

## Scanning Tunnelling Microscopy of Rh<sub>4</sub> and Pt<sub>12</sub> Carbonyl Clusters adsorbed on Graphite

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The images of metal carbonyl clusters such as Rh<sub>4</sub>(CO)<sub>12</sub> and [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] adsorbed on graphite have been observed in well-ordered structures by scanning tunnelling microscopy.

The use of homo- and hetero-metallic carbonyl clusters as precursors has been the subject of recent interest for the preparation of tailored heterogeneous metal catalysts.<sup>1</sup> The catalytic performance of the surface-bound clusters depends on the chemical properties of the supporting materials and the morphology of the cluster is affected by the metal-support interactions.<sup>2</sup> The nature of surface-bound clusters has been studied by means of Fourier transform (F.t.) i.r. and X-ray photoelectron spectroscopy (XPS),<sup>3</sup> EXAFS,<sup>4</sup> and transmission electron microscopy (TEM).<sup>5</sup>

Scanning tunnelling microscopy (STM)<sup>6,7</sup> is a new tool for the observation of solid surfaces and is applicable to surface-bound clusters.<sup>8</sup> In this communication, we report the images of Pt<sub>12</sub> and Rh<sub>4</sub> carbonyl clusters adsorbed on HOPG (Highly Oriented Pyrolytic Graphite).

Our STM system consists of NanoScope I (Digital Instruments Inc.) coupled with a personal computer (NEC PC-9801 VX41). Data are transferred through an analogue-to-digital converter from the NanoScope I to the computer. In the microscope unit, the piezo scanner is tube type and a mechanically sharpened Pt-Ir (80:20%) probe tip is used. The lengths of *x* and *y* axes are estimated directly from the scanning voltage applied to the piezo scanner and are calibrated by the spacing of the graphite.<sup>8</sup> The carbonyl clusters [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] and Rh<sub>4</sub>(CO)<sub>12</sub> were synthesized and purified according to literature methods.<sup>9</sup> [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] and Rh<sub>4</sub>(CO)<sub>12</sub> were dissolved in tetra-

hydrofuran and hexane, respectively, under CO atmosphere. The carbonyl clusters were deposited uniformly by placing a few drops of the solution (0.1 mm) on a freshly cleaved HOPG surface (5 × 5 mm). After removal of the solvent in a CO flow, the sample was transferred to the microscope, and observation by STM was conducted under N<sub>2</sub> atmosphere. Before each observation of the carbonyl clusters on HOPG, the *x* and *y* axes of the image were calibrated with the lattice constant (2.46 Å) of freshly cleaved HOPG. Additionally, surface elemental analysis of the supported Rh<sub>4</sub> cluster was performed by Auger electron spectroscopy (AAS-200: Nichiden-ANELVA Co.).

Figure 1 shows the line-scanning image of [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] with a trigonal prismatic array on HOPG, and Figure 2a shows the top view. The tunnelling current was 0.15 nA and the bias voltage was 96 mV. There are two big scattered humps in the STM images; the lower one (*ca.* 45 × 42 Å) consists of three smaller rowlike structures (*ca.* 12 × 10 Å) (Figure 2b). These humps were not obtained on independent observation of the solvent tetrahydrofuran on HOPG, which implies that they originate from the Pt<sub>12</sub> carbonyl cluster. The size of the central rowlike structure (Figure 2b) is similar to that of a prismatic cluster framework (9 × 15 Å) of [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup>.<sup>9</sup> We suggest that three [Pt<sub>12</sub>(CO)<sub>24</sub>]<sup>2-</sup> aggregate to form the lower hump. Humps were observed reproducibly in the same area in repeat runs.

Figure 3a shows the STM image of Rh<sub>4</sub>(CO)<sub>12</sub> with a

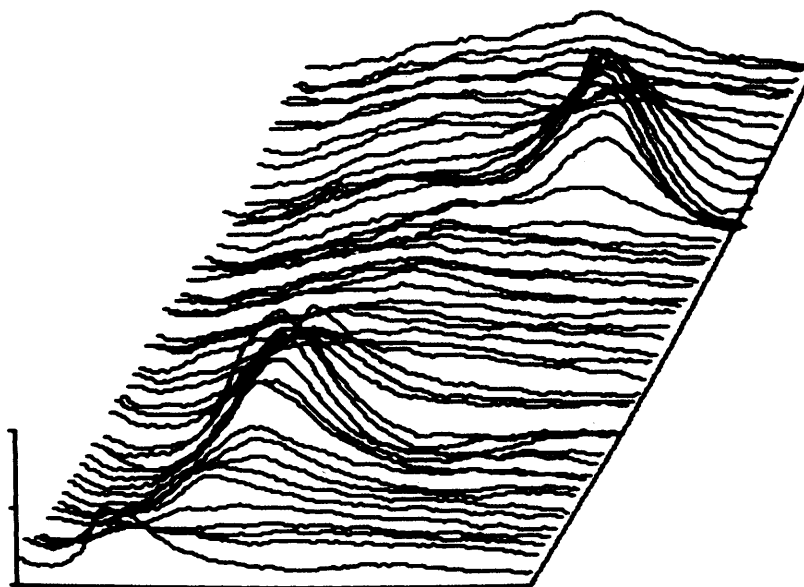
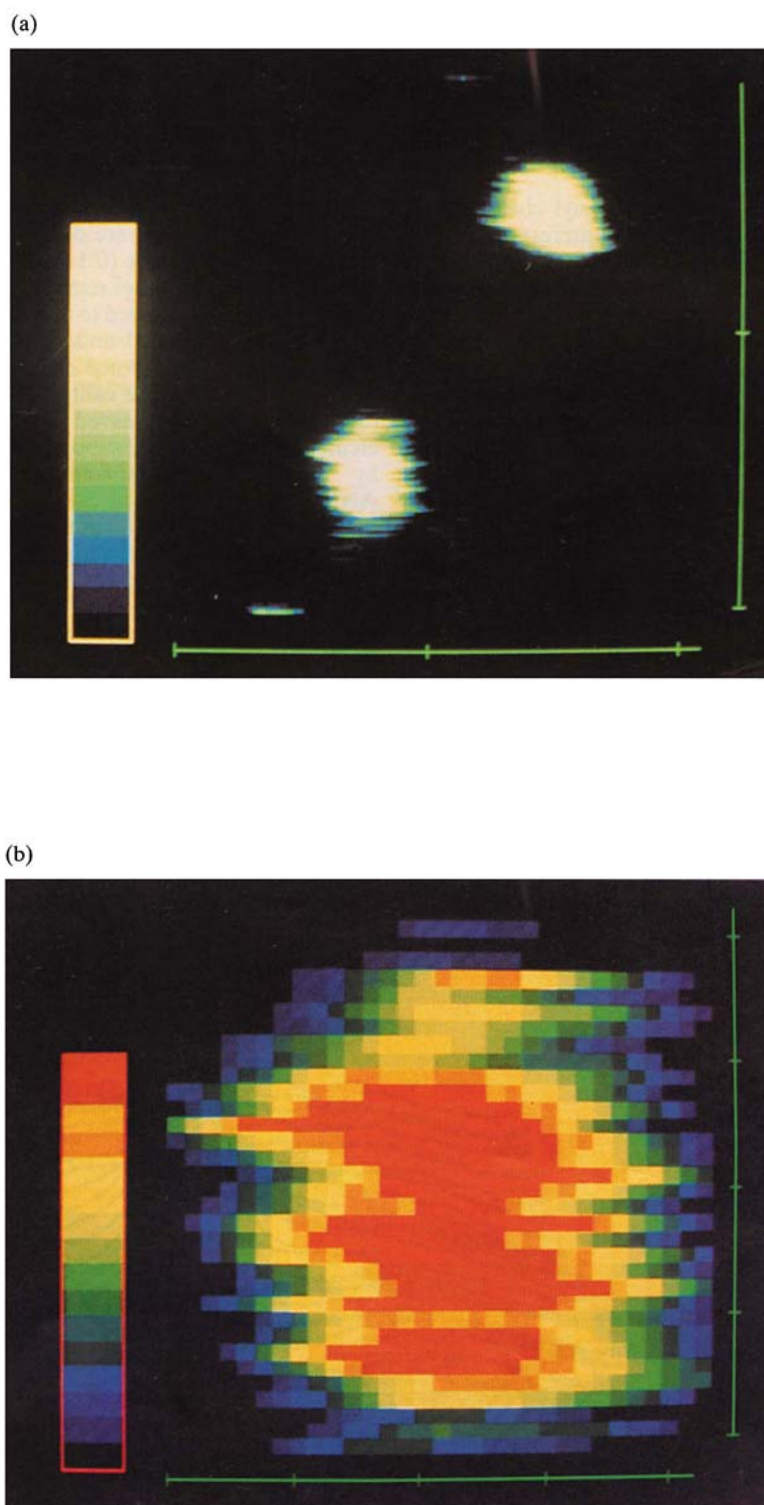
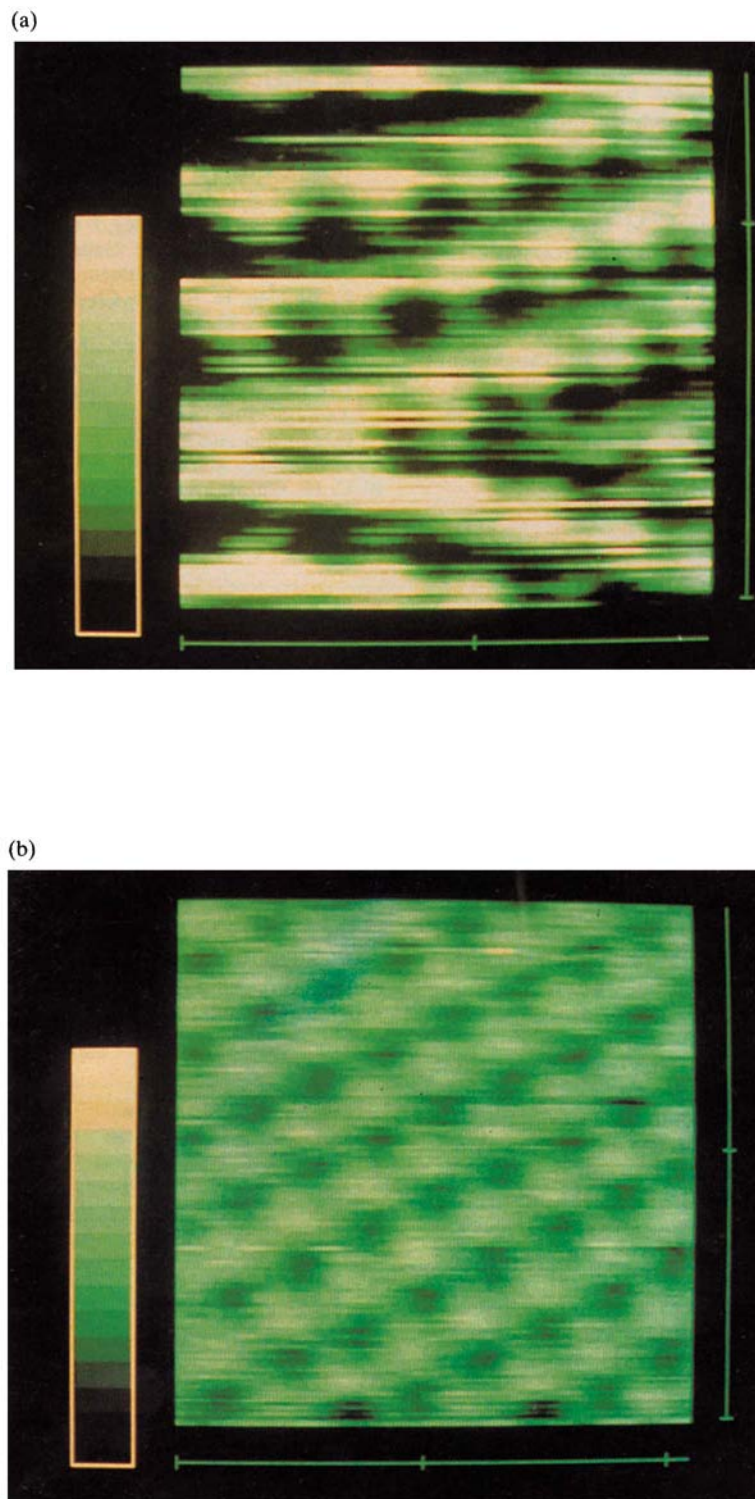


Figure 1. Line scanning STM image of [NEt<sub>4</sub>]<sub>2</sub>[Pt<sub>12</sub>(CO)<sub>24</sub>] on HOPG at 25 °C. Image size: *x* = 210, *y* = 190 Å, *z* = arbitrary unit.



**Figure 2.** Top views of STM images of  $[\text{NEt}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$  adsorbed on HOPG at 25 °C. The height of the STM images is displayed by the colour contrast. (a) Image size:  $x = 210$ ,  $y = 190$  Å. (b) Scaled-up image of the lower hump of (a);  $x = y = 42$  Å.



**Figure 3.** (a) Top view (STM) of  $\text{Rh}_4(\text{CO})_{12}$  on HOPG at 25 °C;  $x = y = 165 \text{ \AA}$ . The height of the STM images is displayed by the colour contrast. (b) Top view of freshly cleaved HOPG surface. Scan area:  $x = 21, y = 19 \text{ \AA}$ .

tetrahedral metal framework, adsorbed on HOPG. The tunnelling current and the bias voltage were 0.15 nA and 95 mV, respectively. In Figure 3a, small humps are set in a regular array, the diameter of one spherical image being *ca.* 12 Å, which is similar to the size of  $\text{Rh}_4(\text{CO})_{12}$ .<sup>10</sup> These humps were not observed on a freshly cleaved HOPG surface under the same conditions (Figure 3b). It is notable that the ordered array of the  $\text{Rh}_4(\text{CO})_{12}$  image seems to be oriented in accordance with the periodic arrangement of the hexagonal units of HOPG. The results suggest that  $\text{Rh}_4(\text{CO})_{12}$  molecules are adsorbed on HOPG under the influence of the orientation of the HOPG surface. Additionally, the individual humps all showed three-fold symmetry. After STM observation, we studied  $\text{Rh}_4(\text{CO})_{12}$ -HOPG using Auger electron spectroscopy and observed a rhodium peak at 301 eV.

The application of STM to clusters adsorbed on HOPG can thus provide images of individual  $\text{Pt}_{12}$  clusters, with information on size and shape, and can show the ordered arrangement of adsorbed  $\text{Rh}_4$  clusters.

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