Synthesis and Electrochemical Activity of Nickel Phosphine Complexes and Polymers Bound to Electrode Surfaces

Marye Anne Fox,* Daniel A. Chandler, and Pei-wei Wang

Department of Chemistry, University of Texas, Austin, Texas 78712

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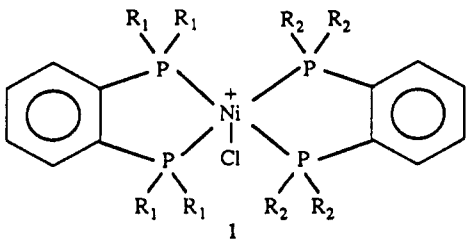
ABSTRACT: More favorable electroactivity (in the reductive electrocatalytic coupling of aryl halides) is observed for adsorbed polymeric nickel phosphine complexes than with their covalently anchored monomeric nickel analogues. Syntheses of the relevant ligands are described and methodology for formation of polyvinylbenzyl chloride bearing pendant bisphosphinobenzene groups and polymers with bisphosphinobenzene incorporated into the backbone is discussed. The electrochemical activities of these ligands and their coordinated nickel complexes provide useful probes for the characterization of the chemically modified electrode surfaces.

Introduction

The attachment of catalytically active molecular reagents to electrode surfaces has contributed significantly to the recent renaissance of electrochemistry. The ability to manipulate the chemical and physical properties of electrode surfaces has broad applications and, driven by clear economic incentives, this area has developed rapidly. Electrode modification is performed in many ways, e.g., chemisorption, covalent bonding, and electrodeposition.[1-3] Most efforts may be thought of as attempts to anchor to an electrode surface a catalyst that has proven to be active under homogeneous conditions and thus to heterogenize the homogeneous catalyst. This approach is especially attractive for use with semiconductor electrodes, where photocorrosion can be a problem and reductive selectivity is lacking.

One of the earliest tactics for deliberate electrode modification relied on a chemisorption,[4] wherein molecules are anchored to a surface through strong electrostatic interactions. Chemisorption has been largely supplanted by the covalent bonding of molecules to surfaces, for example, via silylation.[5-8] An alternate method to immobilize large quantities of a catalytically active reagent near the electrode surface is to incorporate the unit within a polymeric matrix.[9] If the centers can communicate chemically, such a polymer may act as an electron mediator to shuttle charge between the semiconductor surface and an appropriately dissolved redox couple. This configuration can greatly increase the number of catalytic sites and hence the efficiency of electron transfer from electrode to the catalyst.[10]

Nickel phosphine complexes are electrochemically active reduction catalysts:[11] for example, we have recently described the electrocatalytic activity of a family of bis(dialkylphosphino)benzene–nickel complexes 1 for reduction and coupling of aryl halides.[11a,b] In this article we describe strategies for synthetic manipulation of the ligands to attain immobilization of analogues of these complexes on an electrode surface. The contrasting electroactivity afforded by the monomeric and polymeric heterogenized electrocatalysts argues for increased activity of the polymer-modified electrodes in these applications.



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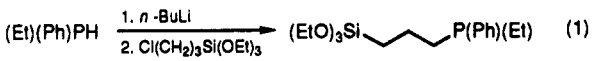
1a: $R_1 = R_2 = Et$
b: $R_1 = R_2 = Me$
c: $R_1 = Me$, $R_2 = Et$

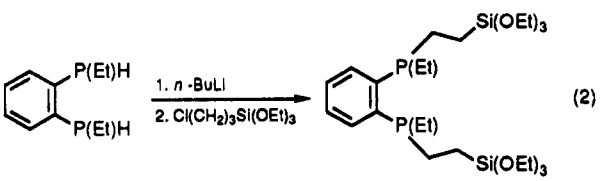
Results and Discussion

Covalent Attachment of Monolayers of Catalyst. A. Silanes. After the hydrosilylation of 4-(ethylphenylphosphino)-1-butene (prepared in 67% yield by the treatment of lithium ethylphenylphosphide with 4-bromo-1-butene) failed,[12] the reaction between an aryl phosphide anion and an alkyl halide silane (e.g., (3-chloropropyl)triethoxysilane) provided a direct route to phosphinosilanes. For example, the reaction between lithium ethylphenylphosphide and (3-chloropropyl)triethoxysilane, eq 1, produced the desired product in 63% yield, with negligible polymer formation.



(1)

Multiple silane linkers could be introduced into multiphosphide anions: with 1,2-bis(ethylphosphino)benzene, a dianion was formed, which upon reaction with (3-chloropropyl)silane, eq 2, produced the desired product **2** in 45% yield.



(2)

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Its nickel(II) chloride complex **3** was compared to its non-silane analogue, chlorobis(*o*-phenylenebis(diethylphosphine))nickel(II) chloride (**1a**). In most respects, the two complexes appeared similar: their ^{31}P NMR and absorption spectra and ionic conductivities indicated that the coordination type and ligand field are the same in each complex, Table I. However, they exhibit very different electrochemical behavior. While the half-potentials for reduction (Ni(II) → Ni(0)) of **3** and **1a** are similar (−1.15 and −1.10 V, respectively), the peak separation for **3** is much larger than for **1a** (500 versus 100 mV), Figure 1. (We have previously reported coulometric

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Table I
Spectroscopic Comparison of Complexes 1a and 3[a]

complex	λ_{max} (ϵ), nm	Λ_M, Ω^{-1} cm^2 mol^{-1}	^{31}P NMR, δ
1a	428 (1150)	87	54.3 (s)
3	428 (1196)	107	55.1 (s)

[a] Absorption spectra and molar conductivities were measured in acetonitrile. ^{31}P NMR (proton decoupled) were measured in $CDCl_3$ and are referenced to phosphoric acid.

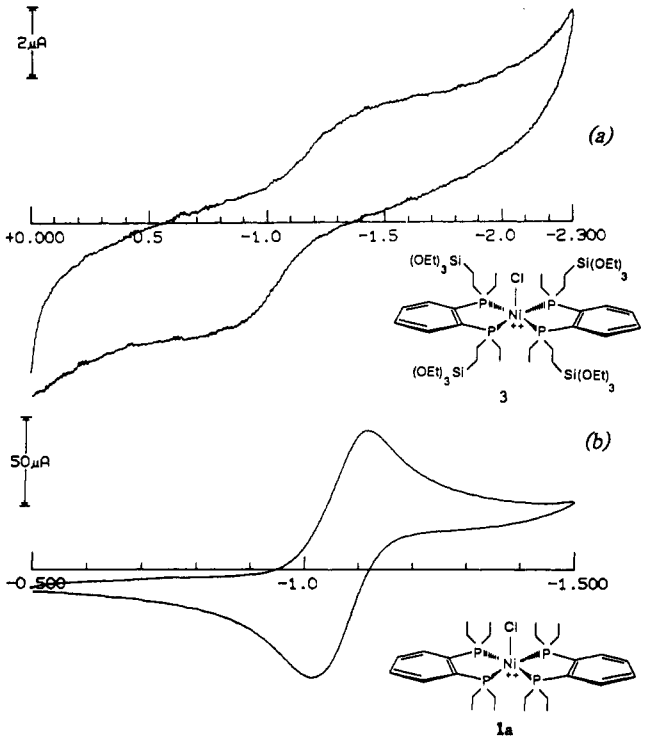


Figure 1. Cyclic voltammograms of complexes (a) **3** and (b) **1a**: 10^{-3} M in acetonitrile containing 0.2 M TBAP, 25 °C, 100 mV/s, at glassy carbon.

evidence that **1a** undergoes a two-electron reduction.[11a] More striking is the huge difference in the two compounds' activities. For a given concentration, the peak current for **3** is less than 5% of that for **1a**.

Electrode fouling to form an insulating polysiloxane is not a likely cause of this behavior: inspection (visually and by XPS, i.e., the absence of surface-adsorbed silicon and phosphorus after rinsing the electrode with ethanol after repeated cycling in the presence of **3**) of a modified carbon electrode showed no sign of film formation. Nor was there any increase in circuit resistance, which normally accompanies electrode fouling. A more plausible explanation for the contrasting electrochemical behavior is that the silane interacts with the metal center. Although the triethoxysilane groups are extremely bulky, their steric effects are probably less important than the coordination of the ethoxy oxygens to nickel,[13] in effect irreversibly sequestering and altering it electronically, Figure 2.

If **2** is exposed to water, oligomerization occurs, as evidenced by a decrease in the expected aryl/ethoxy ratio in the ^{1}H NMR spectrum. Although no evidence could be garnered by surface analysis for associative oligomerization at the electrode surface, the possibility of minor contributions from soluble oligomers to the poor electrochemical behavior cannot be completely ruled out. In such an oligomer, slow kinetics for electrocatalysis would have been expected because of either reduced diffusion rates of the electrocatalyst to the electrode surface or slow electron hopping within the oligomeric cluster.

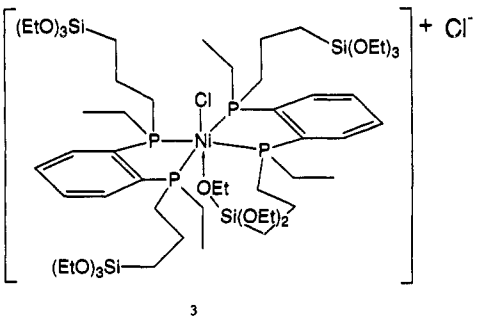


Figure 2. Proposed sequestering of nickel in **3**.

The sequestering ability of the ligand **2** was tested by adding it to a solution of **1a**. Cyclic voltammetry before and after the addition showed the complete suppression of the two distinct reduction waves of **1a**. Only a broad oxidative peak remained, which could be attributed to ligand oxidation. Thus, as handles for surface attachment, the triethoxysilane groups pendant from a bisphosphinobenzene ligand are not electrochemically innocent.

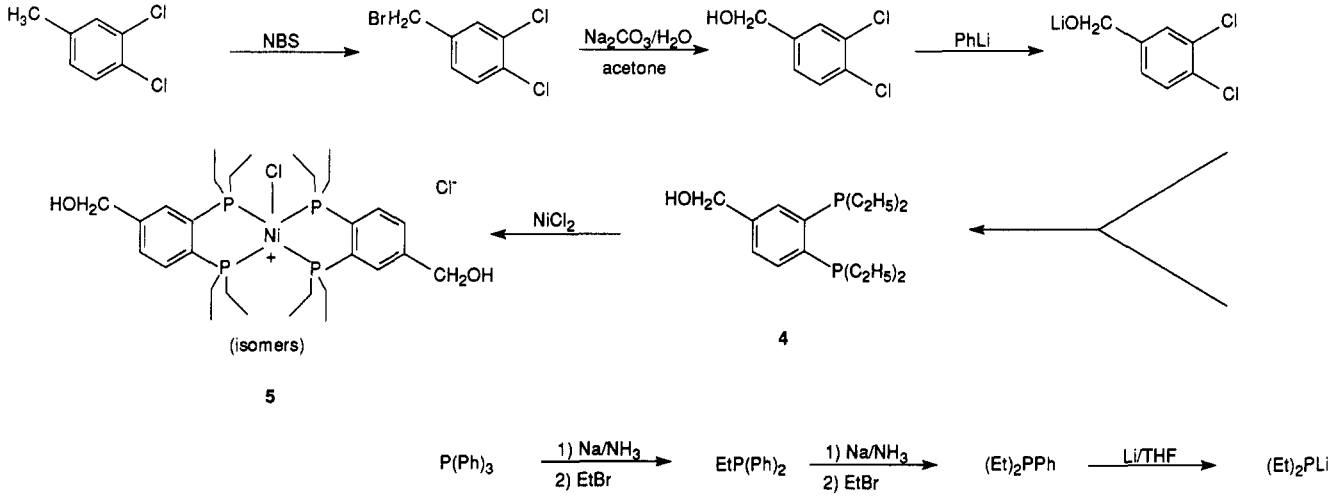
B. Alcohols. Alcohols can be covalently bonded to surfaces by reaction with a previously anchored alkyl or aryl halide (i.e., a Williamson ether synthesis). The resulting ether linkage is durable and electrochemically transparent. Given the effect of the silane group, the number of alcohol groups per ligand was kept to a minimum and the alcohol groups were positioned at a considerable distance from the metal center of the nickel complex to prevent intramolecular coordination.

The convergent synthesis in Scheme I produced ligand **4**, with the remaining products being monosubstituted isomers. Metal complexation[14] in the final separation produced a 2:1 complex as two separable isomers (head-to-head and tail-to-tail alcohols) in an overall 7% yield. The alcohol moiety had no deleterious effect on the complex's electrochemistry. The cyclic voltammogram of the head-to-head isomer **5** (Ni(II) → Ni(0); $E_{1/2}$ = −1.07 V, peak separation = 101 mV) was very similar to that of **1a**, with the small inductive effect of the alcohol group causing $E_{1/2}$ to be shifted slightly more negative. At higher concentrations (>10^{-4} M), peak broadening occurs, presumably because of intermolecular coordination of the alcohol groups with the nickel centers. When an equivalent of methanol was added to solutions of **1a**, peak broadening also occurred.

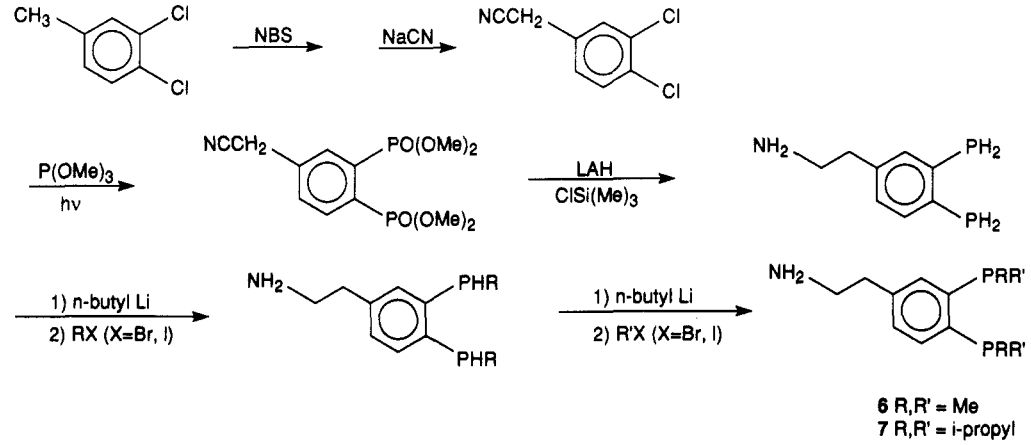
C. Amines. The analogous amines **6** and **7** were prepared by the route shown in Scheme II with only slightly greater difficulty than their unsubstituted analogues. The presence of an amino group profoundly affects the properties of the nickel chloride complexes of these ligands. Their complexes, **8** and **9**, respectively, are considerably less soluble in organic solvents than their models **1a** and **10**; i.e., their absorption spectra show much lower absorptivity than predicted from Beer's law. Aggregates involving intermolecular coordination of the amino groups to nickel, Figure 3, or to the SiO(H) surface, form in solvents with little or no coordinating ability. In low dielectric or strongly coordinating solvents, the amino appendages are unable to compete for coordination sites, and the aggregate breaks up.

In the cyclic voltammogram of **8**, Figure 4, the Ni(III)–Ni(IV) couple is unaffected ($E_{1/2}$ = 0.760 V, peak separation 60 mV), but the Ni(II)–Ni(III) couple becomes much less reversible (peak separation 750 mV), and the Ni(0)–Ni(II) couple is completely absent. In addition to the metal oxidation waves, a third wave (E_p = +1.07 V) corresponding to amine oxidation can be seen. The reduction (Ni(II)

Scheme I
Preparation of the Alcohol-Containing Bis(dialkylphosphino)benzene Ligand 4 and Its Nickel Complex 5



Scheme II
Preparation of Amine-Modified Bisphosphinobenzene Ligands 6 and 7



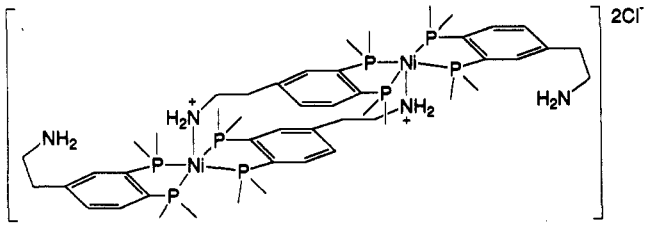


Figure 3. Proposed intermolecular coordination in 8.

→ Ni(0)) requires that an axial coordination site be cleared to enable rearrangement to a tetrahedral species. With the additional coordination of an amine, the nickel center is sequestered and becomes relatively inert to reduction so that a large overpotential is required to induce reduction. The addition of dodecylamine to a solution of **1c** similarly caused the current of the Ni(II)–Ni(0) wave to be greatly diminished. The metal oxidations remained, but their waves were obscured by amine oxidation.

In **9**, a 1:1 Ni/ligand complex is formed. With considerably less coordinative saturation than in **8**, the presence of amino groups is less likely to cause sequestering of the metal center. The cyclic voltammograms of **9** and **10**, Figure 5, show complex reductions with waveshapes dependent on scan rates. Each of the quasi-reversible oxidation waves (Ni(II) → Ni(I) and Ni(I) → Ni(0)) of **10** is split, reflecting geometry changes accessed during the reduction.[11a] Coulometry shows that each wave involves a single electron reduction in both **9** and **10**.[11a] In acetonitrile, where **9** tends to aggregate, the reduction waves are broad and poorly defined, but the peak potentials are shifted only slightly. The Ni(I) → Ni(0) transition, however, is shifted more positive (ca. 175 mV) when an amino group is present. This potential shift may be caused by stabilization of the Ni(0) oxidation state as a result of amine coordination.

In tetrahydrofuran (THF), **9** does not aggregate. It is probable, therefore, that the lower dielectric constant of THF makes the displacement of chloride at a nickel coordination site more difficult. Under these circumstances, the amino appendage has no effect on the electrochemistry: the cyclic voltammograms of **9** and **10** in THF both show waves and peak potentials similar to that shown in Figure 5 for **10**.

Complex **9** can be directly attached to a carbon electrode derivatized by oxidation of the surface, followed by treatment with thionyl chloride. Free ligand **7** was thus anchored to the surface, Scheme III. Electrodes modified with **9** exhibit two weak and very broadened reduction waves (−1.1 and −1.9 V, DMSO). Peak potentials are shifted slightly negative from the values for **10** in solution and the first reduction wave (−1.1 V, Ni(II) → Ni(I)) is barely visible. Presumably, the amino groups are bonded in amide linkages and therefore exert little influence on the metal center. The modified electrode's altered electrochemical character is most likely due to secondary interaction between the complex and the electrode surface.

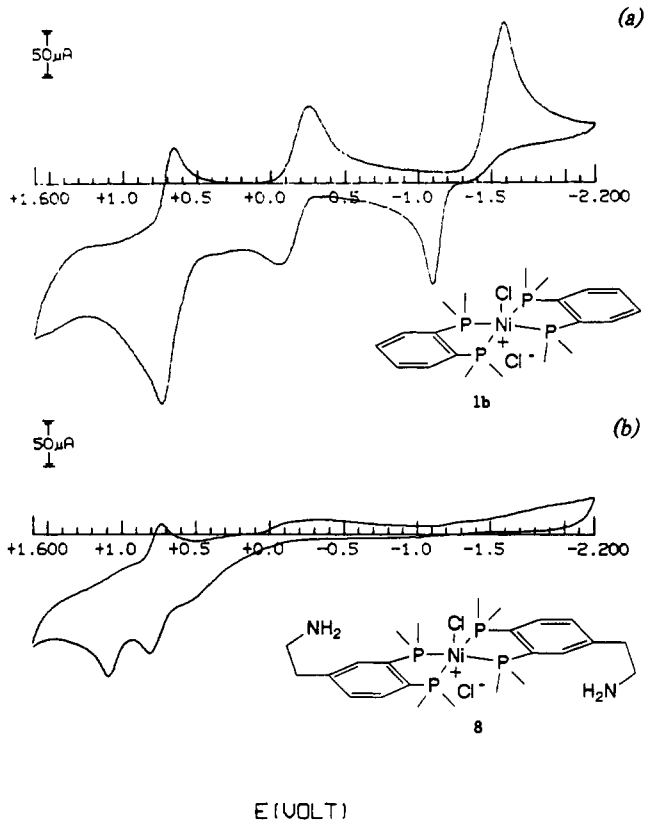


Figure 4. Cyclic voltammograms of (a) **1b** and (b) 8: 10^{-3} M solutions in acetonitrile containing 0.2 M TBAP, 25 °C, 100 mV/s, at glassy carbon.

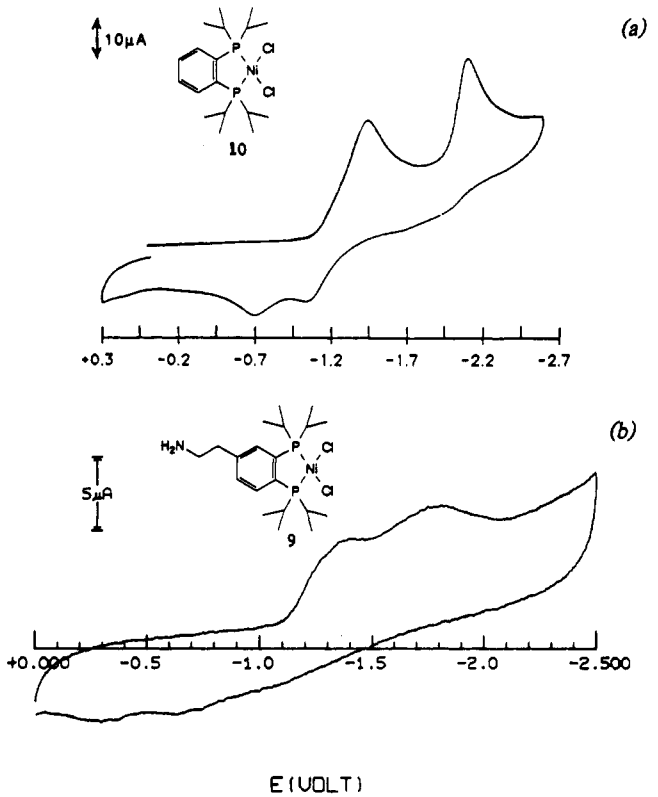
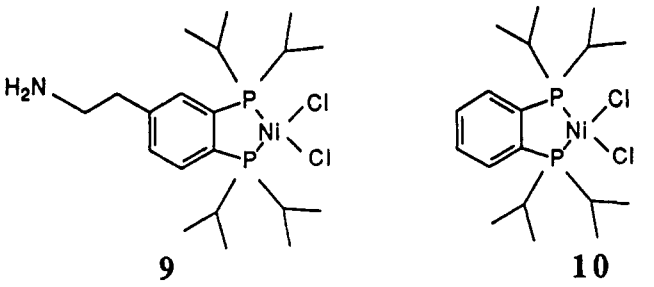
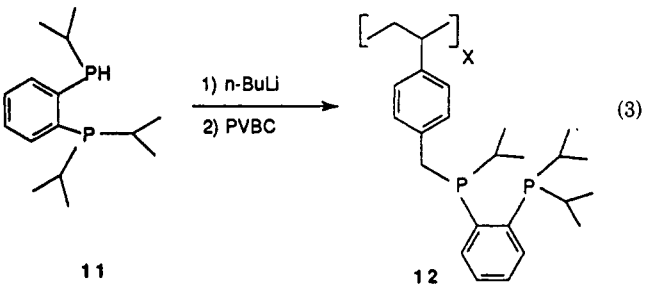


Figure 5. Cyclic voltammograms of (a) **10** and (b) **9**: 10^{-3} M solutions in acetonitrile containing 0.2 M TBAP, 25 °C, 100 mV/s, at glassy carbon.

Attachment of Polymeric Ligands. A. Polyvinylbenzyl Chloride Pendant Bisphosphinobenzene Ligands. Polyvinylbenzyl chloride (PVBC) is commercially available, readily modified by displacement at the benzylic carbon, and electrochemically inert over a considerable potential window. Bisphosphinobenzene ligands can be grafted onto PVBC by nucleophilic substitution of chloride by an appropriately functionalized ligand. Accordingly, PVBC was modified by several routes.

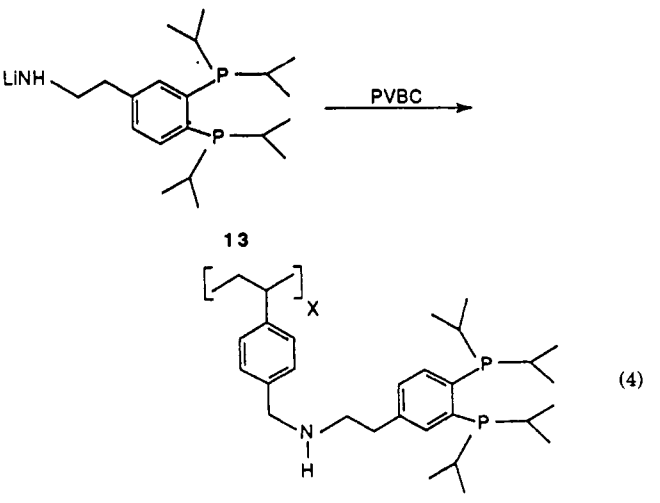


The first involved displacement by a phosphide; however, if a diphosphide forms during this reaction, the polymer will become highly cross-linked (i.e., intractable) and therefore rendered unsuitable for coating electrodes. To prevent cross-linking, the phosphide must therefore be generated from a bisphosphinobenzene that contains one tertiary and one secondary phosphine. Thus, treatment of PVBC with phosphide **11**, eq 3, produced an off-white powder **12** readily soluble in THF, with no evidence of gelation (i.e., no insoluble cross-linked material), in which elemental analysis indicated quantitative substitution.



(3)

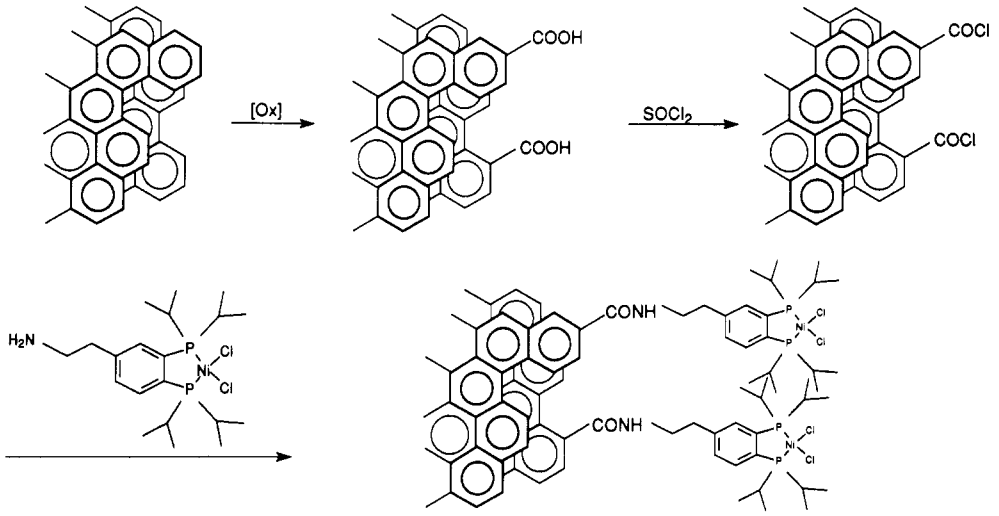
In the second method, a parallel reaction of the amide of 4-(2-aminoethyl)-1,2-bis(diisopropylphosphino)benzene (**13**) produced a light yellow powder **14**, soluble in THF and chloroform, in which elemental analysis indicated that 91% of the benzyl chloride groups had been displaced, eq 4.



(4)

Treatment of **12** and **14** with nickel(II) chloride or nickel(III) perchlorate gave the corresponding nickel complexes

Scheme III
Synthetic Sequence for Covalently Bonding 9 to Glassy Carbon



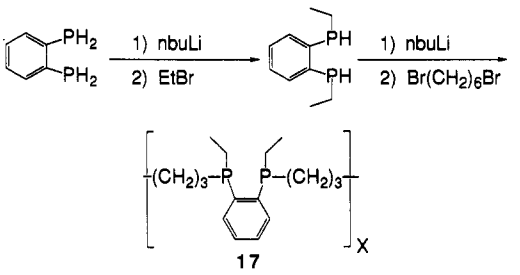
15 and 16 as predominantly insoluble, orange solids. This insolubility can be ascribed to the presence of large domains of highly polar and nonpolar character (the complexation sites and the polymer backbone, respectively) so that a large entropic solvation barrier must be overcome. With nickel perchlorate, two ligand sites may coordinate to a single nickel atom and, in effect, cross-link the resin.

The uncoordinated 12 and 14 were coated onto an electrode by dip- or spin-coating. The resulting films were insoluble in methanol, swelling slightly to permit complexation as a second step. The electrochemical properties of electrodes modified with 15 and 16 were predictably similar since the steric bulk of the ligands in each polymer is roughly equivalent. (Isopropyl and benzylic groups impart an equivalent contribution to cone angles.)[15] Since the 2:1 ligand/metal complexes observed for 1a–1c are supplanted by 1:1 complexes as in 10 when the alkyl groups on phosphorous are bulkier (isopropyl),[11] it is unlikely that 15 or 16 exists as a bis chelated (and hence cross-linked) Ni complex. Treatment with Pd(II) similarly affords the analogous Pd(II) complexes, which exhibit electrochemical behavior parallel to that of the nickel complexes described herein.

The film's metalation level had a significant effect on its electrochemical behavior. Films 15 and 16 metalated with nickel perchlorate are reduced in a single wave (Ni(II) → Ni(0)) in which the observed peak potential varied from one electrode to the next (−1.2 to −1.7 V in acetonitrile; −1.9 to 2.4 V in DMSO) but closely resembles that of uncomplexed nickel perchlorate in solution, Figure 6. Either the polymer matrix is capable of entraining more nickel than can be coordinated with the phosphino ligands or, in the presence of an electric field and coordinating solvents, nickel is dislodged from its phosphine coordination sites.[16] The result is an immobilized population of nickel, which behaves as if the bisphosphinobenzene ligands were not present. In instances of extreme overmetalation, the polymer coating visibly swells to many times its original thickness and takes on a green hue indicative of uncomplexed nickel perchlorate.

Overmetalation could be avoided by exposing the coated electrodes to nickel perchlorate solutions for only short periods (ca. 15–20 min.). In films where the nickel content was maintained at a low level, the reduction potential corresponded well to values observed for 1:1 (ligand/metal) homogeneous complexes (−1.65 V in acetonitrile). Absorption spectra also indicated 1:1 complexation (λ_{max} = 380 nm). The formation of a 1:1 bisphosphinobenzene/nickel perchlorate complex is unusual and is probably the result of the ligand's steric bulk, and its limited degree of translational freedom promote coordinative unsaturation.[17]

Scheme IV
Preparation of a Bisphosphinobenzene Ligand Backbone Polymer 17



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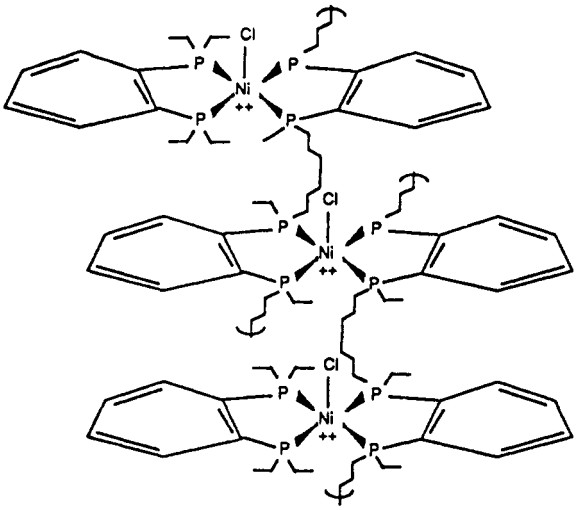
Films obtained by complexation with nickel(II) chloride were sufficiently soluble in acetonitrile and DMSO that they failed to remain immobilized on the electrode to which they were applied. Cyclic voltammetry on trace amounts of polymer complex in solution revealed a two-wave reduction for each of the polymeric nickel chloride complexes. Their peak potentials closely resembled those of 1b.

B. Ligand Backbone Polymers Cross-Linked at Nickel. 1. Poly[1,2-bis(dialkylphosphino)benzene]. Linear, low molecular weight poly[1,2-bis(dialkylphosphino)benzene] was prepared as shown in Scheme IV. Poly[1,2-bis(ethylpropylenephosphino)benzene] (17) was a viscous, colorless oil with a degree of polymerization between 30 and 48.[18] Despite the ready solubility of 17 in aprotic solvents, coordination with Ni(II) produced an intractable, insoluble orange solid 18 (λ_{max} = 428 nm) with 2:1 ligand/metal coordination inducing cross-linking of the resin. These complexes could be deposited on the electrode by spin- or dip-coating a solution of the ligand onto the electrode surface which was then immersed in a solution of the desired Ni(II) salt.

A cyclic voltammogram of 18 exhibited two reduction waves (−1.10 to −1.27 V), but with continued cycling the more negative wave disappears, as the other grows concomitantly. Eventually, this single, fully reversible two-electron wave becomes the only feature present. This change in electrochemical behavior can be attributed to reorganization of initially nonequivalent metal sites,



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principally 1:1 and 2:1 (ligand/metal) coordination but also because of environmental variability caused by residual stresses in the polymer chains.

Once reorganization has been achieved, the electrochemical behavior of the films becomes consistent. This was true regardless of whether the films had been metalated with Ni(II) chloride or Ni(II) perchlorate, since during electrochemical cycling, the metal centers exchange counterions with the electrolyte solution until eventually all counterions are derived from the electrolyte. Electrodes removed from solution, permitted to dry, and resolvated show unaltered behavior compared with the analogous soluble monomeric 2:1 complex. The polymer is somewhat more difficult to reduce since in 18 each metal atom resides at a cross-link juncture. Reduction requires a change in geometry concomitant with or antecedent to electron transfer, which in 18 requires considerable chain reorganization and results in an increased stability of the originally installed oxidation state (Ni(II)) and a coalescing of the Ni(II) → Ni(I) and Ni(I) → Ni(0) processes. Surface-bound monolayers of reversible couples frequently exhibit zero peak potential separation, but despite efforts to make very thin films of 18, peak separations of less than 40 mV could not be attained.

In redox polymers, a self-exchange between neighboring metal sites is possible, Figure 7. In the relatively thick films (2–3 μm) of 18, charge transfer was especially slow, so that the peak currents (i_p) were not proportional to the potential sweep rates ($i_p v^{1/2}$). In most experiments, however, the concentration of redox centers at the electrode surface (Γ) was lower: a coverage of approximately 10^{-8} mol/cm^2 corresponds to approximately 30 monolayers.[19]

2. Poly[1,2-bis(isopropyl-1,2-propylenephosphino)-benzene] (19). A crankshaft polymer with isopropyl substitution 19 was prepared as a glassy solid soluble in nonpolar solvents, Scheme V. Coordination of 19 with nickel(II) produced an orange precipitate that was slightly soluble in coordinating solvents (e.g., THF, acetonitrile, DMSO). The electrochemical behavior of modified electrodes, prepared as described above, was nearly identical with that of uncomplexed nickel perchlorate, as had been observed with grafted perisopropyl-substituted bisphosphino benzene ligands, Figure 6. Efforts to prevent overmetalation of the film were unsuccessful, because films with very low metal content failed to remain immobilized on the electrode surface.

C. Network Cross-Linked Backbone Polymeric Ligands Further Cross-Linked at Nickel: Poly[1,2-bis(ethylpentylenephosphino)benzene] (20). A cross-linked network polymer 20 with steric bulk equivalent to 17 was prepared as shown in Scheme VI as an insoluble, colorless rubber. It could be swelled in organic solvents and metalated by nickel(II) chloride or nickel carbonyl to the analogous nickel-complexed polymer 21. With nickel carbonyl, clean 2:1 complexation was attained, but with Ni(II) salts either 2:1 or 1:1 (ligand/nickel) complexes were formed in about a 43:57 ratio. Exhaustive extraction of the metalated polymer failed to induce leaching. Although the complexes are free to undergo changes in geometry,

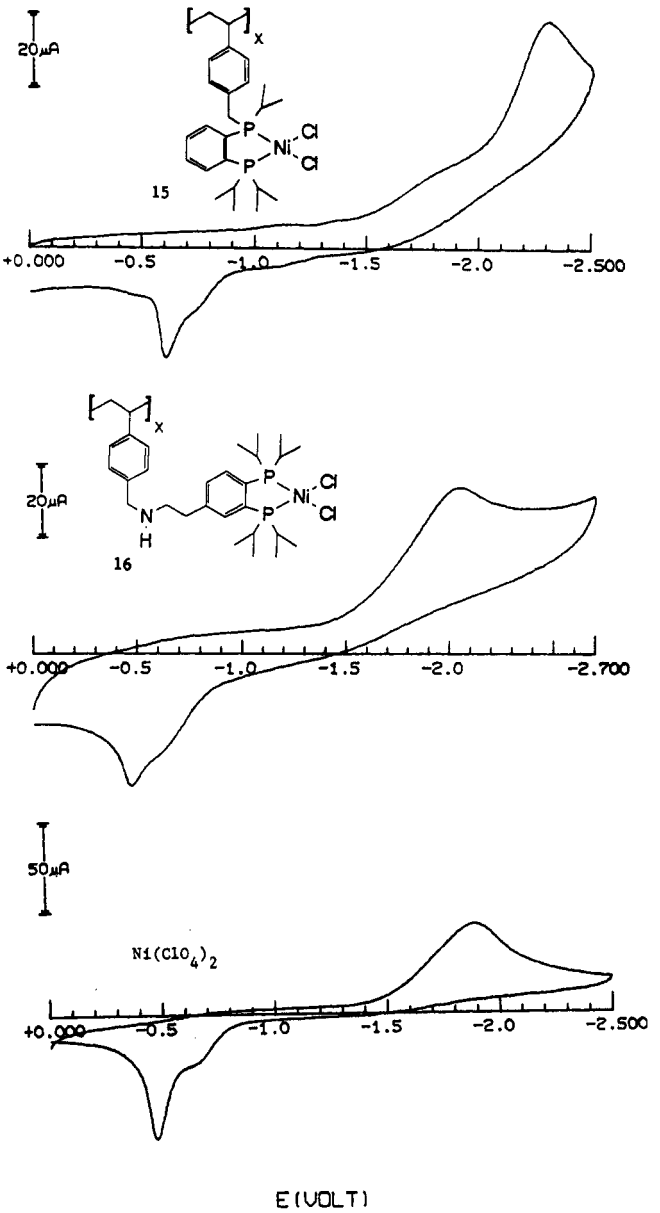


Figure 6. Cyclic voltammograms of (top) glassy carbon modified with 15, (middle) glassy carbon modified with 16, and (bottom) nickel(II) perchlorate as a 10^{-3} M solution at glassy carbon, all in DMSO containing 0.2 M TBATFB, 25 °C, 100 mV/s.

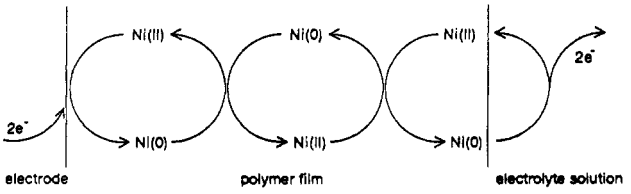
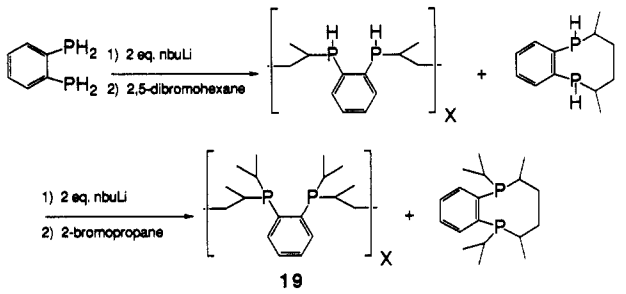


Figure 7. Propagation of charge through a polymeric bisphosphinobenzene–nickel complex containing layer by redox exchange.

Scheme V
Synthesis of Bisphosphinobenzene Ligand Backbone Polymer 19



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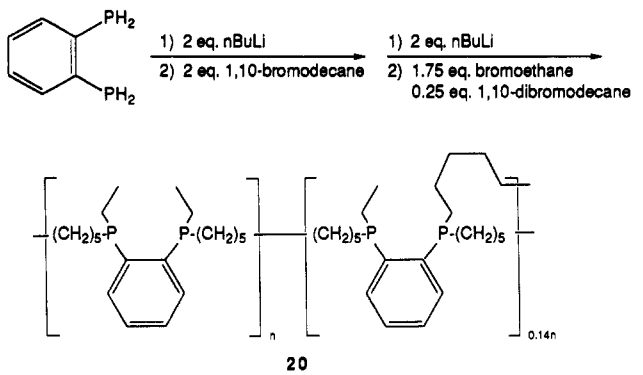
Scheme VI
Preparation of a Cross-Linked Ligand Backbone Polymer 20



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the matrix appears to hold tenaciously to each nickel atom. Similar electroactivity to that seen for **17** was observed in **20**.

Electrocatalytic Reductive Coupling by Polymer 15. Since the reductive coupling of *p*-bromotoluene had been optimized with monomeric ligands,[11b] polymer **15** was examined as a similar electrocatalyst. Although greater variation in attainable turnover number (40–600) was observed in this heterogeneous catalyst, excellent chemical yields (90–97%) of reductive coupling to 4,4′-dimethylbiphenyl were observed at 60 °C in dimethyl sulfoxide upon reduction of **15**, conditions reported to be optimal in the electrocatalysis by [1,2-bis(diisopropylphosphino)benzene]nickel(II) **10**.[11b] Lowered electrocatalytic activity of the polymeric films was ultimately observed, but if the ratio of coupled products to immobilized catalytic sites was held to below 20, the polymeric electrocatalysts could be reused at least four times without appreciable loss of electroactivity. Thus, the immobilized catalyst seems to be somewhat more resistant to the C–P insertion thought to limit turnover number in the monomeric electrocatalyst.

Conclusions

Anchoring of electrocatalytically active bisphosphinobenzene ligands (and their nickel complexes) to electrode surfaces can be accomplished via two general strategies using (1) covalent attachment of coordinating ligands containing "handle" functionalities or (2) irreversible adsorption of polymeric coordinating ligands.

Three different handle groups bearing at least one lone pair of electrons were incorporated into bisphosphinobenzene ligands for use in covalent attachment to electrodes: triethoxysilane, benzyl alcohol, and ethylamine. None of them were completely "innocent" in an electrochemical sense. Attachment of the handle group at a position on the ligand remote from the intended coordination site was necessary for electrocatalytic activity. Alkoxysilanes were the least effective handle, since these groups were ideally positioned for intramolecular coordination to nickel via a seven-membered ring. Even without coordination, the bulky triethoxysilane groups are capable of shielding the metal center and hence blocking electrocatalysis. Both alcohol and amine functionalities could be tolerated in ligands that maintained electroactivity, although formation of polymeric aggregates with amine-derivatized complexes was a problem during solution experiments, and the nickel center appeared to have been sequestered (cf., the silane-containing complexes).

Polymeric analogues of these ligands produced more favorable electrochemical results than did the ligands with handles for covalent attachment. Two strategies for forming polymeric bisphosphinobenzene ligands were effective: covalent displacement of chloride by alkylated bisphosphinobenzene from preformed polyvinylbenzyl chloride or generation of a family of polymers with bisphosphinobenzene in the backbone via α,ω-coupled alkylation at phosphorus. Metalated films of polyvinylbenzyl chloride grafted with bulky perisopropyl-substituted bisphosphinobenzene ligands appeared, however, to include noncomplexed nickel. With a lower nickel content, fewer metal atoms escape coordination. These results demonstrate that a polymer matrix may serve to promote coordinative unsaturation and that the metal content of the matrix is critical in determining its electrochemical behavior.

Electroactivity similar to that observed with the monomeric analogues of these polymer-immobilized catalysts were observed for several of the polymers. While it is extremely difficult to predict the properties of a given heterogenized metal complex a priori, the polymer structure of the adsorbed electrocatalyst provides another adjustable variable to be manipulated in achieving a desired activity.

Experimental Section

General. Proton, carbon-13, and phosphorus-31 NMR were obtained on either a Varian FT80 or General Electric GN-500 spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane for ^{13}C and ^{1}H and are reported relative to phosphoric acid for ^{31}P. Absorption spectra were measured on a Hewlett-Packard 8154A diode array spectrophotometer. Conductivity measurements were made on a Yellow Springs Instruments (YSI Model 32) conductivity bridge. X-ray photoelectron spectroscopy (XPS) was performed on a Vacuum Generators XPS system. A BAS-100 electroanalyzer was used to obtain electrochemical data. All experiments were performed with tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte, a glassy carbon working electrode, and a platinum wire counter electrode. All potentials are referenced to $Ag/AgNO_3$. Unless noted otherwise, all manipulations involving phosphines were conducted under a dry nitrogen or argon atmosphere, and solvents were used as received (spectroscopic grade from Fisher Scientific or Mallinckrodt). Elemental analyses were performed by Galbraith Laboratories.

Reagents for Silane Coupling. 4-(Ethylphenylphosphino)-1-butene. Into a 250-mL round-bottom flask equipped with a stir bar, an argon atmosphere, and a condenser were combined 200 mL of THF (distilled from Na), 8.0 g (37 mmol) of diphenylethylphosphine,[22] and 0.75 g (110 mmol) of lithium wire. The mixture was gently warmed to ca. 50 °C for 24 h, after which time the resulting red solution was filtered through glass wool (under argon) into a clean 500-mL round-bottom flask. The solution was cooled to 0 °C, and 4.0 mL (37 mmol) of 2-chloro-2-methylpropane was added. After 15 min, 5.0 g (37 mmol) of 4-bromo-

1-butene was slowly added by syringe. When the red color had dispersed, the mixture was allowed to warm to room temperature and was washed with 200 mL of degassed water. The organic phase was removed, and two 100-mL portions of diethyl ether were used to extract the aqueous phase. The organic fractions were combined, dried over sodium sulfate, and distilled to produce 4.8 g (67% yield) of the title compound: bp 63–67 °C at 0.6 mmHg; ^{31}P ($CDCl_3$) δ −18.68 (s); ^{13}C ($CDCl_3$) δ 137.8 (d, J = 19 Hz), 132.8 (d, J = 5.5 Hz), 131.8 (d, J = 18 Hz), 128.1 (s), 128.0 (d, J = 10 Hz), 116.1 (d, J = 8.4 Hz), 32.6 (d, J = 14 Hz), 18.7 (d, J = 12 Hz), 9.5 (d, J = 18 Hz). Elemental anal. Calcd for $C_{12}H_{17}P$: H, 8.91; C, 74.97. Found: H, 8.89; C, 74.89.

Attempted Hydrosilylation of 4-(Ethylphenylphosphino)-1-butene. Into a 25-mL reaction tube were combined 15 mL of toluene, 1.9 g (10 mmol) of 4-(ethylphenylphosphino)-1-butene, 2.0 g (12 mmol) of triethoxyhydrosilane, and 0.10 g (0.2 mmol) of chloroplatinic acid hexahydrate dissolved in 2 mL of ethanol (2 mol % of catalyst based on the amount of olefin present). The mixture was frozen, placed under vacuum, and thawed (four cycles) to remove oxygen. The reaction tube was then sealed under vacuum and heated to 150 °C for 8 h in a tube furnace. After cooling, the reaction mixture was examined by ^{1}H NMR. No evidence of hydrosilylation could be detected.

[3-(Triethoxysilyl)propyl]ethylphenylphosphine. Into a 250-mL round-bottom flask equipped with a septum, a stir bar, and an argon atmosphere were combined 100 mL of THF (distilled from Na) and 15 g (110 mmol) of ethylphenylphosphine.[23] The mixture was cooled to −78 °C, and 69 mL of 1.6 M n-butyllithium (110 mmol) was added by syringe. After the n-butyllithium had been allowed to react for 15 min, 27 mL (110 mmol) of 1-chloro-3-(triethoxysilane)propane was slowly added. The reaction mixture was allowed to warm to room temperature and to stir for 1 h. Additional 1-chloro-3-(triethoxysilyl)propane was added (several drops) until the red color had dissipated. The solution was concentrated and distilled to produce 20 g (53% yield) of the desired product: bp 143–149 °C at 0.10 mmHg; ^{31}P ($CDCl_3$) δ −21.04 (s); ^{13}C ($CDCl_3$) δ 138.7 (d, J = 13.6 Hz), 132.0 (d, J = 18 Hz), 130.0 (d), 127.9 (d, J = 6.8 Hz), 57.9 (s), 31.0 (d, J = 12 Hz), 20.4 (d, J = 11.0 Hz), 19.3 (d, J = 15 Hz), 18.0 (s), 12.2 (d, J = 11 Hz), 9.6 (d, J = 14 Hz). Elemental anal. Calcd for $C_{17}H_{31}O_3PSi$: H, 9.12; C, 59.62. Found: H, 9.00; C, 59.55. HRMS, m/e 342.495 15 (calcd 342.494 08).

1,2-Bis[ethyl[3-(triethoxysilyl)propyl]phosphino]benzene (2). Into a 500-mL round-bottom flask equipped with a septum, a stir bar, and an argon atmosphere were combined 200 mL of THF (distilled from Na) and 4.4 g (22 mmol) of 1,2-bis(ethylphosphino)benzene. The mixture was cooled to −78 °C, and 27.75 mL of 1.6 M n-butyllithium in hexanes (44 mmol) was added. After 15 min, 11 mL (44 mmol) of 1-chloro-3-(triethoxysilyl)propane was slowly added. After 1 h, the mixture was concentrated and distilled. The product, 1,2-bis[ethyl[3-(triethoxysilyl)propyl]phosphino]benzene, was obtained in 45.0% yield (6.1 g): bp 180–182 °C at 0.1 mmHg; ^{31}P ($CDCl_3$) δ 144.70 (t, J = 4.2 Hz), 129.7 (t, J = 2.3 Hz), 128.0 (s), 58.0 (s), 57.8 (m), 20.3 (d, J = 3.7 Hz), 19.1 (d, J = 8.0 Hz), 18.0 (s), 12.4 (t, J = 4.2 Hz), 9.6 (t, J = 4.6 Hz). Elemental anal. Calcd for $C_{28}H_{56}O_6P_2Si_2$: C, 55.42; H, 9.30; O, 15.82. Found: C, 53.85; H, 9.04; O, 15.26.

Chlorobis[o-phenylenebis[ethyl[3-(triethoxysilyl)propyl]phosphine]]nickel(II) Chloride (3). Into a 100-mL round-bottom flask were combined 45 mL of acetonitrile and 0.78 g (6.0 mmol) of anhydrous nickel(II) chloride. The solution was degassed with bubbling argon, and 1.8 g (3.0 mmol) of 1,2-bis[ethyl-[3-(triethoxysilyl)propyl]phosphino]benzene was added. The solution was stirred at room temperature for 24 h, after which time the solvent was removed under vacuum. The resulting red, sticky solid was dried under vacuum (85 °C and 0.05 mmHg) for 24 h to produce 7.5 g (93% yield) of a brittle, red solid: mp 244–250 °C (dec); ^{31}P ($CDCl_3$) δ 54.30 (s). Elemental anal. Calcd for $C_{56}H_{112}O_{12}P_4Si_4NiCl_2$: H, 8.4; C, 50.07; O, 14.29. Found: H, 8.15; C, 49.87; O, 14.01.

Reagents for Coupling via Ether Linkages. 4-(Hydroxymethyl)-1,2-bis(diethylphosphino)benzene (4). Diethyllithium Phosphide. Into a 500-mL round-bottom flask equipped with a magnetic stirrer, an argon atmosphere, and a condenser were added 210 mL of tetrahydrofuran (distilled from Na), 34 g (0.22 mol) of diethylphenylphosphine,[24] and 4.7 g (0.67 mol) of lithium ribbon (surface abraded and washed with heptane prior to use). The mixture was cooled to 0 °C and stirred. After 12 h, the dark red solution was filtered to remove excess lithium (accomplished by cannulation through a tube packed with glass wool into a clean, dry, argon-filled flask). To the filtered solution, 16 mL (0.15 mol) of 2-chloro-2-methylpropane was slowly added.

Into a 250-mL round-bottom flask equipped with a magnetic stirrer and an argon atmosphere were combined 11 g (0.06 mol) of 3,4-dichlorobenzyl alcohol and 100 mL of dry tetrahydrofuran. The mixture was cooled to 0 °C, and 64 mL of 0.97 M phenyllithium was added dropwise. The bright yellow solution was allowed to warm to room temperature and was slowly added to the lithium diethylphosphide solution. The resulting brown-purple solution was heated under reflux for 45 min and allowed to cool. Deoxygenated water and diethyl ether (100 mL of each) were added to the reaction mixture. The solution was stirred for 1 h, and the organic layer was removed to a deoxygenated flask containing 65 g of sodium sulfate. After 12 h, the solution was siphoned away from the sodium sulfate and concentrated by stripping off volatiles in a short-path distillation apparatus under an argon atmosphere. The yellow liquid was distilled under vacuum. The desired product was contained in the final fraction as part of a 50:50 mixture with monosubstituted isomers.

Chlorobis[[4-(hydroxymethyl)-o-phenylene]bis(diethylphosphino)]nickel(II) Chloride (5). To a methanol solution containing impure 4, a solution of 0.1 M nickel(II) chloride was added dropwise. As a red color developed, a ^{31}P NMR peak at δ 28.5 ppm was replaced by a new signal at δ 57 ppm. When the former signal had disappeared, the addition was halted. (Care was taken not to add too much nickel chloride to prevent complexation from occurring with the monosubstituted phosphine, which was also present.) The red methanolic solution was then concentrated on a rotary evaporator (not to dryness) and added dropwise to 200 mL of tetrahydrofuran. After stirring for 48 h, the solution was filtered and dried under a stream of argon; 0.03 g of a burnt orange, crystalline product was isolated (54% yield). mp 371–385 °C (dec); ^{31}P($CDCl_3$) δ 57–57 (m). Elemental anal. Calcd for $C_{30}H_{52}P_4NiCl_2 \cdot H_2O$: C, 52.66; H, 7.95. Found: C, 52.81; H, 7.91.

Reagents for Coupling via Amide Linkages. 4-(2-Aminoethyl)-1,2-bis(dimethylphosphino)benzene (6). In a 250-mL round-bottom flask were combined 5 g of powdered sodium cyanide (0.1 mol) and 50 mL of water. The flask was fitted with a condenser, an addition funnel, and a magnetic stir bar. The mixture was warmed in an oil bath at 65 °C until all the sodium cyanide was dissolved. Next, 20 g (83 mmol) of 3,4-dichlorobenzyl bromide dissolved in 100 mL of 95% ethanol was slowly added via the addition funnel. The resulting mixture was heated under reflux for 5 h, allowed to cool, and filtered. The ethanol was stripped off by distillation under a water aspirator vacuum. Upon removal of the ethanol, two layers formed. The organic layer was removed and concentrated, giving a colorless liquid: (3,4-dichlorophenyl)acetonitrile (14 g, 92% yield): bp 145 °C at 0.1 mmHg; ^{1}H δ 3.52 (s), 6.95–6.98 (m), 7.22 (s), 7.25 (s); ^{13}C δ 22.7 (s), 116.7 (s), 127.2 (s), 129.8 (s), 130.0 (s), 131.0 (s), 132.5 (s), 133.2 (s).

A 1.2-L photoreaction vessel equipped with a condenser, a 450-W Conrad-Hanovia medium-pressure mercury vapor lamp, and a quartz immersion well was charged with 170 g (0.914 mol) of (3,4-dichlorophenyl)acetonitrile and 1.0 L (8.48 mol) of trimethyl phosphite (TMP). The solution was magnetically stirred and purged with bubbling argon during the irradiation. Evaporated TMP was replenished as required during the photolysis. The reaction temperature was maintained at 60–70 °C. The total irradiation time was 252 h. Following irradiation, unreacted trimethyl phosphite and (3,4-dichlorophenyl)acetonitrile were removed under vacuum. The resulting viscous, reddish orange oil (260 g, 84%) could not be further purified by distillation or crystallization. ^{31}P ($CDCl_3$) δ 17.10 (s); 23% monosubstituted product was present. By ^{31}P ($CDCl_3$) δ 15.94 (s), the estimated yield of 4-(2-aminoethyl)-1,2-bis(dimethoxyphosphoryl)benzene = 64%.

Dry THF (300 mL distilled from sodium) and 26 g (680 mmol) of lithium aluminum hydride were combined in a 1-L three-neck flask equipped with a mechanical stirrer and an argon atmosphere.

The slurry was cooled to −78 °C, and 86 mL (68 mmol) of chlorotrimethylsilane was slowly added through an addition funnel. After 2 h at room temperature, the mixture was cooled to −30 °C, and 22 g of crude 4-(2-aminoethyl)-1,2-bis(dimethoxyphosphoryl)benzene in 200 mL of THF was slowly added. (Caution: this step is very exothermic and evolves a large amount of hydrogen.) The reaction mixture was stirred for 8 h at room temperature. Excess LAH was quenched by adding 50 mL of H_2O, followed by 150 mL of 2 N NaOH. The organic phase was removed through a cannula, and the aluminum salts were extracted with three 50-mL portions of diethyl ether. The organic fractions were combined, dried over sodium sulfate, and concentrated. Vacuum distillation produced 6.8 g of 4-(2-aminoethyl)-1,2-diphosphinobenzene: colorless oil, bp 110–112 °C at 0.02 mmHg, 47.1%; ^{31}P ($CDCl_3$) δ −123.65 (d) (J = 44 Hz), 125.98 (d) (J = 44 Hz); ^1H ($CDCl_3$) δ 0.79 (s, 2 H), 2.39 (t, J = 6.8 Hz, 2 H), 2.64 (s, J = 6.8 Hz, 2 H), 3.73 (m, 2 H), 4.06 (m, 2 H), 6.75–6.77 (m, 1 H), 7.06–7.18 (m, 2 H); ^{13}C ($CDCl_3$) δ 39.2, 43.1, 127.6, 128.1, 130.1, 135.6, 135.8; HRMS, m/e 185.052 292 (calcd 185.052 321).

Into a 500-mL round-bottom flask equipped with a stir bar, a septum, and an argon atmosphere were combined 150 mL of dry, degassed THF and 5.7 g (31 mmol) of 4-(2-aminoethyl)-1,2-diphosphinobenzene. The solution was cooled to −78 °C and 25 mL (62 mmol) of 2.5 M n-butyllithium in hexanes was added. After 30 min, 8.8 g (63 mmol) of iodomethane was added. Reaction was immediate, as evidenced by the disappearance of red color. Again, 25 mL of 2.5 M n-butyllithium was added, followed in 30 min by 8.8 g of iodomethane. After warming to room temperature for 1 h, the reaction mixture was stirred with 200 mL of 4 N aqueous hydroxide, washed with 200 mL of water, and extracted twice with 100 mL of diethyl ether. The organic layers were combined, dried over sodium sulfate, and concentrated under a stream of argon. Distillation gave 5.6 g (76% yield) of the desired product: bp 140–145 °C at 0.1 mmHg; ^{31}P ($CDCl_3$) −56.39 (s), −56.52 (s). Elemental anal. Calcd for $C_{12}H_{21}P_2N$: C, 59.74; H, 8.77. Found: C, 59.55; H, 8.63.

4-(2-Aminoethyl)-1,2-bis(diisopropylphosphino)benzene (7). Into a 500-mL round-bottom flask equipped with a stir bar were combined 120 mL of dry THF and 3.6 g (20 mmol) of 4-(2-aminoethyl)-1,2-diphosphinobenzene. The solution was cooled to −78 °C and 25 mL (40 mmol) of 1.6 M n-butyllithium in hexanes was added by syringe. After 40 min, 3.7 mL (40 mmol) of 2-bromopropane was added until the red color was discharged. The solution was allowed to warm to room temperature and was then cooled to −78 °C and treated with 25 mL of 1.6 M n-butyllithium, followed by 3.7 mL of 2-bromopropane. Again, the reaction mixture was warmed to room temperature for 40 min. To the reaction flask were added 150 mL each of water and diethyl ether. The organic layer was removed, dried over sodium sulfate, and concentrated. Kugelrohr distillation produced 5.5 g (79%) of the desired product, a light yellow, viscous oil: bp 175–180 °C at 2 μ; ^{31}P ($CDCl_3$) δ −5.78 (s); ^1H ($CDCl_3$) δ 0.60–0.79 (m, 12 H), 0.60–0.99 (m, 24 H), 0.84–0.99 (m, 12 H), 1.36 (s, 2 H), 1.80–1.90 (m, 4 H), 2.49 (t, J = 6.9 Hz, 2 H), 2.73 (t, J = 6.9 Hz, 2 H), 6.84–6.92 (m, 1 H), 7.07–7.08 (m, 1 H), 7.16–7.20 (m, 1 H); ^{13}C ($CDCl_3$) δ 19.5–20.3 (m), 24.9 (d, J_{PC} = 10.0 Hz), 39.7, 43.9, 203.3, 142.0, 137.8, 97.8. Elemental anal. Calcd for $C_{20}H_{37}P_2N$: C, 67.96; H, 10.55; N, 3.97. Found: C, 67.65; H, 10.14; N, 3.79.

Chlorobis[[(2-aminoethyl)-o-phenylene]bis(dimethylphosphino)]nickel(II) Chloride (8). In a 50-mL round-bottom flask equipped with a stir bar, a septa, and an argon atmosphere were combined 570 mg (2.4 mmol) of 4-(2-aminoethyl)-1,2-bis(dimethylphosphino)benzene and 20 mL of acetonitrile. While the mixture was stirred rapidly, a solution of 280 mg (1.2 mmol) of $NiCl_2$·$6H_2O$ dissolved in 15 mL of methanol was rapidly added. After ca. 10 min, a red precipitate was collected by filtration, washed with cold THF, and dried under vacuum for 24 h. The title compound was obtained in 55% yield, mp 355–362 °C (dec); ^{31}P NMR (methanol-d_4) + 44.01 (s). Elemental anal. Calcd for $C_{24}H_{42}P_4N_2NiCl_2$: H, 7.25; C, 49.35. Found: H, 7.12; C, 50.21.

Dichloro[[(2-aminoethyl)-o-phenylene]bis[bis(2-methylpropyl)phosphino]]nickel (9). Into a 25-mL round-bottom flask equipped with a stirrer and a septum were combined 10 mL of methanol and 0.47 g (0.1984 mmol) of $NiCl_2$·$6H_2O$. The solution was deaerated with bubbling argon to remove oxygen. A solution of dichloromethane (5 mL) containing 700 mg (1.984 mmol) of 4-(2-aminoethyl)-1,2-bis(diisopropylphosphino)benzene[11] was added. A red-orange precipitate was collected by vacuum filtration, washed with 0 °C methanol, and dried under vacuum to yield 920 mg (97% yield) of red-orange crystals. The solid appeared to be polymeric in nature—softening and flow temperature 135–140 °C; ^{31}P (pyridine-d_5) δ 79.2 (s); ^1H ($CDCl_3$/pyridine-d_5) 7.47–7.50 (m, 2 H), 7.26 (s, 1 H), 2.59–2.68 (m, 4 H), 3.37 (m, 4 H), 1.00 (s, 1 H), 1.28–1.43 (m, 12 H), 1.01–1.27 (m, 12 H). Elemental anal. Calcd for $C_{20}H_{37}P_2NNiCl_2$·H_2O): C, 47.94; H, 7.85; N, 2.80. Found: C, 47.14; H, 7.23; N, 2.87. Calcd for $C_{20}H_{37}P_2NNiCl_2$: C, 49.73; H, 7.72; N, 2.90. Found: C, 48.53; H, 7.52; N, 2.96.

Carbon Electrode Modification. Covalent Attachment. Glass carbon rod (Atomergic Chemetals Corp., Farmingdale, NY, Grade V10, 3-mm diameter) was cut into 1.5-cm lengths and polished on one end with 50 000-mesh diamond paste (Crystalite Corp., Marina del Rey, CA). The carbon rod was then surface oxidized by heating in air (500 °C, 60 min) or, alternatively, by ashing with an oxygen plasma (10 W at 13.56 MHz, 50–100 μm of Hg [O_2] for 40–60 min. The oxidized carbon cylinders were mounted on the end of $^1/_4$-in. glass (Pyrex) tubing with heat-shrinkable Teflon tubing (Small Parts, Inc., Miami, FL).

A 50-mL three-neck round-bottom flask was fitted with two mounted electrodes (through threaded bushings), a magnetic stir bar, and a condenser. The flask was flushed with argon and 20 mL of sodium-dried toluene containing 3 mL of thionyl chloride (freshly distilled from sulfur) was added. The electrodes were then heated under reflux in this solution for 60 min, after which time they were withdrawn and dried under a gentle stream of argon.

The electrodes were again fitted within a 50-mL three-neck round-bottom flask equipped with bushings, a magnetic stir bar, and a condenser under an argon atmosphere and were heated under reflux in 20 mL of degassed toluene containing 0.22 g (0.6224 mmol) of 7 for 60 min. The toluene solution was then removed from the flask via syringe and degassed. A warm solution of $NiCl_2$·$6H_2O$ in acetonitrile (0.2 M, 65 °C) was added. The electrodes were placed in contact with the solution for 15 min for metalation, withdrawn, dried in a stream of argon, and briefly rinsed in fresh acetonitrile (room temperature) before being dried under vacuum.

Carbon cloth (The Electrosynthesis Co., Inc., East Amherst, NY, Grade GC-10) was modified in an analogous fashion, except that it was cut into 3.5 × 4.5 cm pieces, rolled into cylinders, and held in place by gold-plated alligator clips.

Polymer-Supported Dibromo[1,2-bis(diisopropylphosphino)benzene]nickel(II). Into a 15-mL round-bottom flask equipped with a stir bar, a septum, and an argon atmosphere was added via syringe 0.13 g (0.36 mol) of 7 and 10 mL of THF distilled from Na and degassed with argon. The solution was cooled to −78 °C and 0.21 mL of 1.6 M n-butyllithium in hexanes was added. After 15 min, this yellow-orange solution was transferred to another 15-mL round-bottom flask containing 0.200 g of Merrifield's peptide resin (Aldrich Chemical Co., Madison, WI; 1% cross-linked, 1 mequiv of Cl per gram of resin). This heterogeneous mixture was stirred at room temperature for 1 h with a continuous argon purge to exclude O_2 and to slowly concentrate the solution. A methanol solution of nickel(II) bromide trihydrate (0.3 g in 8 mL) was added. The red solution was stirred for an additional 24 h, after which resin was filtered and washed extensively with methanol. The resulting beads were orange in color, indicating that the metal complex was present on the surface. Heating and stirring in DMSO (24 h, 65 °C) and monitoring the filtered solution by UV-vis spectroscopy (λ_{max} $NiBr_2$·DMSO: 418 700 nm) revealed no leaching of $NiBr_2$.

Pendant Bisphosphinobenzene Ligands. 1-[(Polyvinylbenzyl)-2-propylphosphino]-2-(di-2-propylphosphino)benzene (12). In a 250-mL round-bottom flask equipped with a stir bar and a septa were combined 100 mL of THF (distilled from Na) and 1.72 g (6.42 mmol) of 1-(2-propylphosphino)-2-(di-2-propylphosphino)benzene. The solution was cooled to −78 °C, and 2.67 mL (6.42 mmol) of 2.4 M n-butyllithium in hexanes was added. After 30 min, 0.979 g (6.42 mmol of repeat units) of poly(vinylbenzyl chloride) (60:40 para/ortho isomers, Aldrich) in 25 mL of THF (degassed) was added. The completed reaction

mixture was allowed to warm to room temperature with continued stirring for 24 h. The reaction mixture was transferred to a 500-mL round-bottom flask containing 100 mL of water and 200 mL of diethyl ether (degassed). Following agitation, the organic layer was removed and poured into 300 mL of methanol to precipitate the polymeric product. The supernatant fluid was removed and the polymer was dried under vacuum for 24 h. The product (2.3 g, 94% yield) was a pale yellow solid: ^{31}P (THF) δ -1.73 (d, J = 14.86 Hz), -11.44 (d, J = 14.86 Hz). Elemental anal. Calcd for $C_{24}H_{34}P_2$ (100% benzyl substitution): C, 74.97; H, 8.91; P, 16.11. Found: C, 74.72; H, 9.01; P, 15.93.

Polyvinylbenzyl Chloride Modified with 4-(2-Aminoethyl)-1,2-bis(di-2-propylphosphino)benzene (14). Into a 100-mL round-bottom flask equipped with an argon atmosphere, a stir bar, and a septum were combined 25 mL of THF (distilled from Na) and 0.79 g (2.2 mmol) of 4-(2-aminoethyl)-1,2-bis(di-2-propylphosphino)benzene. The solution was cooled to -78 °C and 1.6 mL (2.2 mmol) of 1.4 M n-butyllithium in hexanes was added. After 15 min, 0.35 g (2.0 mmol) of polyvinylbenzyl chloride (60:40 para/ortho isomers, Aldrich) dissolved in 25 mL of THF was added. The solution was warmed to room temperature and stirred for 2 h. The completed reaction mixture was then transferred to a 250-mL round-bottom flask containing 50 mL of water and 100 mL of diethyl ether. After it was washed, the aqueous layer was removed and the polymer product was precipitated with 100 mL of methanol. The supernatant was removed and the polymer was dried under vacuum for 24 h. The product (0.83 g, 88% yield) was a white, flocculent solid: ^{31}P (THF) δ -5.87 (br). Elemental anal. Calcd for $C_{29}H_{45}P_2$ (100% benzyl substitution): C, 76.45; H, 9.96; P, 13.6. Found: C, 76.27; H, 9.83; P, 13.12. (Corresponds to ca. 91% substitution.)

The corresponding metal complexes **15** and **16** (M = Pd(II) and Ni(II)) were prepared as described in the synthesis of **5** from **4**.

Poly[hexamethylene(ethylphosphinidene)-1,2-phenylene(ethylphosphinidene)]: Linear, Low Molecular Weight Polymer 17. In a 250-mL round-bottom flask equipped with a stir bar, a septum, and an argon atmosphere were combined 100 mL of dry degassed THF and 4.9 g (25 mmol) of 1,2-bis(ethylphosphino)benzene. The mixture was cooled to -78 °C, and 31 mL (49 mmol) of 1.6 M n-butyllithium was slowly added by syringe. After 30 min at -78 °C, 3.8 mL (25 mmol) of 1,6-dibromohexane was rapidly added. The reaction mixture was allowed to warm to room temperature and was stirred until the red color had dissipated. The reaction mixture was cannulated into a 500-mL round-bottom flask containing 100 mL of water and 250 mL of diethyl ether (degassed with bubbling argon). After thorough agitation, the organic layer was removed, dried with sodium sulfate, and concentrated. The product (6.8 g) was an extremely viscous, clear, and colorless oil: ^{31}P (m) (THF) 24.54-29.98 ppm (-29.67). The polymer was readily redissolved in benzene, THF, and chloroform. Elemental anal. Calcd for $(C_6H_{26}P_2)_x$: C, 68.55; H, 9.33. Found: C, 67.7; H, 9.33.

Poly[2,5-hexanediyl(isopropylphosphinidene)-1,2-phenylene(isopropylphosphinidene)]: Branched Polymer 19. In a 100-mL round-bottom flask equipped with a stir bar, a septum, and an argon atmosphere were combined 50 mL of dry, degassed THF and 2.3 g (16 mmol) of 1,2-bisphosphinobenzene. The mixture was cooled to -78 °C and treated with 13 mL (33 mmol) of 2.5 M n-butyllithium in hexanes. After 30 min, 4.0 g (16 mmol) of *meso*-2,5-dibromohexane was added via syringe. The solution was allowed to warm to room temperature for 45 min, after which it was again cooled to -78 °C and treated with 13 mL of 2.5 M n-butyllithium. When 30 min had passed, a mixture of 0.20 g of *meso*-2,5-bibromohexane and 3.83 g of 2-bromopropane were added. The reaction mixture was allowed to warm to room temperature for 2 h. The reaction mixture was then transferred via cannula to a 500-mL round-bottom flask containing 100 mL of water, 300 mL of diethyl ether, and a stir bar (the contents had been previously degassed with bubbling argon). After agitation, the organic layer was removed to another flask and was dried over sodium sulfate, filtered, and concentrated. Approximately 2.9 g (58%) of product was distilled in a Kugelrohr (200 °C at 0.1 mmHg) to yield a clear, colorless, viscous oil (^{31}P ($CDCl_3$) 35.45, 10.03, and -03.72 ppm), presumed to be cyclics and oligomers. The remaining nonvolatile fraction (3.13 g) was a glassy yellow solid, soluble in benzene. ^{31}P NMR -3.72 ppm (m).

Poly[1,10-decanediyl(ethylphosphinidene)-1,2-phenylene(ethylphosphinidene)]: 25% Cross-Linked Network Resin 20. Into a 1000-mL three-neck round-bottom flask equipped with an argon atmosphere, a septum, and a mechanical stirrer were combined 2.0 g (14 mmol) of 1,2-bisphosphinobenzene and 50 mL of dry degassed THF. The solution was cooled to -78 °C and treated with 11 mL (28 mmol) of 2.5 M n-butyllithium in hexanes. After 30 min, 4.1 g (14 mmol) of 1,10-dibromodecane dissolved in 10 mL of THF was added. A red gelatinous mass immediately formed, which was allowed to warm to room temperature and stirred for 1 h. The addition of 0.3 mL of 1-bromopropane caused the gel to break up. After an additional 12 h at room temperature, the reaction mixture had become colorless (although still somewhat heterogeneous). An additional 50 mL of dry degassed THF was added to the solution, and it was again cooled to -78 °C and treated with 11 mL of 2.5 M n-butyllithium. After 30 min, a mixture of 1.0 g (3.5 mmol) of 1,10-dibromodecane and 2.6 g (10 mmol) of 1-bromopropane dissolved in 10 mL of THF were added. The reaction mixture was allowed to stir at room temperature for 12 h.

Workup consisted of adding 150 mL of water and 200 mL of diethyl ether to the reaction flask and stirring for 16 h. Separation of the aqueous and organic layers was facilitated by adding 100 mL of methanol. The aqueous and organic layers were removed, and the remaining white granular solid was extracted several times with THF and methanol. The dried polymer was a white rubber (similar to silicone rubber in consistency): ^{31}P NMR (swollen in $CDCl_3$) very broad peak, -37 ppm. Elemental anal. Calcd for $C_{22.5}H_{38.35}P_2$ (an averaged formula for the theoretical polymer with 25% cross-linking units): C, 72.78; H, 10.52. Found: C, 72.95; H, 10.03.

Poly[1,2-bis(n-propyl-n-decylphosphino)benzene-nickel(0) dicarbonyl] 21. Into a 50-mL round-bottom flask equipped with a stir bar and an argon atmosphere were combined 0.5 g of cross-linked phosphine resin [poly[1,10-decanediyl(ethylphosphinidene)-1,2-phenylene(ethylphosphinidene)] (**20**)] and 25 mL of dry degassed THF. The solution was stirred for 45 min to ensure that the resin was swollen with solvent, and 5 mL of nickel carbonyl was transferred in via cannulation. The mixture was stirred at room temperature for 24 h with a slow purge of argon, after which time the polymer had become purple (almost black). The solvent was cannulated away from the solid (very swollen resin), and the resin was washed and exhaustively extracted with degassed THF. Elemental anal. Calcd for $C_{24.5}H_{38.35}P_2NiO_2$: P, 12.46; Ni, 11.80. Found: P, 11.93; Ni, 10.98. Therefore the atomic P:Ni ratio = 2.09:1 (i.e., each nickel(0) present is coordinated with only one bisphosphinobenzene unit).

Poly[1,2-bis(n-propyl-n-decylphosphino)benzene-nickel(II) dichloride] 21. In a 50-mL round-bottom flask, 0.5 g of cross-linked phosphine resin **20** was combined with 25 mL of degassed MeOH and 1.5 g of $NiCl_2 \cdot 6H_2O$. The addition having been completed, the solution was stirred at room temperature for 16 h, followed by heating under reflux for 24 h. The supernatant fluid was then cannulated from the resulting red solid. After extraction with MeOH, THF, and $CDCl_3$, the solid was dried on a vacuum line. Elemental anal. Calcd for $C_{22.5}H_{38.35}P_2NiCl_2$ (1:1 complexation): P, 12.39; Ni, 11.74. Found: P, 11.27; Ni, 7.42. P:Ni ratio = 2.86:1.

Modification of Carbon Disk Electrodes with Polymeric Phosphines. Electrodes were coated with polymer solutions by either spin-coating a dilute solution (6000 rpm) or dip-coating the relevant phosphine polymer onto the electrode surface from a THF solution (concentrations were typically 0.01 g/mL). Coating operations were performed under an argon atmosphere, and a stream of argon was used to remove excess solvent. Metalation of the electrode was carried out by soaking the polymer-coated electrode in a degassed 0.2 M metal-THF or metal-methanol solution (metal = $NiCl_2 \cdot 6H_2O$ or $Ni(ClO_4)_2$) for 2-12 h. Metalation was self-evident by the orange patina that the electrodes would obtain. Typically, the polymer film would swell very little in methanol, and therefore it required longer metalation times than in THF, but in cases where complexation did not give rise to cross-linking in the polymer film, methanol was preferred. After metalation, the electrodes were briefly washed

with fresh THF or MeOH before being dried under a stream of argon and finally under vacuum.

Preparative Electrocatalytic Reductive Coupling of *p*-Bromotoluene. The preparative coupling and analysis were conducted as described elsewhere,[11b] except that the metal phosphine loaded polymeric films were employed without the addition of any soluble monomeric catalyst. The yields reported in the text are based on consumption of aryl halide as the limiting reagent. Catalytic turnover was calculated from the ratio of diaryl obtained to the fractional deactivation of the polymer sites (as gauged by initial relative electrocatalytic reactivity before and after electrolysis).

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(12) Failure of the hydrosilylation reaction can probably be explained by preferential coordination of the phosphine group to platinum so that the catalyst is totally sequestered and therefore unable to react with olefins. The alternative hydrosilylation route via free radical chemistry (induced by UV light of thermal initiators) produced poor results, as is generally true.

(13) Alcohol and ether molecules bind easily to nickel's sixth coordination site in similar complexes.[11] For example, when methanol was added to an acetonitrile solution of **15**, considerable peak broadening occurs (Ni(II) → Ni(0)).

(14) This complexation was necessary because separation of the mono- and disubstituted products by distillation or chromatography proved to be impossible. It would be difficult to attach this complex to a metal oxide surface via Williamson ether synthesis without disturbing the nickel center. It would be more practical to anchor the free ligand first, followed by metalation. The free ligand could be obtained by decoordination of nickel with sodium cyanide, but this process would further depress an already impractically low yield.

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(16) That metal is leached from its phosphine coordination sites by solvent is unlikely. Extraction of a Merrifield resin (1% crosslinked, which had been modified and metalated in a fashion analogous to that described above for PVBC) for 24 h in hot DMSO failed to remove a sufficient quantity of nickel from the resin to be detected by UV–vis spectroscopy.

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(19) $\Gamma = Q/nFA$, where Q = integrated charge (Coulombs), n = number of electrons in the transition, F = Faraday's constant, and A = electrode area.