

Supporting Information for:

A Versatile Synthesis of $P^R_2N^{R'}_2$ Ligands for
Molecular Electrocatalysts with Pendant Bases in the
Second Coordination Sphere

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General Considerations

Unless otherwise noted, all reactions and manipulations were performed under a N₂ atmosphere using standard glovebox or Schlenk line techniques. Glassware was dried in an oven overnight prior to use. Acetonitrile and tetrahydrofuran (THF) were purified via passage through alumina and molecular sieves. Ethanol was dried over 4 Å molecular sieves. Aniline and triethylamine were distilled from CaH₂ prior to use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was crystallized from methanol and dried under vacuum prior to use. Benzyl chloride was purified by passage through alumina. Methyl iodide was distilled from CaCl₂. [Ni(P^{Ph}₂N^{Ph}₂)(CH₃CN)](BF₄)₂ (**7**) was prepared according to literature methods.¹ All other chemicals were used as obtained from commercial suppliers. Electrochemical measurements were performed on a Gamry potentiostat in an air-tight cell with a glassy carbon working electrode, a Pt counter electrode, and a Ag⁺⁰ wire pseudo reference electrode separated from the bulk solution with a Vycor tip. Benzotrile was used as the solvent and 0.2 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. ¹H and ³¹P{¹H} NMR spectra were obtained on a 300 MHz Varian, 400 MHz Varian or a 500 MHz Joel spectrometer. ¹H NMR spectral data are referenced against the residual solvent signal and are reported in ppm downfield of tetramethylsilane (δ = 0). ³¹P{¹H} NMR spectral data were referenced against an external H₃PO₄ (δ = 0) reference. Elemental analyses were performed by NuMega Labs in San Diego, CA.

Preparation of tris(hydroxymethyl)phosphine (THP, 2)

A large quantity of THP was prepared and isolated for use in the subsequent alkylation reactions. Tetrakis(hydroxymethyl)phosphonium chloride (THPCl, 1) (20 mL, 80% in water, 110 mmol) was dried under vacuum in a 250 mL Schlenk flask. To the resulting oily residue was added 100 mL triethylamine, which precipitated triethylammonium chloride. The supernatant was filtered via cannula into a 250 mL Schlenk flask and dried under vacuum. The resulting oil was dissolved in 10 mL methanol, to which was added 100 mL diethyl ether. This flask was then placed in a freezer at $-40\text{ }^{\circ}\text{C}$ for a week, after which a white precipitate, THP, was observed. This was filtered via cannula, rinsed with ether, and dried to yield 6.58 g THP (53 mmol, 48% yield). Spectral data matched reported values.²

Synthesis of $\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2$ (5)

A 100 mL Schlenk flask was charged with THPCl (6.0 mL, 80% in water, 33 mmol) and the volatiles were removed under vacuum overnight. The resulting oil was dissolved in 50 mL triethylamine and stirred overnight at room temperature, precipitating triethylammonium chloride as a fine white solid. The supernatant was filtered via cannula into a 100 mL Schlenk flask and the volatiles were removed under vacuum. The resulting oil was dissolved in 20 mL THF. To this stirring solution of THP, 1.9 mL CH_3I (30 mmol) was slowly added at $-40\text{ }^{\circ}\text{C}$ via syringe and the reaction was allowed to warm to room temperature overnight. The volatiles were removed under vacuum and the residue was redissolved in 20 mL triethylamine. The solution was stirred overnight, and the precipitation of the triethylammonium iodide salt was observed. The supernatant was filtered via cannula and dried under vacuum to yield $\text{CH}_3\text{P}(\text{CH}_2\text{OH})_2$ as an

oil. This was dissolved in 50 mL dry ethanol, to which was added 2.3 mL aniline (25 mmol). This mixture was stirred at room temperature for one week. A white solid precipitated, and the supernatant was removed via cannula. The solid was rinsed with absolute ethanol and dried to give 3.29 g 3,7-dimethyl-1,5-diphenyl-1,5-diaza-3,7-diphosphacyclooctane ($P^{Me}_2N^{Ph}_2$) (10 mmol, 63% yield).

A sample was prepared for elemental analysis by recrystallization from toluene. Calcd. for $C_{18}H_{24}N_2P_2$: 65.44% C, 7.32% H, 8.48% N. Found: 65.47% C, 7.43% H, 8.47% N. 1H NMR (400MHz, CD_3CN): δ = 7.22 (m, ArH, 4H), 6.70 (m, ArH, 6H), 4.17 (t, J = 14.3 Hz, CH_2 , 4H), 3.44 (dd, J = 14.8 Hz, J = 4.6 Hz, CH_2 , 8H), 1.02 (d, J = 4.4 Hz, CH_3 , 6H). $^{31}P\{^1H\}$ NMR (162MHz, CD_3CN): δ = -61.8 ppm (s).

Synthesis of $P^{Bn}_2N^{Ph}_2$ (6)

Tris(hydroxymethyl)phosphine (0.58 grams, 4.6 mmol) and benzyl chloride (0.53 mL, 4.6 mmol) were dissolved in tetrahydrofuran and stirred overnight in a 100 mL Schlenk flask. This reaction mixture was dried under vacuum and dissolved in triethylamine, and the immediate precipitation of triethylammonium chloride was observed. The supernatant was filtered via cannula into another 100 mL Schlenk flask and dried under vacuum to yield 0.61 grams of oily benzylbis(hydroxymethyl)phosphine. This was dissolved in dry ethanol and refluxed with 0.30 mL aniline (3.2 mmol) overnight, precipitating the ligand 3,7-dibenzyl-1,5-diphenyl-1,5-diaza-3,7-diphosphacyclooctane ($P^{Bn}_2N^{Ph}_2$) as a white solid. This was filtered via cannula, washed with ethanol, dried under vacuum, and purified by recrystallization from toluene to yield 0.15 g $P^{Bn}_2N^{Ph}_2$ (0.31 mmol, 13% yield). Spectral data matched reported values.³

Preparation of $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$

The nickel complexes $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})_n](\text{BF}_4)_2$ ($\text{R} = \text{Me}$, $n = 0$ (**7**) and $\text{R} = \text{Bn}$, $n = 1$ (**8**)) were prepared following the same procedure. The following is a representative example for $[\text{Ni}(\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2)_2](\text{BF}_4)_2$ (**5**). $\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2$ (370 mg, 1.1 mmol) was added to a solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ (340 mg, 0.71 mmol) in 50 mL acetonitrile. The color of this solution immediately turned deep red. This mixture was stirred overnight and solid was precipitated by layering with diethyl ether. The solid was filtered via cannula, rinsed with diethyl ether, and dried under vacuum to yield 0.45 g of microcrystalline red $[\text{Ni}(\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2)_2](\text{BF}_4)_2$ (0.48 mmol, 86% yield).

^1H NMR (500MHz, CD_3CN): $\delta = 7.34$ (t, $J = 8.0$ Hz, ArH, 8H), 7.09 (d, $J = 8.0$ Hz, ArH, 8H), 7.03 (t, $J = 7.3$ Hz, ArH, 4H), 3.74 (d, $J = 14.0$ Hz, CH_2 , 8H), 3.68 (d, $J = 14.0$ Hz, CH_2 , 8H), 1.83 (s, CH_3 , 12H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5MHz, CD_3CN): $\delta = 1.2$ ppm (s). Calculated M/z for $[\text{Ni}(\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2)_2]^{2+}$: 359.1091 ; Found: 359.1088.

Spectral data for complex **8** matched literature values.³

Preparation of $[\text{Ni}(\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2)_2](\text{SO}_3\text{CF}_3)_2$ (**11**) and X-ray Structure Determination

In a 20 mL scintillation vial, $\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2$ (0.107 g, 0.386 mmol) was added to a solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{CF}_3\text{SO}_3)_2$ (0.116 g, 0.192 mmol) in 10 mL acetonitrile. The color of this solution immediately turned deep red. This mixture was stirred overnight. Attempts to isolate solid $[\text{Ni}(\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2)_2](\text{CF}_3\text{SO}_3)_2$ failed as the complex oils out of solution upon layering of diethyl ether into acetonitrile. An analogous microscale reaction performed in a J Young NMR tube (2.2 mg $\text{P}^{\text{Me}}_2\text{N}^{\text{Ph}}_2$, 2.0 mg $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{CF}_3\text{SO}_3)_2$) provided spectroscopic evidence for the complex

with a broad peak in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with $\delta = 1.4$ ppm. X-ray quality crystals of **9** were grown by vapor diffusion of diethyl ether into acetonitrile. Single crystal X-ray structural data was collected at 100K on a Kappa diffractometer equipped with a Bruker Apex detector. The structure was solved by direct methods using SHELXS-97 and refined with full-matrix least-squares procedures using SHELXL-97.⁴

Table S1. X-ray determination details for **11**

Empirical formula	C ₄₂ H ₅₄ F ₆ N ₆ Ni O ₆ P ₄ S ₂	
Formula weight	1099.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C222(1)	
Unit cell dimensions	a = 9.599(4) Å	$\alpha = 90^\circ$.
	b = 19.149(9) Å	$\beta = 90^\circ$.
	c = 26.346(10) Å	$\gamma = 90^\circ$.
Volume	4843(3) Å ³	
Z	4	
Density (calculated)	1.508 Mg/m ³	
Absorption coefficient	0.695 mm ⁻¹	
F(000)	2280	
Crystal size	0.20 x 0.20 x 0.10 mm ³	
Theta range for data collection	2.13 to 25.43°.	
Index ranges	-10 ≤ h ≤ 11, -22 ≤ k ≤ 23, -30 ≤ l ≤ 31	
Reflections collected	14015	
Independent reflections	4418 [R(int) = 0.0404]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9338 and 0.8735	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4418 / 0 / 306	

Goodness-of-fit on F^2	1.142
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0316, wR2 = 0.0725
R indices (all data)	R1 = 0.0427, wR2 = 0.1000
Absolute structure parameter	0.024(17)
Largest diff. peak and hole	0.479 and -0.369 e.Å ⁻³

¹ Märkl, V. G.; Jin, G. Y.; Schoerner, C. *Tetrahedron Lett.* **1980**, *21*, 1409–1412.

² Chatt, J.; Leigh, G. J.; Slade, R. M. *Dalton Trans.* **1973**, 2021–2028.

³ Kilgore, U. J.; Stewart, M. P.; Helm, M. L.; Dougherty, W. G.; Kassel, W. S.; DuBois, M. R.; DuBois, D. L.; Bullock, R. M. *Inorg. Chem.* **2011**, *50*, 10908–10918.

⁴ Sheldrick, G. *Acta Cryst. A* **2008**, *64*, 112–122.