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Covalent Attachment of Diphosphine Ligands to Glassy Carbon Electrodes via Cu-Catalyzed Alkyne-Azide Cycloaddition. Metallation with Ni(II)

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Abstract: Covalent tethering of $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2}$ ligands ($\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2} = 1,5\text{-di-(4-ethynylphenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane}$) to planar, azide-terminated glassy carbon electrode surfaces has been accomplished using a Cu^{I} -catalyzed alkyne-azide cycloaddition (CuAAC) coupling reaction, using a $\text{BH}_3\leftarrow\text{P}$ protection-deprotection strategy. Deprotected, surface-confined ligands were metallated using $[\text{Ni}^{\text{II}}(\text{MeCN})_6](\text{BF}_4)_2$. X-ray photoelectron spectroscopic measurements demonstrate that metallation introduced 1.3 equivalents Ni^{II} per diphosphine onto the electrode surface. Exposure of the surface to a second diphosphine ligand, $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}_2}$, resulted in the removal of Ni from the surface. Protection, coupling, deprotection, and metallation conditions were optimized using solution-phase model systems, with benzyl azide as a model for the azide-terminated carbon surface; these reactions generate a $[\text{Ni}^{\text{II}}(\text{diphosphine})_2]^{2+}$ complex.

Introduction

Soluble coordination complexes of the abundant, inexpensive metal Ni have been developed that catalyze electrocatalytic hydrogen oxidation and production with high rates and energy efficiencies.¹⁻⁴ The strategy for development of these systems leverages the fine control over active site structure and energetics that is typically accessible with homogeneous catalyst systems. This approach does not translate easily to conventional heterogeneous electrocatalysts such as Pt nanoparticles, which cannot yet be readily manipulated and characterized in the same ways. However, heterogeneous systems^{5, 6} are inherently better-suited for implementation in hydrogen fuel cells⁷ and water electrolysis reactors^{8, 9} since the catalyst remains at the electrode surface. Confinement of homogeneous electrocatalysts to electrode surfaces has thus emerged as a compelling goal. That goal is accompanied by a new set of fundamental scientific questions, including whether confinement of a particular class of homogeneous catalysts in a flow reactor is possible, and if so, how such confinement influences catalyst performance and stability.

We report here the exploration of a synthetic route to covalent attachment of complexes belonging to the $\text{Ni}(\text{P}_2\text{N}_2)_2$ family of catalysts (P_2N_2 ligands are 1,5-diaza-3,7-diphosphacyclooctanes with alkyl or aryl substituents at P and N, as shown in Scheme 1), variants of which are electrocatalysts for H_2 production¹⁰⁻¹² and H_2 oxidation.¹³ Artero and co-workers have reported examples where $\text{Ni}(\text{P}_2\text{N}_2)_2$ molecular electrocatalysts have been attached to conductive substrates. In one case they reported covalent binding to carbon nanotubes through an amide linkage,¹⁴ providing electrocatalysts for H_2 production with very high turnover numbers. In a different approach, they used π - π interactions between carbon nanotubes and pyrene groups on the P_2N_2 ligands.¹⁵ Moore and Sharp reported grafting of $\text{Ni}(\text{P}_2\text{N}_2)_2$ complexes to semiconducting materials.¹⁶ Reisner and co-workers reported photocatalytic H_2 generation

with a turnover frequency of $460 \pm 60 \text{ h}^{-1}$ from a $[\text{Ni}(\text{P}_2\text{N}_2)_2]^{2+}$ catalyst immobilized on metal oxide semiconductors.^{17, 18}

Our previous studies¹⁹ show that $\text{Ni}(\text{P}_2\text{N}_2)_2$ complexes can be immobilized onto glassy carbon electrode surface, but these surface-bound coordination complexes can be unstable compared to both their homogeneous counterparts and to heterogeneous systems such as platinum nanoparticles. A clear understanding of the influence of surface attachment on turnover frequency and overpotential will be facilitated by precise control over, and confirmation of, surface attachment at the molecular level. Ideal systems for this purpose will be as similar as possible to their well-characterized homogeneous analogs with respect to molecular structure, electrode surface morphology, and reaction conditions. This paper describes the binding of an alkyne-terminated ligand with a planar, azide-terminated glassy carbon surface, and its subsequent metallation.

Results

Several reports have shown that the Cu-catalyzed alkyne-azide cyclization (CuAAC) reaction²⁰⁻²² (“click” reactions) can be used to attach metal complexes to surfaces.²³⁻²⁷ We describe the binding of a protected, alkyne-terminated ligand with an azide-terminated glassy carbon surface using the Cu-catalyzed alkyne-azide cyclization (CuAAC) reaction,²⁰⁻²² and the subsequent deprotection and metallation of the bound ligand. Conditions for these reactions were selected from experiments using benzyl azide as a model for azide-terminated glassy carbon. Reactions with both the model and the authentic glassy carbon surface are presented in Schemes 1 and 2. We first describe the preparation of the alkyne-terminated ligand, its metallation with Ni^{II} , and catalysis and cyclization results with this complex. We then report the protection-cyclization-deprotection results obtained using benzyl azide, along with catalysis results obtained

with the Ni^{II} complex obtained from the cyclized product. Finally, we describe the results obtained following the same protocol but with the azide-terminated glassy carbon electrode used instead of benzyl azide. These reactions were studied using X-ray photoelectron spectroscopy and electrochemical studies.

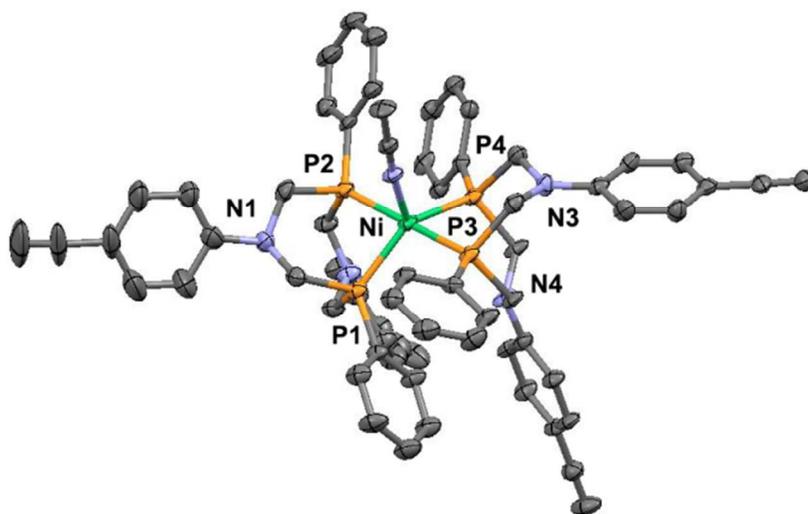
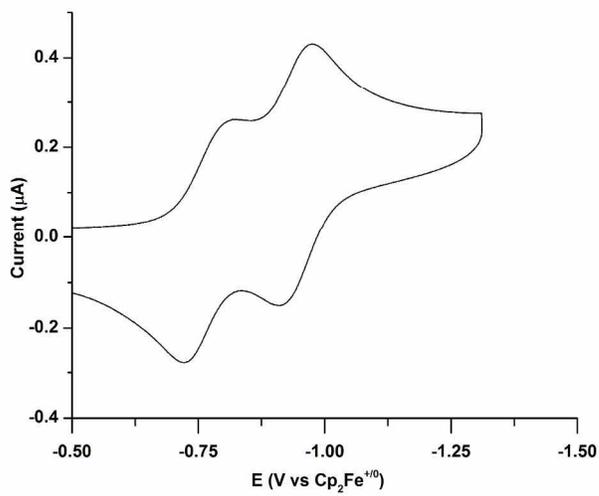
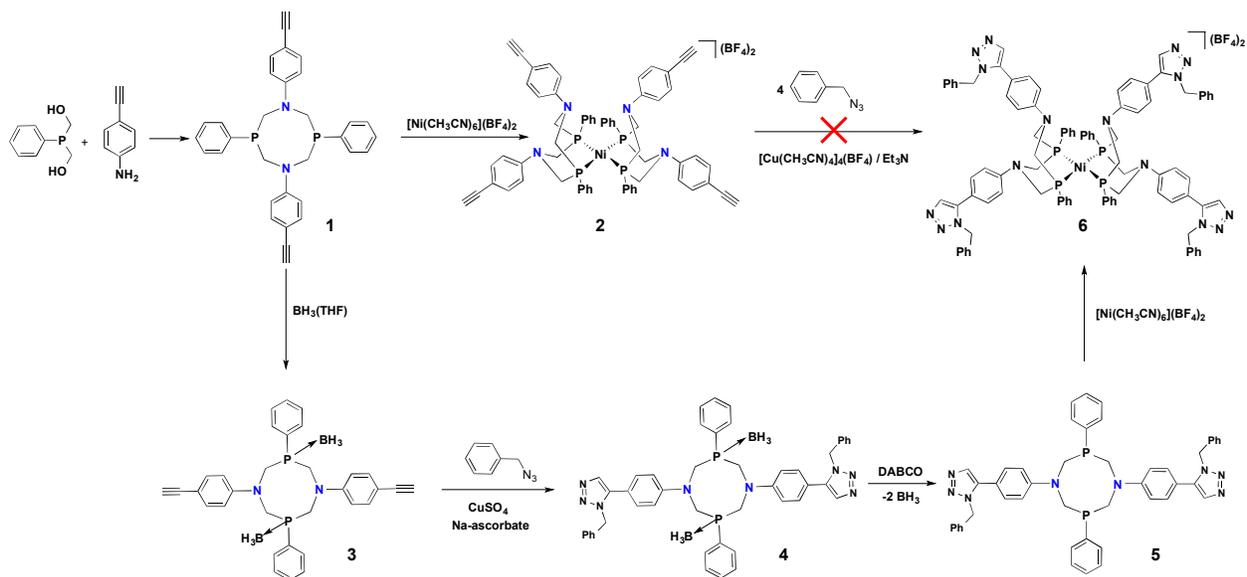


Figure 1. Molecular structure of $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2})_2(\text{MeCN})](\text{BF}_4)_2$ with partial atom numbering. Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms are omitted for clarity.

The diphosphine ligand $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2}$ (**1**) was prepared by condensation of *para*-ethynylaniline with $\text{PhP}(\text{CH}_2\text{OH})_2$. Details are presented in the Experimental Section. Spectroscopic and elemental analysis data are consistent with the structure shown. This ligand complexes cleanly with the Ni^{II} complex $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ to afford $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2})_2(\text{MeCN})](\text{BF}_4)_2$, **2**, which was characterized by NMR spectroscopy, single crystal X-ray diffraction (Figure 1), and elemental analysis. Structural parameters are similar to previously reported variants.^{10,11}

Scheme 1



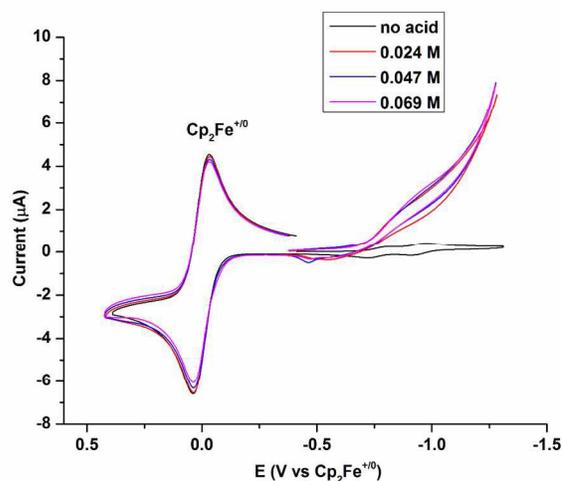


Figure 2: Cyclic voltammograms of 0.5 mM $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{MeCN})](\text{BF}_4)_2$ in MeCN/0.1 M $[\text{}^n\text{Bu}_4\text{N}]\text{PF}_6$ with no acid added (upper) and under catalytic conditions (lower), with incremental addition of $[(\text{DMF})\text{H}]\text{OTf}$. Conditions: 1 mm glassy carbon working electrode, 25 °C, scan rate 100 mV s^{-1} .

The cyclic voltammogram of $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{MeCN})](\text{BF}_4)_2$ exhibits two distinct reversible waves assigned to the Ni(II/I) and Ni(I/0) couples in acetonitrile. A typical voltammogram is shown in Figure 2. Plots of the peak current (i_p) versus $v^{1/2}$ are linear for both waves, indicating that these reactions are diffusion controlled.²⁸ Values of $E_{1/2}$ for the Ni(II/I) and Ni(I/0) couples are -0.77 V and -0.94 V, respectively. The Ni(II/I) values are slightly less negative than those observed¹⁰ at -0.83 V and -1.02 V for $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2]^{2+}$, consistent with the alkynyl group being electron-withdrawing. $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{MeCN})](\text{BF}_4)_2$ is an electrocatalyst for H_2 production using $[(\text{DMF})\text{H}]\text{OTf}$ ($\text{p}K_a = 6.1$ ²⁹ in CH_3CN) as the Brønsted acid. The catalytic activity (Figure 2) was determined from successive voltammograms of solutions in which the acid concentration was systematically increased until the catalytic current (i_{cat}) remained constant (acid concentration independent region). The acid-independent region

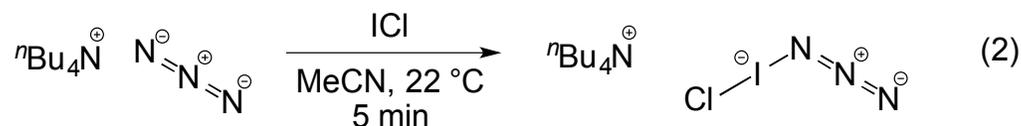
above 0.069 M [(DMF)H]OTf implies a zero-order dependence on acid. The experimentally determined value of (i_{cat}/i_p) of 15 in the acid-independent region can be used in eq. 1 to calculate the turnover frequency for the catalyst, where i_{cat} is measured at -0.95 V. In eq 1,³⁰⁻³² n is the number of electrons involved in the reaction (2 for the catalytic production of H₂), R is the gas constant, T is the temperature in K, F is the Faraday constant, and v is the scan rate in V/s. The turnover frequency determined in this way is 44 s⁻¹.

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk}{Fv}} \quad (1)$$

We did not try to optimize this reaction, as our main intent was to verify that the catalysis by this molecular complex did occur, before our further studies on surface attachment. The half-peak potential of $E_{cat/2}$ of -0.80 V is near the $E_{1/2}$ of the Ni(II/I) couple observed at -0.77 V in the absence of acid. The overpotential at $E_{cat/2}$ was determined to be 400 mV, using the thermodynamic potential for reduction of [(DMF)H]OTf determined by experimental measurements previously.³³

Several different conditions were assayed for the Cu-catalyzed coupling for the reaction of benzyl azide with $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{MeCN})](\text{BF}_4)_2$, including the non-aqueous solvent THF with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ and aqueous solutions with $\text{CuSO}_4/\text{Na-ascorbate}$. None of the conditions produced the desired product, and some gave an intractable brown precipitate with a concomitant loss of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonances. A BH_3 -protected form of the ligand, $(\text{BH}_3\cdot\text{P}^{\text{Ph}})_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2$, (**3**) was prepared by adding two equivalents of $\text{BH}_3\cdot\text{THF}$ at 0 °C to the free ligand **1** in THF solution (Scheme 1). Triazole formation from the BH_3 -protected ligand **3** with benzyl azide proceeded cleanly in THF-H₂O using $\text{CuSO}_4/\text{Na ascorbate}$ to generate the Cu^{I} catalyst, leading to the protected ligand **4**.³⁴ The BH_3 protecting groups were removed using the

amine base 1,4-diazabicyclo[2.2.2]octane (DABCO), giving **5**, which was metallated using $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ as described above for the alkyne-terminated ligand, giving the Ni^{II} complex **6**. The activity for H_2 evolution from **6** is comparable to that observed from **2**.

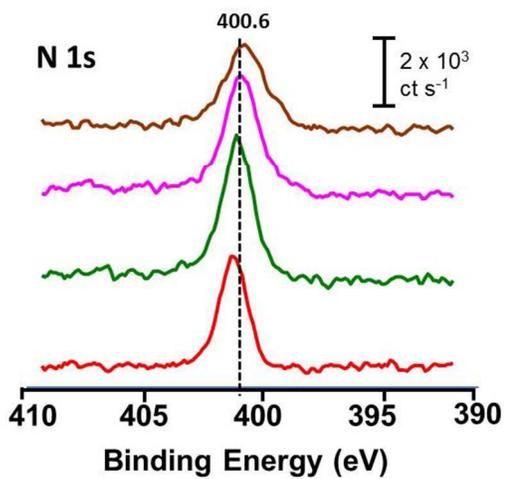


Azide groups were incorporated onto the glassy carbon electrode surface by reaction with *in-situ*-generated $[\text{Cl-I-N}_3]^- [\text{}^n\text{Bu}_4\text{N}]^+$ (eq. 2), as described previously.^{23, 35} Conditions for the CuAAC reaction were optimized as described above, using benzyl azide as a soluble model for all coupling trials. The protection-coupling-deprotection-metallation sequence discussed above was evaluated at each step using XPS measurements, with freshly prepared samples subjected to the entire sequence up to the step of interest, rinsed as described in the Experimental Section, and measured promptly by XPS. These data were compared with authentic $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{MeCN})](\text{BF}_4)_2$, which we reported previously.¹⁹ Quantitative analyses are given in Table 1, and selected photoemission spectra appear in Figure 2.

Table 1. X-ray Photoelectron Spectroscopy (XPS) Data.^a

| Sample | Atom abundance, AT % | | | | | |
|--------|----------------------|-----|------|-----|-----|-----|
| | C | N | O | P | Ni | B |
| 7 | 62.2 | 2.0 | 31.2 | 1.6 | 0.0 | 1.9 |
| 8 | 81.9 | 3.9 | 8.8 | 2.5 | 0.0 | 1.3 |
| 9 | 79.0 | 3.5 | 8.4 | 2.3 | 1.8 | 0.9 |
| 10 | 80.6 | 2.7 | 6.6 | 1.3 | 1.0 | 0.8 |

^aAverage of two measurements. See Figure 3 for high-resolution photoemission spectra.



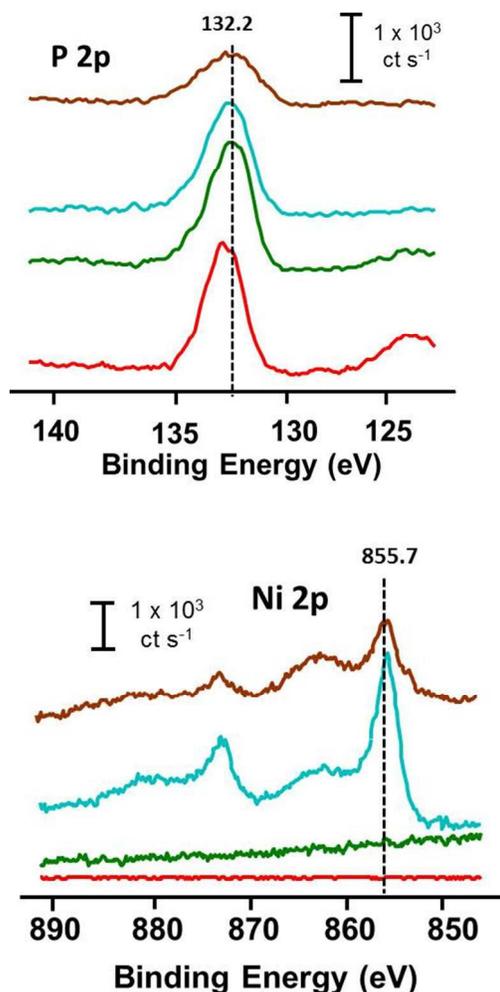
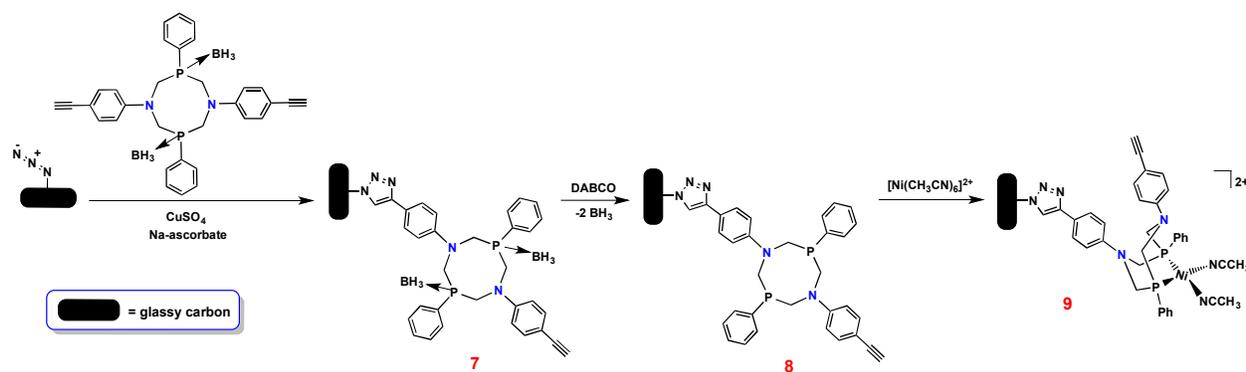


Figure 3: High-resolution photoemission spectra of glassy carbon plate samples in different stages: red = 7; green = 8; blue = 9; brown = 10. See Scheme 2 for identification of sample numbers.

Reaction of $(\text{BH}_3 \cdot \text{P}^{\text{Ph}})_2\text{N}^{\text{C}_6\text{H}_4\text{C}=\text{CH}_2}$ (**3**) with the azide-terminated glassy carbon surface, followed by thorough rinsing, produced a material (**7** in Scheme 2) with B and P present in a 1:1.3 ratio, as determined by XPS. Quantitation of B was based on the high-resolution spectrum showing the B 1s and P 2s lines, and corrected for overlap using the independently measured P 2p line, and thus relies on the relative sensitivity factors of the P 2p and 2s lines, taken³⁶ as 1.59.

Subsequent treatment of this material with DABCO decreased the B:P ratio to 0.5 in sample **8**, indicating removal of some B, as expected for deprotection. If this decrease were due entirely to deprotection, this would indicate that approximately 80% of the P sites were deprotected.

Scheme 2



Reaction of the material prepared in this manner with $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ afforded a sample (**9**) with P:Ni = 1.3, which is less than the value of 2 expected for singly chelated Ni centers (or 4 for doubly chelated Ni centers). This indicates that not all diphosphine ligands engaged Ni, possibly due to the presence of residual B from the protecting group, or to deactivation of the ligands. The overall P abundance was lower by 9% than in the sample (**8**) that had been deprotected but not metallated.

Figure 3 presents the high-resolution photoemission spectrum showing the Ni 2p lines. The $2p_{3/2}$ peak at 855.7 eV corresponds closely with that of the authentic $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{MeCN})](\text{BF}_4)_2$, which appears at 855.5 eV.¹⁹ This differentiates the deposited material from Ni-O species, which have $2p_{3/2}$ lines near 856.5 eV.³⁷ These data do not distinguish between singly and doubly diphosphine-chelated Ni centers.

Exposure of a sample **9** prepared as described above to $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$ afforded a sample with a lower Ni:C ratio (1.3 vs 2.2 Ni per 100 C). This suggests either that the two samples had

different initial Ni concentrations or that some material was leached following introduction of the soluble P_2N_2 ligand. The cyclic voltammogram of **9** with the Ni^{II} -modified electrode shows two reductions, at $E_p = -1.36$ V and -1.77 V, and a single oxidation wave (see Supplementary Information). The Faradic charge passed was low, indicating a very small amount of complex on the surface, consistent with the XPS analysis.

Discussion

Several examples of homogeneous electrocatalysts attached to electrode surfaces were reported recently, motivated by the important technical objective of operating molecular electrocatalysts in flow reactor configurations such as fuel cells.^{19, 24, 38} Many of these surface-confined systems show a significant decrease in activity^{14, 19, 38} on surface binding, with a few notable exceptions.³⁹ Several homogeneous electrocatalyst platforms developed for the production and oxidation¹⁻³ of hydrogen have become the target of covalent attachment efforts, and progress in this area has generated questions whose answers should facilitate the rational development of stable, functional catalyst systems. We have focused on attachment of molecular electrocatalysts to planar electrodes to separate the influence of attachment from the influence of complex electrode surface morphology. The attachment chemistry itself should translate to other carbon electrode materials presenting surface sp^2 carbon atoms.

Homogeneous catalysis provides at least two key advantages: a great deal of structural and dynamic information is available on the catalyst under both non-catalytic and catalytic conditions, and the catalytically active species is structurally uniform, at least initially. These properties allow detailed structure-function hypotheses to be evaluated, accelerating catalyst system development. Our aim in developing the synthetic route presented herein was to achieve

a similar level of detail on the structure and uniformity of catalytically active sites, by covalently attaching a molecular catalyst to a glassy carbon electrode in a well-defined manner. As the initial step in the modification, we chose Chidsey's route²³ wherein azide groups are bound directly to the electrode surface, which likely proceeds by addition of IN_3 across a $\text{C}=\text{C}$ bond, followed by elimination of HI . This method should have some advantages with regard to selectivity, since both reactions proceed in an ionic rather than radical mechanism, as evidenced from the retention of regiochemistry in reactions with *cis* and *trans* disubstituted olefins.^{40, 41} This route precludes nucleation-chain propagation associated with radical routes that can lead to non-random distributions of surface coupling sites.⁴² Subsequent cyclization under copper-mediated alkyne-azide cycloaddition (CuAAC) conditions generates well-defined, stable 1,2,3-triazolyl linkages between the surface and the coupling synthon employed, and this is one of the methods we have pursued for further elaboration of azide-terminated glassy carbon.¹⁹

There are some notable drawbacks to the use of CuAAC to catalyze coupling of phosphines (or their complexes with transition metals) to azides: phosphines not only bind Cu(I) ⁴³ but react readily with azides via the Staudinger iminophosphorane coupling.⁴⁴ Strained-ring alkyne substrates allow AAC coupling without a Cu catalyst or added amine base,⁴⁵ but are time-consuming to prepare and do not solve the problem of iminophosphorane coupling. Phosphine protection using $\text{BH}_3\cdot\text{THF}$ precludes unwanted side reactions at phosphorus,^{46, 47} and deprotection may be accomplished using a strong nitrogen base. We have used this strategy in the present study.

Our studies have shown that: (1) CuAAC can be used to couple alkyne-terminated, BH_3 -protected diphosphine ligands, as we have demonstrated using the soluble coupling partner benzyl azide. (2) Deprotection with a strong nitrogen base (in this case DABCO, see Scheme 1)

proceeds cleanly in solution and with partial removal of BH_3 on the surface (30-50% according to XPS quantification). (3) Metallation of the deprotected, coupled diphosphine ligand with a Ni^{II} reagent proceeds in solution as with related P_2N_2 ligands. Metallation of the electrode-bound diphosphine ligands using the same conditions incorporates Ni, affording a P:Ni ratio of 0.78; considering that deprotection is incomplete; the ratio of deprotected phosphine to Ni on the surface is approximately 2:1, as expected for a surface-bound Ni^{II} species with one diphosphine ligand. Voltammetry shows some Faradaic current, in potential regions similar to a known Ni^{II} mono(diphosphine) complex.⁴⁸ (4) Adding a second diphosphine ligand decreases the surface abundance of Ni and does not change the Ni 2p binding energies. This reaction does not increase the P abundance, indicating that Ni^{II} has been removed from the surface rather than coordinating a second diphosphine ligand. (5) Attempted metallation of the surface-bound diphosphine with a soluble mono(diphosphine) complex does not result in incorporation of Ni. These results indicate that Ni^{II} -P interactions can be labile, an important consideration in the development of these systems.

Experimental Section

General Procedures and Materials. All manipulations were carried out using standard Schlenk or inert-atmosphere glovebox techniques using oven-dried glassware, unless otherwise indicated. Nonaqueous solvents were purified by sparging with N_2 and passage through neutral alumina, using a solvent purification system (PureSolv™, Innovative Technologies, Inc.). $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ ⁴⁹ and $\text{PhP}(\text{CH}_2\text{OH})_2$ ⁵⁰ were prepared using literature methods. All other chemicals were purchased commercially and were used as received. $\text{MeCN-}d_3$ (Cambridge Isotope Laboratories, 99.5% D) was vacuum-distilled from P_2O_5 . $\text{THF-}d_8$ (Cambridge Isotope Laboratories, 99.5% D) was vacuum-distilled from liquid NaK alloy. Acetone (Fisher

ReagentPlus) and $\text{BH}_3 \cdot \text{THF}$ (Aldrich) were used as received. $[\text{Cl-I-N}_3][^n\text{Bu}_4\text{N}]$ was prepared immediately prior to use as previously described³⁵ from $[^n\text{Bu}_4\text{N}]\text{N}_3$ and ICl (Aldrich).

Preparation of glassy carbon substrates for surface modification. Glassy carbon disks (3 mm dia.) encased in poly(chlorotrifluoroethylene) (for voltammetry, BAS Instruments) and $4 \times 10 \times 10$ mm glassy carbon plates (for XPS analysis, SPI-Glas 22 grade, SPI supplies) were lapped and polished on a mechanical wheel (Electron Microscopy Sciences, Model 900) and then cleaned, as previously described.³⁵

Instrumentation and analytical methods. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for ^1H). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external H_3PO_4 . XPS measurements were performed as previously described^{51, 52} using a Physical Electronics Quantera Scanning X-ray Microprobe. Glassy carbon plate samples were mounted for analysis inside a N_2 glovebox interfaced with the vacuum chamber. Surface densities were calculated from XPS data using the method outlined previously.⁵³ The density of glassy carbon was taken as reported by the supplier (1.42 g cm^{-3}). The inelastic mean free path for the C 1s photoelectron (33.85 \AA) was obtained from the Quases-IMFP-TPP2M⁵⁴ material properties database, corrected for the difference in density of the glassy carbon used vs. that listed in the database (1.80 g cm^{-3}).

Electrochemical measurements were conducted using a CH Instruments 620D potentiostat and a standard three-electrode cell (4 or 10 mL shell vial). The counterelectrode was a glassy carbon rod (3 mm dia.; Alfa Aesar). The reference electrode was a silver wire (1 mm dia.; 99.9%, Alfa Aesar) anodized 5 min in aqueous HCl , washed with water and acetone, dried, and suspended in a glass tube containing neutral MeCN ($0.1 \text{ M } [^n\text{Bu}_4\text{N}]\text{PF}_6$) and fitted with a porous Vycor disk. Ferrocene was added as an internal potential standard for all measurements.

Unmodified working electrodes (1 mm dia.; ALS) used for voltammetry of solutions of the Ni complexes and for select control experiments (3 mm dia.; BAS Instruments) in the study of the modified electrodes were polished with diamond paste (0.25 μm , Buehler) on a pad (Buehler MicroCloth) lubricated with ethylene glycol.

X-Ray Crystallography. A crystal of $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{MeCN})](\text{BF}_4)_2$ was mounted on a MiTeGen MicroMounts pin using Paratone-N oil and cooled to 140 K. Data was collected on a Bruker-AXS II CCD diffractometer with 0.71073 Å Mo $K\alpha$ radiation. Cell parameters were retrieved using Bruker APEX II software,⁵⁵ raw data were integrated using SAINTPlus,⁵⁶ and absorption correction was applied using SADABS.⁵⁷ The structures were solved using either direct methods or the Patterson method and refined by a least-squares method on F^2 using the SHELXTL program package. Space groups were chosen by analysis of systematic absences and intensity statistics.⁵⁸ While the electron densities of acetonitrile and Et_2O solvent molecules were found, they could not be modeled because of severe disorder. Final refinement was performed with modification of the structure factors for contribution of the disordered solvent electron densities using the *SQUEEZE* option of *PLATON*.⁵⁹ One of the BF_4^- counterions and one of the $\text{C}_6\text{H}_4\text{C}\equiv\text{CH}_2$ rings were refined with positional disorder. The structural data has been deposited with the Cambridge Crystallographic Data Centre (CCDC 1043367).

Syntheses of 1,5-bis(4-ethynylphenyl)-3,7-bis(phenyl)1,5-diaza-3,7-diphosphacyclooctane ($\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2$) (1). A 100 mL Schlenk flask was charged with solid $\text{PhP}(\text{CH}_2\text{OH})_2$ (514.5 mg, 3.02 mmol) and 20 mL degassed absolute ethanol. The solution was heated for 30 minutes at 70 °C and ethynylaniline (372.1 mg, 3.17 mmol) in 10 mL of degassed ethanol was added slowly into the hot solution over a 30 min period. The solution was heated for another 12 h at 70 °C. The reaction was cooled to room temperature, and a yellowish-white solid product precipitated.

The product was collected by filtration, washed with ethanol (3 × 3 mL) and THF (3 × 1 mL) and dried under reduced pressure for 3 h to afford the final product (250 mg, 33%). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_8): δ -48.7 (s). ^1H NMR (THF- d_8): δ 7.64 (br, 4H), 7.43 (br, 5H), 7.28 – 7.14 (m, 5H), 6.70 (m, 4H), 4.36 (m, 8H), 3.19 (s, 2H). Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{P}_2$: C 76.48; H, 5.62; N 5.57. Found: C, 76.39; H, 5.19; N, 5.10.

$[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ (2). A blue solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ (89.5 mg, 0.18 mmol) in acetonitrile (5 mL) was added to a stirred slurry of $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2$ (180.9 mg, 0.36 mmol) in acetonitrile (5 mL). The blue solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ rapidly changed to orange-red. The resultant solution was stirred overnight, then filtered through a plug of Celite. The solvent was removed under reduced pressure. The red powder was washed with diethyl ether and dried under reduced pressure (210 mg, 92%). Single crystals suitable for X-ray analysis were grown by diffusion of diethyl ether vapor into a concentrated solution of the product in acetonitrile. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 3.58 (s). ^1H NMR (CD_3CN): δ 7.55 (m, 6H), 7.45 (m, 5H), 8.78 (br, 9H), 7.25–7.18 (m, 16H), 4.30 (m, 8H), 3.96 (s, 8H), 3.42 (s, 4H), 2.00 (s, 3H). Anal. Calcd for $\text{C}_{64}\text{H}_{56}\text{B}_2\text{F}_8\text{N}_4\text{NiP}_4$: C, 62.12; H, 4.56; N, 4.53. Found: C, 61.87; H, 4.19; N, 4.72.

1,5-bis(4-ethynylphenyl)-3,7-bis(phenyl)1,5-diaza-3,7-diphosphacyclooctane borane complex ($\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2 \cdot 2\text{BH}_3$) (3). To a solution of the $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2$ (25.5 mg, 0.05 mmol) in THF (2 mL), $\text{BH}_3 \cdot \text{THF}$ (100 μL of 1M THF solution, 0.10 mmol) was added at 0 °C under inert atmosphere. The solution was stirred for 30 minute during which time colorless solution changed to bright yellow. The solvent was removed under reduced pressure. The yellow solid was washed with diethyl ether and dried under vacuum produces an essentially quantitative amount of product. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF) δ 14.5 (s). ^{11}B NMR (THF) δ -39.9.

Preparation of click-ligands in their protected form; CuAAC reaction of benzyl azide with

$\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2 \cdot 2\text{BH}_3$ (4). $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2 \cdot 2\text{BH}_3$ (20 mg, 0.04 mmol) was suspended in THF (2 mL) and degassed water (0.5 mL) was added to this suspension, which was stirred for 30 minutes. Benzyl azide (5 μL , 0.08 mmol) was added into this solution and after 30 minutes of stirring, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (80 μL of 0.1 M aqueous solution, 0.008 mmol, 10 mol% of total alkyne) and Na-ascorbate (6.3 mg, 0.032 mmol, 40 mol% of total alkyne) were added, and stirring was continued for 18 h at room temperature. During this time the color of the solution changed from yellow to off white. The solvent was removed under reduced pressure. The off-white solid was washed and dried under vacuum. The solid material was used with diethyl ether for next reaction without further purification. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF): δ 10.54 (s), -42.9 (s), -48.8 (s).

Deprotection of the ligand: removal of BH_3 to give 5. $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{triazoleCH}_2\text{Ph}}_2 \cdot 2\text{BH}_3$ (20.2 mg, 0.03 mmol) was dissolved in THF (3 mL) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (29.5 mg, 0.30 mmol) was added. The reaction mixture was stirred for 18 hours. The solvent was removed and solid material was washed thoroughly with acetonitrile (3 \times 1 mL) and dried under vacuum to give $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{triazoleCH}_2\text{Ph}}_2$ (5). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF): δ -48.8 (s). ^1H NMR (THF- d_8): δ 7.80 (s, 2H), 7.66 (m, 3H), 7.60 (d, $J = 9$ Hz, 2H), 7.46–7.39 (m, 5H), 7.30–7.24 (m, 5H), 5.51 (s, 4H), 4.40 (m, 4H), 4.26 (m, 4H).

$[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{triazoleCH}_2\text{Ph}}_2)(\text{BF}_4)_2$ (6). A blue solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ (12.4 mg, 0.026 mmol) in acetonitrile (2 mL) was added to a stirred slurry of $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{triazoleCH}_2\text{Ph}}_2$ (5) (20.2 mg, 0.052 mmol) in acetonitrile (3 mL). The blue solution of $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ rapidly changed to orange-red. The resultant solution was stirred overnight, then filtered through a plug of Celite. The solvent was removed under reduced pressure. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 5.77 (s). ^1H NMR

(CD₃CN): δ 8.17 (m, 4H), 7.87 (s, 8H), 7.56–7.05 (br., 46H), 5.67 (s, 8H), 4.32 (m, 8H), 4.02 (s, 8H), 2.00 (s, 3H).

In-Situ Generation of $\text{Bu}_4\text{N}^+[\text{Cl-I-N}_3]^-$ and Reaction of Glassy Carbon Samples with $\text{Bu}_4\text{N}^+[\text{Cl-I-N}_3]^-$ were carried out according to previously reported procedures.^{19,35}

Coupling the azide-modified electrode with $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2 \cdot 2 \text{BH}_3$ to give **7:** In a typical experiment, $\text{P}^{\text{Ph}}_2\text{N}^{\text{C}_6\text{H}_4\text{C}\equiv\text{CH}}_2 \cdot 2\text{BH}_3$ (20 mg, 0.04 mmol) was suspended in degassed THF:H₂O (2 mL, 3:1) in a screw-cap vial, and an azide-treated electrode sample was placed in this solution. CuSO₄·5H₂O (80 μ L of 0.1 M aqueous solution, 0.008 mmol, 10 mol% of total alkyne) and Na-ascorbate (6.3 mg, 0.032 mmol, 40 mol% of total alkyne) were added subsequently and the reaction was continued for 18 h at room temperature. The sample of **7** was then rinsed with MeCN and analyzed by XPS.

Deprotection of the BH₃ complex to give **8.** 1,4-diazabicyclo[2.2.2]octane (DABCO) (29.5 mg, 0.30 mmol) was dissolved in THF (2 mL) in a screw-cap vial and the modified electrode was placed in this solution. The solution was stirred for 6 h at room temperature. The sample of **8** was then rinsed with MeCN and analyzed by XPS.

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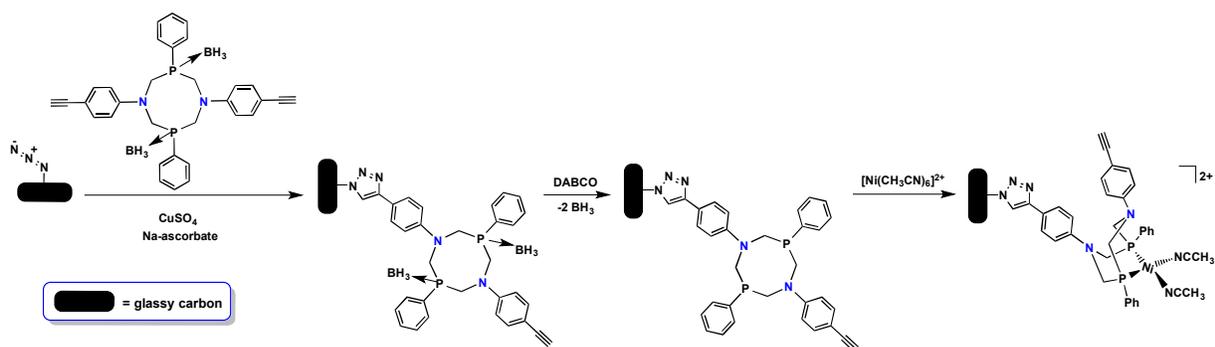
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Graphic for Table of Contents



Text for Table of Contents

Covalent tethering of a P_2N_2 ligand to a planar, azide-terminated glassy carbon electrode surface was accomplished using a Cu^I -catalyzed “click” reaction, followed by metallation with Ni^{II} .