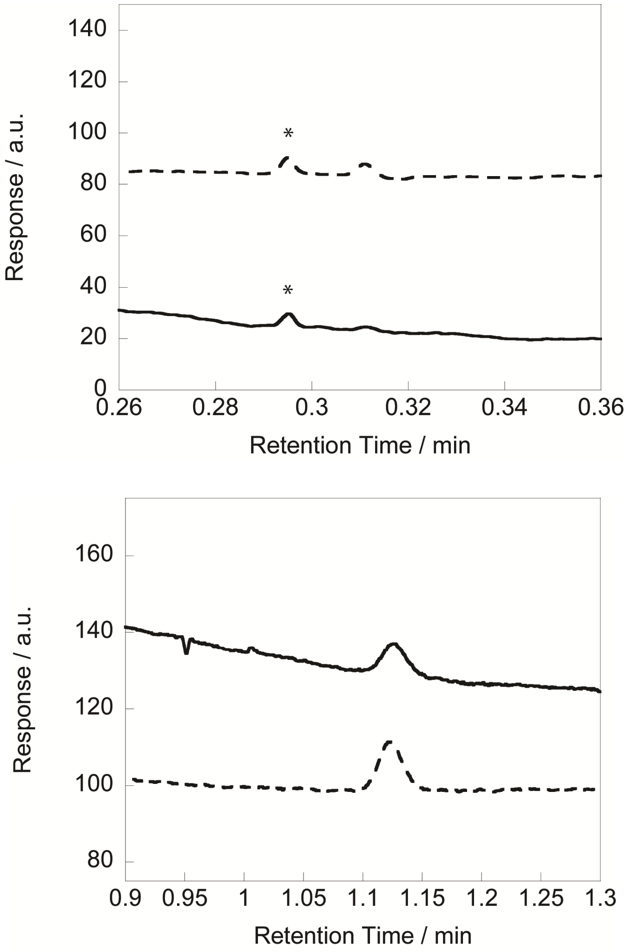

**Fig. S7** Gas chromatogram of **8** after 2 h electrolysis at -1.5 V relative to SCE (▬) and addition of 10 μL $H_2$ after 2 h electrolysis (▪▪▪) in 0.3 M $NBu_4PF_6$ in wet $CH_3CN$, using a glassy carbon rod electrode. $H_2$ (top) and CO (bottom) were identified at 0.31 and 1.15 min, respectively.

**unknown trace component also observed in a blank sample of air*

**Table S1.** Crystallographic Data for Ni complexes **7-10**

| | **[Ni($^{Et}$bimpy)](PF$_6$)$_2$ (7)** | **[Ni($^{Pr}$bimpy)](PF$_6$)$_2$ (8)** | **[Ni$_2$($^{Me}$bimpy)$_2$](OTF)$_2$ (9)** | **[Ni$_2$($^{Et}$bimpy)$_2$](PF$_6$)$_2$·2DME (10)** |
|---|---|---|---|---|
| **Empirical Formula** | $C_{18}H_{16}N_6NiP_2F_{12}$ | $C_{19}H_{18}N_6NiP_2F_{12}$ | $C_{36}H_{28}N_{12}Ni_2F_6O_6S_2$ | $C_{42}H_{48}N_{12}Ni_2P_2F_{12}O_4$ |
| **Formula Weight** | 665.02 | 679.04 | 1020.24 | 1192.28 |
| **Crystal System** | Monoclinic | Trigonal | Monoclinic | Monoclinic |
| **Space Group** | C2/c | R-3 | P2(1)/c | P2(1)/n |
| ***a*** | 10.0790(7) | 33.730(4) | 7.404(17) | 10.6550(15) |
| ***b*** | 19.0802(15) | 33.730(4) | 31.424(7) | 21.779(3) |
| ***c*** | 12.1281(9) | 13.4121(18) | 16.616(4) | 21.880(3) |
| **α (°)** | 90 | 90 | 90 | 90 |
| **β (°)** | 100.4060(10) | 90 | 98.615(4) | 99.063(2) |
| **γ (°)** | 90 | 120 | 90 | 90 |
| ***V(Å$^3$)*** | 2294.0(3) | 12314(3) | 3822.2(15) | 5014.0(12) |
| ***Z*** | 4 | 18 | 8 | 8 |
| **$\rho_{calc}$ (g/cm$^3$)** | 1.926 | 1.536 | 1.773 | 3.159 |
| **μ (mm$^{-1}$)** | 1.106 | 0.866 | 1.190 | 1.828 |
| **2θ$_{max}$ (°)** | 50.66 | 50.74 | 50.70 | 50.9 |
| **Reflections Collected** | 12525 | 94483 | 32458 | 51586 |
| **Independent Reflections** | 2099 | 5384 | 6961 | 9220 |
| **Refl/Param** | 11.45 | 14.91 | 12.06 | 13.94 |
| ***R1*, w*R2* (*I*>2σ)** | 0.0217, 0.0564 | 0.0406, 0.1052 | 0.0518, 0.1058 | 0.0406, 0.0825 |
| ***R1*, w*R2* (all data)** | 0.0220, 0.0566 | 0.0485, 0.1099 | 0.0939, 0.1254 | 0.0837, 0.1003 |
| **Ni-Ni (*Å*)** | | | 2.5087(10) | 2.5790 (6) |

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