

- 834 (1966).
- (5) S. J. Cristol, W. Barasch, and C. H. Tieman, *J. Am. Chem. Soc.*, **77**, 583 (1955).
  - (6) S. J. Cristol, *Acc. Chem. Res.*, **4**, 393 (1971).
  - (7) (a) R. K. Hill and G. R. Newkome, *J. Am. Chem. Soc.*, **91**, 5893 (1969); (b) D. K. Onderka and H. G. Floss, *ibid.*, **91**, 5894 (1969); (c) H. G. Floss, D. K. Onderka, and M. Carroll, *J. Biol. Chem.*, **247**, 736 (1972).
  - (8) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebig's Ann. Chem.*, **560**, 1 (1948).
  - (9) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Am. Chem. Soc.*, **92**, 564 (1970).
  - (10) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).
  - (11) H. Pines and R. H. Kozlowski, *J. Am. Chem. Soc.*, **78**, 3776 (1956). For convenience in handling this volatile diene, it was converted to dimethyl phthalate by Diels-Alder reaction with dimethyl acetylenedicarboxylate as described in this reference before deuterium analysis.
  - (12) E. M. Burgess, H. R. Penton, Jr., and E. A. Taylor, *J. Am. Chem. Soc.*, **92**, 5224 (1970).
  - (13) Cf. G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4609 (1956), and G. Stork and A. F. Dreft, III, *ibid.*, **99**, 3850 (1977).
  - (14) For the use of crown ethers in elimination reactions, see ref 1b. We thank Dr. R. A. Bartsch for suggesting these experimental conditions.
  - (15) R. K. Hill and R. M. Carlson, *J. Org. Chem.*, **30**, 2414 (1965).

Richard K. Hill,\* Mark G. Bock

Department of Chemistry, University of Georgia  
Athens, Georgia 30602

Received September 6, 1977

### Electrode Surface Modification via Polymer Adsorption

Sir:

We are interested in synthesizing electrode surfaces with useful chemical properties. The approach is to chemically bind organic or organometallic compounds to the surfaces of conductors and use these "chemically modified electrodes" to achieve greater specificity in electrode reactions. Recent studies have shown that modifiers, e.g., amines, can be chemically bound to carbon electrodes via the surface oxides.<sup>1-5</sup> Metal oxides, e.g., tin oxide, have been modified by silylation.<sup>6-13</sup> In each case rather stable binding of both electroactive and electroinactive modifiers has been achieved and new chemical properties have been imparted to the electrode. Related studies have shown that electroactive, organic compounds can be strongly adsorbed on platinum<sup>14</sup> and carbon electrodes.<sup>15</sup>

We report here a new approach involving adsorbed polymers. Many polymers strongly adsorb to solids and it appeared that films of one or a few molecular layers could be produced<sup>16</sup> and used independently. The initial experiments reveal the following results. (1) Adsorbed layers of varying thickness can be reproducibly formed using several polymers. (2) Analysis by electron spectroscopy demonstrates that in vacuo the surface is quite uniformly covered and allows an estimate of the layer thickness. (3) These modified surfaces are quite stable and are not destroyed when used in a variety of electrochemical experiments. (4) The polymer layer inhibits electrochemical reactions, but it is shown that reactions can be performed at usual potentials at a surface whose composition is dominated by polymer. (5) An appropriate adsorbed polymer layer can be chemically modified, providing an electroactive surface functionality.

The coating was achieved by dipping platinum wire or sheet into a trifluoroacetic acid solution containing small amounts of ethylene glycol terephthalate polymer (**1**) or a copolymer of 60% lysine, 40% alanine (**2**).<sup>17</sup> After a few minutes the electrode was removed, quickly shaken to remove excess solution and dried in air at 120 °C for 20 min.

Samples coated with **1** (from a 0.03% solution for 7.5 min) were analyzed by scanning Auger electron spectroscopy (AES), providing an elemental analysis of the surface.<sup>18</sup> The spectra showed no fluorine (from trifluoroacetic acid or de-

rivatives), strong carbon and oxygen bands, and markedly attenuated platinum bands. Of the many platinum bands those at 43 and 64 eV and at 1967 eV are of particular interest here. In the spectrum of pure platinum the former pair are some 10 times as intense as the latter. The spectra of the coated samples show the relative intensity of these two pairs to be inverted in comparison with pure platinum. Indeed, the low energy bands are barely detectable. This arises because the electrons ejected at 43 and 64 eV are of relatively low energy so that they have an escape depth of <10 Å. The more energetic electrons analyzed at 1967 eV will, however, escape through some 30 Å.<sup>19</sup> This directly brackets the film thickness between 10 and 35 Å. Etching this sample with an argon ion beam affirms this conclusion. Finally, scanning the sample shows the film to be relatively uniform at the modest resolution of the spectrometer (3-μ electron beam diameter).

There is a correlation between the intensity of the high energy Pt lines and the concentration of the dipping solution. This will be thoroughly explored in a future publication but we note here that AES on the film resulting from a 0.3% solution of **1** showed no high energy platinum lines.

Similar data were obtained using polypeptide **2**. Adsorption from a 0.10% solution of **2** in trifluoroacetic acid, for example, gave a spectrum with no F band, no low energy Pt bands, somewhat depressed high energy Pt lines, and C, N, and O bands of approximately the appropriate intensity considering the polymer structure.

It is of great interest to probe the uniformity of the film. We first note that, although the AES data are averaged over the surface, they are incompatible with a surface thickly covered in some places and uncovered in others. The low energy Pt AES lines are instructive in this regard since they are inhibited by <10 Å of a surface contaminant. If it is assumed that this signal is inversely proportional to the coverage, one concludes that the surface is 99% covered for an electrode prepared from a 0.1% solution of **2** or 0.03% solution of **1**. The question of "narrow, deep holes" is not solved by this approach and, for example, on the 10 Å level there must certainly be such defects. Defects were also sought using a Coates and Welter field emission scanning electron microscope. This secondary imaging instrument is capable of 50-Å resolution. Clean platinum showed a very smooth surface marred only by widely scattered, spheroidal screw defects of up to 4000-Å diameter. Platinum/polyester (from 0.15% solution) and platinum/polyamide (from 0.10% solution) were investigated. The polymer coated surfaces were identical with that of clean platinum. To check this a 70-Å layer of gold was vapor deposited on the polymers before the analysis and, again, the surface appeared as defect free as clean platinum. Irregularities were carefully sought by scanning the surface of the screw dislocations but none could be found. It is concluded that, in vacuo, holes and protrusions of polymer are smaller than the resolution of the instruments.

Platinum sheet/polypeptide electrodes prepared identically with those examined spectroscopically were used for electrochemistry. Cyclic voltammetry experiments were performed using dimethyl sulfoxide, 0.1 M tetraethylammonium perchlorate as solvent, and electrolyte. The reduction of 1 mM *n*-propyl-3,5-dinitrobenzamide was investigated. As expected this compound gave a pair of reversible couples on clean platinum,  $E_{1/2} = -0.76$  V,  $-1.14$  V. The anodic cathodic peak separation was 75 mV. Using platinum/polypeptide a pair of quasi-reversible couples was again seen  $E_{1/2} = -0.76$ ,  $-1.14$  V. Electrodes prepared from dilute, e.g., 0.03%, solutions gave nearly reversible behavior at slow (100 mV/s) sweep rates. At faster sweep rates the peaks broadened consistent with an inhibited electrochemical rate. This behavior has been quantified and will be reported separately. We emphasize here only that electrodes with considerable amounts of polymer on the surface

(equivalent to  $\sim 15 \text{ \AA}$  at full coverage) can be used for electrochemistry. In this situation the electrochemical reactions must be taking place in an environment dominated by the polymer.

To demonstrate that adsorbed layers can be synthetically elaborated, this polypeptide surface was treated with a 1% solution of 3,5-dinitrobenzoyl chloride in acetonitrile, containing 0.5% lutidine. After 1 h at 45 °C the electrode was removed and washed thoroughly by soaking in acetonitrile, methanol, water, and dimethyl sulfoxide. Analysis by x-ray photoelectron spectroscopy (XPS) showed a new N (1s) peak due to the nitro group. Since neither XPS or AES showed a C1 (2p) band after this amidation procedure even though the polylysine surface had a weak band for chlorine before amidation, this indicates a successful reaction. Cyclic voltammetry in  $\text{Me}_2\text{SO}$  produced two reduction peaks on the first scan at  $E_p = -0.79$  and  $-1.23$  V. The corresponding anodic peaks were absent. The integrated current corresponds to  $1.63 \times 10^{-9}$  mol/cm<sup>2</sup> assuming a  $2e^-$  reduction. The background current was negligible, but the true  $n$  value is, of course, unknown. The peak potentials are consistent with a surface bound 3,5-dinitrobenzamide, but it was expected that the process will be reversible as above. Even when the negative going scan was held to  $-0.9$  V avoiding the second wave, no reversibility was seen at sweep rates up to 5.0 V/s. Thus, when attached to the surface, the dinitrobenzoyl anion radical moiety is quite unstable. It has been found previously that, when this species is attached to metal oxides via silylation, reversibility is seen.<sup>11</sup> After a few scans, however, the electroactive surface functionality is also destroyed in this case.

Platinum sheet/polyester electrodes prepared identically with those examined spectroscopically were also used for electrochemistry. We emphasize here the stability and, therefore, the utility of these electrodes for preparative electrochemistry. Steady-state  $i$ - $E$  curves were recorded for mM ferrocene in 50% aqueous ethanol, for 0.07 M ferrocene in ethanol, for oxidation of phenyl acetic acid in 3:7 pyridine-methanol, and for hydrogen evolution in 50% ethanol. Using electrodes coated from 0.03% solution, these curves showed that filming decreased the current density at any potential by about 10% compared with plain platinum. After recording the ferrocene curve (10-min oxidation) and after Kolbe electrolysis of phenyl acetic acid at 100 mA/cm<sup>2</sup> for 30 min, the coated electrodes were rinsed, dried, and reanalyzed by XPS, AES, and CV. These data indicated that the adsorbed polymer was still present. The Kolbe oxidation is an exceptionally rigorous test of film conductance and stability since it shows that high current densities are supported with little added overpotential and that the film is not destroyed under conditions where the electrode is held at a very anodic potential and gas is evolved. We note again that the electrodes are prepared by dipping and there is no polymer added to the electrolysis solution.

There are many points to be fully explored and future publications will demonstrate that a wide variety of metals and polymers give similar results, that interesting electrochemical phenomena are observed and that surface spectroscopy gives some detailed and very useful information about the ultrathin polymer layers.

**Acknowledgment.** Financial support by the National Science Foundation and the General Electric Foundation is gratefully acknowledged. Scanning electron micrographs were generously provided by the Sperry-Univac Corporation. Stimulating discussions and compound **2** were provided by W. Miller.

## References and Notes

- B. F. Watkins, J. R. Behling, E. Kariv, and L. L. Miller, *J. Am. Chem. Soc.*, **97**, 3549 (1975).
- B. E. Firth, L. L. Miller, M. Mitani, T. Rogers, R. Murray, and J. Lennox, *J. Am. Chem. Soc.*, **98**, 8271 (1976).
- J. C. Lennox and R. W. Murray, *J. Am. Chem. Soc.*, **78**, 395 (1977); C. M. Elliot and R. W. Murray, *Anal. Chem.*, **48**, 1247 (1976).
- M. T. Henne, G. P. Royer, J. F. Evans, and T. Kuwana, *J. Electroanal. Chem.*, **80**, 409 (1977).
- M. Fujihira, A. Tamura, and T. Osa, *Chem. Lett.*, 361 (1977).
- P. R. Moses, L. Wier, and R. W. Murray, *Anal. Chem.*, **47**, 1882 (1975).
- P. R. Moses and R. W. Murray, *J. Am. Chem. Soc.*, **98**, 7435 (1976).
- N. R. Armstrong, A. W. C. Lin, M. Fujihira, and T. Kuwana, *Anal. Chem.*, **48**, 741 (1976).
- B. E. Firth and L. L. Miller, *J. Am. Chem. Soc.*, **98**, 8272 (1976).
- M. Fujihira, T. Matsue, and T. Osa, *Chem. Lett.*, 875 (1976).
- J. R. Lenhard and R. W. Murray, *J. Electroanal. Chem.*, **78**, 195 (1977).
- R. J. Burt, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 940 (1976).
- D. F. Untereker et al., *J. Electroanal. Chem.*, **81**, 309 (1977).
- R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, **77**, 1401, 1411 (1973); **81**, 734 (1977).
- A. P. Brown, C. Koval, and F. C. Anson, *J. Electroanal. Chem.*, **72**, 379 (1977).
- Yu. S. Lipatov and L. M. Sergeeva, "Adsorption of Polymers", Wiley, New York, N.Y., 1974.
- Compound **1** was obtained from Polysciences, Inc., Cat. No. 4301, Lot No. 303-125; **2** was supplied by Professor W. Miller.
- T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, N.Y., 1975; D. M. Hercules and J. C. Carver, *Anal. Chem.*, **46**, 133R (1974), and references cited therein.
- This is based upon elemental carbon as an experimental analogue and is widely accepted.<sup>20</sup> We note, however, that very much longer escape depths would be calculated using data obtained from oriented fatty acid monolayers.<sup>21</sup>
- C. J. Powell, *Surf. Sci.*, **44**, 29 (1974).
- B. L. Henke, *J. Phys. (Paris) C*, **4**, 115 (1971).

Larry L. Miller,\* Michael R. Van De Mark

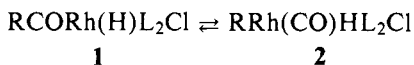
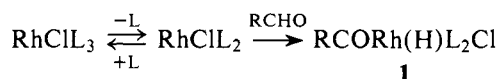
Department of Chemistry, University of Minnesota  
Minneapolis, Minnesota 55455

Received October 17, 1977

## Isolation of a Stable Acylrhodium(III) Hydride Intermediate Formed during Aldehyde Decarbonylation. Hydroacylation

Sir:

The decarbonylation of aldehydes by  $\text{RhCl}(\text{PPh}_3)_3$  has been established as a useful synthetic reaction, appearing in numerous total syntheses of natural products, and is the key step in a method for the stereospecific introduction of angular methyl groups.<sup>1</sup> The mechanism



proposed for decarbonylation involves oxidative addition of the aldehyde C-H bond to form a coordinatively unsaturated complex, an acylrhodium(III) hydride (**1**), as an intermediate. This intermediate can then undergo an acyl-alkyl rearrangement, and subsequent hydrogen transfer to the alkyl group forms *trans*- $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$  and hydrocarbon.<sup>2</sup> The principal support for this proposal comes from studies on the decarbonylation of acid chlorides by  $\text{RhCl}(\text{PPh}_3)_3$ , in which intermediates analogous to **1** and **2** can be isolated.<sup>3</sup> However, prior to this work, no intermediates have been isolated from  $\text{RhCl}(\text{PPh}_3)_3$ -promoted aldehyde decarbonylation reactions.<sup>4</sup>

The cleavage of a carbon-hydrogen bond, as in the formation of **1**, occurs often in organometallic reactions. In some cases (e.g.,  $\text{PtCl}_2$  catalyzed hydrogen-deuterium exchange)<sup>5</sup> carbon-metal bonded species are transient intermediates, while, in others, where a coordinating group is available to form a five-membered chelate (the cyclometalation reaction),<sup>6</sup> ex-