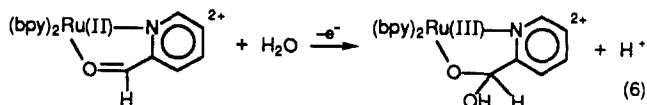additional oxidations were observed out to the solvent window at the various pHs investigated. A plot of $E_{1/2}$ vs pH (i.e., a Pourbaix diagram)[3] for [Ru(bpy)$_2$(2-CHOpy)]$^{2+}$ is shown in Figure 1. The pH dependence observed for the Ru$^{III/II}$ couple in the acidic region of the Pourbaix diagram is due to the redox reaction shown in eq 6, where oxidation of Ru^{II} is coupled to hydrolysis of the coordinated aldehyde. The slope in the acidic region is −60 mV/pH unit, as expected from the Nernst equation.[1] The sta-

bilization of Ru^{III} associated with hydrolysis of the aldehyde ligand can be understood in terms of the lost back-bonding to Ru^{II} upon disruption of the aldehyde π^* system and the enhanced electron-donating ability of the resulting anionic oxygen. At more basic pHs, the Ru^{II} complex undergoes hydrolysis, and the oxidation reaction consists of a simple electron transfer (eq 7).
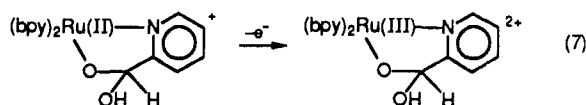
Therefore, no pH dependence is expected at higher pHs, in agreement with Figure 1. The pH at which the two linear portions of the Pourbaix diagram meet corresponds to the pH at which the concentrations of [Ru^{II}(bpy)$_2$(2-CHOpy)]$^{2+}$ and [Ru^{II}-(bpy)$_2$(2-CO(OH)Hpy)]$^+$ are equal, and hence pH = pK_{hy} for eq 5. The data in Figure 1 yielded a pK_{hy} of 6.7 for the Ru^{II} complex.

The hydrolysis constant was also determined by following the electronic spectrum of [Ru(bpy)$_2$(2-CHOpy)]$^{2+}$ as a function of pH. At low pH, the lowest energy metal-to-ligand charge transfer (MLCT) band occurs at 430 nm (7.4 × 10^3 M^{-1} cm^{-1}), while at high pH, the MLCT band is shifted to 500 nm (7.7 × 10^3 M^{-1} cm^{-1}). At intermediate pHs both bands are observed, and the relative intensities reflect the relative concentrations of [Ru-(bpy)$_2$(2-CHOpy)]$^{2+}$ and [Ru(bpy)$_2$(2-CO(OH)Hpy)]$^+$. Analysis of the pH-dependent spectral data by the method of Clarke and Ford[15] yielded a pK_{hy} value of 6.5, in good agreement with the value obtained from the Pourbaix diagram. The hydrolysis constant for [Ru(NH$_3$)$_4$(2-CHOpy)]$^{2+}$ was determined spectrophotometrically by Ford to be 11.8.[12] The decrease in K_{hy} of 5 orders of magnitude upon going from the tetraammine system to the bis(2,2'-bipyridine) system can be understood in terms of π-back-bonding. The aldehyde form of the ligand is stabilized in [Ru(NH$_3$)$_4$(2-CHOpy)]$^{2+}$ by π-back-bonding with Ru^{II}. When the ammine ligands are replaced by 2,2'-bipyridine ligands, 2-CHOpy must compete with the bpy ligands for the available dπ electron density on Ru^{II}. The combined effect of the decreased back-bonding to 2-CHOpy and the enhanced Lewis acidity of the Ru^{II} site is to increase the electrophilicity of the aldehyde carbon,[16] resulting in an increase in the hydrolysis constant. This result suggests that it may be possible to "tune" the hydrolysis constant (and hence the break point in the Pourbaix diagram) by regulating the π-acidity of the spectator ligands.

In summary, the reversible hydrolysis of 2-pyridinecarboxaldehyde coordinated to ruthenium(II) has been used to design a reversible pH-dependent one-electron redox couple such that only one electron-transfer reaction is observed over a relatively large potential region. In addition to providing a chemical means of tuning redox potentials, the coupling of a chemical reaction to an electron-transfer reaction in [Ru(bpy)$_2$(2-CHOpy)]$^{2+}$ illustrates the possibility of regulating chemical reactivity (in this case, carbon–oxygen bond formation) of an organic ligand by

controlling the oxidation state of the coordinate metal.

Oxidation Chemistry of d^0 Organometallic Complexes

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Electron-transfer processes can play an important role in organometallic chemistry.[1,2] Herein, we demonstrate that even d^0 organometallic complexes exhibit a rich redox chemistry and present electrochemical, kinetics, and stereochemical studies that establish a general outer-sphere oxidation process for d^0 group 4 metallocene complexes. This oxidation chemistry closely parallels the reported LMCT photochemistry of these complexes.[3]

Recent observations in our laboratory[4] and others[5,6] indicate that d^0 bis(cyclopentadienyl) dialkyl complexes of Ti and Zr react readily with one-electron oxidants to give products arising from either alkyl radical expulsion or formal reductive elimination. We have observed that the titanacyclobutanes[7] **1** react with one-electron oxidants such as tetrakis(trifluoromethyl)cyclopentadienone (TTFC), Ag$^+$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), or [Cp$_2$Fe]$^+$ (Cp = η^5-cyclopentadienyl) in methylene chloride or acetonitrile, resulting in the quantitative production (by NMR) of the corresponding cyclopropanes (eq 1).[8] Di-

1a: R=t-Bu; R'=H
1b: R=CH$_3$; R'=CH$_3$
1c: R=i-Pr; R'=H

OXIDANT = TTFC, Ag$^+$, TCNQ, [Cp$_2$Fe]$^+$
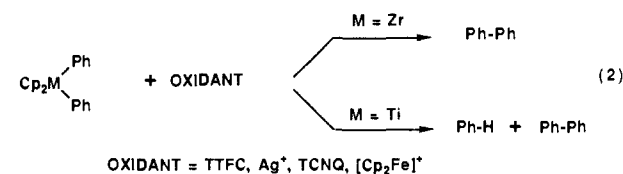
† Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125.
(1) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.
(2) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. Jernakoff, P.; Cooper, N. J. *Organometallics* **1986**, *5*, 747.
(3) (a) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1985**, *24*, 249. (b) Tumas, W.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 6182.
(4) Burk, M. J.; Staley, D. L.; Tumas, W. *J. Chem. Soc., Chem. Commun.*, **1990**, 809.
(5) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *Ibid.* **1986**, *108*, 7410.
(6) Straus, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, *369*, C13.
(7) (a) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (b) Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733. (c) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

(14) *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1981; p D-126.
(15) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 495.
(16) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn & Bacon: Boston, 1973; p 629.
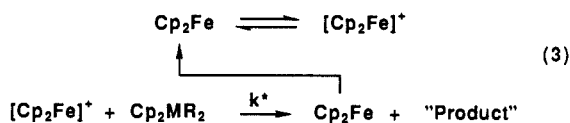
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Communications to the Editor

Table I. Reduction Potentials[a,b]

no.	compd	$E°(0/-)$ redn[c]	$E_{1/2}(0/+)$ oxidn[d]
1a	$Cp_2TiCH_2CH(t\text{-}Bu)CH_2$	-2.05	0.64
2	Cp_2ZrPh_2	-2.05	1.43
3	Cp_2TiPh_2	-1.51	0.96
5	$Cp_2Zr(CH_2Ph)_2$	-2.16	0.60
6	$Cp_2Ti(CH_2Ph)_2$	-1.60	0.65
7	$Cp_2Zr(CH_3)_2$	-2.53	1.31

[a] Potentials (V vs SCE) were measured in 0.1 M $Bu_4N^+BF_4^-$/ CH_3CN against $Ag/AgNO_3$ and ferrocene/ferrocenium references and then corrected to SCE. [b] Reference 9. [c] Reduction wave reversible. [d] Oxidation wave irreversible.

phenylzirconocene (**2**) was found to react under these conditions to produce biphenyl (quantitatively with TTFC).[8] In contrast to this formal reductive elimination chemistry, Jordan and co-workers[5] have reported that Cp_2ZrR_2 (R = CH_3, CH_2Ph) react with Ag^+ or $[Cp_2Fe]^+$ to produce the corresponding cationic complexes $Cp_2ZrR(L)^+$ through an apparent loss of alkyl radical. Similarly, we have found that diphenyltitanocene (**3**) gives predominantly benzene as well as some biphenyl under these conditions.[8] This disparity in product distributions and the general lack of understanding of the oxidation chemistry of d^0 compounds prompted us to explore their electrochemical properties.

Electrochemical studies[9a] of a number of Cp_2MR_2 (M = Ti, Zr; **1–7**) strongly implicate outer-sphere electron-transfer processes in reactions between these d^0 complexes and oxidants. Direct oxidations at platinum electrodes were observed in both acetonitrile and methylene chloride (Table I). In all cases, the oxidations were electrochemically irreversible (scan rates up to 1000 V/s). These complexes also exhibited reversible one-electron reductions with $E°$ values that were independent of the nature of the supporting electrolyte. Cyclic voltammograms of ferrocene compounds in the presence of **1a** or $Cp_2Zr(CH_2Ph)_2$ (**5**) were indicative of an E_rC_i' pathway (eq 3). Rate constants (k^*) for the reaction

$$Cp_2Fe \rightleftharpoons [Cp_2Fe]^+$$

$$[Cp_2Fe]^+ + Cp_2MR_2 \xrightarrow{k^*} Cp_2Fe + \text{"Product"} \quad (3)$$

of **1a** with substituted ferrocenium ions, determined experimentally by cyclic voltammetry (23 °C),[10] decreased monotonically with decreasing driving force: ferrocenium ($E° = 0.41$ V (vs SCE), $k^* = 340$ M^{-1} s^{-1}) > 1-methylferrocenium ($E° = 0.33$ V, $k^* = 180$ M^{-1} s^{-1}) > 1,1'-dimethylferrocenium ($E° = 0.29$ V, $k^* = 140$ M^{-1} s^{-1}). Rate constants for heterogeneous electron transfer from **1a** to a rotating Pt electrode[10c] increased monotonically from 3.6 × 10^{-4} to 1.5 × 10^{-3} cm s^{-1} over the applied potential range 0.53–0.73 V (E vs SCE). Marcus plots of ln k vs E (driving force) are linear with identical slopes ($\alpha = 0.3$) for both homogeneous and heterogeneous electron transfers,[1,11] substantiating an out-

er-sphere electron-transfer process. Similar trends were observed for the homogeneous rates of $Cp_2Zr(CH_2Ph)_2$ (**5**): ferrocenium ($k^* = 1510$ M^{-1} s^{-1}) > 1-methylferrocenium ($k^* = 670$ M^{-1} s^{-1}) > 1,1'-dimethylferrocenium ($k^* = 400$ M^{-1} s^{-1}).[9c]

Bulk electrochemical oxidation of **1** results in the formation of the respective cyclopropane as the only organic product. Biphenyl and benzene were produced from bulk electrolysis[9b] of Cp_2ZrPh_2 and Cp_2TiPh_2. Oxidation of the stereospecifically deuterated[7a] titanacyclobutanes **4** by electrolysis or reaction with TTFC, DDQ, or ferrocenium ion led to the stereospecific formation of cyclopropanes with a high degree of retention of configuration (>15/1 retention/inversion by NMR; eq 4).[12,13] This stereose-
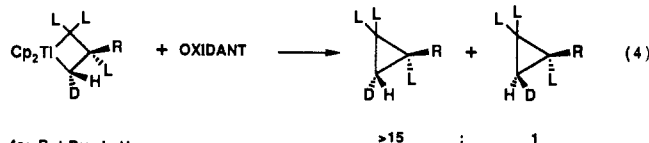
4a: R=t-Bu; L=H
4b: R=i-Pr; L=D
4c: R=i-Pr; L=H

lectivity requires either (a) that the oxidatively induced reductive elimination is concerted or (b) if stepwise, that subsequent cleavage pathways leading to product are faster than C–C bond rotations in any intermediates formed by Ti–C bond homolysis (i.e., very short-lived intermediates). A plausible mechanism for oxidation of d^0 group 4 complexes involves metal–carbon bond homolysis after oxidation of a metal–ligand bond to form the radical–cation pair **8** (eq 5). The observed reaction products would then result from a competition between intramolecular S_H2 coupling (path A) and cage escape (path B)[14] of this intermediate.[15,16]
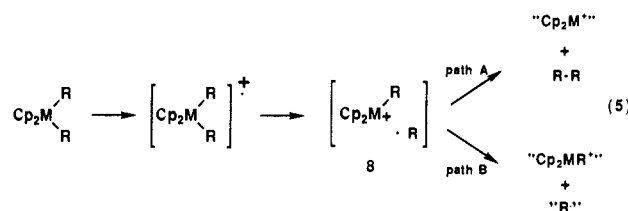
The observation of identical products, stereochemistry, and driving-force dependence of electron-transfer rates (compound **1**) for the electrochemical and chemical oxidation clearly indicates identical reaction pathways and substantiates an outer-sphere electron-transfer process.[15] In addition, the products observed in the chemical and electrolytic oxidations parallel those reported[3] for the ligand-to-metal charge-transfer (LMCT) photochemistry of these group 4 d^0 compounds. This agreement between the oxidation and photochemistry coupled with the reversibility of the electrochemical reductions strongly suggests that the resulting "hole" in a metal–ligand bonding orbital, and not the photoexcited electron, of an LMCT excited state governs the photochemical reactivity.

This oxidation chemistry may find important synthetic applications. Oxidation of a number of bicyclic titanacyclobutanes

(8) Except for reactions involving TTFC (ref 4), the reactions described in eqs 1 and 2 gave intractable organometallic byproducts (presumably paramagnetic halide complexes produced from reactions of Cp_2M^+ and/or Cp_2MR^+ with solvent and/or counterions) that have not yet been characterized.

(9) (a) The electrochemical behavior of most of these complexes was very sensitive to adventitious water and/or oxygen; therefore, it was necessary to work under rigorously inert conditions. Cyclic voltammetry revealed that electrode passivation occurred upon potential excursions into the anodic wave of the Cp_2MR_2 complexes and generally prevented determination of oxidation potentials at very fast scan rates using ultramicroelectrodes. For **1a**, however, we could measure an $E_{1/2}$ of 0.86 V (microelectrode vs SCE) that was significantly positive of the value determined at conventional electrodes, suggesting a very fast chemical reaction following electrooxidation. (b) Due to the extreme hydrolytic sensitivity of **2**, we were unable to determine whether the observed benzene product resulted from electrolytic oxidation or hydrolysis by adventitious water. (c) Due to electrode passivation, heterogeneous rate constants could not be determined for **5**.

(10) (a) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1965**, *10*, 905. (b) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (c) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(11) Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839. Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem.* **1983**, *152*, 1.

(12) In general, the ratio of retention to inversion was greater than 15/1, except for the case of reaction with DDQ, in which the ratio was ca. 7/1.

(13) Grubbs et al. have reported that reaction of **4a** with I_2 leads to nonstereospecific formation of cyclopropanes via two sequential steps with opposite stereospecificity: Ho, S. C. H.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 1533.

(14) At this time, we cannot rule out intermolecular S_H2 reactions of free radicals R• with dialkyls or intermediates after cage escape; however, the observation that these reactions require a stoichiometric amount of oxidant and in some cases are slow implies that any reaction chains must be very short.

(15) For examples of oxidatively induced reductive elimination of d^n systems, see: (a) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 324–326.

(16) For reports on the oxidative cleavage of group 14 alkyls, see: (a) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. (b) Walther, B. W.; Williams, F.; Lau, W.; Kochi, J. K. *Organometallics* **1983**, *2*, 688. (c) Eaton, D. F. *Pure Appl. Chem.* **1984**, *56*, 1191.

(9–11) derived from cyclic olefins leads to the corresponding cyclopropanes, suggesting a new method for end-capping living ring-opening metathesis polymers.[7c] Oxidative cleavage of the numerous Ti and Zr metallacycles in the literature, particularly five-membered-ring systems attainable by cyclizations of alkenes, alkynes, and carbonyl compounds,[17] could provide new routes to hetero- and carbocycles.

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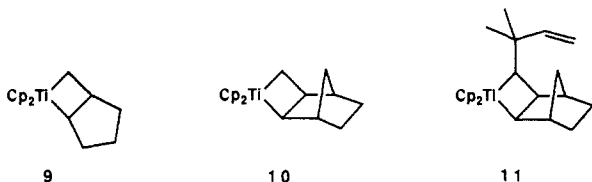
We are currently investigating the redox chemistry and photochemistry of other organometallic complexes as well as examining the synthetic applications of their oxidation chemistry.

Acknowledgment. We are grateful to E. J. Delawski, J. E. Feaster, B. A. Kurtz, and J. A. Suriano for expert technical assistance.

Supplementary Material Available: Experimental methods including electrochemical details and kinetic analyses (5 pages). Ordering information is given on any current masthead page.

(17) Rajanbabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128. Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *Ibid.* **1989**, *111*, 3336. Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

Morphology Control in Electrochemically Grown Conducting Polymer Films. 1. Precoating the Metal Substrate with an Organic Monolayer

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Received April 16, 1990

We report in this communication on a significant increase in the density of an electrochemically grown conducting polymer film obtained by preadsorbing a self-assembling monolayer onto the surface of the electrode substrate.

The properties of electrochemically grown conducting polymer (CP) films have been described recently by many authors. Relatively limited attention has been paid, however, to the mechanism of the film growth process. Park and co-workers have described in a series of recent papers[1] the detection of molecular species (mainly dimers) that serve as intermediates in the film growth process, as well as the products of parallel anodic processes and of film degradation.[1] The results of this last work suggest that the net electrochemical growth rate for a CP film depends on the relative rates of several parallel anodic processes, all of which may be associated with very close onset potentials. To generate the polymer itself from soluble intermediates, the newly formed phase has to (a) nucleate and (b) grow in three dimensions. These are two elementary steps that have been investigated extensively for metal electrodeposition processes, but much less so for the growth of electronically conducting polymers. Important film characteristics that may be strongly affected by the nature

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§ Graduate student visitor from the Department of Materials Research, The Weizmann Institute of Science, Rehovot, Israel.
(1) Shim, Y. B.; Won, M. S.; Park, S. M. *J. Electrochem. Soc.* **1990**, *137*, 538–544 and references therein.

of the nucleation-and-growth process are the morphology and the degree of space filling. These may have, in turn, strong effects on the electrical and electrochemical characteristics of the film. Previous in situ investigations by ellipsometry[2–4] have demonstrated the capability of this optical technique to obtain some information on details of the electrochemical growth of conducting polymer films. Other investigations[5,6] have shown that the quartz crystal microbalance (QCM) is an effective tool for measuring charge efficiencies in the process of CP film growth. We have recently reported a system for simultaneous in situ ellipsometry and QCM measurements.[7] This system allows us to measure continuously the film thickness and mass as two independent parameters and thus follow in situ the density of the film during electrochemical growth.

A significant barrier to polymer growth on a metal surface may originate from poor adhesion between the growing phase and the substrate. This could result in inhibited nucleation and growth of the film along the substrate, preventing the formation of films with good space filling. An example of the optical properties of a film formed under such conditions is given in Figure 1A. This curve is the ellipsometric Ψ vs Δ plot for a film of polyaniline (PANI) grown galvanostatically at a gold electrode substrate. Some familiarity with this type of ellipsometric plot allows an immediate qualitative observation: the small radius of curvature of this plot is testimony for a film with a refractive index very close to that of the electrolyte.[8] A quantitative evaluation of the optical properties and thickness of this film has shown that optical parameters vary somewhat during film growth, but this variation is slight and does not amount to a significant change in film characteristics. The refractive index can be expressed in this case as $\hat{n}_{film} = 1.30 \pm 0.02 + (0.025 \pm 0.015)i$. It is readily seen that this film can be described optically as a "slightly perturbed layer of electrolyte" (the refractive index of the electrolyte at this wavelength is $n = 1.335 + 0i$). Results of a QCM measurement taken simultaneously during the same experiment of galvanostatic growth are shown in Figure 2 (dashed curve). The calculated film density obtained from the division of film mass (QCM) by its thickness (ellipsometry) shows some variations at growth times smaller than 50 min, but for growth times larger than 50 min the evaluated density stabilizes in the range of 1.07–1.08 gr/cm³. Such a low density agrees well with the conclusion reached above from the optical properties of this film, namely, that this is a CP layer with a high electrolyte content and poor space filling.

Suspecting that a surface wetting problem is an important reason for the poor film morphology, we tried to treat the gold surface so as to increase film/substrate adhesion. To achieve that, we adsorbed on the gold substrate a self-assembled monlayer of p-aminothiophenol (PATP)[9] so as to form a uniform monolayer of bound aniline monomers on the electrode. (In general, sulfur-hydrocarbon molecules are adsorbed readily onto gold,[10] and hydrocarbon-thiol self-assembling monolayers were used previously to modify electrode surfaces for other purposes.[11]) Following the coating of the gold surface with this monolayer, we grew on it the film of PANI, using the same galvanostatic growth conditions as in the "bare" gold case. The film that formed now on the gold surface had substantially different properties. The

(2) Redondo, A.; Ticianelli, E. A.; Gottesfeld, S. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 185–203.
(3) Hamnett, A.; Hillman, A. R. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*(4), 329–336.
(4) Greef, R.; Kalaji, M.; Peter, L. M. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 277–289.
(5) Baker, C. K.; Reynolds, J. R. *Synth. Met.* **1989**, *28*, C21–C26.
(6) Hochfeld, A.; Kessel, R.; Schultze, J. W.; Thyssen, A. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1406–1412.
(7) Rishpon, J.; Redondo, A.; Gottesfeld, S. *J. Electroanal. Chem. Interfacial Electrochem.*, in press.
(8) Gottesfeld, S. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1989; Vol. 15, pp 143–265.
(9) Sabatani, E.; Rubinstein, I., to be published.
(10) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.
(11) (a) Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409–413. (b) Sabatani, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *219*, 365–371. (c) Sabatani, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663–6669.