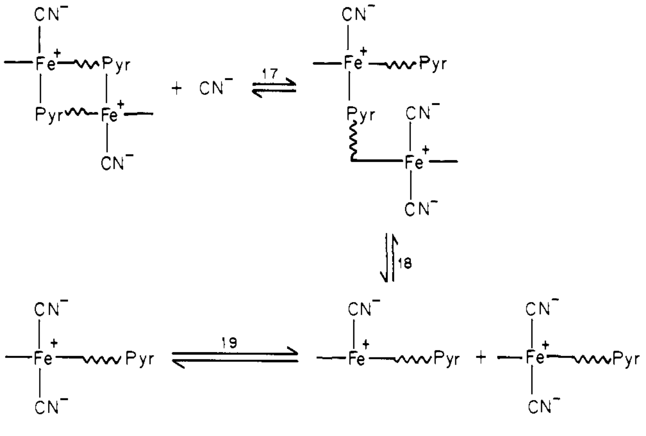
This conclusion is strengthened by a second cooperative reaction, seen in the titration of the dimer $(\mathrm{Hm^+CN^-})_2$ to the monomer $\mathrm{Hm^+(CN^-)_2}$ of $\mathbf{1}^+\mathrm{Cl}^-$. The slope for this titration gives a Hill coefficient of 1.5, consistent with reactions 17–19 (Figure 4).



Reaction 17 is a low-affinity equilibrium due to the neighboring-group effect, which resists the addition of the first but not the second $\mathrm{CN^-}$. It thus appears that the highly stabilized dimer form, $(\mathbf{1}^+\mathrm{CN^-})_2$, dissociates either $\mathrm{CN^-}$ or pyridine in a highly cooperative fashion.

The availability of these simple chemical systems makes possible studies of allosteric effects and the nature of cooperativity. Further studies of the effect of pH, base affinities, etc. on both ligand-induced dimerization and ligand-induced conformational change[6] are underway.

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Registry No. $\mathbf{1}^+\mathrm{Cl}^-$, 82374-44-5; $\mathbf{2}^+\mathrm{Cl}^-$, 72172-03-3.

Preparation and Spectroelectrochemical Characterization of Silicon Electrodes Modified with Molybdenum Dinitrogen Complexes

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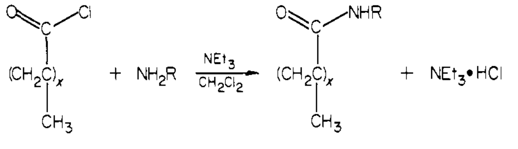
In this paper we report the modification of silicon electrodes with polymer-bound molydenum dinitrogen complexes and the characterization of these electrodes by cyclic voltammetry and Fourier transform–infrared spectroscopy. The condensation of (3-aminopropyl)bis(2-(diphenylphosphino)ethyl)phosphine,[1] **3**, with poly(methacryloyl chloride) produces a methacrylamide polymer with pendant tridentate phosphine ligands (eq 1).[2] In a similar manner reactions of poly(methacryloyl chloride) with Ligands **1** and **2** yield polymers containing monodentate and bidentate phosphine ligands, poly-$\mathrm{P_1}$ and poly-$\mathrm{P_2}$, respectively. Infrared spectra of the products of these condensation reactions have a strong amide carbonyl band at 1668 cm^{-1}. In addition there are acid and acid chloride carbonyl bands at 1710 and 1770 cm^{-1}, respectively, due to the failure of some of the sites of the original polymer to react with the amine functional group of the ligand.[3] These unreacted polymer sites do not interfere with subsequent chemistry, however.



$$[\mathrm{CH_2C(CH_3)(COCl)}]_x + \mathrm{NH_2R} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{NEt_3}} [\mathrm{CH_2C(CH_3)(CONHR)}]_x + \mathrm{NEt_3{\cdot}HCl} \qquad (1)$$

1, $\mathrm{R = CH_2CH_2CH_2PPh_2}$
2, $\mathrm{R = CH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2}$
3, $\mathrm{R = CH_2CH_2CH_2P(CH_2CH_2PPh_2)_2}$

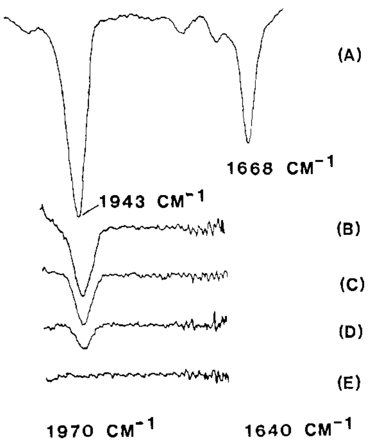


Figure 1. Transmission infrared spectra of a polymer-bound molybdenum dinitrogen complex prepared from 2 equiv of poly-$\mathrm{P_1}$, 1 equiv of poly-$\mathrm{P_3}$, and 1 equiv of $\mathrm{Mo(N_2)_2(PPh_2Me)_4}$ on a 0.1 Ω cm *n*-type Si electrode. Spectrum A was taken in the absence of a supporting electrolyte solution. Spectra B–E are of the same electrode immersed in 0.3 N $\mathrm{LiClO_4}$/methanol solution. Spectrum B was recorded before any cyclic voltammograms were recorded. Spectra C–E were taken after cyclic voltammograms 2, 5, and 6 of Figure 2. The cell path length was 0.5 mm, and each spectrum is the Fourier transform of 200 interferograms.

The lability of the phosphine ligands in $\mathrm{Mo(N_2)_2(PPh_2Me)_4}$[4,5] provides a convenient method for introducing molydenum dinitrogen fragments into poly-$\mathrm{P_1}$, poly-$\mathrm{P_2}$, and poly-$\mathrm{P_3}$. Reaction of poly-$\mathrm{P_3}$ with $\mathrm{Mo(N_2)_2(PPh_2)Me)_4}$ is accompanied by a shift in the infrared stretching frequency of the dinitrogen ligand from 1925 to 1943 cm^{-1}, indicating bonding between the pendant triphosphine ligands and molybdenum. Similar reations of $\mathrm{Mo(N_2)_2(PPh_2Me)_4}$ with poly-$\mathrm{P_2}$, poly-$\mathrm{P_1}$, and a 2:1 mixture of poly-$\mathrm{P_1}$ and poly-$\mathrm{P_3}$ result in the formation of polymer pendant complexes with $\nu_{\mathrm{N_2}}$ 1952 cm, 1925, and 1943 cm^{-1} respectively. Solutions of these reaction mixtures have been evaporated on silicon and carbon electrodes. These electrodes were then washed with hexanes and methanol to remove dimethylphenylphosphine and any unreacted $\mathrm{Mo(N_2)_2(PPh_2Me)_4}$. This procedure results in electrodes coated with polymers containing molybdenum dinitrogen complexes.

A number of spectroscopic methods have been used previously to characterize derivatized electrodes including Auger,[6] ESCA,[7] and ultraviolet and visible spectroscopy,[7,8] We have taken advantage of the strong infrared absorption of coordinated dinitrogen and the infrared transparency of silicon to characterize our de-

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[1] Uriarte, R.,Mazanee, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 79.

[2] Reaction of poly(methacryloyl choride) with amines and alcohols has 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. Fukni, M.; Kitani, A.; Degrand C.; Miller L. L. *Ibid* **1982** *104*, 28.

[3] From infrared absorption data it can be calculated that the mole percents of acid chloride, acid, and amide are 8.4%, 12.3%, and 79.3%, respectively. Anal. Calcd for $\mathrm{C_4H_5OCl}$ (8.4%), $\mathrm{C_4H_6O_2}$ (12.3%), and $\mathrm{C_{35}H_{40}NOP_3}$ (79.3%): C, 71.21; H, 6.87; N, 2.30; P, 15.29; Cl, 0.62. Found: C, 71.33; H, 6.69; N, 2.31; P, 15.07; Cl, 0.69. The ^{31}P NMR spectrum of poly-$\mathrm{P_3}$ is a broad doublet (δ −12.9 relative to external $\mathrm{H_3PO_4}$, $J_{\mathrm{pp}} = 27$ Hz, $\mathrm{CDCl_3}$) and a broad triplet (δ 22.1); the broadness of the resonances presumably result from slow tumbling of the phosphorus atoms upon incorporation into the polymer.

[4] George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285.

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[8] Scott, N. S.; Oyama, N.; Anson, F. C. *J. Electroanal. Chem.* **1980**, *110*, 303.

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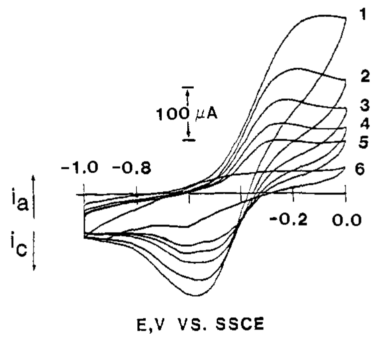

Figure 2. Cyclic voltammograms 1–5 represent five successive scans of the same electrode for which the infrared spectra are shown in Figure 2. Cyclic voltammogram 6 was recorded after the electrode had been potentiostated at 0.0 V for 7 min. The supporting electrolyte solution was 0.3 N $LiClO_4$ in methanol with a SSCE used as the reference electrode. The scan rate for each cyclic voltammogram was 50 mV/s, and the surface area was about 5 cm^2.

rivatized electrodes by transmission FT–IR spectroscopy. Doping silicon results in an increase in conductivity and a decrease in its ability to transmit infrared light. By examining silicon wafers of various doping levels, it was found that those with $\sim$0.1-Ω cm resistivities[9] have a low enough doping level to permit useful transmission infrared studies while maintaining sufficient conductivity to permit cyclic voltammetry.[10,11] This technique allows the combination of a structurally sensitive spectroscopic probe with in situ electrochemical studies.[15]

Spectrum A of Figure 1 is of a silicon electrode modified with a polymer-bound molybdenum dinitrogen complex prepared from 2 equiv of poly-P_1, 1 equiv of poly-P_3, and 1 equiv of $Mo(N_2)_2(PPh_2Me)_4$ as described above. The infrared bands at 1943 and 1668 cm^{-1} are assigned to the ν_{N_2} and ν_{CO} stretching modes of the N_2 ligand and amide group, respectively. The absence of a strong infrared absorption at 1925 cm^{-1} indicates the polymer does not contain a significant amount of residual $Mo(N_2)_2(PPh_2Me)_4$. The remaining infrared spectra of Figure 1 and the cyclic voltammograms of Figure 2 were recorded for this same electrode immersed in 0.3 N $LiClO_4$/methanol solution. The quasi-reversible *i–E* waves of Figure 2 correspond to the oxidation of Mo(0) to Mo(I). The intensity of the amide infrared band at 1668 cm^{-1} is not decreased under these same conditions, confirming that polymer is not lost from the electrode surface. In addition by observing the N_2 infrared band of a polymer-coated electrode immersed in electrolyte solution, it can be observed that the unoxidized polymer is stable for several hours on the electrode surface. These two observations indicate that it is the oxidized form of the dinitrogen complex that is unstable. A similar 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.[16] Presumably a similar process is taking place for the polymer-bound dinitrogen complexes. This accounts for the decrease in the peak current of oxidation and reduction waves with each successive cyclic voltammogram and the corresponding decrease in the intensity of the ν_{N_2} absorption (Figure 1). The correlation between the infrared spectra and cyclic voltammograms in Figures 1 and 2 illustrate that FT–IR spectrocopy can be a valuable probe of reactions occurring on modified silicon electrodes. In addition, a dinitrogen complex has been attached to an electrode surface whose solution analogue is capable of forming ammonia in a cyclic manner.[4,17]

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Registry No. 1, 16605-03-1; **2**, 82638-88-8; **3**, 71734-62-8; poly-P_1, 82638-83-3; poly-P_2, 82638-85-5; poly-P_3, 82638-87-7; $Mo(N_2)_2(PPh_2Me)_4$, 66008-09-1; Si, 7440-21-3; Mo, 7439-98-7; poly(methacryloyl chloride), 26937-45-1.

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[9] We have found resistivities of commercially available silicon wafers to be only a rough guide. A suitable wafer should have a transmittance of 25–45% at 2000 cm^{-1}. A typical electrode with such a transmittance and constructed as described in footnote 10 should have a resistance of 20–80 Ω.

[10] Silicon electrodes were constructed by making an ohmic contact near the edge of a 25-mm diameter silicon wafer (111 orientation, (0.25–0.4 mm thick) with indium solder. A 25-mm glass tube was then attached with epoxy to the back of each silicon wafer. This electrode can then be mounted in an electrochemical cell by using a threaded adapter facing a KBr disk mounted in a similar manner. This configuration allows an IR light beam to pass through the center of the working electrode.

[11] Spectroelectrochemical studies in the far infrared region of the spectrum have been made previously by an internal reflection technique at Ge electrodes (ref 12), by using specular reflectance at Pt electrodes (ref 13), and by using a gold minigrid (ref 14).

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[17] A report of a SnO_2 electrode modified with a molybdenum dinitrogen complex containing two diphosphine ligands has appeared (ref 18), but protonation of this complex does not result in the formation of ammonia (ref 5).

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Cyclohexenones by the Barton Fragmentation of Tertiary Alcohols Derived from Furanone/Alkene Photoadducts

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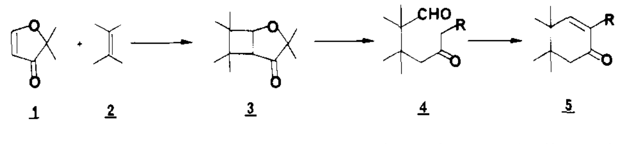
In previous publications we have described the irradiation of 2,2-dimethyl-3(2*H*)-furanone (**1**) with various alkenes **2** and the



conversion of the photoadducts **3** to a variety of synthetically useful intermediates.[2] In the particular case of forming cyclohexenones **5** from **3**, the two published methods involve rather circuitous sequences that incorporate either a Baeyer–Villiger reaction or Beckmann fragmentation in the elaboration procedure. Although the material yields are generally good, the number of discrete synthetic steps involved in each route detracts from the overall viability of the method. We now report an alternative procedure that is more efficient in terms of material yields and synthetic steps and that thus makes the overall method more attractive from a synthetic point of view.

The tertiary alcohols **6** derived from **3** are ideally disposed for an oxidative fragmentation of the C_2–C_3 bond by virtue of the

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[1] (a) Paper No. 10 in the series of photochemical annelations. For 9 see: Baldwin, S. W.; Fredericks, J. E. *Tetrahedron Lett.* **1982**, *23*, 1235. (b) Financial support from the National Institutes of Health (GM 26266) is acknowledged with appreciation.

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