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Modification of Silicon and Carbon Electrodes with Methacrylamide Polymers Containing Covalently Attached Molybdenum Dinitrogen Complexes

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Methacrylamide polymers with pendant monodentate, bidentate, and tridentate phosphine ligands (poly-P_1, poly-P_2, and poly-P_3, respectively) have been synthesized. These polymers react with $Mo(N_2)_2(PPh_2Me)_4$ to form polymers with bound molybdenum dinitrogen complexes. Similarly, $MoCl_3(THF)_3$ reacts with poly-P_3 to form $MoCl_3$(poly-P_3). These polymers have been used to modify silicon and carbon electrodes. These electrodes have been characterized by cyclic voltammetry and FT-IR spectroscopy. The redox chemistry of electrodes modified with $Mo(N_2)_2$(poly-P_3)PPh_2Me and $Mo(N_2)_2$(poly-P_2)$_2$ on silicon and carbon electrodes closely parallels that observed for their solution counterparts. However, reduction of $MoCl_3$(poly-P_3) and $MoCl_3$(poly-P_2)$_2$ on silicon and carbon electrodes does not lead to formation of polymer-bound molybdenum dinitrogen complexes.

Introduction

The conversion of molecular nitrogen and water to ammonia and oxygen is endergonic by 678 kJ/mol of dinitrogen,[1] and hence this reaction constitutes a potentially useful energy-storage reaction utilizing abundant raw materials. If radiant solar energy could be used to drive this reaction, this would provide a means for converting solar energy into a useful, energy-rich chemical. Photoassisted reduction of molecular nitrogen to ammonia at an illuminated GaP cathode immersed in a glyme/$Ti(O$-*i*-$Pr)_4/AlCl_3$ solution with an aluminum anode has been reported.[2] In this case, a large bias was supplied by the aluminum anode and the nature of the active catalyst was poorly defined. We have begun a program to determine whether a chemically modified semiconductor electrode can be used to reduce dinitrogen in a well-defined sequence.[3]

A complex used to modify an electrode for this purpose should possess the following properties: (1) It should be well characterized to permit rational synthetic schemes for electrode modification. (2) It should be moderately stable to air and water to permit survival on an electrode surface. (3) The complex must be capable of reducing nitrogen in a cyclic fashion. On the basis of the information available in the literature, it seemed that complexes of the type Mo(diphos)$L_2(N_2)_2$ and Mo(triphos)$L(N_2)_2$ [where L is a monodentate phosphine ligand, diphos is $Ph_2PCH_2CH_2PPh_2$, and triphos is $PhP(CH_2CH_2PPh_2)_2$] would satisfy these criteria if they could be attached via the diphosphine or triphosphine ligands.[4–6] In this paper we describe the synthesis of such complexes with polymer-bound phosphine ligands, their attachment to carbon and silicon electrodes, and an assessment of their catalytic potential.

Experimental Section

Procedures and Materials. All reactions were carried out by using routine Schlenk and/or glovebox techniques. Filtrations were generally performed with a stainless-steel cannula filter, constructed by first flaring one end of a capillary tube 2 in. long and then sliding the tube over the end of an 18-gauge cannula and finally sealing the tube to the end of the cannula with epoxy. The flared end of the glass tube should extend beyond the end of the cannula, and care should be taken not to plug the cannula with epoxy. Filtrations are performed by covering the flared glass end of the cannula with filter paper attached with nichrome wire, immersing this end in the solution to be filtered, and then forcing the solution through the cannula into a second flask by using a pressure differential in the manner of a normal cannula transfer. Reagent grade dichloromethane was purified by distillation from calcium hydride under nitrogen. Reagent grade methanol was dried over 3A molecular sieves and purged with nitrogen immediately before use. Tetrahydrofuran, toluene, and hexanes were distilled from sodium benzophenone ketyl under nitrogen. Allylamine was distilled immediately before use. Organophosphine reagents (Strem Chemicals, Inc.) and AIBN (2,2′-azobis(2-methylpropionitrile), Aldrich) were used as obtained. Poly(methyacryloyl chloride) was obtained as a dioxane solution from Polysciences, Inc. Dichloromethane was added to the dioxane solution of poly(methacryloyl chloride) and the solvent removed in vacuo. The resultant brown tar was heated at 145 °C under vacuum for 12 h. This procedure produces a solid brown polymer free of dioxane and soluble in dichloromethane. Higher drying temperatures result in the formation of an intractable glass. Tetrakis(diphenylmethylphosphine)bis(dinitrogen)molybdenum(0), $Mo(N_2)_2(PPh_2Me)_4$, and (2-(diphenylphosphino)ethyl)phenylphosphine were prepared by literature methods.[7,8] Silicon wafers were purchased from General Diode, Inc., or Polishing Corp. Platinum and carbon electrodes were purchased from IBM.

Physical Measurements. A Perkin-Elmer 599B spectrometer was used for routine infrared spectra. Samples were prepared by placing 1 drop of an organophosphine ligand between two KBr plates and by evaporating polymer solutions on KBr disks. Spectra of solid polymers were taken of Nujol mulls using KBr or CsI disks. Infrared spectra of modified silicon electrodes were collected on a Nicolet 7000 Fourier transform infrared spectrometer equipped with a liquid-nitrogen-cooled mercury cadmium telluride detector. Typically 250 interferograms were collected for each spectrum.

Electrochemical measurements were carried out with a Princeton Applied Research Model 173 potentiostat equipped with a Model 179 digital coulometer and a Model 175 universal programmer. A Houston Instruments Model 2000 X-Y recorder was used for plotting cyclic voltammograms. Solutions used for electrochemical studies were either 0.2 N $LiClO_4$ in methanol, saturated NEt_4BF_4 in methanol, or 0.3 N NBu_4BF_4 or $LiBF_4$ in tetrahydrofuran. The THF solutions were stored over sodium amalgam prior to use. SCE, SSCE, or Ag/AgCl reference electrodes were used with a platinum-wire counterelectrode and ferrocene as an internal standard. Silicon, carbon-disk (IBM), or platinum-disk (IBM) electrodes were used as working electrodes.

Far-infrared spectroelectrochemical measurements were performed by using a cell whose design is shown in Figure 1. The cell fits into a standard IR cell holder with an extended V-shaped trough. The infrared light beam passes through two windows, one a standard IR-transparent material such as a KBr disk and the other a working

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(1) Bolton, J. R. *Science (Washington, D.C.)* **1978**, *202*, 705.
(2) Dickson, C. R.; Nozik, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 8007.
(3) DuBois, D. L.; Turner, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4989.
(4) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6154. George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285.
(5) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1979**, 2074. Anderson, S. N.; Fakley, M. E.; Richards, R. L. *Ibid.* **1981**, 1973.
(6) A report on a SnO_2 electrode modified with a molybdenum dinitrogen complex containing two diphosphine ligands has appeared, but protonation of the soluble analogue of this complex does not result in the formation of ammonia: Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1797.
(7) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978**, *17*, 1678.
(8) Uriarte, R.; Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79. DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011.

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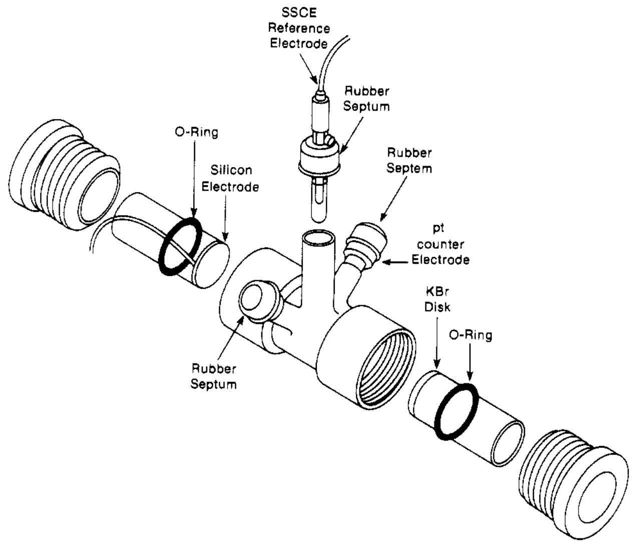

Figure 1. Diagram of the cell used for far-infrared spectroelectrochemical studies.

silicon electrode. Each silicon electrode was constructed by first making an ohmic contact to the silicon wafer by arcing indium solder onto the perimeter of the wafer using a Hewlett-Packard 6181C dc current source. After two isolated contacts were made, the ohmic nature of the contact was verified by observing a linear *i* vs. *E* plot over a 6-V range with little or no hysteresis. Copper wire was attached to the back of the wafer by using indium solder, and a $2^1/_2$ in. long × 25 mm diameter glass tubing was attached to the back of the wafer with epoxy (Epoxi-Patch, 1C white, Hysol Division of Dexter Corp.). The desired resistivity of the silicon wafers to be used for the spectroelectrochemical measurements is 0.1–0.2 Ω cm. The resistivities of all wafers were checked by using a Kulicke & Sofa Model 3007A four-point probe. The percent transmittance varied markedly, from 0% to 60% for wafers approximately 0.3 mm thick, apparently depending on the bulk properties of the crystal. It has been our experience that only 25% of the wafers received in the specified resistivity range are useable, but they can be quickly screened by measuring the infrared transmittance and keeping only those with transmittances of 30% or greater. There also appears to be a crystal orientation effect with the transmittance varying in the order 100 > 111 > 110 for a given resistivity.

Before the silicon electrodes were modified for spectroelectrochemical studies, the silicon wafers were sanded with 600-grit sandpaper, rinsed with water, etched for 2 min in concentrated HF, and finally rinsed successively with water, ethanol, and dichloromethane. The sanding procedure described above results in a rough surface that provides better adhesion for the polymers and more reversible appearing cyclic voltammograms when compared to a highly polished surface.[9] However, this sanding procedure results in a somewhat decreased transmittance due to increased scattering of the infrared light beam. Using electrodes prepared in this manner, we have obtained cyclic voltammograms on a number of complexes with redox potentials between 0.0 and −2.0 V vs. SCE in a variety of nonaqueous solvents with ΔE_p's of 65–120 mV. If the silicon electrodes are scanned more positive than approximately 0 V vs. SCE, irreversible oxidation of the silicon electrode occurs and the electrode is rapidly passivated.

Bulk electrolysis experiments were carried out in a two-compartment cell separated by a medium-porosity sintered-glass frit. Porous carbon-rod electrodes were used as both the working and counterelectrodes, and Ag/AgCl was used as the reference electrode. In a typical experiment 0.1 mmol of $MoCl_3(THF)_3$ (42 mg) was dissolved in 7 mL of 0.5 N NBu_4BF_4/THF solution and 2 equiv of either diphos or poly-P_2 added. After it was stirred for 1 h, this solution was electrolyzed at 0 °C while a stream of nitrogen was bubbled over the cathode. After 3 faradays of current/mol of molybdenum had passed, the electrolysis was stopped. Similarly, solutions containing 0.1 mmol of $MoCl_3(THF)_3$ and 1 equiv of triphos or poly-P_3 and 1 equiv of triphenylphosphine or poly-P_1 per mole of $MoCl_3(THF)_3$ were stirred for 1 h. These solutions were then electrolyzed at 0 °C with nitrogen passing over the electrode until 3 faradays of electricity/mol of $MoCl_3(THF)_3$ had passed.

A JEOL FX90Q FT NMR spectrometer equipped with a tunable, variable-temperature probe was used to collect ^{13}C, ^1H, and ^{31}P NMR spectra. Me_4Si was used as an internal reference for ^1H and ^{13}C spectra. A capillary filled with phosphoric acid was used as an external reference for ^{31}P spectra.

Syntheses. (3-Aminopropyl)diphenylphosphine, NP. Diphenylphosphine (49.55 g) and allylamine (40 mL) were placed in a 250-mL Schlenk flask. The reaction mixture was irradiated with a 300-W Sylvania flood lamp for 1 week with addition of small amounts of AIBN (~10 mg) at 12-h intervals. Excess allylamine was removed by distillation at atmospheric pressure. The remaining reaction mixture was distilled through a Vigreux column. The fraction distilling at 160 °C and 25 μmHg was collected. The yield was 58 g (90%). IR: NH stretch 3360 cm^{-1} (asym), 3280 cm^{-1} (sym); NH bend 1585 cm^{-1}; NH wag 800–870 cm^{-1}. ^1H NMR (C_6D_6): Ph δ 7.4 (m), 7.1 (m); α-CH_2 δ 2.51 (t, J = 7 Hz); β-CH_2 δ 1.45 (m); γ-CH_2 δ 2.0 (m); NH_2 δ 0.48 (s). ^{31}P NMR: δ −16.5. ^{13}C NMR: Ph δ 139 (d, J_{PC} = 13 Hz), 132.7 (d, J_{PC} = 18 Hz), 128.3 (d, J_{PC} = 6 Hz); α-CH_2 δ 43.3 (d, J_{PC} = 13 Hz); β- and γ-CH_2 δ 30.0 (d, J_{PC} = 14 Hz), 25.3 (d, J_{PC} = 12 Hz). Anal. Calcd for $C_{15}H_{18}NP$: C, 74.06; H, 7.46; P, 12.73. Found: C, 74.11; H, 7.58; P, 12.65.

(3-Aminopropyl)phenylphosphine, NPH. Allylamine (27.04 g) and phenylphosphine (46.32 g) were placed in a Schlenk flask and irradiated for 2 weeks. AIBN (~10 mg) was added at 12-h intervals. Unreacted allylamine and phenylphosphine were removed by distillation at atmospheric pressure. The remaining reaction mixture was fractionated by using a Vigreux column. The desired product distilled at 65–70 °C and 25 μmHg. The yield was 29 g (43%). IR: NH stretch 3360 cm^{-1} (asym), 3280 cm^{-1} (sym); NH bend 1585 cm^{-1}; NH wag 800–860 cm^{-1}; PH stretch 2275 cm^{-1}. ^1H NMR (toluene-d_8): Ph δ 7.3 (m), 7.1 (m); PH δ 4.06 (dt, $^1J_{PH}$ = 205 Hz, $^3J_{PH}$ = 7 Hz); α-CH_2 δ 2.42 (t, J = 7 Hz); β- and γ-CH_2 δ 1.6–1.2 (m); NH_2 δ 0.48 (s). ^{31}P NMR: δ 52.3 (s). ^{13}C NMR: α-CH_2 δ 42.7 (d, J_{PC} = 10 Hz); β- and γ-CH_2 δ 32.2 (d, J_{PC} = 8 Hz), 20.3 (d, J = 11 Hz).

(3-Aminopropyl)(2-(diphenylphosphino)ethyl)phenylphosphine, NP_2. Vinyldiphenylphosphine (19.02 g) and NPH (14.98 g) were placed in a Schlenk flask. The reaction mixture was immersed in an oil bath at 110 °C for 3 h. AIBN (10 mg) was added at 1-h intervals. The reaction mixture was fractionated by using a vacuum-jacketed Vigreux column. The desired product distilled at 225–235 °C and 25 μmHg. The yield was 30.30 g (89%). IR: NH stretch 3360 cm^{-1} (asym), 3290 cm^{-1} (sym); NH bend 1585 cm^{-1}; NH wag 790–870 cm^{-1}. ^1H NMR (toluene-d_8): Ph δ 7.4 (m), 7.1 (m); α-CH_2 δ 2.40 (t, J = 6 Hz); β- and γ-CH_2 δ 2.1–1.4 (m); NH_2 δ 0.40 (s). ^{31}P NMR: RPh_2P δ −13.4 (d, J_{PP} = 28 Hz); R_2PhP δ −21.3 (d). Anal. Calcd for $C_{23}H_{27}NP_2$: C, 72.81; H, 7.17; N, 3.69. Found: C, 72.68; H, 7.11; N, 3.58.

(3-Aminopropyl)bis(2-(diphenylphosphino)ethyl)phosphine, NP_3. This ligand was prepared as described in ref 8. Spectral data were in agreement with published data.

Poly[(3-aminopropyl)bis(2-(diphenylphosphino)ethyl)phosphine methacrylamide], poly-P_3. Poly(methacryloyl chloride) (0.84 g) was dissolved in dichloromethane (150 mL) and added to a 0.215 M solution of NP_3 in toluene (37 mL). Triethylamine (2 mL) was added and the reaction mixture stirred at room temperature for 10 days. The reaction mixture was filtered with a stainless-steel cannula filter to remove triethylamine hydrochloride, and the volume of the filtrate was reduced to 20 mL in vacuo. A white tar was precipitated by addition of methanol (60 mL). The solvent was decanted via cannula and the white tar redissolved in dichloromethane. Again, a white tar was precipitated by addition of methanol. After the supernatant was decanted off, the white tar was dried under vacuum for 1.5 h and then washed with 50 mL of hexanes to produce a white solid that was collected by filtration and dried in vacuo at 50 °C for 3 h. The yield was 1.75 g. IR: NH stretch 3200–3350 cm^{-1}; CO stretch 1768 (acid chloride, 8.4%), 1710 (acid, 12.3%), 1665 cm^{-1} (amide, 79.3%). The percentages of acid chloride, acid, and amide are based on the relative

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(9) Presumably the rough surface contains a number of surface states in the band gap that facilitates charge transfer across the interface of the electrode.

(10) Reactions of poly(methacryloyl chloride) with amines and alcohols have been used to generate other polymers of interest for electrode modification: Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487. Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728.

area under the different CO absorption bands, assuming all have the same extinction coefficient. ^{1}H NMR ($CDCl_3$): Ph δ 7.2 (s); CH_2 δ 1.0–2.5 (br m). ^{31}P NMR: RPh_2P δ −12.9 (d, J_{PP} = 27 Hz); R_3P δ −22.1 (t). Anal. Calcd for $C_{35}H_{40}NOP_3$ (amide unit, 79.3%), $C_4H_6O_2$ (acid unit, 12.3%), and C_4H_5OCl (acid chloride unit, 8.4%): C, 71.21; H, 6.87; N, 2.30; P, 15.29; Cl, 0.62. Found: C, 71.33; H, 6.96; N, 2.31; P, 15.07; Cl, 0.69.

Poly[(3-aminopropyl)(2-(diphenylphosphino)ethyl)phenylphosphine methacrylamide], poly-P_2. This polymer was prepared by a procedure identical with that for poly-P_3. IR: NH stretch 3200–3400 cm^{-1}; CO stretch 1770 (acid chloride, 6%), 1710 (acid, 11%), 1665 cm^{-1} (amide, 83%). ^{1}H NMR ($CDCl_3$): Ph δ 7.25 (s); NCH_2 δ 3.1 (m); CH_2 and CH_3 δ 2.1–0.8 (br m). ^{31}P NMR: R_2PhP δ −21.3 (d, J_{PP} = 29 Hz); RPh_2P δ −13.0 (d). Anal. Calcd for $C_{27}H_{31}NOP_2$ (amide unit, 83%), $C_4H_6O_2$ (acid unit, 11%), and C_4H_5OCl (acid chloride unit, 6%): C, 71.63; H, 6.95; N, 3.00; P, 13.28; Cl, 0.55. Found: C, 71.47; H, 6.95; N, 3.10; P, 13.38; Cl, 0.74.

Poly[(3-aminopropyl)diphenylphosphine methacrylamide], poly-P_1. This polymer was also prepared by a procedure identical with that for poly-P_3. IR: NH stretch 3300–3450 cm^{-1}; CO stretch 1770 (acid chloride, 3%), 1713 (acid, 16%), 1665 cm^{-1} (amide, 81%). ^{1}H NMR ($CDCl_3$): Ph δ 7.27 (s); NCH_2 δ 3.25 (m); CH_2 and CH_3 δ 2.0–0.9 (br m). ^{31}P NMR ($CDCl_3$): δ −16.7 (s). Anal. Calcd for $C_{19}H_{22}NOP$ (amide unit, 81%), $C_4H_6O_2$ (acid unit, 16%), C_4H_5OCl (acid chloride unit, 3%): C, 72.06; H, 7.09; N, 4.81; P, 9.31; Cl, 0.42. Found: C, 72.21; H, 7.18; N, 3.94; P, 9.28; Cl, 0.48.

$Mo(N_2)_2$(poly-P_3)PPh_2Me. A solution of $Mo(N_2)_2(PPh_2Me)_4$ (0.96 g) dissolved in THF (75 mL) was added to a THF solution of poly-P_3 (0.61 g in 150 mL). The resulting reaction solution was kept at 0–4 °C for 48 h. Solvent was removed in vacuo and the resulting solid washed with 3 × 100 mL of hexane and 100 mL of THF. The resulting brown solid was dried under vacuum for 3 h and then ground with a mortar and pestle to produce a yellow powder. The yield was 0.47 g. IR: N_2 stretch 1943 cm^{-1}; CO stretch (amide) 1668 cm^{-1}. No solution NMR was observable for the reaction mixture except for the displaced diphenylmethylphosphine. Elemental analysis found: Mo, 9.23; P, 12.17. This corresponds to a Mo/P ratio of 1.00/4.08.

$Mo(N_2)_2$(poly-P_2)$_2$. $Mo(N_2)_2(PPh_2Me)_4$ (0.40 g) was dissolved in THF (40 mL), and the resultant mixture was added to a THF solution of poly-P_2 (0.40 g in 100 mL). The reaction solution was stirred at 0 °C for 48 h. The volume of the reaction mixture was reduced to ca. 15 mL, and hexane (75 mL) was added to precipitate an orange powder. The resulting solid was collected by filtration, washed with four 75-mL aliquots of hexanes, and dried under vacuum for 6 h. The yield was 0.45 g. IR: N_2 stretch 1945 cm^{-1}; CO stretch (amide) 1665 cm^{-1}. Elemental analysis found: Mo, 7.63; P, 10.11. Mo/P ratio is 1.00/4.13.

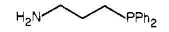
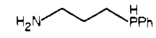
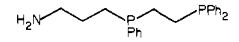
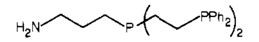
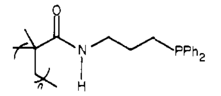
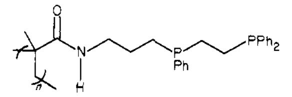
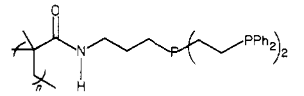
Reaction of $Mo(N_2)_2(PPh_2Me)_4$ with poly-P_1. $Mo(N_2)_2(PPh_2Me)_4$ (0.43 g) was added to a THF solution of poly-P_1 (0.66 g in 75 mL). The reaction solution was stirred for 48 h at 0 °C. The volume of THF was reduced to 20 mL in vacuo, and hexane (60 mL) was added slowly to precipitate a yellow powder. The powder was collected by filtration and washed with three 50-mL portions of hexane. The yellow solid was dried under vacuum for 4 h. The yield was 0.59 g. IR: N_2 stretch 1920 cm^{-1}; CO stretch (amide) 1665 cm^{-1}. Elemental analysis found: Mo, 2.70; P, 7.90. Mo/P ratio is 1.00/9.11.

$MoCl_3$(poly-P_3). $MoCl_3(THF)_3$ (0.21 g) was added to a THF solution of poly-P_3 (0.30 g in 100 mL). The reaction mixture was stirred overnight. The yellow precipitate that formed was collected by filtration and washed with two 50-mL aliquots of THF. The yellow solid was dried in vacuo for 3 h. The yield was 0.33 g. IR: CO stretch 1665 cm^{-1} (amide); MoCl stretch 300, 285 cm^{-1}. Elemental analysis found: Mo, 10.92; P, 10.74; Cl, 12.27. Mo/P/Cl ratio is 1.00/3.04/3.04.

Preparation of Solutions of $MoCl_3$(poly-P_2)$_2$. To a solution of poly-P_2 in THF (119 mg/25.0 mL) was added 52 mg of $MoCl_3(THF)_3$. The reaction solution was stirred for 2 h and then used to modify electrodes without further study.

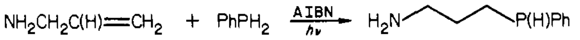
Modification of Electrodes. Solutions for modifying electrodes were prepared as described above with the exception that the concentrations of all reactants were 10^{-3} M. Micropipets were used to place quantitative amounts of polymer solutions on the various electrodes. The area of a typical silicon electrode was 6 cm^2. The areas of platinum and glassy-carbon electrodes were approximately 1 cm^2. After the solvent from the reaction mixture had evaporated, the electrodes were washed with hexanes and dried for 1–24 h. After drying, the electrodes were again rinsed with either THF or methanol, depending on the solvent to be used for the electrochemical experiment.

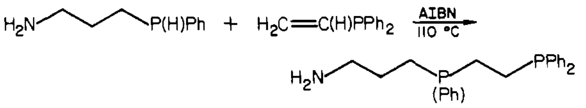
Table I

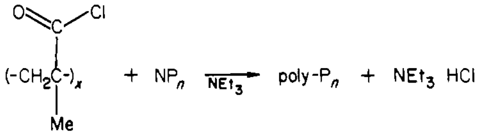
ligand structure	abbreviation
	NP
	NPH
	NP$_2$
	NP$_3$
	poly-P$_1$
	poly-P$_2$
	poly-P$_3$

Results

Ligand and Polymer Synthesis. In order to develop a general method for modifying electrode surfaces with monodentate, bidentate, and tridentate phosphine ligands, we have synthesized the aminophosphine ligands shown in Table I. These ligands are most conveniently prepared by free-radical addition of a P–H bond to a vinylphosphine or allylamine.[8] Equations 1 and 2 illustrate the synthesis of two such ligands. Characterization data for the new ligands listed in Table I are as expected and are given in the Experimental Section.


(1)


(2)


(3)

Additions of the aminophosphine ligands NP, NP$_2$, and NP$_3$ to poly(methacryloyl chloride) solutions result in formation of a methacrylamide polymer with pendant monodentate (n = 1, poly-P$_1$), bidentate (n = 2, poly-P$_2$), and tridentate (n = 3, poly-P$_3$) phosphine ligands (reaction 3).[9] The progress of these reactions can be conveniently monitored by observing a decrease in the intensity of the infrared absorption band of the acid chloride at 1770 cm^{-1} and the growth of a new band at 1665–1670 cm^{-1}, indicating formation of the desired amide. The reaction is not quantitative as indicated by the presence of the acid chloride carbonyl band at 1770 cm^{-1} in the product. Workup of the product in undried alcohol results in conversion of part of the unreacted acid chloride to the acid (ν_{CO} = 1710 cm^{-1}). If the extinction coefficients for the acid chloride, acid, and amide CO infrared absorptions are all assumed to be equal, an estimate can be made of approximately 80% conversion to the amide. Analytical data for these polymers are also consistent with approximately 80% conversion (see Experimental Section). The relative percentages of acid, acid chloride, and amide vary slightly from preparation to preparation and appear to be a function of the poly(methacryl chloride) supplied by the manufacturer. These reaction can be driven to completion under more forcing conditions such as heating the neat reaction mixture to 140 °C for several hours; however, the resulting polymers are insoluble glasses

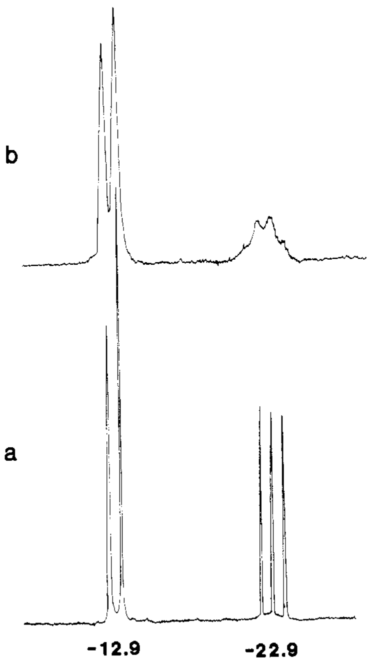
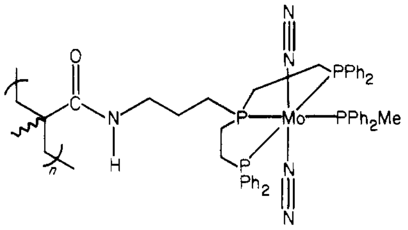


Figure 2. ^{31}P spectra of (a) NP_3 and (b) poly-P_3 illustrating the broadening that occurs upon binding of phosphine ligands to polymer.

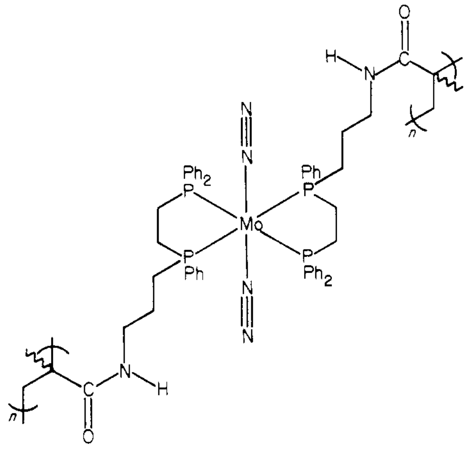
and are not suitable for reaction with metal complexes.

The proton-decoupled ^{31}P NMR spectrum of NP_3 and poly-P_3 are shown in Figure 2. It can be seen that the resonances of poly-P_3 are unshifted but broadened when compared to unbound NP_3, presumably reflecting a slower tumbling rate for the phosphorus atoms upon incorporation into the polymer. This effect is more pronounced the closer the phosphorus atom is to the backbone of the polymer. The triplet corresponding to the central phosphorus atom is broadened more than the doublet of the terminal phosphorus atoms. Similar broadening effects were noted for poly-P_1 and poly-P_2 compared to their respective free ligands.

Reaction of poly-P_3 with $Mo(N_2)_2(PPh_2Me)_4$ results in a shift in the dinitrogen stretching frequency in the IR spectrum from 1925 to 1943 cm^{-1}, indicating binding between poly-P_3 and molybdenum. On the basis of elemental analysis of this polymer, the phosphorus to molybdenum ratio is 4.08 to 1.00. This ratio is consistent with all three phosphorus atoms of the pendant tridentate ligand entering the coordination sphere of molybdenum and in addition indicates that all of the triphosphine ligands in the polymer are available for coordination. If the ligand acted as a bidentate ligand with a dangling diphenylphosphino group or if some of the ligands did not bind to molybdenum, then the phosphorus to molybdenum ratio would be expected to be greater than 4 to 1. The ^{31}P NMR spectrum of the reaction solution has only a sharp resonance for the displaced diphenylmethylphosphine. The failure to observe resonances of coordinated phosphine ligands is presumably due to even greater broadening than was observed for poly-P_3. This severe broadening prevents any structural information from being obtained by NMR. On the basis of the phosphorus to molybdenum ratio and the observation of only one band in the IR spectrum assignable to coordinated dinitrogen, which is consistent with a *trans*-dinitrogen complex, the basic polymer unit is assigned structure **1**.



1



2

In a similar manner the reaction of 2 equiv of poly-P_2 with $Mo(N_2)_2(PPh_2Me)_4$ results in a shift in the infrared stretching frequency of the band assigned to the *trans*-$Mo(N_2)_2$ unit from 1925 to 1952 cm^{-1}. Again the reaction appears to be quantitative with no unreacted $Mo(N_2)_2(PPh_2Me)_4$ on the basis of infrared spectra, and a molybdenum to phosphorus ratio of 1.00 to 4.13 on the basis of elemental analysis. The structural unit of the polymer for $Mo(N_2)_2(\text{poly-}P_2)_2$ is believed to be that of **2** on the basis of the infrared and analytical data. The reaction of $Mo(N_2)_2(PPh_2Me)_4$ with poly-P_1 does not result in any detectable shift of the infrared band at 1925 cm^{-1}. This is as expected since the (diphenylphosphino)propyl group of the polymer-bound phosphine is nearly identical with the (diphenylphosphino)methyl group that it displaces. Elemental analysis of the polymer-bound complex gives a Mo/P ratio of 1.00/9.11. This indicates that in contrast to poly-P_2 and poly-P_3 a significant portion (~50%) of the ligands (of poly-P_1) are not bound to molybdenum. A ^{31}P NMR spectrum of the reaction mixture after 48 h at 0 °C showed the presence of approximately equal amounts of unbound poly-P_1 and diphenylmethylphosphine.

poly-P_3 reacts with $MoCl_3(THF)$ to form $MoCl_3(\text{poly-}P_3)$, the polymer analogue of $MoCl_3(\text{triphos})$.[4] The infrared spectrum of this polymer in Nujol has two bands at 300 and 275 cm^{-1}. By comparison $MoCl_3(\text{triphos})$ also has two bands at 300 and 275 cm^{-1}. These bands are assigned to MoCl stretching vibrations. Elemental analysis of this polymer gives a Mo/Cl/P ratio of 1/3.04/3.04 consistent with its formulation.

Characterization and Reactions of Modified Electrodes. All of the metalated polymers discussed above are insoluble once they have precipitated from the reaction solution. Because of this feature, reaction solutions were used for modifying electrode surfaces. In a typical experiment an aliquot of the reaction solution was evaporated on the electrode to produce polymer coatings ranging from 1×10^{-9} to 1×10^{-7} mol/cm^2. These electrodes were rinsed repeatedly with hexanes, allowed to dry for at least 1 h, and then rinsed in either THF or methanol depending on which solvent was to be used for the electrochemical experiment.

Glassy-carbon and Pt electrodes were characterized by cyclic voltammetry. Silicon electrodes were characterized by both cyclic voltammetry and transmission FT-IR spectroscopy. On the basis of infrared spectroscopy, silicon electrodes modified with $Mo(N_2)_2(\text{poly-}P_3)PPh_2Me$ (~10^{-7} mol/cm^2) have a half-life upon exposure to air of about 1 h. However, these same electrodes are stable under an inert atmosphere for at least 1 wk. The infrared bands observed at 1943 and 1668

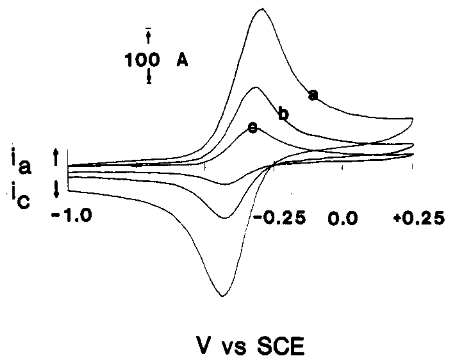


Figure 3. Cyclic voltammograms of $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ on glassy-carbon electrodes: (a) 50 mV/s; (b) 20 mV/s; (c) 10 mV/s. Electrolyte solution was saturated NEt_4BF_4 in methanol.

cm^{-1} are assigned to the ν_{N_2} and ν_{CO} stretching modes of the N_2 ligand and the amide group, respectively. The persistence of both of these bands for hours after immersion in methanol indicates that the polymer does not dissolve appreciably from the electrode surface and that the molybdenum(0) dinitrogen complex is stable in this environment. This situation changes quickly when cyclic voltammetry is performed. Figure 3 shows the cyclic voltammetry of $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ on a glassy-carbon electrode as a function of sweep rate. The wave observed at -0.38 V vs. SCE is assigned to the oxidation of $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ to $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me^+$, consistent with redox potentials of other molybdenum dinitrogen complexes. For example, $E_{1/2}$'s for $Mo(N_2)_2(dppe)_2$ and $Mo(N_2)_2(PPh_2Me)_4$ are -0.24 and -0.53 V vs. SCE, respectively.[11] In Figure 3 it can be seen that at slower sweep rates the cathodic portion of the wave is smaller than the anodic peak. This is consistent with an EC mechanism in which the electrochemical oxidation of $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ is followed by an irreversible chemical reaction. Oxidation of $Mo(N_2)_2(dppe)_2$ (where dppe is 1,2-bis(diphenylphosphino)ethane) in a homogeneous solution results in loss of N_2 via a dissociative mechanism with a half-life of 2–3 s.[12] Presumably the chemical step following the oxidation of the surface-bound $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ is also loss of dinitrogen. Infrared spectra of silicon electrodes taken after no more electrochemical activity is observed for the modified electrode indicates complete loss of the dinitrogen complex as no absorption is observed at 1943 cm^{-1} nor are any new infrared absorptions observed in the 1800–2200-cm^{-1} region. However, the intensity of the amide carbonyl band at 1668 cm^{-1} is unchanged. This indicates that the loss of electrochemical activity of the derivatized electrode is not due to dissolution of the oxidized form of the polymer from the electrode surface.

Similar spectroelectrochemical measurements were carried out on carbon and silicon electrodes modified with $Mo(N_2)_2(poly\text{-}P_2)_2$ and $Mo(N_2)_2(poly\text{-}P_1)_4$. Infrared stretches for coordinated dinitrogen ligands were observed at 1952 and 1925 cm^{-1}, respectively. Half-wave potentials of -0.37 V, $Mo(N_2)_2(poly\text{-}P_2)_2$, and -0.40 V, $Mo(N_2)_2(poly\text{-}P_2)_4$, were obtained by cyclic voltammetry for the Mo(0)/Mo(I) couple. Both $Mo(N_2)_2(poly\text{-}P_2)_2$- and $Mo(N_2)_2(poly\text{-}P_1)_4$-modified electrodes showed a decay in the intensity of the dinitrogen infrared band when repeated cyclic voltammograms were recorded. From the criteria described for $Mo(N_2)_2(poly\text{-}P_3)(PPh_2Me)$, this decay is also believed to be due to loss of coordinated N_2 upon oxidation of the surface-bound dinitrogen complex. The spectroelectrochemical results described here for $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$, $Mo(N_2)_2(poly\text{-}P_2)_2$, and $Mo(N_2)_2(poly\text{-}P_1)_4$ indicate a close similarity of the oxidation chemistry of surface-bound and homogeneous dinitrogen complexes.

The homogeneous species, $Mo(N_2)_2(triphos)PPh_3$, can be protonated to form ammonia according to reaction 4.[4] To

$$\underset{\mathbf{3}}{2Mo(N_2)_2(triphos)PPh_3} + 8HBr \rightarrow 2NH_4Br + \underset{\mathbf{4}}{2MoBr_3(triphos)} + 3N_2 + 2PPh_3 \quad (4)$$

determine the similarity in reactivity of the surface-bound $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ and its solution analogues with acids, electrodes modified with $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ were treated with gaseous HCl and aqueous HCl, HBr, or H_2SO_4. When large excesses of strong acid (e.g., 30 mL of HCl gas) were added to a 10 mL of methanol or THF solution in which the derivatized electrodes were immersed, ~90% of the polymer was lost from the electrode surface as estimated by infrared spectroscopy. When smaller amounts of acid were added to the electrolyte solution in contact with the modified electrodes (e.g., 20–100 μL of 6 N HCl), the infrared band assigned to coordinated dinitrogen disappeared while the polymer remained bound to the electrode. However, it was not possible to detect formation of a MoCl bond because the detector of the FT-IR spectrometer does not extend below 400 cm^{-1}.

In the homogeneous system $MoBr_3(triphos)$ (**4**), formed in reaction 4, can be reduced with sodium amalgam to regenerate the original dinitrogen complex, reaction 5, completing a cycle

$$\underset{\mathbf{4}}{MoBr_3(triphos)} + PPh_3 + N_2 \xrightarrow[THF]{Na(Hg)} \underset{\mathbf{3}}{Mo(N_2)_2(triphos)PPh_3} + 3NaBr \quad (5)$$

for the generation of ammonia from N_2.[4,13] To see if reaction 5 or analogous reactions could be carried out electrochemically, a number of bulk electrolysis experiments were performed on reaction mixtures of $MoCl_3(THF)_3$ and the appropriate phosphine ligands. In our hands, electrochemical reduction of a reaction mixture containing $Mo(Cl)_3(THF)_3$, triphos, and triphenylphosphine at a carbon electrode did not result in the formation of $Mo(N_2)_2(triphos)PPh_3$ with an infrared stretching frequency at 1955 cm^{-1}. Instead, a dinitrogen complex with an infrared stretching frequency at 1970 cm^{-1} was formed. This complex is apparently an impurity in reaction 5.[4] However, a solution of $MoCl_3(THF)_3$, poly-P_3, and triphenylphosphine can be electrochemically reduced under identical conditions to form $Mo(N_2)_2(poly\text{-}P_3)PPh_3$, as indicated by the presence of an infrared stretching frequency at 1955 cm^{-1} in the isolated product. No band is observed at 1970 cm^{-1}. When the ratio of intensities of the infrared bands for the N_2 and amide carbonyl groups of $Mo(N_2)_2(poly\text{-}P_3)PPh_3$ formed by electrochemical reduction is used and that ratio is compared to the ratio observed for $Mo(N_2)_2(poly\text{-}P_3)PPh_2Me$ prepared by the ligand-substitution method described earlier, it can be estimated that the percentage of molybdenum sites reduced to $Mo(N_2)_2(poly\text{-}P_3)PPh_3$ is between 5 and 10%. Similar electrolysis experiments carried out on solutions containing $MoCl_3(THF)_3$, poly-P_3, and poly-P_1 did not result in the formation of detectable amounts of molybdenum dinitrogen complexes. The electrochemical reduction of a solution of $MoCl_3(THF)_3$ and 2 equiv of diphos results in the efficient generation of $Mo(N_2)_2(diphos)_2$ as determined by comparing the infrared and ^{31}P NMR spectra of the product

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with those of an authentic sample of $Mo(N_2)_2(diphos)_2$. In contrast, repeated attempts to reduce solutions of $MoCl_3(THF)_3$ and 2 equiv of poly-P_2 did not produce any detectable amounts of molybdenum dinitrogen complex.

On the basis of results obtained in solution, it seemed most likely that if we were to observe formation of a dinitrogen complex on an electrode surface by electrochemical reduction of a molybdenum(III) precursor it would be with electrodes modified with $MoCl_3$(poly-P_3) immersed in solutions containing triphenylphosphine. Silicon and glassy-carbon electrodes coated with 1×10^{-9} to 1×10^{-7} mol/cm^2 of $MoCl_3$(poly-P_3) were immersed in 0.00, 0.01, and 1.0 M solutions of PPh_3 in THF (0.3 N NBu_4BF_4) and the electrode potential swept slowly (1–2 mV/s) from 0 to −2.5 V vs. SCE while N_2 was bubbled over the electrode surface. These electrodes were then held at the fixed potential of −2.5 V for 15–30 min. No new redox waves were observed at −0.4 V, nor were any new infrared stretches observed in the 1900–2000-cm^{-1} region indicative of formation of a molybdenum dinitrogen complex. Similar results were obtained with electrodes modified with solutions of $MoCl_3$(poly-P_2)$_2$. Fixing the potential of $MoCl_3$(poly-P_2)$_2$-modified electrodes at −2.5 V for 15–30 min did not result in the formation of any new infrared stretches in the 1900–2000-cm^{-1} region or new redox waves at ∼−0.4 V. If these electrodes were potentiostated at −2.5 V in electrolyte solutions not stored over sodium amalgam, a new infrared band formed at 1967 cm^{-1}. This new band is not due to formation of a dinitrogen complex since it is also generated when the reduction is carried out under helium. We tentatively assign this new band to formation of a molybdenum hydride with the proton source arising from impurities in the supporting electrolyte.

Discussion

The objective of the research described in this paper was to determine whether reactions 4 and 5, which are well characterized in solution, would also occur at a modified electrode. In this paper the attachment of analogues of **3** and **4**, $MoCl_3$(poly-P_3) and $Mo(N_2)_2$(poly-P_3)PPh_2Me, to electrode surfaces has been described. The redox chemistry of $Mo(N_2)_2$(poly-P_3)PPh_2Me and $Mo(N_2)_2$(poly-P_2)$_2$ attached to electrode surfaces closely parallels that of their solution analogues, showing a reversible oxidation followed by an irreversible loss of N_2 from the molybdenum(I) species formed. Protonation of $Mo(N_2)_2$(poly-P_3)PPh_2Me and $Mo(N_2)_2$(poly-P_2)$_2$ attached to electrode surfaces results in the disappearance of the N_2 stretch from the infrared spectrum as is observed for their solution analogues. However, reduction of $MoCl_3$(poly-P_2)$_2$ or of $MoCl_3$(poly-P_3) at the electrode surface in the presence of triphenylphosphine or poly-P_1 does not lead to formation of detectable amounts of dinitrogen complexes.

The failure to observe formation of $Mo(N_2)_2$(poly-P_3)PPh_3 upon reducing $MoCl_3$(poly-P_3) on modified electrodes in the presence of triphenylphosphine is due to low conversion of the molybdenum(III) sites to the dinitrogen complex. As discussed above, the electrolytic reduction of the solutions of $MoCl_3$(poly-P_3) and triphenylphosphine resulted in only 5–10% conversion of the available Mo(III) sites in the polymer to a dinitrogen complex. A similar yield on the electrode surface would be at or below the limit of our ability to detect formation of an N_2 compound by FT-IR spectroscopy. The sodium amalgam reduction of $MoCl_3$(triphos) to produce $Mo(N_2)_2$(triphos)PPh_3 gives higher yields when the reaction is carried out at low molybdenum concentrations (∼10^{-2} M) and high N_2 pressures (∼5 atm).[13] To obtain a similar N_2 to molybdenum ratio for our heterogeneous system would require pressures of 100–1000 atm due to the high local concentration of $MoCl_3$(poly-P_3) at the electrode surface (∼1 m). With current cell designs we are unable to obtain such pressures. The most likely side reaction would appear to be formation of a complex in which a phenyl ring is bound in an η^6 fashion to molybdenum. Such complexes are formed in high yields when the amount of nitrogen in solution is restricted significantly.[14] Other problems associated with trying to use this system for catalytic reduction of dinitrogen to ammonia are the large negative potentials required to reduce the starting Mo(III) species to Mo(0) (more negative than −2.0 V) and what appears to be preferential hydride formation in the presence of a proton source. A source of protons would be necessary for the operation of a catalytic cycle.

Although the conversion of N_2 to ammonia in a stepwise fashion at a modified electrode has not been demonstrated with this sytem, a general method for modifying electrodes with polydentate phosphine metal complexes has been developed. This modification procedure involves four steps. First, the appropriate monodentate, bidentate, or tridentate aminophosphine ligand is synthesized. Second, the primary amine functional group can be reacted with poly(methacryloyl chloride) to form methacrylamide polymers with pendant monodentate, bidentate, and tridentate phosphine ligands. Third, these polymers can be metalated by appropriate exchange reactions. Finally, evaporation of solutions of the polymers bearing pendant metal phosphine complexes results in a general method for modifying a variety of electrode surfaces. The extension of this approach to a number of other transition metals will be the subject of future publications.

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