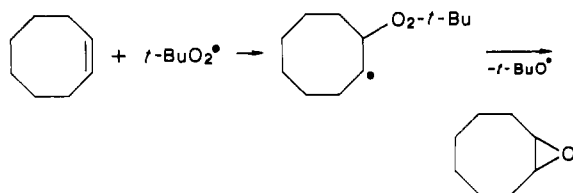


Figure 1. Decomposition of TBHP: (A) in the presence of **4** (2.2×10^{-3} M); (B) in the presence of **5**. (C) in the presence of kaolinite clay. All of the above experiments were carried out with imidazole (0.026 M). The concentration of TBHP was determined iodometrically.

Scheme III



In contrast to the findings with cyclohexene, the cyclooctene oxide formation may occur not only via the oxometal route, but also by a free-radical pathway, which is shown in Scheme III.^{13,14} Our results with **4** and **5** indicate nearly identical yields of cyclooctene oxide. To delineate the relative importance of the above pathways with **4** and **5**, experiments were conducted with radical inhibitor **6**. As shown in Table I, addition of the inhibitor led to a sharp drop in epoxide yield with **4**, while no change was observed with **5**. These results therefore suggest that epoxide formation occurs predominantly via the oxometal route with **5**, while the reverse is true with **4**.

In conclusion, the above study has demonstrated that the radical pathway for TBHP decomposition, leading either to side-product formation with cyclohexene or to epoxide formation with cyclooctene, is suppressed on the clay-adsorbed catalyst and that, instead, the oxometal route for epoxidation is the predominant reaction pathway. We note however, that the reactions with **5** are more sluggish than those with **4**. Anchoring of **4** is beneficial when TBHP is the oxidant, while no such advantage accrues with oxidants such as PhIO, which in any case yield epoxides cleanly via the oxometal route.

Acknowledgment. We thank IEL Limited for financial support and Dr. P. K. Ghosh for extremely helpful discussions.

Registry No. **4**, 117340-85-9; **6**, 128-37-0; TBHP, 75-91-2; PhIO, 536-80-1; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

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Schiff Base Complex Formation on a Copper Surface Detected by Raman Scattering

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Received December 17, 1987

Metal complex formation at a metal surface is a little understood process that is important in such fields as corrosion inhibition and supported heterogeneous catalysis. A major problem is in the identification in situ of the species formed in surface films, which may on occasion be as thin as monolayers. By using surface Raman spectroscopy with a system in which the complex but not the ligand contains a chromophore, we have been able to observe complex formation on a copper surface and observed a subsequent reaction at the surface. In the process we have found behavior that may yet prove of value in investigations of the nature of the enhancement in surface enhanced resonance Raman scattering (SERRS).

Various molecules adsorbed on metal surfaces have been observed by using surface enhanced Raman scattering (SERS).¹ There is a molecular specificity resulting from the nature of the metal to adsorbate bond, and the nature of the surface is critical, with some form of surface roughness usually required.² This is usually accompanied in solution at an electrode by applying oxidation-reduction cycles (ORC's) to obtain a surface roughened by etching and redepositing metal atoms.³ The purpose of this roughening appears to be to enable localized surface electron waves to be propagated and to aid in reemission. The natural frequencies of these waves is dependent on the metal, and with visible lasers the effect is more efficient with silver and to a lesser extent copper and gold. Such structured surfaces provide intense scattering that is voltage dependent. From the viewpoint of a chemist, the technique is limited in that the signals depend so heavily on the nature of the surface that many chemical reactions of interest cannot be followed either because during reaction the surface anneals and quenches the SERS signal or because the potentials required for SERS are incompatible with the reaction to be studied.

However, creation of a resonance chromophore on complex formation may enable detection of a Raman signal from a few monolayers due to resonance enhancement even in a wavelength region where the surface would not be expected to be SERS active. Essentially, this resonance is a molecular property and would be expected to be less surface sensitive. It may, in some circumstances, be no more than a molecular resonance. However, in some cases it may be equivalent to the "chemical effect" of the charge-transfer term of SERS,^{4,5} and by using radiation in a wavelength range where this effect is not expected to be strong, it may be possible to disentangle these two terms.

Here we report the use of this method to follow the formation of a complex with an aldehyde at a copper/copper oxide surface. We further follow the formation of a Schiff base complex by the addition of *o*-aminophenol to the aldehyde-treated surface. A wavelength of excitation coincident with electronic transitions of the bulk complexes in the blue is used.⁶

A carefully polished and treated copper working electrode was used in a modification of a three-electrode cell described previously.⁷ It was cycled five times between 0 and -0.1 V vs SCE

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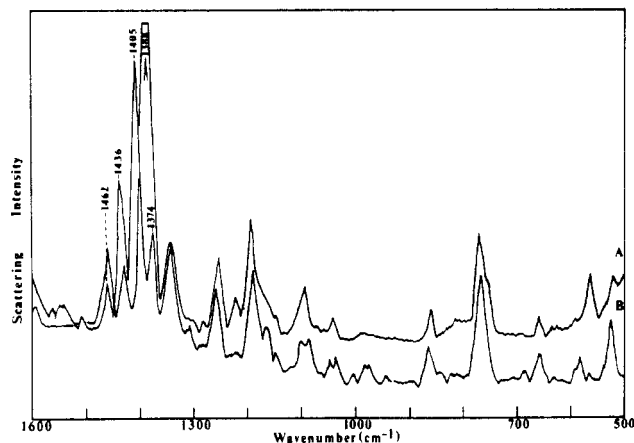


Figure 1. Raman spectra of bis(2-hydroxy-1-naphthaldehydato)copper(II) as a free compound (A) and as a layer on a copper metal surface (B).

in an aqueous ethanolic solution of 0.1 M 2-hydroxy-1-naphthaldehyde in saturated K_2SO_4 as electrolyte. The electrode was thoroughly washed with distilled water to remove all ligand and ethanol and was immersed in distilled water or 0.1 M K_2SO_4 before measurement. Schiff base complex formation was completed by adding *o*-aminophenol in aqueous ethanol and washing off ligand and solvent as before. One hundred milliwatts of 457.9-nm excitation was provided by a 171 Spectra Physics argon ion laser. Scattering of 90° was detected by using an Anaspec Modified Cary 81 instrument with a cooled photomultiplier. Film thicknesses were determined by atomic absorption measurements of the film dissolved off in DMSO. They indicated a surface layer coverage of between 1 and 3 monolayers.

A copper metal surface in aqueous solution is covered with a thin layer of copper(I) oxide with some copper(II) ions at the interface between the surface and solution. On addition of 2-hydroxy-1-naphthaldehyde, a copper(II) complex would be expected to form. The resonance Raman spectrum of a fresh surface obtained by electrochemical treatment followed by addition of the ligand is comparable to the spectrum obtained from a solid sample of bis(2-hydroxy-1-naphthaldehydato)copper(II), clearly indicating a similar species (Figure 1). There are, however, salient modifications: for example, the emergence of a new band at 1374 cm^{-1} , a marked relative increase of the pair of bands between 1400 and 1500 cm^{-1} , and a shift of $+17\text{ cm}^{-1}$ for the strongest band at about 1400 cm^{-1} . It would seem that the surface-bound complex retains the trans configuration and the 2:1 stoichiometry of the bulk complex, since more extensive modifications would have been expected if either had changed. However, the changes noted are significant and probably reflect steric restraints imposed by coordination to a fifth site, which in this case would involve metal ion complexing to oxide or hydroxide ions, or water molecules on the surface.

From Figure 2, it may be seen that the formation of the Schiff base complex is not instantaneous and that the gradual disappearance of the band at 1405 cm^{-1} and the appearance of the band at 1393 cm^{-1} are effective indicators of conversion of bis(2-hydroxy-1-naphthaldehydato)copper(II) to a copper Schiff base. The characteristic C=N stretch of Schiff bases at approximately 1600 cm^{-1} is also clearly resolved in Figure 2C. Comparison of the free Schiff base complex spectrum with the spectrum of the complex on the electrode shows that there is no appreciable difference between the surface and bulk species. Thus, the modifications found in the aldehyde where a smaller, more mobile ligand is involved are not carried through to the more rigid Schiff base.

Varying the electrode potential between 0 and -0.6 V vs SCE produced little change in the Raman spectra of both the aldehyde

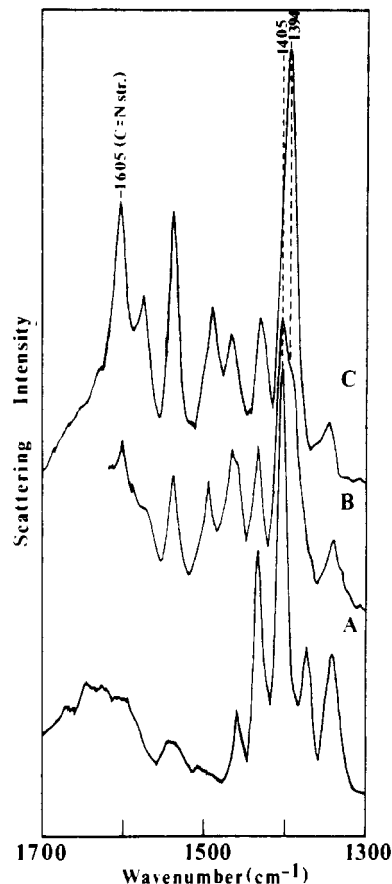


Figure 2. Raman spectra showing the formation of a copper(II) Schiff base on a copper surface by addition of *o*-aminophenol to a preformed layer of bis(2-hydroxy-1-naphthaldehydato)copper(II) (A). Spectrum B represents an intermediate stage and spectrum C the final product.

complex precursor and the Schiff base complex. In this experiment there is little indication of a voltage dependence, and consequently the method can readily be used to examine reactions at the metal surface in a wide range of conditions.

Previous studies of metal complex formation at a metal surface have used ligands such as phenanthroline⁸ and bipyridyl⁷ to complex with ions generated electrochemically from metal surfaces. These studies are usually carried out in the presence of the ligand, and the signals are similar to those of the bulk complex and can be removed by anodization. It seems likely that the signals are from complexes in solution and/or complexes adsorbed with little change at the electrode surface. In this study we have observed frequency and intensity changes that indicate the formation of new species on the surface. These moieties remain attached to the surface even after removal of the ligand and anodization within reasonable voltage limits. The significance of this study is that it uses Raman spectroscopy to reveal a form of surface complexation in which the surface plays an active part in the nature of the complex formed.

Thus, by the choice of systems in which a resonant chromophore is formed on complexing at a surface, surface resonance Raman spectroscopy provides a powerful tool to probe relatively inaccessible surface reactions. It is likely that the chemistry can be extended to include other Schiff base ligands and perhaps other ligands involving other chromophores. In addition, there appear to be important ramifications for theoretical models explaining enhancement of Raman scattering because the Raman spectra presented were recorded by using blue excitation, where SERS from copper is expected to be weak.⁹ The high-quality spectra obtained from these electrodes appear to result from efficient

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competition from the resonant scattering of the molecules with the optical deenhancement from the copper surface.

Registry No. *o*-Aminophenol, 95-55-6; 2-hydroxy-1-naphthaldehyde, 708-06-5.

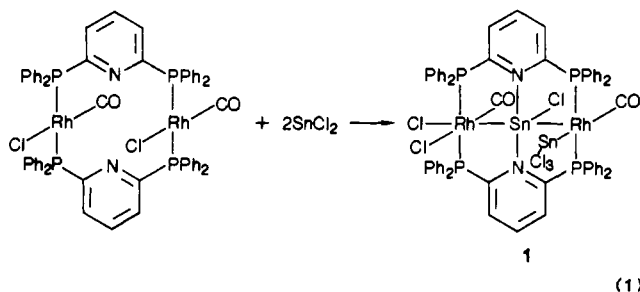
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Novel Oxidation Resulting from the Reaction of Tin(II) Chloride with $\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2$: Structure of $\text{Ir}_2(\text{CO})_2(\text{SnCl}_3)_2(\mu\text{-S})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2$

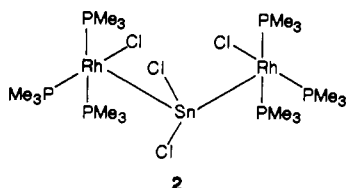
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Received June 13, 1988

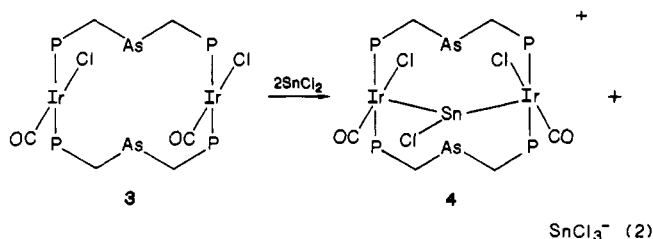
Tin(II) chloride is known to interact with complexes of the platinum metals and to enhance their catalytic activity.¹ Frequently this occurs through the insertion into M-Cl bonds to give M-SnCl₃ groups. Recently, however, several new modes of bonding of tin(II) chloride with platinum metal complexes have been found. Reaction 1, which involves a rhodium metallo-



macrocycle, yields **1** in which two modes of interaction are seen. One tin(II) chloride forms a SnCl₃⁻ group in an entirely normal fashion, while another tin(II) chloride has entered the center of the macrocycle and transferred a chloride ligand (via oxidative addition) to the rhodium on the left side.² Tin(II) chloride reacts with 2 equiv of Rh(PMe₃)₃Cl to yield the novel unbridged Rh-Sn-Rh chain compound **2**.³ The metallomacrocycle, Ir₂(CO)₂Cl₂(μ-Ph₂PCH₂As(Ph)CH₂PPh₂)₂ (**3**), reacts with tin(II) chloride to give the deep blue/green adduct **4** via eq 2.^{4,5} Com-



(CO)₂Cl₂(μ-Ph₂PCH₂As(Ph)CH₂PPh₂)₂ (**3**), reacts with tin(II) chloride to give the deep blue/green adduct **4** via eq 2.^{4,5} Com-



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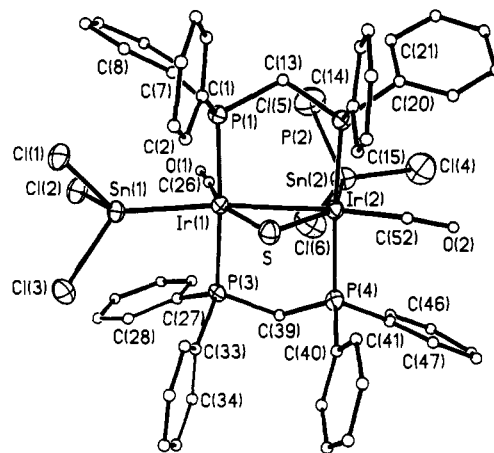
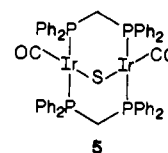


Figure 1. Perspective view of $\text{Ir}_2(\text{CO})_2(\text{SnCl}_3)_2(\mu\text{-S})(\mu\text{-dpm})_2$ showing 50% thermal contours for the heavy atoms and uniform, arbitrarily sized circles for carbon and oxygen.

pound **4** has the tin complexed by the two iridium ions; no Sn-As bonds are present. In order to explore the effects of orientation and separation of the two Ir coordination planes on the ability to bind tin(II) in this fashion, we undertook an examination of the reaction of tin(II) chloride with the A-frame complex $\text{Ir}_2(\text{CO})_2\text{Cl}_2(\mu\text{-S})(\mu\text{-dpm})_2$ (**5**) (dpm is bis(diphenylphosphino)-



methane). This complex has a much shorter Ir...Ir separation (~3.15 Å estimated from the rhodium analogue⁷) than that in the metallomacrocycle **3** (where a similar estimate is ~5.4 Å⁸) and has the iridium coordination planes inclined at an angle of 75° rather than nearly parallel as in **3**.

Results

Addition of an excess of tin(II) chloride in methanol to a purple solution of $\text{Ir}_2(\text{CO})_2(\mu\text{-S})(\mu\text{-dpm})_2$ in dichloromethane/methanol immediately produces a yellow solution. When allowed to stand for 24 h, this produces green crystals of $\text{Ir}_2(\text{CO})_2(\text{SnCl}_3)_2(\mu\text{-S})(\mu\text{-dpm})_2$ (**6**) in 81% yield. These have no significant solubility in any common organic solvent, although they do impart a faint greenish color to dimethyl sulfoxide, benzene, and toluene. Because their intense color was somewhat similar to that of **4**, we suspected that they might have a similar structure. The infrared spectrum (Nujol), however, shows carbon monoxide stretching vibrations at 2031 m, 1998 vs and 1978 s cm⁻¹. The increase in these values compared to those of **1** (1918 s, 1902 vs cm⁻¹)⁶ suggests that the original complex has undergone oxidation in some fashion.

Crystals of 6·1.5CH₂Cl₂ suitable for X-ray diffraction were available directly from the original preparation. Atomic positional parameters are given in Table I. Table II contains selected bond distances and angles. Figure 1 shows a perspective view of the molecule.

The complex retains the A-frame structure present in **1** with two trans-dpm bridges and a bridging sulfide. Two SnCl₃⁻ ligands have been added to the molecule (which has undergone a net

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