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Communications

Surface Coordination Chemistry of Well-Defined Platinum Electrodes.[1,2] Surface Polyprotic Acidity of Pt(111)($2\sqrt{3}\times2\sqrt{3}$)R30°-CNH

Sir:

We are currently investigating the interaction of halides and pseudohalides with structurally and chemically well-defined platinum single-crystal surfaces in aqueous solutions as a means of understanding electrochemical processes at the molecular level.[3-5] We wish to describe here new studies, based on low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), of the reaction of Pt(111) with dilute aqueous solutions of metal cyanides. We have found the following: (i) Surface coordination of the CN^- ligands occurred spontaneously to form a highly ordered ionic layer, which underwent cation exchange without compositional loss or structural rearrangements. (ii) This cyanide layer exhibited polyprotic behavior; at pH ≤ 9 it is only partially deprotonated to form a lattice of isolated anions surrounded by neutral hydrogen isocyanide (HNC) molecules. (iii) At higher pH, a second stage of ionization was observed, yielding a lattice of adjacent, negatively charged CN^- species.

This is the first structural and chemical study of ion coordination from solution onto well-defined metal surfaces; it has important ramifications in surface coordination chemistry,[1,2] electrical double-layer structure,[4,5] and electrocatalysis.[7]

Experimental Section.[3-6] The Pt(111) single crystal was oriented and polished such that all six faces were crystallographically equivalent. Surface cleanliness was attained by Ar^+ ion bombardment followed by thermal annealing at 700 °C; verification was by LEED and AES. The crystal was isolated in an argon-filled antechamber for immersion into various reagent solutions; reaction time was 180 s. Following immersion and evacuation, the surface was again characterized by LEED and AES.[3-6] Solutions were prepared from Ar-saturated pyrolytically distilled water.[8]

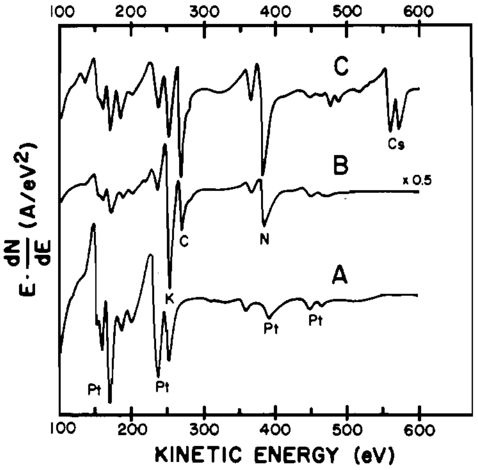

Figure 1. Auger electron spectra: (A) Pt(111); (B) Pt(111)($2\sqrt{3}\times2\sqrt{3}$)R30°-CNK, twofold attenuation due to intense K peak; (C) Pt(111)($2\sqrt{3}\times2\sqrt{3}$)R30°-CNCs. experimental conditions: incident beam 11° from surface plane; 2000 eV; cylindrical mirror analyzer; modulation amplitude 5 V.

Quantitative Auger spectra were obtained with a cylindrical mirror analyzer.[3-6] The surface coverage of the *i*th element, θ_i (Γ_i/Γ_{Pt}, where Γ_i is the surface concentration of the *i*th element and $\Gamma_{Pt(111)}$ = 2.49 nmol cm^{-2}) was extracted from numerical double-integrals, I_x, of the modulated spectra according to[5]

$$\theta_i \equiv \frac{\Gamma_i}{\Gamma_{Pt}} = \frac{I_i/I_{Pt}}{I_I/I_{Pt}}\left[\frac{G_I}{G_i}\right]\frac{\Gamma_I}{\Gamma_{Pt}} \qquad (1)$$

where the *subscript* I is the element iodine. Values of Auger electron yield factors, G, for different elements have been tabulated.[5] Normalization of I_i by I_{Pt}, the Pt signal amplitude at 160 eV, eliminated fluctuations due to differences in sample position relative to the analyzer, while normalization with respect to I_I/I_{Pt} for a well-characterized iodine adlattice[10] served to calibrate spectrometer detectivity. Further information on AES[3,5,9] and on LEED[3,11] experiments has been presented elsewhere.

Results and Discussion. Figure 1A shows the Auger spectrum of clean Pt(111); only transitions assignable to Pt[12] can be seen. The LEED pattern characteristic of this untreated surface[13] is

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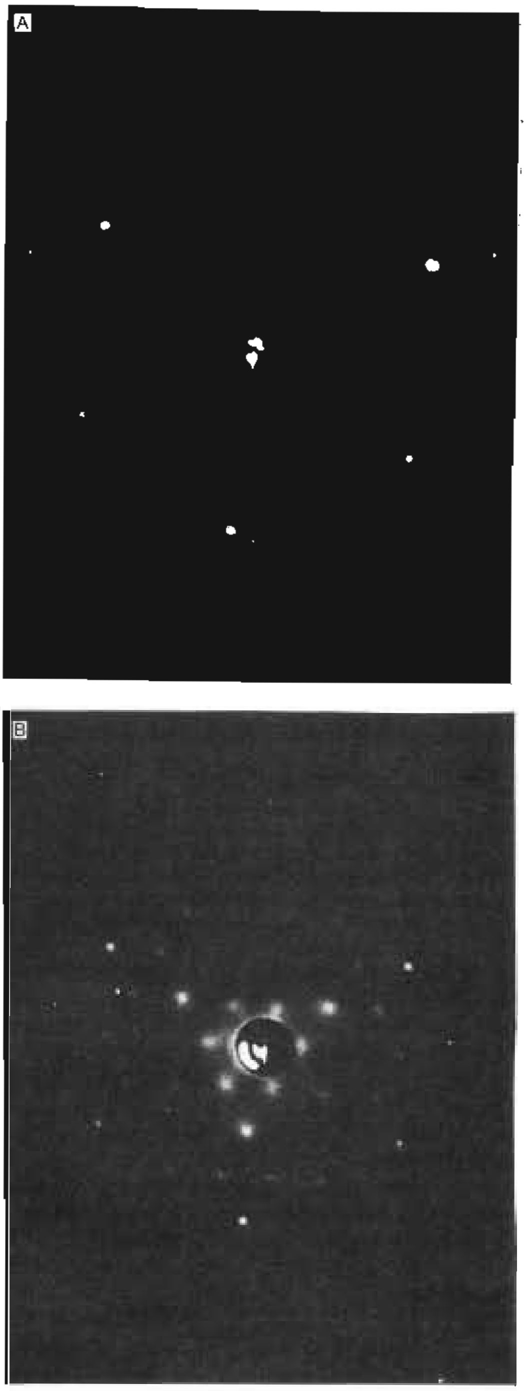

Figure 2. LEED patterns: (A) Pt(111), 66 eV; (B) Pt(111)(2√3×2-√3)R30°-CNK, 68 eV, cyanide adsorbed from 10^{-4} M aqueous KCN.

shown in Figure 2A. The LEED pattern that resulted after immersion of the clean surface in 0.1 mM aqueous KCN is displayed in Figure 2B; this pattern corresponds to the real lattice structures, Pt(111)(2√3×2√3)-CNK[4] (cf. Figure 4 below). The Auger spectrum for the latter surface layer is given in Figure 1B, where the presence of Auger peaks due to K, C, and N is obvious.[4] Ion exchange[5] of the K^+ counterions by Cs^+ ions (0.1 mM CsCl in neutral solutions) produced *no* changes either in the LEED pattern or in the C and N Auger peak intensities (Figure 1C); displacement of K^+ by Cs^+ was indicated by disappearance of the K Auger peak and emergence of the Cs doublet. Quantitation of the metal counterion retained by the anionic cyanide layer was more convenient with Cs since the K Auger peak overlapped with the C peak (Figure 1B).

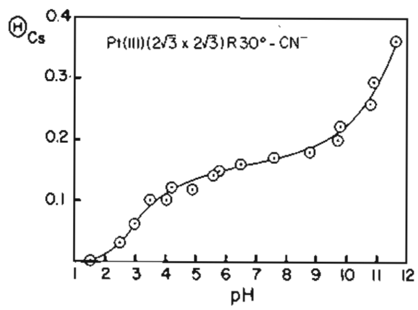

Figure 3. Cs^+ cation packing density, θ_{Cs}, at Pt(111)(2√3×2√3)-R30°-CN^- as a function of pH. Experimental conditions: 10^{-4} M aqueous CsCN.

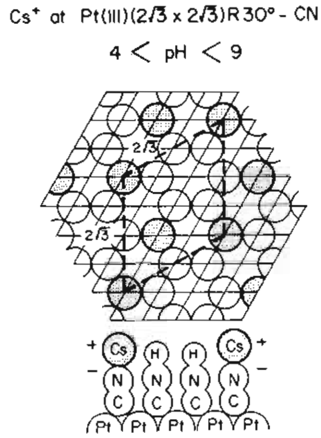

Figure 4. Surface structure of Pt(111)(2√3×2√3)-CsCN at 4 ≤ pH ≤9. Shaded circles represent CsCN ion pairs; open circles represent HNC neutral molecules.

Quantitative measurement[5] of C, N, and Cs coverages from the Auger spectrum in Figure 1C gave $\theta_N = 0.8 \pm 0.1$, $\theta_C = 0.6 \pm 0.1$, and $\theta_{Cs} = 0.21 \pm 0.02$. The C Auger peak was attenuated by a factor of 0.8 due to scattering by the N atoms which are atop the Pt-bonded C atoms[14] in the vertically attached cyanide layer.[5] Taking $\theta_{CN} = \theta_N$, the Cs^+/CN ratio was therefore 0.2/0.8 = 0.25; this ratio indicates that, in neutral solutions, the cyanide layer is only partially ionized.

The effect of pH on the amount of Cs^+ retained by the cyanide layer is shown in Figure 3: (i) Below pH 3, no Cs^+ was retained because the large excess of H^+ ions in solution ($\geq 10^{-2}$ M H^+ compared with 10^{-4} M Cs^+) displaced Cs^+ ions from the surface. (ii) Between pH 4 and 9, the amount of Cs^+ retained was virtually unchanged, with $Cs^+/CN = 0.25$ as in Figure 1C. (iii) Above pH 9, θ_{Cs} increased rapidly with pH, indicating further (base-induced) deprotonation of the cyanide layer.

The above results demonstrate that a single surface-coordinated layer of CN^- ligands behaves as a polyprotic acid. Combined analysis of LEED and AES data strongly suggests that the first stage of dissociation occurs readily (as for strong acid) to form a lattice of isolated CN^- ions surrounded by neutral hyrdogen isocyanide (CNH) molecules. (Although free CNH has not been isolated, the existence of metal–C-coordinated CNH has been postulated to explain the stepwise acid dissociation[15] of $H_2Fe(CN)_6^{2-}$ and the infrared spectra of anhydride complex cyanide acids;[16] the linkage isomerism of the CN^- ligand itself is well-known.[17]) The most probable surface structure for this partially dissociated layer is depicted in Figure 4; it is stable toward further

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deprotonation up to about pH 9. The observed resistance to full ionization is due to a reluctance of the cyanide layer to form an energetically unfavorable lattice consisting of adjacent, mutually repelling anions.

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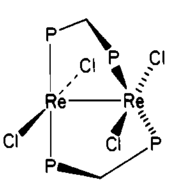
Stabilization of Dinuclear Multiply Bonded Complexes Containing π-Acceptor Ligands: The Dirhenium(II)–Isocyanide System

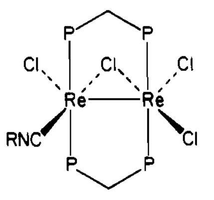
Sir:

The cleavage of metal–metal bonds of dinuclear and trinuclear complexes by the π-acceptor ligands CO, NO, RNC (R = alkyl), and ArNC (Ar = aryl) is an important facet of multiple-metal–metal-bond chemistry.[1-3] In several instances these reactions have provided excellent synthetic routes to mononuclear complexes although little is yet known about their mechanisms. In this communication we report on the novel chemistry that is emerging from our studies of the reactions between the triply bonded dirhenium(II) complexes $Re_2X_4(LL)_2$ (X = Cl, Br; LL = dppm, dppe, arphos)[4] and isocyanide ligands. Dinuclear complexes that can be considered as intermediates in the bond cleavage process have been isolated, including the first example of a multiply bonded molecular A-frame-like complex, $Re_2Cl_4(dppm)_2(CN\text{-}t\text{-}Bu)$.

While the $Re\equiv Re$ bond of $Re_2X_4(PR_3)_4$ (X = Cl, Br; PR_3 = monodentate tertiary phosphine) is readily cleaved by CO and RNC ligands to give mononuclear species,[2a,e,5] the complexes $Re_2Cl_4(LL)_2$, which contain the intramolecular bridging ligands dppm, dppe, or arphos, should be much more resistant to conversion to mononuclear fragments.[6] We find that this is the case. The reaction of $Re_2Cl_4(dppm)_2$ (**1**)[7] with 1 equiv of *tert*-butyl isocyanide (*t*-BuNC) in acetone for 30 min produces the red-brown 1:1 adduct **2** in very high yield (~90%). Analogous complexes have been obtained with use of the isocyanides MeNC and xylNC (xyl = xylyl). Recrystallization of **2** from dichloromethane–diethyl ether gave crystals of the CH_2Cl_2 hemisolvate $Re_2Cl_4(dppm)_2(CN\text{-}t\text{-}Bu)\cdot 0.5CH_2Cl_3$.[8] This diamagnetic complex is a nonelectrolyte in acetone and exhibits a well-defined 200-MHz ^1H NMR spectrum in CD_2Cl_2 that integrates in accord with this stoichiometry.[9] The *t*-BuNC resonance is a sharp singlet at $\delta = +0.97$ (9 H), while the methylene protons of the dppm ligands appear as a basic AB pattern with superimposed P–H coupling ($\delta_A = +5.78$ (2 H); $\delta_B = +5.60$ (2 H); $J_{AB} = 12.7$ Hz; $J_{PH} = 4.8$, 5.1 Hz). This spectral pattern accords with **2** possessing an A-frame type structure.[10-13] This has been confirmed by an X-ray crystal structure analysis.[14] Unfortunately, refinement of the structure has been frustrated by a disorder problem that involves the Cl and *t*-BuNC ligands trans to the bridging Cl ligand. All that can be said at this time is that the Re–Re distance in **2** is somewhat longer than in the parent complex **1** (2.234 Å).[15] The electrochemical properties of **2**, as measured by cyclic voltammetry (in 0.2 M Bu_4NPF_6–CH_2Cl_2 with a Pt-bead electrode),[16] show the presence of two couples ($E_{1/2} = +0.21$ and $+1.30$ V vs. SCE), both of which correspond to one-electron oxidations. Both processes are characterized by $i_{p,c}/i_{p,a}$ ratios of unity and constant $i_p/\nu^{1/2}$ ratios for sweep rates (ν) between 50 and 400 mV/s in accord with diffusion control. Values for the potential separations between coupled anodic and cathodic peaks (ΔE_p) were 100 mV at $\nu = 200$ mV/s, and they increased with increase in sweep rate. These properties are consistent with the electron-transfer processes being electrochemically quasi-reversible. Chemical reversibility has been demonstrated by the oxidation of **2** (and its MeNC and xylNC analogues) to paramagnetic $[Re_2Cl_4(dppm)_2(CNR)]PF_6$ using $NOPF_6$ or $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in CH_2Cl_2.[17] The ready accessibility of two one-electron oxidations in **2** is a property that is characteristic of multiply bonded dirhenium species where the HOMO is an orbital of metal π or δ character.[3,7] Accordingly,



1 (P⌒P = dppm)



2 (P⌒P = dppm, R = *t*-Bu)

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(4) Ligand abbreviations are as follows: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; arphos = 1-(diphenylphosphino)-2-(diphenylarsino)ethane.

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(8) Anal. Calcd for $C_{55.5}H_{54}Cl_5NP_4Re_2$: C, 47.32; H, 3.86; Cl, 12.58. Found: C, 46.57; H, 3.90; Cl, 12.82. IR (CH_2CH_2): $\nu(C\equiv N)$ 2133 s cm^{-1}.

(9) The $^{31}P\{^1H\}$ NMR spectrum of **2** in 3:1 CH_2Cl_2–acetone-d_6 (vs. 85% aqueous H_3PO_4 with positive chemical shifts downfield) showed an AA′BB′ pattern. Simulation of this spectrum gave the following parameters: $\delta_A = -6.39$; $\delta_B = -11.23$; $J_{AA'} = 232.3$ Hz; $J_{BB'} = 212.1$ Hz; $J_{AB} = 79.7$ Hz; $J_{AB'} = 1.2$ Hz.

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(17) The properties of $[Re_2Cl_4(dppm)_2(CN\text{-}t\text{-}Bu)]PF_6$, which are characteristic of complexes of this type, are as follows: IR (CH_2Cl_2) $\nu(C\equiv N)$ 2151 s cm^{-1}; IR (Nujol) $\nu(C\equiv N)$ 2149 s cm^{-1}; CV (in 0.2 M TBAH–CH_2Cl_2) $E_{1/2}(ox) = +1.32$ V and $E_{1/2}(red) = +0.21$ V vs. SCE; X-band ESR (CH_2Cl_2 glass at −160 °C) broad complex signal between 500 and 4000 G centered at $g \approx 2.85$; μ_{eff} (CH_2Cl_2 solution) 1.4 μ_B; elect absorption spectrum λ_{max} (in CH_2Cl_2) 770 ($\epsilon = 130$), 494 ($\epsilon = 1080$), 1175 nm ($\epsilon = 900$).

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