natural tylosin (vide infra). To complete the synthesis, **6** was selectively reduced (4.0 equiv of Dibal, CH_2Cl_2, –78 °C, reduction of dienone and γ-lactone) and oxidized (1.3 equiv of DDQ, benzene, 25 °C) to produce *O*-mycinosyltylonolide (**1**) in 76% overall yield. Synthetic **1** was identical in all respects with an authentic sample obtained by degradation of tylosin as described below.

Mild acid hydrolysis of tylosin (**7**) (Scheme I) (dilute HCl, THF, 25 °C or AcOH–THF–H_2O, 25 °C) detaches only mycarose from the molecule producing *O*-mycinosyl-*O*-mycaminosyltylonolide (**8**) in 90% yield.[10] Both the highly methoxylated mycinose and the basic, N-containing mycaminose are resistant to acid hydrolysis under normal conditions that will allow survival of the rest of the molecule. A Polonovski type degradation of **8** [(a) 1.1 equiv of *m*-CPBA, CH_2Cl_2, 0 °C, 0.5 h followed by 8.0 equiv of $(CF_3CO)_2O$ and 8.0 equiv of pyridine, 0 °C, 0.5 h and then aqueous $KHCO_3$ workup and 1.0 equiv of anhydrous K_2CO_3, MeOH, O °C, 1 h)], however, furnished *O*-mycinosyltylonolide (**1**) in 76% yield after chromatographic purification. The same compound (**1**) was also produced by direct degradation of tylosin (**7**) under the above conditions (65% yield).[11] MnO_2 (excess, CH_2Cl_2, 48 h) oxidation of *O*-mycinosyltylonolide (**1**) led to compound **6** in high yield (87%).

So that the potential of *O*-mycinosyltylonolide (**1**) as a precursor to tylosin (**7**) could be demonstrated, a number of final chemical maneuvers were performed. Thus, reaction of (**1**) with ethylene glycol in the presence of camphorsulfonic acid as catalyst yielded the acetal **9** as a major product (65%),[12] liberating the C-5 hydroxyl for selective glycosidation. Although molecular models as well as chemical evidence indicate that no protection of the C-3 hydroxyl group should be needed, protection of the mycinose-bound hydroxyl might be necessary for steric-reactivity reasons for such glycoside formation attempts. Selective blockade of this hydroxyl was, therefore, sought and achieved by treating **9** sequentially with (a) phenylboronic acid (1.2 equiv, benzene, azeotropic removal of water at reflux to form a cyclic boronate ester at C-3 and C-5), (b) *tert*-butyldimethylsilyl chloride (excess imidazole, DMF, 25 °C), and (c) acetone–H_2O (3:1, 25 °C, 1 h) to remove the boronate furnishing compound **10** in 72% overall yield.

This highly efficient and stereocontrolled total synthesis of *O*-mycinosyltylonolide (**1**) clearly demonstrates the advantageous utilization of carbohydrates in the construction of the 16-membered ring macrolide antibiotics.[13–15] At present, no practical methodology exists for completing the remaining disaccharide, mycaminose-containing unit, due to the well-recognized problems of glycosidation of N-containing sugars.[16] New strategies directed toward this goal are currently under way in these laboratories.

Acknowledgment. We express our many thanks to Drs. George T. Furst and Tom Terwilliger of the Department of Chemistry, University of Pennsylvania, for their spectroscopic assistance and helpful discussions. Our thanks are also due to Dr. J. F. Downing of Lilly Research Laboratories, Eli Lilly and Co., Greenfield, IN, for a generous gift of tylosin. This work was financially supported by the National Institutes of Health (Grant GM 26879), Merck Sharp & Dohme, the A. P. Sloan Foundation, and the Camille and Henry Dreyfus Foundation.

Registry No. 1, 80879-01-2; **2**, 80879-02-3; **2**, α isomer, 80924-99-8; **3**, 80879-03-4; **4**, 80879-04-5; **5**, 80879-05-6; **6**, 80879-06-7; **7**, 1401-69-0; **8**, 11032-98-7; 9, 80879-07-8; **10**, 80879-08-9.

Supplementary Material Available: A listing of the physical properties of key intermediates (2 pages). Ordering information is given on any current masthead page.

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[10] Hamill, R. L.; Haney, M. E., Jr., Stamper, M.; Wiley, P. F. *Antibiot. Chemother.* (*Washington, D.C.*) **1961**, *11*, 328.

[11] Similar conditions were used by Masamune in the degradation of *O*-mycaminosyltylonolide in his elegant preparation of tylonolide, the aglycon of tylosin: Masamune, S.; Hayase, Y.; Chan, W. K.; Sobczak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 7874.

[12] Concomitantly, the isomeric hydroxyethyl furanoside was also formed as a minor product and separated from **9** chromatographically.

[13] For an elegant carbohydrate approach to the erythromycins see: Hanessian S. *Pure Appl. Chem.* **1977**, *49*, 1201.

[14] (a) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *Tetrahedron Lett.* **1979**, 2327. (b) Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 1224. (c) Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 1224.

[15] For independent work in this area see: (a) Ziegler, F. E.; Gilligan, P. J.; Chakraborty, U. R. *Tetrahedron Lett.* **1979**, 3371. (b) Ziegler, F. E.; Gilligan, P. J. *J. Org. Chem.* **1981**, *46*, 3874. (c) Tatsuta, K.; Amemiya, Y.; Maniwa, S.; Kinoshita, M. *Tetrahedron Lett.* **1980**, 2837. (d) Tatsuta, K.; Amemiya, Y.; Kanemura, Y.; Kinoshita, M. *Tetrahedron Lett.* **1981**, *22*, 3997.

[16] Although Tatsuta et al. have succeeded in attaching the similar disaccharide unit on carbomycin B, the reported glycosidation yields are rather low: Tatsuta, K.; Tanaka, A.; Fujimoto, K.; Kinoshita, M.; Umezawa, S. *J. Am. Chem. Soc.* **1977**, *99*, 5826.

Synthesis and Characterization of a New Surface Derivatizing Reagent To Promote the Adhesion of Polypyrrole Films to n-Type Silicon Photoanodes: *N*-(3-(Trimethoxysilyl)propyl)pyrrole

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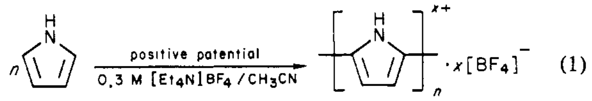
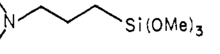
Received December 21, 1981

Four research groups have suggested that "polypyrrole"[1] formed by anodic polymerization of pyrrole, eq 1, can be used to protect



(1)

n-type semiconductors from photoanodic decomposition.[2–5] A problem encountered in the use of the polypyrrole is that it is not persistently attached to the surface,[2] though it does appear that adhesion to n-type Si is improved by metallization of the surface prior to anodic polymerization of the pyrrole.[4,5] Generally, polypyrrole can be peeled from the substrate to give free standing films.[1] Work in this laboratory has established that $(RO)_3Si$ groups can be used to anchor redox-active polymers to surfaces to protect against photocorrosion.[6] We now report the synthesis, characterization, and application of *N*-(3-(trimethoxysilyl)-propyl)pyrrole, I, as a photoanode derivatizing reagent that can



I

be covalently anchored to the electrode via reaction of surface OH groups (eq 2).[7] The pendant pyrrole functionality can then be used as the initiation site for polymerization of pyrrole, thereby serving to covalently anchor the polypyrrole (eq 3). This sort

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[1] (a) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854. (b) Diaz, A. F.; Castillo, J. J. *Ibid.* **1980** 397. (c) Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1979/1980**, *2*, 329. (d) Diaz, A. F.; Vasquez Vallejo, J. M.; Martinez Duran, A. *IBM J. Res. Dev.* **1981**, *25*, 42.

[2] Noufi, R.; Tench, D.; Warren, L. F. *J. Electrochem. Soc.* **1980**, *127*, 2310; **1981**, *128*, 2596.

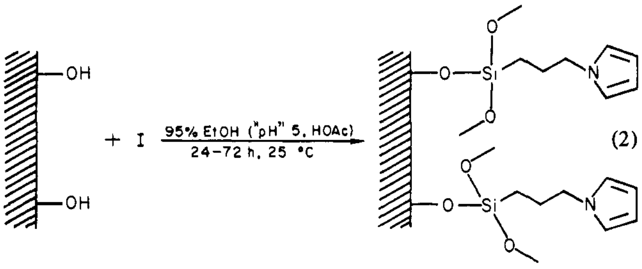
[3] Noufi, R.; Frank, A. J.; Nozik, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 1849.

[4] Skotheim, T.; Lundstrom, I.; Prejza, J. *J. Electrochem. Soc.* **1981**, *128*, 1625.

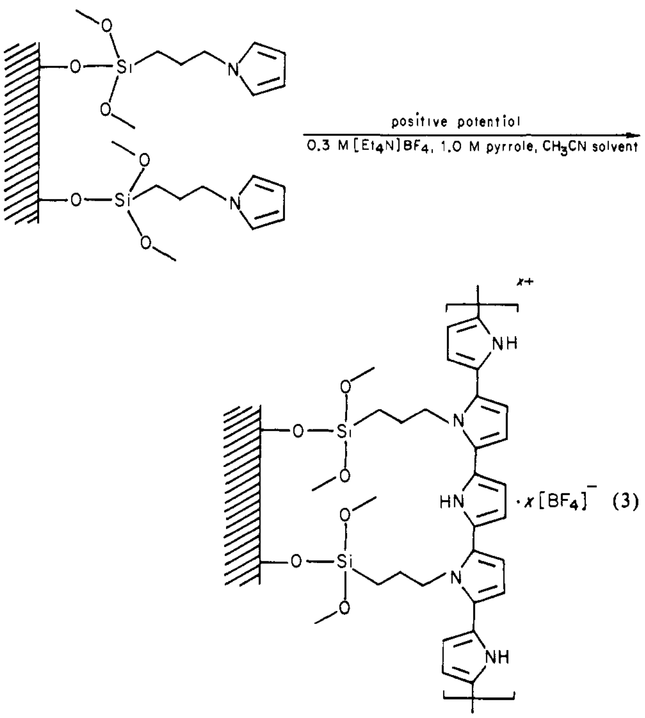
[5] Fan, F. R. F.; Wheeler, B.; Bard, A. J.; Noufi, R. *J. Electrochem. Soc.* **1981**, *128*, 2042.

[6] (a) Bocarsly, A. B.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3390. (b) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *Ibid.* **1979**, *101*, 1378; (c) Bolts, J. M.; Wrighton, M. S. *Ibid.* **1978**, *100*, 5257.

[7] (a) Moses, P. R.; Wier, L.; Murray, R. W. *Anal. Chem.* **1975**, *47*, 1882. (b) Murray, R. W. *Acc. Chem. Res.* **1980**, *12*, 135 and references therein.



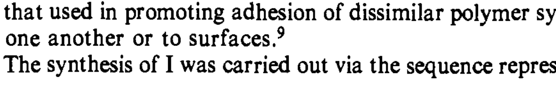
(2)



(3)

of concept has been previously applied to bind electroactive ferrocene to surfaces by beginning with a reagent that will covalently bind a polymer to the surface.[8] Further, the concept is similar to that used in promoting adhesion of dissimilar polymer systems to one another or to surfaces.[9]

The synthesis of I was carried out via the sequence represented



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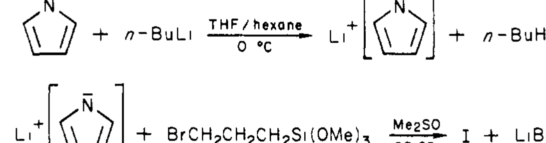

(5)

by eq 4 and 5 adapted from the preparation of *N*-alkylpyrroles.[10] The compound was purified by distillation and determined to be pure by ^{1}H NMR and mass spectroscopy.[11]

Both Pt and n-type Si electrodes have been functionalized with various combinations of I and polypyrrole. Key results relate to pretreated[12] Pt and *n*-type Si electrodes first functionalized with I and then coated with polypyrrole by anodic polymerization of 1.0 M pyrrole in CH_3CN/0.3 M $[Et_4N]BF_4$ (eq 3). Functionalization of electrodes with I can be effected according to eq 2 by soaking pretreated Pt or n-type Si in 95% EtOH ("pH ≈ 5") with HOAc containing 0.02 M I at 25 °C for 24–72 h. Figure 1 shows a comparison of the Auger spectra[13] of (a) n-type Si functionalized only with polypyrrole by anodic polymerization,

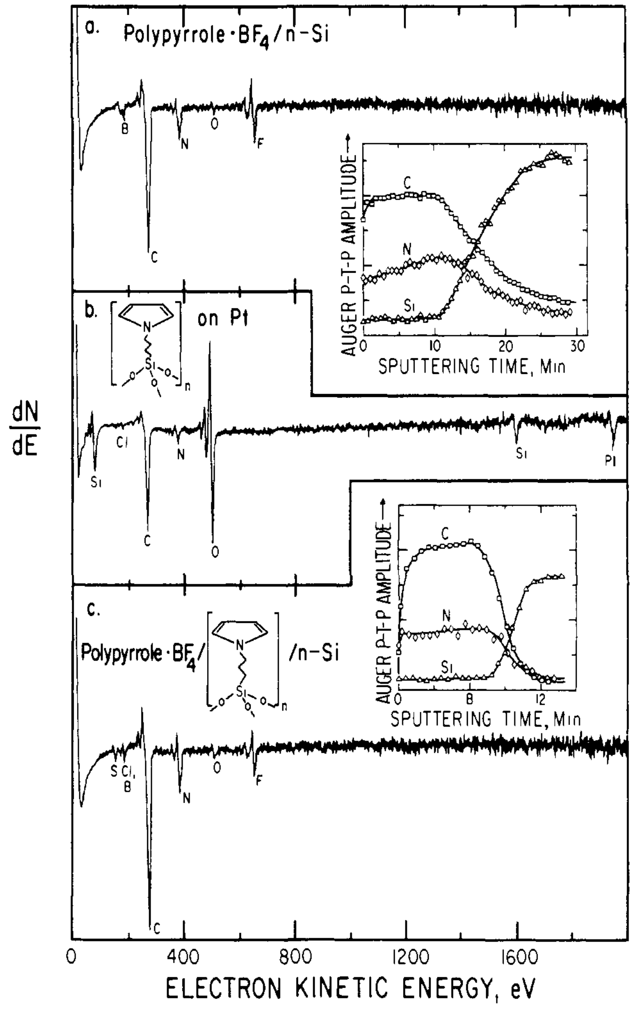

Figure 1. Auger spectra of modified electrode surfaces: (a) n-Type Si modified with polypyrrole by photoanodic oxidation of stirred 1.0 M pyrrole in 0.3 M $[Et_4N]BF_4/CH_3CN$ at an electrode potential of +0.85 V vs. SCE under white light, ~40 mW/cm^2, illumination to give a current density of ~0.1 mA/cm^2. The electrode was withdrawn after passing ~10^{-2} C/cm^2. The inset shows the depth profile analysis of the electrode showing the time dependence of the peak-to-peak amplitude of the Auger signals for Si (×2), N (×5), and C(×1) while sputtering with Ar$^+$ ions. (b) Pretreated Pt functionalized with I according to eq 2; coverage is low; note presence of Pt signal. (c) n-Type Si functionalized first with I according to eq 2 followed by modification with polypyrrole as for the electrode shown in a. Note that the depth profile analysis (Si, ×2; N, ×5; C, ×2) is very similar to that in a, consistent with a very thin layer of material from I between the polypyrrole and the n-type Si.

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(8) Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487.

(9) Cameron, G. M.; Marsden, J. G. *Chem. Brit.* **1972**, *8*, 381 and references therein.

(10) Synthesis of I adapted from: Hobbs, C. F.; McMillan, C. K.; Papadopoulos, E. P.; Van der Werf, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 43.

(11) The ^{1}H NMR (δ, $CDCl_3$, 60 MHz) data are as follows: (1) the pyrrole ring protons appear as an AA′BB′ set with $J_{AB} = J_{AB'}$, giving a pair of triplets at 6.07 (2 H) and 6.60 (2 H); (2) the $Si(OMe)_3$ is associated with a singlet at 3.58 (9 H); (3) the pair of protons on the C adjacent to Si appear as a multiplet at 0.64 (2 H); (4) the pair of protons on the C adjacent to the N appear as a triplet at 3.89 (2 H); (5) the pair of protons on the middle C of the propyl chain appear as a complex multiplet at 1.92 (2 H). These data confirm the structure as formulated in I and are consistent with ^{1}H NMR spectra of other *N*-alkylpyrroles; cf., Stadtler spectrum no. 4973 and Aldrich spectrum no. C9,135-2 of *N*-*n*-butyl-2,5-dimethylpyrrole and *N*-(2-cyanoethyl)pyrrole, respectively. The mass spectrum, *m/z* (rel intensity), of I is correct: 229 (100); 230 (17.7); 231 (4.9).

(12) n-Type single-crystal Si was mounted as electrodes as previously described,[6] pretreated by a 15-s etch in HF followed by rinsing with distilled H_2O, immersion into 10 M NaOH for 60 s, and rinsing with H_2O and then with acetone. Smooth Pt was pretreated as described in the literature: Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 195.

(13) Auger spectra and depth profiles were obtained on a Physical Electronics Model 590A scanning Auger spectrometer under conditions described elsewhere: Bruce, J. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 74. Bookbinder, D. C.; Bruce, J. A.; Dominey, R. N.; Lewis, N. S.; Wrighton, M. S. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6280. Depth profiling using an Auger spectrometer has been previously described: Palmberg, P. W. *J. Vac. Sci. Technol.* **1972**, *9*, 160. Holloway, D. M. *Ibid.* **1975**, *12*, 392. Davis, R. E.; Faulkner, L. R. *J. Electrochem. Soc.* **1980**, *128*, 1349.

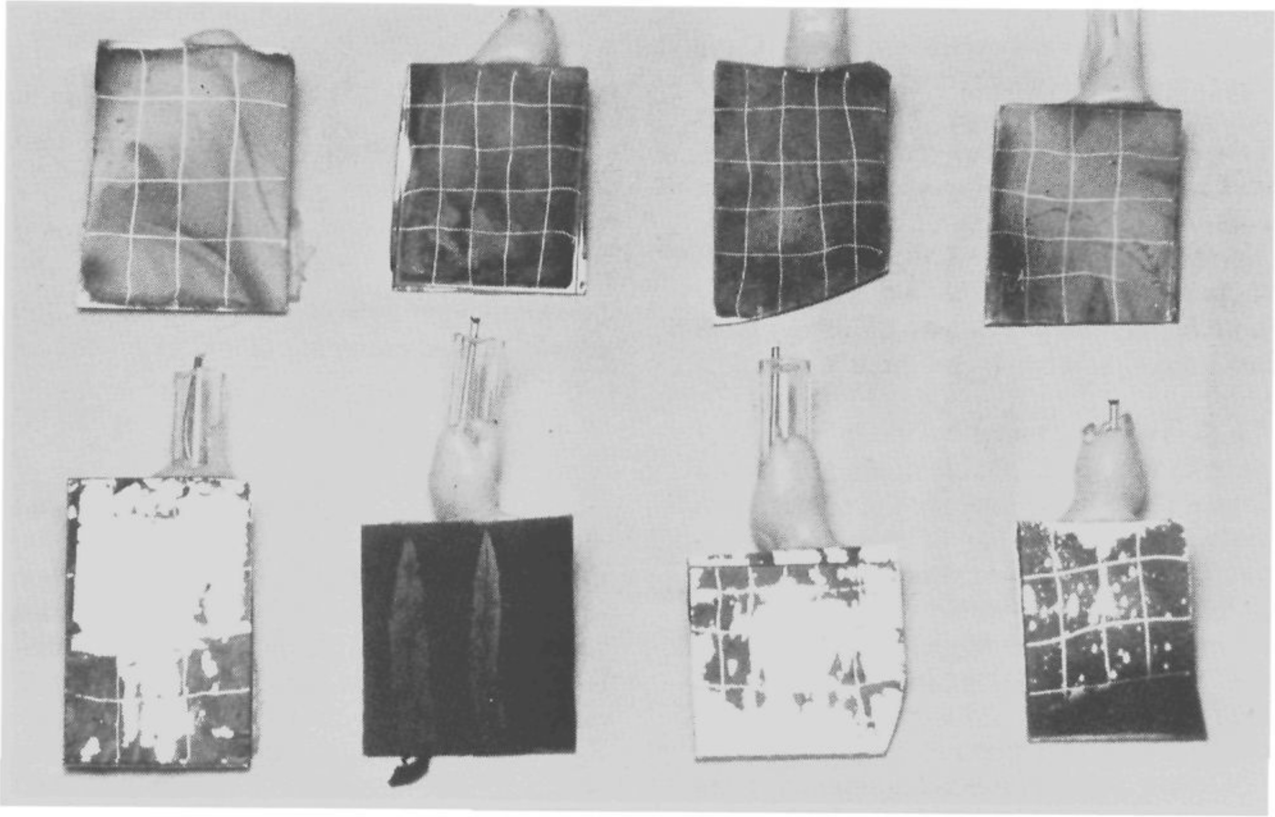
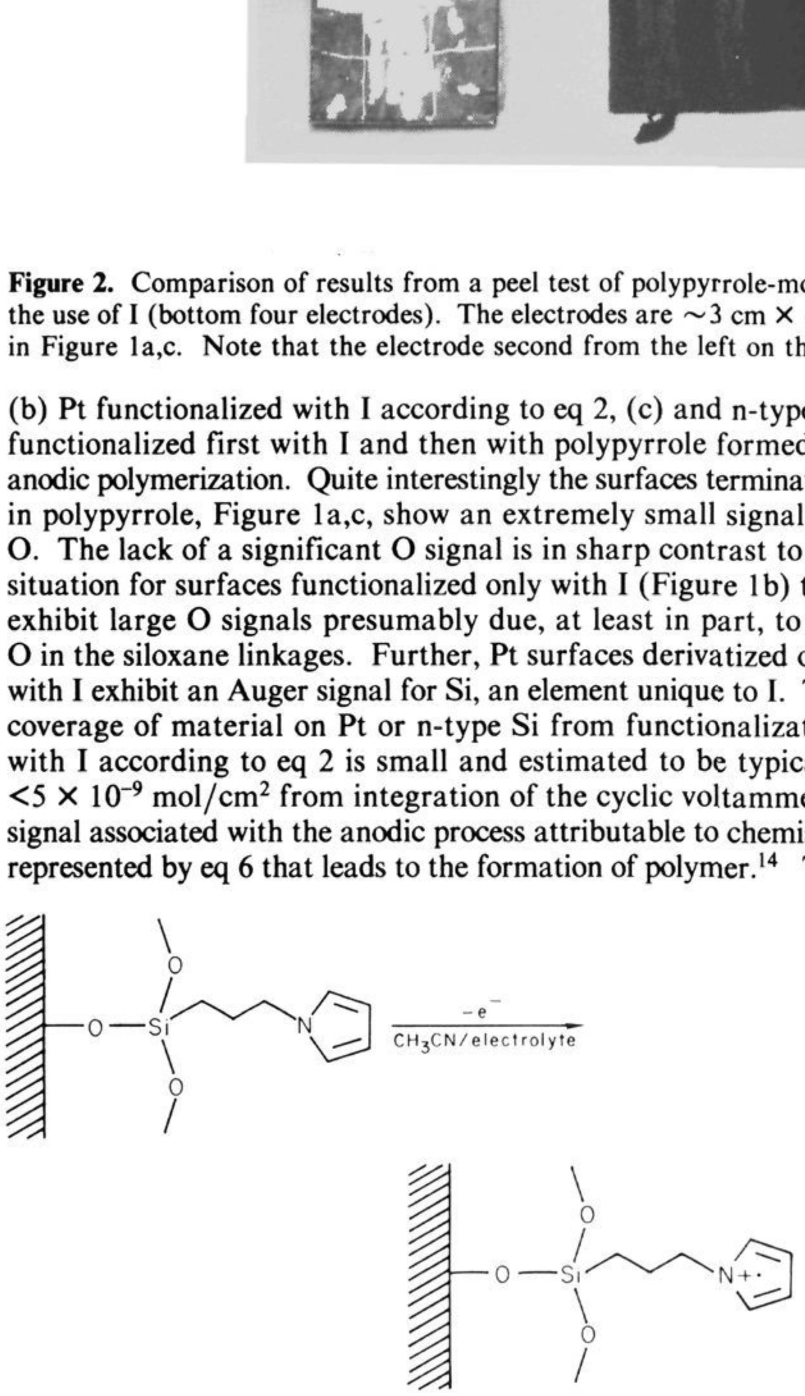


Figure 2. Comparison of results from a peel test of polypyrrole-modified n-type Si electrodes modified first with I (top four electrodes) and without the use of I (bottom four electrodes). The electrodes are ~3 cm × ~3 cm and have been coated with polypyrrole as were the electrodes characterized in Figure 1a,c. Note that the electrode second from the left on the bottom shows peeling of the polypyrrole without doing the peel test.

(b) Pt functionalized with I according to eq 2, (c) and n-type Si functionalized first with I and then with polypyrrole formed by anodic polymerization. Quite interestingly the surfaces terminating in polypyrrole, Figure 1a,c, show an extremely small signal for O. The lack of a significant O signal is in sharp contrast to the situation for surfaces functionalized only with I (Figure 1b) that exhibit large O signals presumably due, at least in part, to the O in the siloxane linkages. Further, Pt surfaces derivatized only with I exhibit an Auger signal for Si, an element unique to I. The coverage of material on Pt or n-type Si from functionalization with I according to eq 2 is small and estimated to be typically $<5 \times 10^{-9}$ mol/cm^2 from integration of the cyclic voltammetry signal associated with the anodic process attributable to chemistry represented by eq 6 that leads to the formation of polymer.[14] The low coverage from functionalization of electrodes with I according to eq 2 is consistent with the ability to see the Pt Auger signal of the substrate. Further, the depth profile analyses shown as insets in Figure 1a,c do not differ significantly except for the thickness of the polypyrrole layer; in particular, the presence of the thin layer of material from derivatization with I prior to the polypyrrole formation is not detected in the Auger scan or in the depth profile. In the depth profile the signal for Si (as well as for O, omitted from the figure for clarity) shows no increase prior to the start of the decline of C and N signals. The main point is that the layer from I is thin. This is possibly important inasmuch as the conductivity of poly(*N*-alkylpyrrole) is much lower than for polypyrrole itself.[1]



(6)

The Auger depth profiles of n-type Si/I/polypyrrole interfaces do show that the O signal increases concomitant with the increase in the Si signal. This O signal then declines while Si increases to a value associated with bulk Si. Thus, there does appear to be an SiO_x layer between the polypyrrole/I interface and the bulk Si. However, when polypyrrole is deposited onto n-type Si without pretreating with I, there is no significant SiO_x layer found in the depth profile. Thus, it is apparent that the photoanodic polymerization of 1.0 M pyrrole competes effectively with SiO_x formation under the conditions used. The SiO_x layer found for n-type Si first pretreated with I likely originates from thermal SiO_x growth during the derivatization procedure represented by eq 2.

Auger spectroscopy does suggest that surfaces can be persistently functionalized with I according to eq 2. Additionally, transmission Fourier transform infrared spectroscopy of n-type Si functionalized with I provides molecular specific information showing that the surface bears the *N*-alkylpyrrole functionality.

The important consequence of first treating n-type Si surfaces with I (eq 2) followed by modification with polypyrrole (eq 1) is that the adhesion of the thick, conducting, polypyrrole overlayer is dramatically improved. Inasmuch as I is oxidizable with a peak current at +1.3 V vs. SCE at Pt while pyrrole is oxidizable at +0.8 V vs. SCE,[14] we have used sufficiently positive potentials to ensure that the material from I can be oxidized to begin polymerization of pyrrole as represented in eq 3. Figure 2 illustrates the typical results from a peel test[15] of n-type Si (similar results obtain for Pt) electrodes with and without the inner layer of material from

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(14) The irreversible oxidation of 7 mM I in CH_3CN/0.1 M [n-Bu_4N]ClO_4 occurs with a peak at ~+1.3 V vs. SCE on linear sweep at 50 mV/s at Pt. After functionalization of pretreated Pt with I a similar scan in CH_3CN/0.1 M [n-Bu_4N]BF_4 exhibits an anodic peak in the same region. At freshly HF-etched, illuminated n-type Si the anodic peak for oxidation of I in solution appears at ~+0.3 V vs. SCE whereas n-type Si derivatized with I exhibits a surface wave at ~+0.6 V. The positive shift for derivatized n-type Si may be due to some growth of SiO_x during derivatization. Oxidation of pyrrole occurs with an onset at ~+0.8 V vs. SCE at Pt peaking at ~1.2 V and onsets at ~0.2 V vs. SCE at illuminated n-type Si.

(15) (a) "Paint Technology Manuals 5. Testing of Paints"; Oil & Colour Chemists' Association, Rheinhold: New York, 1965; p 81. (b) Lewis, A. F.; Forrestal, L. J. In "Characterization of Coatings: Physical Techniques, Part I"; Myers, R. R., Long, J. S., Eds.; Marcel Dekker: New York, 1969; Vol. 2, p 73. (c) Morgan, W. M. "Outlines of Paint Technology"; CRC Press: Ohio, 1969; p 380; (d) Pascoe, M. W. In "Aspects of Adhesion 3"; Alner, D. J., Ed.; CRC Press: Cleveland, OH, 1967; p 86.

I. The peel test consists of cutting through the polymer overlayer on the electrode to produce a grid of polypyrrole squares. Clear adhesive tape[16] is then applied and smoothed to remove any air bubbles; the tape is then peeled off the surface. For the electrodes functionalized with I we observe no obvious removal of the polypyrrole, whereas when I is not used as a "primer", the polypyrrole either peels spontaneously upon attempting to cut through the polymer (see electrode second from left on the bottom) or is efficiently removed by the adhesive tape. The peel test was done by removing the tape both rapidly and slowly with the same results for electrodes functionalized first with I: no gross removal of polypyrrole is observed.

Treatment of n-type Si with I followed by the formation of polypyrrole improves the durability of the electrode in aqueous electrolytes when it is used as a photoanode for the oxidation of I^- or Fe^{2+}(aq) compared to the durability of electrodes functionalized only with polypyrrole. Conditions, current density, and electrolytes are similar to those reported earlier.[2-5] For example, in one experiment an n-type Si/I/polypyrrole photoanode at +0.41 V vs. SCE in 0.15 M $FeCl_3$/0.5 M $FeCl_2$/1 M HCl gave an initial photocurrent of 7.6 mA/cm^2 that remained constant, or slightly greater, for 25 h. In a parallel experiment with an n-type Si/polypyrrole photoanode, having nearly the same amount of polypyrrole on the surface, photocurrent declined from 6.5 to 1.8 mA/cm^2 in less than 18 h. We attribute the improvement in durability to less H_2O/electrolyte undermining of the polymer when it is covalently anchored to the surface. Detailed studies of durability will be reported in a full paper.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. We thank R. N. Dominey for assistance with the FTIR studies and J. A. Bruce for assistance with the Auger spectroscopy.

Registry No. I, 80906-67-8; pyrrole, 109-97-7; 1-bromo-3-trimethoxysilylpropane, 51826-90-5.

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(16) Scotch (3M) Brand 810 Magic Transparent Tape (part no. 021200-07378) was used for all peel tests.

Pyridine Coordination Chemistry of Nickel and Platinum Surfaces

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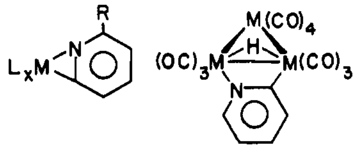
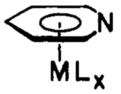
Received November 6, 1981

Pyridine–transition-metal coordination chemistry for molecular species is largely characterized by a conventional σ-donor and π-acceptor interaction of the nitrogen atom with the metal atom.[1] However, in zerovalent or low-valent, coordinately unsaturated mononuclear[2a] and cluster[2b] complexes, there is a potential for subsequent interactions, **1**, whereby a chelating α-pyridyl or a bridging α-pyridyl complex may form.



In addition, there are several isolated examples[3] of π-$C_5H_5NML_3$ complexes, **2**, in which pyridine or a substituted pyridine is an η^6-ligand for a metal atom in a low oxidation state.



Pyridine coordination chemistry at metal surfaces has been studied by spectroscopic[4] and diffraction[5] techniques, but the available data do not allow unqualified structural interpretations. We present here results of an ultra-high-vacuum study[6] of pyridine chemistry on various crystal planes of nickel and platinum. Through isotopic labeling studies, an important interaction via α-pyridyl bonding has been incisively established for some specific crystal planes. These data provide a fundamental understanding of a catalytic reaction, namely H–D exchange processes, observed[10] for pyridine and deuterium with metallic catalysts.

Pyridine adsorbed on the nickel(100) surface at 25 °C, and approximately monolayer[11] coverage exhibited partial (~50%)[12a]

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(1) Pyridine is a medium-strength field ligand. It lies between ammonia and ethylene in the ligand spectrochemical series.

(2) (a) Cp_2TiR (R = alkyl) reacts with substituted pyridines to give chelating α-pyridyl complexes: Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53. (b) $Os_3(CO)_{12}$ reacts with pyridine to give $Os_3(CO)_{11}NC_5H_5$. By thermal activation and with further reaction with pyridine, the following transformations have been observed: $Os_3(CO)_{11}NC_5H_5 \xrightarrow{\Delta} HOs_3(\mu_2\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}$ $(+NC_5H_5) \rightleftharpoons HOs_3(\mu_2\text{-}\eta^2\text{-}NC_5H_4)(CO)_9(NC_5H_5) \rightleftharpoons H_2Os_3(\mu_2\text{-}\eta^2\text{-}NC_5H_4)_{22}(CO)_8 \rightarrow Os_2(\mu_2\text{-}\eta^2\text{-}NC_5H_4)_2(CO)_6$ (Yin, C. C.; Deeming, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2091.

(3) Timms, P. L. *Angew. Chem.* **1975**, *87*, 295; Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273. Simons, L. H.; Riley, P. E.; Davis, R. E.; Lagowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1044. Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1976**, *15*, 2735. Biederman, H.-G.; Öfele, K.; Tajtelbaum, J. *Z. Naturforsch., A* **1976**, *31B*, 321. Biederman, H.-G.; Öfele, K.; Schuhbauer, N.; Tajtelbaum, J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 639.

(4) (a) Kishi and Ikeda examined the ultraviolet spectra of pyridine chemisorbed on titanium, iron, and nickel films and considered two possible modes of bonding: (i) bonding solely through the nitrogen atom and (ii) bonding through the nitrogen atom and through the aromatic system (Kishi, K.; Ikeda, S. *J. Phys. Chem.* **1969**, *73*, 2559). (b) Kishi et al. in a later study of pyridine chemisorption on nickel and iron films decided that the earlier film studies related to partially oxidized metal film surfaces. They examined the X-ray photoelectron spectra of pyridine on nickel and iron films at 10^{-6}–10^{-8} torr and proposed binding of the pyridine to the unoxidized surfaces through the aromatic system of the pyridine (Kishi, K.; Chinomi, K.; Inoue, Y.; Ikeda, S. *J. Catal.* **1979**, *60*, 228). (c) Morrow et al. from an infrared study of pyridine chemisorbed on silica-supported metals proposed α-pyridyl bonding for Pt, Ir, Os, Rh, and Ru. For nickel, simple bonding only through the nitrogen atom of pyridine was proposed: Morrow, B. A.; Cody, I. A.; Moran, L. E.; Palepu, R. *J. Catal.* **1976**, *44*, 467. (d) Very weak bonding of pyridine to Ag(110) and polycrystalline Ag has been established: Kelemen, S.; Kaldor, A. *Chem. Phys. Lett.* **1980**, *73*, 205. Eesley, G. L. *Phys. Lett. A* **1981**, *81A*, 193. Eesley, G. L.; Simon, D. L. *J. Vac. Sci. Technol.* **1981**, *18*, 629. (e) Demuth et al. studied pyridine chemisorbed on Ag(111) by high-resolution electron energy loss and UV photoemission spectroscopy and proposed a state with a slight tipping of the C_5N ring to bring the N atom close to the surface plane and then at higher coverages a more weakly bound state with primarily metal–nitrogen bonding: Demuth, J. E.; Christman, K.; Sanda, P. N. *Chem. Phys. Lett.* **1980**, *76*, 201.

(5) Gland and Somorjai reported that pyridine forms poorly ordered structures on Pt(111) and Pt(100). On the basis of work-function studies, they proposed bonding of the pyridine through the nitrogen atom: Gland, J. L.; Somorjai, G. A. *Surf. Sci.* **1973**, *38*, 157. *Adv. Colloid Interface Sci.* **1976**, *5*, 205.

(6) For the experimental strategy, experimental procedure, and cleaning procedures, see ref 7, 8, and 9, respectively.

(7) Muetterties, E. L. *Angew. Chem.* **1978**, *90*, 577; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 545.

(8) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767, 773.

(9) Friend, C. M.; Gavin, R. M.; Muetterties, E. L.; Tsai, M.-C. *J. Am. Chem. Soc.* **1980**, *102*, 1717.

(10) Moyes and Wells studied the exchange reaction between D_2 and pyridine over Mn, Co, Ni and W films and over powdered iridium and platinum (Moyes, R. B.; Wells, P. B. *J. Catal.* **1971**, *21*, 86). Selectivity to exchange at the 2 and 6 position of the pyridine ring was observed with nickel (at 42 °C), by far the most selective catalyst.

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