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Earl L. Muetterties

October 1980

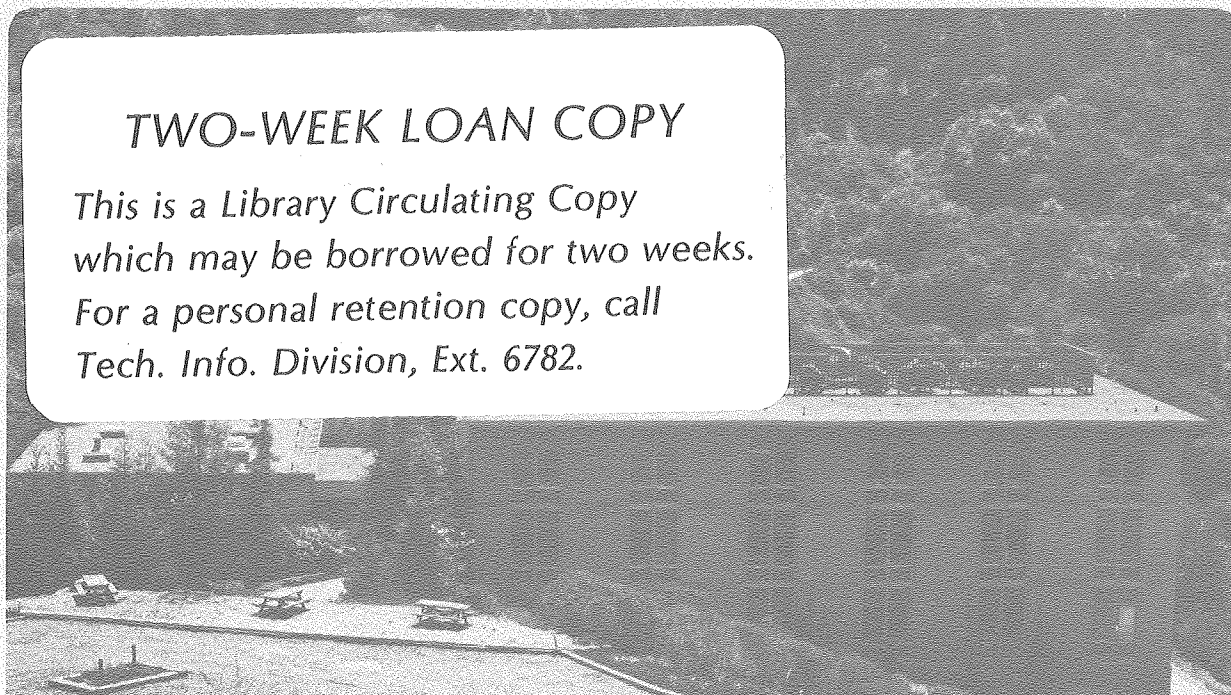
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The Coordination Chemistry
of Metal Surfaces

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Abstract

In coordinately unsaturated molecular metal complexes, carbon-hydrogen bonds of the peripheral ligands may, if the stereochemistry allows, closely approach a metal center so as to develop a three-center two-electron bond between the carbon, the hydrogen, and the metal atoms, C-H-M. In some instances, the interaction is followed by a scission of the C-H bond whereby the metal is effectively oxidized and discrete M-H and M-C σ bonds are formed. This class of metal-hydrogen-carbon interactions and reactions is shown to be a common phenomenon in metal surface chemistry. Ultra high vacuum studies of nickel and platinum with simple organic molecules like olefins, and arenes are described. These surface chemistry studies were done as a function of surface crystallography and surface composition. The discussion is largely limited to the chemistry of methyl isocyanide, acetonitrile, benzene and toluene. Molecular orbital calculations are presented that support the experimental identification of the importance of C-H-M metal bonding for metal surfaces.

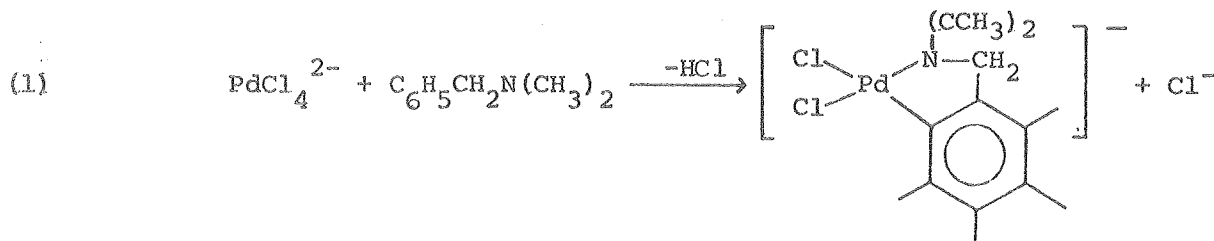
Introduction

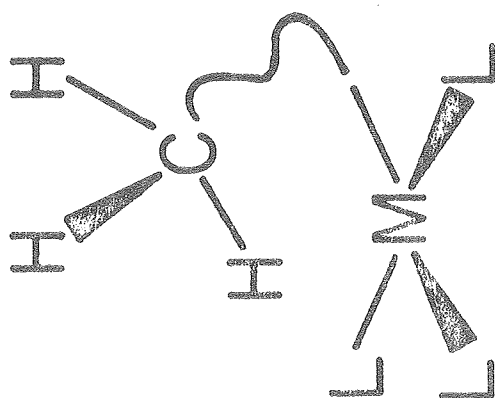
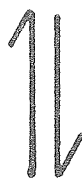
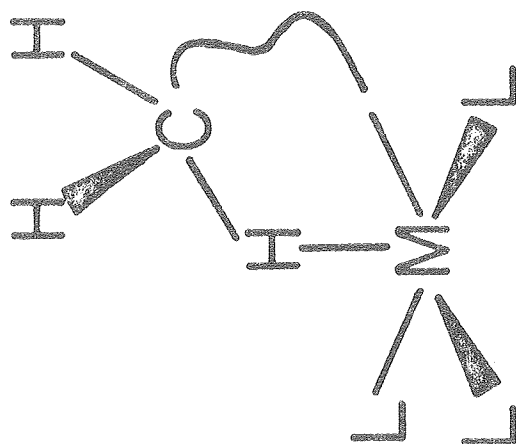
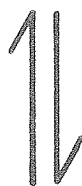
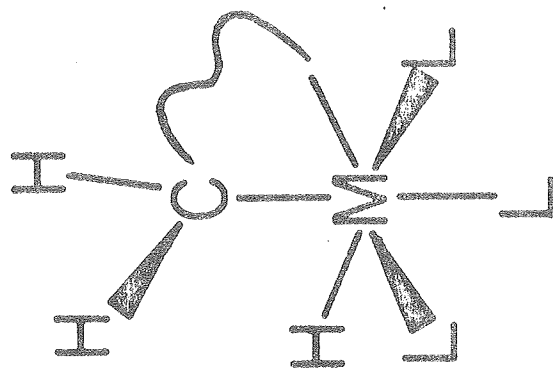
A relatively common interaction in molecular coordination or organo-metallic compounds that nominally are coordinately unsaturated is the formation of a three-center two-electron bond between a metal center in the compound and a C-H bond of a hydrocarbon, a hydrocarbon fragment, or a hydrocarbon derivative that is a ligand in the complex. This interaction can be the prelude, the intermediate or transition state, to a subsequent reaction in which the CH hydrogen atom is transferred to the metal center and a direct σ bond is formed between the carbon atom and the metal atom. Internal oxidative addition of CH is a term often applied to this subsequent reaction step. The overall sequence is schematically outlined in 1. Factors

1

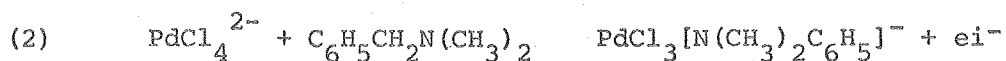
that materially affect the forward and back rate constants in step 2 of 1 have not been adequately elucidated except that step two is especially favored if the formal oxidation state in the oxidized product is easily accessible. Hence, favorable and established reaction couples are $\text{Fe}(0) \rightleftharpoons \text{Fe}(\text{II})$, $\text{Ru}(0) \rightleftharpoons \text{Ru}(\text{II})$, $\text{Co}(\text{I}) \rightleftharpoons \text{Co}(\text{III})$, $\text{Nb}(\text{III}) \rightleftharpoons \text{Nb}(\text{V})$, $\text{Ta}(\text{III}) \rightleftharpoons \text{Ta}(\text{V})$, and $\text{Ti}(\text{II}) \rightleftharpoons \text{Ti}(\text{IV})$ with the $d^8 \rightleftharpoons d^6$ couple the most common one.

The first example of the internal CH oxidation addition came from organic research with diazobenzene and PdCl_4^{2-} . Cope and Siekman^{1a} discovered the palladation reaction of diazobenzene in 1965. The palladation reaction is





general to a variety of organic nitrogen compounds such as benzyldialkylamines (equation 1) whereby the nitrogen compound is converted to a five-membered ring metallocycle ostensibly through a first step shown in equation (2) of amine displacement of the chloride ligand.

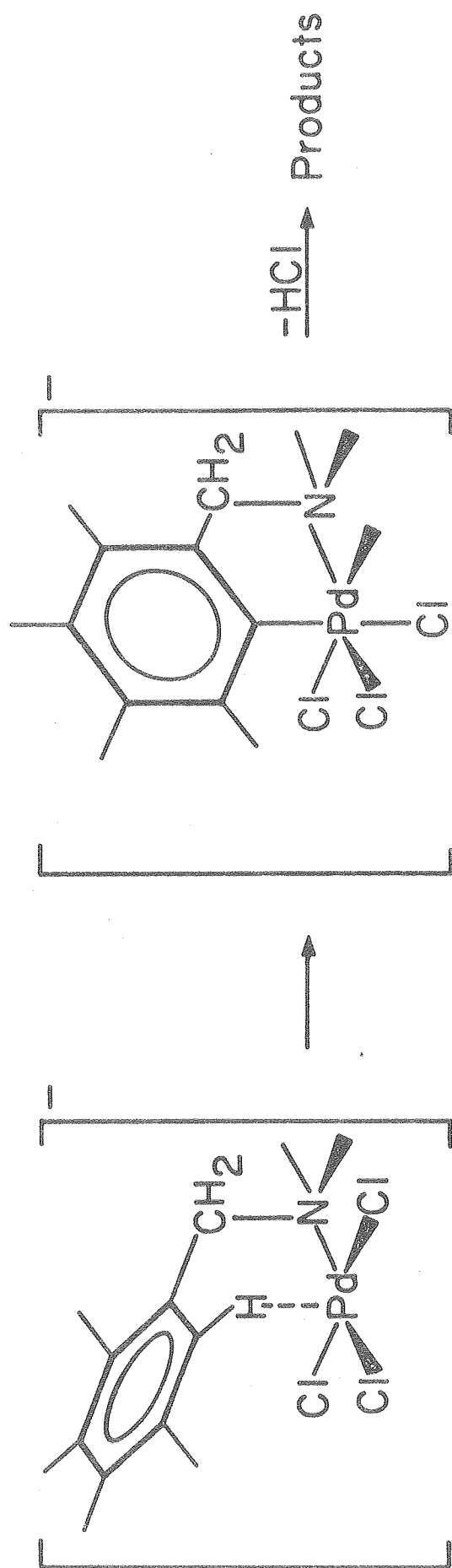


Later steps can be envisioned as in 2. Presently, the list of such internal

2

C-H oxidative addition reactions is large and involves such ligands as triaryl phosphites and phosphines, trialkylphosphines, cyclopentadienyl, benzene and olefins (olefin $\rightleftharpoons$ allyl).² In addition, there is a large number of coordination compound in which the intermediate state, discussed above, with the multicenter C-H-M bond have been established by crystallographic studies--the H-metal bond distance has varied from the very short, 1.75Å,⁴ to the long but apparently still bonding range of ~1.9-2.5Å.⁵

This established C-H chemistry in molecular coordination compounds should have its formal analog in metal surface chemistry. Carbon-hydrogen bond-cleavage is a common reaction at metal surfaces but it does not comprise mechanistically the simple collision of a hydrocarbon such as methane with a metal surface (vide infra). Methane neither reacts with nor is chemisorbed on a metal surface under moderate conditions. However, propylene does chemisorb, and then C-H bonds may be broken, depending upon the nature of the metal surface. Generally, the sequence at the surface comprises first the formation of a coordinate bond between a surface metal atom(s) and



some functionality in the organic molecule. Then, if C-H hydrogen atoms of the chemisorbed molecule can closely approach the surface metal atoms, the three center C-H-M bond should develop (the surface is typically coordinatly unsaturated unless overladen with contaminant elements like carbon or sulfur) leading to an activation of the C-H bond and possible subsequent C-H bond cleavage.

Saturated hydrocarbons other than methane do react with metal surfaces at 20°C. Clean metal surfaces such as ruthenium adsorb saturated hydrocarbons and effect dehydrogenation of the hydrocarbon, e.g., cyclohexane is converted to benzene. In these cases, perhaps the initial chemisorption process comprises the formation of several C-H-metal three-center two-electron bonds.

I present data from our recent experimental and theoretical studies of metal surfaces that implicate the very same sequential steps described above for C-H bond activation in molecular coordination and organometallic complexes.

Experimental

Nearly all the experiments described were performed in an ultra high vacuum chamber at pressures of about 10^{-10} torr. The specific equipment and experimental procedures used have been described elsewhere.^{8,9} Experimental protocol for the thermal desorption experiments and for the chemical displacement reactions is presented below. All these experiments were repeated with a control, blank experiment with a metal crystal that had the front and exposed face covered with gold; the sides and back of the crystal were exposed.^{8,9} These blank experiments were performed to ensure that all thermal desorption and chemical displacement experiments monitored only the surface chemistry of the front exposed face of the metal

crystal under study.

Gas exposures were performed with a variable leak valve equipped with a dosing "needle" such that the gases could be introduced in close proximity to the surface, thus minimizing background contamination. Two separate valve-needle assemblies mounted symmetrically with respect to the mass spectrometer were used to introduce the different gases in displacement reactions. This avoided contamination of the displacing gas in the leak valve. During displacement reactions, the crystal face was directed 45° away from the line of sight of the mass spectrometer ionizer (so as to face the second valve assembly). This configuration decreased the mass spectrometer signal of gases evolved from the crystal during a displacement reaction as compared to a thermal desorption. The time interval between the two gas exposures in a displacement reaction was between 1-5 minutes. Oxide formation on nickel (111) and (100) was effected by a prolonged exposure (5-10 min.) of the crystal to 5×10^{-8} torr of O_2 with a crystal temperature of $\sim 350^\circ C$. The oxide was ordered with a $c(2 \times 2)$ low energy electron diffraction pattern. Carbon contaminated surfaces were prepared by thermally decomposing benzene on the nickel surface. The carbon overlayer was ordered but the diffraction pattern was complex. It did not correspond to a graphitic ring structure. Approximate carbon coverages were estimated using Auger calibration curves based on thermally decomposed benzene.¹⁰

All chemicals used were free by mass spectrometric criterion of any significant impurities. Isotopically labeled compounds were purchased or prepared; see references 8 and 9 for their isotopic characterization.

Chemisorption state modeling by extended Huckel molecular orbital calculations were made in a collaborative study with R.M. Gavin, and full details of these calculations will be published elsewhere.

Discussion

Surface Crystallography and Composition

Platinum¹¹ and nickel^{8,9,12} have been the metal surfaces examined in our surface science studies to date. The surface coordination chemistry has been examined as a function of surface crystallography and surface composition. Surfaces specifically chosen for an assay of metal coordination number and of geometric effects were the three low Miller index planes (111), (110), and (100) as well as the stepped 9(111)x(111) and stepped-kinked 7(111)x(310) surfaces (both platinum and nickel are face centered cubic). These surfaces are depicted in Figures 1-5. The coordination chemistry generally was established for these five clean surfaces and for their carbon, sulfur and oxygen contaminated surfaces.

Chemistry of Benzene and Toluene

One of our best defined chemical systems for C-H bond activation and C-H bond scission is that of benzene and toluene on nickel surfaces.⁹ The chemistry was a sensitive function of surface crystallography and of surface composition.⁹

Chemisorption of benzene on the flat (111) and (100) surfaces was fully molecular (dissociative) below 100°C and ~150-200°C, respectively. For each surface, the benzene was quantitatively displaced from the crystal surface by trimethylphosphine below these temperatures. Furthermore, when these experiments were effected with $C_6H_6 + C_6D_6$ mixtures, only C_6H_6 and C_6D_6 molecules were displaced. Thus, no reversible C-H (or C-D) bond breaking occurs on these clean surface within the time scale of the experiments (minutes).¹⁴ However, irreversible bond breaking¹⁴ does occur at temperatures above 100°C and 150°C for the (111) and (100) surfaces, respectively, as shown by thermal desorption experiments where only a fraction

of the benzene molecules reversibly desorbed: ~20% on Ni(111) with a maximum at 115 - 125°C and ~40% on Ni(100) with a maximum at ~220°C. In each case thermal decomposition of the chemisorbed benzene to H_2 + Ni-C was a competitive process to thermal desorption. Thermal desorption experiments with C_6H_6 + C_6D_6 mixtures on these two surfaces yielded in the fraction that reversibly desorbed only C_6H_6 and C_6D_6 molecules. No H-D exchange was observed.¹⁴

The stepped nickel 9(111)x(111) and stepped-kinked Ni 7(111)x(310) surfaces displayed a benzene coordination chemistry that was quantitatively and qualitatively identical with that of the Ni(111) surface except that not all the benzene was displaced by trimethylphosphine indicating that either a small percentage (~10%) of the benzene on these surfaces either was present in different environments or was dissociatively⁹ chemisorbed (see later discussion of stereochemistry). Benzene chemisorption behavior on Ni(110) was similar to that on Ni(111) except that the thermal desorption maximum was lower, ~100°C and that trimethylphosphine did not quantitatively displace benzene from the Ni(110)- C_6H_6 surface. In these experiments, no H-D exchange was observed with C_6H_6 + C_6D_6 mixtures.

The benzene surface chemistry was not qualitatively altered by the presence of carbon or sulfur impurities (up to ~0.2-0.3 monolayer); only the benzene sticking coefficient was lowered by the presence of such impurity atoms. Surface oxygen atoms present as oxide oxygen reduced the benzene sticking coefficient to near zero values at 20°C.

Toluene surface coordination chemistry was quite different from that of benzene. Toluene chemisorption on all the clean surfaces was thermally irreversible. In addition, toluene was not displaced from these surfaces by trimethylphosphine nor by any other potentially strong field ligand

examined to date, e.g., carbon monoxide or methyl isocyanide. In the thermal decomposition of toluene on these surfaces (attempted thermal desorption experiments), there were two thermal desorption maxima for H_2 (or D_2 from perdeuterotoluene) with the exception of the $Ni(110)$ surface. This is illustrated in Figure 6 for $Ni(111)-C_7D_8$. Experiments with the deuterium labeled molecules, $C_6H_5CD_3$ and $C_6D_5CH_3$ incisively delineated the molecular details of toluene chemisorption and decomposition on the nickel (111), stepped, stepped-kinked, and (100) surfaces. Following the D_2 formation from $Ni(111)-C_6H_5CD_3$, there was a single desorption maximum for D_2 at $\sim 130^\circ C$; none was detected in the higher temperature region. For $Ni(111)-C_6D_5CH_3$, no D_2 appeared in the low temperature range ($\sim 130^\circ C$) and there was a single desorption maximum at $\sim 185^\circ C$. These experiments are illustrated in Figure 7 (compare with Figure 6 for the $Ni(111)-C_7D_8$ decomposition). Thus, no aromatic C-H (or C-D) bonds in toluene chemisorbed on $Ni(111)$ are broken below temperatures of $\sim 150^\circ C$ whereas all aliphatic C-H (or C-D) bonds are broken and the hydrogen atoms desorb as H_2 (or D_2) below $150^\circ C$.¹⁵ The experiments do not establish the temperatures at which aliphatic C-H bonds are first cleaved but all these processes are completed by $130-150^\circ C$.¹⁵ Essentially the same behavior and the same desorption maxima were observed for the $C_6H_5CD_3$ and $C_6D_5CH_3$ decompositions on the stepped $9(111) \times (111)$ and stepped-kinked $7(111) \times (310)$ surfaces. The same behavior was observed for the two labeled toluenes on the flat (100) surface: Single D_2 desorption maxima were observed with the temperature maximum of $110^\circ C$ for $C_6H_5CD_3$ and of $230^\circ C$ for $C_6D_5CH_3$. In sharp contrast, toluene thermal decomposition on the super-stepped (110) surface (Figure 4) gave only a single H_2 (or D_2 for C_7D_8) desorption maximum at $150^\circ C$.

Impurity atoms do perturb the character of the toluene thermal

decomposition on the flat surfaces. At carbon or sulfur coverage levels of 20% or higher on Ni(100), where an ordered $c(2 \times 2)$ low energy diffraction pattern was obtained and where the impurity atoms reside over four-fold sites, the differentiation between aliphatic and aromatic C-H bond cleavage rates was lost. Under these conditions, only a single hydrogen desorption maximum was observed.

Stereochemical Features of Benzene and Toluene Coordination Chemistry

Benzene forms an ordered chemisorption state on the flat Ni(111) and Ni(100) surfaces at 20°C with unit cells of $(2\sqrt{3} \times 2\sqrt{3})R 30^\circ$ and $c(4 \times 4)$, respectively.¹⁶ The symmetry data do not fix the registry of the benzene with respect to the metal atoms nor the orientation of the ring plane to the surface plane. However, basic coordination principles would suggest that the benzene ring plane should be parallel to the surface plane. In Figures 8 and 9, possible registries of the benzene with respect to the metal atoms are presented. For the Ni(111) surface, one of the more favorable registries has the C_6 centroid directly over a single metal atom. This registry provides for optimal overlap of not only the π and π^* with metal surface orbitals but also for the development of three-center two-electron bonds between the C-H hydrogen atoms and surface metal atoms (this registry places each hydrogen atom directly over a nickel atom and rotation by 30° places the hydrogen atoms nearly directly over 2-fold bridging (Ni-Ni) sites. Electronic¹⁷ and vibrational^{16,18} spectroscopic data are consistent with these basic formulation of chemisorbed benzenes in planes parallel to these two flat nickel surfaces. Importantly, this configuration does not allow close¹⁹ approach of hydrogen atoms to surface metal atoms in the 20°C chemisorption state - hence the absence of C-H bond breaking on these flat

surfaces. However at elevated temperatures, thermal excitation of C-H bonds for C-H bond bending and of C_6 plane tipping can bring the C-H hydrogen atoms closer to the surface metal atoms - with consequent C-H bond breaking that, in fact, was observed to be a significant process competitive with the (reversible) benzene thermal desorption process.

On the slightly irregular $9(111) \times (111)$ and $7(111) \times (310)$ surface, most of the chemisorbed benzene molecules should be in planes parallel to the terrace section planes and, in this context, the chemistry should be and was analogous to that on the (111) surface. However, because of the steps some of the C-H hydrogen atoms can approach surface metal atoms very closely and C-H bond scission should ensue (Figure 10). This stereochemical feature was clearly evident in the slightly less than quantitative displacement of benzene from these surfaces by trimethylphosphine in contrast to the quantitative displacement on the fully flat (111) and (100) surfaces. For the fully ruffled, or super-stepped, (110) surface, close approach of C-H hydrogen and facile C-H bond scission should be more extensive - and apparently was, based on the thermal desorption and chemical displacement experiments. The specific stereochemical features of the $Ni(110)-C_6H_6$ chemisorption state(s) cannot be characterized with our available data.

Toluene should coordinate initially in a stereochemical fashion analogous to benzene on the flat surfaces. This orientation will necessarily bring an aliphatic C-H hydrogen atom of the methyl group very close to the surface. Again C-H bond cleavage should be facile. Cleavage would then generate a benzyl species in which, if all carbon atoms lie in a plane parallel to the surface, all carbon atoms can interact with the surface metal atoms

as can the seven hydrogen atoms in three-center two-electron C-H-M bonds. This is a probable stereochemistry for the toluene chemisorption state (dissociative) at 20°C on the flat surface. It is a representation that is fully consistent with all of our experimental data. When the surface was substantially perturbed by the presence of impurity atoms, like C or S, the characteristic toluene surface chemistry established with the labeled molecules, $C_6H_5CD_3$ and $C_6D_5CH_3$ was lost.

Our data suggest a basis for selective H-D exchange between toluene and D_2 centered at the methyl site. Actually, Crawford and Kemball earlier had established such selectivity for toluene and D_2 on evaporated nickel films with sintered films showing higher selectivity, by one order of magnitude, than unsintered films (ostensibly the sintered films had a higher percentage of metal atoms in (111) or (100) type environments than did the unsintered films). We have also established that irregular nickel surfaces show essentially no selectivity.²² All these results, with "irregular" surfaces under normal pressure conditions, are fully consistent with our ultra high vacuum studies.

Ethylene and Acetylene

On nickel (111), both ethylene and acetylene are irreversibly chemisorbed; neither can be thermally desorbed. We also find that trimethylphosphine cannot displace ethylene or acetylene from these surfaces. There have been suggestions that ethylene and acetylene are not present on the surface as molecules but as molecular fragments.²³ For a flat surface, we would initially expect that both molecules would chemisorb such that the C-C bond vectors would be parallel to the surface plane. The hydrogen atoms should be significantly farther²⁴ from the surface than for the benzene case discussed above. Hence on ground state considerations and the benzene

surface data, C-H bond scission for ethylene and for acetylene should not be a facile process at least at 20°C. However, torsional twisting of these molecules, bound in the conventional π fashion, about the C-C bond will, of course, be a lower energy process than for ring tipping or ring deformation for benzene chemisorbed on a flat surface. If these barriers are quite low, then C-H bond scission should be facile at 20°C. At this point, the basic molecular details of ethylene and of acetylene chemisorption on nickel surfaces are not definitively established and further experimental data are required. We do anticipate that propyne or propylene chemisorption would be dissociative in character because of the easier close approach of methyl hydrogen atoms to the surface (by formal analogy to the benzene and toluene systems discussed above).

Our studies of olefin and acetylene chemisorption states on platinum surfaces is presently incomplete. Ethylene and acetylene chemisorption on platinum (111) are complicated by the apparent presence of more than one chemisorption state (indicated by thermal desorption studies). When C_2H_4 and C_2D_4 are chemisorbed on Pt(111), the small fraction of ethylene thermally desorbed as ethylene comprises nearly a statistical mixture of all possible $C_2H_xD_{4-x}$ molecules. Thus we see here reversible C-H (and C-D) bond breaking on this flat platinum surface. In an analogous experiment with C_2H_2 and C_2D_2 , only a small extent of H-D exchange was observed for the small fraction of acetylene molecules that reversibly desorb from this surface.¹¹

Acetonitrile and Methyl Isocyanide⁸

Acetonitrile forms an ordered chemisorption state on the fully flat nickel surfaces, a p(2x2) and a c(2x2) on Ni(111) and Ni(100), respectively. Acetonitrile thermal desorption from these two surfaces was nearly quantitative (a small amount of acetonitrile decomposed at the temperatures characteristic

of the reversible thermal desorption from these surfaces. Importantly from an interpretive context, acetonitrile was quantitatively displaced from these two flat low Miller index planes by trimethylphosphine.⁸ However, the displacement was not quantitative (only 90-95% complete) from the stepped and stepped-kinked surfaces. For the super-stepped (110) surface, chemisorption was nearly irreversible and no acetonitrile could be displaced from this surface by trimethylphosphine.

For the ordered p(2x2) and c(2x2) states on Ni(111) and Ni(100), respectively, the acetonitrile must be bound solely through the CN nitrogen atom and the CN vector must be largely normal to the surface planes. As shown in Figure 11, such stereochemistry maintains the methyl hydrogen atoms well removed from the surface metal atoms even with nominal departures from a surface-N-C angle of 90° and with CH₃ group bending at the nitrile carbon atom. Near step or kink sites, a close approach of methyl hydrogen atoms can occur (Figure 11) and this probably accounts for the slightly different behavior of acetonitrile on the stepped or stepped-kinked surface relative to that for the (111) surface: probably some acetonitrile molecules initially chemisorbed near such surface irregularities as steps undergo irreversible C-H bond cleavage reactions and hence are not displaced by the phosphine. Fully consistent with this stereochemical interpretation was the thermal reactivity of acetonitrile on the super-stepped (110) surface and the nondisplacement of the nitrile from this surface by the phosphine.

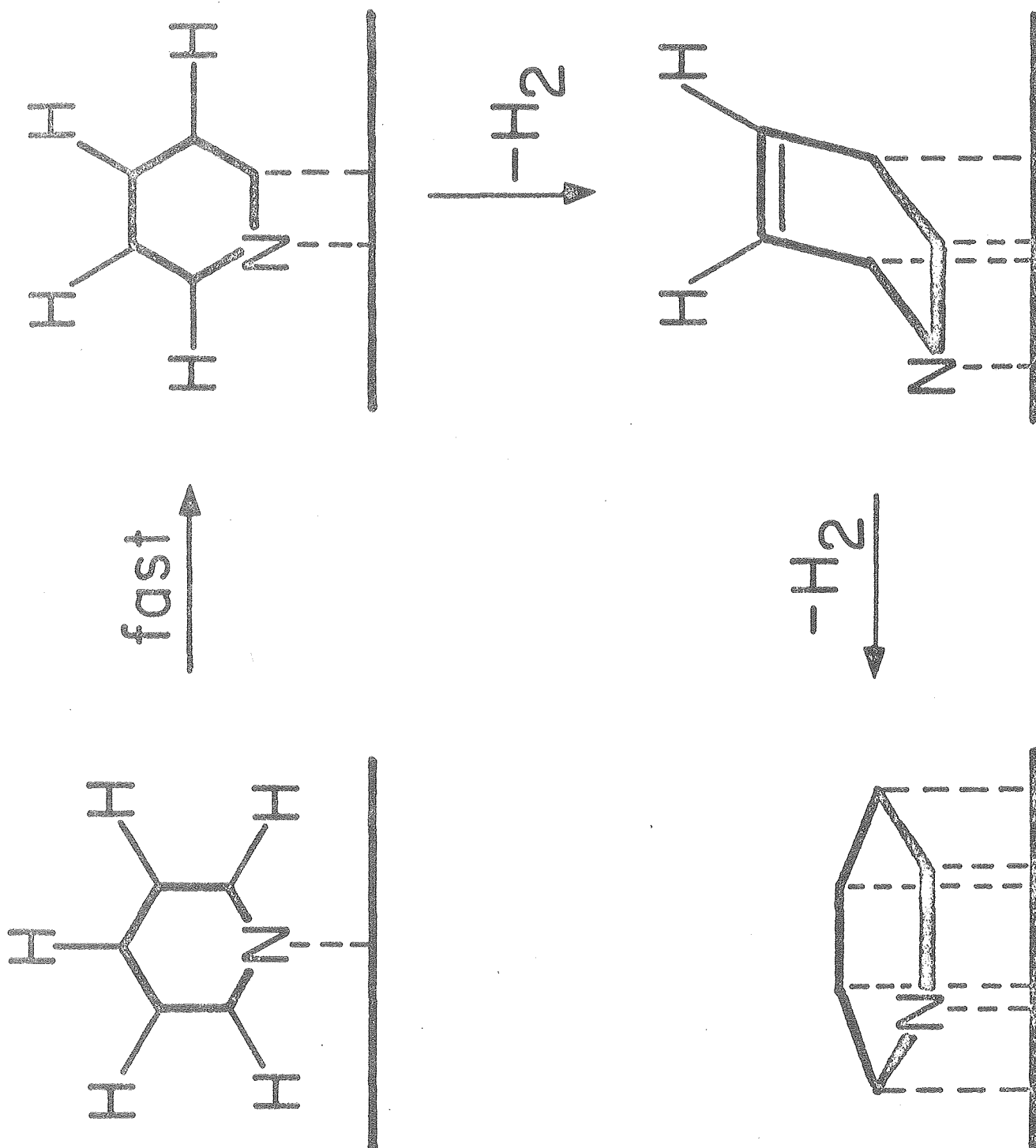
The precise registry of the nitrile nitrogen atom with respect to surface metal atoms has not been established. Normally acetonitrile is bound in coordinately saturated mononuclear metal compounds or clusters through the nitrogen atom to a single metal atom.⁸ However, the ordered chemisorption states for CH₃CN on

Ni(111) and Ni(100) are coordinately unsaturated. Possibly the nitrogen atom may lie at bridging sites, e.g., the three-fold site on the (111) and four-fold site on the (100) surface. We plan vibrational studies of these surface states and these may be informative about this stereochemical feature.

Methyl isocyanide was irreversibly chemisorbed on all the clean nickel surfaces. Based on the tendency of isocyanides to bind through both the carbon and the nitrogen atoms in coordinately unsaturated metal clusters,^{25a} we would expect the N-C bond vector of methyl isocyanide chemisorbed on the flat nickel (111) and (100) surfaces to be more or less parallel to the surface with both the isocyanide carbon and nitrogen atoms bonded to surface metal atoms.⁸ This stereochemistry necessarily allows methyl hydrogen atoms to closely approach surface metal atoms and allows for facile, irreversible C-H bond scission--a postulate fully consistent with the experimental data.⁸

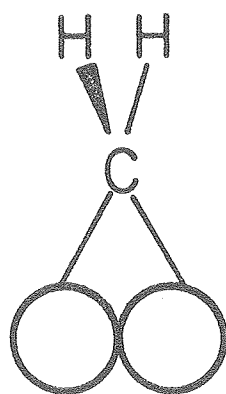
Trimethylphosphine

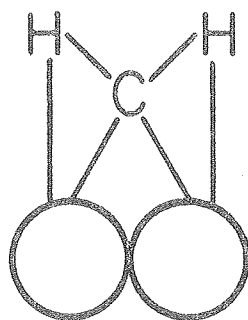
Trimethylphosphine is very strongly chemisorbed on all the nickel surfaces. On the Ni(111) surface, thermal decomposition occurs readily and CH_4 and H_2 are desorbed as decomposition products with desorption maxima at 90 and 98°C respectively. Chemisorption of this phosphine initially must involve a donor-acceptor interaction centered at the phosphorus atom. Models show that the methyl hydrogen atoms can then closely approach the surface metal atoms. Cleavage of C-H bonds probably occurs at or near 25°C, and P-C-Ni bonds are then irreversibly formed. This surface chemistry qualitatively mirrors that of trimethylphosphine in the coordinately unsaturated complex, $\text{Fe}[\text{P}(\text{CH}_3)_3]_4$, which is primarily $\text{HFe}[\eta^2\text{-CH}_2\text{P}(\text{CH}_3)_2][\text{P}(\text{CH}_3)_3]_3$ in the solution state.^{25b}

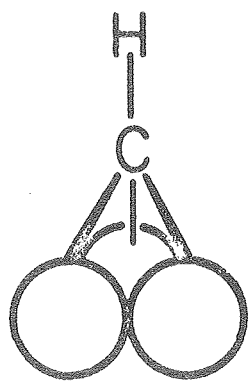


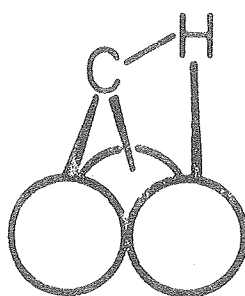
Hydrocarbon Fragments - Modeling by Molecular Orbital and Cluster Chemistry

A basic guideline for metal surface coordination chemistry with respect to hydrocarbon or hydrocarbon derivatives may be formulated as follows: If the stereochemistry of the chemisorption state allows C-H hydrogen atoms to closely approach surface metal atoms then the chemisorption state should be further stabilized by the formation of a three-center two-electron C-H-metal bond. This effect should be more pronounced the more electron deficient the metal surface. There should be an activation of the C-H bond and the hydrogen atom should become more protonic in character. If the C-H bond is sufficiently weakened by this interaction then C-H bond cleavage should result. Certainly, all our metal surface studies point to the importance of this stereochemical feature in determining the chemistry of chemisorbed molecules. One further illustrative example that is incompletely defined as yet is that for pyridine on the Ni(100) and Pt(111) surfaces where the pyridine is irreversibly chemisorbed and three hydrogen thermal desorption maxima of relative intensities 1:2:2 were observed.^{11,12} These data suggest that pyridine initially chemisorbs in a plane normal to the surface bonding through the nitrogen atom. This places the α - CH hydrogen atoms close to surface metal atoms and C-H bond cleavage should occur very readily (at 20°C or slightly higher temperatures) to form a pyridyl species.^{11,12} At high temperatures, ring tipping so as to ultimately lie in a plane parallel to the surface may then occur in two stages as shown in 3:









Studies with deuterium labeled pyridines are in progress to confirm or refute this hypothesis.

If the above generalization is correct, then simple extended Hückel molecular orbital calculations for the surface chemisorption states of simple hydrocarbons or hydrocarbon fragments should sense this tendency for multicenter C-H-metal bonds to form (these particular calculations are inappropriate for modeling features of the C-H bond cleavage step). We²⁶ have examined this aspect for the nickel (111) surface and find that multicenter C-H-metal bond formation does appear to be important. For example, in the case of the CH₂ fragment the lowest energy site for bonding was found to be the two-fold site as would be expected from coordination principles but that stereochemistry 4 was of higher energy than 5 simply because of the

4

5

added stabilization in 5 of the multicenter C-H-M interactions (all known dinuclear and cluster complexes with CH₂ ligands have form 4 because these complexes are coordinately saturated²⁸). For the methylidyne fragment, CH, the three center site, 6, is explicably more stable than the two-center and sitting

6

atop a single metal atom site when the C-H vector was fixed normal to the surface plane. However, the most stable stereochemistry was 7 where the carbon is off

7

the three-fold site toward a two-fold site and the C-H vector is tipped so as to generate a multicenter C-H-M bond. In fact, every system tested so far by these calculations exhibits a stabilization as C-H-metal interactions are generated for these coordinately unsaturated surfaces. The more complex benzene system is presently under study to see if a most favorable registry (Figures 8 and 9) can be identified by this calculational procedure and how it conforms to those symmetric registries discussed above and in Figure 8 and 9.

Cluster modeling of possible chemisorption states and of possible intermediate states in surface reactions can to a first approximation be useful in guiding experiments or interpretations of experimental data for surface reactions.²⁷⁻²⁹ One important and enlightening result^{7,30,31} in metal carbide cluster chemistry will be used here to illustrate this particular point because it bears directly on the importance of multicenter C-H-M bonding for hydrocarbon fragments in metal chemistry.

Oxidation of the iron carbide cluster anion, $\text{Fe}_4\text{C}(\text{CO})_{12}^{2-}$ (Figure 12), yielded the coordinately unsaturated and thermally very reactive $\text{Fe}_4\text{C}(\text{CO})_{12}$ cluster; both reactant and product have a four coordinate carbide carbon atom. When the oxidation is carried out at $\sim 0^\circ\text{C}$ in the presence of hydrogen, hydrogen addition occurred to give a new cluster with both a C-H and a Fe-H-Fe hydrogen site. The methylidyne or CH ligand was not simply bound to iron atoms through the carbon atom--a type of bonding (see 6 above) conventionally found in clusters such as $\text{HCCo}_3(\text{CO})_9$.³² Such a conventional

bonding would have given, for the open butterfly array of four iron atoms, a coordinately unsaturated cluster. Instead, both the carbon and the hydrogen atoms of the methylidyne ligand were bound to iron atoms as shown in Figure 13--with the additional C-H-Fe multicenter bonding a coordinately saturated cluster obtains. The stereochemical feature of the CH ligand in this cluster is analogous in form to the molecular orbital prediction for CH on a metal surface. Furthermore, there are spectroscopic data³³ for CH chemisorbed on Ni(111) that suggest that the CH vector is tipped with respect to the surface normal and is ostensibly similar to γ and to the CH ligand in the iron cluster. Another structural point of interest in a chemical context is that the C-H bond distance in the methylidyne ligand in the cluster is rather long, 1.18 Å. The bond lengthening suggests C-H bond activation--a point borne out by the established cluster chemistry where (A) there is fast exchange between hydrogen atom sites in the cluster, i.e., between the C-H-Fe and the Fe-H-Fe sites and (B) the C-H hydrogen atom is quite protonic in character and is removed by the weak base methanol to form $[\text{HFe}_4\text{C}(\text{CO})_{12}]^-$.³⁰

Multicenter bonding of a CH_3 group in a metal cluster has also been established.³⁴ In $\text{H}(\text{CH}_3)\text{Os}_3(\text{CO})_{10}$, the CH_3 group is sigma bonded to one osmium atom in the cluster and is also bonded through a multicenter Os-C-H-Os bond to a second. Without the latter interaction the cluster would have been coordinately unsaturated. The CH bond in this cluster is activated: The methyl derivative in solution is in equilibrium with a second cluster that has a methylene ligand, $\text{H}_2(\text{CH}_2)\text{Os}_3(\text{CO})_{10}$. The methylene ligand bridges two osmium atoms in the cluster (Figure 14). This cluster chemistry with the facile and reversible C-H bond cleavage reaction illustrates the two steps postulated in the beginning of this article: the formation of a multicenter C-H-M bond which

effects C-H bond activation and the subsequent (and reversible) step of C-H bond activation.

We seek in our cluster chemistry further examples of facile C-H bond activation and bond scission. Other established examples of such hydrocarbon chemistry had been reviewed earlier.²⁷

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References and Notes

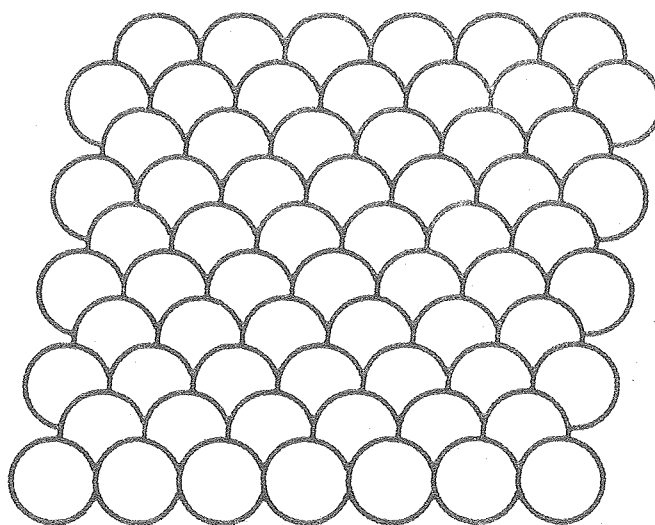
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(b) A.C. Cope and E.C. Friedrich, J. Am. Chem. Soc., 90 909 (1968).
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13. In surface science literature, the terms associative and dissociative chemisorption are used to denote chemisorption processes that respectively occur without and with fragmentation of the molecule.
14. In the realm of ultra high vacuum experiments, the concentration or activity of surface species is relatively low at least with respect to

those present on surfaces at near normal pressures. Accordingly, carbon-hydrogen bond scission reactions are typically irreversible; the hydrogen surface activity is apparently too low for the reverse reaction to proceed at measurable rates. However, with extension of the ultra high vacuum studies to real surfaces at normal pressures, reversible C-H bond scission may be and has been observed.

15. Desorption of hydrogen atoms as H_2 on these surfaces is an activated process and minimally requires temperatures of about $130^\circ C$ (since the desorption process is second order in hydrogen atoms, the desorption temperature is dependent upon surface coverage by hydrogen atoms). In the decomposition experiments, there was no detectable H-D isotope effect upon the H_2 (or D_2) desorption temperature maxima.
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19. That is, close in a relative sense. Actually the C-H hydrogen atoms probably are slightly out of the C_6 plane towards the metal surface so as to develop better C_6H_6 π and π^* overlaps and to achieve stronger three-center two-electron C-H-M bonds. In $C_6H_6Cr(CO)_3$, such a displacement of hydrogen atoms has been established from an X-ray and neutron crystallographic study.²⁰
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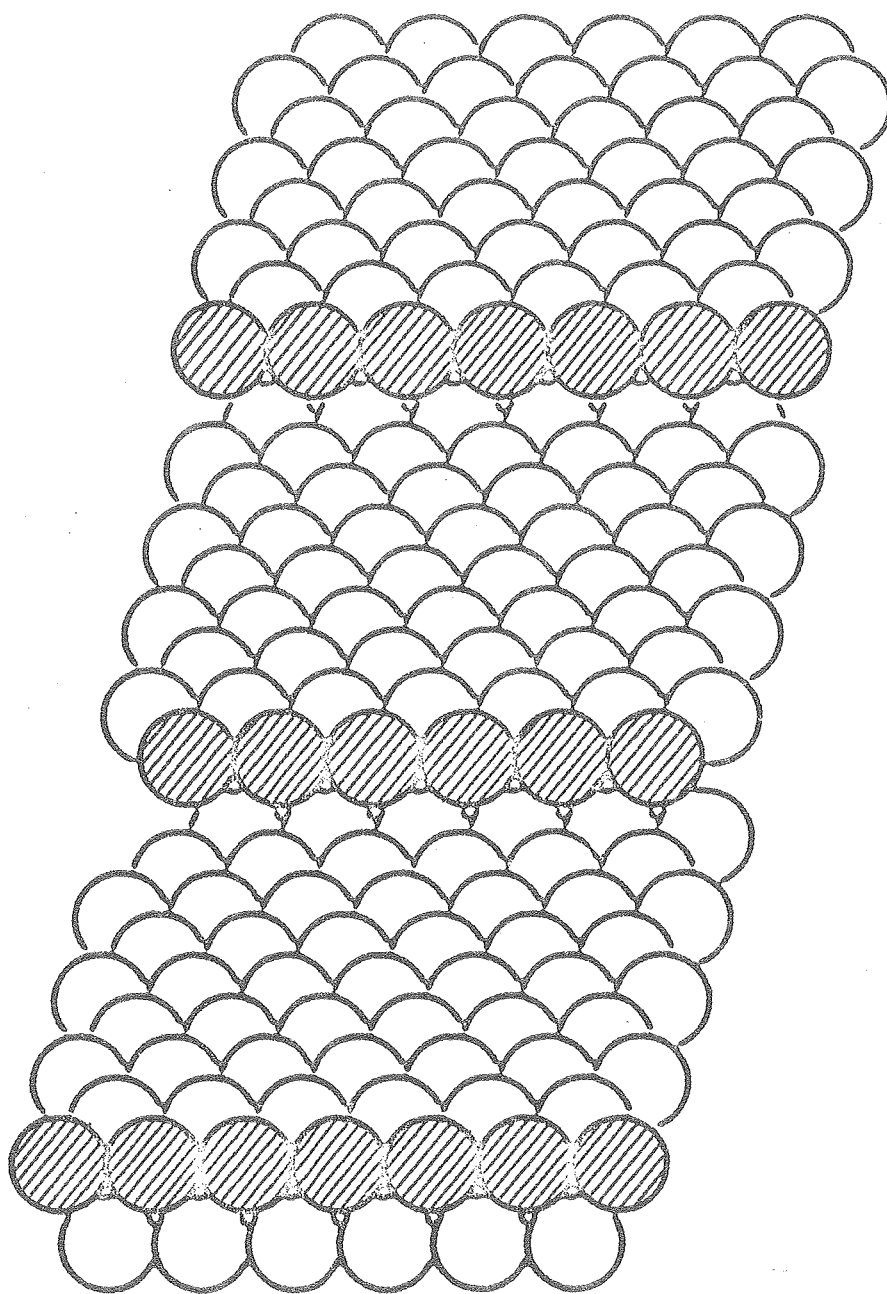
- accompanied the basic chemisorption process, cf. M.G. Cattania, M. Simonetta, and M. Tescari, *Surf. Sci.*, 82 L615 (1979); J.E. Demuth, *Surf. Sci.*, 76 L603 (1978); P. Klimesch and M. Henzler, *Surf. Sci.*, 90 57 (1979); and references therein.
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 32. D. Seyferth, *Adv. Organomet. Chem.*, 14 98 (1976).
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Figure 1: This is a perspective of the thermodynamically most stable crystal plane for face centered cubic, the (111) low Miller index plane. All surface atoms have nine nearest neighbors compared to twelve for the bulk atoms.



XBL 804-9137

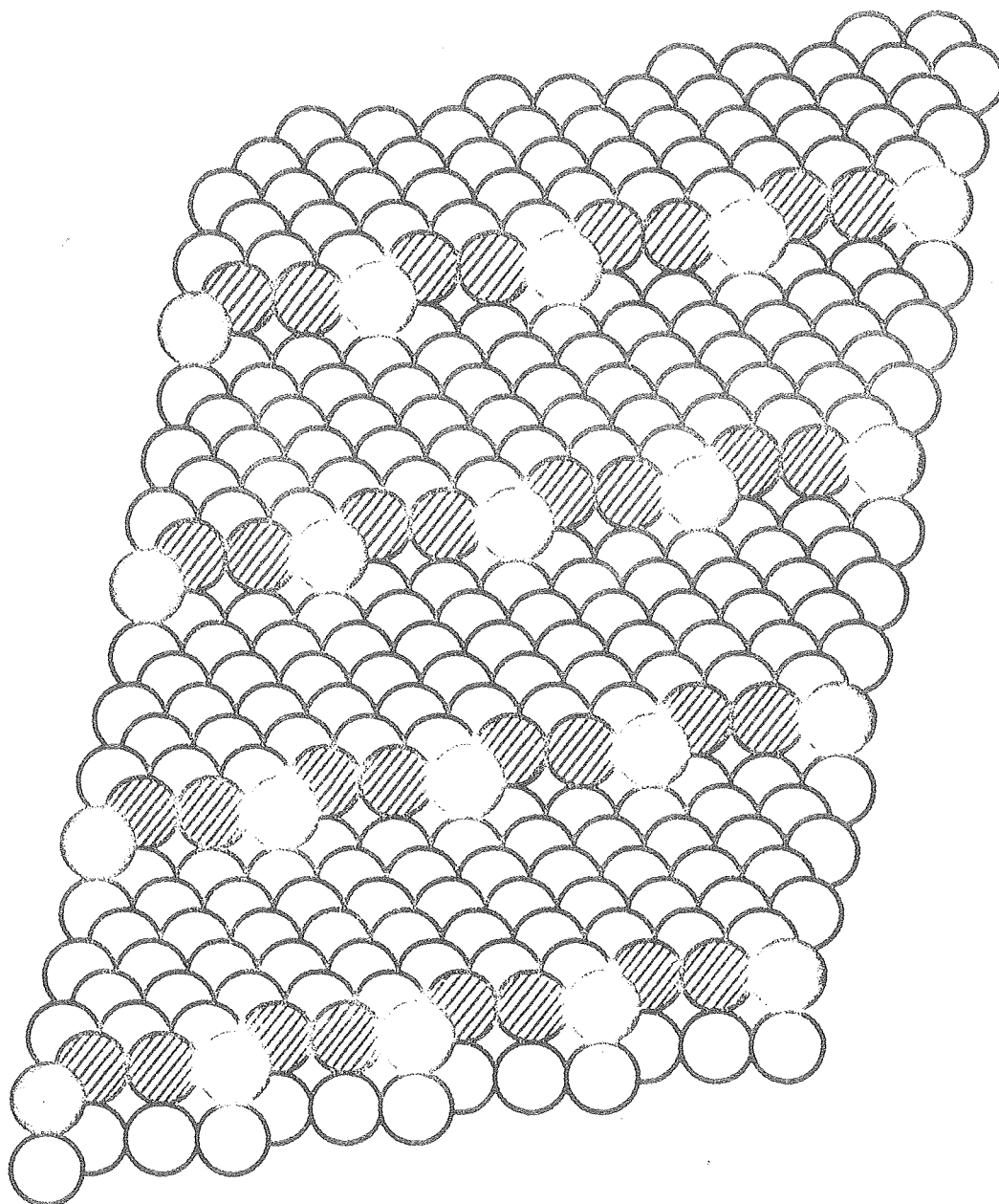
Figure 2. The most common type of imperfection site on a (111) crystal plane is steps. This illustration shows the perspective of regularly placed steps on the (111) surface. Every ninth row is a step--the step atoms are shaded--and this may indexed as $9(111)x(111)$. The coordination number of step atoms is seven.



XBL 802-8091A

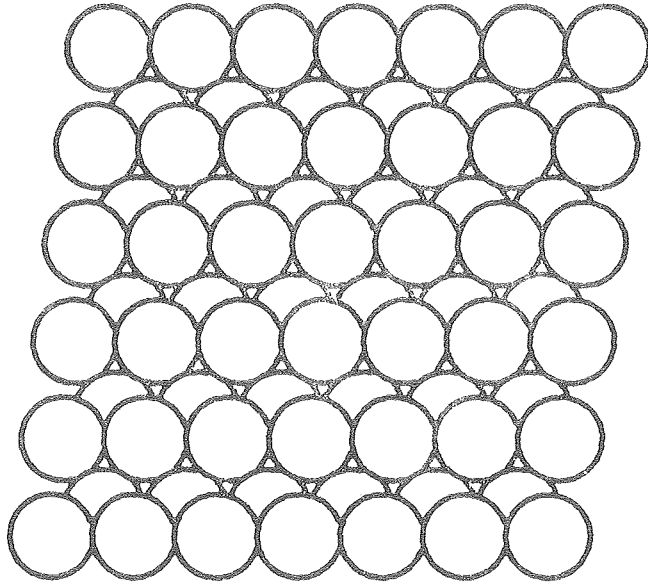
Figure 3: The other common imperfection site on a (111) surface is a kink.

This $7(111) \times (310)$ surface shown in perspective is a regularly stepped and kinked surface with a step sequence beginning every seventh row and with a kink site at every third atom in the row. The atoms in kink sites have a coordination number of six (black spheres).



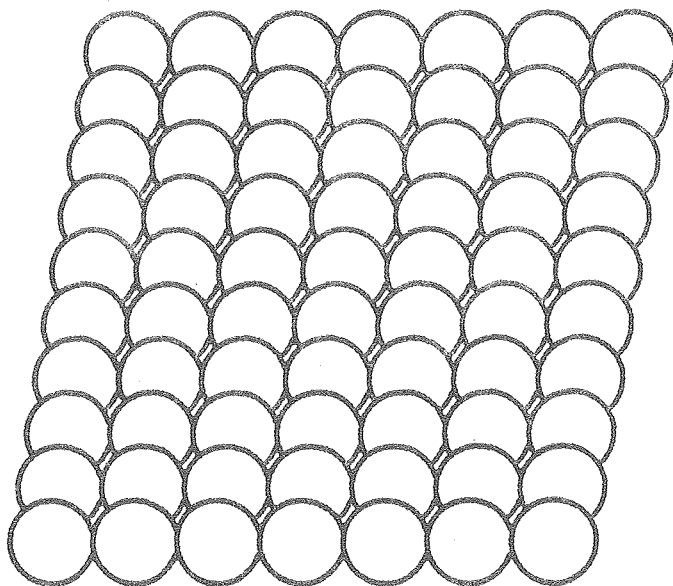
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Figure 4: This (110) low Miller index plane is like a super-stepped surface-- every other row is a step. The coordination numbers of surface metal atoms in the crests and troughs of this stepped or ruffled surface are six and eleven, respectively.



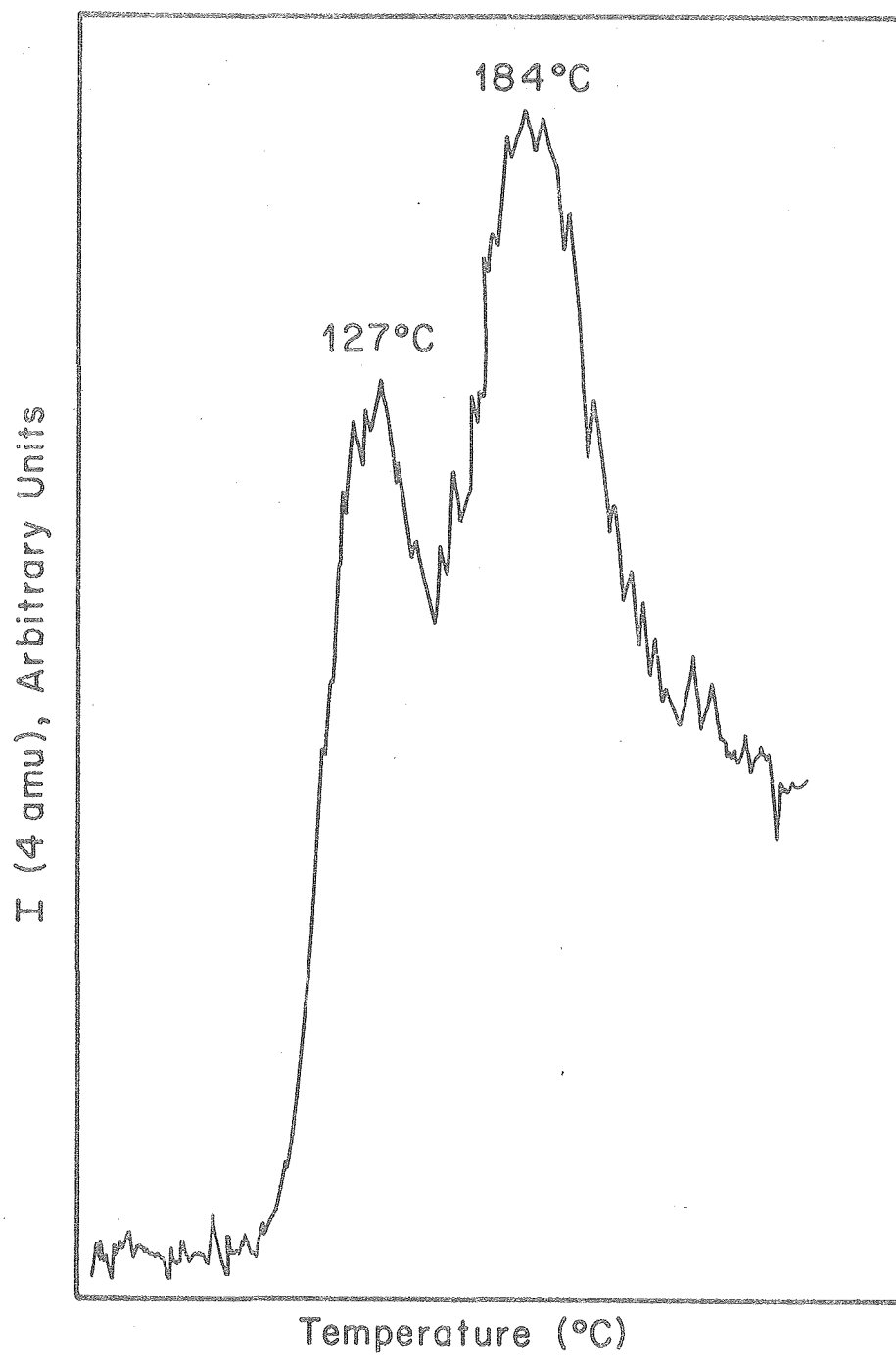
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Figure 5: This representation is for the flat (100) plane where the surface atoms have a coordination number of eight.



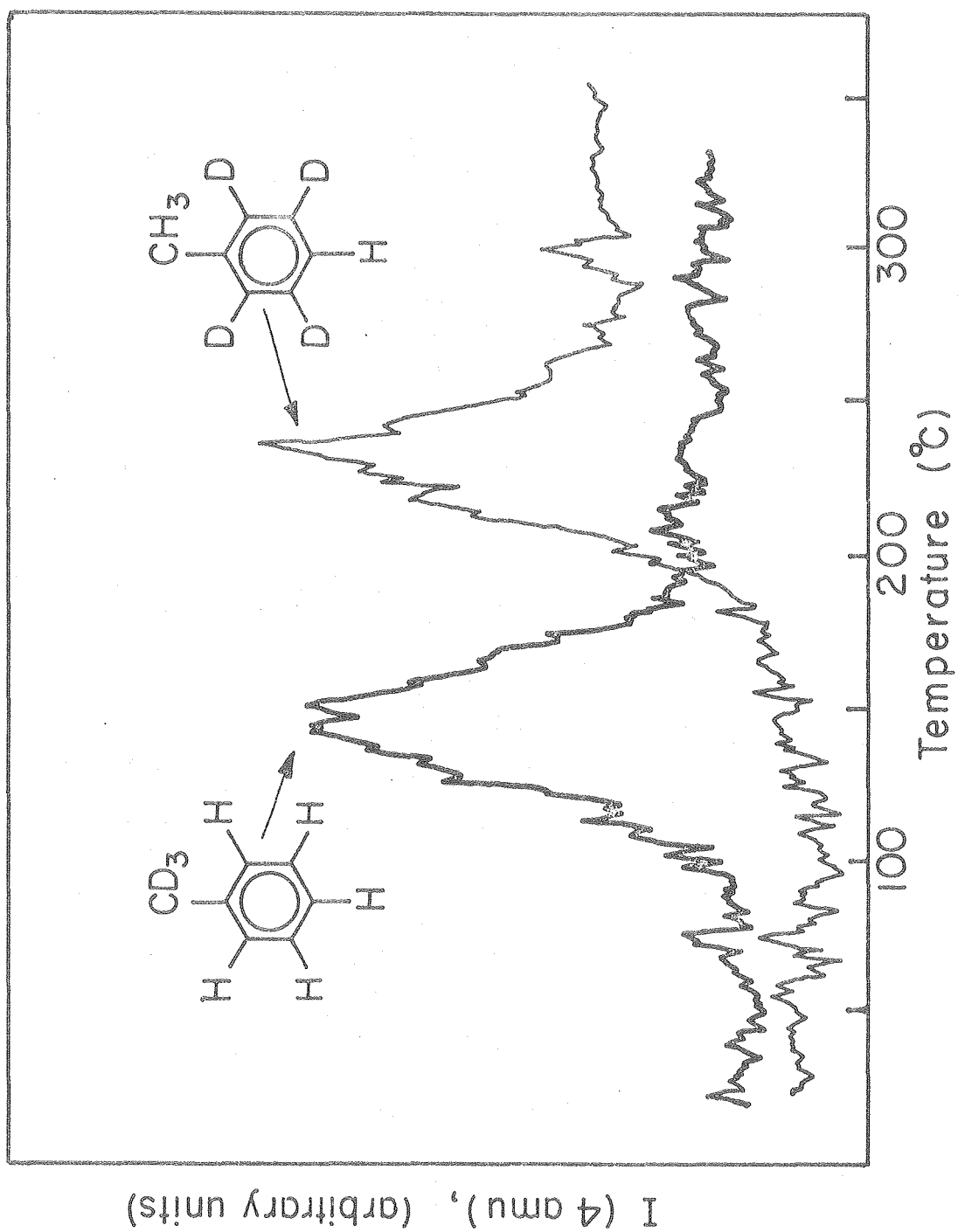
XBL 804-9135

Figure 6: This is the thermal desorption curve for the desorption of D_2 from the thermal decomposition of perdeuterotoluene on the (111) surface. In this experiment, mass four is monitored by mass spectrometry as a function of temperature (the crystal was heated at a linear rate of $25^\circ/\text{sec}$).



XBL 804-9449

Figure 7: In the two thermal desorption experiments plotted above, deuterium mass four, was monitored as a function of crystal temperature in the thermal decomposition of $C_6H_5CD_3$ and of $C_6D_5CH_3$ on the Ni(111) surface.



XBL 804-9446

Figure 8: The figure illustrates possible symmetric registries between chemisorbed benzene and the metal atoms in the (111) nickel surface. Shown are registries with the C_6 centroid over a single nickel atom, over a two-fold site and over a three-fold site. Because the distance between hydrogen atoms at para positions in the benzene molecule is virtually identical to twice the nickel atom diameter, the registry with the C_6 centroid atop a single nickel atom is precise (upper left). Overlaps with the π and π^* benzene orbitals and metal surface orbitals should be excellent. In one rotational form, the hydrogen atoms of the benzene lie directly over single nickel atoms so as to generate multicenter C-H-Ni bonds. The van der Waals extension of the benzene molecule (dotted line) is virtually identical with the space occupied by the central nickel atoms and the surrounding six nickel atoms. Another form generated from the above by a rotation of 30° has the C-H hydrogen atoms lying nearly above the two-fold sites (lower left). Either of these may be the most stable registry for benzene on this surface.

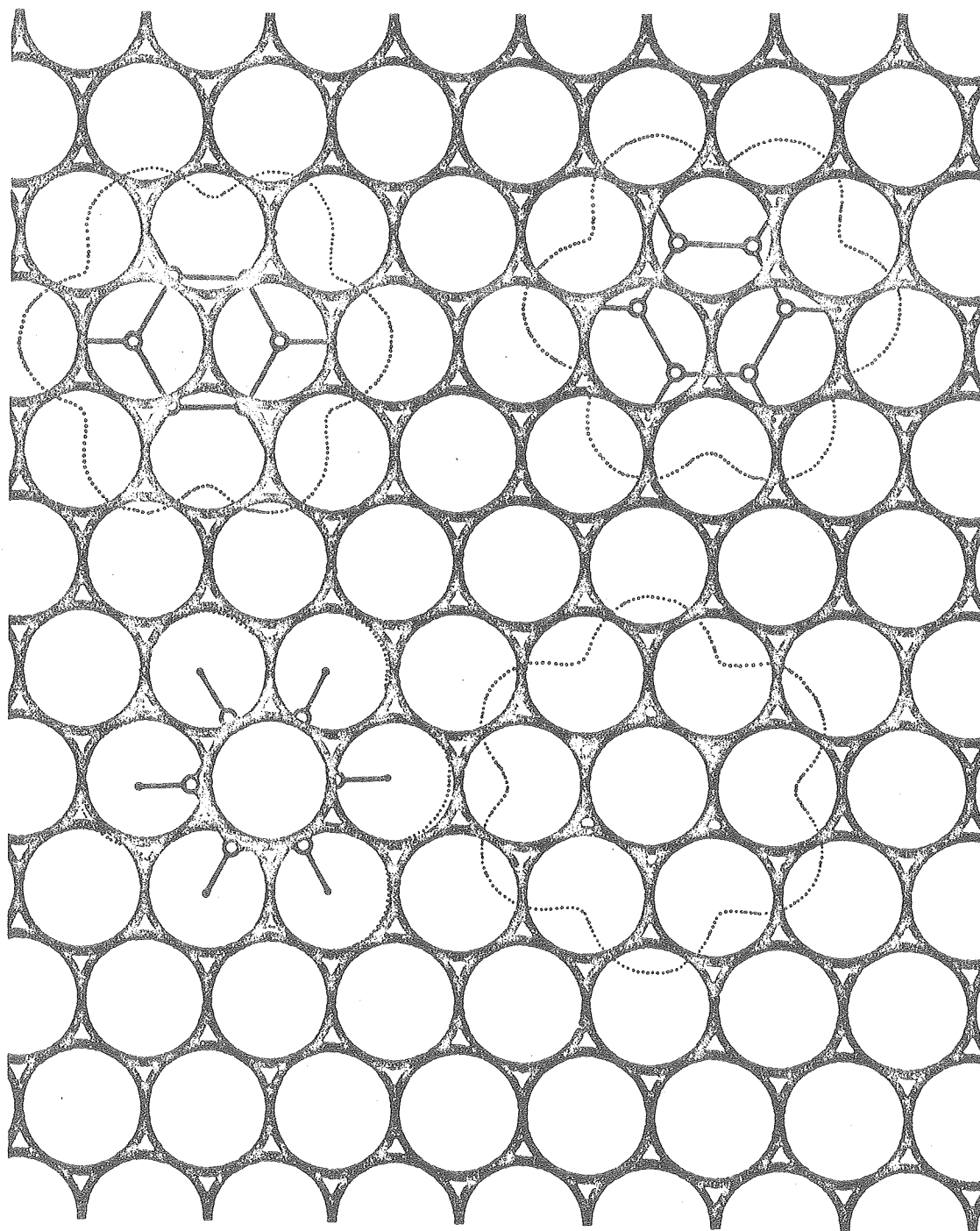


Figure 9: Shown above are some of the more symmetrical registries of the benzene molecule with respect to the Ni(100) lattice plane. Although none of these registries can have as close a 1:1 correspondence of H-Ni atom positions as on the (111) surface (Figure 8), benzene appears to be more strongly bound⁹ on this surface than on the (111) surface.

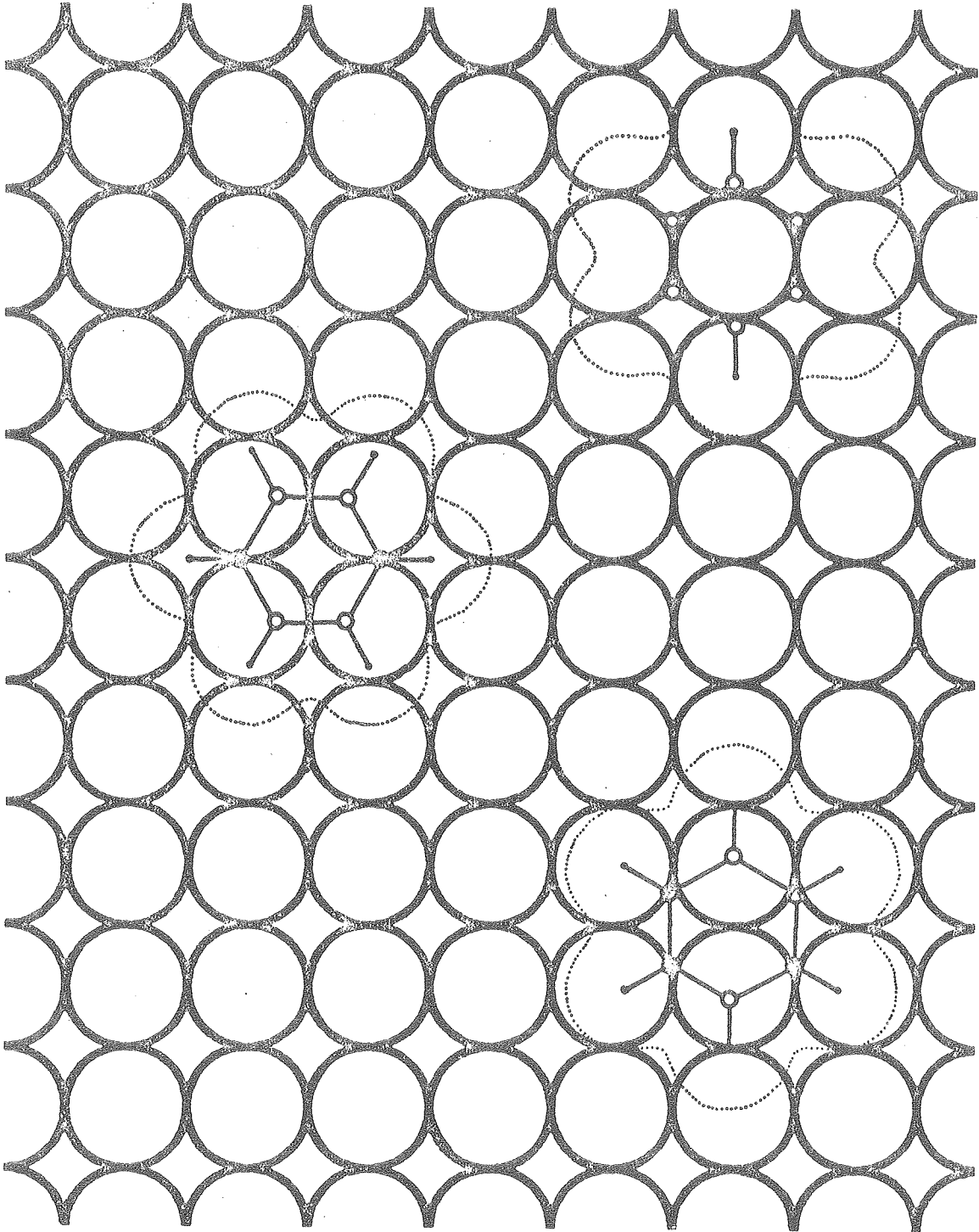


Figure 10: Here is an exaggerated representation of benzene molecules chemisorbed near stepped or stepped-kinked sites where C-H hydrogen atoms may closely approach metal atoms in the next plane. This can account for the higher reactivity (C-H bond breaking) observed for benzene on such irregular stepped or stepped-kinked surfaces.

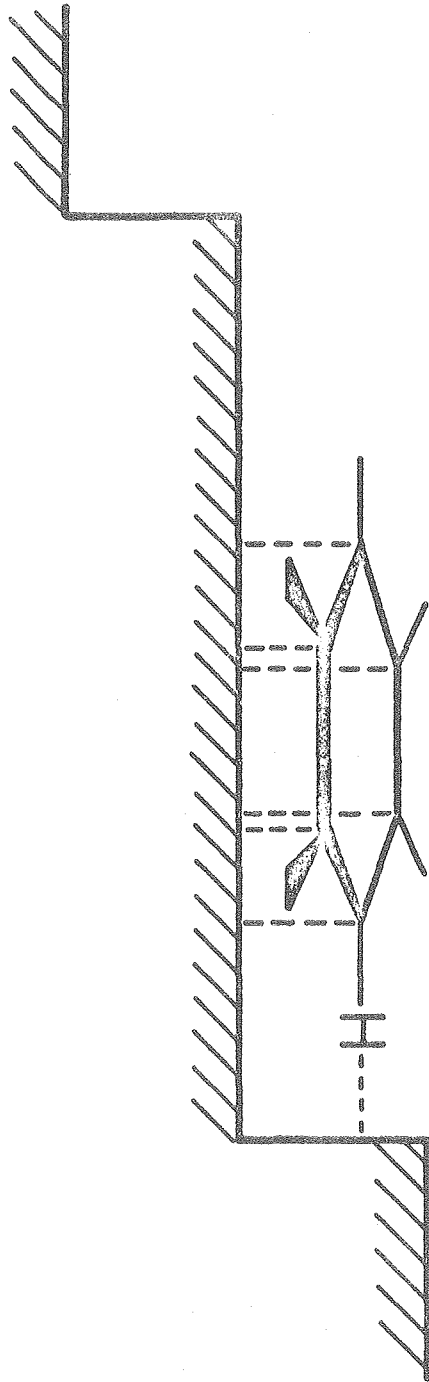


Figure 11: On the flat (111) and (100) surfaces, acetonitrile is bonded to surface metal atoms only through the nitrogen atom, and the CN bond vector is more or less normal to the surface. Thus, methyl hydrogen atoms cannot easily closely approach surface metal atoms even through vibrationally excited states as shown schematically at the left in the Figure. However, acetonitrile molecules bound near step or kink sites can have methyl hydrogen atoms in positions from which there can be a facile close approach of these hydrogen atoms to the surface metal atoms. This geometric or stereochemical feature explains the reactivity (irreversible C-H bond breaking processes) observed for acetonitrile on the stepped, stepped-kinked, and super-stepped (110) nickel surfaces.

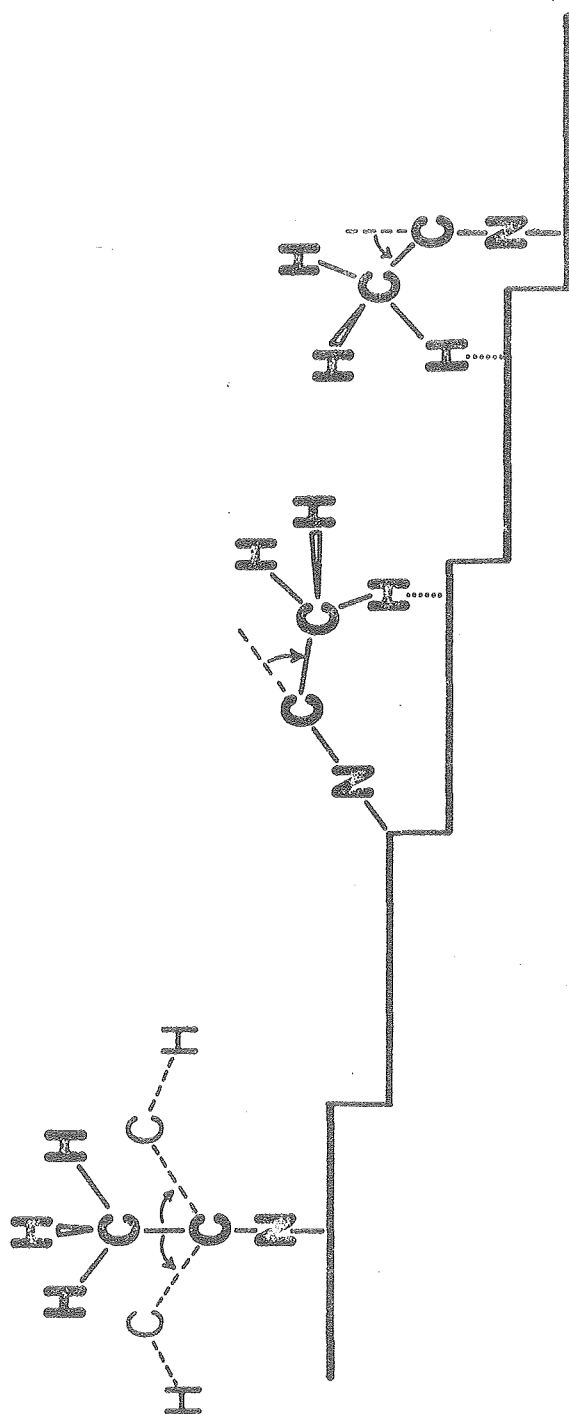


Figure 12: In $[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$, the iron atoms form a butterfly array with the carbide carbon atom centered above the wings.³⁰ The carbide carbon atom has the very low coordination number of four, a feature showed only by this cluster and the related cluster $[\text{HFe}_4\text{C}(\text{CO})_{12}]^-$.³⁰ Each iron atom has three terminally bound CO ligands.

2-

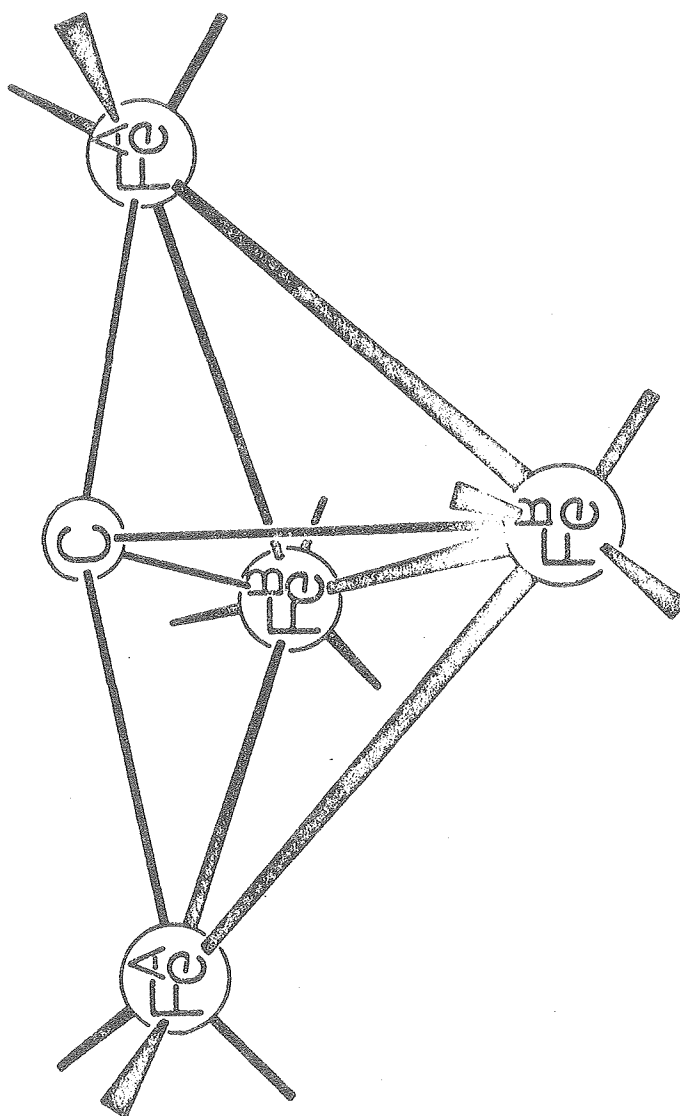


Figure 13: This is the structure of $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$, minus the twelve carbonyl ligand atoms, as determined by a neutron crystallographic study.³¹

The most notable features of this structure center on the methylidyne, CH, ligand which forms a strong, closed three-center two-electron bond with the apical iron atom, Fe(1). There are two molecules in the asymmetric unit. The distances shown are for molecule (1); no experimentally significant differences exist between the two molecules. Each iron atom in this cluster has three terminally bound carbonyl ligands.

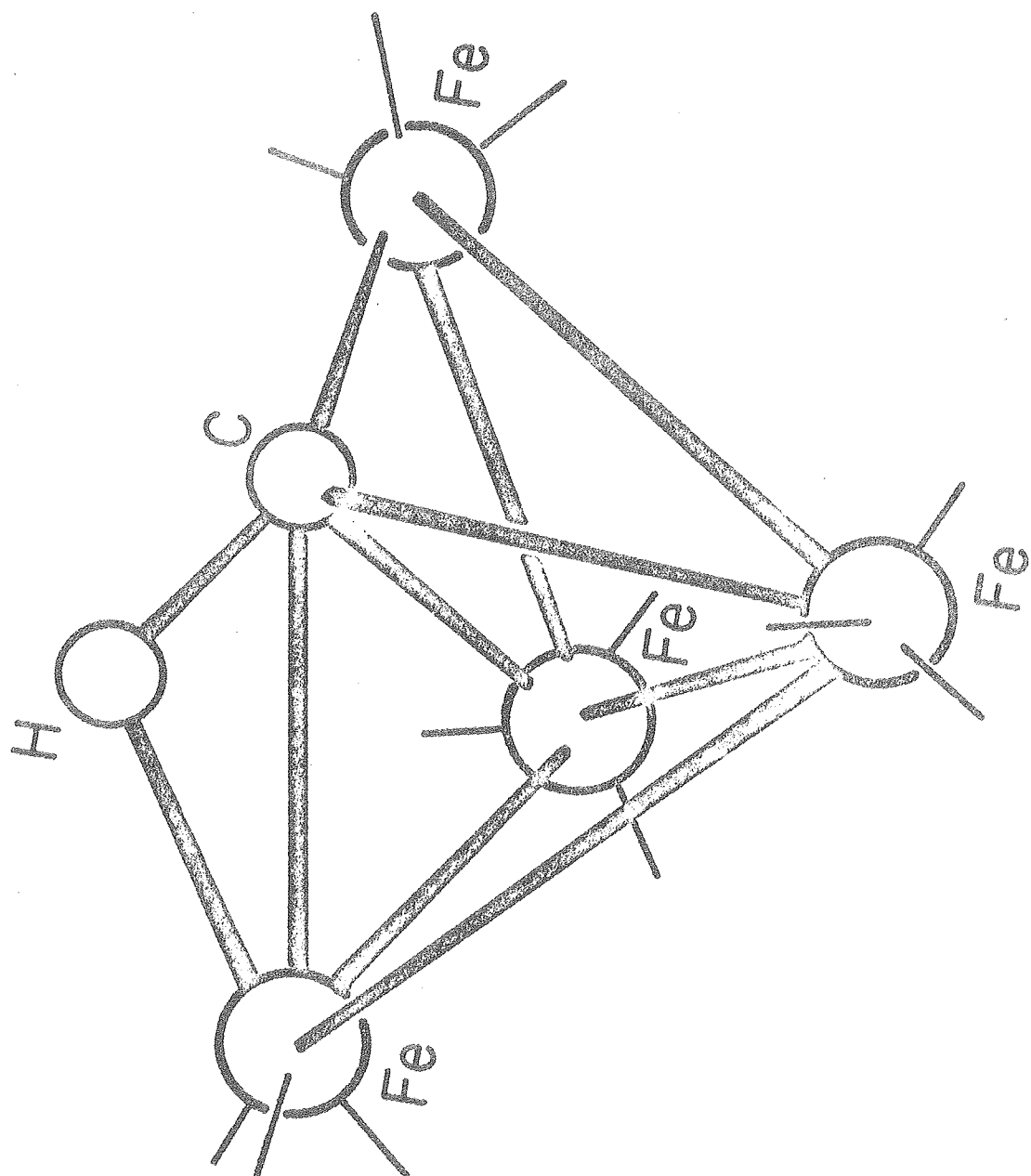


Figure 14: Here is a representation of the equilibrium solution of two cluster molecules, one a methylene and the other a methyl species, which rapidly interconvert. The methylene structure on the right has been established by crystallographic analysis. The precise structure of the methyl derivative on the left has not as yet been crystallographically defined but NMR spectroscopic data have reasonably established that the methyl group unsymmetrically bridges between two osmium atoms with a three-center, two-electron C-H-Os interaction.

