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THE MOLECULAR STRUCTURE OF HYDROCARBON MONOLAYERS ON METAL SURFACES

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ABSTRACT

Recent studies of the molecular structure and chemical bonding of organic monolayers on metal surfaces are reviewed. Most of the research is concentrated on alkenes and alkynes adsorbed on Platinum and Rhodium. The applications of Low Energy Electron Diffraction, High Resolution Electron Energy Loss Spectroscopy and Thermal Desorption Spectroscopy provided most of the structural and bonding information in studies that utilized single crystal metal surfaces.

Hydrocarbon monolayers exhibit a rich and diverse structural chemistry that may be correlated to analogous organometallic clusters. Alkylidyne ($\equiv C-(CH_2)_n-CH_3$) bonding predominates near 300K on Pt and Rh although a variety of different molecular conformations is found.

Perhaps the most pronounced characteristic of the organic monolayers is the temperature dependent variation of their structure and bonding. The bonding also varies markedly across the periodic table; much stronger for the early transition metals (W, Fe) and much weaker on Ag and Cu than on Pt and Rh. These temperature- and metal-dependent trends are altered to some extent when considering different crystallographic planes for the metal surface. Finally the possible directions that this field of research may take are discussed.

INTRODUCTION

The molecular basis of many macroscopic surface phenomena, including lubrication, adhesion, wettability and hydrocarbon catalysis is established by studies of the structure and chemical bonding of monolayers of adsorbed hydrocarbons. During the past decade a major effort has been underway in our laboratory to better understand, on the molecular level, the structure and bonding of organic molecules to transition metal surfaces. These studies were carried out using single crystal surfaces that were characterized by many of the new surface science techniques.

The adsorbed hydrocarbon monolayers were examined by Low Energy Electron Diffraction (LEED), High Resolution Electron Energy Loss Spectroscopy (HREELS) and Thermal Desorption Spectroscopy (TDS). Studies, so far, concentrated on alkene and alkyne monolayers adsorbed mostly on Platinum and Rhodium.

In this paper we review what is known about the structure and bonding of organic monolayers on transition metal surfaces; their temperature dependent character, their structure sensitivity to different crystallographic planes of the metal surface and the variation of their bonding to metals across the periodic table will be discussed. Finally, we point out possible new avenues of research for the near future that this growing field may follow.

II. TECHNIQUES

Several surface science techniques have been applied recently to investigate the structure of adsorbed monolayers of molecules;[1-3] we mention in particular Ultraviolet Photoemission Spectroscopy (UPS), Low Energy Electron Diffraction (LEED), High Resolution Electron Energy Loss Spectroscopy (HREELS), and Surface Extended X-ray Absorption Fine-Structure Spectroscopy (SEXAFS). All these techniques take advantage of the surface sensitivity of low energy electrons (20-500eV). A low energy electron interacts so strongly with a metal lattice that it can only penetrate a few atomic layers into the crystal; as a result, any electron that is backscattered from the metal will carry information about the near surface region only (~5 atomic layers). These techniques all require an Ultra High Vacuum (UHV) environment to ensure that the metal surface is not contaminated by residual gas adsorption and that the electron has a large enough mean free path in the gas phase. In Table I, we emphasize the strengths and weaknesses of these techniques since many of the methods are very complementary and provide very different information.

Our laboratory has relied mainly on LEED and HREELS to study the structure of adsorbed hydrocarbons on Pt and Rh. Although LEED was discovered already in 1927 by Davisson and Germer[4] and its potential as a surface structural tool recognized at that time, it did not become a common technique until the early 1970's.[5] Probably the two most important reasons for this long delay is that a complicated theory was needed to model electron diffraction in a multiple scattering situation and that the development of an ultra-high vacuum technology had to wait for

our space exploration program of the early 60's. The LEED analysis is conceptually similar to X-ray crystallography; the major distinction between the two methods is that a low energy electron has about 10^6 times the scattering cross-section of an X-ray photon. This gives a low energy electron the surface sensitivity that an X-ray photon lacks, but also complicates the diffraction process. An incident electron will probably scatter from a few metal atoms before leaving the crystal so that the quite straight forward kinematic scattering in X-ray crystallography no longer holds; to properly account for this multiple scattering in electron diffraction, a much larger computational effort is required.

Figure 1 describes the LEED experiment where an incident low energy electron beam is back diffracted from a metal and the different diffraction beams appear as spots on a luminescent screen. The spot intensities for any beam can then be measured as a function of the incident beam energy or incident angle and the characteristic peaks that appear in the resulting intensity vs voltage (I/V) plot or intensity-angle plot contain the structural information of interest. Figure 2 shows how this structural information is extracted. The experimental I/V curves are compared to calculated ones that assume particular model geometries; that geometry which gives best agreement between theory and experiment is considered the correct one. The agreement is generally measured by a reliability factor[6] just as in x-ray crystallography, though a straightforward visual inspection is also sometimes used. Typically, a few tens of plausible models are tested and hundreds of I/V curve comparisons must then be made; the number of trial geometries

is limited in the more complicated cases by the large computational effort needed to properly account for the multiple scattering of the low energy electrons. This method has been the most productive one to date for determining bond lengths and bond angles at surfaces; however, it does not detect hydrogen atoms, requires an ordered overlayer, and increases quickly in computational cost as the surface unit cell grows.

To complement the advantages and disadvantages of LEED, one can study the same or very similar hydrocarbon overlayers with HREELS. HREELS has evolved in the last decade into one of the most versatile qualitative structural tools available to the surface scientist; the first application of this technique can be traced to the work of Propst and Piper[7] in 1967. Ibach[8] should be credited for improving the energy resolution of the incident and detected electrons so that it became possible to routinely measure the vibrational energies of adsorbed species. In HREELS, a low energy (1-10eV) electron can gain or lose a quantum of vibrational energy (0-500 meV) when striking the surface; these low energies are measured and represent the vibrational spectrum of an adsorbed molecule.

Since most the specularly reflected electrons only see the dynamic dipole moment of a surface vibration from a long distance (~ 100Å), a simple dipole scattering selection rule can be invoked in the case of a flat metal surface; this rule states that only the vibrations with a dynamic dipole moment perpendicular to the surface can be measured. As an example, Fig. 3 shows vibrational spectra[9a] of CO on Rh(111); we see only Rh-C (480cm^{-1}) and CO stretch (1870, 1990 cm^{-1}) frequencies but not the bending vibrations. According to the selection rule, this

suggests a CO axis oriented perpendicularly to the surface; while the observed Rh-C stretching vibration indicates that the molecule stands with the carbon end bound to the surface. In this case, even the adsorption site can be inferred from the CO stretching frequency; the 1990 and 1870 cm^{-1} frequencies imply that CO bonds to one (atop) or two (bridge) top layer metal atoms.

HREELS, though not a quantitative tool as yet, can probe the structure of disordered overlayers and is quite sensitive to hydrogen atoms present on the surface. Since long-range order is not required, coverage dependent phenomena can be studied as well as coadsorption behavior. However the complicated vibrational spectra of hydrocarbon overlayers must be assigned to particular vibration modes and the structural interpretation of the measured vibrational frequencies should be calibrated and confirmed by LEED. So in the straightforward example shown in Fig. 3 we must first assign the 1990 and 1870 cm^{-1} vibrations to be C-O stretches and then interpret the frequencies to indicate a CO molecule bound to one or two Rh atoms, respectively. In summary then, we see that HREELS and LEED complement each other and in combination provide a very powerful structural method.

Thermal Desorption Spectroscopy[10] (TDS) has also been used in our laboratory to support the LEED and HREELS measurements. This method provides valuable information on the heat of adsorption for molecules that can desorb intact from the metal surface or on the onset temperature for decomposition reactions which occur when the adsorbed molecules can not desorb intact. In a typical experiment the metal, which is covered by a monolayer of some adsorbate, is heated to obtain a linear

temperature ramp. The desorption rate of the entire molecule or its fragments can be monitored with a quadrapole mass spectrometer (QMS) that is attached to the UHV chamber. Later in this paper, we will discuss the hydrogen desorption spectra illustrated in Fig. 10, these spectra were obtained from alkene (C_nH_{2n}) overlayers on the Pt(111) surface. Most the adsorbed hydrocarbons dissociate into a carbon residue and desorbing hydrogen gas. The peak hydrogen desorption rates (labeled A, B, and C) shown in Fig. 10 actually mark the transitions to the more dehydrogenated hydrocarbon structures as the temperature is increased.

III. NOVEL BONDING OF ALKENES TO THE Rh AND Pt SURFACES

We shall now review what has been learned about the nature of the surface chemical bond for ethylene, propylene, and 2-butene monolayers on the (111) faces of Rh and Pt. These two systems serve as a good introduction to hydrocarbon adsorption on metals. They demonstrate the rich and diverse chemistry of such overlayers and provide a firm foundation to discuss hydrocarbon adsorption on other surfaces.

(i) Adsorption on Rh(111)

Ethylene (C_2H_4): Using LEED[11] and HREELS,[9b] the surface structure of the ethylene overlayer that forms at 240K on the Rh(111) surface has been determined in our laboratory. The hydrocarbon adsorbs in a (2x2) lattice of surface sites; the (2x2) notation implies a unit cell of the same orientation as that of the Rh(111) surface and twice as large in both directions. Figure 4 shows the ethylidyne species ($\equiv C-CH_3$) that forms inside the (2x2) unit cell; the alkene undergoes a hydrogen shift to leave one carbon atom bonded to three Rh atoms above a hollow site on the surface, while the other carbon atom is fully saturated with hydrogen.

This surface ethylidyne group has many analogues in Organometallic Chemistry; as can be seen in Fig. 4, the carbon-carbon bond distance as well as the carbon covalent radius for the rhodium-carbon bond agree within experimental uncertainty with the values for ethylidyne trinuclear clusters. Although not indicated in Fig. 4, we should realize that the (111) surface of face-centered cubic (fcc) metals provides two different types of hollow sites when we consider the top two metal

layers; one site has a metal atom below it (hcp hollow) and the other does not (fcc hollow). Our LEED analysis clearly shows that ethylidyne sits above the hcp hollow, even though the HREELS data could not discriminate between these two subtly different sites.

Propylene (C_3H_6): Next we consider propylene adsorption on the Rh(111) surface and in particular the structure that forms between 230-270K.[12] LEED indicates that here again an alkylidyne species [$\equiv C-(CH_2)_n-CH_3$] appears and sits above an hcp hollow site. The propylidyne structure has an extra methyl group on the hydrocarbon chain, compared to ethylidyne. We find from the diffraction experiments that all methyl groups lock into a $(2\sqrt{3} \times 2\sqrt{3})$ R30° superlattice as shown in Fig. 5; the superlattice unit cell is drawn in the figure and the notation again refers to the rhombic cell of the clean Rh(111) surface. Also in Fig. 5 we see that the methyl groups appear to be attracted to each other, possibly by Van der Waals forces, and do not significantly interact with the metal atoms. The corresponding packing energy for the superlattice of methyl groups must be fairly large to overcome the thermal energy that could disorder it. Preliminary force field calculations[13] of this propylidyne overlayer using standard Van der Waals interactions do indeed, at least qualitatively, support our structural result. It should come as no surprise to us that these Van der Waals structures can appear in hydrocarbon overlayers since the importance of these forces in hydrocarbon crystals is well established.[14] The straight-chain, aliphatic hydrocarbons (C_nH_{2n+2}) have axes that run parallel to each other to maximize the Van der Waals attraction between

molecules and to minimize the Van der Waals repulsion between non-bonding atoms within each molecule. This repulsion also keeps the carbon skeleton of gas phase n-paraffins in a zig-zag, trans conformation and its axis straight.[14]

2-butenes (C_4H_8): Cis- and trans-2-butene give a poorly ordered (2x2) lattice of butylidyne on Rh(111); the presence of butylidyne was inferred from thermal desorption spectroscopy (TDS).[12] This will be discussed more fully in the next section where we consider the temperature dependence of the hydrocarbon metal bond. To better understand the nature of this structure, we plan to begin HREELS studies on this system in the near future.

(ii) Adsorption on Pt(111)

Ethylene (C_2H_4): Using LEED[15] again, the ethylene-derived structure found on the Pt(111) surface at 300K is very similar to that on Rh(111). HREELS work[16] and an Angle Resolved Ultraviolet Photoemission Spectroscopy (ARUPS)[17] study confirm the ethylidyne structure that was proposed by LEED. Figure 6 includes this ethylidyne structure; the bond distances are slightly different than those found for ethylidyne or propylidyne on Rh(111) and these different results are compared in Table II. Two possible explanations can account for the small discrepancy. (1) The alkylidyne species on the Pt surface occupies an fcc rather than hcp hollow; the absence of the second layer metal atom under the alkylidyne group on the surface could change the relevant bond distances.[11] (2) The differences in measured bond distances represent the experimental uncertainty of the LEED experiment.

Propylene (C_3H_6): Although propylene does give a propylidyne species on the Pt surface as indicated in Fig. 6, the methyl groups of this overlayer are randomly oriented.[18] This is clearly seen in Fig. 7 where the diffraction beam intensities for the ethylene and propylene derived overlayers are nearly identical; only if the methyl groups of propylidyne were disordered could the intensity curves for these two overlayers be so nearly identical. Thermal Desorption Spectroscopy was used to exclude the possibility of partial fragmentation of propylidyne into ethylidyne plus a disordered carbon phase.

We recall that the propylidyne layer on Rh formed a $(2\sqrt{3}x2\sqrt{3})R30^{o}$ superlattice of ordered methyl groups in addition to the (2x2) lattice of adsorption sites. Why does this superlattice not appear for the Pt overlayer since Pt and Rh differ by only 4% in their metallic radii? We thought this structural change could be caused by the temperature difference of the two overlayers. Cooling the Pt overlayer could "freeze in" the methyl superlattice since the entropy term ($T\Delta S$) in the free energy would become less influential. However, when we cooled the Pt surface to 240K, the propylidyne overlayer still did not order into a superlattice. Alternatively, we tried heating the propylidyne layer on Rh and hoped to see the methyl superlattice disorder, but instead found an irreversible order-order transition to a different state with a c(4x2) lattice.

Force Field calculations at zero temperature[13] on the propylidyne layers of Pt and Rh(111) show only slight differences in the packing energy of these hydrocarbon molecules due to the small change in substrate lattice constants. However, these calculations only consider

the enthalpy (ΔH) and not the entropy ($T\Delta S$) term in the free energy. Entropy considerations may play an important role in determining the transition temperature for ordering the methyl groups into a superlattice and only further experiments at still lower temperatures will provide us with a complete description of the propylidyne structure on Pt(111).

2-Butenes (C_4H_8): Figure 6 also illustrates the butylidyne complex that forms after adsorption of cis-or trans-2-butene on the Pt(111) surface at room temperature;[18] this alkylidyne phase on Pt(111) does produce a $(2\sqrt{3}x2\sqrt{3})R30^{o}$ superlattice. A possible structure for this butylidyne layer is drawn in Fig. 8. However, Force Field calculations[13] suggest that the γ-carbon in neighboring butylidyne species $C(\alpha)-C(\beta)H_2 - C(\gamma)H_2 - C(\delta)H_3$ rotate towards each other by 30° just as we found for propylidyne on Rh(111) with LEED. These calculations further indicate the δ-carbon in the methyl group may tilt away from its neighbors. A LEED analysis of this butylidyne overlayer is presently underway in our laboratory to confirm this model which is favored by Force Field calculations just as we did for propylidyne on Rh(111).

IV. TEMPERATURE DEPENDENCE OF THE SURFACE CHEMICAL BOND

One of the most fascinating features of surface chemistry is the large number of different overlayer structures that can form with changing temperature. The bonding of hydrocarbons to metal surfaces is no exception to this rule and in fact presents a clear demonstration of the rich structural chemistry that exists on surfaces. The sequence of alkene (C_nH_{2n}) structures that occurs with increasing temperature has some general features which we shall now point out. No matter how reactive a particular metal may be, a hydrocarbon will physisorb at low enough temperatures (typically below 50K). The molecule is only weakly bound to the surface by Van der Waals forces (with an adsorption energy of a few kcal/mole) and is relatively undistorted from its gas phase structure. Upon heating, a series of chemisorbed species will form that make actual chemical bonds to the top layer metal atoms and are much more strongly bound to the surface (with adsorption energies ranging from 10 to 100kcal/mol). In this state, the alkene has already undergone a significant structural rearrangement and possibly lost some hydrogen atoms. As the crystal temperature continues to increase, the carbon skeleton fragments with a further loss of hydrogen. CH_x species now present on the surface can then dehydrogenate and sometimes form surface carbides, in which carbon is embedded in the metal lattice. Finally at even higher temperatures, a graphite overlayer can be produced that is fully dehydrogenated.

Let us now consider the temperature-dependent adsorption of ethylene on the Rh and Pt(111) crystal faces. Table III summarizes the sequence of chemisorbed structures that form at different tempera-

tures and should serve as a helpful guide in the following discussion. At 100-290K, ethylene[19] is found to lie parallel to the surface with each carbon atom σ-bonded to two neighboring Pt atoms, while the metal-carbon bonds probably lie in a plane perpendicular to the surface. The carbon atoms are thought to be nearly sp^3 hybridized which leaves the carbon-hydrogen bond slightly inclined to the surface. This phase of ethylene does not exhibit long-range order and therefore does not produce a clear diffraction pattern; so LEED cannot be used to study this system even though all the ethylene molecules have the same local geometry.[18] Since HREELS probes only the local, and not the long-range, structure of overlayers, it was used to obtain the approximate molecular geometry of adsorbed ethylene described above.

Between 290 and 500K, the ethylene overlayer forms the ethylidyne species on Pt(111) as discussed in the previous section and illustrated in Fig. 6. We should note that ethylene has now lost one hydrogen atom (which can desorb from the surface at these temperatures) and has the remaining hydrogens bonded to only one carbon atom. Above 500K, the carbon-carbon bond of ethylidyne is broken and CH groups appear on the surface;[20] this phase persists to about 700K when a layer of graphite begins to form on the Pt surface and all the hydrogen from the overlayer has desorbed. Since the CH groups are disordered on the surface, HREELS was again solely used to detect this species, while the graphite layer is recognized by a characteristic LEED pattern as has been observed on many other metals with LEED.[21,22]

The graphite unit cell is about 13% smaller than the rhombic cell of the top layer Pt atoms and is only slightly compressed ($\sim$1-2%) from

the bulk graphite due to the strong carbon-carbon and weak carbon-metal bonding. The graphite layer is found to have preferred orientations with respect to the Pt surface;[22] in one orientation, the graphite unit all vectors lie in the same direction as those for the top Pt layer. Since the graphite cell is slightly smaller, a "coincidence" between metal and graphite layers occurs at a distance of every 9 Pt atoms. This concidence lattice is inferred from the (9x9) LEED pattern that appears after graphite formation. From a catalytic point of view, the transition from a CH species to graphite has very serious consequences. The CH group is reactive and quite active in carrying out hydrogen transfer during many important catalytic processes;[23] while the very stable graphite layer is too inert and only serves to poison catalytic reactions. Naturally, the ability to control or to adjust this transition would find considerable use in the catalytic technology.

The sequence of ethylene structures which form on the Rh(111) face is very similar to those on Pt, but it shows that Rh is a slightly more reactive metal. An ethylidyne phase already appears at 230K on the Rh surface while this conversion occurred at 300K on Pt. Our LEED results[11] clearly indicate that ethylidyne sits above a different hollow site on Rh than that for Pt; and this may be caused by the coadsorbed hydrogen layer that forms when ethylene converts to ethylidyne. This hydrogen layer may not form on Pt because the ethylidyne conversion happens above the hydrogen desorption temperature.

As the Rh surface is heated to 270-450K, the (2x2) overlayer cell changes to a c(4x2). The structure of the hydrocarbon species in this c(4x2) cell is presently being studied in our laboratory; preliminary evidence[9b] indicates another ethylidyne lattice may exist as indicated in Fig. 9. At 450K ethylidyne on Rh[9b] fragments to a CH species compared to 500K for Pt.[20,23] As in the case of Pt, this CH group present on the Rh surface will also convert to graphite at 700K;[21] yet in this case, only a (12x12) coincidence lattice between the graphite and Rh layers is formed. (We recall that a variety of graphite metal orientations were possible on Pt.)

We conclude this section with a discussion of the behavior of the larger molecular weight hydrocarbons adsorbed on Rh and Pt as a function of temperature. The situation is well illustrated in Fig. 10; here Thermal Desorption Spectra (TDS) obtained in our laboratory[24] are shown for ethylene, propylene, and the 2-butenes adsorbed on the Pt(111) surface. In these curves, the rate of hydrogen desorption is measured with a mass spectrometer as the crystal temperature is uniformly increased. Three peaks appear in each of the spectra in Fig. 10 and correspond to structural transitions in the hydrocarbon overlayers. These peaks are very similar for all the alkenes which indicates that propylene and the 2-butenes behave like ethylene with increasing temperature. The desorption peak labeled (A) that occurs at 300K corresponds to the conversion to alkylidyne from the parallel-bonded alkene species with the release of one hydrogen atom. This peak occurs at identical temperatures for all the alkenes studied. Similarly, the broad desorption peak labeled (C) between 600 and 700K appears in all

the curves and corresponds to the transition from CH groups to a graphite overlayer. In addition, the ethylene overlayer has a sharp desorption peak (B) at 500K that was found by HREELS to correspond to fragmentation of the carbon skeleton; interestingly, this peak is seen to shift to 420K for propylidyne and 380K for butylidyne indicating that the larger hydrocarbons are more susceptible to decomposition. A similar set of TD spectra[12] has recently been collected in our group for the C_2,C_3 and C_4 alkenes adsorbed on Rh(111) indicating that the C_3 and C_4 hydrocarbons also behave like ethylene on this surface.

These two well-studied systems clearly demonstrate the variety of hydrocarbon structures that can be explored on surfaces. The similarities and trends in bonding for different hydrocarbons adsorbed on two separate metals suggest that the underlying principles involved may be uncovered as more systematic work is carried out on still other hydrocarbon overlayers.

V. ALKYNE MONOLAYERS (ACETYLENES)

Acetylene and Methylacetylene overlayers on the Rh and Pt(111) surfaces have also been studied with HREELS[9b,19] and LEED;[12,18,25] a summary of the temperature-dependent structures that form with these molecules can be found in Table IV. Below 270K for Rh and 300K for Pt, acetylene forms a (2x2) lattice; it is parallel bonded to the surface and each carbon atom probably di-σ bonds to two neighboring metal atoms as in the low temperature ethylene phase. The carbon atoms would be roughly sp^2-hybridized and have a double bond between them. The hydrogen atoms would then bend away from the C-C axis and the remaining π-orbital can interact with a third metal atom. This π-bonding tilts the plane of the distorted molecule towards the surface. Such π-bonding is well-documented in x-ray crystallography work with cluster compounds.[26] The exact location of the acetylene complex above the surface as well as the carbon-metal and carbon-carbon distances could not be accurately determined by the LEED or HREELS studies that were carried out.

The di-σ, π bonded acetylene will convert to a vinylidene species ($=C=CH_2$) when heated to near room temperature; this has been observed for Pt with HREELS.[19] To form the vinylidene group, a hydrogen shift occurs and the lower carbon atom presumably σ-bonds to two neighboring metal atoms. Due to the appearance of certain vibrational modes in the HREEL spectra, the carbon-carbon axis is thought to be tilted toward the surface. This tilt would allow the π-orbital of vinylidene to interact weakly with a third metal atom on the surface. The vinylidene species is very reactive and will in the presence of coadsorbed hydrogen

quickly convert to ethylidyne ($\equiv C-CH_3$).[15,19] One additional hydrogen must be incorporated into vinylidene before the ethylidyne species can form. The thermal desorption,[9b,27] angle-resolved[17] and integrated Ultraviolet Photoemission,[28] LEED,[12,29] and HREEL[9b,19] spectra are identical for the ethylene and acetylene derived overlayer of ethylidyne proving that these layers are indeed the same.

The strong correspondence and analogy that exists between Organometallic and Surface chemistry is clearly evident in these hydrocarbon transitions. A very similar sequence of acetylene complexes have been observed for triosmium acetylene clusters. Acetylene reacts with $H_2Os_3(CO)_9$ (I) to give $HOs_3(CHCH_2)(CO)_{10}$ (II)[30] that upon mild heating yields $H_2Os_3(C{=}CH_2)(CO)_9$ (III).[30] Cluster (III) is equivalent to the surface vinylidene structure. Paralleling the surface case, an ethylidyne complex, H_3Os_3 $(CCH_3)(CO)_9$ (IV)[31] is formed by bubbling H_2 through a refluxing n-heptane solution of (III) for 24 hours.

Thus, the transitions of acetylene to vinylidene upon mild heating and of vinylidene to ethylidyne in the presence of hydrogen is the same on the metal surface and in the cluster compounds. This example illustrates the utility of studies in cluster chemistry for understanding some of the complicated chemical processes that can occur on surfaces.

Methylacetylene behaves similar to that of acetylene. A (2x2) lattice of parallel-bonded methylacetylene forms below room temperature on the Pt(111) surface. Methylacetylene adopts the same bonding geometry as acetylene except that one of the hydrogens of acetylene is now replaced by a methyl group; its structure is illustrated in

Fig. 11. This structure has been inferred by the near identity of LEED intensity curves obtained from the acetylene and methylacetylene overlayers.[18] Since the presence of the extra methyl group in methylacetylene does not alter the intensity curves, we believe that this group is disordered. The rotation about the unsaturated carbon-carbon bond of the off-axis chemisorbed methylacetylene is probably fairly unhindered; this tumbling motion would sway the inclined methyl group and should make it appear disordered in our diffraction experiments.

Upon heating, the di-σ, π-bonded methylacetylene complex probably converts to 1-propenylidene ($=C=CH_2CH_3$) though this disordered phase has not yet been examined with HREELS. This species then converts to propylidyne at room temperature in the presence of coadsorbed hydrogen.[18] This propylidyne layer is identical to the one prepared from propylene adsorption at room temperature on Pt(111).

When methylacetylene is adsorbed on the Rh(111) face between 230 and 270K, a $(2\sqrt{3}x2\sqrt{3})$ R30^{o} structure appears. Our LEED results[12] indicate that methylacetylene is still di-σ, π bonded to the surface in a (2x2) lattice; however now the methyl groups order into a $(2\sqrt{3}$ x $2\sqrt{3})$ R30^{o} superlattice, presumably due to intermolecular Van der Waals interactions. This structure is reminiscent of propylidyne adsorption on Rh(111), but the exact location of the methyl groups will have to await the completion of our LEED analysis now underway.

VI. ELECTRONIC EFFECTS IN HYDROCARBON BONDING ON TRANSITION METAL SURFACES.

With the structural information available for hydrocarbon adsorption on the (111) faces of Rh and Pt, we shall now compare and contrast these results with other crystal faces of Pt and Rh as well as with the other metal surfaces that are beginning to be studied. Two important findings should be anticipated. (1) Very similar alkene structures form on the (100) and (111) faces of Rh and Pt. (2) The metal surfaces become more reactive as we move to the left in the transition metal series; that is, near 300K, the adsorbed alkenes are undistorted on the Ag and Cu, rehybridized on Pt, Rh, Pd, and Ni, and fully dissociated on the low Miller index faces of Fe and W. This suggests that the electronic character of a given metal may play a more important role than its surface geometry in determining the structure and bonding of adsorbed hydrocarbons.

Ethylene adsorption on Pt(100) has recently been investigated with HREELS.[32] The (100) surface of face-centered cubic crystals exposes a square mesh of metal atoms; the four-fold hollow site that exists on this face is not as well suited for ethylidyne adsorption as the three-fold hollow present on the (111) face. Yet the vibrational spectra obtained for ethylene on the (100) and (111) faces of Pt are nearly identical. This can only be possible if ethylidyne forms on both these crystal faces. Our group has also investigated ethylene adsorbed on Rh(100); the Thermal Desorption Spectra and LEED patterns[12] are strikingly similar to those found for Pt and suggest that ethylidyne may form on the Rh(100) surface as well.

The presence of ethylidyne on both (100) and (111) fcc surfaces demonstrates the extreme stability of this particular complex. In fact, alkylidyne species may be the dominant form of hydrocarbon bonding on a number of different metals. A recent HREELS study[33] reports the formation of ethylidyne on the Pd(111) surface since the vibrational spectrum of ethylene on Pd(111) is again nearly identical to that on Pt and Rh. The thermodynamic stability of alkylidynes is also readily apparent in cluster compounds where a large number of different synthetic pathways all lead to the same trinuclear ethylidyne complexes.[34] In addition, these complexes display an unusual resistance to oxidation and thermal decomposition.[34]

Other than Rh and Pt, the only transition metal to have been studied extensively with respect to hydrocarbon adsorption is Nickel. At temperatures below 200K, ethylene di-σ bonds to the Ni(111) surface[35] in a way very similar to Pt(111). The HREEL spectra from these two surfaces closely resemble each other with one notable exception. One C-H stretching vibration for ethylene on Ni is shifted to a lower frequency and is broadened by 200-300 cm^{-1}. This behavior, that is commonly observed in hydrogen-bonded liquids, implies that the hydrogen atoms in ethylene interact strongly with the surface Ni atoms. This hydrogen-metal bonding promotes C-H bond scission; an acetylene species is formed already at 200K along with a coadsorbed layer of hydrogen that is released. Dehydrogenation is favored on the Ni surface due to the strong interaction between the hydrogen on the adsorbed ethylene and the metal, while the formation of an alkylidyne species is

preferred on Pt and Rh where this hydrogen-metal interaction is not detectable.

The acetylene layer that forms on Ni(111) between 200-400K orders into a (2x2) lattice at a coverage near 1/4 monolayer. This structure is being investigated with HREELS[36] and LEED.[37] The acetylene is strongly rehybridized and the carbon atoms appear to lie above neighboring hollow sites. The carbon-carbon axis is not parallel to the surface but inclined by ~20°; this μ-bonding arrangement has also been observed in Organometallic Chemistry.[26] The inclination of the carbon-carbon bond of the adsorbed acetylene may be caused by the different nature of the two neighboring hollow sites. We recall that fcc(111) surfaces provide two different hollow sites, one with a second layer atom (hcp hollow) and another with a third layer atom below it (fcc hollow).

The acetylene complex that forms on the Ni(111) surface is quite different from that on the Rh or Pt(111) face. We remember that acetylene di-σ, π̄ bonds to neighboring Pt or Rh atoms and that the carbon-carbon axis is parallel to the surface. Two possible explanations for these differences are the following. (1) The greater distance between adjacent three-fold hollow sites on Pt(111) (1.60Å) or Rh(111) (1.55Å) than on Ni(111) (1.43Å) may not allow optimal overlap of the molecular (s,p) and metal (d) orbitals; (2) or, the different geometries may arise from the difference in the Ni and Rh or Pt wavefunctions that participate in forming the molecular orbitals with the adsorbed hydrocarbon.

As the acetylene layer on Ni(111) is heated above 400K, C-H species are detected by HREELS;[38] the vibrational spectrum of this species is nearly identical to those obtained on Rh[9b] and Pt(111)[20]

under similar conditions. With still further heating, a graphite layer forms. In this case the graphite and nickel unit cells match in size and a simple (1x1) LEED pattern is observed.[39]

HREELS[40,41] and AES[42] studies on acetylene adsorption on the (100), (110), and (111) faces of tungsten indicate partial dissociation of the hydrocarbon layer at room temperature. At low coverages, the hydrocarbons are completely dissociated, while at higher coverages a di-σ bonded structure forms that is probably very similar to the parallel-bonded species we found on Pt and Rh(111). The carbon fragments probably modify the electronic and structural properties of the tungsten surface to allow molecular adsorption. Tungsten carbide has been observed to have very similar catalytic[43] and electronic[44] characteristics to Platinum. It is tempting to consider that low coverage dissociation of ethylene occurs due to adsorption on the very reactive bare tungsten surface whereas the di-σ bonded ethylene that forms at higher coverages may be due to adsorption on a tungsten carbide surface which behaves much like Platinum.[42] This system is certainly worthy of further experimental and theoretical work. Preliminary studies on acetylene and ethylene adsorption on the low miller index faces of iron[45,46] indicates that these surfaces may act much like tungsten. Thermal desorption spectra[45] obtained show that a mixture of molecularly and dissociatively adsorbed acetylene exists at 300K, while Photoemission spectra[46] indicate that acetylene and ethylene will already decompose on the bare α-Fe(100) surface at only 100K.

All these observations fit the general trend that metal surfaces became more reactive as we move towards the upper left hand corner of

the transition metal series. (e.g. towards Fe and W). Now we will consider adsorption of acetylene and ethylene on Cu and Ag that appear at the right hand side of the transition metal series and again confirm the above-mentioned trend. Acetylene adsorption on Cu(111) has been investigated with UPS;[47] the acetylene species is weakly bound to the surface and desorbs intact at 370K. The spectra indicate that adsorbed acetylene is not significantly distorted from its gas phase structure and that it interacts with the metal surface solely through its π-orbitals. This contrasts sharply with acetylene adsorbed at similar temperatures on Platinum or Rhodium where significant rehybridization, large adsorption energies, and a substantial distortion from the gas-phase structure all occur. Experiments on Ag(111)[48] parallel those on Cu; here ethylene desorbs already below 200K and does not appear to be distorted, according to UPS and X-ray Photoelectron Spectroscopy (XPS) studies. Once again, the bonding of the unsaturated hydrocarbon to the surface via its π-orbital.

Thus three different regimes of hydrocarbon bonding to metal surfaces are seen; W and Fe are very reactive and at room temperature dissociate adsorbed acetylene or ethylene by C-C bond breaking. This strong interaction appears to be moderated by the electronic influence of the atomic carbon layer that forms on the bare metal; the metal carbide layer (with probably one carbon atom per surface W or Fe atom[42]) acts like a clean Platinum surface. The Pt, Rh, Pd, and Ni metals do not dissociate the adsorbed hydrocarbons into smaller carbon fragments at room temperature, but the gas phase structure is distorted or rearranged. On Ni, acetylene is strongly rehybridized and μ-bonds to

the (111) surface, while ethylene will dehydrogenate to chemisorbed acetylene at room temperature. On the (111) and (100) faces of Pt, Rh, and probably Pd, acetylene forms either vinylidene or ethylidyne species depending on the amount of coadsorbed hydrogen present on the surfaces. Although the carbon-hydrogen and carbon-metal bonds are easily broken, the carbon skeleton is seen to remain intact below 400K. The surfaces of Ag and Cu illustrate the third regime of hydrocarbon bonding where adsorbed acetylene is not significantly distorted from its gas phase structure and desorbs as the intact molecule. Further studies of hydrocarbon bonding on other transition metals and other crystal faces will provide a better understanding of the geometric and electronic effects on the structure of hydrocarbon monolayers.

VII. DIRECTIONS FOR THE NEAR FUTURE.

Studies of the structure and bonding of hydrocarbon monolayers that were carried out so far suggest several interesting avenues of research for the near future. The temperature dependence of hydrocarbon bonding on the more reactive transition metal surfaces (W, Fe, Re, Mo, etc.) is poorly understood. Low temperature (<100K) studies need to be carried out to monitor the sequence of hydrocarbon structures that may form as well as the nature of sequential rearrangement and bond breaking as the temperature is increased.

Often, high pressures are necessary to force the molecules to remain on the surface as the temperature is increased. The high pressure-high temperature regime is where most catalytic reactions are carried out. It would be of great value to study the adsorbed layer <u>after</u> a high pressure catalyzed reaction by quenching to low temperatures before pressure reduction needed to carry out the surface studies. Perhaps reaction intermediates or less strongly bound surface species can be identified this way.

As surface science techniques are refined more information should become available on the bonding of larger molecular weight hydrocarbons on metal surfaces. These include aromatic, cyclic and heterocyclic molecules, long chain alkanes, alkenes, alcohols and acids. Studies of adsorbed organic molecules that contain polar groups for strong surface bonding could elucidate the molecular details of lubrication and adhesion.

Promoters such as potassium or chlorine are routinely used in the chemical technology to improve the activity, selectivity and the

stability of metal catalysts;[49a] yet the influence of promoter-metal charge transfer on the bonding of adsorbed hydrocarbons is poorly understood.[49b,c] Studies of co-adsorbed promoter-hydrocarbon monolayers would be of considerable value.

Structure sensitivity is an issue of great importance in catalysis; the properties of catalysts can be dramatically altered as the dispersion of metal particles on a support is varied. This indicates that the geometry of the metal particles on the support plays an important role in determining its catalytic properties. The dispersion on identical catalysts can be modelled with different faces of single-crystal samples. To date, most hydrocarbon studies on well-characterized single crystals have used only the low miller-index faces, which are smooth and compact. Fig. 12 shows some stepped and kinked surfaces that occur for the higher miller indices. The atoms beneath the step or kink edge have a higher coordination number and can be more reactive than the terrace atoms in some cases.[50] For example, the dehydrogenation and hydrogenation reactions of acetylene on Ni show extreme structure sensitivity.

We recall that acetylene μ-bonds to Ni(111) at room temperature. The stepped Ni(5(111)x($\bar{1}$10)) surface dehydrogenates acetylene to a metastable C_2 fragment that on further annealing to 200K forms an atomic carbon layer.[51] On the Ni(111) surface C-C bond-breaking occurs first at 400K to form C-H groups, while on the Ni(5(111)x($\bar{1}$10)) face C-H bond breaking is seen to happen before C-C bond scission. Similarly, the stepped surface has a markedly higher hydrogenation activity for acetylene than the flat one when coadsorbed hydrogen is present. It

is our hope that studies of the bonding of hydrocarbon monolayers on stepped and kinked surfaces will further elucidate the structure sensitivity of their surface chemical bonds.

ACKNOWLEDGEMENT

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LIST OF FIGURES

Fig. 1. Schematic of LEED experiment. Low-energy electrons striking the crystal are backdiffracted on a phosphorescent screen; the unit cell of any surface structure can be found by examining the diffraction spot positions on the screen.

Fig. 2. Illustration of the method used in a LEED analysis. The spot intensities are measured as a function of electron wavelength (or energy); these intensity vs. voltage (I/V) profiles are then compared to theoretical curves that assume a particular model geometry. The geometry that gives best agreement between theory and experiment is considered the correct one.

Fig. 3. Typical HREEL spectra obtained from CO adsorbed on Rh(111). The peak assignments are given in the text.

Fig. 4. An ethylidyne ($\equiv CCH_3$) species forms on the Rh(111) surface between 240 and 270K; a comparison is made between the bond angles and distances found for this structure by LEED and those for corresponding organometallic compounds.

Fig. 5. The propylidyne phase that appears on the Rh(111) surface between 240 and 270K can order its methyl groups into a superlattice; the $(2\sqrt{3} \times 2\sqrt{3})$ R30° unit cell drawn indicates the periodicity of this superlattice.

Fig. 6. Alkylidyne species also form on the Pt(111) surface above 300K with ethylene, propylene, and 2-butene adsorption. The relevant bond distances are shown.

Fig. 7. The intensity vs. voltage (I/V) profiles for the room temperature phases of ethylene and propylene on Pt(111) are shown. The near identity of these curves indicates that propylene forms a propylidyne structure. The alkynes (C_2H_2 and C_3H_4) will also yield an alkylidyne phase at 300K in the presence of coadsorbed hydrogen.

Fig. 8. The butylidyne phase on Pt(111) orders its ethyl groups into a $(2\sqrt{3} \times 2\sqrt{3})$ R30° superlattice. The ethyl groups orient themselves to optimize their Van der Waals interactions.

Fig. 9. A comparison of the c(4x2) and (2x2) lattices of ethylidyne on Rh(111).

Fig. 10. Thermal Desorption Spectra (TDS) for ethylene, propylene, and 2-butene layers on Pt(111). The hydrogen desorption rate is plotted against the crystal temperature. This illustration is taken from reference 24.

Fig. 11. The di-σ,π bonded methylacetylene species that forms on the Rh and Pt(111) surface is shown.

Fig. 12. The flat (111), stepped (755), and kinked (10,8,7) surfaces can exhibit very different hydrocarbon bonding. The highly coordinated metal atoms beneath the step and kink edges tend to be more reactive.

Table I. Commonly used structural methods in surface science

Acronym	LEED[1]	HREELS[2]	SEXAFS[3]	NPD[3]	UPS[3]
Full Name:	Low energy electron diffraction	High resolution electron energy loss spectroscopy	Surface extended X-ray absorption fine-structure spectroscopy	Normal photoelectron diffraction	(Angle - integrated) Ultraviolet photoemission spectroscopy
Sensitive to:	Atomic positions	Molecular configuration	atomic positions	Atomic positions	Electronic structure
Underlying Principle:	Electron diffracts from atomic cores	Electron energy gain or loss by interaction with the dynamic dipole moment or short-range forces of surface vibrations	Emitted electron diffracts from nearby atomic cores	Photoelectron diffracts from nearby atomic cores	Photoelectron emission from molecular orbitals
Advantages:	Measures bond distances (± 0.05-0.1Å) and bond angles (±10-15°)	Identifies molecular species present on surface and its adsorption site; detects hydrogen	Measures bond distances (± 0.03)	Measures bond distances (± 0.05-0.1Å) and bond angles (±10-15°) and probes bond symmetry	Measures binding energy of molecular orbitals
Dis-advantages:	Requires long range order; complicated multiple scattering occurs	Not quantitative; difficult to assign vibrational modes	Synchrotron radiation required	Synchrotron radiation required	d-band emission and relaxation effects complicate interpretation of spectra

Table II. Comparison of bond distances of ethylidyne ($\equiv C-CH_3$) adsorbed on the Rh and Pt(111) surfaces, determined by LEED.

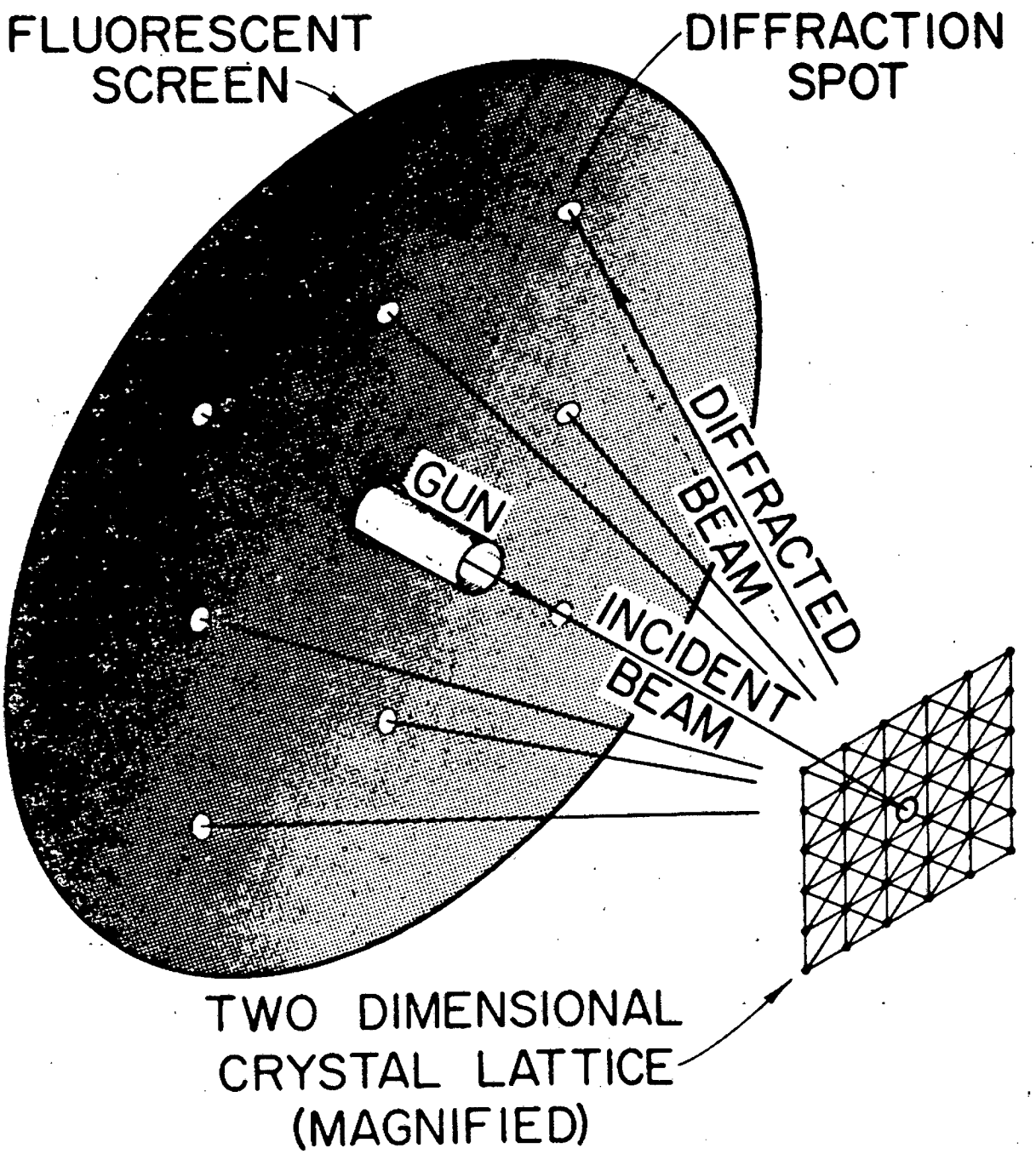
	Rh(111)	Pt(111)
C-C distance	1.45 (5)	1.50
M-C distance	2.03 (4)	2.00
Carbon radius in M-C bond	0.69	0.61
$\measuredangle$CCM	130°	127°

Table III. Irreversible structural transitions for ethylene on Rh and Pt(111) that occur with increasing temperatures.

	Rh(111)	Pt(111)
I. Intact Carbon Skeleton Below 300K		
Structure	Ethylidyne ($\equiv CCH_3$)	di-σ bonded (H_2C-CH_2)
Temperature range	<230-270K	<140-290K
LEED pattern	(2x2)	disordered
Technique(s) used	LEED,[11] HREELS[9b]	HREELS[19]
II. Intact Carbon Skeleton Between 300-450K		
Structure	Ethylidyne (?) ($\equiv CCH_3$)	ethylidyne ($\equiv CCH_3$)
Temperature range	270-420K	290-450K
LEED pattern	c(4x2)	(2x2)
Technique(s) used	LEED,[12] HREELS[9b]	LEED[15], HREELS,[15,16] ARUPS[17]
III. Carbon-Carbon Bond Scission		
Structure	$\equiv$CH species	$\equiv$CH species
Temperature range	420-700K	450-700K
LEED pattern	disordered	disordered
Technique(s) used	HREELS[9b]	HREELS[20]
IV. Total Dehydrogenation		
Structure	graphite	graphite
Temperature range	700K	700K
LEED pattern	(12x12)	(9x9)+ other graphite-Pt registries
Technique(s) used	LEED,[21]	LEED[22]

Table IV. Irreversible structural transitions for acetylene on Rh and Pt(111) that occur with increasing temperature.

	Rh(111)	Pt(111)
I. Rehybridized Species		
Structure	di-σ, π bonded (HC=CH)	di-σ, π bonded (HC=CH)
Temperature range	230-270K	140-350K
LEED pattern	(2x2)	(2x2)
Technique(s) used	HREELS[9b]	HREELS,[19] LEED[25]
II. Hydrogen-Shift Species		
Structure	Vinylidene (=C=CH_2)	Vinylidene (=C=CH_2)
Temperature range	>270K	>350K
Hydrogen needed?	No	No
LEED pattern	Disordered	Disordered
Technique(s) used	Predicted from strong similarity for Rh and Pt(111)	HREELS[19]
III. Hydrogen-addition Species		
Structure	Ethylidyne (?) ($\equiv CCH_3$)	Ethylidyne ($\equiv CCH_3$)
Temperature range	270-420K	290-450K
Hydrogen needed?	Yes	Yes
LEED Pattern	c(4x2)	(2x2)
Technique(s) Used	LEED,[11] HREELS[9b]	LEED,[15] HREELS,[16] ARUPS,[17]



$$\underset{\sim}{k}' = \underset{\sim}{k} + \underset{\sim}{G}$$

XBB 708-3583

Fig. 1

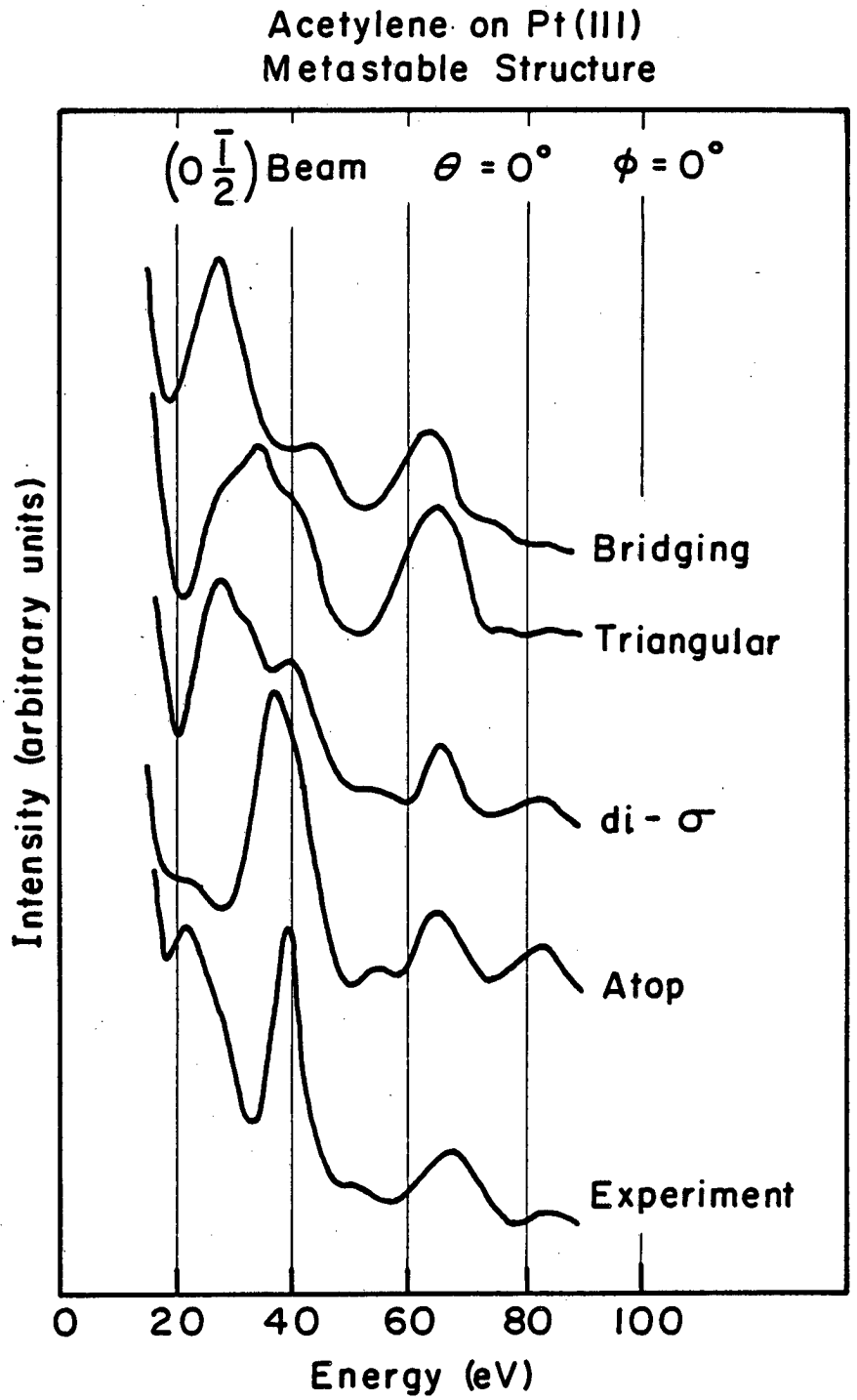

Acetylene on Pt(111)
Metastable Structure
$(0\frac{1}{2})$ Beam
$\theta = 0°$
$\phi = 0°$
Bridging
Triangular
di - σ
Atop
Experiment
Intensity (arbitrary units)
0
20
40
60
80
100
Energy (eV)
XBL 772-5068

Fig. 2

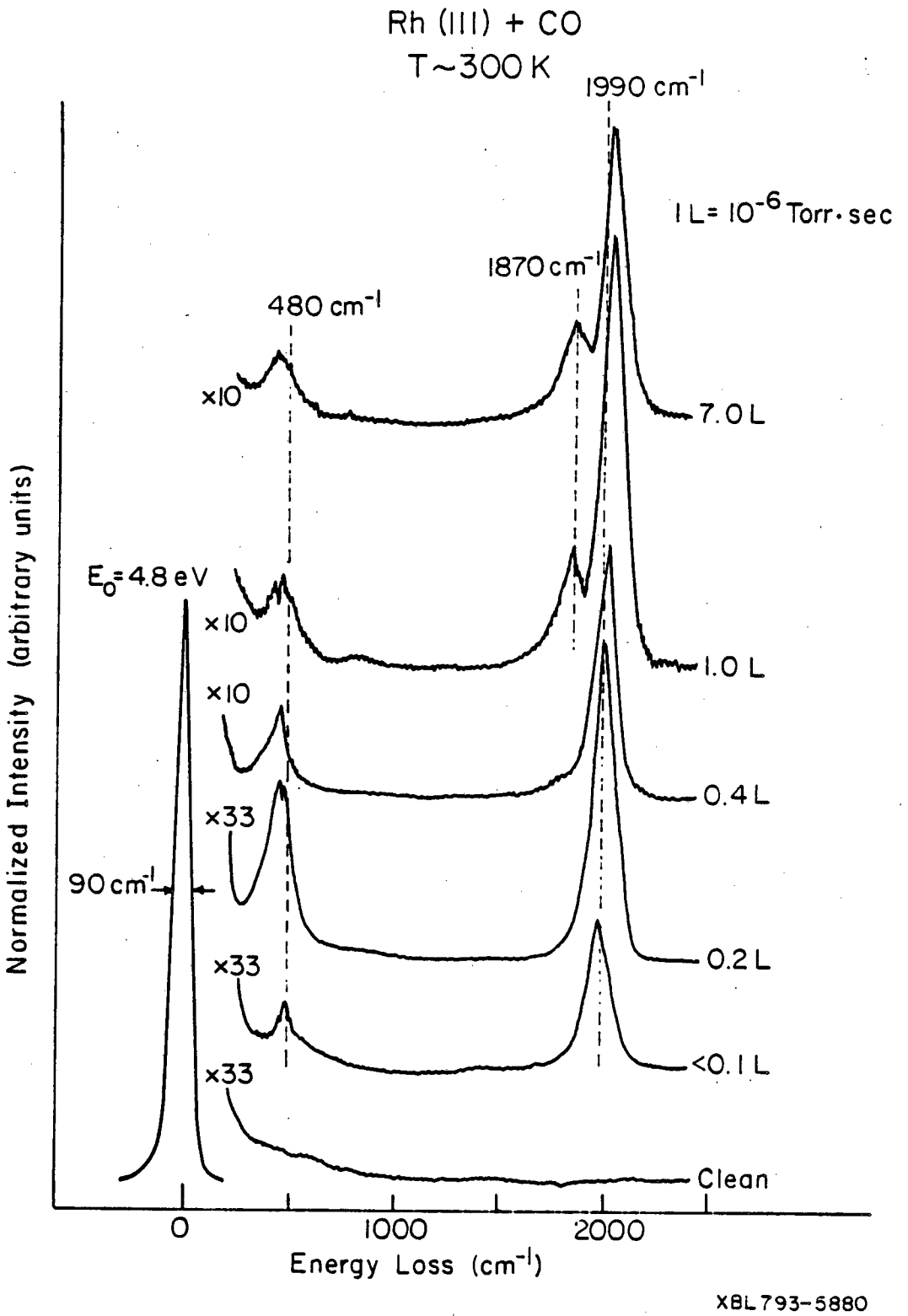
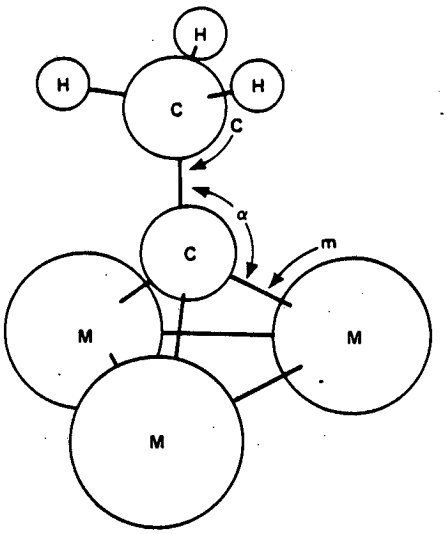

Rh (111) + CO
T~300 K
1990 cm⁻¹
1 L= 10⁻⁶ Torr·sec
1870 cm⁻¹
480 cm⁻¹
×10
7.0 L
E₀=4.8 eV
×10
1.0 L
×10
0.4 L
×33
90 cm⁻¹
0.2 L
×33
<0.1 L
×33
Clean
Normalized Intensity (arbitrary units)
0
1000
2000
Energy Loss (cm⁻¹)
XBL 793-5880

Fig. 3

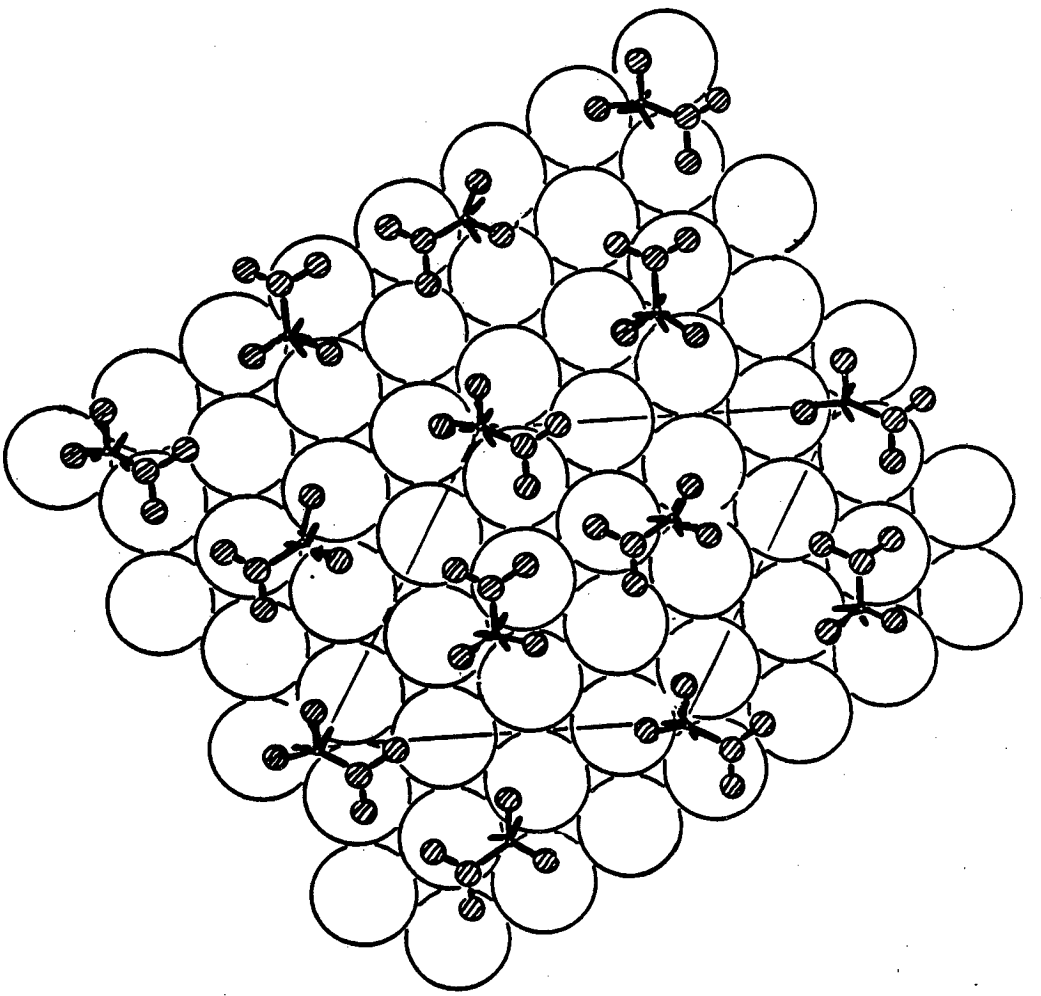
Bond Distances and Angles for Ethylidyne Species



Ethylidyne Species	C[Å]	m	Measured Metallic Radius, r_M	Carbon Covalent Radius, r_C	α[°]
$Co_3(CO)_9CCH_3$	1.53 (3)	1.90 (2)	1.20	0.66	131
$H_3Ru_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.42	0.66	128
$H_3Os_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.42	0.66	128
$[P(C_6H_5)_3]Co_3(CO)_8CCH_3$	1.50 (2)	1.92 (1)	1.25	0.66	131
$[\pi\text{-}C_6H_3Me_3]Co_3(CO)_6CPh$	1.48 (2)	1.89 (2)	1.23	0.66	132
$[\pi\text{-}C_8H_8]Co_3(CO)_6CPh$	1.48 (2)	1.89 (2)	1.23	0.66	132
Rh(III) + (2×2) CCH_3	1.45 (5)	2.03 (4)	1.34	0.69	130
$H_3C - CH_3$	1.54			0.77	110
$H_2C = CH_2$	1.33			0.68	122
$HC \equiv CH$	1.20			0.60	180

XBL 821-5004

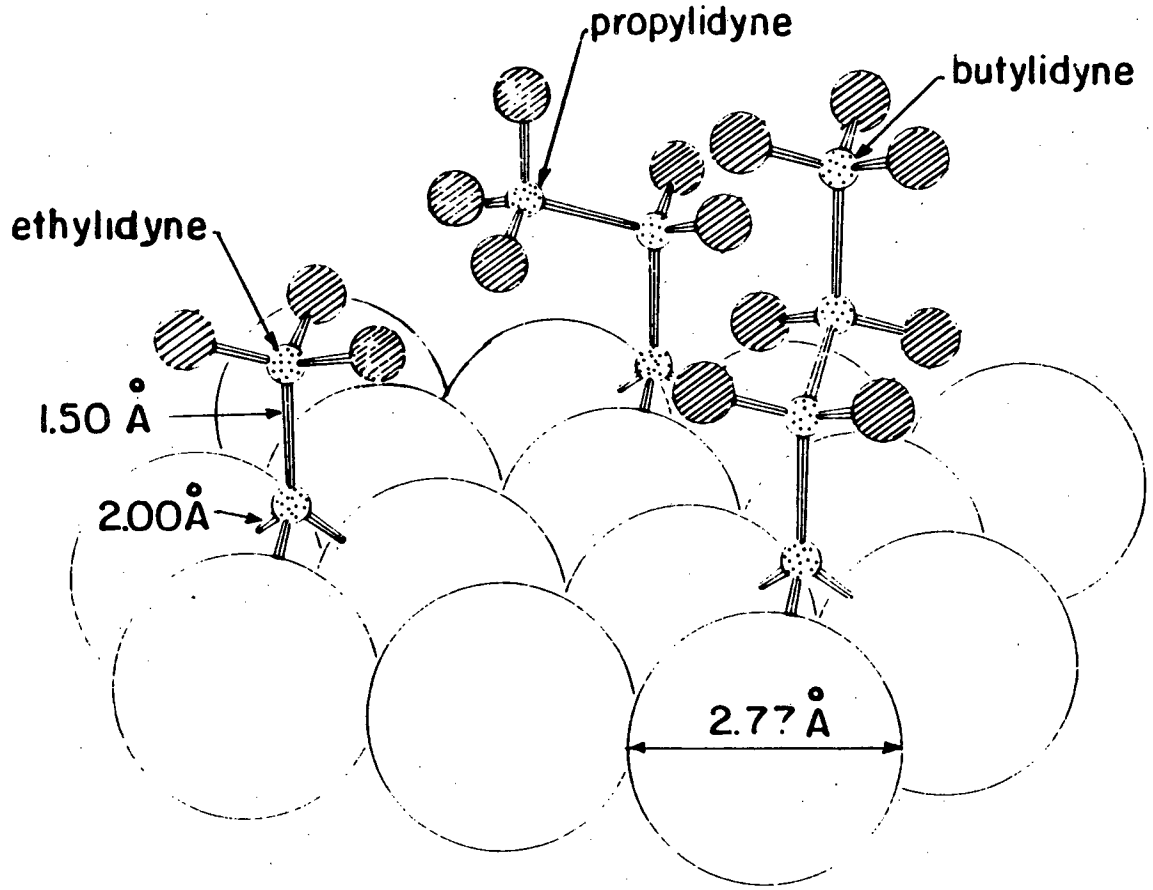
Fig. 4



Rh(111) + $(2\sqrt{3} \times 2\sqrt{3})R30°$ (propylidyne)

XBL 821-5101

Fig. 5



Pt (III) + ethylidyne, propylidyne and butylidyne

Fig. 6

XBL 8110-6882

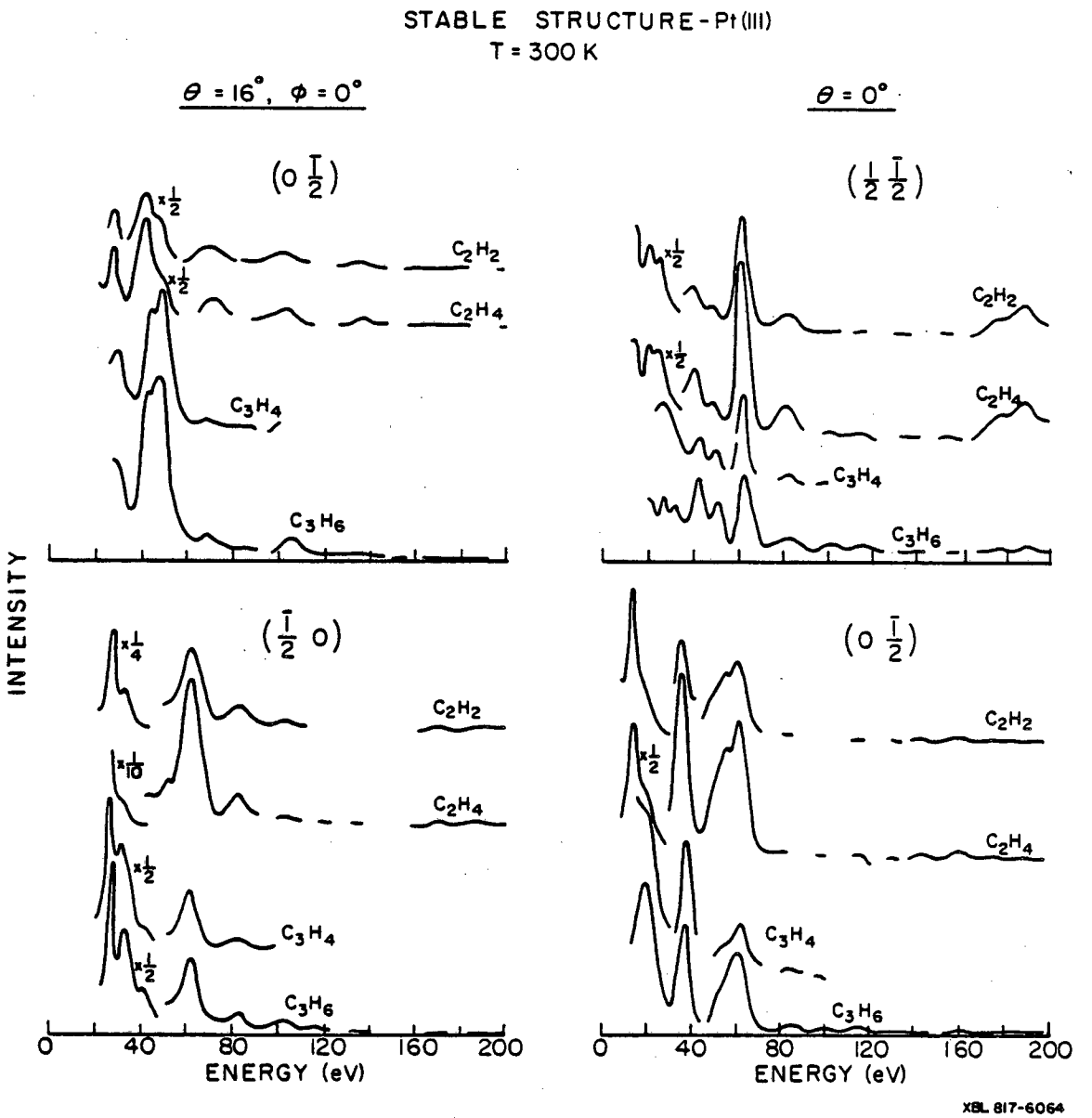
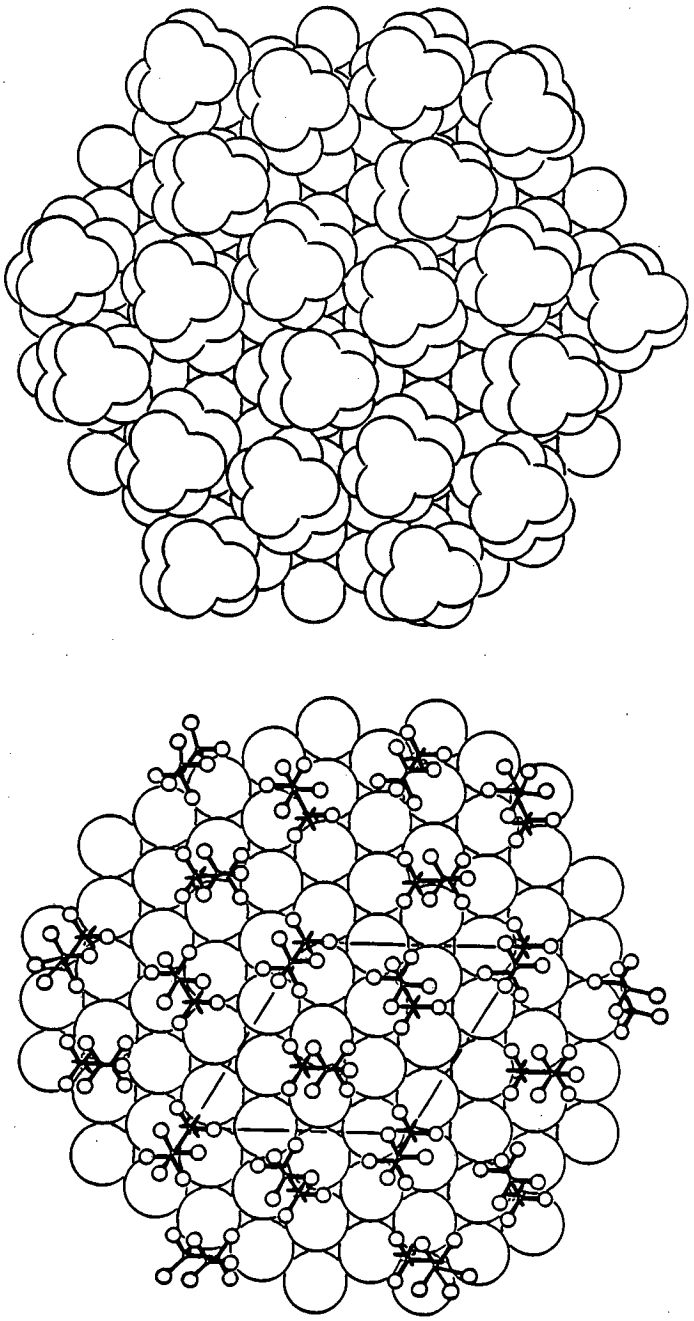

STABLE STRUCTURE-Pt(III)
T = 300 K
θ = 16°, φ = 0°
θ = 0°
(0 1̄/2)
(1/2 1̄/2)
(1̄/2 0)
(0 1̄/2)
C2H2
C2H4
C3H4
C3H6
INTENSITY
ENERGY (eV)
0
40
80
120
160
200
XBL 817-6064

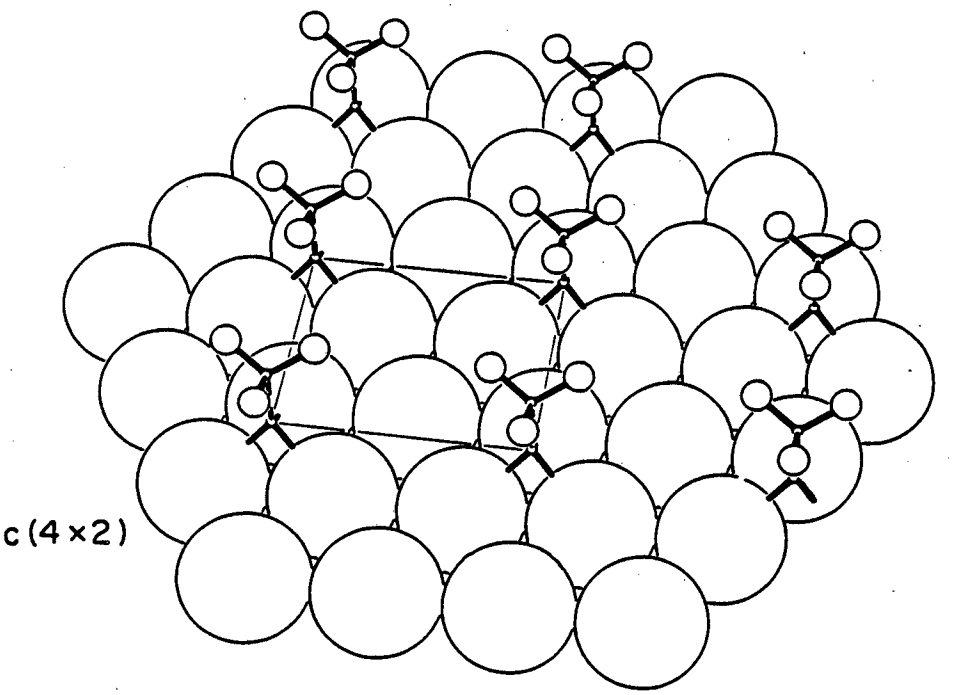
Fig. 7

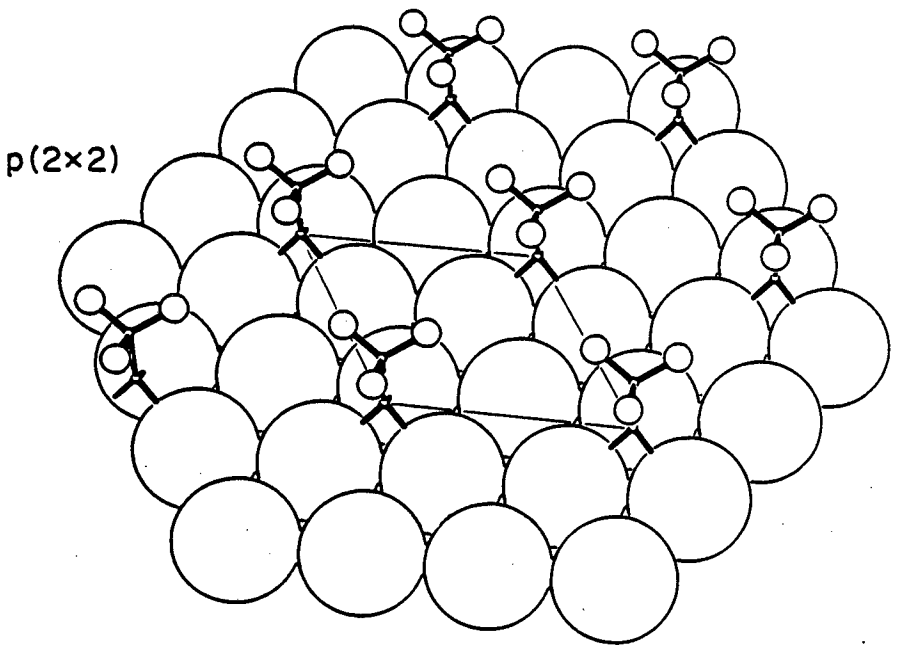


fcc (111) + $(2\sqrt{3} \times 2\sqrt{3})$ R30° C_4H_7 (butylidyne)

XBL 813-5411

Fig. 8





fcc (111) + C_2H_3 (ethylidyne)

XBL813-5407

Fig. 9

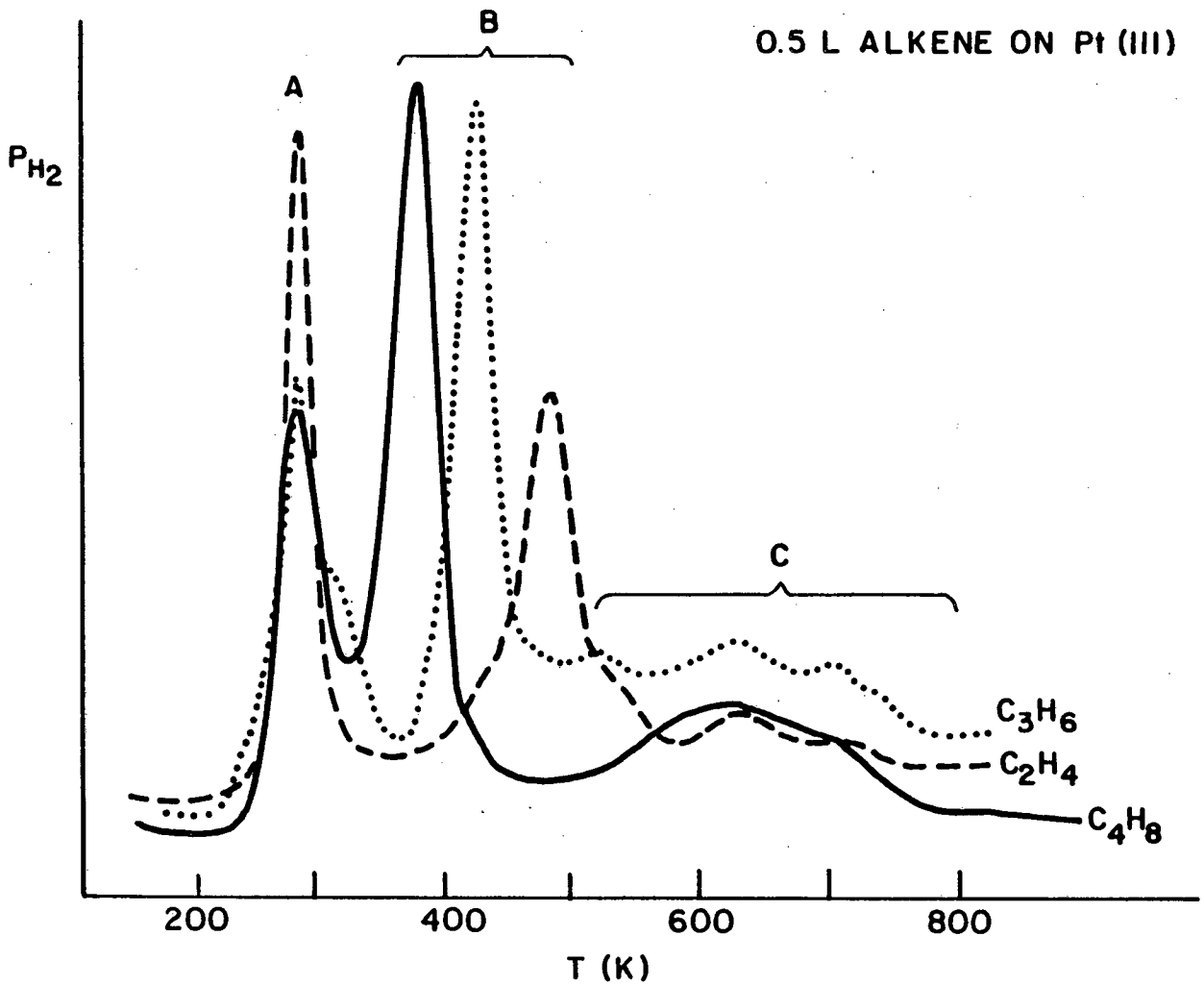
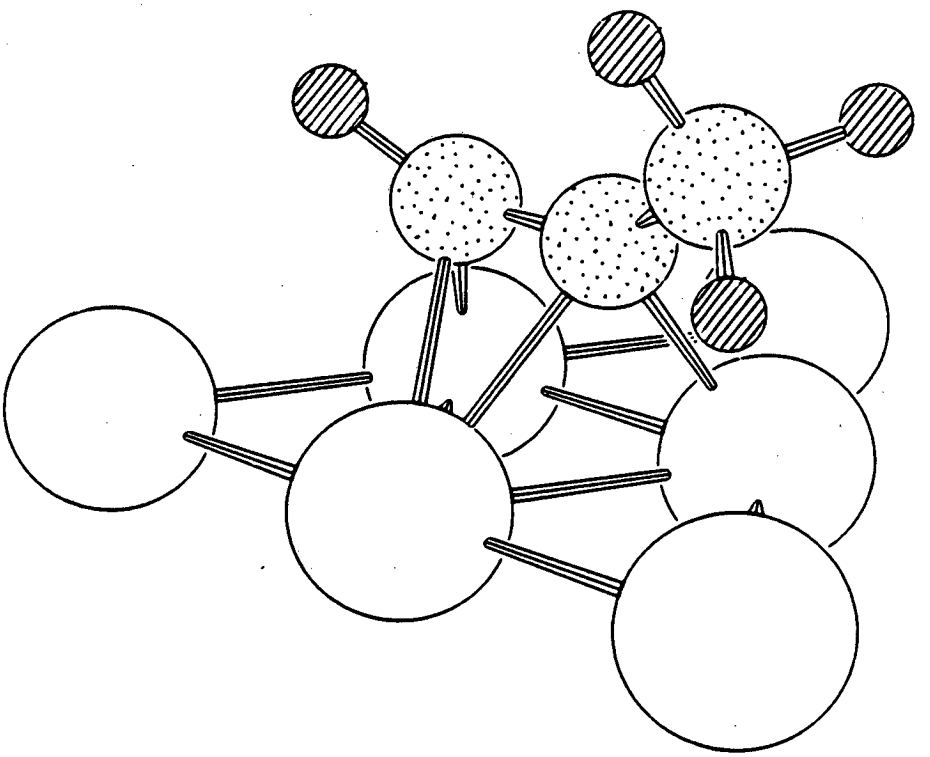


Fig. 10

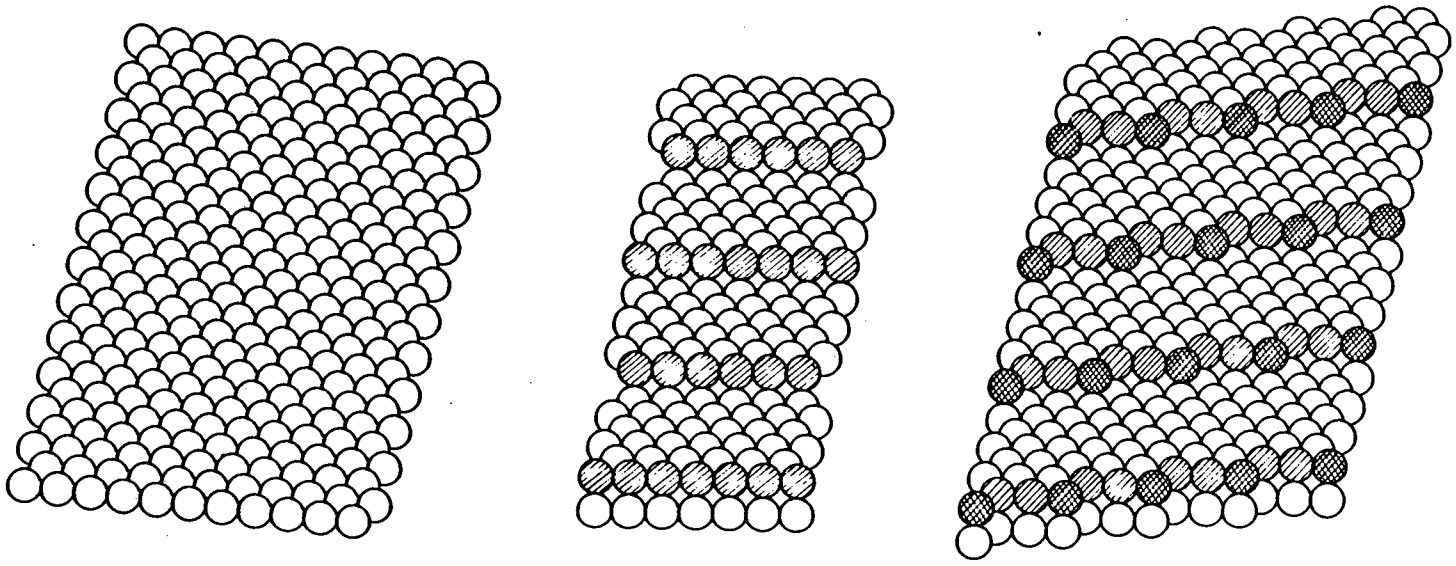
XBL 814-5475



Metastable methylacetylene

XBL 817-6067

Fig. 11



XBL 806-10430

Fig. 12

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