

The formation of the cyclohexadienone **4a** is the result of an unprecedented "para"-two-alkyne annulation. Reduction of **4a** with zinc and acetic acid gave the phenol **9a** which was found not to be identical with the phenol **2a** also isolated from this reaction. Although phenol products resulting from the incorporation of two molecules of alkyne, a carbon monoxide and a carbene ligand, have been observed before, they have only been reported with the regiochemistry indicated by **2** in which the carbene and carbon monoxide ligands are introduced in adjacent positions in the newly formed aromatic nuclei.¹⁰ The "para"-two-alkyne phenol (and diene) products were observed for the reactions in entries a, b, c and f in Table I. The assignment of their structures was made for the phenols **2b** and **9b** on the basis of NOE experiments and ¹³C labeling experiments which are discussed in the Supplementary Material. Possible mechanisms to account for the formation of para-two-alkyne phenols include a [4 + 2] cycloaddition of an alkyne to the vinylcarbene complex intermediate **11** and a [4 + 2] cycloaddition to the vinylketene complexed intermediate **17**. Current studies are directed to determine how the reaction conditions can lead to differentiation between "para"- and "ortho"-two-alkyne annulated products.

The uniqueness of the transformations leading to the 2-vinylcyclopentene-1,3-diones and para-two-alkyne phenols should promote further study of the mechanistic issues and synthetic opportunities raised by these initial observations.

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Supplementary Material Available: Spectral data for all new compounds, structural assignment of the phenols **2** and **9**, and X-ray diffraction data for compound **3a** (21 pages). Ordering information is given on any current masthead page.

Combining Spontaneous Molecular Assembly with Microfabrication to Pattern Surfaces: Selective Binding of Isonitriles to Platinum Microwires and Characterization by Electrochemistry and Surface Spectroscopy

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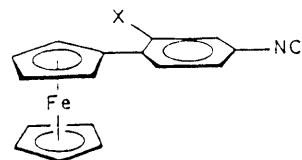
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We wish to report selective modification of the Pt microelectrodes of a microfabricated array by using redox reagents I and II having an isonitrile, -NC, functional group, Scheme I. Building



I, X = H;
II, X = Cl.

on studies of macroscopic surface chemistry,¹ selective coordination chemistry of RSH and RCOOH has been recently used to assemble monolayers of long chain hydrocarbons or perfluorocarbons onto mixed-metal microwire arrays.² Our new results demonstrate the ability to combine microfabrication and surface coordination chemistry to pattern a surface with *redox active molecular reagents*.

The rationale for investigating the binding of RNC reagents to Pt is that RNC is isoelectronic with CO which is known to bind firmly to Pt.³ It has already been shown that gas-phase CH₃NC will bind to (111) Pt⁴ and (111) Rh⁵ in the manner implied in Scheme I. A large number of RNC transition metal complexes are known,⁶ and these can be viewed as derivatives of CO complexes. Importantly, RNC ligands offer considerable diversity in properties via variation in R.⁷ While a few functional groups, e.g., -SH or olefin, have been used to bind redox reagents to electrode surfaces,^{1a,d,e} the use of the -NC group for surface attachment has not been explored.

Electrochemical and surface spectroscopic techniques have been used to establish the binding of I and II to Pt electrode surfaces. I and II were prepared from the corresponding ferrocenylanilines³ and incorporate the reversible redox function (the ferrocenyl group) and unique elements (e.g., Fe in I or Cl in II) to facilitate surface analysis by X-ray photoelectron spectroscopy, XPS,⁸ or Auger electron spectroscopy, AES.⁸ Typically, pretreated Pt⁹ was exposed to ~1 mM I or II in CH₃CN solvent for 5 min at 298 K under Ar, removed, and washed thoroughly with CH₃CN, prior to analysis. XPS shows the Fe 2p_{3/2}, 707.9 eV, and N 1s signals, 398 eV, at intensities consistent with about one monolayer of intact RNC. The same modification and analysis procedure using phenylferrocene, containing no -NC group, shows no surface-confined Fe-containing material. Fourier transform infrared spectroscopy, FTIR, shows the -NC vibration at 2137 cm⁻¹ for I bound to Pt¹⁰ vs 2127 cm⁻¹ for I in CH₂Cl₂. For comparison,

(1) (a) Hubbard, A. T. *Chem. Rev.* 1988, 88, 633 and references cited therein. (b) Allara, D. L.; Nuzzo, R. G. *Langmuir* 1985, 1, 45. (c) Allara, D. L.; Nuzzo, R. G. *Langmuir* 1985, 1, 52. (d) Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* 1988, 332, 426. (e) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 191. (f) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559. (g) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321 and the references on thiol adsorption cited therein.

(2) (a) Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science* 1989, in press.

(3) (a) Russell, J. W.; Overend, J.; Scanlon, K.; Severson, M.; Bewick, A. *J. Phys. Chem.* 1982, 86, 3066. (b) Russell, J. W.; Severson, M.; Scanlon, K.; Overend, J.; Bewick, A. *J. Phys. Chem.* 1982, 87, 293. (c) Golden, W. G.; Kunimatsu, K.; Seki, H. *J. Phys. Chem.* 1984, 88, 1275. (d) Kunimatsu, K.; Golden, W. G.; Seki, H.; Philpott, M. R. *Langmuir* 1985, 1, 245. (e) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G., II; Philpott, M. R. *Surf. Sci.* 1985, 158, 586.

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(7) (a) Grundmann, C. In *Methoden der Organischen Chemie*; Folbe, J., Ed.; Thieme-Verlag: Stuttgart, 1985; p 1611. (b) Skorna, G.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 259. (c) *Isonitrile Chemistry*; Ugi, I., Ed.; Academic: New York, 1971.

(8) Experimental details concerning synthesis, XPS, and AES are given in the Supplementary Material.

(9) Commercial Pt, vacuum deposited Pt, or microelectrodes were sonicated for ~30 min in each of the three solvents of increasing polarity (usually hexane, CH₂Cl₂, and CH₃OH) followed by an O₂ plasma treatment in a Harrick PDC-23G for 1-5 min, 0.3 Torr at medium power (40 W), and used immediately.

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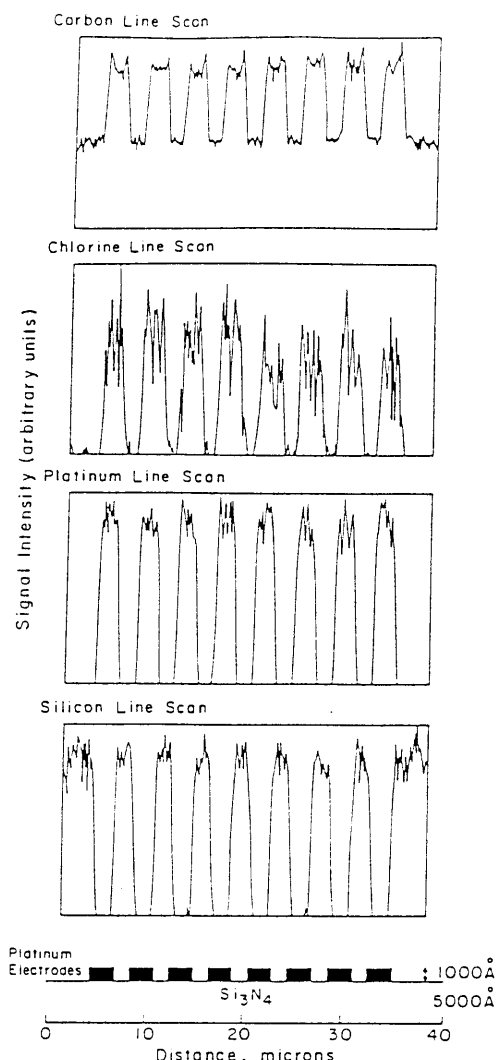
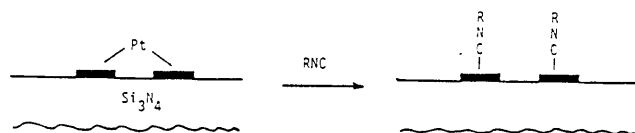


Figure 1. Four AES element line scans (C, Cl, Pt, Si) across a Pt microelectrode array derivatized with II. Scans are aligned with a scale showing positions of microelectrodes. The data show Cl from II to be found on the Pt microwires not on the Si_3N_4 . The electrochemical characterization shown in Figure 2 is for the same array but prior to analysis by AES.

Scheme 1. Cross Sectional View of Pt Microwire Array Selectively Modified with RNC



we find the $-\text{NC}$ vibration in $\text{W}(\text{CO})_5(\text{CNR})$ ($\text{CNR} = \text{I}$) to be at 2143 cm^{-1} in CH_2Cl_2 . Thus, XPS, FTIR, and comparison of behavior of I and II with phenylferrocene show that the $-\text{NC}$ group does yield surface-confined material. Linear sweep cyclic voltammetry in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{PF}_6$ at 258 K shows a reversible, persistent ($>1 \text{ h}$) wave at $+0.6 \text{ V}$ vs Ag and coverage of $2.4 \pm 0.2 \times 10^{-10} \text{ mol/cm}^2$. Therefore, the data are consistent with spontaneous attachment of about one monolayer of I or II to Pt surfaces via the $-\text{NC}-\text{Pt}$ linkage.

Patterning in two dimensions using the spontaneous attachment of II to Pt has been demonstrated by using Pt microelectrode arrays. Each microfabricated¹¹ array consists of eight, individually

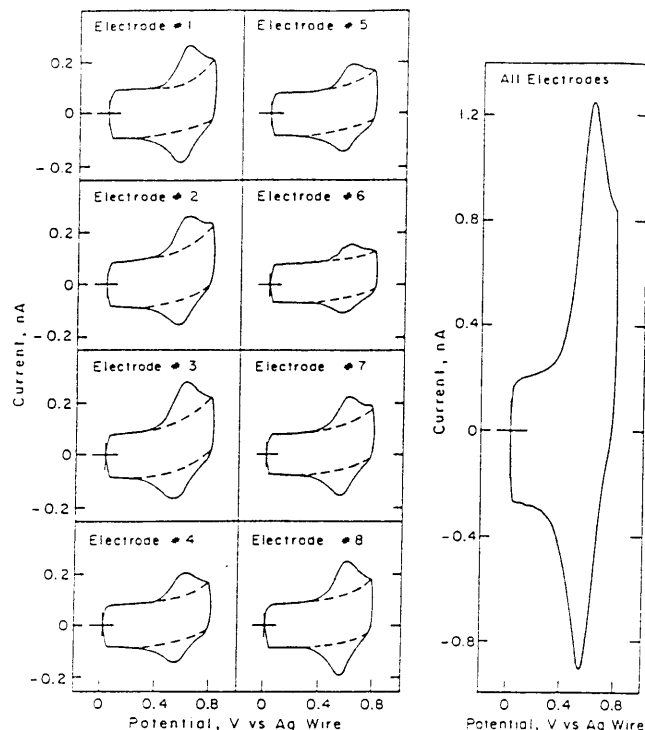


Figure 2. Cyclic voltammetry (500 mV/s) of II adsorbed to eight Pt microelectrodes in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{PF}_6$ at 258 K.

addressable, Pt microelectrodes ($\sim 2 \mu\text{m}$ wide, $\sim 90 \mu\text{m}$ long, $\sim 0.1 \mu\text{m}$ thick) separated from each other by $1.4 \mu\text{m}$ on a flat Si_3N_4 substrate. Immersion of a pretreated Pt microelectrode array into a 1 mM CH_3CN solution of II for 5 min, followed by thorough washing with CH_3CN , results in a surface where the ferrocenyl units are in place on Pt but *not* on Si_3N_4 . XPS and AES provide evidence for selective (at least 100:1) attachment of I and II to Pt vs Si_3N_4 . XPS shows no detectable $\text{Fe } 2p_{3/2}$ signal in Si_3N_4 regions of the chip, whereas Pt regions have an easily observed $\text{Fe } 2p_{3/2}$ signal.

AES is a higher lateral resolution ($\sim 50 \text{ nm}$) technique than XPS ($\sim 150 \mu\text{m}$) and allows detection of the unique element Cl from II only on the Pt, Figure 1. In particular, the Cl from II is shown to be in registration with the Pt in an element line scan, whereas no Cl from II is detected in the Si_3N_4 region. The C line scan shows substantial enrichment of C on the Pt, consistent with uptake of II on the Pt. Like XPS, AES shows a strong selectivity ($>100:1$) of II for Pt vs Si_3N_4 . Linear sweep cyclic voltammetry, Figure 2, as on macroscopic Pt electrodes, shows a reversible, cyclic voltammetry wave at $+0.6 \text{ V}$ vs Ag. The eight Pt microelectrodes each show electroactive molecules, $\sim 2.4 \pm 0.3 \times 10^{-10} \text{ mol/cm}^2$, or about one monolayer.

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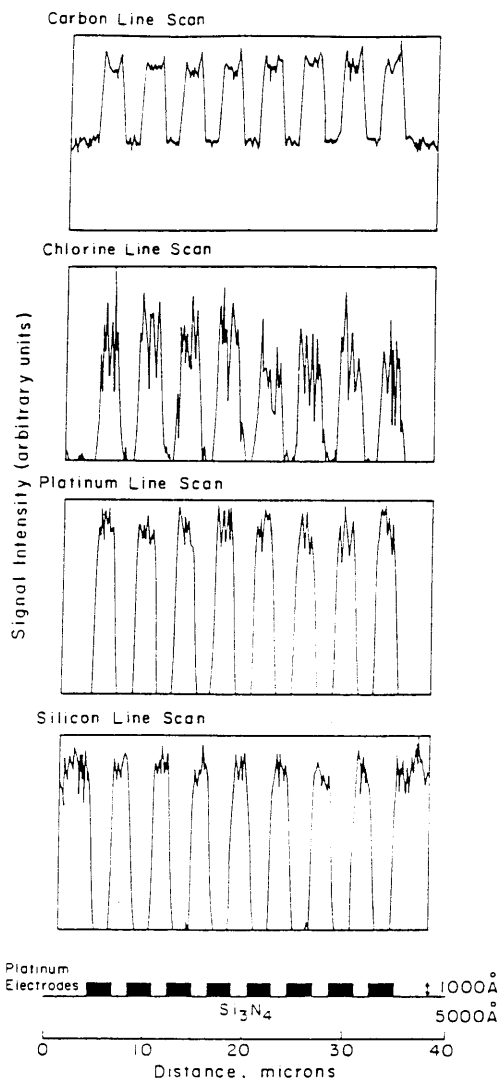
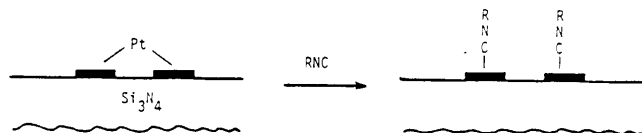


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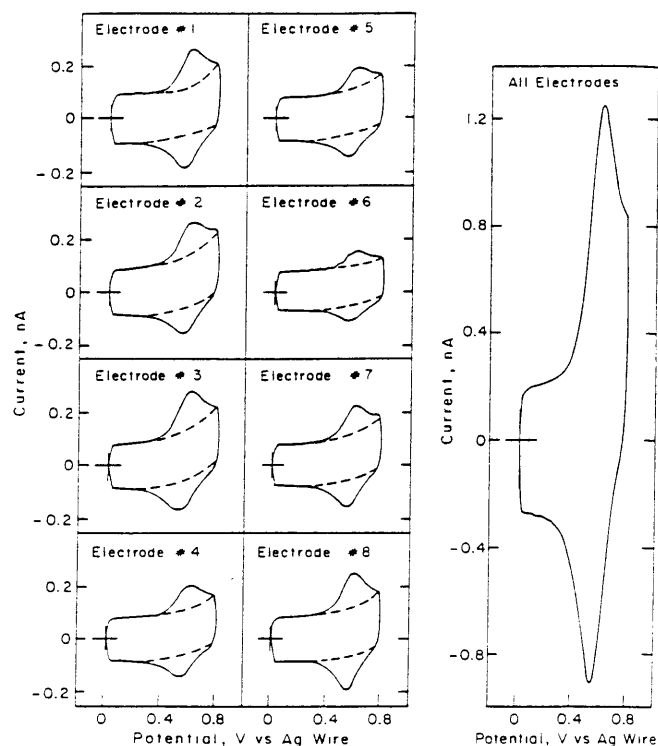


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