# Nickel Phosphine Catalysts with Pendant Amines

# for the Electrocatalytic Oxidation of Alcohols

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#### **General Procedures.**

All manipulations were performed under N<sub>2</sub> using standard glovebox and Schlenk technique. Protio solvents were purchases anhydrous from Fischer and Aldrich and further dried on a solvent drying system. Acetonitrile- $d_3$  was purchased from Cambridge Isotopes Laboratories and distilled from P<sub>2</sub>O<sub>5</sub>. The amines were purchased from Aldrich, dried over KOH or CaH<sub>2</sub> and stored under inert atmosphere until use. Phosphines were purchases from Aldrich and Strem and used as received. Alcohols and benzaldehyde were purchased form Aldrich and were degassed and dried over 3 A molecular sieves. Complexes **1-Ph**, **1-Bn**, **1-'Bu**, and **2** were synthesized by literature methods.<sup>1</sup> The P<sup>tBu</sup><sub>2</sub>N<sup>tBu</sup><sub>2</sub> ligand was synthesized by the below procedure modified from Liu et al.<sup>2</sup> All NMR spectra were collected on a Varian 500 MHz spectrometer at 25 °C in CD<sub>3</sub>CN unless otherwise noted and referenced versus tetramethylsilane (<sup>1</sup>H, 0.0 ppm) or H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P, 0.0 ppm).

**Synthesis of P<sup>tBu</sup><sub>2</sub>N<sup>tBu</sup><sub>2</sub>.** A 250 mL Schlenk flask was loaded with paraformaldehyde (1.80 g, 60.0 mmol) and 125 mL of ethanol. The flask was degassed and placed under N<sub>2</sub> before adding tertbutylphosphine (3.9 mL, 2.7g, 30 mmol) and heating to 75 °C for 5 hours. Neat tertbutylamine (3.2 mL, 2.2g, 30 mmol) was added slowly before leaving the reaction to stir at 22 °C for approximately 18 hours. The solvent was removed under vacuum and the resulting sticky white solid was dissolved in 10 mL diethylether, layered with 10 mL acetonitrile, and stored at -35 °C to yield white crystalline solid (39-76% yield). The <sup>31</sup>P NMR spectrum matches that from the previously reported synthesis.<sup>2</sup>

#### Electrochemistry

**Cyclic voltammetry.** All electrochemical experiments were performed in 1.0 mL 0.1 M <sup>n</sup>BuN<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN under dry N<sub>2</sub> at 21 °C using a CH instruments model 620D or 660C potentiostat with a standard three-electrode configuration. This includes a 1 mm PEEK-encased glassy carbon rod as the working electrode, a glassy carbon rod counter electrode, and a silver wire in electrolyte separated from the main solution by a Vycor frit as a pseudo-reference. Scans were collected at 50 mV/s unless otherwise noted and all potentials are referenced versus  $Cp_2Fe^{+/0}$  (0.0 V).

Bulk Electrolysis. Bulk electrolyses were performed in 1.0 or 10.0 mL solution of 0.1 M <sup>n</sup>BuN<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN under dry N<sub>2</sub> at 21 °C using an EC Epsilon BASi potentiostat equipped with a PWR-3 Power Module with a standard three-electrode configuration. This included a glassy carbon foam as the working electrode, a nichrome wire as the counter electrode, and a silver wire as the pseudo-reference electrode. The counter electrode and pseudo-reference electrode were suspended in 0.1 M <sup>n</sup>BuN<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN and separated from the main solution by a glass and Vycor frit, respectively. See images below. These catalysts are known to oxidize stoichiometric quantities of alcohol without applied potential or chemical oxidant, and therefore current efficiencies were calculated assuming that the Ni(II) precatalyst oxidizes a molar equivalent of alcohol without external potential. The non-exhaustive electrolysis was performed over 30 minutes, and the TON for oxidation of benzyl alcohol by 1-<sup>t</sup>Bu was determined to be 3.1 by integration of the benzaldehyde resonances in the <sup>1</sup>H NMR spectrum relative to a 1,3,5trimethoxybenzene as an internal standard. Benzoic acid (or benzoate) was not observed, but would not be expected in the absence of a significant concentration of water. The average catalytic turnover frequency during electrolysis was 6 h<sup>-1</sup>, which is not equivalent to that from

the cyclic voltammetry results due to the mass transport limitations in an electrolysis experiment. Specifically, most of the catalyst is not near the electrode surface in an electrolysis, and the average turnover frequency accounts for all of the catalyst in the bulk of the solution.

**Electrolyte and Conjugate Acid.** The turnover frequencies of the 1-catalyzed oxidization of diphenylmethanol to benzophenone was measured by NMR spectroscopy using  $Cp*_2FeBF_4$  as a chemical oxidant by the same method as described in ESI reference 1a. The addition of 0.06 M Et<sub>3</sub>NHBF<sub>4</sub> or Et<sub>4</sub>NBF<sub>4</sub> resulted in an observed turnover frequency of 54-57 h<sup>-1</sup> versus the reported value of 26.8 h<sup>-1</sup> reported in reference 3. This increase in turnover frequency may be the result of increased polarization of the solvent medium. This rate increase is unlikely the result of acid (Et<sub>3</sub>NH<sup>+</sup>) because it is also observed with Et<sub>4</sub>NBF<sub>4</sub>.





**Figure S1.** A photograph of the electrodes (left) used in bulk electrolysis including the nichrome counter electrode (A), the silver pseudo-reference electrode (B), the carbon foam working electrode (C), and the 1 mm disk carbon electrode used for pre- and post-electrolysis cyclic voltammograms (D). The bulk electrolysis setup (right) in the reaction solution wired for bulk electrolysis.

The TOF is calculated using eq 3 from the main text. The initial current  $(i_p)$  is measured from the Ni(II/I) reduction wave before addition of alcohol or base, and catalytic current  $(i_{cat})$  is measured from Ni(II/I) oxidation wave after the addition of alcohol and base as is shown in Figure S2.



**Figure S2.** Cyclic voltammogram of complex  $1^{-t}Bu$  (black, 3.7 mM) and complex  $1^{-t}Bu$  with upon addition of BnOH and Et<sub>3</sub>N (blue) with the  $i_p$  and  $i_{cat}$  measurements show. The arrows indicate the starting potential and direction of each scan. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 3.7 mM  $1^{-t}Bu$ , 57 mM BnOH, and 115 mM Et<sub>3</sub>N.



**Figure S3.** Cyclic voltammogram of complex 1-<sup>*t*</sup>**Bu** (black, 4.0 mM) and complex 1-<sup>*t*</sup>**Bu** with upon addition of BnOH (red, 43 mM BnOH), indicating no background oxidation of benzyl alcohol in the absence of base, even in the presence of the catalyst. The voltammograms were collected in 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s.

### **Kinetic Data**



**Figure S4.** A linear trend in the plot of catalytic current ( $i_{cat}$ ) versus catalyst concentration for **1**-<sup>*t*</sup>**Bu** indicates a first-order dependence with respect to catalyst concentration. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 57 mM BnOH and 115 mM Et<sub>3</sub>N.



**Figure S5.** The plot of  $i_{cat}/i_p$  versus Et<sub>3</sub>N concentration (mM) indicates an approximate independence with respect to base concentration. Et<sub>3</sub>N concentration was examined from 0.0072 M to 0.22 M. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 0.37 mM **1-**<sup>*t*</sup>Bu and 42 mM BnOH.



**Figure S6.** The plot of  $i_{cat}/i_p$  versus benzyl alcohol concentration (mM). Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 0.37 mM **1-'Bu** and 84 mM Et<sub>3</sub>N.



**Figure S7.** The plot of  $[BnOH]^{1/2}$  (M<sup>1/2</sup>) versus TOF (s<sup>-1</sup>) resulting in a roughly linear trend indicating a half-order dependence with respect to [BnOH]. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 0.37 mM **1-'Bu** and 84 mM Et<sub>3</sub>N.



**Figure S8.** The plot of  $i_{cat}/i_p$  versus iPr<sub>2</sub>EtN (mM) concentration indicates an initial dependence on iPr<sub>2</sub>EtN concentration followed by independence with respect to base concentration. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 0.38 mM 1-<sup>*t*</sup>Bu and 42 mM BnOH.

Alcohol	$i_{\rm cat}/i_p$	
iPrOH	2.22, 2.70	
iPrOD	2.48, 2.41	
iPrOD-d8	2.28, 2.46	

**Table S1.** Currents Enhancements of the Catalytic Oxidation of 2-Propanol Isotopologs by  $Ni(P^{tBu}_2N^{tBu}_2)(CH_3CN)_2(BF_4)_2$  with Et<sub>3</sub>N.<sup>a</sup>

<sup>a.</sup> Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s with 0.37 mM **1-**<sup>*t*</sup>Bu, 42 mM alcohol, and 84 mM Et<sub>3</sub>N.



**Figure S9.** Cyclic voltammograms of complex  $1^{-t}Bu$  in the presence of Et<sub>3</sub>N and BnOH to determine catalysts stability under these conditions, in the absence of applied potential. The cyclic voltammograms were collected at 1 hour intervals. The decrease in oxidative current may be due to catalyst deactivation. The arrows indicate the starting potential and direction of each scan. Conditions: 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s, 0.55 mM  $1^{-t}Bu$ , 57 mM MeOH, and 115 mM Et<sub>3</sub>N. Potentials are referenced versus Cp<sub>2</sub>Fe<sup>+/0</sup> (0.0 V).



**Figure S10.** Cyclic voltammogram of complex 1-<sup>*t*</sup>**Bu** (black, 2.7 mM) and complex 1-<sup>*t*</sup>**Bu** with upon addition of MeOH and Et<sub>3</sub>N (blue). The arrows indicate the starting potential and direction of each scan. Conditions: 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s, 3.7 mM 1-<sup>*t*</sup>**Bu**, 42 mM MeOH, and 84 mM Et<sub>3</sub>N. Potentials are referenced versus  $Cp_2Fe^{+/0}$  (0.0 V).



**Figure S11.** Cyclic voltammogram of complex **1-**<sup>*t*</sup>**Bu** (black), the resulting catalytic wave after addition of Et<sub>3</sub>N and BnOH (blue), and the catalytic wave upon addition of 39 mM benzaldehyde (BzH). The arrows indicate the starting potential and direction of each scan. The addition of benzaldehyde results in a minor decrease in catalytic current possibly due to product inhibition. Conditions: 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN scanning at 50 mV/s, 0.37 mM **1-**<sup>*t*</sup>**Bu**, 42 mM BnOH, 84 mM Et<sub>3</sub>N, and 39 mM benzaldehyde. Potentials are referenced versus Cp<sub>2</sub>Fe<sup>+/0</sup> (0.0 V).

## References

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