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Stereochemistry in the
Coordination Chemistry of Metal Surfaces

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Abstract

The stereochemistry of metal surface coordination chemistry is discussed with respect to the chemisorption states of hydrogen, carbon monoxide, nitriles, isocyanides, pyridine, benzene, acetylenes and olefins. A stereochemical comparison is made with the binding of such species on metal surfaces with the binding in discrete molecular clusters.

Introduction

Molecules can bind with metal surfaces in relatively complex fashions^{1,2} with multicenter metal-ligand atom interactions. Initial binding may be followed by one or a series of bond scissions to yield an array of molecular fragments bound to single or to several metal atoms.^{2,3} Presently available spectroscopic and diffraction techniques for surface studies do not easily yield the precise structural and stereochemical definition of the techniques applicable to molecules and to bulk structures.³ I describe here the status of stereochemical definition of metal surface chemisorbed species and the possible stereochemical relationships between these species and those bound to metal atoms in discrete or molecular mononuclear and polynuclear²⁻⁸ metal complexes. A set of relatively simple molecules, hydrogen, carbon monoxide, nitriles, isocyanides, pyridine, benzene, acetylenes and olefins is discussed

in the contexts of stereochemistry in metal surface coordination chemistry² and of the metal surface-metal cluster analogy.²⁻⁴ The latter consideration is of significance on several bases. Because molecules or molecular fragments can and sometimes do bind to more than one metal atom in a cluster, the comprehensive stereochemistry of ligand-metal interactions in clusters provides a series of potential (and simple) models of metal-ligand stereochemistry at metal surfaces that are useful in the attempts to structurally interpret spectroscopic, diffraction and chemical data for metal surface chemisorption states. Secondly, there should be instances where stereochemical features or trends in clusters and in surfaces will diverge. Identification of such systems with subsequent delineation of the factor or factors responsible will assist in establishing the "boundary conditions" for the valid application of a localized bonding model to surface chemisorption states.

Hydrogen Chemisorption State

Hydrogen chemisorption on most transition metals is dissociative⁹ at 300 K in that the H-H bond is severed and the individual hydrogen atoms are directly bonded to metal atoms at the surface. Conceptually, this is the simplest stereochemical problem but it is very difficult to resolve experimentally because most surface physical techniques do not sense the presence of the hydrogen nuclei. Even a "vibrational" technique now in an extensive stage of development--analysis of energy loss in electrons inelastically scattered from the metal surface¹⁰--does not always sense vibrational excitation of hydrogen atoms chemisorbed on the late transition metals.^{11,12} For nickel(100), hydrogen forms an ordered 2 x 2 structure and the hydrogen atom explicably lies in the hollow, four-fold bridging site

as judged by electron loss spectroscopic studies^{11,12} (see Figure 1).

Analysis of low energy electron diffraction data from a nickel(111) surface with chemisorbed hydrogen established that the unit cell is twice as large as that of the two dimensional surface unit cell of nickel(111) and that the larger unit cell is not rotationally disjoint from the nickel surface atom unit cell.^{13,14} Registry of the two cells is not established unequivocally although it has been suggested that the hydrogen atoms lie over every other unfilled three-fold site and over every other filled three-fold site (Figure 2).¹⁴

We¹⁵ are in the process of applying molecular orbital theory to this issue of where a hydrogen atom would be most favorably (energetically) placed on the (111) surface of nickel. Preliminary results suggest that the ordering should be 3-fold sites > 2-fold sites > sitting atop individual nickel atoms (Figure 2). Differentiation between filled and unfilled 3-fold sites will require a precise quantitative calculation; this more subtle stereochemical issue will not be resolved by such an approximate theoretical analysis. Interestingly, qualitative considerations suggest that a more stable configuration would be the placement of the hydrogen atoms in the subsurface octahedral holes of the (111) nickel face. There then would be a seeming inconsistency with the interpretation¹⁴ of the low energy electron diffraction data; however, both chemisorption states should be present with their concentrations a function of surface coverage, and the diffraction studies would detect only the surface bridging sites. An electron loss study of hydrogen on platinum(111)^{16a} detected a loss at 500 cm^{-1} that was ascribed to hydrogen atoms at surface three-fold sites. A similar suggestion for hydrogen on palladium(111) was made from infrared studies^{16b} of films.

Precise structural and stereochemical data for hydridometal clusters are especially revealing and possibly suggestive. In three-atom and four-atom-tetrahedral metal clusters, the hydrogen atom is never in the center of the cluster (the center interstice is too small to accommodate a hydrogen atom) but is in one of three possible positions: (1) terminally bound to a single metal atom (analog of the sitting atop a single metal atom for the surface case), (2) bridging between two metal atoms (analog of the two-fold site for a close-packed metal surface), and (3) bridging between three metal atoms (analog of a (111) surface plane three-fold site).² Of these cluster hydrides structurally characterized to date, bridging hydride ligands are more common than terminal hydride ligands. In the only octahedral metal cluster hydrides for which the hydrogen atom positions are unequivocally established (by X-ray and neutron crystallographic studies), the hydrogen atoms are in the octahedral hole! These clusters include the biocuboctahedral cluster hydrides,^{17a} $\text{Ni}_{12}(\text{CO})_{21}\text{H}^{3-}$ and $\text{Ni}_{12}(\text{CO})_{21}\text{H}_2^{2-}$, and the octahedral^{17b} $\text{Co}_6(\text{CO})_{15}\text{H}^-$ cluster. A similar placement is established for the hydride ligand in the octahedral Nb_6H unit of $\text{Nb}_6\text{I}_{11}\text{H}$.¹⁸ Thus the data for clusters and the qualitative considerations would suggest that, at least for the later transition metals like nickel and platinum, chemisorbed hydrogen should first go below the surface in the octahedral holes provided that the activation energy for migration from surface sites to these octahedral holes is not too high--a large activation energy for such a migration is not anticipated. The next sites to be filled should be the three-fold surface sites. However, our molecular orbital calculations¹⁵ actually show that that three-fold sites are favored over octahedral holes and predict the former are filled before the octahedral holes. Perhaps, with CO chemisorbed on the nickel(111) surface (analog of the nickel carbonyl hydride clusters), the relative energy for three-fold and for octahedral hole sites would be transposed. 3

The mechanistic significance of subsurface hydrogen atoms in the chemistry of metal surfaces could be significant. For example, the catalytic hydrogenation of acetylenes to give olefins of largely *cis*-stereochemistry is explicable if a bound acetylene is "attacked" from below the surface by hydrogen atoms. Analogous stereochemical features of aromatic hydrocarbon hydrogenation (e.g., formation of largely *cis* dimethylcyclohexanes from xylenes) at metal surfaces would also follow from such considerations. However, "attack" by surface hydrogen atoms would yield the same *cis* stereochemistry in hydrogenation products of olefins and arenes provided that the olefinic C-C bond and the C₆ arene plane are largely parallel to the surface. Attack from below the surface, nevertheless, does raise the interesting possibility that effectively only one surface metal atom might be required per olefin hydrogenation sequence whereas more than one surface atom is required if the hydrogen atoms are all above the surface.

Carbon Monoxide

Like chemisorbed hydrogen atoms, the chemisorbed carbon monoxide molecule could reside in the 3-fold, 2-fold or 1-fold sites (Figure 2) normal to the (111) faces of a face-centered cubic metal with the carbon atom directly bonded to the metal atom or atoms. The basic electronic features of these interactions would be fully analogous to those of mononuclear or polynuclear metal carbonyls. Carbon monoxide cannot penetrate the surface as a molecule but it can, and does with the more electropositive metals like iron, chemisorb with scission of the carbon-oxygen bond and these individual atoms then can move into and below the surface at least at elevated temperatures.

For associatively chemisorbed carbon monoxide on metals like nickel,

palladium, platinum, rhodium, ruthenium and iridium, the precise stereochemistry is not well defined. Interpretations of complimentary low energy electron diffraction,¹⁹ angle resolved photoemission^{20a} and energy loss²⁶ data agree in placing the carbon atoms atop single nickel atoms in the (100) nickel surface (Figure 1) although in the first analysis,¹⁹ the CO vector was set substantially off the normal to the surface plane. The behavior of the palladium(100) surface in CO chemisorption is apparently quite different than nickel. Here the experimental data for the ordered and centered (4x2) -45° structure are consistent only with CO bridging between two palladium atoms^{20b} (Figure 1). This divergent behavior of CO on nickel and palladium surfaces is really quite unexpected--more specifically, it is surprising that the CO molecule is not bridge bonded on nickel(100).

Recently, the analysis of energy loss in electrons inelastically scattered from metal crystal faces on which carbon monoxide is chemisorbed has provided an extensive set of data that identify the energy associated with the stretching of the C-O bond in the chemisorbed carbon monoxide molecule. The results are interesting and the apparent stereochemical implications are not always simple and not necessarily expected from qualitative considerations. Before discussing these results, it is instructive to consider the well established stereochemical features of metal carbonyl clusters.²

The binding of carbon monoxide to metal atoms in metal clusters includes

- (i) Terminal 2-center M-CO bonding with a ν_{CO} range of ~2150 to 1950 cm^{-1} in neutral clusters.

- (ii) "Edge" bridging 3-center bonding, analogous to

the 2-fold potential binding site in a close packed metal surface (Figure 2), with a ν_{CO} range of ~1880 to 1740 cm^{-1} in neutral clusters.

- (iii) Face bridging 4-center M_3 -CO bonding with the CO vector normal to the M_3 centroid, analogous to the 3-fold potential binding site in a close packed metal surface (Figure 2), and with a ν_{CO} range of ~ 1840 to 1620 cm^{-1} in neutral clusters.

These are the three established, idealized classes of metal-CO interactions in metal clusters; aberrant forms with unequal M-C distances are known for the two classes of bridging CO interactions,² and these are, in a sense, intermediate states between the idealized forms. The energy difference between terminal and edge (3-center) bridging sites can be quite small since studies²¹ of intramolecular CO exchange between such sites have established activation energies as low as ~ 8 kcal/mole which represents a maximum value for the energy difference between terminal and edge bridging CO bond energies in these particular cases. In other cases, the activation energy for intramolecular site exchange is greater than 20 kcal/mole which might indicate very large energy differences between bonding types.²¹ Typically, the appearance of bridge bonding is more common in the clusters of first row transition metals than those of the second row which in turn are more common than in those of the third row. This shift appears to be largely electronic in origin. Bridge bonding is more effective than terminal bonding for carbon monoxide in removing electron charge from the metal centers. This electronic effect is especially evident in the shift from terminal to bridge bonding upon increasing the formal negative charge on the cluster or upon increasing the number of strong σ donor ligands like phosphines or phosphites.

In addition to the above cited three idealized classes of carbon monoxide bound to metal atoms in clusters, there is a striking example²² of a carbonyl ligand bound through both the carbon and the oxygen atoms to metal atoms in a cluster as structurally²² depicted in Figure 3. Conceptually, this cluster can be viewed as an intermediate between the associative and dissociative chemisorption states of carbon monoxide on a metal surface.

Much of the information about carbon monoxide chemisorbed states on metal surfaces has come from recent electron energy loss studies although complimentary reflectance infrared studies have been made in certain cases. One typical feature of these studies is that the apparent CO stretching frequency of chemisorbed carbon monoxide increases with increasing coverage of the surface by the carbon monoxide. For example, the frequency for CO on Ru(001) (hexagonal close packed) dramatically and smoothly shifts from 1980 to 2080 cm^{-1} as surface coverage increases.^{23a} One possible interpretation of this shift is that the stereochemistry smoothly shifts in registry (between surface metal atom and C(CO) atom two dimensional structures) from bridging to terminal ("sitting atop a single metal atom) binding as surface coverage increases. This registry explication is distressing to me--a coordination chemist--because the useful concept of directed bonding is inapplicable and because the approximation of a localized molecule-surface metal atom's interaction would appear to be of limited validity. I consider these possibilities to be relatively improbable especially for the case of low surface coverages simply because the fundamental chemical bond and directed valence concepts, which are successful in explaining structure and stereochemistry for the gas, liquid, solution and solid states, should not suffer complete revocation in their application to surface chemistry. Perhaps, at high coverages particularly above one monolayer a more delocalized interaction will obtain since there will be a relatively large separation between the upper layers and the metal surface atoms and since nonbonded interactions between the adsorbed molecules will be more significant.

A more attractive explanation for the CO frequency shifts with surface coverage is that the efficacy of the interaction of metal surface orbitals with the CO π^* orbital is significantly reduced as the extent of the CO

surface coverage increases (cf. discussion by Bradshaw and Hoffmann^{25c}). Unresolved, however, is the issue of a stereochemical interpretation of the absolute values for the CO stretching frequencies--are the values to a first approximation correlatable with the ranges (cited above) associated with terminal, edge-bridging, and face-bridging CO ligands in molecular metal clusters? More appropriate would be the M-C stretching frequencies but unfortunately these are rarely pure M-C stretching modes. Vibrational spectroscopic interpretations were relatively ineffective in correctly resolving fundamental structural and stereochemical issues in the early days of molecular structure studies but hopefully this scenario will not be repeated in the more subtle and demanding area of surface structure determination.

Carbon monoxide chemisorption on Pt(111) is on the basis of electron loss and reflection infrared studies very different from the chemisorption of this molecule on Ni and Pd(111) surfaces.²⁴ For CO on Pt, there is a single loss at $\sim 2075\text{ cm}^{-1}$ within the temperature range of 150 to 300 K for very low CO coverage. This loss shifts slightly on increasing coverage to about 2100 cm^{-1} and also a new loss appears at 1870 cm^{-1} . The initial high energy CO vibration was ascribed to CO at sitting atop a single platinum atom and the lower energy vibration to CO bridging two platinum atoms. Interestingly, a stepped platinum surface $6(111) \times (111)$ also shows a major CO absorption at $2075\text{--}2100\text{ cm}^{-1}$. (Both the flat and the stepped surfaces also exhibit a common high energy thermal desorption peak for CO at $\sim 520\text{--}540\text{ K}$ --this peak is the sole peak for low CO coverages on the stepped surface and is the minor peak, the major one is at $\sim 460\text{ K}$, for the flat surface.)

For nickel^{25a,b} and palladium^{25c} (111) surfaces, the carbon monoxide molecules chemisorbed under conditions of low coverage exhibit a relatively low CO stretching frequency. Nickel at 140 K exhibited a loss at 1810 cm^{-1}

at low CO coverages and this loss shifted to $\sim 1910 \text{ cm}^{-1}$ with increasing coverages. It has been proposed^{25b} that initially CO goes to the three-fold bridging sites on Ni(111) and then shifts to two-fold sites at higher coverages. Palladium(111) shows in reflectance infrared studies a relatively constant CO stretching frequency at 1823 cm^{-1} with low CO surface coverages at 300 K. At higher coverages a very broad CO absorption band (~ 100 wave numbers) centered around 1870 cm^{-1} is evident and the peak narrows and progressively shifts to $\sim 1946 \text{ cm}^{-1}$ at very high coverages. Bradshaw and Hoffmann^{25c} proposed that on palladium(111) the CO goes initially to three-fold sites and then shifts to two-fold sites at intermediate coverages.

Thus there is an apparent, similarity in stereochemistry for the CO chemisorption states on Ni(111) and Pd(111). The proposals that, at low CO coverages, the carbon monoxide is at three-fold sites are consonant with basic coordination chemistry principles. At low coverages, the surface energy (or in the jargon of coordination chemistry "the coordination unsaturation of the surface atoms") should be most effectively reduced by coordination of the CO molecules to a maximum of metal atoms--i.e., at three-fold bridging sites. The proposed platinum-CO stereochemistry at low CO coverages seems anomalous.

The ostensibly simple stereochemical problem of CO chemisorption states on close packed metal surfaces seems to be relatively complex. Complimentary studies of these CO chemisorption states by other spectroscopic and diffraction techniques may be required for a full resolution of the stereochemistry--this has been done for the case of CO on Ni(100) (where the consensus has CO bound to single nickel atoms and not in bridging sites as would be expected at low CO coverages on the basis of coordination principles). The experimental and interpretational difficulties in this

area are substantial. More than one chemisorption state may obtain under a set of temperature and coverage conditions--especially at high coverages. Such multiple chemisorption states can present problems because one spectroscopic or diffraction technique may be particularly sensitive to one state and another technique to another state. Surface coverage by a molecule on a crystal can--at best--be only semi quantitatively estimated yet the vibrational studies show the sensitivity of the absorption characteristics to coverage. In addition, the single crystal faces are not atomically perfect. Since vibrational absorption intensities can vary substantially it is conceivable--but perhaps unlikely--that the absorption intensities for chemisorbed molecules bound at "imperfection sites" might be larger than for those bound in the normal crystal plane.

Alkyl Cyanide (nitrile) and Isocyanide Chemisorption

Chemisorption of CH_3CN on the Ni and Pt(111) surfaces leads to weakly bound states.²⁷ Both chemisorption processes are largely thermally reversible and the desorption temperature for the Ni(111) CH_3CN state, the more tightly bound of the two, is about 385 K. In the nickel case, the CH_3CN surface structure is ordered; there is a 2x2 unit cell (Figure 2).²⁷ For both these metals, the CH_3CN molecule appears to be normal to the surface. The nitrogen atom probably is bound at three-fold sites. In coordination chemistry, acetonitrile is a weakly bound ligand that typically is bonded to single metal atoms through the nitrogen atom.²⁸

The isomer of acetonitrile, methyl isocyanide, is strongly bound to the nickel and platinum(111) surfaces.²⁷ The binding to the nickel surface is thermally irreversible (hydrogen is evolved at 380-480 K) and there is no evidence for displacement of the bound isocyanide molecule by other molecules like CO and acetylene. Methyl isocyanide chemisorption on platinum(111) is in part

thermally reversible and the reversible desorption temperature maximum is 500 K.^{27b}

In cluster chemistry, an isocyanide can bind to a single metal atom in a 2-center, 2-electron type of interaction or to two metal atoms in a bridging 3-center, 2-electron type of interaction.² Nmr studies of intramolecular isocyanide ligand site exchange in dinuclear metal complexes indicate that the energy difference between terminal and bridging sites is not very large (10-20 kcal/mole).²¹ However, an isocyanide ligand can also bind, in a multi-electron fashion, through both the carbon and nitrogen atoms as in $\text{Ni}_4[\text{CNC}(\text{CH}_3)_3]_7$,²⁹ and this multi-center, multi-electron type of binding can be quite robust. Hence, in the strong and thermally irreversible chemisorption of CH_3NC on nickel(111), the carbon and nitrogen atoms are probably bound to surface metal atoms. This would then place the hydrogen atoms of the methyl group closer to the metal surface than in the CH_3CN case where the CN group is normal to the surface. As established³⁰ in coordination chemistry, close approach of ligand carbon-hydrogen bonds to an unsaturated metal center can lead to a facile internal oxidative-addition of C-H to the metal atom to form σ M-C and M-H bonds. This type of process could account for the thermal irreversibility of CH_3NC chemisorption on nickel and the evolution of hydrogen at the characteristic temperature for hydrogen desorption from a nickel surface as sketched in 1.³¹

An alternative³² to initial associative CH_3NC chemisorption would be a dissociative process whereby CH_3 and CN fragments would be bound initially to the surface.

Since the CH_3NC chemisorption on platinum is in part thermally reversible, a distinction between associative and dissociative chemisorption could be achieved for this case by isotopic labelling studies, e.g. chemisorption of a mixture of CD_3NC and $\text{CH}_3\text{N}^{13}\text{C}$ and mass spectrometric analysis of the thermally desorbed isocyanide (nitrile³³).³⁴

Pyridine

Pyridine strongly chemisorbs on metal surfaces. Infrared studies³⁵ indicate that the chemisorption process is dissociative with scission of the α carbon-hydrogen bond to form a pyridyl species as in 2 with metal-carbon

2

and metal-nitrogen bonds. In addition, low energy electron diffraction studies³⁶ of pyridine chemisorbed on platinum(111) suggest a large angle between the plane of the C_5N ring and the surface plane; and a large work function change³⁶ on chemisorption strongly implicates an interaction of nitrogen atom with the surface metal atoms. An interaction like 2 or a single N-Pt donor acceptor interaction are consistent with the data. Chemisorption of pyridine on nickel(111)³⁷ is thermally irreversible, a property expected in a dissociative chemisorption process that would generate species like 2.

In mononuclear metal coordination chemistry, pyridine typically functions as a base or donor ligand. In metal cluster chemistry, pyridine can

function as a simple donor molecule and also can react in a "dissociative" fashion to give pyridyl cluster derivatives. The latter function is shown in the pyridine reactions with osmium carbonyl clusters³⁸ where the product, $\text{HOs}_3(\text{CO})_{10}\text{NC}_5\text{H}_4$, has a heavy atom structure exclusive of the terminally bound carbonyl groups as shown in 3, with the C_5N plane essentially normal to the Os_3

3

plane. Thus the correspondence in function and stereochemistry between surface and cluster pyridine chemistry appears to be high.

In the pyridine chemisorption process on metal surfaces, the following reaction sequences are the most probable ones. Initial interaction between pyridine and a metal surface should be localized largely at the donor nitrogen atom to give a donor acceptor complex with the C_5N ring plane more or less normal to the surface. Ring rocking in the C_5N plane will bring the α -hydrogen atoms close to metal surface atoms. Thus a subsequent C-H bond scission to give 2 and M-H surface species may occur. This secondary process is more likely to occur the more electropositive the metal and may proceed at high rates even at 20°C. For the more electronegative metals, like platinum, the rates for the C-H scission may become appreciable only at elevated temperatures and even may be lower than molecular dissociation rates whereby reversible or partly reversible thermal desorption will occur.

Aromatic Hydrocarbons

Chemisorption of benzene on nickel and platinum low Miller index surfaces has been studied rather extensively by low energy diffraction, photoemission and electron energy loss techniques. All structural conclusions from these studies agree.^{36,39} A π binding between the benzene and the surface metal atoms has been proposed with the C_6 ring more or less parallel to the metal surface--although some tilting of the rings for the Pt(111) surface has been suggested from an analysis of low energy electron diffraction and Auger electron spectroscopic data.^{39a}

There are at least four idealized structures for monocyclic aromatic hydrocarbons, 4-7,⁴⁰ in molecular arene-coordination chemistry.

4

5

6

7

In mononuclear transition metal chemistry, the η^6 -arene-metal class, 4, is by far the largest and, although bond energies vary widely, the M- η^6 -arene bond energy is large with respect to those of the other classes, the bond energy may be as large as 80 kcal/mole.⁴³ The diene-like, η^4 interaction between the arene and a metal in structural class 5 has been crystallographically defined for only about seven molecular complexes⁴³--the metal- η^4 -arene bond energy is not established for any complex but these bond energies should be somewhat lower than for the η^6 -arene-metal bond. The olefinic or η^2 -arene-metal class, 6, is established only for d^{10} transition metal complexes and the bond strengths for these are relatively low.⁴³ One quite curious type of structure found for $\text{Pd}_2\text{X}_2 \cdot (\text{arene})_2$ ($\text{X} = \text{AlCl}_4$ or Al_2Cl_7) complexes⁴⁴ is shown in 7. In effect, this is a special case of η^2 -arene-metal binding with a nearly square planar coordination geometry about each palladium atom.

Development of metal cluster arene coordination chemistry is in a relatively early stage. In ruthenium cluster chemistry, there are examples,⁴⁵ specifically arene- $\text{Ru}_6(\text{CO})_{14}$ species, of an arene bound in an η^6 -fashion to a single ruthenium atom in the cluster. In addition, the reaction of benzene with $\text{Os}_3(\text{CO})_{10}$ yields a "benzyne" derivative, $\text{H}_2\text{Os}_3(\text{C}_6\text{H}_4)(\text{CO})_9$, in which a C_6H_4 unit is sigma bound to two osmium atoms and the ring is tilted toward the Os_3 plane through interactions of ring π orbitals and orbitals of the third osmium atom (Figure 4).⁴⁶ This reaction and the resultant complex represent a simple model of dissociative benzene chemisorption on a metal surface and of the stereochemistry of the benzene fragment (benzyne)-metal surface interaction.

We suggest that most initial interactions of benzene with metal surfaces are with the benzene π orbitals and that the benzene ring will be more or less parallel to the surface. With thermal excitation, ring hydrogen atoms may come in close proximity to the metal atoms at the surface. At this stage,

carbon-hydrogen bond scission may occur to generate surface bound species such as C_6H_4 (Figure 4) or C_6H_5 (bridging between two or more metal surface atoms). This secondary process again would be more favorable with the more electropositive metals. In fact, benzene chemisorption on Ni(111) is thermally irreversible whereas on Pt(111) it is largely reversible. When the temperature of a (111) nickel crystal face with chemisorbed benzene is raised, hydrogen--and no other gaseous species--is evolved at ~540 K.³⁷

Alkyl substituted benzenes should behave in a largely analogous fashion to benzene; however, there is the possibility of the hydrogen atoms of the alkyl substituents interacting with metal surface atoms while a parallel relation between arene ring planes and surface planes is largely maintained. Significantly, catalytic studies have shown that for alkyl substituted benzene molecules, the alkyl C-H hydrogen atoms generally exchange more rapidly with deuterium than do aromatic C-H hydrogen atoms on most metal surfaces.^{47,48} A common intermediate may be, at least initially, a π or η^3 -benzylic type species wherein a largely parallel orientation of arene and metal surface planes is retained.⁴⁹

Olefins and Acetylenes

One of the distinctive properties of metal surfaces is facile scission of carbon-hydrogen bonds. Rapid H-D exchange in D_2 -alkane reaction mixtures, dehydrogenation, and hydrogenation all occur at 300 K over clean transition metal surfaces. This property, though obviously of great technological utility, significantly complicates stereochemical analysis of the chemisorption of alkanes, alkenes and alkynes on metal surfaces--especially on the more electropositive metal surfaces. Thus, it is not surprising that a stereochemical definition of such hydrocarbon chemisorption process has not been

achieved. Most carefully studied has been acetylene and ethylene chemisorption on Pt(111) where the ordered chemisorption surface structure appears to involve not C_2H_2 or C_2H_4 but either a CH_3CH or CH_3C species.⁵⁰

The interaction of acetylene or ethylene with a mononuclear metal complex is almost invariably a σ - π interaction of the acetylene or olefin bonding and antibonding π orbitals (Figure 5) and the metal orbitals with both acetylenic, or olefinic, carbon atoms within bonding distance of a single metal atom. The interactions of these hydrocarbon π orbitals should also predominate in the initial step of acetylene or olefin chemisorption on a metal surface. For the olefin, this state or a metallocycle like species, 8,

8

probably will be maintained unless or until hydrogen addition or abstraction reactions begin to occur as discussed below. Acetylenes, however, may undergo rehybridization at the acetylenic carbon atoms and form strong σ carbon-metal bonds with two or more surface metal atoms as has been observed in acetylene-cluster complexes (Figure 6); a simple η^2 -acetylene interaction is rarely observed in isolable cluster complexes.

Beyond the above stages, hydrogen addition or abstraction may occur. The hydrogen atom source in addition reactions may be either the ubiquitous hydrogen (H_2) "impurities" present in metal systems isolated from air or oxygen or the chemisorbed olefin or acetylene molecule through hydrogen transfer (e.g., $3C_2H_4(\text{metal surface}) \rightarrow C_2H_6(g) + 2CH_3C(\text{metal surface})$).

On a tungsten surface, ethylene chemisorbs at very low temperatures to give

some intact C_2H_4 species which is progressively dehydrogenated with temperature increase to give hydrogen gas and a tungsten surface with only carbon on it. Similar gross observations are typical for C_2H_2 or C_2H_4 chemisorption on other metal surfaces.

The interaction of ethylene with the osmium cluster $H_2Os_3(CO)_{10}$ is instructive: Here the implicated or established steps are

The starred species, the reactant hydride, vinyl, vinylidene and carbyne complexes, have been detected, isolated and crystallographically defined (Figure 7).⁵¹⁻⁵⁴ Similar reaction sequences can be envisaged for C_2H_4 -metal surface reactions.

A special point should be addressed here in this section. This is the issue of alkyl radical interactions at a metal surface. In mononuclear metal coordination chemistry, an alkyl radical is bound in a simple two-center, two-electron fashion. However, a CH_3 group may bridge between two metal

atoms in dimeric (e.g., $\text{Al}_2(\text{CH}_3)_6$) or polynuclear species through a two-electron, 3-center bond. In principle, this multi-center type of bonding could also be extended to a four-center structure with a CH_3 group bridging three metal atoms (or above three-fold sites in close packed metal surfaces). There is now evidence that there may be an extensive alkyl metal cluster chemistry which should be instructive as a crude, simple model of stereochemistry and chemistry for alkyl species chemisorbed on metal surfaces. Recently Calvert and Shapley⁵⁵ prepared a methyl derivative of an osmium cluster, $\text{CH}_3\text{Os}_3(\text{H})(\text{CO})_{10}$, in which the CH_3 group is unsymmetrically bridge bonded between two osmium atoms, $\text{Os}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}-\text{Os}$. This species is rather like an intermediate or transition state in the activation (and ultimate scission) of a carbon-hydrogen bond. Most significantly, this methyl derivative is, in solution, in equilibrium with a methylene-hydride cluster (Figure 8). This discovery in metal cluster chemistry provides a possible simple model for the nearly pervasive phenomenon of hydrogen atom lability in chemisorbed hydrocarbons.

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FIGURE 1.

The top view of a (100) face of a close-packed metal. For this face, there are three different binding sites for a ligand atom which are denoted as (A), (B) and (C). Position (A) represents the two-center, two-electron site ("sitting atop" site), position (B) represents the three-center, two-electron bridging site and position (C) the five-center site in which the ligand atom is bound to four equivalent metal atoms. In the shaded areas to the left are depicted two possible 2x2 unit cells for a chemisorbed ordered layer. In the lower left is a cell based on a registry with the four-fold sites so that ligating atoms would be at the four-fold sites. Above is an alternative 2x2 unit cell based on ligating atoms at sitting atop positions. To the right is a representation of the centered (4x2)-45° unit cell. Here the unit cell of the ordered chemisorbed layer is rotated 45° from the unit cell of the (100) metal surface. This centered 4x2 unit cell is established for the ordered chemisorption state of carbon monoxide on palladium.

FIGURE 2.

A view looking down the first two layers of a (111) face of a cubic close-packed metal (face-centered cubic), e.g., nickel, palladium or platinum. Shown by shading are two possible 2x2 unit cells for an ordered chemisorbed state on this metal surface. The one at the upper left is based on ligating atoms bound to the "empty" three-fold sites (i.e., over the octahedral subsurface holes). The one in the lower right is based on ligating atoms at filled three-fold sites (i.e., situated over subsurface tetrahedral holes). The two-fold site is labelled X in the upper right hand corner of the drawing.

FIGURE 3.

This drawing depicts the iron atom skeleton of the cluster ion $\text{HFe}_4(\text{CO})_{13}^{1-}$. Only one of the 13 carbonyl ligands is shown and this is the carbonyl in which the carbon atom is bonded to the four iron atoms and the oxygen atom is also bound to one of the iron atoms. The remaining 12 carbonyl ligands are terminally bound to the iron atoms, three to each iron atom and their approximate positions are shown by the single lines on the periphery of the spheres that represent the iron atoms.

FIGURE 4.

The cluster complex, $\text{H}_2\text{Os}_3(\text{C}_6\text{H}_4)(\text{CO})_9$, is formed in the high temperature reaction of benzene with the unsaturated metal cluster $\text{Os}_3(\text{CO})_{10}$. Each of the osmium atoms is bound in a conventional two-centered-two electron manner with three carbonyl ligands. The two hydride ligands are directly bound to osmium atoms. The remaining C_6H_4 fragment is in effect σ bound to two of the osmium atoms through the two adjacent benzyne carbon atoms of the ring and the third osmium atom is bonded through an overlap of metal orbitals with the $p(\pi)$ orbitals of the two benzyne carbon atoms.

FIGURE 5.

The conventional representation for the interaction of the π and π^* orbitals of an acetylenic or an olefinic molecule with the d orbitals of a transition metal in η^2 -olefin-metal complexes.

FIGURE 6.

Acetylene complexes with trinuclear metal clusters invariably involve the interaction of orbitals associated with acetylenic carbon atoms with orbitals associated with all three metal atoms. Two different orientations of the acetylenic C-C vector with respect to the ring triangle has been observed and these two idealized skeletal models are shown above with only the core M_3C_2 atoms included. Each carbon atom bears an alkyl or aryl substituent (not shown) that is directed above at an angle of about 30° to the C-C vector.

FIGURE 7.

In this figure, the structure and stereochemistry for a series of osmium cluster hydrides and their hydrocarbon derivatives are depicted. For the hydrocarbon set, the stereochemistry of the M_3-C_2 interactions is shown for a series of related hydrocarbon fragments-- $CH=CH_2$, $C=CH_2$ and $C-CH_3$. The osmium atoms are shown as shaded circles. Hydrogen and carbon atoms are labelled with the exception of structure 7c where the two carbon atoms simply are represented by solid circles. Structure 7a shows the stereochemistry of the two hydride hydrogen atoms in the cluster, $H_2Os_3(CO)_{10}$. The orientation of the terminally bound carbonyl groups are shown by solid lines attached to the shaded osmium circles. In 7b, the heavy atom and hydrogen atom stereochemistry for the cluster, $HOs_3(CO)_{10}(CH=CH_2)$ is depicted, and in 7c the positions of the heavy atoms in the cluster, $H_2Os_3(CO)_9(C=CH_2)$, are shown. The positions of the nine carbonyls which are attached in a terminal fashion to the three osmium atoms are shown by the lines directed out from the shaded osmium circles. Hydrogen atom positions have not been established in the $H_2Os_3(CO)_9(C=CH_2)$ cluster by crystallographic studies; however, spectral studies indicate that the carbon atom at the left bears two hydrogen atoms and the one to the right, none. In 7d the carbon atom, osmium atom and hydride hydrogen atom positions in the cluster $H_3Os_3(CO)_9CCH_3$ (based on the crystallographic analysis of the ruthenium analog) are shown. Not depicted in this skeletal representation are the nine carbonyl ligands--simply for clarity purposes; each osmium atom is terminally bonded to three carbonyl ligands.

(a)

(b)

(c)

(d)

FIGURE 8.

Representation of the equilibrium solution species for a cluster that has the composition $\text{Os}(\text{CO})_{10}\text{CH}_4$. The methylene structure on the right has been established by crystallographic analysis. The precise structure of the methyl derivative on the left has not as yet been crystallographically defined but nmr spectroscopic data clearly indicate that the methyl group is in an unsymmetric bridging position because of a three-center, two-electron C-H-Os interaction.

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the text, and (2) it may reflect two or more chemisorption sites which differ in thermal behavior. Multiple chemisorption sites are, of course, feasible for a given crystal face. In addition, no real metal crystal face is atomically uniform.³ Imperfections at the crystal face can give rise to multiple chemisorption sites. For example, a real (111) crystal face of a face-centered cubic metal will have irregularities at the microscopic and the atomic (a common imperfection would be the presence of steps due to cutting angle imprecision) levels.

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