Chem. Rev. 1995, 95, 2651–2693

An Organometallic Guide to the Chemistry of Hydrocarbon Moieties on Transition Metal Surfaces

Francisco Zaera

Department of Chemistry, University of California, Riverside, California 92521

Received June 26, 1995 (Revised Manuscript Received September 11, 1995)

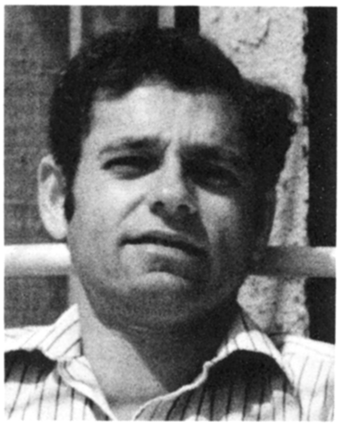
Contents

I. Introduction

In this review what is known about the chemistry of hydrocarbon molecules on transition metal surfaces will be surveyed. A battery of new surface science techniques has been used to study the solid–gas interface, but only recently has a picture started to emerge for the surface chemistry of adsorbed organic molecules. Even though a few reviews have already been published on this subject,[1-5] a comprehensive and systematic description of these systems is still lacking. Here we will discuss the results reported to date on the structure and reactivity of the different types of hydrocarbon moieties that form on transition metal surfaces. One of the goals of this review is to provide an organometallic guide for the possible interactions of hydrocarbons with transition metals with the idea of examining their relation to the corresponding surface chemistry. We will however limit our review of the organometallic literature to the information relevant to the surface systems, and also narrow the field to cover only molecules with carbon and hydrogen atoms; compounds containing other atoms (O, S, N) will be excluded.

It is our belief that there is a close relation between organic ligands in organometallic compounds and their counterparts on solid surfaces in terms of both structure and reactivity. Even though physicists originally described the behavior of metals in terms of a completely delocalized electronic structure, later studies have differentiated between the sp delocalized band responsible for the electrical conductivity and other physical properties of the metals and the d electrons, which were found to be reasonably localized in terms of both energy and space (Figure 1).[6-9] Since the chemistry of most transition metals is dominated by their d orbitals, the localization of those orbitals around the individual atoms of a solid surface is then expected to lead to localized bonding. Several experimental observations have proven this true in many systems. For one, the vibrational normal modes associated with bonds between surfaces and adsorbates usually display well-defined frequency values,[10-13] and there are well-defined electronic

0009-2665/95/0795-2651$15.50/0



Francisco Zaera received his degree of Licenciate in Chemistry from the Simón Bolívar University in Caracas, Venezuela, in 1979. He then went to the University of California, Berkeley, and obtained his Ph.D. degree under the supervision of Professor Gabor A. Somorjai in 1984. This was followed by a two-and-a-half year appointment as Assistant Physicist at the National Synchrotron Light Source, in Brookhaven National Laboratories, where he worked in collaboration with a research group from the Corporate Research Laboratory of the Exxon Research and Engineering Company headed by Dr. John L. Gland. From there he moved to his present position at the University of California, Riverside, where he is now a Professor of Chemistry. His main research interests are in the fields of surface chemistry and heterogeneous catalysis.

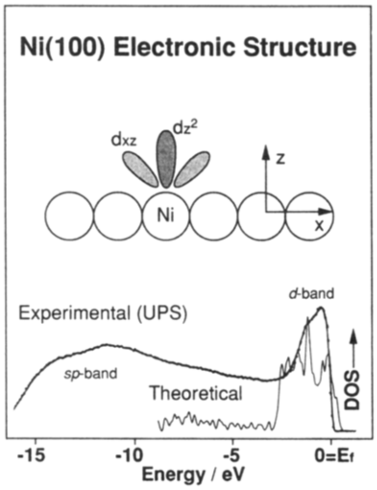


Figure 1. Ultraviolet photoelectron spectrum (UPS, thick trace) and calculated valence electron density of states (thin trace) for clean Ni(100) surfaces. This figure highlights both the narrow range of energies and the spatial localization of the d band in transition metal surfaces.[9] It is this geometrical and energetic localization of the d orbitals in surfaces that explains the localized nature of the bonding in adsorbates and that allows for the building of a close analogy between surface and organometallic systems.

levels associated with those bonds as well.[12,14,15] In addition, molecules chemisorbed on single crystals often arrange themselves in periodic patterns in registry with the substrate structure; analysis of the diffraction patterns obtained from those systems show that the local geometry of the adsorbed molecules is well defined.[16,17] All this means that, to a first approximation, we can expect to see the same type of organic moieties on surfaces and in organometallic systems. This analogy has of course some limitations, since there are other parameters that need to be taken into consideration when interpreting the chemistry observed in both surfaces and discrete compounds, namely, coordination numbers (or the number of metal atoms bonded to one molecule), the effect of ligands on the electronic structure of the central atom, and steric effects. Surfaces may also offer additional bonding sites not available in discrete clusters and can even reconstruct to accommodate adsorbates. We will address those issues briefly in this review as well.

The present review is organized in the following manner. First, a brief discussion of the experimental techniques used to characterize both organometallic and surface systems is presented. A discussion of the coordination and structure of the different types of organic moieties, first in organometallic compounds and then on metal surfaces, follows. Here the systems are classified according to the type of bonding between the molecules and the metals: both σ- and π-bonded ligands are described according to their coordination number. Next, the different elementary steps that such systems can undergo are summarized: C−H and C−C bond-breaking and bond-forming reactions, isomerizations, and others. Again, the chemistry of organometallic compounds is discussed first, and the surface chemistry is presented subsequently. A brief description of a few key nonelementary reactions is also given, including some catalytic processes. Lastly, a brief discussion on the main similarities and differences found so far between surface and organometallic systems, and on possible future directions for this field, is offered.

II. Experimental Methods

Even though bonding in most chemisorption systems is localized, the different local structures of the metal atoms present on the surface of a given solid make these systems intrinsically more complex than their organometallic analogs. The use of single crystals with well-characterized structures has therefore been adopted in recent years in order to simplify surface studies. In addition, most chemisorption experiments are nowadays performed under so-called ultrahigh vacuum (UHV) conditions, that is, under pressures in the $10^{-9}-10^{-10}$ Torr range, in order to keep the substrates clean for reasonably long periods of time.[17-19] This is the type of work reviewed here.

The characterization of organometallic systems relies on well-developed techniques such as X-ray and neutron diffraction, NMR, and infrared spectroscopies. Unfortunately, most of those probes are not applicable to the small single-crystal systems described above. A group of alternative surface-sensitive techniques based on the use of electrons and other particles has been developed in recent years for surface studies. These include low-energy electron diffraction (LEED) and surface-extended X-ray absorption fine structure (SEXAFS) for structural determinations, photoelectron (UPS and XPS), electron energy-loss (EELS) and work function measurements for characterization of electronic levels, secondary ion mass (SIMS), Auger electron (AES) and ion scattering (ISS) spectroscopies for compositional analysis, high-resolution electron energy-loss (HREELS) and reflection-absorption infrared (RAIRS) spectroscopies for vibrational studies, and temperature-programmed desorption (TPD) for reactivity determinations, to name a few.[20,21] Unfortunately, none of those techniques is yet capable of providing the information necessary for reaching the type of definitive conclusions regarding the structure or the reactivity of chemisorbed moieties that are typical in inorganic chemistry. This is why a good understanding of both the similarities and the differences between surface and organometallic systems is crucial in developing the chemical intuition needed to interpret the data from surface studies.

III. Coordination and Structure

A. Single Metal–Carbon σ Bonding

1. Alkyls

The synthesis of organometallic compounds with alkyl ligands via the direct oxidative addition (C–H bond scission) of saturated hydrocarbons to metal atoms is in general not practical because of the low reactivity of those alkanes. There are, however, several easier routes for the synthesis of alkyl–metal organometallic complexes, such as, for instance, the oxidative addition of alkyl halides to metal centers.[22–25] For years metal alkyls other than $(CH_3)_3PtI$ could not be isolated, but it is now known that this was not due to a weak metal–carbon bond, but to the fact that there are a number of facile decomposition pathways available for these compounds (which will be discussed later). By coordinating deactivating ligands to the metal center, many alkyl metallic compounds have been isolated since.

Most alkyl groups form a single σ bond with one metal atom through a two-electron donation, and occupy a single coordination site. However, there are also cases where those groups bond to multicenter complexes in a bridge configuration. Bridging alkyl groups are common among main-group elements such as aluminum,[26] but have also been observed in a few transition metal complexes. There seems to be a competition between this bridging of alkyl groups, which has been seen mainly with first-row metals, and the formation of metal–metal multiple bonds, which is favored by 4d and 5d elements.[27–29] Apart from the simplest bridging configuration possible, via a two-electron three-center bond between the metals and the carbon atom,[27–29] two other types of bridging compounds have been observed with transition metals, one where the carbon atom coordinates to one of the metal atoms while the C–H bond displays an agostic interaction with a second, and another where the alkyl group is in a planar configuration, sandwiched between the two metals.[30–32]

Alkyl halide insertion reactions can also be induced on transition metal surfaces.[33] There have been a large number of studies reported recently on the chemistry of simple alkyl halides over well-defined surfaces for a variety of transition metals, including tungsten,[34] iron,[35] ruthenium,[36] cobalt,[37] rhodium,[38] nickel,[39–44] palladium,[45–48] platinum,[49–58] copper,[59–65] silver,[66–69] and gold.[70,71] At liquid nitrogen temperatures alkyl halides usually adsorb molecularly, but in most cases they can be easily activated, either thermally[33] or photolytically,[72] to produce alkyl groups on the surface. The cleavage of C–I bonds in particular generally requires activation energies of 5 kcal/mol or less,[73,74] and usually occurs at temperatures below 200 K.[40,41,50,52,61,62] Evidence for the formation of alkyl moieties after this bond-scission step comes from a range of techniques, mostly X-ray photoelectron (XPS), static secondary ion mass (SSIMS), and vibrational (HREELS and RAIRS) spectroscopies.[39–42,49,52–54,68,74,75] According to data from infrared experiments, the alkyl chains initially orient themselves flat on the surface in order to maximize their interaction with the metal, but reorient to a perpendicular configuration at higher coverages, presumably because van der Waals interactions between the hydrocarbon chains dominate in that regime.[44,51,64,76] There is no direct information on either the bonding geometry or the coordination of the alkyl groups to the surface available to date. On the one hand, both the low metal–carbon stretching frequency observed in vibrational studies[77–79] and some theoretical calculations[80–82] suggest that alkyls may adsorb on hollow sites, but other calculations explain the experimental results by an on-top configuration instead.[83,84]

There have been several attempts to develop alternative synthetic routes for alkyl groups on metal surfaces. A few research groups have used chemisorbed azocompounds as alkyl precursors, but since the surface chemistry of those compounds is far more complex than initially expected, there have been no cases where alkyl moieties have been produced cleanly in this manner.[85–91] A second approach consists of dosing alkyl radicals produced in the gas phase by decomposition of the same azocompounds.[92,93] This route has proven to work quite well for generating methyl groups, but has so far not been extended to other alkyl moieties. A third method involves the preparation of alkyl groups by using alkane molecular beams,[94] but again, only methyl moieties have been synthesized this way. Other attempted procedures include the soft landing of alkyl cations,[95] the direct deposition of organometallic complexes containing alkyl ligands,[96–100] the hydrogenation of olefins, either with gaseous hydrogen atom via an Eley–Rideal reaction,[101] or by a Langmuir–Hinshelwood mechanism with adsorbed hydrogen,[102] and the bombardment of adsorbed alkanes with low-energy electrons.[103] All these methods are in their initial stages of development.

Finally, a few words need to be said about the stability of alkyl fragments. As mentioned earlier, metal–carbon σ bonds are not inherently weak; compounds with alkyl ligands are kinetically unstable only because there are a number of decomposition routes readily available to them.[104,105] The metal–carbon dissociation energy for gas-phase metal–CH_3 fragments ranges from about 30 kcal/mol (for Mn and Fe) to 60 kcal/mol (for Ni and Cu).[106] In organometallic compounds those energies vary from 28 kcal/mol in $Pt(CH_2)_3Cl_2$[107] to 30 kcal/mol in $Mn(CH_3)(CO)_5$,[108] 39 kcal/mol in $Pt(CH_3)_3(\eta^5\text{-}C_5H_5)$,[109] and 53 kcal/mol in $Re(CH_3)(CO)_5$.[108] On surfaces, to the best of our knowledge, values for metal-alkyl bond energies exist only for methyl and ethyl moieties, and only for surfaces of four transition metals, namely, Pt(111),[110,111] Ni(100),[40,41,112,113] Cu(111), Cu(100), and Cu(110),[59,62] and Fe(100);[102] in all those cases the metal–carbon energy is approximately 30 kcal/mol. The numbers listed above are within the range predicted by extrapolating the known values for M–N and M–O bond strengths, and are sufficiently large to allow for the isolation of alkyl complexes provided that their decomposition can be suppressed. Also worth noticing is the fact that the bond energies for a given metal have similar values regardless of the type of system being studied, whether it is a gas-phase radical, a gas or a liquid organometallic complex, or a hydrocarbon moiety adsorbed on a solid surface, as long as the oxidation state of the metal is not changed. Finally, it is interesting to point out that, at least in the case of copper, the metal–methyl bond energy (33 kcal/mol) is much closer to that for the cation $Cu-CH_3^+$ (30 kcal/mol) than for the neutral $Cu-CH_3$ molecule (58 kcal/mol), and since the main difference between the two gas-phase molecules is the lack of s electrons in the ionized metal, it could be argued that on the surface the alkyl–metal bond involves an s electron from the metal.

2. Vinyls, Acetylides, and Aryls

In addition to alkyl groups, unsaturated hydrocarbons can also σ bond to one or more metal centers to form alkenyl (vinyl), alkynyl (acetylide), or aryl ligands. Homoleptic vinyl complexes (containing only one type of ligand) are common among main elements,[114,115] but rare on transition metals.[116,117] Other vinyl compounds can be prepared by oxidative addition of vinyl halides,[118–120] by insertion of coordinated acetylene,[121,122] by transmetalation,[122] or by decarbonylation of acrylic compounds.[123] When coordinated to one metal center, the metal–carbon bond has a pure σ character,[117] but this type of ligand is more commonly seen in clusters, and in those compounds an additional interaction between the π orbital and a second metal atom is usually observed.[124–126]

There are, to the best of our knowledge, only four examples where vinyl groups have been cleanly isolated and well characterized on solid transition-metal surfaces. In one case the vinyl moieties were prepared by thermal dehydrogenation of ethylene on Ni(100) around 175 K. The formation of the surface vinyl species was first inferred from laser-induced desorption (LID) kinetic experiments with partially labeled compounds,[127] and later confirmed using vibrational spectroscopy.[128] By using near-edge X-ray absorption spectroscopy (NEXAFS), the C–C axis was determined to be at 35° to the surface normal, and the molecular plane oriented at 60° from that surface (Figure 2).[129] Although the exact coordination of the carbon to the surface was not determined, the observed geometry does suggest some π interaction with the metal surface. The other examples come from recent reports on the synthesis of vinyl groups by direct decomposition of chemisorbed vinyl halides on Pt(111),[130,131] Cu(100),[132] and Ag(111)[66] surfaces. Other reports claim to have isolated surface vinyl species after either electron bombardment[133] or thermal decomposition[134,135] of adsorbed ethylene, on Ag(111) and Pt(100), respectively, but the thermal desorption and photoelectron spectroscopy data presented in those cases was not accompanied by any structural or vibrational characterization of the surface species.

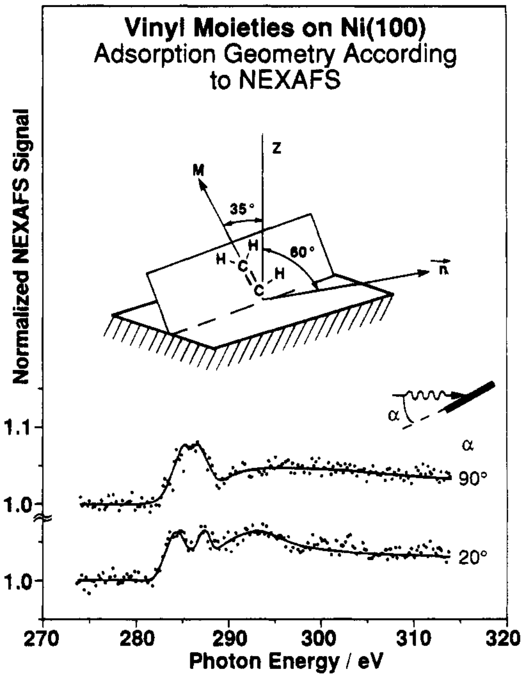


Figure 2. Near-edge X-ray absorption fine structure (NEXAFS) spectra from vinyl species adsorbed on Ni(100), as produced by heating a layer of about 15% of saturation of ethylene on that surface to 180 K.[129] These data were used to determine that vinyl moieties bond to the surface with their molecular plane at 60° and their C–C bond tilted about 35° from the normal.

Acetylide compounds behave in general in a way similar to that of the vinyl counterparts. Acetylides are most often prepared either by substitution of a coordinated halide with an acetylenic anion (such as in a Grignard reagent),[23] or by the oxidative addition of the acetylenic C–H bond in coordinated alkenes.[136] The metal–carbon bond in mononuclear acetylide compounds has a single σ character,[137] but in clusters these σ-bonded acetylides are capable of additional π bonding with neighboring metal atoms.[138] The stability of the mononuclear compounds depends on the nature of the R group in the β position, which follow the order aryl > hydrogen > alkyl.[23] These changes can be explained by the greater electronegativity of aryl groups compared to that of either H or alkyls and by the reduction in negative charge of the triple bond in the aryl case by virtue of its resonant delocalization. Many acetylides tend to polymerize, and acetylides of the form M_2C_2 are frequently explosive, especially when the metal is Cu, Ag, or Au.[23]

The formation of acetylides on metal substrates has usually been seen in association with the decomposition of chemisorbed ethylene, acetylene, or benzene molecules, but in most cases the evidence offered for the presence of this moiety on the surface has not been compelling. High-resolution electron energy-loss spectroscopic (HREELS) data has been interpreted as to indicate the presence of acetylide moieties in the following cases: (1) after decomposition of ethylene on Pd(111) and Pd(100) at 450 K,[139] on Ni(100) and Ni(110) around 300 K,[140,141] on Ru(0001) at 360 K,[142] on Ir(111) around 500 K,[143] and on Rh(100) at 300 K;[144,145] (2) following dehydrogenation of propylene on Rh(111);[144,146] (3) after fragmentation of chemisorbed benzene on Rh(111) above 400 K;[147] and (4) after decomposition of acetylene on Ni(100)[140] and Rh(111).[148] Although these assignments have been based on only a few vibrational modes, the proposed structures are consistent with similar cluster compounds.

Finally, there are a substantial number of known σ-bonded transition metal aryl compounds.[149-151] Transition metal aryl bonds can be made by a variety of synthetic methods, such as the use of aryl Grignard, lithium, or mercury reagents,[152,153] and the oxidative addition of aryl halides[154-156] (or even aryl C−H bonds[157]) to metal complexes. The monometallic compounds usually display M−C distances typical of single bonds, but in a few cases a considerable shortening of this bond has been found,[158] presumably because of the significant amount of back donation of the metal d electrons into the π^* phenyl orbital. Aryl compounds are quite reactive, readily converting to biphenyl derivatives and other products.[159] The decomposition mechanism for this is not well understood, but seems to involve the hydrogens in the *ortho* position, because adding *ortho* substituents to an aryl ligand results in a higher kinetic stability of the organometallic compound.[23] Aryl compounds are also believed to be intermediates in the formation of η^6-arene complexes in some cases.[149]

Almost no examples are known for aryl fragments on surfaces. Thus far phenyl groups have been prepared via the decomposition of halobenzenes on copper, silver, and nickel surfaces,[160-164] by thermal decomposition of benzene on Os(0001)[165] and Ni(110),[166] and by electron bombardment of adsorbed benzene on Ag(111).[133,160] On the basis of HREELS and NEXAFS data, a tilted geometry has been suggested for those systems.

B. Multiple Metal−Carbon σ Bonding

1. Carbenes

Saturated hydrocarbon moieties can also bond to metal centers via multiple σ bonds. For example, CR_2 fragments can coordinate directly to one metal atom in organometallic complexes to form what nominally would be a double bond.[167,168] These compounds are generically called carbenes, but in cases where the R groups are composed exclusively of carbon and hydrogen atoms they are referred as either alkylidenes or (substituted) methylidenes. There are in fact two types of metal−carbene complexes, those where bonding occurs through the donation of the electron lone pair of the carbene free radical into the d orbitals of the metal (the so-called Fischer type),[167] and those in which the double bond is formed by the sharing of electrons between the carbon and the metal atom(s) (the Schrock type).[169] This separation is more than just a question of semantics, since each type displays a quite distinct reactivity pattern. The "true carbene" (Fischer) type is stabilized by keeping the metal in a low oxidation state, and is readily attacked by nucleophilic reagents at the carbene carbon atom. The Schrock type, on the other hand, exists mostly in metals in high oxidation states and can react either with an electrophilic reagent at the carbon atom or with a nucleophilic group at the metal center.[24,170] The difference can alternatively be viewed in terms of the nature of the interaction between the ligand and the metal: while the first type is formed by electrophilic carbene ligands which exist as singlets in their free radical state, the second type, the most common for alkylidenes, originates from nucleophilic radicals in their triplet, most stable gas-phase state.[119]

Single-metal carbene compounds are fairly unstable and commonly require the presence of at least one element other than carbon (usually oxygen, sulfur, or nitrogen) on the carbene carbon.[168] There are very few examples of stable monometallic alkylidene complexes,[171] even though a theoretical study does suggest that the carbene−metal bond energy should be of the order of 50 kcal/mol, higher than that in coordinated ethylene, acetylene, N_2, or CO.[172,173] Some Schrock carbene complexes with less than 18 electrons are further stabilized by having the proton on the carbene atom bend backward toward the metal, so the C−H bond becomes longer and interacts strongly with the metal center while the metal−carbon double bond becomes shorter.[174]

A more stable form of carbenes exists in metal clusters with the carbon atom bonded in a bridge configuration between two metal atoms.[175] Bridged methylenic structures can be prepared by the addition of a variety of reactants to metal complexes, including dihalo alkanes,[176,177] diazo compounds,[178] and even ketenes,[179] although the use of this last reagent is not advisable because of its lack of selectivity. A few additional indirect synthetic methods, such as the addition of olefins and acetylenes and the use of organolithium and dimethyl magnesium reagents, have been reported in the literature as well.[175] The bridging carbene structures are usually symmetric, with an internal M−C−M angle of about 80° and an external R−C−R angle around 105°. Molecular orbital calculations have revealed an electronic structure for these systems best described by a CR_2 unit formally added to a metal−metal double bond: apart from a σ donation from the methylene group into the metal orbitals, there is also an electron transfer from the M−M σ bond to a carbon orbital with π symmetry which reduces the formal metal−metal bond from double to single character.[180] This interpretation is supported by results from photoelectron spectroscopy experiments.[181]

There have only been a handful of examples reported for the isolation and characterization of alkylidene groups on solid surfaces. Vibrational spectroscopic data from studies on the decomposition of diazo methane on Ru(0001) were initially assigned to the formation of methylene on the surface,[182] but later reinterpreted as possibly resulting from dimerization to ethylene. Additional vibrational results have been reported for methylene formation from ketene on Fe(110),[183] Ru(0001),[184] and Pt(111),[185] and from diiodo methane on Rh(111)[186] and Mo(110).[187] Supporting SSIMS data has been reported for the formation of methylene from ketene on Pt(111),[188] and indirect evidence for the synthesis of CH_2 surface moieties has been obtained by TPD from diazo methane on Pt(111),[189] from diiodo methane on Mo(110),[187] Ni(100),[112] Pd(100),[190] Cu(110),[191] and Cu(100),[192] and from chloro iodo methane on Pt(111).[193] In most cases the decomposition of the precursor takes place at low temperatures: methylene formation from either ketene or diazo methane on Ru(0001), or from diazo methane on Pt(111), occurs immediately upon adsorption around 100 K, and C−C bond scission in ketene takes place below 150 K on Pt(111). The decomposition of CH_2I_2 is presumed to be equally facile; it probably occurs below 200 K. Only in the case of ketene on Fe(110) has methylene formation been proposed to occur at higher temperatures (still below 390 K). Ethylidene moieties have also been isolated and characterized by infrared spectroscopy after thermal activation of 1,1-diiodoethane on Pt(111).[194]

2. Carbynes

Similar to CR_2 moieties, it is also possible to attach CR groups directly to metal atoms. The resulting complexes are called carbynes in general, and alkylidynes when R is a carbon-containing fragment. As in the case of carbenes, it is also possible to differentiate between two types of coordination, namely, one in which the carbyne donates its two free electrons in the sp orbital to the metal center(s) and shares the third p electron with three other in two of the d orbitals of the metal, and another in which it forms what would be nominally considered a triple bond by sharing its three electrons (one in each of the one sp and two p orbitals) with the metal atoms.[24] There have been reports of stable alkylidyne compounds in complexes with one[170,195] and two[138,196] metal centers, but by far the most stable type is one where the alkylidyne is located at the center of the triangle formed by three metal atoms.[197−199] These compounds can be prepared by using the corresponding 1,1,1-trihaloalkanes, by decomposition of acetylenic or alkylidene complexes, or by substitution of R groups in existing alkylidyne compounds.[198] Their electronic configuration is still a matter of some debate, but it is by and large believed that the carbon atom attached to the metal is sp hybridized and bonds to all three metal atoms via delocalized molecular orbitals.[200,201]

Alkylidyne species are also quite common in chemisorption systems. CH groups may form via the decomposition of methyl[79] or larger hydrocarbon moieties on W(110),[202] Ru(0001),[142] Rh(111),[144,146,148] Ni(111),[203] Pd(111),[204] Pd(100),[205] and Pt(111),[206] and ethylidyne forms cleanly after thermal activation of ethylene on Pt(111),[13,207] Pt(100),[208,209] Rh(111),[210] Rh(100),[144] Pd(111),[211] Ru(0001),[212] and Ir(111)[143] single crystals as well as on supported platinum,[213] palladium,[214] and nickel[215] surfaces. In fact, ethylidyne has been one of the most studied moieties in surface science in recent years; a wide range of structural,[207,216,217] electronic,[218−220] and vibrational[13,221] techniques have been used for that purpose. The general findings from this work can be summarized as follows (Figure 3): (1) ethylidyne chemisorbs with the lower carbon atom located at the center of a 3-fold hollow site (4-fold for square lattices) and with the C−C bond parallel to the surface normal; (2) the C−C bond distances are on the order of 1.50 Å, close to those of single bonds in organic compounds; (3) the most intense and characteristic vibration seen in all cases is the symmetric methyl deformation (umbrella) mode at about 1335−1360 cm^{-1}, the same as in discrete organometallic complexes; (4) the bonding to the surface is most likely through a simultaneous donation of electrons from a carbon p orbital perpendicular to the metal d band (a_1 symmetry) and a back-donation of metal d electrons to an empty carbon p orbital parallel to the surface (e symmetry). A recent microcalorimetric study of ethylidyne on (1×2)-Pt(110) estimates the overall binding energy of the metal−carbon interaction to be about 160 kcal/mol.[222]

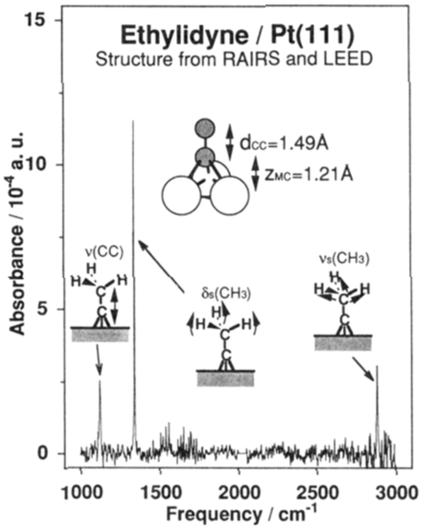


Figure 3. Reflection−absorption infrared spectrum (RAIRS) from a saturation layer of ethylidyne on Pt(111), prepared by exposing the surface to ethylene at room temperature.[559] The three vibrational modes characteristic of ethylidyne moieties are clearly seen here, namely, the C−C stretching at 1118 cm^{-1}, the symmetric methyl deformation (umbrella mode) at 1339 cm^{-1}, and the symmetric C−H stretching at 2883 cm^{-1}. Also shown in this figure is the structure of the carbon backbone of ethylidyne, as determined by low-energy electron diffraction experiments:[217] the C−C bond stands in the middle of a 3-fold hollow site perpendicular to the surface, and is about 1.49 Å long (a distance typical of single bonds) and 1.21 Å above the surface plane.

The formation of larger alkylidynes (n-propylidyne, n-butylidyne, isobutylidyne, and n-pentylidyne) by thermal conversion of the corresponding olefins was initially inferred from TPD and LEED results[223−225] and later corroborated by vibrational spectroscopy.[146,226−229] Studies on long-chain alkylidyne have so far been carried out only on Pt(111), Rh(111), and Ru(0001) surfaces.

3. Vinylidenes and Metallacycles

Metal complexes containing unsaturated carbenes such as vinylidenes are quite reactive, but can nevertheless be isolated. They are usually prepared either by conversion of terminal alkynes, or by protonation or alkylation of metal acetylides.[230] Many mononuclear vinylidene complexes are now known, but the metal cluster version is generally more stable, to the point that conversion of the former to the latter can sometimes be driven by just heating the initial compound.[231,232] The M−C−C bond angle in mononuclear compounds is usually linear, even though bent configurations with angles as acute as 167° have been reported,[233,234] but in clusters with three or more metal atoms the coordination is essentially bridged. Bonding in vinylidene complexes is similar to that in other carbenes, namely, via a simultaneous σ donation from the ligand to the metal and back-donation from the metal d orbitals to the π^* orbital of the C−C double bond. The interaction with the π system fixes the molecular plane of the vinylidene moiety at a tilted configuration with respect to the metal plane of the complex,[235−238] and creates an activation barrier for its rotation of the order of 5 kcal/mol.[239,240]

On metal surfaces vinylidenes are likely intermediates in the decomposition of chemisorbed alkenes or alkynes. The most convincing report of the isolation of vinylidene moieties on surfaces is that on Pd(111),[204,241] in which vibrational and X-ray absorption data were interpreted as indicative of a di-σ bonded species with additional π interaction to a third metal atom. This structure is consistent with that observed in organometallic clusters: the vibrational data was successfully compared to that of the model compounds $H_2Os_2(\mu\text{-}C{=}CH_2)(CO)_9$ and $Ru_2(C_2H_5)_2(\mu\text{-}C{=}CH_2)(CO)_3$.[124,126,138] In another example, infrared data showed that the decomposition of vinyl iodide on Pt(111) yields a mixture of vinylidene and acetylene on the surface around 140 K.[131] Vinylidene was also postulated to be one of a group of compounds present on an unreconstructed Pt(100) surface after annealing adsorbed ethylene at 300 K, but the data analysis in that case was complicated by the overlap of vibrational bands from other species in the spectra.[209] On supported platinum catalysts, NMR measurements have been interpreted as to reflect the conversion of acetylene to vinylidene.[242] Vinylidene species may also be stabilized on surfaces by coadsorption with other species: the formation of vinylidene from both ethylidyne at 350 K on oxygen-passivated Ru(0001)[243] and ethylene decomposition on CO-covered Ni(100)[244] have both been suggested in the literature. Finally, early claims on the formation of vinylidene from ethylene on Pt(111),[245,246] Ni(111),[247] and Fe(100)[248] have been reconsidered.

Metallacycles containing three to seven atoms are also well known in organometallic chemistry,[249] the most common being those with either three or four carbon atoms. Although these cyclic compounds could be regarded as metal complexes with a chelating alkyl group occupying two coordination positions, their chemistry is usually quite different than that of dialkyl compounds. Cyclic compounds can be made by a variety of synthetic routes, including the use of Grignard type[249] or other bifunctional alkylating agents (such as dihalides),[250] the reduction of allyl or four-carbon rings,[251,252] the use of cyclometallation reactions,[253−255] and the addition of either cyclopropanes (for the formation of metallacyclobutanes)[256] or two olefins (for metallacyclopentanes).[257] The rings in most metallacycles have all carbon atoms in the same plane, but in many instances that plane does not include the metal. This often results in either puckered[258] or "open envelope" [259] type configurations which, in the case of rings with five or more atoms, are usually unstable toward the formation of either cyclic organic compounds[260] or olefins.[261] Unsaturated cyclic compounds in which the π electrons are delocalized around the ring are also quite common,[262,263] although *cis*-butadiene ligands may also bond via two single bonds and form metallacyclopent-3-enes.[264] A number of metallacycles with more than one metal atom where alkyl chains one to four carbon atoms long act as bridging agents between the metal centers have also been characterized.[265]

A recent elegant piece of work has shown how *cis*-3,4-dichlorocyclobutene can be used to prepare a C_4H_4 group on Pd(111) surfaces.[266,267] Metallacycles have also been prepared by thermal decomposition of diiodoalkanes on aluminum[268] and, more recently, on Ni(100)[269] surfaces. In the latter case, the formation of cyclic surface species with three to six carbon atoms was inferred from TPD experiments.[269] Many other reports claim to have isolated metallacycles on surfaces as well, but those experiments have by and large been based on the decomposition of heterocycles such as thiophene, and such systems are so complex that the many techniques used to characterize them have not yielded definitive proof for the formation of the proposed intermediates.[270−274] The general belief is that when thiophene decomposes on surfaces such as Pt(111), Pt(100), Pt(210), Ni(100), Rh(111) or Ru(0001), it loses the sulfur atom and forms a five-membered ring with a metal atom. This ring usually retains both its aromaticity and its planarity, and is tilted with respect to the surface. Bonding to the substrate involves the first and fourth carbon atoms, and has di-σ character. The degree of dehydrogenation of the α-C atoms is not known, but it appears to be extensive. It is worth mentioning that this thiophene decomposition pathway is not universal: on other surfaces the first step has been suggested to be the removal of an α hydrogen with retention of the sulfur atom.[275,276] This latter mechanism has some support in the organometallic literature.[277]

C. π Bonding

1. Olefins

Since the preparation in 1827 of Zeise's salt, $K[(\eta\text{-}C_2H_4)PtCl_3]\cdot H_2O$, a large number of complexes with side-bonded olefins have been isolated for virtually all transition metals. Given that this field has already been extensively reviewed,[278] only the most salient points relevant to the surface systems will be mentioned here. Some of the most important synthetic routes to alkene complexes are (1) direct coordination of olefins to unsaturated metal atoms, (2) ligand substitution, and (3) β-hydride elimination of alkyl complexes. The structural details of the products can be summarized as follows:[279] (1) the C−C bond distance in the coordinated olefin is significantly longer than in the free molecule; (2) the substituents around the double bond bend away from the metal, breaking the original planarity of the molecule (that is, the carbon atoms rehybridize); (3)

the carbon atoms involved in the olefin double bond are essentially equidistant from the metal atom; (4) the double bond aligns in one of four geometries depending on the structure of the overall complex, namely, in the plane of trigonal planar compounds, perpendicular to the plane of square planar complexes, in the equatorial plane of trigonal bipyramidal configurations, or parallel to one of the axes of octahedral compounds. In all cases the bonding is sideways and is described by the Dewar–Chatt–Duncanson model where the filled π molecular orbital of the olefin donates electron density to an empty valence d orbital of the metal while another filled metal d orbital back-donates into the empty π^* antibonding orbital of the double bond.[280] According to this model, the degree of back-donation determines the strength of both the metal–carbon and the carbon–carbon bonds, which in fact follow opposite trends: one weakens at the expense of the other. All kinds of complexes can be obtained this way, from compounds with a pure π interaction, to molecules with an essentially metallacyclopropane character. In metal clusters olefins usually coordinate in the same way as in mononuclear complexes, that is, via a π donation/π back-donation to one of the metal atoms, but in those cases the ligand is quite fluxional, as it can both rotate and twist about its metal–ligand axis as well as move to other metal atoms.[281] In addition, multimetal olefin complexes can also bind in a di-σ configuration to two metal atoms with additional π interaction to a third metal center.[227,282]

Ethylene chemisorption on transition metal surfaces has been studied extensively as well.[283,284] Two types of molecularly adsorbed species have been identified, in analogy to the two bonding extremes mentioned above: di-σ metallacyclic, and π-bonded olefinic. The degree of double-bond character retained upon adsorption varies smoothly from one end to the other with the nature of the metal systems; by using a criteria based on the relative values of the frequencies for the C–C stretching and CH_2 deformation vibrational modes,[285,286] systems have been found for the whole range of rehybridization. The reported cases to date go from essentially C–C single-bonded species, as on Pt(111),[287] Rh(100),[286] Fe(111),[288] Ru(0001),[212] Ni(111),[289] Ni(110),[141] W(100),[290] and Pd(100),[205] to adsorbates with a large double-bond character, as on Cu(100),[291] Cu(111),[292] Cu(110),[293] Ag(100),[294] Pd(111),[295] Pd(110),[296] Fe(110),[297] and Ni(100).[128] As it can be seen from this list, ethylene adsorption normally leads to significant rehybridization toward a single-bond character, and retention of the double-bond character occurs mainly in late transition metals, but this trend can be modified by coadsorption of species such as oxygen or carbon atoms.[298–301] It is also interesting to note that sometimes both types of adsorption are observed on the same surface: on Pt(111), for instance, a transition from π- to di-σ-bonded ethylene takes place around 50 K,[302] and both species presumably coexist at saturation coverages around liquid nitrogen temperatures.

Much less information is available on the adsorption of heavier olefins. Propene, the four isomeric butenes, 1-pentene, cyclopentene, and cyclohexene all adsorb in di-σ configurations on Pt(111), at least above 100 K.[227–229,303,304] A sp^2-to-sp^3 rehybridization occurs in all those compounds during adsorption, and the appearance of soft C–H modes in the vibrational spectra of the cyclic structures suggests a slight puckering of the ring.[303] Propene chemisorbed on Rh(111) seems to have more of a π character in the same temperature range,[146] and both π and di-σ species were detected on Ru(0001).[305] Lastly, isobutene binds in a tilted triple-coordinated state on Ni(111).[306]

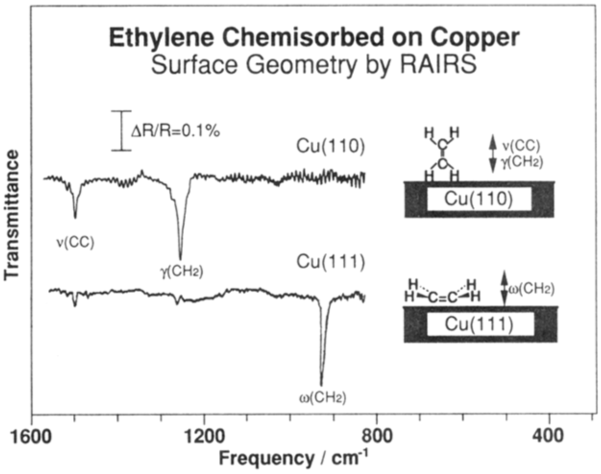


Figure 4. Reflection–absorption infrared spectra (RAIRS) for ethylene adsorbed on Cu(110)[293] and Cu(111)[292] surfaces. Three vibrational modes are seen in those spectra, namely, the out-of-plane CH_2 deformation at 910 cm^{-1}, the in-plane (scissors) CH_2 deformation at 1261 cm^{-1}, and the C–C stretching at 1522 cm^{-1}. However, the relative intensities of the three bands within each spectrum are dramatically different. On the basis of the surface selection rule that applies to RAIRS on metals,[899] those changes can be related to changes in adsorption geometry. It was determined that while the molecular plane of ethylene is oriented parallel to the surface on Cu(111), it seems to be standing up in a perpendicular configuration on Cu(110).

There has been a reasonably large amount of work carried out on the structural characterization of chemisorbed olefins on metal surfaces. Most systems are believed to have the C–C double-bond plane parallel to the surface regardless of the electronic configuration for bonding.[220,307–312] There are only two known exceptions to this rule reported to date. The first is ethylene on Ni(100) which, according to NEXAFS studies, binds with its C–C bond parallel to the surface but with its molecular plane tilted by 50°, suggestive of a di-σ/π three-atom interaction.[129] The second example refers to ethylene on copper (Figure 4), where vibrational studies have shown flat adsorption on Cu(111)[292] and Cu(100),[291] but perpendicular on Cu(110).[293,313] This last case has been recently contested, because results from photoelectron diffraction experiments suggest that the olefin may lie flat even on the Cu(110) surface,[314] but it is possible that this discrepancy is due to the reconstruction of the Cu(110) surface under some circumstances. Whatever the actual situation may be, these data suggest that crystallographic orientations play an important role in determining adsorption geometries, perhaps because they control the spatial orientation of the d orbitals of the metal.

2. Alkynes, Dienes, and Allyls

Alkynes bind to metals in a similar manner as olefins. However, because of their larger electronegativity, there is more back-donation of metal d electrons to the empty π^* antibonding orbitals in the alkynes, and therefore, the bonding to the metal is stronger. In organometallic compounds, two main observations support this statement: (1) the substituents in the C−C triple bond tend to fold away from the metal by up to 40°, and (2) the metal−carbon distances shorten by as much as 0.07 Å compared to the corresponding alkene complex.[174,279] Moreover, although alkynes coordinated to one metal-atom center are generally regarded as two-electron donors, the extra π bond allows for a four-electron donation, especially in coordinatively unsaturated complexes.[315−317] This is even more likely in compounds with more than one metal atom, where acetylenic compounds tend to coordinate in a bridging configuration. In two-center complexes, for instance, two types of geometries have been observed, with the C−C bond oriented either parallel[318,319] or perpendicular[320] to the metal−metal axis (the latter being the most common). In clusters with three or more metal atoms, the basic di-σ bridging coordination is complemented by a π interaction to one or two additional atoms. In these latter compounds the alkyne can still be considered a four-electron donor, even though it is clear that both the metal−alkyne interaction and the C−C bond distance increase with increasing number of metal atoms, indicating that the electron-density transfer is larger than in the case of one or two metal centers.[321−324]

The molecular adsorption of acetylene has been characterized for a number of surfaces.[283,284] Based mainly on vibrational data, two types of adsorption geometries have been proposed: coordination to four atoms (for W(110), Fe(111), Fe(110), Ru(0001), Ni(111), Ni(100), Pd(100), Cu(111), Cu(100), and Cu(110)[202,284]), in a similar way as in Os and Co tetrametallic complexes,[321−324] and di-σ bridging coordination to either one or two adjacent metal centers with extra π interaction to the side atoms (on Ru(0001), Rh(111), Ni(110), Pd(111), Pd(110) and Pt(111) surfaces), like in $(C_2H_2)Os_3(CO)_{10}$.[325] The first class is best exemplified by the adsorption of acetylene on Ni(111), for which structural information has been obtained by using both LEED and photoelectron spectroscopies.[326,327] In that case the acetylene molecule was found to sit parallel to the surface and in a crossed bridge site such that the two carbon atoms occupy nonequivalent hollow sites (Figure 5). The C−C distance ranges from 1.44 to 1.50 Å (essentially a single bond), while the spacing between the molecule and the first nickel layer has been reported to be either 2.0[326] or 1.4 Å.[327] The second coordination type is illustrated by the adsorption of acetylene on Pt(111), where a LEED structural analysis places the molecule lying flat on the surface but coordinated to a single metal atom (Figure 5),[328] with metal−carbon and carbon−carbon bond distances of 2.5 and 1.3 Å respectively (in line with what would be expected for a carbon−carbon double bond). A more recent NEXAFS determination sets the C−C bond length at about 1.45 Å,[308] a value both much different than that measured from LEED and outside the range expected from what is known in the organometallic literature, but this may be explained by the complications in the X-ray absorption measurements arising from the weak cross section of the shape resonance associated with this system.[329] The flat adsorption geometry for acetylene on Pt(111) has also been confirmed by ARUPS data.[220] For acetylene on Pd(111), on the other hand, a combination of UPS and NEXAFS measurements led to the conclusion that the C−C axis is tilted by more than 20°,[330] with a CCH angle of about 117°, and a C−C bond length close to 1.3 Å (the same as on platinum). Other UPS studies have shown that the hybridization of the carbon atoms in acetylene changes from essentially sp^2 on Ni(111), Pd(111), and Pt(111), which corresponds to a C−C bond length of the order of 1.35−1.40 Å and a HCH angle between 120 and 130°, to close to a sp structure on Ni(110), which corresponds to values of about 1.3 Å and 150° for the parameters mentioned above.[331]

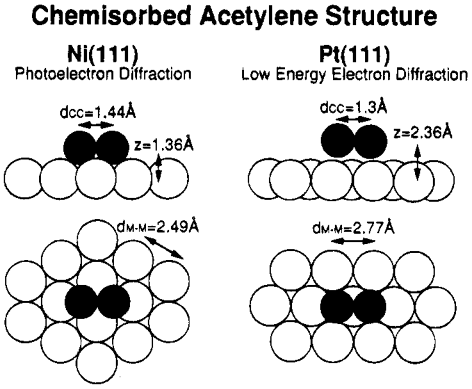


Figure 5. Structural details for acetylene adsorption on transition metal surfaces. The results from photoelectron diffraction experiments on Ni(111) exemplify one type of adsorption where the molecule sits on a bridge site with its carbon atoms on 3-fold hollow sites.[312] The molecular axis lies flat 1.36 Å above the surface plane, and the C−C bond distance, which is about 1.44 Å, corresponds to a single bond. Another adsorption configuration is illustrated by the results from low-energy electron diffraction (LEED) experiments on Pt(111), where the acetylene sits on top of a single platinum atom.[328] The C−C in that case is also parallel to the surface plane, but the molecule sits at a larger distance from the metal, at about 2.36 Å, and the C−C bond is much shorter, about 1.3 Å. Neither technique allowed for the determination of the position of the hydrogen atoms.

Conjugated alkenes such as butadiene could be considered as four-electron donors, since both olefinic bonds can coordinate to the central metal atom, but the actual bonding is better regarded as the result of the interaction of the delocalized π system of the diene with the d orbitals of the metal, especially when the ligand is in the *cis* configuration.[264,332] The main structural features of inorganic conjugated-alkene complexes can be summarized as follows: (1) the bond between the inner carbon atoms of the diene is shorter than the average of the outer ones; (2) both inner and outer carbon atom pairs are each equidistant from the metal; (3) the inner carbons are closer to the metal center; (4) the four carbons are coplanar, with C−C−C bond angles ranging from 114 to 121°; and (5) the substituents in the C_1 and C_4 positions tend to be twisted out of the four-carbon plane. All of these observations can be rationalized by a structure somewhere between a bent di-σ *cis*-metallacyclo-3-pentene with some additional π interaction and a *cis*-η^4-diene.[333] Binding of butadiene in the *trans* configuration is rare, but it has been observed in a few circumstances, both in mononuclear complexes[334,335] and in clusters.[336] Bonding in those cases is likely to be via a π interaction, and their conversion to the *cis* configuration is facile.

Only a few studies have dealt with the determination of the structural details of butadiene adsorbed on metal surfaces. Vibrational data for butadiene on Pt(111) was interpreted in terms of a 1,2-di-σ species, which supposedly forms at 170 K and converts into a tetra-σ coordinated moiety by 300 K.[228] This hypothesis is supported by some theoretical calculations done for Pt(110).[337] On Mo(100), on the other hand, both NEXAFS and ARUPS data suggest that the molecular orbitals are only minimally perturbed upon adsorption at low temperatures, and that the butadiene plane is oriented at about 40° from the surface plane; heating of this layer to 200 K induces a transformation to a moiety with an electronic configuration similar to that of gas-phase *trans*-2-butene.[338] Finally, the adsorption of 1,3-cyclohexadiene on Pt(111) is accompanied by a significant rehybridization of the carbon atoms involved. The adsorbate–surface interaction in that case seems to be better described by assuming two separate di-σ coordinations rather than one overall π bond to the surface.[339]

Allyl ligands usually bind to a metal center in either η^3 or a π coordination modes; in both cases the neutral allyl ligand acts as a three-electron donor.[174,279] Discrete compounds with allyl ligands are quite easy to make: they can be prepared by treating metal complexes with Grignard, allyl halide, or allyl alcohol reagents, by hydride abstraction from coordinated alkenes, or by protonation of 1,3-diene ligands.[340-343] Structural studies have indicated that, as long as there is no clear asymmetry imposed on the molecule by other ligands, the allyl group itself is quite symmetric: both C–C bonds are about the same length, the C–C–C bond angle has a value around 120° (typical of a sp^2 hybridization), and the metal atom is located approximately at the centroid of the allylic triangle. In substituted allylic ligands the substituents are in general bent away from the C_3 plane, most commonly toward the metal.[315-317] In cyclic ligands such as cyclopentadienyls, however, the part of the ring that does not contribute to the allylic interaction usually bends away from the metal.[344] Allyl ligands are also well known to bridge two metal atoms, but the details of the geometrical arrangement in these cases depend on the overall structure of the compound.[318,319]

The best examples for well-characterized allylic species on metal surfaces are those on Ag(110), where allyl chloride decomposes to form an allylic moiety around 180 K,[345] and where isobutene reacts with oxygen to produce a small amount of a π-2-methyl allyl species.[346] The vibrational data from the first study was interpreted as being the result of a η^3-π coordination with the molecular plane parallel to the surface. On Al(100), the decomposition of 3-bromo-1-propene around 310 K yields the same allylic species.[268] An intermediate allylic species has also been observed during the dehydrogenation of both cyclohexane and cyclohexene on Pt(111).[304,347,348]

3. Arenes

Many aromatic ligands, cyclopentadienyl ions and benzene rings in particular, π bond quite easily to metal complexes.[320] Arene metal compounds are readily prepared by reacting metal complexes directly with the aromatic molecule, a procedure that can lead to the displacement of three terminal carbonyls or other more labile ligands.[349] In metal clusters, the benzene ring usually coordinates in a similar geometry to that of the mononuclear complexes,[350] but there are some multicenter metallic compounds where the aromatic ligands coordinate in either a bridge, on-edge position within a metal triangle,[351-354] or by capping a triangular face.[355-358] Alternative (and perhaps more interesting) synthetic routes for arene complexes start from either dienes[359] or alkynes;[119] we will discuss the dimerization and trimerization reactions involved in those processes in a subsequent section.

Arenes (benzene complexes) usually bind to transition metals in a η^6 six-electron π-donating configuration which depletes most of the π electron cloud of the molecule and therefore reduces its aromaticity. The benzene ring usually retains its planar configuration, but occasionally this charge donation causes Kekulé bond distortions where either the C–C bond distances become unequal[321-324] or the ring bends into boat[360] or butterfly[325] geometries, and where any groups directly attached to the benzene ring bend away from their normal planar position.[279] A few cases have been reported where the aromatic ligand coordinates in either η^4 [361,362] or η^2 [363,364] configurations; in the former case the bonding resembles that of any other *cis*-diene.

It is generally accepted that benzene adsorption on metal surfaces at low temperatures is molecular, that the aromatic ring usually orients itself flat on the surface, and that the adsorption process can induce noticeable changes in the shape of the ring.[365] A flat adsorption geometry has been reported for benzene on Cu(100),[366] Cu(110),[367] Cu(111),[367,368] Ag(110),[369,370] Ag(111),[366] Ni(111),[371] Ni(110),[372,373] Pd(111),[374,375] Pt(111),[376,377] Pt(100),[378] Rh(111),[379] Ir(111),[380,381] and Mo(110).[365] Vibrational data indicates that the symmetry of the molecule can be lower than the pseudo (local) C_{6v} expected for top-site coordination on (111) surfaces of fcc metals, suggesting that it may involve more than one metal atom (either a bridge or a hollow site). Structural LEED studies on Rh(111) and Pt(111) surfaces have not only corroborated that conclusion, but have also shown that not all the C–C bonds within the molecule have the same length (Figure 6). Alternating values were seen in the case of Rh,[382,383] and two opposite shorter bonds were observed on Pt (a bridge configuration).[384] There is some controversy about the length of the C–C bonds in these systems: the LEED studies yielded average values ranging from 1.52 to 1.72 Å (the latter being significantly longer than a single bond), but more recent NEXAFS studies on Pt(111) resulted in a value of 1.40 Å.[367,376] C_{3v} symmetry has also been

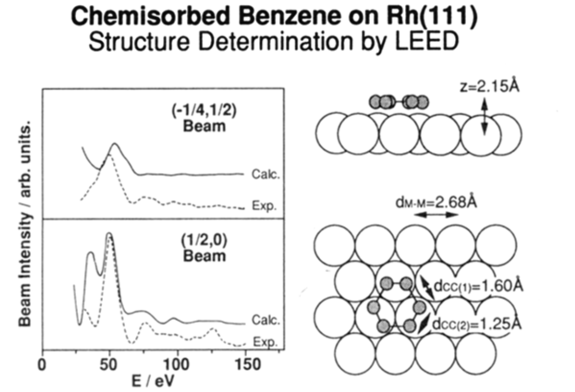


Figure 6. Low-energy electron diffraction (LEED) intensity vs voltage data used to determine the structure of benzene adsorbed on Rh(111).[382] A Kekulé distortion is seen in this system, where the C−C bonds rearrange to achieve alternating distances of 1.25 and 1.60 Å. A different (not shown) distortion is seen on Pt(111), where two opposite bonds become shorter than the rest.[384] The molecular plane in both cases is parallel to the surface.

calculated from ARUPS results for benzene on Re(0001),[5] Os(0001),[385] Ir(111),[381] Ni(111),[386,387] Pt(111) and Pt(110),[388] and even a C_{2v} symmetry has been reported on Ni(110),[372] but, in contrast with the LEED results, ARUPS studies of benzene on Rh(111),[389,390] Rh(100),[390,391] Pd(111),[392] Pd(100),[393,394] and Pd(110)[395] single crystals have all yielded the pseudo-C_{6v} symmetry suggestive of on-top coordination on a single metal atom; the discrepancy between the ARUPS and LEED results is still unresolved. In high-symmetry cases, however, there could still be some rehybridization on the carbon atoms and some bending of the C−H bonds upward from the molecular plane.[374] Lastly, a combination of NEXAFS, UPS, and XPS studies have led to the conclusion that at low temperatures and high coverages benzene adopts a tilted configuration on both Pd(111)[396] and Pd(110),[395] with the molecular plane inclined between 10° and 30° with respect to the metal surface.

Much less is known about the coordination of other aromatic compounds to metal surfaces.[377,392,397−399] On the basis of vibrational data it was concluded that toluene adsorbs molecularly on Pt(111) with the ring parallel to the surface,[397] but a NEXAFS study suggested that the ring is tilted instead, at least at 300 K.[377] These two claims could be reconciled if it is assumed that the high-temperature species is in fact a σ-bonded benzyl moiety; indirect evidence for this has been recently reported by Domagala et al.[400] *m*-Xylene adsorbed on Pd(111) presumably lies flat on the surface,[392] the same as the cyclopentadienyl moiety believed to form from the decomposition of cyclopentene on Pt(111).[401] Polycyclic molecules, which often coordinate through one ring in mononuclear complexes,[402,403] also seem to bond flat on metal surfaces. An exception to this is tetracene on Cu(100), which adsorbs with the molecular plane in a perpendicular orientation.[366]

D. Agostic Bonding

1. Alkanes

Because of their intrinsic stability, alkanes have proven difficult to activate. Nevertheless, several examples have been reported in the literature for the conversion of saturated molecules to other compounds, both in organometallic complexes and on solid surfaces. The initial chemical interaction of an alkane with a metal center has been proposed to involve a three-center two-electron bond between a filled C−H bonding orbital and an unfilled metal d orbital. Theoretical calculations indicate that d^{10}-ML_3 and d^{10}-ML_2 systems should be particularly effective in activating alkanes and that such a reaction may take place by first forming an intermediate with a M−H−C angle larger than 130°.[404] This idea is supported by the large number of stable complexes displaying this type of intramolecular interaction (the so-called agostic bonding) that have been isolated.[405,406]

Kinetic studies on intramolecular activation reactions also suggest the formation of a reactive η^2(C−H) alkane intermediate.[407,408] Although such an alkane complex has not yet been isolated, evidence is accumulating for its formation during reductive elimination reactions (C−H bond-forming steps) and, as required by the principle of microscopic reversibility, during alkane oxidative additions (C−H bond-breaking steps). For instance, recent isotope-labeling studies have shown that the reductive elimination of methane from methyl tungsten hydride complexes is intramolecular and that hydrogen scrambling between the methyl and the hydride ligands is faster than methane elimination. This suggests that such scrambling requires the formation of a weakly held methane−tungsten complex.[409] Also, intermolecular reactions between organometallic intermediates and saturated hydrocarbons are usually favored over activation of C−H bonds within coordinated ligands.[410-412] A feature common to all these reactions seems to be the generation of a low-coordination, highly reactive complex with high electron density at the central metal. Such an unstable intermediate can in fact be photolytically generated in situ in an alkane solvent.[410] Oxidative addition of alkanes has also been induced on bare metal atoms, either by radiating the metal in an alkane matrix,[413,414] or by gas-phase generation of metal−alkane clusters.[415,416]

Evidence is also available for the complexation of alkanes on surfaces. Any molecule can, of course, be condensed at low enough substrate temperatures, but the fact that many metal-based catalysts are good promoters for alkane H−D exchange and hydrogenolysis reactions is a clear indication that the alkane−metal interaction is stronger than a purely van der Waals attraction. Alkane activation has also been reported on single-crystal surfaces under vacuum, in some cases via the formation of a weakly bonded alkane−metal intermediate. On Ni(100) surfaces, for instance, molecular beam experiments have shown that while the angular distribution of the scattered methane has the specular shape typical of direct inelastic scattering, butane displays a cosine dependence indicative of complete energy exchange with the surface, and both ethane and propane exhibit a behavior intermediate between those two extremes.[417] More recent studies have extended these conclusions to other surfaces, and have helped in the estimation of some adsorption energies. It was

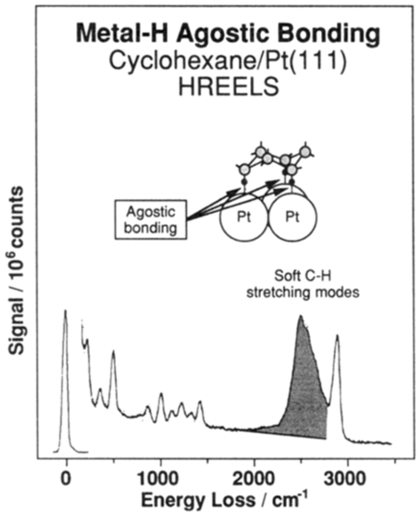


Figure 7. High-resolution electron energy-loss spectrum (HREELS) for cyclohexane adsorbed on Pt(111) at low temperatures.[347] The broad and intense "soft-mode" seen around 2500 cm^{-1} in this spectrum was initially assigned to an agostic interaction between some of the C−H bonds of the molecule and the surface atoms, but has later been reinterpreted as the result of a mild repulsive interaction between the metal and each of the three C−H bonds oriented directly toward the surface (the molecule is believed to maintain its chair configuration).

found that the heat of molecular adsorption starts around 4−5 kcal/mol for methane, and increases at the rate of an additional 1−2 kcal/mol per methylene group in heavier alkanes.[418] Because this trend parallels that of the heats of vaporization of alkanes, it is reasonable to assume that the alkane chains adsorbs approximately flat on the surface. Infrared data support this conclusion.[419]

Temperature-programmed desorption experiments have confirmed the molecular beam results mentioned above. They have also shown that the probability for alkane decomposition (relative to its desorption) increases with increasing molecular weight.[420−422] The extent of this decomposition depends on the structure of the surface: open, "corrugated" surfaces can be several orders of magnitude more reactive than flat, "smooth" ones.[418] Further evidence of a chemical interaction between the molecule and the metal atoms comes from the development of a new, intense and broad band in the C−H stretching region of the vibrational spectra for cyclic alkanes (Figure 7). These new "soft" modes, which have frequency values as low as 2600 cm^{-1} (more than 200 cm^{-1} below those of the gas-phase molecule), have been observed for cyclohexane on Ru(0001),[423] Ni(111),[424] Pd(111),[425] Pt(111),[347,426] Pt(100),[427] Cu(111),[428] and Cu(100).[429] It was initially suggested that these modes were due to an attractive interaction between the C−H bond and the metal, but more recently they have been explained in terms of a geometrical match between the axial C−H bonds and the surface lattice.[430] It is now believed that the cyclohexane molecules adsorb in their chair configuration, with three of the axial hydrogens directed straight down to the surface and that the interaction between each C−H bond and the surface is in fact mildly repulsive. Similar soft modes have also been observed for cyclopentane chemisorbed on Pt(111),[430,431] where the molecular ring is believed to be oriented parallel to the surface, but no low C−H stretching frequencies have been seen in smaller rings.[432,433]

2. Others

Although no metal−alkane inorganic adducts have hitherto been isolated, there is ample evidence for the intramolecular interaction of C−H bonds with metallic centers in complexes with saturated ligands. Early studies on a number of compounds containing polypyrazolyl ligands resulted in the observation of both unusual NMR chemical shifts and low C−H stretching frequencies.[434] Further proof of the interaction of aliphatic hydrogens with metal centers came from the observation of short M−HC distances in neutron-diffraction structural studies,[435] and clear evidence for the existence of agostic interactions in metal compounds with alkylidene[436] and alkyl[437] ligands was presented soon after. Agostic interactions have since been observed in a large number of compounds and are now well accepted.[405,406] Metal clusters with agostic interactions have been isolated as well; one particularly interesting example of this relates to the interconversion of methyl to methylene reported in a triosmium cluster.[438]

As in the case of alkanes, the structural and spectroscopic data for agostic systems reported thus far are consistent with the description of the metal−HC system in terms of a three-center, two-electron bond. Ab initio calculations have provided a theoretical framework to support this hypothesis.[439,440] The minimum requirement for agostic interactions is for the metal center to have an empty orbital to receive the two electrons of the C−H bond. It is presumed that this orbital has essentially d character and that its energy and disposition approach those of the C−H bonding orbital. Moreover, the metal atom could not have reached its maximum coordination number; on the basis of steric considerations it is expected that the formation of agostic bonds is favored in metals having coordination numbers of six or less. Calculations for the agostic interaction between the β C−H and the metal in ethyl ligands indicate that the coordination geometry is optimized when the $M-C_\alpha-C_\beta$ angle is on the order of 90°, the M−H distance is short (around 2.23 Å for Ti and 2.13 Å for Pd), and the $C_\beta-H_\beta$ distance is large (1.11−1.13 Å, about 0.05 Å longer than the other C−H bonds within the same ligand). Agostic distortions have in fact been seen experimentally in coordinated methyl groups. In one example, the $Ta-C_\alpha-H_\alpha$ angle was measured to be close to 100°.[437] In spite of the relatively strong nature of the agostic interaction, which has a binding energy of the order of 10 kcal/mol,[406] agostic hydrogens are easily displaced by other donor groups if there are no steric constraints.

The existence of agostic interactions on surfaces has again been suggested by computer calculations[83,441] and supported by the appearance of soft modes in the C−H stretching region of the vibrational spectra. For methyl groups on Ni(111)[94] and Pt(111)[49,442,443] surfaces, broad bands have been reported around 2600−2700 cm^{-1}. On the other hand, a series of theoretical calculations for the CH_3/Ni(111) system has suggested that there is little direct interaction between the C–H bonds and the metal and that the mode softening observed experimentally is due to charge donation from the metal into an C–H antibonding orbital instead.[80,444,445] C–H vibrational mode softening has been observed for longer alkyl chains on Cu(111) surfaces as well, but since the strong metal–HC interaction seems to also involve the α carbon in that case, it could again be argued that it results from a charge donation between the metal and the adsorbate, and not from an agostic interaction.[78]

IV. Reactivity

A. C–H Bond Activation

1. Alkanes

Developing methods to convert alkanes into other more useful compounds has proven to be a great challenge. Any reaction that involves alkanes must start with the scission of one of its C–H bonds, a process that requires energies of about 100 kcal/mol. It was reported some time ago that saturated hydrocarbons could be activated by soluble platinum salts at relatively high temperatures,[446,447] but since no hydrido–alkyl metal complexes were detected in any of those studies, the reaction was proposed to require the formation of free radicals. The first reported example of an intermolecular addition of an alkane C–H bond into a metal compound was that induced by an intermediate produced via the photolytic activation of $(Me_5Cp)Ir(PMe_3)(H)_2$.[410] This reaction yields a hydrido-metal complex with the increase in coordination number and nominal oxidation state of the metal center expected in oxidative addition reactions. A few more reports have appeared in the literature for this type of C–H bond addition,[323,448] but such a reaction is still regarded as difficult.

The mechanism by which organometallic complexes activate alkanes is still far from understood. For instance, it is not entirely clear why C–H bonds do not add as readily as hydrogen molecules. It is currently believed that the main reason for this difference is that M–C bonds are in general weaker than M–H bonds.[449,450] Indeed, oxidative addition is favored in systems where the resulting M–C bond is strong.[451] The activation of arenes by $(Me_5Cp)Ir(PMe_3)(H)_2$, for example, is about four times faster than the activation of cyclohexane with the same complex,[410] and primary carbon atoms in aliphatic alkanes are about three times more reactive than those in secondary positions (in spite of their higher bond energy), in this latter case perhaps because of the difference in steric hindrance.

Much research points to the idea that alkane activation by organometallic compounds requires the formation of a weak intermediate complex. Although direct evidence for the formation of alkane–metal adducts is not yet available, the initial metal–HC interaction is believed to be agostic. For one, there are a large number of examples of stable complexes containing intramolecular agostic interactions.[405] In particular, the characterization of catalytic cyclic dehydrogenation reactions with $Ir(H)_2(P(p\text{-}PhF)_3)_2(OOCCF_3)$ has led to the isolation of an agostic alkyl hydride similar to the one expected to form in the initial alkane activation step of that cycle.[452] Additional kinetic and mechanistic studies of intramolecular alkane activation by metal complexes have also supported the idea of the formation of a reactive intermediate prior to the C–H bond-breaking step.[407,408] In most cases the scission of saturated C–H bonds requires complexes with labile ligands, so they can be easily released to produce the electron-deficient electrophilic metal centers needed for three-center two-electron agostic interactions.[323]

Alkane activation can also be induced on solid metal surfaces. Most alkanes physisorb on metal surfaces at low temperatures, but they usually desorb molecularly upon heating of the sample;[419,420] as mentioned above, alkane chemisorption requires the breaking of at least one C–H bond. One indication of the ability of metal surfaces in activating saturated C–H bonds is the fact that they are good catalysts for H–D exchange, dehydrogenation, isomerization, and hydrogenolysis of alkanes.[453–455] Vacuum studies on the adsorption and activation of alkanes on metal surfaces, by molecular beams as well as by more conventional adsorption–desorption techniques, have raised several issues related to the nature of the activation step. For one, the C–H bond scission may occur directly upon collision of the incoming gas molecule with the surface, or, alternatively, it may involve the formation of a weakly adsorbed intermediate trapped on the surface. Many molecular beam studies have provided evidence for the first mechanism and have shown that the critical factor in determining the efficiency of the activation is the rate of energy transfer from the translational and internal degrees of freedom of the molecule to a particular C–H bond; the energy stored by the surface seems to be of little importance for this process.[77,417,456,457] An early study by Stewart and Ehrlich revealed that vibrational modes are the most likely source of energy for the dissociation of methane on rhodium (which provide about 7 kcal/mol),[458] and Rettner et al. found that only the normal component of the translational energy of methane is important for the C–H bond breaking on W(110).[456] This latter conclusion has been later extended to the activation of both methane[459–462] and other alkanes[417,457,463,464] on a variety of metal surfaces (Figure 8).

It has been suggested that direct alkane activation occurs via a tunneling mechanism.[461,465–467] For one, the sticking probability of the alkane often increases monotonically with increasing kinetic energy, it does not display the threshold expected for cases where the kinetics are dominated by an activation barrier (Figure 8).[456] In addition, the observed shifts in the translational energy needed to activate CH_4 vs CD_4, or C_2H_6 vs C_2D_6, are usually on the order of 5 kcal/mol, much larger than the differences in their zero-point energies.[468] Kinetic arguments, on the other hand, have been used to propose that the energy and angle dependence of the sticking coefficient of methane observed experimentally may be related to the strongly peaked desorption profile of methane desorption from reductive elimination of methyl with hydrogen (the reverse of the oxidative addition of methane) instead.[469,470] In any case, most of these

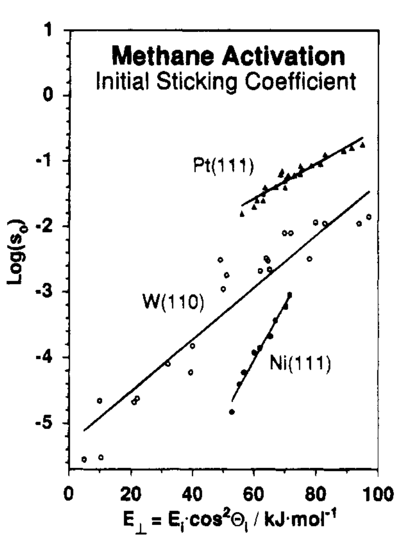


Figure 8. Initial sticking coefficients for the dissociative adsorption of methane on Pt(111),[462] W(110),[456] and Ni(111).[94] These data, obtained by using supersonic molecular beams, displays the exponential dependence of the sticking coefficient on the perpendicular component of the translational energy of the impinging methane molecules that argues for a direct tunneling mechanism for methane activation at high energies. Other evidence, however, suggests the possibility of a second, precursor-mediated, pathway at lower energies where the actual C−H bond scission is preceded by an agostic interaction between one of the C−H bonds of a weakly adsorbed methane and a metal atom.

experiments used supersonic beams with narrow distributions of high energies, and given that only a small fraction of the gas molecules in a typical catalytic mixture (those at the high energy tail of the Boltzmann distribution) have such energies, the probability of any collision-induced alkane activation process would be expected to be low. This has been confirmed by high-pressure experiments, which have yielded values for the sticking probability of methane as low as 10^{-10}–10^{-12}.[471−475]

Other molecular beam work has provided evidence for a precursor-mediated alkane activation mechanism. The trapping probability of ethane on Ir(110)-(1×2), for instance, shows only a weak dependence on the angle of incidence of the beam, suggesting that the momentum of the incoming molecules is rapidly transferred to the surface.[464] In some cases alkane dissociation is also assisted by an energy transfer from the surface: on both platinum and rhodium, for example, the sticking probability of methane depends on the temperature of the surface in an Arrhenius manner when the kinetic energy of the gas molecules is low, and displays an activation energy of between 5 and 10 kcal/mol.[461,476] Lastly, physisorbed methane can be activated by collisions with other impinging molecules (a "hammering" effect),[477] and some chemisorbed heavier alkanes can be activated directly by heating of the substrate.[478−481]

Trapping-mediated surface reactions most likely proceed via a three-center two-electron intermediate similar to that proposed in organometallic systems.[83,84,441,482,483] The activation barrier associated with the decomposition of alkanes on metal surfaces is in most cases lower than 20 kcal/mol,[471−474,484] less than one-fifth of the C−H bond energy in hydrocarbon molecules. This suggests that an initial electronic interaction between the alkane and the surface weakens these C−H bonds prior to reaction. In addition, chemical trends similar to those reported for organometallic systems have also been observed on surfaces. First, alkane activation is facilitated by electron deficiency at the metal center. There is a clear correlation between the position of the metal in the periodic table and its reactivity: early transition metals are particularly efficient in dissociating medium-size alkane chains,[422] and iridium dissociates both methane and ethane more efficiently than platinum.[418] Second, there is a structure sensitivity associated with this reaction: for any given metal, rough surfaces are in general more active than close-packed ones.[418,421] Lastly, the coadsorption of additives such as alkali metals or chalcogens can activate nominally inert substrates for alkane decomposition.[485] On the other hand, an isotope labeling study of alkane decomposition on Pt(110)-(1×2) indicated that secondary and tertiary carbon atoms within aliphatic hydrocarbons react faster than primary carbons,[486,487] an order opposite to that in organometallic complexes but in accord with the differences in bond energy.

The oxidative addition of alkanes into metal surfaces most likely leads to the formation of chemisorbed alkyl groups. Thus far this has been corroborated only in one instance, for the case of methane on Ni(111), where vibrational spectroscopy was used to identify the resulting methyl groups.[488]

2. Alkyls

By far the most common decomposition pathway in complexes with alkyl ligands is the loss of a hydrogen atom from the second carbon from the metal center (the β position).[489−491] This so-called β-hydride elimination reaction is believed to take place in a concerted step, via a planar four-center transition state which decomposes to form an (η^2-alkene)metal−hydride complex. Normally this complex then releases a free alkene,[492,493] but in some cases the coordinated olefin intermediate can be isolated.[494,495]

β-Hydride elimination reactions are usually reversible,[23,496] and in many cases part of isomerization[497] and H/D scrambling[498,499] processes. In cases where hydrogen scrambling is not a problem, isotopic labeling experiments have successfully proven that hydrogen abstraction is usually highly selective at the β position, and that the reaction displays a normal kinetic isotope effect.[500] In dialkyl complexes the decomposition products normally consist of a 1:1 alkane/alkene mixture, which is produced by a β-hydride elimination step followed by the reductive elimination of the second alkyl ligand.[493,501]

Several aspects of the mechanism for the β-H elimination have already been elucidated. First, the leaving hydrogen atom has a negative ion character. This has been shown by studies on the effect that changing the substituent groups on the β carbon has on the reaction:[502,503] electron-withdrawing substituents suppress the reaction, while electron-donating groups enhance its rate. Second, the large negative entropy changes associated with the transition state are consistent with a cyclic intermediate.[504] And third, the stereochemistry for the reaction is also consistent with a *syn* elimination from that intermediate.[505]

One of the key features of the mechanism for β-hydride elimination is that it leads to an increase in the coordination number of the metal center. The reaction is therefore inoperative in coordinatively saturated compounds: any 18-electron complex has to lose at least one ligand in order to open a site for the elimination products.[492,497,506–508] In 16-electron complexes, on the other hand, an additional coordination site is usually available, except in Pd(II) and Pt(II) compounds, which tend to avoid the 18-electron configuration.[493] β-Hydride elimination may also be hindered by steric effects when the alkyl groups are either too bulky,[509] or have a rigid structure not capable of arranging into the planar configuration required for the transition state.[510] Cyclopentyl groups, for instance, dehydrogenate at a rate several orders of magnitude faster than cyclohexyl ligands.[511,512] The activation energy for the β-hydride elimination reaction ranges from 5[490] to 30 kcal/mol,[509] depending on the magnitude of these electronic and steric effects. Its selectivity may also be affected by these parameters, and the preferential formation of 1-alkenes (the most common product), *trans*-2-alkenes (in some Cr compounds[513]), or even the less stable *cis* isomers (in bulky clusters[514]) may all be observed depending on the specific case.

β-Hydride elimination is also the most favorable alkyl decomposition reaction on surfaces. One of the best early examples of this was provided by temperature-programmed desorption studies on the decomposition of partially labeled ethyl iodides on Pt(111). It was shown that the thermal activation of ethyl groups on that surface leads to the exclusive release of a deuterium atom in the case of CD_3CH_2I, but of normal hydrogen from CH_3CD_2I instead.[50,111,515] The preference for the β-H elimination pathway has since been established for ethyl groups on Al(100) and Al(111),[516,517] Fe(100),[102] Ni(100),[41] Pd(100),[48] Pt(111),[50,111,515,518] Cu(100), Cu(111) and Cu(110),[63,519,520] and Au(100) and Au(111).[71,521] Larger alkyl groups decompose by the same mechanism. The selectivity for β- over either α- or γ-hydride elimination was clearly demonstrated on both Cu(110)[64] and Ni(100)[42] surfaces by isotope labeling studies (Figure 9), and additional studies highlighted the ease with which β-elimination occurs on other surfaces for straight alkyl chains of up to six carbons,[44,63,71,517] as well as for branched species such as isopropyl and isobutyl.[44,96]

The details of the mechanism for β-H eliminations on metal surfaces have been addressed by a few research groups. An elegant series of experiments using fluorine-substituted propyl groups on Cu(111) have demonstrated the anionic nature of the leaving hydrogen in the same way as previously reported for organometallic systems.[522] The positive charge that develops on the β carbon in the transition state is also stabilized by electron-donating groups such as alkyls, making the reaction on either propyl or butyl species faster than on ethyl groups.[516] This promotion by alkyl substitution at the β position was seen directly in the selective production of 2-hexene over 1-hexene from 2-iodohexane on Cu(100).[523] The fact that on Cu(100) β-H elimination is much faster in 3-hexyl groups than in cyclohexyl moieties indicates that molecular strain also hinders the reaction, and suggests a cyclic transition state.[524] Finally, a molecular cluster calculation for the decomposition of isobutyl decomposition on aluminum surfaces favors a four-center planar intermediate.[512]

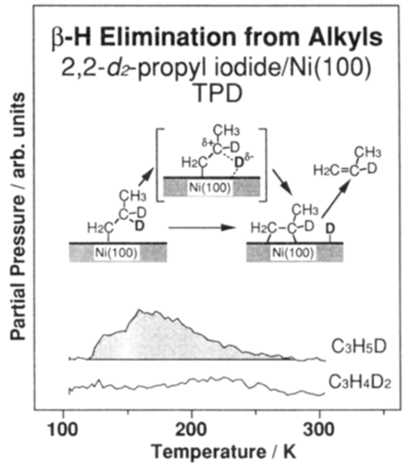


Figure 9. Propene temperature-programmed desorption (TPD) spectra from 2,2-dideuteriopropyl iodide on Ni(100).[42,44] Alkyl iodides are commonly used in these studies as precursors for the preparation of alkyl groups on metal surfaces, since the C−I bond is easily activated at temperatures below 200 K.[73] The selective desorption of $CH_3CD{=}CH_2$ from the 2,2-dideuteriopropyl group that forms in this case indicates that β-hydride elimination reactions are highly preferred over α- or γ-H eliminations (which would produce either D_0 or D_2-propenes). β-Hydride elimination is in fact one of the most common reactions followed by alkyl groups on metal surfaces.

The activation barrier for β elimination ranges from 24 to 37 kcal/mol on aluminum,[516] but is less than 10 kcal/mol on most transition metal surfaces.[41,42,50,519,522] This difference is paralleled by differences in the thermodynamics of the reaction, and therefore may be related to the affinity of the different surfaces for atomic hydrogen. Also, the elimination of a deuterium atom from an ethyl group is about 10 times slower than the elimination of a normal hydrogen on either Cu(100)[519] or Fe(100)[102] surfaces; since normal primary isotope effects can at the most account for a factor of 5, the remaining difference must be due either to tunneling or to secondary effects. The reaction rate can be reduced further by "caging" effects, because a large ensemble of atoms is required to accommodate the resulting products;[525] this may be related to the increase in coordination number required for the reaction in organometallic systems. Some other significant trends have been observed: (1) The desorption temperature of alkenes from alkyl groups on Ni(100) shifts to higher temperature with increasing chain length, perhaps because of the increase in adsorption energy of the products.[44] (2) Branched alkyls yield more alkenes than linear ones (relative to the alkane produced by the competing reductive elimination reaction), and they do so at lower temperatures. This effect can be explained at least in part by steric and entropic arguments.[44] (3) Open surfaces are normally more active than close-packed ones: the formation of ethylene from ethyl peaks around 240 K in temperature-programmed desorption on Cu(100), but only about 225 K on Cu(110).[526] This difference may be correlated to the requirement of low-coordination numbers for the β-H elimination in organometallic complexes. (4) β-H elimination is easier on earlier transition metals: it occurs below 200 K on nickel, palladium, or platinum surfaces, at around 230–250 K on copper, and at about 260–310 K on gold. (5) Most metals are efficient at promoting β-hydride elimination reactions, but a few late transition metals tend to favor the reductive elimination route instead. On silver in particular alkyl groups couple with 100% efficiency,[68] perhaps because the low affinity of silver for hydrogen inhibits any hydride elimination steps; the same lack of elimination activity has been reported in silver complexes.[527]

Hydride elimination from the α position, i.e., from the carbon bonded to the metal, is generally much less favorable than from the β carbon, but it is operative in ligands with no β hydrogens such as methyl, neopentyl, and benzyl.[489–491] The simplest case of an α-H elimination step is the conversion of methyl to methylene groups. In contrast to the olefin produced in β-elimination reactions, though, the methylene moiety that results from α-H abstraction is not stable in free form, and therefore remains coordinated to the metal. Moreover, methylene–hydride complexes are usually unstable and therefore difficult to isolate. In spite of the lack of direct evidence for the mechanism for this reaction, some kinetic data suggest that α-elimination is facile in early transition metal complexes, even in some coordinated alkyl moieties with β-hydrogens.[513,528,529] A few coordinatively unsaturated methyl complexes can also exist in equilibrium with their corresponding methylene hydride isomer, a process that promotes fast H–D exchange at the α position.[451,530] The same methyl–methylene equilibrium can also be attained in clusters,[531] but in dialkyl organometallic compounds the formation of carbene ligands is usually accompanied by the subsequent elimination of an alkane molecule in a disproportionation reaction which may take place either through the formation of a metal hydride intermediate or directly via a four-center activated complex (where the α-abstraction step is bypassed).[532] Intermolecular α-hydride abstraction reactions are possible as well.[533,534]

On surfaces, alkyl α-hydride elimination reactions have so far only been observed in methyl groups. The conversion of methyl moieties to methylene groups was clearly established on Pt(111) by reflection–absorption infrared spectroscopy (RAIRS).[52,535] Indirect evidence for such a reaction in other cases comes from temperature-programmed desorption[36,40,47,62] and photoelectron spectroscopy[37] experiments. The multiple H–D exchange seen for methyl groups on Pt(111) suggests an activation barrier of less than 10 kcal/mol for the dehydrogenation of those moieties.[110,536] A fast alkyl–alkylidene equilibrium may also be one of the key steps in the mechanism of H–D exchange reactions in alkanes on transition metal catalysts.[453,537]

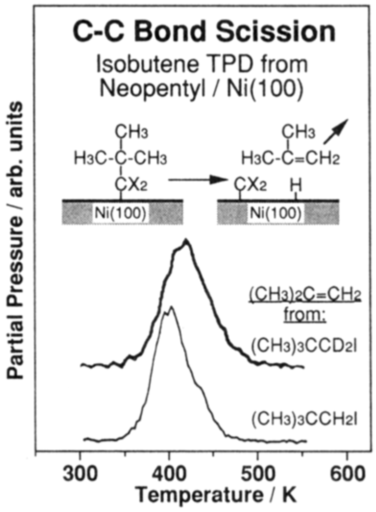


Figure 10. Isobutene temperature-programmed desorption (TPD) spectra from neopentyl iodide on Ni(100).[539–541] This is perhaps the best surface science example for C–C bond-scission reactions. The mechanism of this reaction is still not well understood, but the fact that only normal isobutene is formed even when starting with 1,1-dideuterioneopentyl iodide indicates that the bond that breaks is that between the α and β carbons. It is also quite likely that at least one dehydrogenation step precedes this C–C cleavage, since a normal kinetic isotope effect is seen for the overall reaction (the peak shifts by about 30 K to higher temperatures in the α-deuterated neopentyl case)

Elimination at positions further along the carbon chain, whenever possible, usually yields cyclic products.[174] The selectivity for γ- versus α-hydride elimination in inorganic compounds depends on the nature of the metal complex. For example, neopentyl tantalum compounds tend to form stable methylenic species via an α-hydride elimination step,[171] but analogous platinum complexes undergo elimination at the γ position to yield metallacyclobutane compounds instead.[538] It has been suggested that γ eliminations are favored by low-valence late transition metals.

No direct evidence is yet available for γ-elimination reactions on surfaces. A recent study has identified the production of isobutene from decomposition of neopentyl moieties on Ni(100),[539] which additional isotope labeling experiments showed occurs by dissociation of the C–C bond closer to the surface (Figure 10).[540,541] Since the C–C bond cleavage presumably occurs after a number of α-H eliminations, this result suggests that α hydrogens are substantially more reactive than γ hydrogens.

3. Vinyls, Acetylides, and Aryls

Mononuclear transition metal vinyl complexes are rare, but a few vinyl containing clusters, which represent solid surfaces more closely, have been prepared. Coordinated vinyl groups dehydrogenate by either α- or β-hydride elimination steps to yield vinylidene[542–545] or acetylene,[542] respectively. Unfortunately, little is known about the factors that control the selectivity between those two reaction pathways. On surfaces the mechanism for vinyl dehydrogenation seems to depend on the nature of the transition metal: infrared experiments indicated that the thermal activation of vinyl moieties on

Pt(111) leads to the formation of a mixture of vinylidene and acetylene around 140 K,[131] while a preference for pure acetylene formation at much higher temperatures, about 275 K, was seen on Ni(100).[128]

Much less is known about the dehydrogenation of either acetylides or aryl moieties, in part because they tend to decompose via alternative paths such as protonation or alkylation at the α or β carbons (to form either acetylene, vinyl, or arene ligands), or rearrangement to vinylidene complexes.[119] An intramolecular *ortho* hydride abstraction from the phenyl ligand of a tantalum compound yields the corresponding η^2-benzyne complex,[119] suggesting a chemistry similar to that of vinyl moieties. Little is understood about these reactions on surfaces too. Acetylides usually dehydrogenate completely to hydrogen and surface carbon, but it is not yet clear how this reaction proceeds; in many cases the final nature of the remaining surface carbon is not even known.[139,141−144,147] Benzyne formation from benzene decomposition has been reported on Os(0001)[165] and on Mo(110),[365] but the mechanism for the dehydrogenation of chemisorbed aryl moieties is still a mystery.

4. Carbenes, and Carbynes

Carbene ligands are very reactive, especially in monometallic complexes. Thermal decomposition of Fischer-type carbene complexes usually leads to the formation of either one or both of two possible types of alkenes, namely, those formed by ligand dimerization,[546] and/or those produced by a 1,2 shift rearrangement.[195,547−549] Schrock-type carbenes (which include most alkylidenes), on the other hand, normally react via an α-hydride elimination step to yield the coordinated carbyne (alkylidyne), either spontaneously, via an intramolecular reductive-elimination step,[550,551] or after induction by an external base.[552] The intramolecular α-hydride abstraction is believed to occur in one concerted step, starting from a structure with an agostic interaction between the metal and at least one of the α C−H bonds.[323] Neutron scattering studies have indicated that in tantalum−alkylidene complexes the precursor to this hydride elimination already has a highly distorted sp^2-hybridized α carbon, a Ta−C distance shorter than that of a typical double bond, a Ta−H distance only slightly longer than that in metal hydrides, and a C−H distance significantly longer than those in typical hydrocarbons.[436] Both infrared and NMR experiments have also highlighted the existence of C−H bonds with low stretching frequencies and ^{13}C−H coupling constants. It is interesting to note, although, that theoretical studies have revealed that the complete transfer of the α hydrogen to the tantalum center is symmetry forbidden, which explains why the original reactants are so stable.[323] Hydride abstraction from a bridging carbene can yield an unsaturated and very reactive bridging carbyne with a pronounced carbonium ion character.[174]

Carbynes bind in an analogous way to carbenes, and display similar chemistry.[119] For instance, carbynes can be made to react with either nucleophiles or electrophiles, or to undergo electrocyclic reactions in less reactive solvents. In polynuclear clusters they also rearrange in geometrical configurations which facilitate dehydrogenation reactions. For example, according to neutron and X-ray diffraction studies, the strong interaction in a Fe$_4$ methylidyne butterfly complex between the hydrogen of the methyne and a wing of the frame results in a very short Fe−H distance and a long C−H bond. This suggests a three-center two-electron (agostic) bond between that CH and the metal frame which facilitates the removal of methyne hydrogen by weak bases such as methanol. Moreover, NMR studies indicate that a methyne hydrogen can exchange sites with a second bridged hydrogen within the same molecule.[323] Since larger alkylidynes do not have α hydrogens, they can only dehydrogenate at other positions further away in the chain, a reaction that does take place in molybdenum[553] and tungsten[554] monometallic compounds, but that is more common in bridging multicenter complexes. In one case, μ-bridged ethylidyne diiron complexes react with acids (or bases) to produce the corresponding μ-vinylidene compound.[555−557] A similar conversion has recently been suggested in a triplatinum ethylidyne cluster.[558]

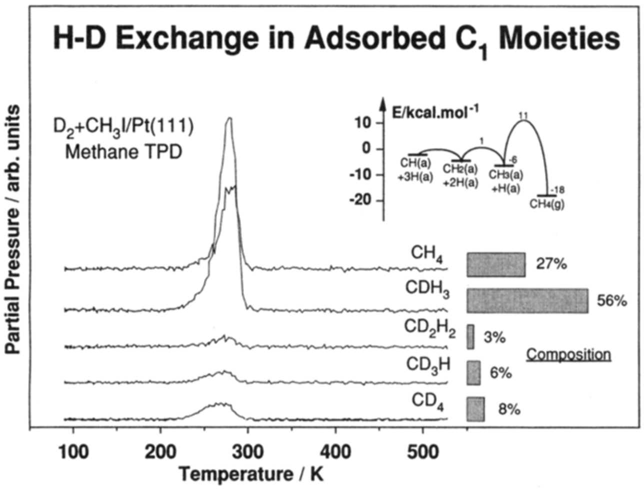


Figure 11. Methane temperature-programmed desorption (TPD) spectra from methyl iodide on a deuterium-predosed Pt(111) surface.[110,535,536] The product distribution shown in the right-hand side highlights the fact that even though close to 85% of the desorbing methane is composed of the CH_4 and CH_3D that results from direct reductive elimination of normal methyl groups with coadsorbed hydrogen or deuterium atoms, there is an additional 8% of CD_4 produced by extensive H−D exchange in the surface methyl groups prior to methane formation. An analysis of the kinetic data obtained from these experiments led to the energy diagram shown in the upper right-hand corner.

The dehydrogenation of methylene groups on metal surfaces has only been inferred indirectly. On Pt(111), for instance, the extensive H−D exchange of methyl groups observed in temperature-programmed desorption experiments has led to the conclusion that methylene and methylidyne moieties must be present in equilibrium on that surface (Figure 11).[110,535,536] Coadsorption of CH_2I_2 with D_2 on Ni(100) does not lead to any significant exchange, but since methylene groups do eventually dehydrogenate to carbon and hydrogen, methylidynes are likely intermediates on that surface too.[112] Recently, it has been shown that on Pt(111) ethylidene dehydrogenates easily (below 200 K) at the α position, but this reaction also produces ethylene and ethyl groups, and may occur via bimolecular steps.[194] Little is known about the mechanism for carbyne decomposition (in spite of the extensive studies reported on the chemistry of alkylidynes). Ethylidyne is known to undergo H−D exchange, at least on platinum and rhodium surfaces, but the participation of an initial β-dehydrogenation step in the mechanism of that reaction seems unlikely.[559] Alkylidynes do dehydrogenate to other species on most transition metals above 400 K, but the mechanism for this process is also unknown.

5. Olefins

Little is known about the breaking of C−H bonds in π ligands coordinated to discrete compounds. Olefin−metal complexes are fairly stable but, if the olefinic ligand within a monometallic complex reacts, it usually does so by interacting with either nucleophilic or electrophilic agents to form new ligands such as aldehydes, ketones, vinyl ethers, vinyl acetates, amines, and olefin dimers.[560] Oxidative addition reactions are not common in these compounds, but can be induced by carrying the reaction out in polar solvents or by substituting the vinylic hydrogen with more electronegative elements.[560] Vinyl bromides, for instance, can undergo oxidative addition at a metal center to form the corresponding complex. Details on the mechanism for the carbon−halide bond scission have been difficult to obtain, because the rates of isomerization of many vinyl halide complexes are either too rapid for isolation of intermediates other than the vinyl adduct, or too slow to accurately measure reaction rates. The reaction between *cis*- or *trans*-β-bromo styrene and cobalt, platinum, or nickel complexes occurs with retention of configuration at the trigonal carbon,[120,561−564] and *trans*-1,2-dichloro ethylene also reacts with either PtL_4 or PdL_4 ($L = Ph_2MeP$) complexes to afford the *trans*-2-chloro vinyl adduct.[565] These oxidative addition reactions are presumably preceded by coordination of the reactant, since a variety of π complexes have indeed been isolated and shown to undergo a unimolecular rearrangement to the oxidative adduct.[566,567] The conversion of $L_2Pt(F_2C{=}CFBr)$ into *cis*-$L_2PtBr(CF{=}CF_2)$, on the other hand, follows a first-order kinetics that depends linearly on the Grunwald−Winstein solvent parameter, suggesting a S_N1 mechanism instead.[567] Similar conflicting results have been obtained in studies on the activation of unsaturated C−H bonds: Jones and Feher have reported an example where η^2-arene coordination precedes the C−H bond-scission step in the aromatic ligand,[568] but Stoutland and Bergman found another case in which the attack of the vinyl C−H bond in ethylene occurs before any π complexation.[569]

A few examples are also known for the oxidative addition of olefins to cluster compounds. The $Os_3(CO)_9(SMe)(H_2C{=}CH_2)$ complex, for instance, converts to the corresponding vinyl complex.[570] Reactions of ethylene with either $H_2Os_3(CO)_{10}$[571] or $Os_3(CO)_{12}$[572] also yield $HOs_3(CO)_{10}(CH{=}CH_2)$ and $H_2Os_3(CO)_9(CH{=}CH_2)$, respectively, but there is no direct evidence available for the formation of an initial ethylene−osmium complex in those cases. Other examples of olefin addition include the reactions of ethylene and $Ru_3(CO)_{12}$,[573] propylene and $Os_3(CO)_{12}$,[236,574,575] hexadiene and $Ru_3(CO)_{12}$,[576,577] cycloocta-1,5-diene and $Ir_4(CO)_{12}$,[578,579] cyclooctene and $M_3(CO)_{12}$ (M = Ru or Os),[580,581] and bicyclo[3.2.1]-octa-2,6-diene and $Ru_3(CO)_{12}$;[582] complexes with either vinylidene or acetylenic ligands, most likely originating from the conversion of an initial vinyl intermediate, were isolated in all those cases. It is quite possible that metal clusters facilitate C−H bond activation reactions in coordinated olefins because they provide the framework for a multiply coordinated final vinyl product; the scission of vinylic C−H bonds in preference to allylic ones gives a clear indication of the unique chemistry generated by the presence of several metal atoms in a complex.[583] The contrast between this α-hydride abstraction chemistry in clusters and the overriding cyclometalation reaction preferred in mononuclear systems[157] may provide some clues for understanding the analogous surface processes.

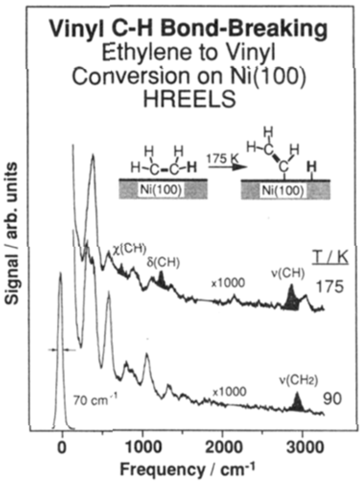


Figure 12. High-resolution electron energy-loss spectra (HREELS) from molecular ethylene adsorbed at low temperatures on Ni(100) and for the vinyl species that forms after annealing that surface to 175 K.[128] The conversion of ethylene to vinyl can be clearly seen by the differences between these two spectra, which include the development of new peaks for the C−H stretching and in- and out-of-plane deformation modes around 2920, 1405, and 760 cm^{-1}, respectively. Additional laser-induced desorption (LID) kinetic experiments indicate that this reaction is most likely an elementary oxidative-addition step.[127]

Olefin dehydrogenation reactions are apparently easier on transition metal surfaces than in the corresponding organometallic compounds. Perhaps one of the best examples for this type of reaction is the conversion of adsorbed ethylene to vinyl species that occurs on Ni(100) around 175 K (Figure 12).[127−129,584] Kinetic studies proved that the ethylene−vinyl conversion in that case is unimolecular, and that it displays strong normal primary and secondary isotopic effects, suggesting that the reaction is an elementary step. More commonly, chemisorbed ethylene converts directly to ethylidyne around room temperature. This latter reaction has so far been observed on single-crystal surfaces of ruthenium,[212] rhodium,[144] iridium,[143] palladium,[211] and platinum.[13,207−210] Although the mechanism for ethylidyne formation is still controversial, it most likely involves two or more steps. Some evidence has suggested that vinyl may be an intermediate in this process,[585] but more recent work favors the formation of either ethyl or ethylidene instead.[559,586]

6. Alkynes, Dienes, and Arenes

The chemistry of alkynes coordinated to metallic centers resembles in many ways that of olefins. When terminal acetylenes are π bonded to a transition metal, they tend to rearrange into the tautomeric vinyl complex, presumably by going through a σ-coordinated acetyl intermediate.[587] For instance, $Rh(PR_3)_2(Cl)(HC{\equiv}CPh)$ exists in equilibrium with its σ-alkynyl(hydrido) isomer, and this equilibrium shifts toward the latter compound upon addition of pyridine to the solution.[588] In another example, propyne reacts with the highly nucleophilic $Ir(Cl)(PPh_3)_3$ complex to form a stable σ-acetylenic iridium(II) hydride.[589] In clusters the oxidative addition of the C−H acetylenic bond of terminal alkynes commonly yields either μ^2- or μ^3-alkynyl complexes.[583] For instance, the reaction of phenyl acetylene with $H_2Os_3(CO)_{10}$ produces $HOs_3(\mu^2\text{-}C{\equiv}CPh)(CO)_{10}$,[544] and the reaction of *tert*-butylacetylene with $Ru_3(CO)_{12}$ gives $HRu_3(\mu^3\text{-}C{\equiv}C^tBu)(CO)_9$.[590,591] Even 2-butyne coordinates to $H_2Os_3(CO)_{10}$ and converts to the corresponding μ^3-1-methyl allenyl complex.[592]

The thermal activation of acetylene on transition metal surfaces usually leads to its complete dehydrogenation (at least under vacuum) via a series of ill-defined steps. The intermediate products from this conversion depend on both the nature and the crystallographic orientation of the surface.[283,284] Several reports, some still contested, claim to have identified a single step for the transformation of chemisorbed acetylene into an acetylide moiety. Vibrational and electronic spectroscopic data have been used to support this mechanism on Rh(111)[148] and Rh(100),[144,145] Ir(111),[143] Ni(100),[140,593,594] Ni(110),[141] and Pd(100).[139] A similar reaction has also been reported on Pd(111), but the details of the chemistry of acetylene on that surface are still being debated.[330,595] Most of the reports mentioned above show that the α-hydride elimination of adsorbed acetylene takes place at reasonably high temperatures, above 400 K in some cases, and is often followed by some yet undetermined polymerization steps.

Dienes in metal complexes, like other unsaturated π-coordinated ligands, rarely undergo hydride elimination reactions, but rather react with either electrophilic or nucleophilic reagents.[560,596,597] The poor reactivity of the vinyl C−H bonds in dienes becomes particularly evident in ligands with allylic hydrogens, for which allyl formation is the only reaction observed. Examples of this can be seen in the chemistry of tricarbonyl(*cis*-penta-1,3-diene)iron, which upon treatment with Ph_3C^+ yields a dienyl complex,[560] of cyclopentadiene with nickel complexes, which produces a mixed η^3,η^5-complex after a sequence of reactions that starts with the oxidative addition of one cyclopentadiene molecule to form a cyclopentadienyl hydride complex,[598] and of a cyclooctadiene−ruthenium complex, which also converts into the corresponding dienyl complex.[599] No examples are yet available for the elimination of terminal hydrogens in dienes adsorbed on surfaces.

Oxidative additions of arene C−H bonds to metals have been known since 1965, when Chatt and Davidson reported the reaction between naphthalene and a ruthenium complex to yield the corresponding aryl compound.[600] The more widespread occurrence and earlier observations of arene vs alkane C−H bond activation has led to the general belief that kinetic factors, namely, prior η^2-arene coordination, are responsible for the different reactivity of the two types of bonding.[601] In particular, Jones and Feher have demonstrated that η^2-arene coordination is required for the activation of a C−H bond in a benzene−Rh complex.[568] The small kinetic isotope effect seen in the activation of benzene by $(Me_5Cp)Ir(PMe_3)$ also suggests an early transition state for the C−H addition, perhaps something like an initial agostic interaction, as in the reactions with dihydrogen and alkyl species.[410,602] On the other hand, since the difference in strength between metal−aryl and metal−alkyl bonds is greater than that between hydrogen−aryl and hydrogen−alkyl bonds, the case could also be made for thermodynamics been the dominant factor driving the arene activation.[450,568,603]

The decomposition of benzene and of other arenes on transition metal surfaces has proven to be quite complex. The final products from these reactions, after the formation of a series of intermediates, are almost always hydrogen and surface carbon. The nature of those intermediates depend on the metal, but are mostly of the C_nH type.[144,147] Surface coverages can also affect the decomposition mechanism. In some cases the adsorption geometry of benzene changes, from flat lying at low coverages to a tilted configuration near saturation,[369,395,396,604] inducing a transition from an initial π resonant bonding to the η^2 configuration supposedly involved in the C−H bond activation in organometallic complexes. Recent reports have in fact offered some evidence for the formation of a benzyne (C_6H_4) intermediate during the decomposition of benzene on Os(0001)[165] and Mo(110) surfaces.[365]

7. Allylic and Benzylic Bonds

The activation of C−H bonds in olefins and substituted aromatic ligands can occur either at the vinylic/aromatic or at the allylic/benzylic positions. The selectivity between the two in principle depends on a number of kinetic, thermodynamic, electronic, and steric/geometric factors, but since the allylic/benzylic C−H bond is considerably weaker than the vinylic/aromatic C−H bond (D(H-allyl) = 89 kcal/mol vs D(H-vinyl) ≥ 108 kcal/mol, and $D(H\text{-}CH_2Ph)$ = 85 kcal/mol vs D(H-Ph) = 110 kcal/mol[605]), the former are in general more reactive. On the basis of this knowledge it is easy to understand why allyl ligands can be easily prepared from coordinated alkenes. For instance, the π-olefinic $Ni(PPh_3)C_3H_6$ complex equilibrates with its allyl hydride isomer $NiH(PPh_3)C_3H_5$ at temperatures as low as −40 °C,[606] and several substituted olefins react with certain palladium and iridium complexes to yield similar allyl products.[607,608] The detection of π-benzyl complexes has also been reported, either by itself, or in equilibrium with its

η^1-benzyl isomer,[609,610] and examples for dienes were mentioned before.

To the best of our knowledge, the only clear example known so far for the conversion of olefins to allyl moieties on surfaces comes from the thermal activation of cyclohexene on Pt(111), where the C_6H_9 intermediate isolated between 180 and 280 K was identified by vibrational spectroscopy as an allylic species,[304,347,348] but the reaction of isobutene with oxygen-predosed Ag(110) seems to produce a small amount of an allylic species as well.[346] The scission of C−H bonds in substituted benzenes was shown to be regiospecific on Ni(111), Ni(100), Pd(111), Pd(100), and Pt(111) surfaces.[399,611−614] The benzylic hydrogen is always removed first in those molecules, suggesting that the initial adsorption geometry of the ring is tilted, and that perhaps a π-benzyl intermediate forms after activation.[400] Even the decomposition of diphenylethane molecules on Pt(111) yields 1,2-diphenylethylene selectively.[615]

B. C−H Bond Formation

1. Alkyls

One of the most common reactions both in organometallic alkyl hydride complexes and on alkyl surface systems is the recombinatory reductive elimination of the alkyl group with hydrogen to yield a free alkane. This reaction is in principle reversible (the reverse reaction being the oxidative addition step discussed previously), but usually goes only in one direction. The oxidative addition/reductive elimination equilibrium is determined by the overall thermodynamics of the system, and therefore depends on the relative stability of the product (an A−B molecule) compared to that of the initial reactant (a M(A)(B) complex). This is why, on the one hand, alkyl halides add easily to metal centers but alkyl−halide adducts rarely eliminate back the free halide and, on the other, alkanes rarely oxidatively add to metals but alkyl−hydride complexes commonly eliminate alkanes. The reductive elimination of either an alkyl and a hydride or two alkyl groups is exothermic: elimination of methane from $Pt(PH_3)_2(CH_3)H$, for instance, releases an estimated 19 kcal/mol at room temperature.[119]

The reductive elimination of alkanes in metal complexes takes place with ease regardless of if the two ligands are bonded to the same or to two different metal centers. There are nevertheless some requirements for this elimination reaction, which in the case of mononuclear compounds are rather obvious. For one, the two ligands to be eliminated must be coordinated *cis* to each other.[616] Also, since the reaction is nominally accompanied by the reduction of the metal center, it is favored by additional positive charge on that metal.[617−619] For the same reason, the removal of σ-donor ligands usually accelerates the reaction,[620−622] although there are some notorious exceptions to this rule.[623,624] Lastly, elimination from three- or five-coordinate complexes is easier than from four- (planar) or six- (octahedral) coordinated compounds.[625,626]

The formation of C−H bonds in reductive elimination reactions is in general favored over H−H and C−C reductive couplings.[627] The preference for C−H over H−H bond formation can be explained entirely by thermodynamic arguments, but C−C coupling reactions, which are even more exothermic than the C−H counterparts, are slower because the transition state requires the reorientation of two highly directional carbon-sp^3 hybrid orbitals.[628] Both the lack of isotopic scrambling in experiments with mixed labeled compounds and the preservation of the stereochemistry of the coupling alkyl groups have also proven that reductive eliminations are in general concerted and that they occur without previous dissociation of the metal−carbon bond.[629,630] The observation of inverse kinetic isotope effects in some cases suggests the formation of a σ adduct between the resulting alkane and the metal prior to dissociation,[450] but the evidence for such an intermediate is not compelling.

Examples have been reported for intramolecular reductive elimination reactions in gold, silver, copper, manganese, and cobalt complexes.[631−634] The elimination of two organic ligands from a pair of metal atoms already joined by a bond, however, is symmetry forbidden, and therefore quite rare.[635] R−H elimination from two metal centers has been observed, but only after a β-hydride elimination step. For example, the decomposition of $[Mo(NMe_2)_2(CH_2CD_3)]_2$ affords the formation of a one-to-one mixture of ethylene $CH_2{=}CD_2$ and ethane CH_2DCD_3.[501] The same type of β-hydride elimination−reductive elimination reaction sequence is common in dialkyl mononuclear compounds.[493]

The hydrogenation of chemisorbed alkyl groups on transition metal surfaces has been reported on a number of systems. These C−H reductive elimination reactions are common on most metals, but compete unfavorably with C−C coupling reactions on late transition metals[67] and are overtaken by dehydrogenation reactions to surface carbon and hydrogen on early transition elements.[34] The yield for the self-hydrogenation of methyl moieties to methane is quite high, between 50 and 75%, on Ru(0001),[36] Ni(100),[39,40] Ni(111),[636] Pd(100),[637,638] Pt(111),[49,52] Cu(100),[639] Cu(110),[62] and Cu(111)[61] single-crystal surfaces as well as on films of iron, nickel, palladium, lead, gold, and copper.[70,640] Ethane formation by ethyl elimination is a less selective reaction, because β-hydride elimination dominates in most cases where β hydrogens are available.[50,54,516] Significant alkane desorption does occur at about the same temperature as olefin formation on surfaces with high ethyl coverages, suggesting that a disproportionation reaction similar to that discussed above for dimolybdenum complexes is likely to take place on surfaces as well. Heavier alkyl groups generally behave in a fashion similar to ethyl moieties.[64,516]

The reductive elimination of alkanes can be greatly enhanced by coadsorbing hydrogen (or deuterium) on the surface: the thermal activation of methyl moieties on hydrogen-precovered Pt(111)[110] and Ni(100)[112] surfaces leads to methane yields of nearly 100%, and the conversion of ethyl iodide to ethane increases by a factor of 5 on Pt(111) after similar hydrogen treatments.[111] These increases in yield with hydrogen coadsorption are also accompanied by

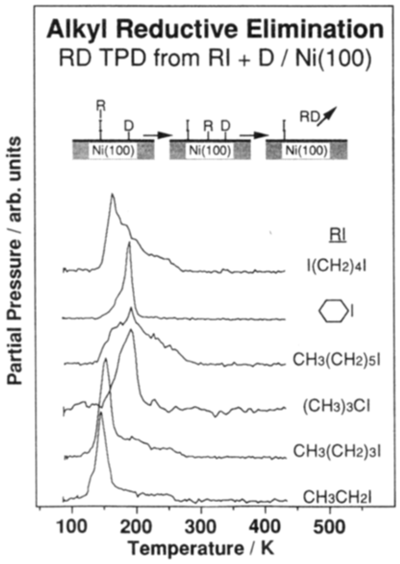


Figure 13. Monodeuterated alkane temperature-programmed desorption (TPD) spectra from a series of alkyl iodides adsorbed on deuterium-predosed Ni(100) surfaces.[641] This figure shows the ease with which most alkyl groups undergo reductive elimination reactions with coadsorbed hydrogen (or deuterium): significant amounts of monodeuterated alkanes are produced below 200 K from linear alkyls such as ethyl, *n*-butyl, and *n*-hexyl, branched alkyls such as *tert*-butyl, and cyclic alkyls such as cyclohexyl. Double-coordinated metallacycles such as the metallacyclopentane formed by decomposing 1,4-diiodobutane also hydrogenates to the corresponding 1,4-dideuteriobutane. Alkyl−hydrogen reductive elimination reactions are common on most transition metal surfaces.

a reduction of the energy barrier for the overall reaction, reflecting the fact that the rate-limiting step for alkane production is actually the C−H bond formation when hydrogen is present on the surface (which requires about 5−6 kcal/mol on either nickel or platinum), and not the processes responsible for supplying the required surface hydrogen, as in the self-hydrogenation case. Other alkyl groups can be eliminated as alkanes in a similar manner (Figure 13).[641]

2. Other σ-Bonded Species

The hydrogenation of σ-bonded hydrocarbon species other than alkyls has not been studied in detail. In general, both vinyl and acetylide ligands tend to incorporate hydrogen atoms at the β position. For instance, hydride addition to the $Cp_2Ru_2(CO)_3(\sigma\pi\text{-}CH{=}CH_2)^+$ complex predominantly yields the μ-CHMe product,[642] even though some complexed ethylene is produced in that case as well. The formation of olefins (the α-addition product) in these systems is enhanced by the presence of bulky groups on the vinyl ligand, as in the case of a tetraruthenium μ-vinyl complex with the β carbon of the vinyl attached to a diruthenium carbene.[643] Analogously, acetylides are quite reactive toward electrophiles and undergo protonation at the β carbon: they form stable vinylidene complexes in the presence of acids.[554] The acetylide hydrogenation to vinylidene is common in monometallic complexes as well as in metal clusters.[544] This step is key in the tautomeric isomerization of acetylides to vinylidenes and is facilitated by either a formal positive charge on the metal, or a basic catalyst.[644−647] Finally, aryl−hydride complexes may undergo a reductive elimination step similar to that in alkyl−hydrides to yield arenes,[560] but since metal−aryl bonds are stronger than metal−alkyl bonds, the equilibrium in these cases favors the aryl−hydride side of the equation.[119]

On surfaces, the hydrogenation of vinyl groups produces ethylene preferentially;[130] no cases have been reported to date for hydride addition to the β carbon. Phenyl groups, prepared by decomposition of iodobenzene, can be hydrogenated to benzene on Ni(100)[163] and Cu(111)[162] surfaces. Given that not many examples exist for the clean isolation of acetylides on metal surfaces, little is known about the reactivity of those moieties.

Hydrocarbon groups multiple σ-bonded to organometallic compounds can be hydrogenated as well. In the case of carbenes and carbynes this often occurs via a migratory insertion into a metal−H bond, and results in hydrogen addition at the α carbon. Intramolecular reactions of this type appear to be facile, and are considered to be in many respects analogous to the migratory insertion of carbonyls. For one, the rate of reaction can be increased in both cases by placing a positive charge on the complex. Also, both conversions are often reversible, as in the case of the equilibrium between the methyl and methylene−hydride forms,[530] or even between the alkyl−olefin and alkylidene−alkyl tautomers,[529] of tantalum-based complexes. An interesting example of such reversible interconversions involving a late transition metal is that of a pentacoordinated Ir(III) complex.[648] Similar equilibria are also known in clusters: the $H_2Os_3(\mu^2\text{-}CH_2)(CO)_{10}$ complex, for example, exists in tautomeric equilibrium with its $HOs_3(\mu^2\text{-}CH_3)(CO)_{10}$ isomer.[531] Alkylidyne−hydride complexes can exist in equilibrium with their corresponding carbene isomers the same way, especially in early transition metal compounds, and interchange via an agostic interaction between the carbene and the metal center.[551] Alkylidyne clusters can even be hydrogenated all the way to the free alkane.[649,650] Several pieces of evidence suggest that in those cases the rate constants for the successive C−H bond formation steps increases in the sequence $k(CX + H) < k(CHX + H) < k(CH_2X + H)$.

Temperature-programmed desorption studies for methylene hydrogenation reactions on Mo(110),[187] Rh(111),[186] Ni(100),[112] Pd(100),[190] Pt(111),[188,535] and Cu(110)[62] have shown that methane formation occurs around 300, 260, 230, 180, and 280 K respectively, indicating that methylene hydrogenation on transition metals is facile. In fact, the formation of methane from chemisorbed methylene is often limited by the decomposition steps that provide the required surface hydrogen; the hydrogenation steps themselves are much less activated. TPD experiments with diiodo methane on Ni(100), for instance, have shown that methane desorption occurs at lower temperatures and with higher yields in the presence of coadsorbed hydrogen.[112] Additional experiments with coadsorbed deuterium have also indicated that the methylene conversion to methane occurs in two separate steps, via the sequential reductive elimination of methylene and methyl species with the coadsorbed hydrogen (deuterium), and that the latter is rate limiting, as in organometallic systems. On Pt(111) methylidyne hydrogenation is so fast that an equilibrium between methylidyne and methylene is rapidly established on the surface.[536] The estimated activation energy for methyl formation from methylene in that case is less than 6 kcal/mol, while that for methane production from methyl is about 17 kcal/mol (Figure 11). Hydrogenation products have also been detected for ethylidene on Pt(111).[194]

Because alkylidyne groups are quite stable on metal surfaces, their hydrogenation is much more difficult to achieve. The reaction can be driven under atmospheric pressures of hydrogen,[651,652] but it has never been observed under vacuum conditions. Nevertheless, ethylidyne exchanges its hydrogens with surface deuterium,[223,559] and although the mechanism for that reaction has yet to be determined, it is logical to think that it most likely starts with a hydrogenation step (see later).

Exposure of vinylidene complexes either to acids or to hydrogen gas leads to the incorporation of hydrogen atoms at the β position, the same as for vinyls and acetylides, and yields alkylidynes.[545,653–656] Hydrides can also add at the α carbon to produce vinyl derivatives, but only if the complex is not readily deprotonated by bases.[657] The formation of alkylidynes dominates in cluster systems, and has also been observed on both Pd(111)[204] and Pt(111).[131] In the latter case, however, the vinylidene to ethylidyne conversion involves the formation of an ethylene intermediate on the surface.

3. Olefins

The homogeneous catalytic hydrogenation of olefins is one area within the field of organometallic chemistry that has received a great deal of attention. Many catalysts have been developed for this purpose but, unfortunately, very few have shown to be of practical use to date.[658–661] A few special cases are worth mentioning here. For example, Wilkinson's catalyst, a $RhCl(PPH_3)_3$ complex discovered in 1964 by Wilkinson and Coffey, is the best known and most remarkable homogeneous olefin hydrogenation catalyst,[659,662] because it displays unique regioselective and stereoselective properties not matched by any known heterogeneous counterpart. A family of cationic rhodium catalysts also yields high enantioselectivity in asymmetric hydrogenation processes,[663] and a highly stable iridium catalyst has been developed for the fast reduction of hindered olefins under oxygen atmospheres.[664] A few of these homogeneous systems are used for specific synthetic processes, but heterogeneous catalysts are in general preferred because organometallic compounds are usually more sensitive to impurities, tend to promote olefin rearrangements, and are quite expensive and difficult to recover.

The majority of the organometallic olefin hydrogenation catalysts available nowadays are coordinatively unsaturated, since vacant sites are usually required for both the complexation of the substrate (the olefin) and the incorporation of the hydrogen atoms. Mechanistic studies indicate that hydrogenation occurs in a stepwise fashion, via the incorporation of one hydrogen atom at a time.[119,665] The limiting step in most cases is the migratory insertion of the coordinated olefin into a metal–H bond (the reverse of the β-hydride elimination reaction discussed before),[666–668] which is believed to require a four-center coplanar transition state with an agostic hydrogen atom simultaneously bonded to a carbon atom and the transition metal center. Such a mechanism justifies the selective *cis* addition of the M–H bond to the olefin seen in most cases. The possibility of isolating the resulting alkyl intermediate and of studying its subsequent reductive elimination to the alkane is generally limited by the fast rate of the latter reaction. This is, however, not the case in cationic rhodium compounds, where the elimination controls the overall process at low temperatures.[669] An alternative mechanism has been proposed in a few cases, mostly for conjugated olefins, which include the formation of an alkyl free radical,[670] but this pathway is not common, and since it is not relevant for comparisons with surface reactions, will not be discussed here.

The order in which the reactants coordinate to the metal center during the hydrogenation reaction seems to depend strongly on the nature of the catalyst. In Wilkinson's catalyst, for example, a hydrogen molecule adds oxidatively to the metal center first to form a dihydride, and the olefin coordinates to this intermediate afterward.[666,667] In some rhodium cationic catalysts, on the other hand, it is the olefin that ligates first.[669] In both cases the addition of the hydrogen molecule is dissociative and leads to the formation of a dihydride complex, but in other systems the formation of a monohydride complex takes place via a nonoxidative, one-step heterolytic cleavage instead.[671] Regardless of the order in which the ligands coordinate to the metal, however, the olefin usually needs to be attached to the metal before reacting (except in cases where a free radical is involved, see above), and the strength of this metal–olefin bond ultimately controls the selectivity of the catalyst. Consequently, terminal olefins, which are more strongly bonded to the metal, are in general more reactive than alkenes with internal C–C double bonds, and the *cis* isomers are usually more reactive than the *trans* counterparts.[119]

The hydrogenation of olefins (of ethylene in particular) on single-crystal metal surfaces has also been studied in great detail.[586,672–674] These studies include the characterization of the thermal chemistry of olefins chemisorbed on both clean[223,287,302,675] and hydrogen- and/or deuterium-predosed[189,676–680] surfaces under vacuum as well as catalytic work under atmospheric pressures.[652,681–683] The thermal activation of alkenes on late transition metal surfaces almost always yields some alkane, even under vacuum conditions. This self-hydrogenation is initiated by the decomposition of some of the chemisorbed olefins on the surface and is followed by the incorporation of the resulting hydrogen atoms into other alkene molecules. In the presence of surface hydrogen, the initial step is bypassed, and ethane is formed at lower temperatures and with higher yields.[676,678,679] The incorporation of hydrogen into the olefin takes place in two consecutive steps, as indicated by the fact that

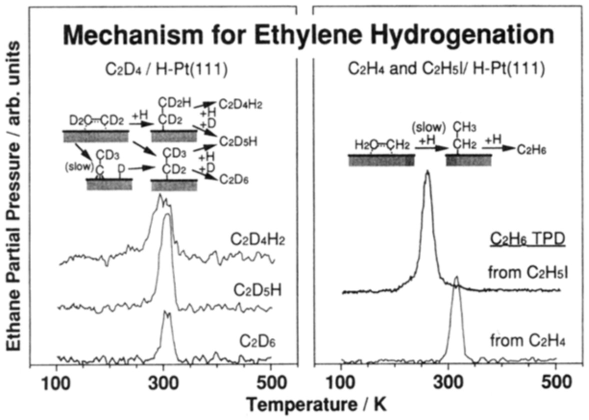


Figure 14. Ethane temperature-programmed desorption (TPD) studies for ethylene hydrogenation on Pt(111).[50,111,679] The use of isotopic labeling has allowed for the identification of some of the mechanistic details of this reaction. The left panel, for instance, shows that C_2D_6, C_2D_5H, and $C_2D_4H_2$ are all produced from perdeuterioethylene coadsorbed with normal hydrogen, indicating that ethylene hydrogenation is a stepwise reaction. The most likely mechanism for this reaction is one where the ethylene molecules are first inserted into metal–hydrogen bonds to form alkyl groups, and where those alkyl species then undergo a reductive elimination step with an additional hydrogen atom to yield ethane. The right panel shows that the desorption of ethane from ethyl groups takes place at much lower temperatures than from ethylene, which means that the initial alkyl formation is rate-limiting in olefin hydrogenation. The ethyl intermediates can also undergo a β-hydride elimination step, leading to the fast ethylene–ethyl interconversion that explains the extensive H–D exchange observed in adsorbed ethylene.

the hydrogenation of ethylene on platinum surfaces predosed with a mixture of hydrogen and deuterium yields a mixture of C_2H_6, C_2H_5D, and $C_2H_4D_2$ (Figure 14).[679] The first step in the conversion of alkenes to alkanes must be a migratory insertion of the olefin into a metal–hydrogen bond, which produces an alkyl moiety, and the second the reductive elimination of that alkyl with an additional surface hydrogen. The lack of any clear evidence for stereoselectivity in the addition of the hydrogen atoms into the double bond even in rigid molecules such as bicyclo[2.2.2]octene or norborane[684] provides convincing proof for the formation of the alkyl intermediate. One study has reported the *syn* addition of two deuteriums to the *endo* face of the double bond of norbornadiene coordinated to a dimethylplatinum moiety,[685] but that reaction is believed to occur on a solid Pt surface after transfer of the ligand from the complex; the results were consistent with the mechanism proposed above where the formation of a surface alkyl moiety is followed by interchange with surface hydrogen atoms. Lastly, the absence of any alkyl buildup on the surface during the reaction indicates that the first step must be rate limiting, in the same way as in organometallic compounds. The faster rate of the alkyl–hydrogen reductive elimination step has also been demonstrated by temperature-programmed desorption experiments (Figure 14).

The order in which the hydrogen and the ethylene are adsorbed on the surface in vacuum studies also changes the kinetics of the hydrogenation reaction.[678] This is because there is a geometrical constraint on the way the olefin and the hydrogen atoms need to adsorb on the surface for the reaction to occur. In connection with this, recent laser-induced desorption kinetic studies have shown that at low enough temperatures the extent of the H–D exchange in ethylene coadsorbed with deuterium on Pt(111) (a reaction believed to start by the migratory insertion of the olefin into the M–H bond, see below) is limited to a fraction of the total molecules and results in the incorporation of an average of only about one deuterium atom per ethylene.[686] This suggests that the mobility of hydrogen on the surface is hindered by the olefin and that the reaction only takes place within reactants adsorbed in close proximity to each other. Other complications have also been identified for the mechanism of the catalytic hydrogenation of ethylene under atmospheric pressures. In experiments using normal ethylene and deuterium, for example, ethane molecules with up to six deuterium atoms are produced (the main product being D_1-ethane). Strongly bound carbonaceous deposits (ethylidyne moieties in the case of ethylene) also form on the surface within seconds of initiating the reaction; the role of those moieties in the overall mechanism is still a matter of debate.[586,652,681,682,687]

4. Alkynes, Dienes, Arenes, and Allyls

Although not common, coordinated alkynes may sometimes undergo migratory insertion reactions into metal–hydrogen bonds in a similar fashion to that of alkenes.[688-690] The insertion is usually *syn*, so the stereochemistry of the carbons is retained,[691] but the initially formed *cis*-vinyl complex can then isomerize to the *trans* tautomer (possibly via a η^2-vinyl intermediate) if there is a vacant coordination site on the metal center.[692] On the basis of both theoretical and experimental results, the reaction has been proposed to take place via a four-center transition state involving the metal, the metal-coordinated hydrogen, and the two acetylenic carbons.[693,694]

The migratory insertion of conjugated dienes into metal–hydrogen bonds is much easier than that of simple olefins, mostly because they result in the formation of a stable π-allylic complex;[597,695] the intramolecular character of this reaction is usually manifested in the stereoselectivity of the product. Arenes can also be hydrogenated with organometallic catalysts: some of those catalysts are capable of promoting hydrogenation of all but one aromatic ring in polycyclic compounds,[696–698] while others can also hydrogenate benzene and other simple monocyclic molecules.[699–704] The reaction in the latter case is slow, usually starts after an induction period, and only proceeds for a few turnovers. High stereoselectivity has been reported in some cases,[701–704] but detailed studies are sparse, and the homogeneous nature of some of the reactions is doubtful.

Some allyl complexes are highly electrophilic and can therefore be easily attacked by a variety of nucleophiles and electrophiles to yield the corresponding olefin. In the case of nucleophilic attacks, the addition always occurs at the noncomplexed side of the ligand. Olefin isomerization presumably proceeds via an allyl complex intermediate.[596,597]

The hydrogenation of acetylene on single-crystal surfaces under vacuum has so far been reported on

Ru(0001),[705] Pd(100) and Pd(111),[706,707] and Pt(111).[708] The unequivocal identification of a surface intermediate could not be made in any of those studies, but self-hydrogenation to ethylene was observed in temperature-programmed desorption experiments on platinum and palladium. Hydrogen coadsorption facilitates the production of a small amount of ethylene on Ru(0001) around 175 K, presumably by first forming a vinyl intermediate around 150 K. Also, only $C_2H_2D_2$ desorbs from deuterium-predosed Ru(0001) surfaces, indicating that no H–D scrambling occurs in that system, but all D_2-, D_3-, and D_4-ethylenes are produced on Pd(111), supposedly by H–D exchange via a vinylidene intermediate.[707] The studies on palladium also highlighted the structure sensitivity of the hydrogenation reaction: ethylene formation occurs around 300 K on Pd(100), around 320 K on Pd(111), and not at all on Pd(110). A small amount of ethane is also produced from acetylene on Pt(111).

To the best of our knowledge no hydrogenation reactions have been reported for either dienes or arenes on transition metal surfaces. One example is available in the literature for the insertion of allyl groups into M–H bonds, that of the π-allylic C_6H_9 species that results from cyclohexene decomposition on Pt(111); that species incorporates a deuterium atom from the surface and desorbs as the olefin if bismuth is dosed after the first dehydrogenation step.[304]

C. C–C Bond Activation

Oxidative addition steps on metal centers like those discussed above for carbon–hydrogen bonds can in principle take place with carbon–carbon single bonds as well. Cyclopropane and a few other strained compounds do indeed react this way,[251,256,709–712] but in compounds with unstrained C–C bonds such cleavage is rare because the overall process is highly endothermic.[119] Recent observations have lead to the suggestion that dehydrogenation steps on the coordinated hydrocarbon moiety are required to assist subsequent C–C oxidative additions.[252] There are nevertheless some examples where this is not the case. For instance, a methyl group can be abstracted from a 1,1-dimethyl cyclopentadiene iridium complex,[713] and some aliphatic coordinated ligands can be converted to olefins via alkyl elimination at the β position.[714–717]

β-Alkyl elimination steps are usually exothermic, but are not common because they compete unfavorably with β-hydride elimination. That obstacle can be overcome by blocking the β position (by using ligands without β hydrogens), or by choosing systems where olefin removal from the complex is favored (a condition needed to drive the equilibrium in the desired direction). β-Alkyl eliminations are well known for aluminum complexes in connection with Ziegler–Natta processes,[718,719] and are feasible in some organolanthanides as well.[714,715] *Exo*-Ring opening, a related reaction, occurs in both alkyl–scandium[716] and platinum complexes.[717]

Metallacycles, on the other hand, quite often decompose via C–C bond breaking steps, via the equivalent of a β-carbene elimination step. The most common reaction of metallacyclobutanes in particular is their reversible fragmentation to the olefin–carbene isomer.[720] Metallacycles are often unstable and exist only as transient short-lived intermediates in olefin metathesis reactions,[721] but have been isolated in a few cases.[722] Olefins can also form reversibly from metallacyclopentanes.[723] Theoretical calculations suggest that the transition state for metathesis requires the planes of the olefin and the carbene to be parallel to each other,[724] and some indirect experimental evidence is available to support this idea: most carbene–olefin complexes in which the carbene is perpendicular to the C–C bond are quite stable.[436,725] A few exceptions to this rule have been reported recently.[726]

Carbon–carbon oxidative addition of double and, more commonly, triple bonds in unsaturated hydrocarbons coordinated to metal clusters are possible. For example, the activation of the carbon–carbon double bond in ethylene yields bridging methylenes in many bimetallic complexes.[727] Reported cases for the activation of triple bonds include the reaction between the hexanuclear $Os_6(CO)_{18}$ cluster and diphenyl acetylene to form $Os_6(CO)_{16}(\mu_3\text{-CPh})(\mu_4\text{-CPh})$,[728] the thermal conversion of the tetranuclear alkyne complex $Os_3WCp(H)(\mu_3\text{-RCCR}')(CO)_{10}$ to the bis(alkylidyne) $Os_3WCp(H)(\mu_3\text{-CR})(\mu_3\text{-CR}')(CO)_9$ complex,[729] and the addition of alkynes to other trimetallic clusters.[730,731] Presumably, the alkyne needs to rotate during this reaction from its initial parallel coordination mode to a perpendicular configuration in order to migrate to the edge of the cluster, which is the initial step toward the C–C bond activation.[730] A few examples have also been reported for this reaction in complexes with only two metal centers.[732,733]

In heterogeneous systems carbon–carbon bond scission steps are the basis for well-established catalytic processes such as hydrocarbon hydrogenolysis, but nevertheless, little is known about the mechanism of this reaction. The activation of alkanes and other saturated and unsaturated compounds seems to almost always be initiated by the breaking of C–H bonds, as only highly dehydrogenated species seem prone to C–C cleavage. Perhaps the cleanest and most interesting example of a C–C bond-breaking reaction in surface science is the decomposition of neopentyl groups to isobutene on Ni(100) surfaces (Figure 10).[539] That reaction was shown to have an activation energy barrier on the order of 22 kcal/mol, much higher than that for β-hydride elimination steps on the same surface. The mechanism by which the olefin is formed has not yet been determined, but, given that the decomposition of α,α-dideuterioneopentyl groups only yields normal isobutene (without any deuterium substitutions), a direct β-methyl elimination step can be discarded.[540,541] A β-methyl elimination step was also proposed for the formation of propylene from isobutyl moieties on aluminum surfaces,[96] but no direct proof was provided to support that hypothesis. A third example of C–C bond scission reactions on surfaces is the conversion of a C_4H_4 cyclic moiety to vinylidene on Pd(111),[266] a reaction that takes place around 250 K, most likely via an initial ring-opening step to form acetylene.

Although to the best of our knowledge there are no other reported cases for isolated carbon–carbon bond-scission steps, those reactions take place in almost all hydrocarbon/transition metal surface systems at high temperatures. Decomposition reactions are usually molecule or functional group specific below 400 K, but most hydrocarbon moieties seem to decompose to the same fragments above 500 K. Unfortunately, high-temperature activation of adsorbed carbonaceous moieties often produces a mixture of species on the surface, making the characterization of those species quite difficult. Vibrational and temperature-programmed desorption studies have narrowed down the possible candidates to CH, C_2H, and/or partially hydrogenated polymeric carbon rings and chains. As a case in point, heating ethylene, acetylene, or benzene on ruthenium,[142,212] rhodium,[144,147] nickel,[203] palladium,[204,205] or platinum[144] surfaces above 500 K all produce a mixed layer of CH and CCH fragments. The formation of methylidyne (CH) clearly requires the breaking of at least one C–C bond, but the available data indicate that this only occurs after extensive dehydrogenation if at all.[734]

D. C–C Bond Formation

1. Reductive Elimination of Alkyls

Carbon–carbon bond-formation steps are the reverse of C–C activation reactions, and usually occur by one of two paths, either by reductive elimination (or C–C coupling, the reverse of the oxidative addition step discussed before), or by migratory insertion. Thermodynamically C–C coupling is favored over C–H and H–H elimination reactions, but kinetically the need for the reorientation of the two highly directional carbon-sp^3 hybrid orbitals often makes those reactions slow.[628] A well-known example of a C–C coupling is the alkane formation from dialkyl mono-metallic complexes,[712] a reaction that requires the two outgoing ligands to be oriented *cis* to each other.[616] The elimination rate is enhanced both by a large positive charge at the metal center[618,619] and by prior coordination of another ligand.[626] Apparently this enhancement is due not only to the formal two-electron reduction of the metal center induced by the elimination, but also to geometrical effects related to the spatial distribution of the d orbitals in the metal: elimination from three- and five-coordinated complexes is much easier than from planar four-coordinated ones.[735] This also explains the differences in the way reductive elimination reactions take place in different metals. For example, four-coordinated $Ni(PR_3)_2R_2$ compounds lose a R–R alkane directly, but the equivalent Pd(II) and Au(III) complexes normally release one of the phosphine ligands first,[616,621] and Pt(II) complexes usually react only after the previous oxidative addition of an alkyl halide.[736]

C–C coupling reactions are believed to be elementary and to take place intramolecularly, at least in monometallic complexes.[616] The elimination of two organic moieties coordinated to different metal centers within the same compound is rare, and in the case of bimetallic complex is in fact symmetry forbidden.[635] A great deal of indirect evidence also suggests that the formation of the C–C bond proceeds with retention of stereochemistry,[737] and that the stability of the product often enhances the reaction rate. This is why both vinyl–alkyl[738] and vinyl–vinyl[739] eliminations, which yield coordinated olefins, are faster than alkyl–alkyl couplings. Octanuclear organocopper clusters produce biaryls via the Ullmann coupling reaction,[740,741] while hexanuclear alkyl–aryl mixed complexes yield the alkyl–benzene cross-coupling product instead.[742] The formation of a σ alkane–metal complex prior to the release of the free hydrocarbon molecule has also been suggested in some alkyl–alkyl elimination reactions.[743]

Reductive eliminations often compete with disproportionation reactions. Late transition metals in general favor C–C coupling over β-hydride or C–H reductive elimination steps. Alkyl–silver complexes yield dialkyl compounds almost exclusively. Iron compounds, on the other hand, usually produce alkane/alkene mixtures, and copper, gold, nickel, rhodium, platinum, and palladium compounds all produce varying mixtures of alkanes, alkenes, and dialkanes depending on the nature of the other ligands.[489,712]

The reductive elimination of alkyl groups on surfaces is known on late transition metals only (Figure 15). For example, the thermal activation of methyl, ethyl, *n*-propyl, and isopropyl on Ag(111) surfaces yields ethane, butane, *n*-hexane, and 2,3-dimethyl butane respectively, all with 100% selectivity.[66–68] On palladium,[637] copper,[61,62,191,639] and gold[71,521,744] surface coupling reactions compete with hydride elimination steps, especially at low alkyl coverages.[71,521] The rate of C–C coupling also seems to be directly related to the strength of the metal–carbon bond: the weaker the bond is, the faster the coupling.[744] Methyl groups couple with high efficiency on Au(100) or Au(111) surfaces unless sites are blocked by other ligands,[744] but other alkyl groups disproportionate to a large extent, which means that the activity for C–C coupling on gold must be somewhere between that for the α- and β-hydride elimination steps. The activation energies for both reactions are quite similar on copper, on the order of 20 kcal/mol, suggesting that the selectivity toward reductive elimination reactions may at least in part be determined by the ability of the metal to activate dehydrogenation reactions.[63] Also, coupling reactions are bimolecular, and therefore have kinetics that may depend strongly on the concentrations of the surface reactants. Finally, the rates for the coupling of CH_2 and CH_3 moieties is faster on Cu(100) than on Cu(110), indicating that the structure of the surface plays an important role in determining the kinetics of these reactions as well (Figure 15). It is conceivable that the actual C–C surface recombination step is fast and that the rate for alkyl dimerization is controlled by the diffusion of the reactants on the surface.

In terms of relative rates for C–H vs C–C bond-forming reactions, it was found that coadsorption of hydrogen with phenyl groups on Cu(111) completely

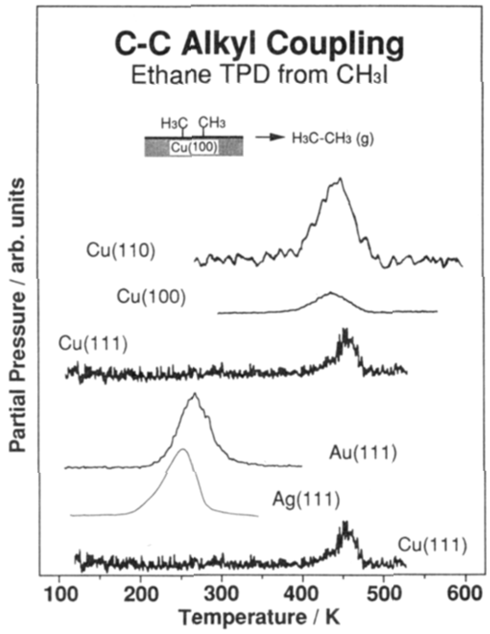


Figure 15. Ethane temperature-programmed desorption (TPD) spectra from methyl iodide adsorbed on Cu(110),[62] Cu(100),[192] Cu(111),[63] Au(111),[744] and Ag(111),[67] showing the relative ease with which C−C alkyl coupling reactions occur on late transition metal surfaces. Silver is an extreme case where the coupling not only occurs at lower temperatures than on any other metal, but where it also takes place with 100% efficiency. Some ethane also forms on copper and gold surfaces, but only in competition with the products of α-hydride and alkyl−hydrogen reductive elimination reactions. This figure also shows how the maxima for ethane formation shifts from around 440 K on Cu(100) to 445 and 450 K on Cu(110) and Cu(111), respectively. Although these temperatures depend somewhat on the initial methyl surface coverage, there is a clear difference in reaction rate on surfaces with different crystallographic orientations. This may be associated with the ease with which alkyl groups diffuse across surfaces.

inhibits biphenyl formation at the expense of benzene production;[162,745] C−H reductive eliminations steps are clearly favored in that case. On the other hand, phenyl groups act as efficient traps for alkyl radical intermediates: all methyl, ethyl, propyl, butyl, and neopentyl groups couple with phenyl moieties below 160 K to yield the corresponding alkyl benzene, indicating that alkyl−aryl coupling is favored over alkyl−alkyl formation.[746] Other metals may promote coupling as well. For instance, the thermal activation of methyl moieties yields ethylidyne moieties on Pt(111)[747] and Ru(0001)[36] surfaces at high coverages. Although it is not yet clear what the mechanism for that reaction is, it most likely starts by an initial α-H elimination on methyl groups to produce methylidyne. No other alkyl coupling examples have been reported under vacuum to date.[33]

2. Other Eliminations

Reductive elimination from metallacycles usually yields cyclic compounds. A rhenium cyclopentane complex, for instance, undergoes sequential ring contraction and reductive elimination steps to produce methyl cyclopropane.[250] A better example is that of a nickel cyclopentane complex, which undergoes a reductive elimination step directly to yield cyclobutane.[260] This latter system is particularly interesting, because it proves that the product selectivity is controlled by the coordination number and/or the geometry of the molecule. For example, while a 14-electron, three-coordinate complex undergoes β-hydride elimination to butene, a 16-electron, four-coordinated compound decomposes via reductive elimination to cyclobutane, and an 18-electron, five-coordinated complex reacts by C−C bond scission to yield ethylene.[260]

Multiply coordinated ligands can C−C couple as well. Some Fischer carbenes, for instance, can reductively eliminate to yield olefins,[195] and dialkylidyne complexes can produce acetylenes, both in monometallic[748,749] and in cluster[750−752] compounds. In π ligands, diolefin complexes can oxidative couple to metallacyclopentane, most likely via the formation of a metallacyclopropane intermediate,[753] and diacetylene compounds produce the corresponding unsaturated metallacycle (metallol) complex.[754] In the homogeneous conversion of acetylenes to benzenes, which is commonly catalyzed by metal complexes,[755,756] blocking of the side reactions and use of bulky substituents allows for the isolation of C_2 and C_4 intermediates.[755]

Decomposition of metallacycles leads to the elimination of cyclic hydrocarbons on silver[66] and nickel[269] surfaces, but not on aluminum[268] or palladium.[266] On Ag(111), cyclopropane is produced from $Cl(CH_2)_3I$ decomposition (presumably via the formation of a metallacyclobutane).[66] Vinyl and phenyl groups also reductively eliminate on Ag(111) to butadiene and biphenyl, respectively,[133] and 1,5-hexadiene forms by coupling of allyl groups on Ag(110).[345] Perhaps more interesting, butadiene is produced with 100% efficiency from vinyl on Cu(100),[132] even though hydride eliminations seem to dominate on other hydrocarbon−copper systems. Cycloalkenes from cyclopropene to cyclohexene are produced on Ni(100) by thermal decomposition of the corresponding 1,*n*-diiodoalkane compounds.[269] Methylene moieties couple very efficiently on silver[66] and copper[62,639] surfaces, but not at all on either nickel[112] or platinum[193] substrates. Finally, CH groups dimerize to acetylene above 250 K on Ni(111).[79]

Perhaps the most interesting C−C coupling reaction reported so far on surfaces is the trimerization of acetylene on Pd(111).[595,706,707,757,758] A series of elegant isotope-labeling, structural, and reactivity studies have shown that this reaction takes place via an initial oxidative coupling of two acetylene molecules to form a $Pd-C_4H_4$ metallocycle followed by the coupling of such an intermediate with a third acetylene to benzene. Several pieces of evidence support this mechanism: (1) C_4 products desorb from palladium surfaces exposed to acetylene molecular beams;[758,759] (2) several C_4 molecules, mostly butene, are also produced by thermal activation of acetylene when coadsorbed with hydrogen;[760] (3) thermal activation of acetylene coadsorbed with either sulfur[761] or oxygen[762] yields thiophene or furan, respectively; (4) thermal activation of mixtures of normal and fully deuterated acetylenes yields benzene molecules with even number of deuterium atoms exclusively;[763] and (5) the reaction between the palladium C_4 intermediate prepared by decomposition of 3,4-*cis*-dichlorocyclobutene and acetylene produces benzene.[763] Acetylene trimerization has also been observed on nickel-,[764] copper-,[765] and tin-modified platinum[766] surfaces, but no mechanistic details were provided in the reports of those cases.

3. Migratory Insertion

The other common type of C−C bond-formation reaction is the migratory insertion of carbenes or olefins into metal−carbon bonds. Carbene insertion in organometallic complexes has been recognized only recently, and is not yet well understood. Several examples have been reported for what looks like an alkyl−carbene insertion, but in most cases the presumed alkyl−carbene complex was generated in situ (usually from a dialkyl compound), and only the insertion product was identified.[767−769] This reaction can in principle repeat itself in a catalytic cycle to produce polymers, but this seems to be common only in the heterogeneous systems related to the Fischer−Tropsch process.[770−772] The insertion of coordinated alkenes into metal−alkyl bonds is also possible, and is in fact pivotal in the Heck reaction, where palladium is complexed sequentially with an alkyl (R) group and an olefin ($R''_2C{=}CR'H$) to produce a palladium hydride compound and the enlarged alkene ($R''_2C{=}CR'R$),[773] in the Cramer mechanism for olefin dimerization,[774] and in the Cossee mechanism for Ziegler−Natta polymerizations.[775−777] All these reactions occur via *syn* additions with retention of configuration,[778] but the regiochemistry depends on the steric and/or electronic details of the complex, so that the new alkyl ligand can be formed by bonding of the old alkyl group to either the most (Markovnikov) or the least (anti-Markovnikov) crowded carbon atom in the olefin .[775,779] Alkyl−olefin insertions are thermodynamically more favorable than hydrido−olefin insertions, but kinetic factors usually shift the selectivity toward the latter reactions.[780,781] Alkynes can also be inserted into metal−alkyl bonds with anti-Markovnikov regiospecificity via a *cis* addition step,[782,783] in this case to yield metal−vinyl derivatives,[689,690,694,784] and thanks to the high stability of the resulting π complex, the insertion of conjugated dienes and other extended olefinic systems is even more facile.[695] Olefin insertion into metal−carbene bonds produces metallacyclobutane complexes; this reaction is not only common, but often reversible, and believed to be the basis for metathesis processes.[721,785] Also possible, although less common, is the insertion of alkynes into metal−carbenes or metal−μ-alkylidenes; these reactions yield unsaturated cyclic complexes[786] or allylic ligands,[787,788] respectively. The latter two processes could in fact be the same, and the difference could just be due to a subsequent rearrangement of the product.[789,790]

The only clear example of a migratory insertion reaction on metal surfaces is that of methylene into copper−alkyl bonds on copper single crystals (Figure 16). For instance, the thermal activation of mixtures of methyl and methylene groups coadsorbed on Cu(110) yields significant amounts of ethylene, which is produced by β-hydride elimination from the ethyl moieties resulting from carbene insertion into the $Cu{-}CH_3$ bond.[62] On Cu(100) the activation of CH_2 + CD_3 mixtures produces both D_2-ethylene and D_3-propylene, the latter by two consecutive insertion steps (Figure 16), and coadsorbed CH_2 + C_2D_5 mixtures yield D_4-propylene.[192] Olefin metathesis has been reported on both metal oxides and molybdenum metallic foils, but no mechanistic details are available for those cases.[791] Finally, polymerization of hydrocarbon moieties takes place on several metal surfaces at high temperatures. Hydrocarbon decomposition on Pt(111) substrates, for instance, ultimately yields graphitic layers,[216,792] but the mechanism for that reaction is far from understood.

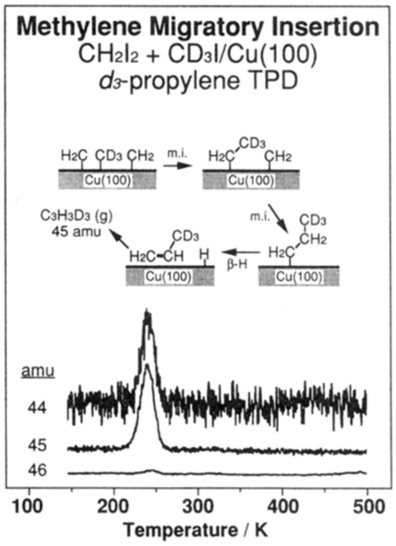


Figure 16. Propene temperature-programmed desorption (TPD) spectra from a Cu(100) surface dosed with a mixture of diiodo methane and perdeuteriomethyl iodide. This figure illustrates the ease with which methylene migratory insertion reactions occur on copper surfaces. The relative peak intensities for the 44, 45, and 46 amu traces correspond to those of 3,3,3-trideuterioprop-1-ene, indicating that the trideuterio olefin is the major C_3 product in this case.[192] The proposed mechanism for this reaction, shown schematically at the top of this figure, consists of two sequential methylene migratory insertions into an alkyl−metal bond (a methyl first and an ethyl in the second step) followed by the β-hydride elimination from the resulting trideuteriopropyl species.

E. Isomerization

Apart from hydrogenation−dehydrogenation steps, coordinated hydrocarbon moieties can also undergo isomerization reactions. One of the most common pathways for such tautomerism is via the shift of a hydrogen atom from one carbon to the next.[793,794] In particular, the interconversion of coordinated acetylene into vinylidene moieties within organometallic complexes has received significant attention over the past decade.[644−647,795−803] Several calculations indicate that metal-coordinated vinylidene ligands may be more stable than their acetylene counterparts, in spite of the fact that the opposite is true for the free gas-phase moieties.[797,799] The relative stability of these ligands is in fact controlled by several factors, including the d electron count in the metal center,[644] which is why their interconversion can indeed occur in both directions.

The mechanism for the vinylidene−acetylene isomerization reaction is far from resolved. Two routes have been extensively discussed in the literature, the direct hydrogen "slippage" from one carbon to the next,[797] and the two-step conversion via an alkynyl intermediate.[232] The latter did gain some support after the isolation of several alkynyl(hydrido) complexes,[645–647,795,796] but the prohibitively large barrier calculated for such a process makes the conversion of this hydrido–acetylide into vinylidene unlikely.[801] In the end, both mechanisms may be operational depending on the characteristics of the system, since 18-electron filled-shell acetylene complexes cannot undergo the C–H oxidative addition step necessary to make the hydrido intermediate anyway. There has also been some discussion on the effect of the metal cluster size on the viability of the acetylene–vinylidene conversion. Such a transformation was calculated to be unlikely for binuclear complexes,[797] but has nevertheless been observed experimentally in a few systems.[802,803] The isomerization of nonterminal alkyne complexes to allyl compounds has been reported as well.[800]

The conversion of both alkenes into alkylidenes[643,804–806] and alkenyls into alkylidynes are also possible.[557,643,806–810] As in the case of the alkyne–vinylidene isomerization, the alkenyl–alkylidyne tautomerism is believed to often follow a two-step mechanism, since the reaction is in many instances driven by the addition of protons to the solution.[806,808] On the other hand, isotope labeling experiments provided strong evidence for a direct 1,2 hydrogen shift within the hydrocarbon moiety in a triosmium complex, without the direct participation of any of the metal atoms.[810] Also, the rearrangement of alkylidynes to alkenyl complexes is accelerated by a higher degree of alkyl substitution at the β carbon of the hydrocarbon ligand,[557] and the kinetic product from the conversion of metal complexes with 1,2-disubstituted alkenes are the alkylidyne compounds.[809] Theoretical calculations on the latter suggest a transition state with a bridging hydrogen and a positive charge localized at the β position.[811]

There have not been many reported instances of simple isomerization reactions on surfaces. One of the earliest examples of this was the intramolecular rearrangement of chemisorbed acetylene to vinylidene that occurs on Pd(111) between 220 and 270 K[139,204,241,595] and on supported platinum around room temperature.[242] On Pt(111), the thermal decomposition of vinyl moieties yields acetylene and vinylidene moieties simultaneously, but there is no evidence for the interconversion of one species into the other.[131] The most studied case involving hydrogen tautomerism in surface chemistry is by far the conversion of ethylene to ethylidyne;[586] this is a complex reaction and will be discussed in detail in the next section. Acetylene can also isomerize to ethylidyne if hydrogen is coadsorbed on the surface,[204,210,705] in the case of supported platinum via the formation of vinylidene.[812,813] Other types of isomerizations, such as C–C double- or triple-bond migration, *cis–trans* isomerization in olefins, and shifts of methyl and other carbon-containing fragments are all known in organometallic systems,[597,801,814] but have, to the best of our knowledge, never been observed in surface science studies.

Other more complex isomerization reactions have also been reported. Coordinated cyclic compounds, for instance, sometimes undergo ring-expansion or ring-contraction reactions. A cycloheptatrienyl–Cr(CO)$_3$ cation, for instance, reacts with cyclopentadienyl ions to yield the ring-contracted chromium–benzene neutral complex.[323,560] Labeling experiments proved that the arene six-membered ligand in that case is formed from the tropylium ring rather than from the cyclopentadienyl ring.[597] Adsorbed cycloheptatriene was also shown to yield benzene on a carbon-passivated W(100) surface.[815] In another example, 1,3,5,7-tetramethylcyclooctatetraene reacts spontaneously when coordinated to a Fe(CO)$_3$ complex to produce the corresponding [4.2.0]bicyclic compound,[816,817] and a similar ring contraction has been recently reported on Pt(111) surfaces.[818] Finally, the conversion of 1-methylcyclopentene to benzene has been observed on Ni(100).[163]

F. Multiple-Step Reactions

1. Dehydrogenation

In addition to the studies of elementary steps discussed in the previous sections, some research has been carried out on more complex surface reactions. Reactions involving multiple hydrogenation–dehydrogenation, hydrogen shift, and H–D exchange steps have received special attention in recent years. The conversion of alkenes to alkylidynes mentioned in the previous section falls in this category. This reaction, which takes place on almost all late transition metal surfaces, is believed to follow a multistep mechanism that includes a 1,2 hydrogen-shift step. Unfortunately, it has not yet been possible to determine the actual sequence of elementary steps that take place in that reaction. TPD, NEXAFS, SSIMS, and RAIRS experiments all have proven that ethylidyne formation follows first-order kinetics,[585,819–824] but recent studies have pointed to two kinetic regimes for the decomposition of ethylene, a slow one at saturation, and a faster one at lower coverages.[825] This means that the rate of ethylene disappearance diverges from that of ethylidyne formation in the low coverage regime, suggesting that another species accumulates on the surface. Nevertheless, no intermediates have been isolated for this reaction to date. Also, recent studies have indicated that the mechanism of this reaction is more complicated than initially thought. For example, a recent STM study has shown that the kinetics for the conversion of ethylene to ethylidyne on Pt(111) may depend on the availability of the appropriate ensemble of metal atoms, since the reaction appears to take place preferentially on the boundaries between the islands formed by ethylene and ethylidyne.[216] Infrared and laser-induced desorption experiments with labeled ethylene and deuterium have shown that ethylene exchanges its hydrogen atoms simultaneously during the formation of ethylidyne as well.[559,686]

Several pathways have been proposed in the literature for the conversion of ethylene to ethylidyne (Figure 17).[144,205,287,518,585,826–828] Any mechanism that tries to explain this reaction must include at least two steps in order to account for the changes that

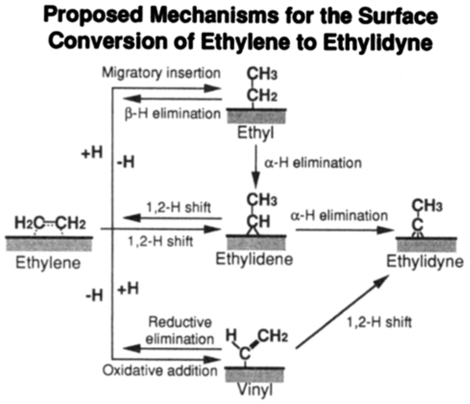


Figure 17. Proposed mechanisms for the conversion of adsorbed ethylene into ethylidyne species on transition metal surfaces.[586] Three intermediates have been suggested for this reaction, namely, ethyl, ethylidene, and vinyl species. The lack of a significant buildup of any species other than ethylene and ethylidyne during ethylidyne formation argues for a mechanism with an initial slow step or, more likely, for a fast equilibrium between ethylene and a second species. Ethylidyne and ethylene are both much more stable than any of the other proposed species, so if such an equilibrium were to be established, the second moiety would have to be present in small concentrations on the surface at all times during the ethylene conversion. In addition, given that the rate for ethylidyne formation is independent of the surface coverage of coadsorbed hydrogen,[686] the most likely mechanism for ethylidyne formation is that involving ethylidene. Note, however, that an equilibrium between ethylene and ethyl must also exist on the surface, since such interconversion is believed to be responsible for the extensive ethylene H−D exchange that takes place concurrently.

take place within the surface moieties, namely, (1) a removal of a hydrogen atom (the breaking of a C−H bond), and (2) a transfer of a second hydrogen from one carbon to the other. Two straightforward sequences can be proposed for this, one where the hydrogen transfer is followed by the hydrogen removal, in which case an ethylidene ($CHCH_3$) intermediate is formed, and a second one where the hydrogen removal occurs first, and a vinyl-like ($CH{=}CH_2$) intermediate is involved instead. Precedents for the first step of both schemes exist in the organometallic literature,[557,643] but results from kinetic experiments with trideuterioethylene ($CHD{=}CD_2$) on Pt(111) ruled out the simple two-step irreversible sequence via an ethylidene intermediate,[585] and studies on the surface chemistry of vinyl iodide argue against the idea of a pathway involving vinyl intermediates as well.[131] A third proposal is that ethyl groups may coexist in small concentrations on the surface throughout the course of the reaction,[4,144,829] perhaps in equilibrium with the adsorbed ethylene. This equilibrium would not only explain the ease with which ethylene exchanges its hydrogen atoms, but could also account for the formation of ethylidyne via a short-lived ethylidene intermediate. On the other hand, recent RAIRS experiments have shown that the rate of ethylidyne formation is not affected by the presence of coadsorbed hydrogen on the surface.[686] At the present time, the best mechanism appears to be one involving a direct ethylene−ethylidene fast interconversion followed by the α-elimination of ethylidene to ethylidyne, but more work is needed to resolve this issue.

Another good example of the type of reactions that most likely involve multiple steps is the dehydrogenation of alkenes to alkynes, the best example being the dehydrogenation of ethylene to acetylene on Ni(111).[289,424,830−832] According to secondary ion mass spectrometric studies, the acetylene formation begins around 165 K and is over by about 215 K, at which point all the surface ethylene has been consumed and the resulting acetylene starts to dehydrogenate to other species.[831,832] Recent structural experiments suggest that the two hydrogen atoms could be lost simultaneously from the ethylene molecule in a concerted step, either via *cis* elimination with translation of the molecule to a new adsorption site, or by *trans* elimination and rotation around the symmetry axis of the molecule along the surface normal.[311] This is consistent with the fact that no intermediates have been identified for this reaction. It is interesting to note that the mechanism of dehydrogenation reactions depends on the structure of the surface (at least under vacuum), since the thermal activation of ethylene on Ni(100) and Ni(110) crystals yields vinyl and acetylide species, respectively.[128,141] This structure sensitivity may be related to the need for a reasonably large ensemble of metal atoms in order for the reaction to occur: the adsorption of ethylene and acetylene involves a minimum of four and two surface nickel atoms, respectively,[311,327] and each extra hydrogen requires one hollow site with another three Ni atoms. In the case of the dehydrogenation of cyclohexane on platinum, the blocking of surface sites by gold deposition increases the selectivity for cyclohexene over benzene production, presumably because a larger site is required to accommodate the extra hydrogen atoms from benzene formation (Figure 18).[833] Since such large ensembles are difficult to emulate with organometallic clusters, it may be difficult to reproduce these surface reactions in the homogeneous phase.

2. Hydrogenation

The most widely studied example of a hydrogenation reaction is the conversion of ethylene to ethane. Temperature-programmed desorption experiments on Pt(111) have shown that ethylene self-hydrogenates around 300 K at saturation coverages (Figure 14). The reaction yield, however, is quite low, on the order of a few percent.[223] Ethylene self-hydrogenation has also been observed on Ni(111) under high pressures,[675] and on Pd(111) in molecular beam studies at room temperature.[834] On the other hand, no detectable ethane formation from adsorbed ethylene has been observed on nickel,[141,594,831] palladium,[205,835,836] rhodium,[286] iridium,[837] or ruthenium[142] single-crystal surfaces under vacuum. This self-hydrogenation reaction could in principle occur via the direct disproportionation of two adsorbed ethylene molecules, but isotope-labeling experiments indicate that it takes place by incorporation of surface hydrogen atoms (either from decomposition of ethylene, or from hydrogen adsorption from the background) instead.[676,679]

Coadsorption of hydrogen with ethylene on the surface enhances the ethane yield on Pt(111),[676,679] and induces ethylene hydrogenation on Ni(100),[678]

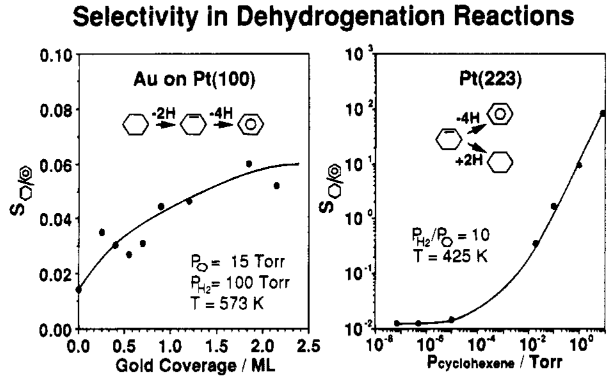


Figure 18. Selectivity results for hydrogenation–dehydrogenation reactions with cyclohexane and cyclohexene on platinum single-crystal surfaces. The left panel displays changes in selectivity for cyclohexene over benzene formation from cyclohexane dehydrogenation on Pt(100) as a function of epitaxially deposited gold coverage.[833] The relative increase in cyclohexene formation with increasing gold site-blocking indicates that dehydrogenation reactions require large metal ensembles on the surface and that the more extensive the dehydrogenation is, the larger the ensemble needs to be (because additional space is required to accommodate the leaving hydrogen atoms). The right panel shows the dramatic changes in selectivity for cyclohexene conversion with total pressure on Pt(223), from benzene production, which is favored at low pressures, to cyclohexane formation, which dominates at high pressures. This selectivity change is again due to the effect that site blocking has on dehydrogenation reactions: under high pressures the surface is covered with a layer of hydrocarbon species which selectively poisons dehydrogenation over hydrogenation reactions.

Ni(110),[838] Rh(111),[286] and Fe(100).[839] Experiments with deuterium and with deuterated ethylene have demonstrated that hydrogenation is stepwise, occurring via the migratory insertion of ethylene into a metal–hydrogen bond followed by the reductive elimination of the resulting alkyl intermediate with a second coordinated hydrogen atom (Figure 14).[679] The first step in this mechanism is believed to be rate limiting and the second to most likely compete with the β-hydride elimination that regenerates the original ethylene molecule.[679] The activation energies for the ethyl formation (migratory insertion) and ethane desorption (reductive elimination) steps have been estimated to be about 13 and 5 kcal/mol respectively on Pt(111),[111] and around 10 kcal/mol and less than 5 kcal/mol on Ni(100).[41] Although all these observations are consistent with what is known about catalytic hydrogenation in homogeneous phases,[119] the surface systems are still unique in that the local arrangement of the adsorbed species (ethylene and hydrogen atoms) affects the hydrogenation kinetics: both the yield and the desorption temperature of the resulting ethane change considerably depending on the dosing order of the reactants.[678] This suggests that hydrogen mobility in these crowded substrates plays an important role in determining the rate of the overall process.

Ethylene formation from acetylene provides another good example of a hydrogenation reaction. Acetylene self-hydrogenation has been observed only on palladium[706,840] and platinum[708] single-crystal surfaces. Of particular interest is the fact that ethylene is produced on Pd(100) and Pd(111), but not on Pd(110).[706,840] Hydrogen coadsorption enhances the production of hydrogenated compounds on all surfaces, as in the case of ethylene. On palladium, for instance, coadsorbed hydrogen shifts the selectivity from acetylene trimerization (to benzene) to ethylene production.[707] On Pt(111), ethylene formation is also accompanied by a small amount of ethane desorption,[708] but on palladium this does not happen because of the particular ease with which ethylene desorbs from that metal;[841] presumably this is the reason why palladium is such a selective catalyst for partial hydrogenation reactions. A small amount of ethylene can also be produced by thermal activation of acetylene coadsorbed with hydrogen on Ru(0001).[705] Isotope labeling and surface characterization experiments suggest that the hydrogen incorporation in all these cases is stepwise: on Ru(0001), for example, the identification of a vinyl intermediate was inferred from vibrational data.

A third example of unsaturated hydrocarbon hydrogenation is that of cyclohexene. On platinum single crystals, the thermal activation of cyclohexene coadsorbed with hydrogen leads to the production of some cyclohexane, but only in small quantities; the preferred product is benzene.[842,843] However, this selectivity changes by several orders of magnitude as the total pressure is increased even if the hydrogen-to-cyclohexene ratio is kept constant, to the point that cyclohexane becomes the dominant product under atmospheric pressures (Figure 18).[842–844] The hydrogenation of more stable surface moieties such as alkylidenes and alkylidynes is also possible. Methylene moieties, for instance, hydrogenate on Pt(111),[52,188] Ni(100),[112] and Rh(111)[186] in a stepwise manner, via the sequential formation of methyl and methane. On nickel in particular, it was shown that the limiting step is not the migratory insertion step that yields the methyl intermediate, but the subsequent reductive elimination of that methyl with surface hydrogen to produce methane. Methylidyne can also be hydrogenated all the way to methane on Pt(111) in a stepwise sequence of reactions where the final hydrogen incorporation step is rate limiting.[536] Ethylidyne, on the other hand, is much more difficult to hydrogenate. This reaction seems to be possible on Pt(111)[651] but not on Rh(111),[652] and only above room temperature and under atmospheric hydrogen pressures.

3. H–D Exchange

In the presence of surface deuterium hydrogenation–dehydrogenation reactions are often accompanied by H–D exchange. For example, when ethylene is coadsorbed with deuterium on Ni(100)[678] or Pt(111),[559] significant exchange is observed. This reaction could in principle take place via an initial oxidative addition of the alkene followed by a reductive elimination of the resulting vinyl with a deuterium atom, but most likely proceeds via an initial insertion of the coordinated olefin into a metal–deuterium bond and a subsequent β-H elimination from the resulting ethyl intermediate.[119] On Pt(111), mixtures of normal and fully deuterated ethylenes show H/D scrambling even in the absence of coadsorbed hydrogen or deuterium, probably because the decomposition of some of the adsorbed ethylene provides the H and D atoms required for the exchange.[559] Hydrogen (or deuterium) atoms also exchange in alkyl groups on Pt(111), but not on Ni(100); in fact, almost 10% of the methane produced by hydrogenation of normal methyl groups with deuterium on Pt(111) under vacuum is fully deuterated (Figure 11).[535] A fast equilibrium between methylidene and methylidyne may be responsible for the extent of that exchange.[536] Much less (although still noticeable) exchange is also observed in ethyl groups on Pt(111).[111]

Examples of H–D exchange reactions in alkylidynes include those of ethylidyne on Pt(111),[223,559,687,845] Rh(111),[652,824] and Ir(111),[677] and of propylidyne on Pt(111).[846] Because this reaction requires a large ensemble of surface atoms, however, it is usually slow at saturation coverages; only atmospheric pressures lead to significant exchange in that case.[652] On the other hand, appreciable exchange takes place under vacuum at submonolayer alkylidyne coverages.[223,559,687] Also, H–D exchange is a couple of orders of magnitude slower in propylidyne than in ethylidyne, signaling that steric effects are important in determining the rate of the reaction.[846] Nevertheless, exchange occurs by incorporation of one deuterium at the time in all cases. Several mechanisms have been proposed: (1) the direct formation of an alkylidene by α-deuterium incorporation, followed by migration of a β hydrogen to the α position (to yield the monodeuterated alkene), formation of an alkylidene with one deuterium in the β position (by the reverse reaction), and α-elimination to the monodeuterated alkylidyne; (2) the loss of a β hydrogen from the alkylidene to form an α-deuterated vinyl followed by hydrogen incorporation at the β position; (3) the concerted β-hydride elimination and α–β hydrogen shift in the alkylidene; or (4) the initial alkylidyne–vinyl rearrangement prior to the formation of either alkylidene or alkene. The first two mechanisms are unlikely because alkylidenes are less stable than either alkenes[559] or vinyls,[131] and the third because it does not satisfy the principle of microscopic reversibility (the transition state should be at the middle of a symmetrically looking reaction coordinate), but the fact is that there is not enough experimental data to assess the validity of any of these proposals with any certainty.

G. Other Reactions

Another possible way in which alkyls and other hydrocarbon moieties bonded to metal centers may decompose is via the homolytic scission of the metal–carbon bond to yield free radicals. However, because of its high activation barrier (the energy of the carbon–metal bond), this reaction is not common: in the case of alkyl moieties, energies on the order of 30–50 kcal/mol are required both in organometallic compounds[107–109] and on surfaces.[40,62,102,110,111] Theoretical studies predict that this reaction should take place mainly on early transition metals,[847] but most experimental examples reported so far come from complexes of platinum,[109,743,848] nickel,[849] copper,[850,851] and silver.[852] Only one example has at present been reported for this type of reaction on solid surfaces, namely, that of the desorption of methyl groups from Cu(111) surfaces.[59] The Cu–CH_3 bond in that case cleaves at around 470 K (which corresponds to an activation energy of about 29 kcal/mol), in one of a family of parallel reactions that also include the conversion of methyl to methane, ethylene, and propylene. The formation of free alkyl radicals from other chemisorbed hydrocarbons, on the other hand, can be close to isoenergetic; methyl radicals, for instance, are ejected into the gas phase after activation of methyl iodide on Cu(111)[59,60,63,746] and Ni(100),[76] and of methoxy on Mo(100).[853]

Organic ligands in metal complexes may also be displaced by either nucleophiles or electrophiles. The simplest case of a nucleophilic attack is the transfer of a coordinated alkyl from one molecule to another which lacks such ligand. This reaction is reasonably facile and follows a S_N2 mechanism with inversion of configuration at the carbon atom.[854,855] Cleavage of σ alkyl–metal bonds by other nucleophiles is much less common (because the metals involved usually are poor leaving groups), but it can be promoted by increasing the oxidation state of the metal.[856,857] On the other extreme, the removal of an organic ligand from a transition metal by an electrophile is most commonly done by using protons.[858,859] In that case the reaction retains the stereochemistry of the leaving group,[629,860] presumably because it occurs via an attack and coordination of the electrophile to the metal center prior to the reductive elimination step.[119] Both halogens (X_2) and mercuric halides (HgX_2) also favor this type of reaction, but if a sufficiently good electrophile is produced during the process (i.e., X^- during an X_2 cleavage reaction), the selectivity shifts toward the direct attack on the α carbon to displace the metal with inversion of stereochemistry (an S_N2 mechanism).[861] Again, only a few examples are available on metal–surface systems for either nucleophilic or electrophilic attacks on hydrocarbons. One example is the displacement of propyne, propylene, or trimethylbenzene (but not *hexa*-methyl benzene) by triethylphosphine on Pd(111).[612] Trimethylphosphine is also capable of displacing a number of adsorbates on copper surfaces,[862] and the ability of bismuth to displace many chemisorbed moieties has been used to develop a method for adsorbate identification based on a variation of temperature-programmed desorption spectroscopy.[863,864] Finally, a closely related reaction, the concerted displacement of the iodine atom in alkyl iodides by adsorbed hydrogen to produce the corresponding alkane, has been seen on Ni(100) substrates.[865]

H. Catalytic Processes

1. Dehydrogenation

Transition metal surfaces are well-known catalysts for a wide variety of hydrocarbon conversion reactions. Many experiments have been carried out on single-crystal surfaces in order to establish a connection between the insights obtained using modern surface-sensitive techniques under vacuum and this catalytic activity. A recent publication reviews most of this work, which includes studies on CO methanation, olefin hydrogenation, dehydrogenation, hydrogenolysis, isomerization and cyclization of alkanes, and acetylene cyclotrimerization.[683] In view of this, only the most important conclusions reached so far in terms of mechanisms for hydrocarbon catalytic processes will be summarized here.

The most studied dehydrogenation reaction in surface science has been the conversion of cyclohexane. This process has been characterized on platinum,[866] ruthenium,[867] and tungsten[868] single crystals. Benzene is the major product in all the cyclohexane conversion reactions reported to date, but cyclohexene, *n*-hexane, and other lighter alkanes are often produced in smaller quantities. Both the dehydrogenation activity and its selectivity are quite sensitive to the structure of the surface, indicating that reasonably large ensemble sites with specific geometries are involved. Indeed, studies on gold–platinum alloys with different compositions proved that dehydrogenation and hydrogenolysis reactions require different geometrical arrangements on the surface.[833,869,870] Cyclohexene is an intermediate in the transition from cyclohexane to benzene, and its yield can be enhanced by blocking surface sites with gold atoms (Figure 18). On the basis of the UHV studies reviewed above, both cyclohexyl and allyl moieties have been proposed as additional intermediates for this reaction.

Other alkanes, once activated and converted into alkyl species, dehydrogenate further with ease. Given the fast rates of hydrogenation and dehydrogenation reactions under the conditions used in most reforming experiments, however, an equilibrium is usually reached between alkanes and alkenes within a few minutes.[871] Furthermore, given the high hydrogen pressures in the reaction mixtures during catalysis, the equilibrium is generally almost completely shifted toward the alkane.[872] In the case of cyclohexene, where dehydrogenation to benzene competes with hydrogenation to cyclohexane, the selectivity between these two paths changes dramatically with total pressure, even if the H_2/cyclohexene ratio is kept constant: the production of benzene dominates at low pressures (10^{-7} Torr), but cyclohexane is formed almost exclusively under high pressures (10^2 Torr) (Figure 18).[842] At low pressures these reactions proceed over clean metal surfaces, and therefore are structure sensitive,[873] but under atmospheric pressures they become structure insensitive, presumably because the continuous presence of about a monolayer of strongly bound carbonaceous species blocks the surface defects.[874,875] This behavior is general in hydrocarbon reforming reactions.[672,674,874,875]

2. Hydrogenation

The best known class of hydrogenation reactions is that of alkenes. Olefin hydrogenation has been studied for ethylene on Pt(111),[681] Rh(111),[144] Ni(100), Ni(111), and Ni(110),[876] for propylene on Ir(111) and Ir(110)-(1×2),[877] for 1,3-butadiene on Pt(100), Pt(110), and Pt(111),[878,879] and for cyclohexene on Pt(111), Pt(223),[844] and Pt(100).[833] The studies on ethylene hydrogenation over Pt(111) have shown that the active catalytic surface in these processes is not clean, but completely covered with a layer of strongly bound hydrocarbon moieties (ethylidyne in the case of ethylene hydrogenation).[681,682] The role of these moieties in the hydrogenation mechanism is still controversial. The idea of ethylidyne being a direct intermediate in the conversion of ethylene to ethane was ruled out by kinetic measurements using ^{13}C- and ^{14}C-labeled compounds, which proved that ethylidyne hydrogenates at a rate several orders of magnitude slower than ethylene.[651,880] The ethylidyne layer does completely cover the surface of the catalyst during the reaction under certain conditions, impeding the adsorption of additional ethylene directly on the metal, but it does not affect the kinetics of the ethylene hydrogenation, since reactions on clean and ethylidyne-presaturated surfaces display identical rates, and since the catalyst does not deactivate over time.[681] These observations led to the initial suggestion that ethylidyne may serve the double role of passivating the metal, preventing the fragmentation of adsorbed ethylene molecules and acting as a transfer agent for atomic hydrogen from the surface to the alkene.[586]

It is logical to think that the same clean metal surface capable of dehydrogenating ethylene to ethylidyne cannot be responsible for catalyzing a mild reaction such as olefin hydrogenation. Indeed, the molecular desorption of ethylene under vacuum never exceeds 20%, and it only happens at coverages close to saturation; complete decomposition takes place at lower coverages. Furthermore, of the 20% of the ethylene that does desorb molecularly, only approximately 5% originates from a weak state similar to that expected to exist under atmospheric pressures.[586] With respect to the idea of ethylidyne acting as a hydrogen transfer agent, this is supported by the fact that ethylidyne is capable of undergoing H–D exchange at the methyl group (at low coverages only under vacuum, but even at saturation under atmospheric pressures). However, since the exchange is several orders of magnitude slower than ethylene hydrogenation, the β hydrogens can be ruled out as hydrogenating agents, and therefore, if ethylidyne were to facilitate the catalytic hydrogenation of ethylene, it would need to undergo an interconversion with another surface species. On the basis of these ideas an equilibrium between ethylidyne (CCH_3) and ethylidene ($CHCH_3$) was originally proposed,[681] but this hypothesis has not yet been adequately tested.

Alternatively, ethylidyne could merely be a spectator species present on the surface during ethylene hydrogenation, which could still take place via the same stepwise mechanism as under vacuum, either on defects or on the platinum sites opened by the removal of ethylidyne. The fact that the activation energy for ethylene hydrogenation is about the same under vacuum and in catalytic conditions support this hypothesis.[586] Also, no ethylidyne buildup is seen on Pd-supported catalysts under certain conditions.[880] The absolute rates for olefin hydrogenation are much higher at high pressures than under vacuum, but the reaction probabilities per alkene molecule impinging on the surface are not: for ethylene that probability is about 2×10^{-2} at 300 K under vacuum, but only 4×10^{-8} at high pressures. If the same mechanism is operative in both pressure regimes, therefore, the catalytic reaction must take place on specific bare metal sites amounting to less than 0.001% of the total surface atoms, and such low concentrations of surface sites are difficult to detect with the surface sensitive equipment available nowadays. More work is needed to distinguish between these two mechanistic views.[586]

3. H–D Exchange

The catalytic exchange of hydrogens for deuteriums in hydrocarbon molecules over single-crystal metals has so far only been studied for a few alkanes on platinum single-crystal surfaces.[674,843,881,882] The kinetic parameters for ethane H–D exchange on Pt(111), namely, the activation energy and the pressure dependence of the rate law, were found to be the same as for polycrystalline foils and supported catalysts. One of the most interesting results from the single-crystal studies is that the product distribution displays an U-shape with maxima at the mono and perdeuterated alkanes. Since Pt(111) surfaces are smooth, there is no reason to believe that there is more than one type of site available for the reaction, and therefore the bimodal product distribution seen in these studies strongly argues for a mechanism where the formation of a common initial intermediate, presumably an alkyl moiety, is followed by two competitive reaction paths. The monodeuterated product can be easily accounted for by the immediate reductive elimination of the alkyl groups by surface deuterium. The production of a large amount of fully deuterated alkane, on the other hand, requires at least two more surface intermediates. Recent NMR and high-resolution mass spectrometric analysis of the ethane products after exchange on polycrystalline samples suggests that one of those intermediates is the adsorbed olefin (Figure 19);[883,884] this is, in fact, to be expected given the ease with which β-hydride elimination occurs in alkyl fragments. The other intermediate has tentatively been identified by low-energy electron diffraction experiments as alkylidyne,[882] the product of thermal activation of alkenes on clean Pt(111) surfaces.

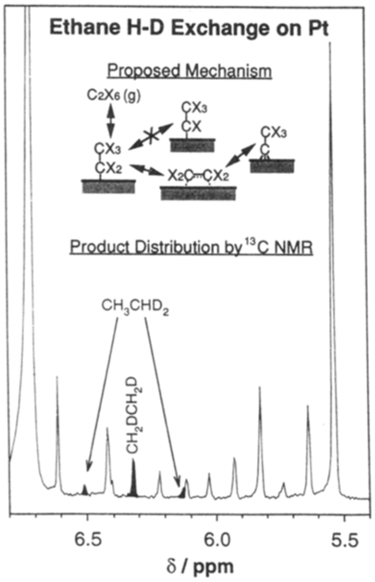


Figure 19. ^{13}C NMR analysis of the ethane product distribution obtained after H–D exchange between normal ethane and deuterium over a platinum foil.[884] The product distribution from these experiments is U-shaped, with maxima at the D_1- and D_6-ethanes. The production of the single-exchanged ethane is explained by an ethane oxidative addition to the surface to produce ethyl moieties on the surface followed by the reductive elimination of that ethyl with surface deuterium. The formation of such large quantities of perdeuterioethane, however, requires the formation of at least two other intermediates on the surface. Since the NMR data show that CH_2DCH_2D is produced preferentially over CH_3CHD_2, it is reasonable to propose ethylene as a second intermediate. This can in fact be easily understood given the ease with which alkyl groups decompose via β-hydride elimination steps. Additional low-energy electron diffraction results on Pt(111) suggest that ethylidyne could be the third surface species in this mechanism.[882]

4. Hydrogenolysis, Isomerization, and Cyclization

Alkane hydrogenolysis has perhaps been the most studied reaction on single crystals under catalytic conditions. Ethane hydrogenolysis has been characterized on Ni(100) and Ni(111),[885] Pt(111),[882,886,887] Ir(111) and Ir(110)-(1×2),[888] Ru(0001) and Ru(1,1,-10),[889] Re(0001),[887] and W(100),[890] as well as on a few alloys. The activation energy for this reaction ranges from about 18 to 50 kcal/mol, much higher than that for hydrogenation–dehydrogenation processes because higher energies are required to break C–C than C–H bonds. This observation has led to the proposal of several mechanisms where dehydrogenation steps precede the breaking of the hydrocarbon chain; the breaking of the C–C bond most likely occurs only in highly dehydrogenated surface species. In addition, the majority of the hydrogenolysis reactions are structure sensitive, being faster on open surfaces, and take place in the presence of a carbonaceous layer on the surface of the catalyst. Studies on the hydrogenolysis of propane, butane, neopentane, *n*-hexane, *n*-heptane, cyclopropane, methylcyclopropane, methylcyclopentane, and cyclohexane have provided additional mechanistic information for this reaction.[683] For instance, the selectivity between 2- and 3-methylpentane production by methylcyclopentane ring opening reflects the relative importance of selective and nonselective C–C bond-breaking steps directly.[872,891] Due to the limitations of the experimental techniques available at the present time for such studies, however, data on in situ identification of intermediates during catalytic reactions by spectroscopic means are scarce.

Many hydrogenolysis studies include data on the competing isomerization and/or cyclization reactions.[683] Skeletal rearrangements are usually favored over hydrogenolysis reactions.[872] Cyclization steps to aliphatic and aromatic compounds are also observed for chains with five or more carbon atoms. The conversion of *n*-hexane over platinum surfaces, for instance, yields significant quantities of methyl cyclopentane and benzene, and the isomerization to methyl pentanes in this system also proceeds via the formation of a C_5 ring.[892] Once again, direct information on the surface intermediates is not available.

5. Other C–C Bond-Forming Reactions

An interesting reaction involving C–C bond-formation steps is the cyclotrimerization of acetylene over palladium catalysts.[893] This reaction is surface sensitive, being about five times faster on Pd(111) than on Pd(110). Also, it appears as if the high-pressure reaction takes place via the formation of a C_4 intermediate on the bare metal, the same as under vacuum.[791] However, since acetylene trimerization competes with its conversion to vinylidene, the rate for benzene formation under catalytic conditions is possibly limited by the availability of surface sites, as is the case in olefin hydrogenations.

Another type of reaction involving C−C bond-formation steps is the Fischer-Tropsch process. Unfortunately, the conversion of CO−hydrogen gas mixtures to hydrocarbons on single-crystal metal surfaces has only been studied in detail on nickel substrates, where the main reaction product is methane.[894] The initial rate-limiting step in that case is the dissociation of the C−O bond, which is followed by the stepwise hydrogenation of the resulting carbidic carbon. The fact that only methane is formed on these nickel surfaces indicates that hydrogen incorporation in all carbide, methylidyne, methylene, and methyl intermediates is much faster than C−C coupling or methylene insertion reactions. Methane is also the main CO hydrogenation product on other surfaces, but longer chain hydrocarbons do form on Co(0001), Co(11$\bar{2}$0) and Co(10$\bar{1}$2),[895] Rh(111),[896] Fe(111),[897] and Mo(100).[898] As in the case of nickel, the relative selectivity between chain growth and chain termination (alkane formation) in these cases depends on the relative rates of the reductive elimination and methylene migratory insertion steps. Finally, propylene can also undergo a metathesis reaction on either Mo(100) or molybdenum foils to yield ethylene and butene.[791]

V. Conclusions

Throughout this review we have attempted to systematically survey the present knowledge on both the structure and the thermal chemistry of hydrocarbon moieties on surfaces. In particular, analogies have been drawn, when possible, between surface and organometallic systems. Many examples were indeed found for this. In terms of the structure of the adsorbed hydrocarbons, for instance, single σ-bonded species such as alkyls, alkenyls, aryls, and acetylides, multiple σ-bonded moieties such as alkylidenes, alkylidynes, vinylidenes, and metallacycles, and π-bonded molecules such as alkenes, alkynes, dienes, allyls, and arenes, have all been seen both in organometallic complexes and on metal surfaces. With respect to reactivity, examples of these similarities were seen in the conversion of alkyl groups to olefins by β-hydride elimination and in their reduction with hydrogen or other alkyl moieties to yield alkanes.

As already mentioned in the introduction, the similarities in chemical behavior between hydrocarbon ligands in organometallic complexes and hydrocarbon species adsorbed on surfaces can be justified by the localized nature of the chemical bond between the metal atoms and the hydrocarbon moieties on surfaces. There are, however, some differences between these two types of systems worth discussing in some detail. For example, the C−H bonds in unsaturated adsorbates such as olefins are easier to activate on surfaces than on discrete metal complexes. The conversion of adsorbed neopentyl groups to isobutene is also difficult to explain in terms of known organometallic processes. C−C coupling and methylene and olefin migratory insertion reactions are apparently easier with coordinated ligands than with chemisorbed fragments on solid surfaces, at least under vacuum. Finally, heterogeneous systems catalyze a much larger number of reactions than their organometallic counterparts, but they usually exhibit much poorer selectivity toward any given pathway. These differences can be addressed by elaborating on the initial model for surface bonding discussed above, since several parameters need to be considered in order to fine-tune the description of the hydrocarbon−metal bonding. First of all, since the electronic structure of metals is quite complex, it cannot be simply divided into sp and d electronic bands, because those two bands do not only interact with each other but are also affected by the surrounding environment. For example, peripheral ligands do affect the chemistry of organometallic complexes. An extreme of this is the so called *trans* effect, by which a change in the nature of the ligand opposite to the hydrocarbon moiety being investigated modifies the strength of its metal−carbon bond. Another factor to consider in inorganic complexes is the formal oxidation state of the central metal atom(s). These variations do not have direct parallels on surfaces, but the electronic structure of solids can be modified to some extent by the coadsorption of electron-donating or electron-withdrawing elements such as alkaline metals or halides, respectively, or by alloying two or more metals. Much research activity in the surface science community is nowadays focused on the study of these effects.

Differences in coordination geometry between solids and organometallic compounds are important in the determination of hydrocarbon reactivity as well. Clearly, ligands are much less affected by steric hindrance in organometallic complexes than on surfaces. This may be the reason why both reductive elimination and migratory insertion steps occur at a faster rate in metal complexes, especially if they involve two hydrocarbon moieties. On the other hand, coordination in organometallic systems is somewhat limited by the 18-electron-per-metal-atom rule that they need to obey; due to the delocalized nature of electrons in solids, the adherence to this rule on surfaces is less strict. Also, surfaces offer a wide variety of metal atom ensembles which are hard to emulate with discrete metal clusters; this difference is critical in reactions such as dehydrogenation or skeletal rearrangements, which require large catalytic ensembles. Furthermore, the spatial orientation of the metal atomic orbitals in surfaces is fixed by the structure of the bulk, so they are exposed in different orientations depending on the crystallographic plane of the chosen surface. This effect constitutes a major reason for the structure sensitivity observed in many catalytic reactions. Lastly, changes in surface coverage not only affect the relative rates of unimolecular and bimolecular reactions, but can also induce adsorbate−adsorbate interactions, and even modify the electronic characteristics of the surface; high surface coverages usually lead to appreciable changes in both adsorption energies and reaction rates. More research is needed in order to learn to exploit these differences.

Research on the chemistry of hydrocarbons on surfaces is still in its infancy, and much work is needed to obtain a complete understanding of the parameters that control the structure and reactivity in those systems. For one, systematic studies are required on the chemisorption and conversion of moieties on different crystallographic orientations of the same metal and on different metals across the periodic table in order to establish reactivity trends. In fact, although this point was not emphasized throughout our review, a few of those systematic variations have already been identified. The relative selectivity between C–C coupling and hydride elimination in alkyl groups for instance, increases from left to right in the periodic table d series: β-hydride elimination dominates the chemistry of those alkyl species on platinum and nickel surfaces, but competition with coupling reactions take place on copper and gold, and exclusive C–C bond formation occurs on silver. Both the identification of other trends and the explanation of the ones already reported await the gathering of more experimental results.

Inorganic chemists can also help in the understanding of surface systems and in connecting the knowledge from discrete molecules to solids. In particular, more work is needed in the area of cluster chemistry in order to be able to design compounds with a given metallic core and to study the reactivity of ligands on those frames. Systematic studies as a function of variables such as size, structure, and coordination numbers can greatly enhance our understanding of the changes in hydrocarbon chemistry that occur in going from single atoms to solid surfaces. Finally, more refined structural and dynamic theoretical studies can help in deciding on the relative stability of closely related chemisorbed species and can aid in determining what other parameters control the selectivity among reactions with comparable activation energies. The payoff of all this will be an increased understanding of the many processes that involve surface reactivity. This, of course, includes heterogeneous catalysis, but also encompasses a range of other technologies, from tribology to electrochemistry and chemical vapor deposition. A better understanding of the surface chemistry in those systems will in turn result in the potential for designing new and better processes, not merely by trial and error, but in a systematic and knowledgeable way.

VI. Acknowledgments

We would like to thank Brian E. Bent, Nancy Gleason, Ton. V. W. Janssens, and Wilfred T. Tysoe for their help in proofreading this manuscript. Financial support for this research was provided by grants from the National Science Foundation and the Department of Energy.

VIII. References

(1) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
(2) Albert, M. R.; Yates, J. T., Jr. *The Surface Scientist's Guide to Organometallic Chemistry*; American Chemical Society: Washington, 1987.
(3) Zaera, F. *J. Mol. Catal.* **1994**, *86*, 221.
(4) Bent, B. E.; Somorjai, G. A. *Adv. Colloid Interface Sci.* **1989**, *29*, 223.
(5) Netzer, F. P.; Ramsey, M. G. *Crit. Rev. Solid State Mater. Sci.* **1992**, *17*, 397.
(6) Posternak, M.; Krakauer, H.; Freeman, A. J.; Koelling, D. D. *Phys. Rev. B* **1980**, *21*, 5601.
(7) Plummer, E. W.; Salaneck, W. R.; Miller, J. S. *Phys. Rev. B* **1978**, *18*, 1673.
(8) Conrad, H.; Ertl, G.; Knozinger, H.; Küppers, J.; Latta, E. E. *Chem. Phys. Lett.* **1976**, *42*, 115.
(9) Hoffmann, R. *Solid and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988.
(10) Eischens, R. P.; Pliskin, W. A. *Adv. Catal.* **1958**, *10*, 1.
(11) Richardson, N. V.; Bradshaw, A. M. *Surf. Sci.* **1979**, *88*, 255.
(12) Demuth, J. E.; Ibach, H. *Surf. Sci.* **1979**, *85*, 365.
(13) Skinner, P.; Howard, M. W.; Oxton, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1203.
(14) Rabalais, J. W. *Principles of Ultraviolet Photoelectron Spectroscopy*; John Wiley & Sons: New York, 1977.
(15) Plummer, E. W.; Loubriel, G.; Rajoria, D.; Albert, M. R.; Sneddon, L. G.; Salaneck, W. R. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 35.
(16) Ertl, G.; Küppers, J. *Low Energy Electrons and Surface Chemistry*; VCH: Weinheim, 1985.
(17) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
(18) Zangwill, A. *Physics at Surfaces*; Cambridge University Press: Cambridge, 1988.
(19) Hudson, J. B. *Surface Science: An Introduction*; Butterworth-Heinemann: Boston, 1992.
(20) Woodruff, D. P.; Delchar, T. A. *Modern Techniques of Surface Science*; Cambridge University Press: Cambridge, 1986.
(21) Niemantsverdriet, J. W. *Spectroscopy in Catalysis: An Introduction*; VCH: Weinheim, 1993.
(22) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, 1977.
(23) Green, M. L. H. *Organometallic Compounds*; Methuen: London, 1968; Vol. II [The Transition Elements].
(24) Cotton, F. A.; Wilkinson, G.; Gaus, P. L. *Basic Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1987.
(25) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.
(26) Holton, H.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Chem. Commun.* **1976**, 425.
(27) Kruger, C.; Sekutowski, J.; Berke, H.; Hoffmann, R. *Z. Naturforsch. B, Anorg. Chem.* **1978**, *33B*, 1110.
(28) Hursthouse, M. B.; Malik, K. M. A.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 826.
(29) Andersen, R. A.; Carmore-Guzumbra, E.; Gibson, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 2204.
(30) Waymoth, R. B.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050.
(31) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.
(32) Park, J. W.; Mackenzie, P. B.; Schafer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6402.
(33) Zaera, F. *Acc. Chem. Res.* **1992**, *25*, 260.
(34) Zhou, X.-L.; Yoon, C.; White, J. M. *Surf. Sci.* **1988**, *206*, 379.
(35) Benziger, J. B.; Madix, R. J. *J. Catal.* **1980**, *65*, 49.
(36) Zhou, Y.; Henderson, M. A.; Feng, W. M.; White, J. M. *Surf. Sci.* **1989**, *224*, 386.
(37) Steinbach, F.; Kiss, J.; Krall, R. *Surf. Sci.* **1985**, *157*, 401.
(38) Solymosi, F.; Klivényi, G. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64/65*, 499.
(39) Zhou, X.-L.; White, J. M. *Surf. Sci.* **1988**, *194*, 438.
(40) Tjandra, S.; Zaera, F. *Langmuir* **1992**, *8*, 2090; **1993**, *9*, 880.
(41) Tjandra, S.; Zaera, F. *Surf. Sci.* **1993**, *289*, 255.
(42) Tjandra, S.; Zaera, F. *Langmuir* **1994**, *10*, 2640.
(43) Maesh, E. P.; Tabares, F. L.; Schneider, M. R.; Gilton, T. L.; Meier, W.; Cowin, J. P. *J. Chem. Phys.* **1990**, *92*, 2004.
(44) Tjandra, S.; Zaera, F. *J. Am. Chem. Soc.* **1995**, *117*, 9749.
(45) Solymosi, F.; Kiss, J.; Révész, K. *J. Phys. Chem.* **1990**, *94*, 2224.
(46) Solymosi, F.; Kiss, J.; Révész, K. *J. Chem. Phys.* **1991**, *94*, 8510.
(47) Solymosi, F.; Révész, K. *Surf. Sci.* **1993**, *280*, 38.
(48) Kovács, I.; Solymosi, F. *J. Phys. Chem.* **1993**, *97*, 11056.
(49) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci.* **1987**, *184*, L325.
(50) Zaera, F. *Surf. Sci.* **1989**, *219*, 453.
(51) Zaera, F.; Hoffmann, H.; Griffiths, P. R. *J. Electron Spectros. Relat. Phenom.* **1990**, *54/55*, 705.
(52) Zaera, F.; Hoffmann, H. *J. Phys. Chem.* **1991**, *95*, 6297.
(53) Hoffmann, H.; Griffiths, P. R.; Zaera, F. *Surf. Sci.* **1992**, *262*, 141.
(54) Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, *214*, 227.

(55) Roop, B.; Lloyd, K. G.; Costello, S. A.; Campion, A.; White, J. M. *J. Chem. Phys.* **1989**, *91*, 5103.

(56) Liu, Z.-M.; Costello, S. A.; Roop, B.; Coon, S. R.; Akhter, S.; White, J. M. *J. Phys. Chem.* **1989**, *93*, 7681.

(57) Liu, Z.-M.; Akhter, S.; Roop, B.; White, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 8708.

(58) Ukraintsev, V. A.; Harrison, I. *J. Chem. Phys.* **1993**, *98*, 5971.

(59) Lin, J.-L.; Bent, B. E. *J. Phys. Chem.* **1993**, *97*, 9713.

(60) Lin, J.-L.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2849.

(61) Lin, J.-L.; Bent, B. E. *J. Vac. Sci. Technol. A* **1992**, *10*, 2202.

(62) Chiang, C.-M.; Wentzlaff, T. H.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 1836.

(63) Lin, J.-L.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 6943.

(64) Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. *J. Am. Chem. Soc.* **1993**, *115*, 308.

(65) Magrini, K. A.; Gebhard, S. C.; Koel, B. E.; Falconer, J. L. *Surf. Sci.* **1991**, *248*, 93.

(66) Zhou, X.-L.; White, J. M. *J. Phys. Chem.* **1991**, *95*, 5575.

(67) Zhou, X.-L.; Solymosi, F.; Blass, P. M.; Cannon, K. C.; White, J. M. *Surf. Sci.* **1989**, *219*, 294.

(68) Zhou, X.-L.; White, J. M. *Catal. Lett.* **1989**, *2*, 375.

(69) Zhou, X.-L.; White, J. M. *Surf. Sci.* **1991**, *241*, 270.

(70) Ali, A.-K. M.; Saleh, J. M.; Hikmat, N. A. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2391.

(71) Paul, A.; Yang, M. X.; Bent, B. E. *Surf. Sci.* **1993**, *297*, 327.

(72) Zhou, X.-L.; Zhu, X.-L.; White, J. M. *Acc. Chem. Res.* **1990**, *23*, 327.

(73) Tjandra, S.; Zaera, F. *J. Vac. Sci. Technol. A* **1992**, *10*, 404.

(74) Lin, J.-L.; Bent, B. E. *J. Phys. Chem.* **1992**, *96*, 8529.

(75) Zaera, F.; Hoffmann, H.; Griffiths, P. R. *Vacuum* **1990**, *41*, 735.

(76) Zaera, F.; Tjandra, S. *J. Phys. Chem.* **1994**, *98*, 3044.

(77) Ceyer, S. T.; Beckerle, J. D.; Lee, M. B.; Tang, S. L.; Yang, Q. Y.; Hines, M. A. *J. Vac. Sci. Technol. A* **1987**, *5*, 501.

(78) Lin, J.-L.; Bent, B. E. *Chem. Phys. Lett.* **1992**, *194*, 208.

(79) Yang, Q. Y.; Maynard, K. J.; Johnson, A. D.; Ceyer, S. T. *J. Chem. Phys.* **1995**, *102*, 7734.

(80) Schule, J.; Siegbahn, P.; Wahlgren, U. *J. Chem. Phys.* **1988**, *89*, 6982.

(81) Yang, H.; Whitten, J. L. *Surf. Sci.* **1991**, *255*, 193.

(82) Siegbahn, P. E. M.; Panas, I. *Surf. Sci.* **1990**, *240*, 37.

(83) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *Surf. Sci.* **1995**, *324*, 345.

(84) Burghgraef, H. Ph.D. Thesis, Technical University of Eindhoven, The Netherlands, 1995.

(85) Hanley, L.; Guo, X.; Yates, J. T., Jr. *Surf. Sci.* **1990**, *232*, 129.

(86) Hanley, L.; Guo, X.; Yates, J. T., Jr. *J. Phys. Chem.* **1989**, *93*, 6754.

(87) Gebhard, S. C.; Frueh, J. L.; Ellison, G. B.; Koel, B. E. *Surf. Sci.* **1995**, submitted for publication.

(88) Berlowitz, P.; Yang, B. L.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1986**, *171*, 69.

(89) Weldon, M. K.; Friend, C. M. *Surf. Sci.* **1994**, *310*, 95.

(90) Jentz, D.; Trenary, M.; Peng, X. D.; Stair, P. *Surf. Sci.* **1995**, *341*, 282.

(91) Gleason, N.; Jenks, C. J.; Bent, B. E.; Zaera, F. *Surf. Sci.* **1995**, submitted for publication.

(92) Smudde, G. H., Jr.; Peng, X. D.; Viswanathan, R.; Stair, P. C. *J. Vac. Sci. Technol. A* **1991**, *9*, 1885.

(93) Chiang, C.-M.; Bent, B. E. *Surf. Sci.* **1992**, *279*, 79.

(94) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. T. *J. Chem. Phys.* **1986**, *85*, 1693.

(95) Strongin, D.; Mowlem, J. *Chem. Phys. Lett.* **1991**, *63*, 175.

(96) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634.

(97) Lee, T. R.; Whitesides, G. M. *Acc. Chem. Res.* **1992**, *25*, 266.

(98) Kovács, I.; Iost, N.; Solymosi, F. *J. Chem. Phys.* **1994**, *101*, 4236.

(99) Pansoy-Hjelvik, M. E.; Xu, R.; Gao, Q.; Weller, K.; Feher, F.; Hemminger, J. C. *Surf. Sci.* **1994**, *312*, 97.

(100) Paul, A.; Bent, B. E.; Seidler, P. F. *J. Am. Chem. Soc.* **1995**, submited for publication.

(101) Xi, M.; Bent, B. E. *J. Vac. Sci. Technol. B* **1992**, *10*, 2440.

(102) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 2780.

(103) White, J. M. *Langmuir* **1995**, in press.

(104) Yagupsky, G.; Mowat, W.; Shortland, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1970**, 1369.

(105) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organometal. Chem.* **1970**, *25*, C36.

(106) Armentrout, P. B.; Georgiadis, R. *Polyhedron* **1988**, *7*, 1573.

(107) Hall, P. W.; Puddephatt, R. J.; Seddon, K. R.; Tipper, C. F. H. *J. Organometal. Chem.* **1974**, *81*, 423.

(108) Brown, D. L. S.; Connor, J. A.; Skinner, H. A. *J. Organometal. Chem.* **1974**, *81*, 403.

(109) Egger, K. W. *J. Organometal. Chem.* **1970**, *24*, 501.

(110) Zaera, F. *Surf. Sci.* **1992**, *262*, 335.

(111) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 8350.

(112) Tjandra, S.; Zaera, F. *J. Catal.* **1993**, *144*, 361.

(113) Tjandra, S.; Zaera, F. *Langmuir* **1994**, *9*, 880.

(114) Masetti, G.; Zerbi, G. *Spectrochim. Acta* **1970**, *26A*, 1891.

(115) Kaesz, H. D.; Stone, F. G. A. *Spectrochim. Acta* **1959**, *15*, 360.

(116) Beverwijk, C. D. M.; Van Der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organometal. Chem. Rev.* **1970**, *A5*, 215.

(117) Cardin, C. J.; Cardin, D. J.; Roy, A. *J. Chem. Soc., Chem. Commun.* **1978**, 899.

(118) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fijioka, A.; Kodama, S.-I.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

(119) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987.

(120) Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.

(121) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202.

(122) Cardin, C. J.; Cardin, D. J.; Kelly, J. M.; Norton, R. J.; Roy, A. *J. Organometal. Chem.* **1977**, *132*, C23.

(123) Falbe, J. *New Synthesis with Carbon Monoxide*; Springer Verlag: New York, 1980.

(124) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1983**, 639.

(125) Caddy, P.; Green, M.; Smart, L. E.; White, N. *J. Chem. Soc., Chem. Commun.* **1978**, 839.

(126) Andrews, J.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *Inorg. Chem.* **1982**, *21*, 2874.

(127) Hall, R. B.; Bares, S. J.; DeSantolo, A. M.; Zaera, F. *J. Vac. Sci. Technol. A,* **1986**, *4*, 1493.

(128) Zaera, F.; Hall, R. B. *Surf. Sci.* **1987**, *180*, 1.

(129) Zaera, F.; Fischer, D. A.; Carr, R. G.; Gland, J. L. *J. Chem. Phys.* **1988**, *89*, 5335.

(130) Liu, Z.-M.; Zhou, X.-L.; Buchanan, D. A.; Kiss, J.; White, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 2031.

(131) Zaera, F.; Bernstein, N. *J. Am. Chem. Soc.* **1994**, *116*, 4881.

(132) Yang, M. X.; Eng, J., Jr.; Kash, P. W.; Flynn, G. W.; Bent, B. E.; Holbrook, M. T.; Bare, S. R.; Gland, J. L.; Fischer, D. A. *J. Phys. Chem.* **1995**, submitted for publication.

(133) Zhou, X.-L.; Schwaner, A. L.; White, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 4309.

(134) Fischer, T. E.; Kelemen, S. R. *Surf. Sci.* **1977**, *69*, 485.

(135) Clarke, T. A.; Gay, I. D.; Law, B.; Mason, R. *Faraday Discuss. Chem. Soc.* **1975**, *60*, 119.

(136) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.

(137) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46.

(138) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

(139) Kesmodel, L. L.; Waddill, G. D.; Gates, J. A. *Surf. Sci.* **1984**, *138*, 464.

(140) Zaera, F.; Hall, R. B. *J. Phys. Chem.* **1987**, *91*, 4318.

(141) Stroscio, J. A.; Bare, S. R.; Ho, W. *Surf. Sci.* **1984**, *148*, 499.

(142) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554.

(143) Marinova, T. S.; Kostov, K. L. *Surf. Sci.* **1987**, *181*, 573.

(144) Bent, B. E. Ph.D. Thesis, University of California, Berkeley, 1986.

(145) Slavin, A. J.; Bent, B. E.; Kao, C.-T.; Somorjai, G. A. *Surf. Sci.* **1988**, *206*, 124.

(146) Bent, B. E.; Mate, C. M.; Crowell, J. E.; Koel, B. E.; Somorjai, G. A. *J. Phys. Chem.* **1987**, *91*, 1493.

(147) Koel, B. E.; Crowell, J. E.; Bent, B. E.; Mate, C. M.; Somorjai, G. A. *J. Phys. Chem.* **1986**, *90*, 2949.

(148) Mate, C. M.; Kao, C.-T.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1988**, *197*, 183.

(149) Zeiss, H. H.; Sneeden, R. P. A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 435.

(150) Sarry, B.; Velling, P. *Z. Anorg. Allg. Chem.* **1976**, *426*, 107.

(151) Keim, W. *J. Organometal. Chem.* **1968**, *14*, 179.

(152) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.

(153) Cross, R. J. *Organometal. Chem. Rev.* **1962**, *2*, 97.

(154) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

(155) Bunnett, J. F. *Quart. Rev. Chem. Soc.* **1958**, *12*, 1.

(156) Blum, J.; Weitzberg, M. *J. Organometal. Chem.* **1976**, *122*, 261.

(157) Parshall, G. *Acc. Chem. Res.* **1975**, *8*, 113.

(158) Carroll, W. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1978**, 825.

(159) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

(160) Zhou, X.-L.; Castro, M. E.; White, J. M. *Surf. Sci.* **1990**, *238*, 215.

(161) Zhou, X. *J. Chem. Phys.* **1990**, *92*, 5612.

(162) Xi, M.; Bent, B. E. *Surf. Sci.* **1992**, *278*, 19.

(163) Tjandra, S.; Zaera, F. To be published.

(164) Myli, K. B.; Grassian, V. H. *J. Phys. Chem.* **1994**, *98*, 6237.

(165) Graen, H. H.; Neuber, M.; Neumann, M.; Illing, G.; Freund, H.-J.; Netzer, F.-P. *Surf. Sci.* **1989**, *223*, 33.

(166) Huntley, D. R.; Jordan, S. L.; Grimm, F. A. *J. Phys. Chem.* **1992**, *96*, 1409.

(167) Fischer, E. O. *Adv. Organometal. Chem.* **1976**, *14*, 1.

(168) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545.

(169) Schrock, R. R. *Acc. Chem. Res.* **1977**, *12*, 98.

(170) Ushio, J.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5892.

(171) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(172) Schaefer, H. F., III. *Acc. Chem. Res.* **1977**, *10*, 287.
(173) Herrmann, W. A.; Ziegler, M. L.; Weidenhammer, K.; Biersack, H.; Mayer, K. K.; Minard, R. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 164.
(174) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988.
(175) Herrmann, W. A. *Adv. Organometal. Chem.* **1982**, *20*, 159.
(176) Summer, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.
(177) Herrmann, W. A.; Schweizer, I.; Creswick, M.; Bernal, I. *J. Organometal. Chem.* **1979**, *165*, C17.
(178) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.
(179) Hong, P.; Nishii, N.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1972**, 993.
(180) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29.
(181) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852.
(182) George, P. M.; Avery, N. R.; Weinberg, W. H.; Tebbe, F. N. *J. Am. Chem. Soc.* **1983**, *105*, 1393.
(183) McBreen, P. H.; Erley, W.; Ibach, H. *Surf. Sci.* **1984**, *148*, 292.
(184) Henderson, M. A.; Radloff, P. L.; White, J. M.; Mims, C. A. *J. Phys. Chem.* **1988**, *92*, 4111.
(185) Mitchell, G. E.; Radloff, P. L.; Greenlief, C. M.; Henderson, M. A.; White, J. M. *Surf. Sci.* **1987**, *183*, 403.
(186) Klivényi, G.; Solymosi, F. *Surf. Sci.* **1995**, in press.
(187) Weldon, M. K.; Friend, C. M. *Surf. Sci.* **1994**, *321*, L202.
(188) Radloff, P. L.; Mitchell, G. E.; Greenlief, C. M.; White, J. M.; Mims, C. A. *Surf. Sci.* **1987**, *183*, 377.
(189) Berlowitz, P.; Yang, B. L.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1985**, *159*, 540.
(190) Solymosi, F.; Kovács, I. *Surf. Sci.* **1993**, *296*, 171.
(191) Chiang, C.-M.; Wentzlaff, T. H.; Jenks, C. J.; Bent, B. E. *J. Vac. Sci. Technol. A* **1992**, *10*, 2185.
(192) Lin, J.-L.; Chiang, C.-M.; Jenks, C. J.; Yang, M. X.; Wentzlaff, T. H.; Bent, B. E. *J. Catal.* **1994**, *147*, 250.
(193) Zhou, X.-L.; Liu, Z.-M.; Kiss, J.; Sloan, D. W.; White, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3565.
(194) Janssens, T. V. W.; Zaera, F. *J. Phys. Chem.* **1995**, submitted for publication.
(195) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857.
(196) Davis, D. L.; Dyke, A. F.; Felder, A. E.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organometal. Chem.* **1980**, *198*, C43.
(197) Voyevodskaya, T. M.; Pribytkova, I. M.; Ustynyuk, Y. A. *J. Organometal. Chem.* **1972**, *37*, 187.
(198) Seyferth, D. *Adv. Organometal. Chem.* **1976**, *14*, 97.
(199) Canty, A. J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R. *J. Chem. Soc., Chem. Commun.* **1972**, 331.
(200) Miller, D. C.; Brill, T. B. *Inorg. Chem.* **1978**, *17*, 240.
(201) Chesky, P. T.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 4419.
(202) Backx, C.; Willis, R. F. *Chem. Phys. Lett.* **1978**, *53*, 471.
(203) Demuth, J. E.; Ibach, H. *Surf. Sci.* **1978**, *78*, L238.
(204) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.
(205) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 105.
(206) Baro, A. M.; Ibach, H. *J. Chem. Phys.* **1981**, *74*, 4194.
(207) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *J. Chem. Phys.* **1979**, *70*, 2180.
(208) Ibach, H. In *Int. Conf. Vib. in Ads. Layers*; Jülich, 1978; pp 64–75.
(209) Hatzikos, G. H.; Masel, R. I. *Surf. Sci.* **1987**, *185*, 479.
(210) Dubois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234.
(211) Kesmodel, L. L.; Gates, J. A. *Surf. Sci.* **1981**, *111*, L747.
(212) Barteau, M. A.; Broughton, J. Q.; Menzel, D. *Appl. Surf. Sci.* **1984**, *19*, 92.
(213) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1985**, *89*, 3606.
(214) Beebe, T. P., Jr.; Albert, M. R.; Yates, J. T., Jr. *J. Catal.* **1985**, *96*, 1.
(215) Lapinski, M. P.; Ekerdt, J. G. *J. Phys. Chem.* **1988**, *92*, 1708.
(216) Land, T. A.; Michely, T.; Behm, R. J.; Hemminger, J. C.; Comsa, G. *J. Chem. Phys.* **1992**, *97*, 6774.
(217) Starke, U.; Barbieri, A.; Materer, N.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1993**, *286*, 1.
(218) Koestner, R. J.; Stöhr, J.; Gland, J. L.; Horsley, J. A. *Chem. Phys. Lett.* **1984**, *105*, 332.
(219) Freyer, N.; Pirug, G.; Bonzel, H. P. *Surf. Sci.* **1983**, *126*, 487.
(220) Albert, M. R.; Sneddon, L. G.; Eberhardt, W.; Greuter, F.; Gustafsson, T.; Plummer, E. W. *Surf. Sci.* **1982**, *120*, 19.
(221) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, *56*, 267.
(222) Stuck, A.; Wartnaby, C. E.; Yeo, Y. Y.; King, D. A. *Phys. Rev. Lett.* **1995**, *74*, 578.
(223) Salmerón, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, *86*, 341.
(224) Koestner, R. J.; Frost, J. C.; Stair, P. C.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *116*, 85.
(225) Koestner, R. J.; Van Hove, M. A.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 203.
(226) Wang, D.; Li, Y.; Liu, H.; Zhai, R.; Guo, X. *Catal. Lett.* **1989**, *2*, 9.
(227) Avery, N. R.; Sheppard, N. *Surf. Sci.* **1986**, *169*, L367.
(228) Avery, N. R.; Sheppard, N. *Proc. R. Soc. Lond. A* **1986**, *405*, 27.
(229) Avery, N. R.; Sheppard, N. *Proc. R. Soc. Lond. A* **1986**, *405*, 1.
(230) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organometal. Chem.* **1983**, *22*, 129.
(231) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403.
(232) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organometal. Chem.* **1977**, *137*, 55.
(233) Kirchner, R. M.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1667.
(234) Roper, W. R.; Waters, J. M.; Wright, L. J.; van Meurs, F. *J. Organometal. Chem.* **1980**, *201*, C27.
(235) Brun, P.; Dawkins, G. M.; Green, M.; Kills, R. M.; Salaün, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 966.
(236) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.
(237) Farrar, D. H.; John, G. R.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Chem. Commun.* **1981**, 886.
(238) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.
(239) Berke, H. *Chem. Ber.* **1980**, *113*, 1370.
(240) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
(241) Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T. *J. Phys. Chem.* **1994**, *98*, 2134.
(242) Wang, P.-W.; Slichter, C. P.; Sinfelt, J. H. *Phys. Rev. Lett.* **1984**, *53*, 82.
(243) Hills, M. M.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597.
(244) Akhter, S.; White, J. M. *Surf. Sci.* **1987**, *180*, 19.
(245) Demuth, J. E. *Surf. Sci.* **1979**, *80*, 367.
(246) Ibach, H.; Hopster, H.; Sexton, B. *Appl. Surf. Sci.* **1977**, *1*, 1.
(247) Hemminger, J. C.; Muetterties, E. L.; Somorjai, G. A. *J. Am. Chem. Soc.* **1979**, *101*, 62.
(248) Brucker, C.; Rhodin, T. *J. Catal.* **1977**, *47*, 214.
(249) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.
(250) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.
(251) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461.
(252) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.
(253) Whitesides, G. M.; Reamey, R. H.; Brainard, R. L.; Izumi, A. N.; McCarthy, T. J. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 56.
(254) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448.
(255) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425.
(256) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.
(257) Puddephatt, R. J. *Comments Inorg. Chem.* **1982**, *2*, 69.
(258) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.
(259) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3106.
(260) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1978**, *100*, 2418.
(261) Ozawa, F.; Yamamoto, A.; Ikariya, T.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1482.
(262) Churchill, M. R.; Wasserman, H. J. *J. Organometal. Chem.* **1984**, *270*, 201.
(263) Erker, G.; Krüger, C.; Müller, G. *Adv. Organometal. Chem.* **1985**, *24*, 1.
(264) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.
(265) Krause, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2972.
(266) Patterson, C. H.; Mundenar, J. M.; Timbrell, P. Y.; Gellman, A. J.; Lambert, R. M. *Surf. Sci.* **1989**, *208*, 93.
(267) Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F.; Yao, J. M.; Saldin, D. K.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T. *Surf. Sci.* **1993**, *295*, 277.
(268) Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 1143.
(269) Tjandra, S.; Zaera, F. To be published.
(270) Heise, W. H.; Tatarchuck, B. J. *Surf. Sci.* **1989**, *207*, 297.
(271) Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44.
(272) Netzer, F. P.; Bertel, E.; Goldmann, A. *Surf. Sci.* **1988**, *201*, 257.
(273) Stöhr, J.; Gland, J. L.; Kollin, E. B.; Koestner, R. J.; Johnson, A. L.; Muetterties, E. L.; Sette, F. *Phys. Rev. Lett.* **1984**, *53*, 2161.
(274) Zaera, F.; Kollin, E. B.; Gland, J. L. *Langmuir* **1987**, *3*, 555.
(275) Schoofs, G. R.; Preston, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313.
(276) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75.
(277) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.
(278) Ittel, S. D.; Ibers, J. A. *Adv. Organometal. Chem.* **1976**, *14*, 33.
(279) Redhouse, A. D. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1982; Vol. I [The Structure, Preparation, Thermochemistry and Characterization of Organometallic Compounds], pp 1–41.
(280) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

(281) Gallop, M. A.; Johnson, B. F. G.; Keeler, J.; Lewis, J.; Heyes, S. J.; Dobson, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 2510.
(282) Matheson, T. W. Unpublished results.
(283) Bertolini, J. C.; Massardier, J. In *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1984; Vol. 3B [Chemisorption Systems], pp 107–136.
(284) Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589.
(285) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 3183.
(286) Bent, B. E.; Mate, C. M.; Kao, C.-T.; Slavin, A. L.; Somorjai, G. A. *J. Phys. Chem.* **1988**, *92*, 4720.
(287) Steininger, M.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.
(288) Seip, U.; Tsai, M. C.; Küppers, J.; Ertl, G. *Surf. Sci.* **1984**, *147*, 65.
(289) Lehwald, S.; Ibach, H. *Surf. Sci.,* **1979**, *89*, 425.
(290) Hamilton, J. C.; Swanson, N.; Waclawski, B. J.; Celotta, R. J. *J. Chem. Phys.* **1981**, *74*, 4156.
(291) Nyberg, C.; Tengstal, C. G.; Anderson, S.; Holmes, M. W. *Chem. Phys. Lett.* **1982**, *87*, 87.
(292) McCash, E. M. *Vacuum* **1990**, *40*, 423.
(293) Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. *Surf. Sci.* **1992**, *277*, L89.
(294) Arvanitis, D.; Baberschke, K.; Wenzel, L.; Döbler, U. *Phys. Rev. Lett.* **1986**, *57*, 3177.
(295) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1982**, *120*, L461.
(296) Chesters, M. A.; McDougall, G. S.; Pemble, M. E.; Sheppard, N. *Appl. Surf. Sci.* **1985**, *22/23*, 369.
(297) Erley, W.; Baro, A. M.; Ibach, H. *Surf. Sci.* **1982**, *120*, 273.
(298) Backx, C.; de Groot, C. P. M.; Biloen, P. *Appl. Surf. Sci.* **1980**, *6*, 256.
(299) Bandy, B. J.; Chesters, M. A.; James, D. I.; McDougall, G. S.; Pemble, M.; Sheppard, N. *Philos. Trans. R. Soc. London A* **1986**, *318*, 141.
(300) Kostov, K. L.; Marinova, T. S. *Surf. Sci.* **1987**, *184*, 359.
(301) Stuve, E. M.; Madix, R. J. *Surf. Sci.* **1985**, *160*, 293.
(302) Hugenschmidt, M. B.; Dolle, P.; Jupille, J.; Cassuto, A. *J. Vac. Sci. Technol. A* **1989**, *7*, 3312.
(303) Avery, N. R. *Surf. Sci.* **1984**, *146*, 363.
(304) Henn, F. C.; Diaz, A. L.; Bussell, M. E.; Hugenschmidt, M. B.; Domagala, M. E.; Campbell, C. T. *J. Phys. Chem.* **1992**, *96*, 5965.
(305) Chesters, M. A.; Horn, A. B.; Ilharco, L. M.; Ransley, I. A.; Sakakini, B. H.; Vickerman, J. C. *Surf. Sci.* **1991**, *251/252*, 291.
(306) Hammer, L.; Dötsch, B.; Brandenstein, F.; Fricke, A.; Müller, K. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *54/55*, 687.
(307) Demuth, J. E. *IBM J. Res. Develop.* **1978**, *22*, 265.
(308) Stöhr, J.; Sette, F.; Johnson, A. L. *Phys. Rev. Lett.* **1984**, *53*, 1684.
(309) Carr, R. G.; Sham, T. K.; Eberhardt, W. E. *Chem. Phys. Lett.* **1985**, *113*, 63.
(310) Horsley, J. A.; Stöhr, J.; Koestner, R. J. *J. Chem. Phys.* **1985**, *83*, 3146.
(311) Bao, S.; Hofmann, P.; Schindler, K.-M.; Fritzsche, V.; Bradshaw, A. M.; Woodruff, D. P.; Casado, C.; Asensio, M. C. *J. Phys.: Condens. Matter* **1994**, *6*, L93.
(312) Bao, S.; Hofmann, P.; Schindler, K.-M.; Fritzsche, V.; Bradshaw, A. M.; Woodruff, D. P.; Casado, C.; Asensio, M. C. *Surf. Sci.* **1995**, *323*, 19.
(313) Kubota, J.; Kondo, J. N.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1994**, *98*, 7653.
(314) Bradshaw, A. M. Personal communication.
(315) Laine, R. M.; Moriarty, R. E.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 1402.
(316) Mason, R.; Wheeler, A. G. *J. Chem. Soc. A* **1968**, 2549.
(317) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.
(318) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1977**, 178.
(319) Frisch, P. D.; Posey, R. G.; Khare, G. P. *Inorg. Chem.* **1978**, *17*, 402.
(320) Silverthorn, W. E. *Adv. Organometal. Chem.* **1975**, *13*, 47.
(321) Gervasio, G.; Rossetti, R.; Stanghellini, P. L. *Organometallics* **1985**, *4*, 1612.
(322) Koshland, D. E.; Myers, S. E.; Chesik, J. P. *Acta Crystallogr., Sect. B* **1977**, *33*, 2013.
(323) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985.
(324) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 2516.
(325) Anson, C. E.; Keiller, B. T.; Oxton, I. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Chem. Commun.* **1983**, 470.
(326) Casalone, G.; Cattania, M. G.; Merati, F.; Simonetta, M. *Surf. Sci.* **1982**, *120*, 171.
(327) Bao, S.; Hofmann, P.; Schindler, K.-M.; Fritzsche, V.; Bradshaw, A. M.; Woodruff, D. P.; Casado, C.; Asension, M. C. *Surf. Sci.* **1994**, *307*, 722.
(328) Kesmodel, L. L.; Baetzold, R.; Somorjai, G. A. *Surf. Sci.* **1977**, *66*, 299.
(329) Horsley, J. A. Personal communication.
(330) Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Lambert, R. M.; Yao, J. M.; Saldin, D. K.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T. *Surf. Sci.* **1992**, *268*, 1.
(331) Demuth, J. E. *Surf. Sci.* **1979**, *84*, 315.
(332) Churchill, M. R.; Mason, R. *Adv. Organometal. Chem.* **1967**, *5*, 93.
(333) Cotton, F. A.; Day, V. W.; Frenz, B. A.; Hardcastle, K. I.; Troup, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 4522.
(334) Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462.
(335) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344.
(336) Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 1976.
(337) Maurice, V.; Minot, C. *Langmuir* **1989**, *5*, 734.
(338) Bredael, G.; Tysoe, W. T.; Zaera, F. *Langmuir* **1989**, *5*, 899.
(339) Hugenschmidt, M. B.; Diaz, A. L.; Campbell, C. T. *J. Phys. Chem.* **1992**, *96*, 5974.
(340) Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.
(341) Martin, H. A.; Jellinek, F. *J. Organometal. Chem.* **1968**, *12*, 169.
(342) Green, M. L. H.; Nagy, P. L. I. *Adv. Organometal. Chem.* **1964**, *2*, 325.
(343) Abel, E. W.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1973**, 1706.
(344) Huttner, G.; Brintzinger, H.; Bell, L. G.; Friedrich, P.; Bejenke, V.; Neugebauer, D. *J. Organometal. Chem.* **1978**, *145*, 329.
(345) Carter, R. N.; Anton, A. B.; Apai, G. *J. Am. Chem. Soc.* **1992**, *114*, 4410.
(346) Ayre, C. R.; Madix, R. J. *Surf. Sci.* **1992**, *262*, 51.
(347) Land, D. P.; Erley, W.; Ibach, H. *Surf. Sci.* **1993**, *289*, 237.
(348) Parker, D. H.; Pettiette-Hall, C. L.; Li, Y.; McIver, R. T., Jr.; Hemminger, J. C. *J. Phys. Chem.* **1992**, *96*, 1888.
(349) Angelici, R. J. *Synthesis and Techniques in Inorganic Chemistry*; Saunders: Philadelphia, 1977.
(350) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682.
(351) Bennett, M. J.; Cotton, F. A.; Legzdins, P. *J. Am. Chem. Soc.* **1967**, *89*, 6797.
(352) Lyerla, J. R.; Fyfe, C. A.; Yannoni, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 1351.
(353) Humphries, A. P.; Knox, S. R. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1523.
(354) Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 321.
(355) Mills, O. S.; Paulus, E. F. *J. Organometal. Chem.* **1968**, *11*, 587.
(356) Howard, J. A. K.; Kennedy, F. G.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1979**, 839.
(357) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1979**, 506.
(358) Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; McCamley, A.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1988**, 1071.
(359) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
(360) Radonovich, L. J.; Zuerner, E. C.; Efner, H. F.; Klabunde, K. J. *Inorg. Chem.* **1976**, *15*, 2976.
(361) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *28*, 2049.
(362) Churchill, M. R.; Mason, R. *Proc. R. Soc. Lond. A* **1966**, *292*, 61.
(363) Allegra, G.; Casagrande, T.; Immizi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289.
(364) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31.
(365) Liu, A. C.; Friend, C. M. *J. Chem. Phys.* **1988**, *89*, 4396.
(366) Yannoulis, P.; Dudde, R.; Frank, K. H.; Koch, E. E. *Surf. Sci.* **1987**, *189/190*, 519.
(367) Bader, M.; Haase, J.; Frank, K.-H.; Ocal, C.; Puschmann, A. *J. Phys. [Paris]* **1986**, *47*, C8–491.
(368) Xi, M.; Yang, M. X.; Jo, S. K.; Bent, B. E.; Stevens, P. *J. Chem. Phys.* **1994**, *101*, 9122.
(369) Solomon, J. L.; Madix, R. J.; Stöhr, J. *Surf. Sci.* **1991**, *255*, 12.
(370) Liu, A. C.; Stöhr, J.; Friend, C. M.; Madix, R. J. *Surf. Sci.* **1990**, *235*, 107.
(371) Aminpirooz, S.; Becker, L.; Hillert, B.; Haase, J. *Surf. Sci.* **1991**, *244*, L152.
(372) Ramsey, M. G.; Steinmüller, D.; Netzer, F. P.; Schedel, T.; Santaniello, A.; Lloyd, D. R. *Surf. Sci.* **1991**, *251/252*, 979.
(373) Huber, W.; Weinelt, M.; Zebisch, P.; Steinrück, H.-P. *Surf. Sci.* **1991**, *253*, 72.
(374) Ohtani, H.; Bent, B. E.; Mate, C. M.; Van Hove, M. A.; Somorjai, G. A. *Appl. Surf. Sci.* **1988**, *33/34*, 254.
(375) Waddill, G. D.; Kesmodel, L. L. *Phys. Rev. B* **1985**, *31*, 4940.
(376) Horsley, J. A.; Stöhr, J.; Hitchcock, A. P.; Newbury, D. C.; Sette, F. *J. Chem. Phys.* **1985**, *83*, 6099.
(377) Johnson, A. L.; Muetterties, E. L.; Stöhr, J. *J. Am. Chem. Soc.* **1983**, *105*, 7183.
(378) Richardson, N. V.; Palmer, N. R. *Surf. Sci.* **1982**, *114*, L1.
(379) Mate, C. M.; Somorjai, G. A.; Tom, H. W. K.; Zhu, X. D.; Shen, Y. R. *J. Chem. Phys.* **1988**, *88*, 441.
(380) Netzer, F. P.; Bertel, E.; Matthew, J. A. D. *Surf. Sci.* **1980**, *92*, 43.
(381) Mack, J. U.; Bertel, E.; Netzer, F. P. *Surf. Sci.* **1985**, *159*, 265.
(382) Van Hove, M. A.; Lin, R.; Somorjai, G. A. *Phys. Rev. Lett.* **1983**, *51*, 778.
(383) Lin, R. F.; Blackman, G. S.; Van Hove, M. A.; Somorjai, G. A. *Acta Crystallogr., Sect. B* **1987**, *43*, 368.
(384) Ogletree, D. F.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1987**, *183*, 1.

(385) Netzer, F. P.; Graen, H. H.; Kuhlenbeck, H.; Neumann, M. *Chem. Phys. Lett.* **1987**, *133*, 49.
(386) Lloyd, D. R.; Quinn, C. M.; Richardson, N. V. *Solid State Commun.* **1977**, *23*, 141.
(387) Huber, W.; Steinrück, H.-P.; Pache, T.; Menzel, D. *Surf. Sci.* **1989**, *217*, 103.
(388) Somers, J.; Bridge, M. E.; Lloyd, D. R.; McCabe, T. *Surf. Sci.* **1987**, *181*, L167.
(389) Bertel, E.; Rosina, G.; Netzer, F. P. *Surf. Sci.* **1986**, *172*, L515.
(390) Netzer, F. P.; Rosina, G.; Bertel, E.; Saalfeld, H. *Surf. Sci.* **1987**, *184*, L397.
(391) Neumann, M.; Mack, J. U.; Bertel, E.; Netzer, F. P. *Surf. Sci.* **1985**, *155*, 629.
(392) Netzer, F. P.; Mack, J. U. *J. Chem. Phys.* **1983**, *79*, 1017.
(393) Nyberg, G. L.; Richardson, N. V. *Surf. Sci.* **1979**, *85*, 335.
(394) Hofmann, P.; Horn, K.; Bradshaw, A. M. *Surf. Sci.* **1981**, *105*, L260.
(395) Netzer, F. P.; Rangelov, G.; Rosina, G.; Saalfeld, H. B.; Neumann, M.; Lloyd, D. R. *Phys. Rev. B* **1988**, *37*, 10399.
(396) Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Lambert, R. M.; Wang, L. P.; Tysoe, W. T. *Surf. Sci.* **1990**, *232*, 259.
(397) Abon, M.; Bertolini, J. C.; Billy, J.; Massardier, J.; Tardy, B. *Surf. Sci.* **1985**, *162*, 395.
(398) Grassian, V. H.; Muetterties, E. L. *J. Phys. Chem.* **1987**, *91*, 389.
(399) Wilk, D. E.; Stanners, C. D.; Shen, Y. R.; Somorjai, G. A. *Surf. Sci.* **1993**, *280*, 298.
(400) Domagala, M. E.; Campbell, C. T. *Langmuir* **1994**, *10*, 2636.
(401) Avery, N. R. *Surf. Sci.* **1984**, *137*, L109.
(402) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427.
(403) De, R. L.; Von Seyerl, J.; Zsolnai, L.; Huttner, G. *J. Organometal. Chem.* **1979**, *175*, 185.
(404) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.
(405) Brookhart, M.; Green, M. L. H. *J. Organometal. Chem.* **1983**, *250*, 395.
(406) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.
(407) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.
(408) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.
(409) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897.
(410) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.
(411) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.
(412) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094.
(413) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393.
(414) McCafferty, J. G.; Ozin, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 7351.
(415) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.
(416) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.
(417) Hamza, A. V.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 25.
(418) Weinberg, W. H. *Langmuir* **1993**, *9*, 655.
(419) Chesters, M. A.; Gardner, P.; McCash, E. M. *Surf. Sci.* **1989**, *209*, 89.
(420) Salmerón, M.; Somorjai, G. A. *J. Phys. Chem.* **1981**, *85*, 3835.
(421) Wittrig, T. S.; Szuromi, P. D.; Weinberg, W. H. *J. Chem. Phys.* **1982**, *76*, 3305.
(422) Liu, A. C.; Friend, C. M. *J. Chem. Phys.* **1987**, *87*, 4975.
(423) Hoffmann, F. M.; Felter, T. E.; Thiel, P. A.; Weinberg, W. H. *Surf. Sci.* **1983**, *130*, 173.
(424) Demuth, J. E.; Ibach, H.; Lehwald, S. *Phys. Rev. Lett.* **1978**, *40*, 1044.
(425) Waddill, G. D.; Kesmodel, L. L. *Chem. Phys. Lett.* **1986**, *128*, 208.
(426) Chesters, M. A.; Gardner, P. *Spectrochim. Acta* **1990**, *46A*, 1011.
(427) Lamont, C. L. A.; Borbach, M.; Stenzel, W.; Conrad, H.; Bradshaw, A. M. *Chem. Phys. Lett.* **1994**, *230*, 265.
(428) Chesters, M. A.; Parker, S. F.; Raval, R. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *39*, 155.
(429) Chesters, M. A.; Parker, S. F.; Raval, R. *Surf. Sci.* **1986**, *165*, 179.
(430) Avery, N. R. *Surf. Sci.* **1985**, *163*, 357.
(431) Hoffmann, F. M.; O'Brien, E. V.; Hrbek, J.; Paola, R. A. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *29*, 301.
(432) Felter, T. E.; Hoffmann, F. M.; Thiel, P. A.; Weinberg, W. H. *Surf. Sci.* **1983**, *130*, 163.
(433) Hoffmann, F. M.; Upton, T. H. *J. Phys. Chem.* **1984**, *88*, 6209.
(434) Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 2493.
(435) Brown, R. K.; Williams, J. M.; Schultz, J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981.
(436) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.
(437) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K.; Schultz, A. J.; Williams, J. M.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1986**, 1629.
(438) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.
(439) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625.
(440) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.
(441) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *J. Chem. Phys.* **1994**, *101*, 11012.
(442) Zhou, Y.; Feng, W. M.; Henderson, M. A.; Roop, B.; White, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 4447.
(443) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci.* **1991**, *248*, 279.
(444) Zheng, C.; Apeloig, Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 749.
(445) Yang, H.; Whitten, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 6442.
(446) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725.
(447) Shilov, A. E. *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Riedel: Dordretcht, 1984.
(448) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, 624.
(449) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.
(450) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.
(451) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.
(452) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.
(453) Kemball, C. *Catal. Rev.* **1971**, *5*, 33.
(454) Anderson, J. R.; Baker, B. G. In *Chemisorption and Reactions on Metallic Films*; Anderson, J. R., Ed.; Academic Press: London, 1971; Vol. 2, pp 63–210.
(455) Sinfelt, J. H. *Adv. Catal.* **1973**, *23*, 91.
(456) Rettner, C. T.; Pfnür, H. E.; Auerbach, D. J. *Phys. Rev. Lett.* **1985**, *54*, 2716.
(457) McMaster, M. C.; Madix, R. J. *Surf. Sci.* **1992**, *275*, 265.
(458) Stewart, C. N.; Ehrlich, G. *J. Chem. Phys.* **1975**, *62*, 4672.
(459) Brass, S. G.; Reed, D. A.; Ehrlich, G. *J. Chem. Phys.* **1979**, *70*, 5244.
(460) Rettner, C. T.; Pfnür, H. E.; Auerbach, D. J. *J. Chem. Phys.* **1986**, *84*, 4163.
(461) Luntz, A. C.; Bethune, D. S. *J. Chem. Phys.* **1989**, *90*, 1274.
(462) Schoofs, G. R.; Arumainayagam, C. R.; McMaster, M. C.; Madix, R. J. *Surf. Sci.* **1989**, *215*, 1.
(463) Szuromi, P. D.; Engstrom, J. R.; Weinberg, W. H. *J. Chem. Phys.* **1984**, *80*, 508.
(464) Mullins, C. B.; Weinberg, W. H. *J. Chem. Phys.* **1990**, *92*, 3986.
(465) Yang, H.; Whitten, J. L. *J. Chem. Phys.* **1992**, *96*, 5529.
(466) Swang, O.; Faegri, K., Jr.; Gropen, O.; Wahlgren, U.; Siegbahn, P. E. M. *Chem. Phys.* **1991**, *156*, 379.
(467) Luntz, A. C.; Harris, J. *J. Vac. Sci. Technol. A* **1992**, *10*, 2292.
(468) Verhoef, R. W.; Kelly, D.; Mullins, C. B.; Weinberg, W. H. *Surf. Sci.* **1994**, *311*, 196.
(469) Ukraintsev, V. A.; Harrison, I. *Surf. Sci.* **1993**, *286*, L571.
(470) Ukraintsev, V. A.; Harrison, I. *J. Chem. Phys.* **1994**, *101*, 1564.
(471) Winters, H. F. *J. Chem. Phys.* **1975**, *62*, 2454.
(472) Schouten, F. C.; Gijzeman, O. L. J.; Bootsma, G. A. *Surf. Sci.* **1979**, *87*, 1.
(473) Brass, S. G.; Ehrlich, G. *Surf. Sci.* **1987**, *187*, 21.
(474) Beebe, T. P., Jr.; Goodman, D. W.; Kay, B. D.; Yates, J. T., Jr. *J. Chem. Phys.* **1987**, *87*, 2305.
(475) Hanley, L.; Xu, Z.; Yates, J. T., Jr. *Surf. Sci.* **1991**, *248*, L265.
(476) Brass, S. G.; Ehrlich, G. *J. Chem. Phys.* **1987**, *87*, 4285.
(477) Beckerle, J. D.; Johnson, A. D.; Yang, Q. Y.; Ceyer, S. T. *J. Chem. Phys.* **1989**, *91*, 5756.
(478) Chan, C.-M.; Van Hove, M. A.; Weinberg, W. H.; Williams, E. D. *Surf. Sci.* **1980**, *91*, 440.
(479) Szuromi, P. D.; Engstrom, J. R.; Weinberg, W. H. *J. Phys. Chem.* **1985**, *89*, 2497.
(480) Land, D. P.; Pettiette-Hall, C. L.; McIver, R. T., Jr.; Hemminger, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 5970.
(481) Bussell, M. E.; Henn, F. C.; Campbell, C. T. *J. Phys. Chem.* **1992**, *96*, 5978.
(482) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *Faraday Discuss.* **1993**, *96*, 337.
(483) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *Chem. Phys.* **1993**, *177*, 407.
(484) Schouten, F. C.; Kaleveld, E. W.; Bootsma, G. A. *Surf. Sci.* **1977**, *63*, 460.
(485) Chen, J. G.; Weisel, M. D.; Hardenbergh, J. H.; Hoffmann, F. M.; Mims, C. A.; Hall, R. B. *J. Vac. Sci. Technol. A* **1991**, *9*, 1684.
(486) Weinberg, W. H.; Sun, Y.-K. *Science* **1991**, *253*, 542.
(487) Weinberg, W. H.; Sun, Y.-K. *Surf. Sci.* **1992**, *277*, L39.
(488) Lee, M. B.; Yang, Q. Y.; Ceyer, S. T. *J. Chem. Phys.* **1987**, *87*, 2724.
(489) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.
(490) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.
(491) Cross, R. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, pp 559–624.
(492) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1426.

(493) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.
(494) Bönnemann, H.; Grard, C.; Kopp, W.; Pump, W.; Tanaka, K.; Wilke, G. *Angew. Chem.* **1973**, *85*, 1024.
(495) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.
(496) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1962**, 5075.
(497) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.
(498) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 5811.
(499) Chatt, J.; Coffey, R. S.; Gough, A.; Thomson, D. T. *J. Chem. Soc. A* **1968**, 190.
(500) Evans, J.; Schwartz, J.; Urquhart, P. W. *J. Organometal. Chem.* **1974**, *81*, C37.
(501) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138.
(502) Egger, K. W.; Cocks, A. T. *Trans. Faraday Soc.* **1971**, *67*, 2629.
(503) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53.
(504) Egger, K. W. *J. Chem. Soc. A* **1971**, 3603.
(505) Li, M.-Y.; San Filippo, J., Jr. *Organometallics* **1983**, *2*, 554.
(506) Churchill, M. R.; Schrock, R. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 647.
(507) Reger, D. L.; Culberston, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789.
(508) Yagupsky, G.; Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1392.
(509) Kruse, W. *J. Organometal. Chem.* **1972**, *42*, C39.
(510) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.
(511) Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200.
(512) Rudakov, E. S.; Tishchenko, N. A. *Kinet. Catal., Engl. Trans.* **1991**, *32*, 274.
(513) Sneeden, R. P. A.; Zeiss, H. H. *J. Organometal. Chem.* **1971**, *26*, 101.
(514) Glaze, W. H.; Lin, J.; Felton, E. G. *J. Org. Chem.* **1966**, *31*, 2643.
(515) Zaera, F. *J. Am. Chem. Soc.* **1989**, *111*, 8744.
(516) Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 1137.
(517) Dubois, L. H.; Bent, B. E.; Nuzzo, R. G. In *Surface Reactions*; Madix, R. J., Ed.; Springer Verlag: Berlin, 1994; Vol. 34 of the Springer Series in Surface Sciences, pp 135–183.
(518) Lloyd, K. G.; Campion, A.; White, J. M. *Catal. Lett.* **1989**, *2*, 105.
(519) Jenks, C. J.; Xi, M.; Yang, M. X.; Bent, B. E. *J. Phys. Chem.* **1994**, *98*, 2152.
(520) Jenks, C. J.; Chiang, C.; Bent, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 6308.
(521) Yang, M. X.; Jo, S. K.; Paul, A.; Avila, L.; Bent, B. E.; Nishikida, K. *Surf. Sci.* **1995**, *325*, 102.
(522) Forbes, J. G.; Gellman, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 6277.
(523) Jenks, C. J. Ph. D. Thesis, Columbia University, 1992.
(524) Teplyakov, A. V.; Bent, B. E. *J. Am. Chem. Soc.* **1995**, *117*, 10076.
(525) Jenks, C. J.; Paul, A.; Smoliar, L. A.; Bent, B. E. *J. Phys. Chem.* **1994**, *98*, 572.
(526) Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. to be published.
(527) Whitesides, G. M.; Bergbreiter, D. E.; Kendall, P. E. *J. Am. Chem. Soc.* **1974**, *96*, 2806.
(528) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.
(529) Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481.
(530) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.
(531) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.
(532) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.
(533) Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.
(534) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.
(535) Zaera, F. *Langmuir* **1991**, *7*, 1998.
(536) Zaera, F. *Catal. Lett.* **1991**, *11*, 95.
(537) Anderson, J. R. *Rev. Pure Appl. Chem.* **1957**, *7*, 165.
(538) Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948.
(539) Zaera, F.; Tjandra, S. *J. Am. Chem. Soc.* **1993**, *115*, 5851.
(540) Tjandra, S.; Zaera, F. To be published.
(541) Tjandra, S. Ph.D. Thesis, University of California, Riverside, 1994.
(542) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organometal. Chem.* **1974**, *80*, C53.
(543) Cooksey, C. J.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 1718.
(544) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.
(545) Bryan, E. G.; Jackson, W. G.; Johnson, B. F. G.; Keland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organometal. Chem.* **1976**, *108*, 385.
(546) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.
(547) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.
(548) Bodner, T.; Cutler, A. R. *J. Organometal. Chem.* **1981**, *213*, C31.
(549) Bly, R. S.; Bly, R. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1046.
(550) McLain, S. J.; Wood, C. D.; Messerle, L. M.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962.
(551) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.
(552) Guggenburger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935.
(553) Gill, D. S.; Green, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1037.
(554) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474.
(555) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911.
(556) Casey, C. P.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 7197.
(557) Jacobson, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1626.
(558) Rashidi, M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 1636.
(559) Janssens, T. V. W.; Zaera, F. *Surf. Sci.* **1995**, in press.
(560) Pruchnik, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum: New York, 1990.
(561) Cassar, L.; Giarrusso, A. *Gazz. Chim. Ital.* **1973**, *103*, 793.
(562) Johnson, M. D.; Meeks, B. S. *J. Chem. Soc. B* **1971**, 185.
(563) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667.
(564) Nguyen van Duong, K.; Gaudemer, A. *J. Organometal. Chem.* **1970**, *22*, 473.
(565) Johnson, B. F. G.; Lewis, J.; Jones, J. D.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 34.
(566) Bland, W. J.; Burgess, J.; Kemmitt, R. D. W. *J. Organometal. Chem.* **1968**, *15*, 217.
(567) Burgess, J.; Hunt, M. M.; Kemmitt, R. D. W. *J. Organometal. Chem.* **1977**, *134*, 131.
(568) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.
(569) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.
(570) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Organometal. Chem.* **1981**, *213*, 249.
(571) Keister, J. B.; Shapley, J. R. *J. Organometal. Chem.* **1975**, *85*, C29.
(572) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407.
(573) Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. M. *J. Chem. Soc., Chem. Commun.* **1974**, 807.
(574) Deeming, A. J. *J. Organometal. Chem.* **1978**, *150*, 123.
(575) Tachikawa, M.; Shapley, J. R. *J. Organometal. Chem.* **1977**, *124*, C19.
(576) Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E.; Milone, L.; Valle, M. *J. Chem. Soc., Chem. Commun.* **1972**, 545.
(577) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221.
(578) Pierpont, C. G.; Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 616.
(579) Stuntz, G. F.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 2596.
(580) Canty, A. J.; Johnson, B. F. G.; Lewis, J. *J. Organometal. Chem.* **1972**, *43*, C35.
(581) Canty, A. J.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 2056.
(582) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Organometal. Chem.* **1972**, *36*, C43.
(583) Deeming, A. J. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; John Willey & Sons: Chichester, 1980; pp 391–469.
(584) Tjandra, S.; Zaera, F. *Langmuir* **1991**, *7*, 1432.
(585) Zaera, F. *J. Am. Chem. Soc.* **1989**, *111*, 4240.
(586) Zaera, F. *Langmuir* **1995**, in press.
(587) Berke, H. *Z. Naturforsch. B.: Anorg. Chem., Org. Chem.* **1980**, *35B*, 86.
(588) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414.
(589) Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* **1977**, *30*, 1213.
(590) Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organometal. Chem.* **1972**, *39*, 169.
(591) Catti, M.; Gervasio, G.; Mason, S. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2260.
(592) Deeming, A. J. *J. Organometal. Chem.* **1977**, *128*, 63.
(593) Demuth, J. E. *Surf. Sci.* **1980**, *93*, 127.
(594) Zhu, X.; Castro, M. E.; Akhter, S.; White, J. M.; Houston, J. E. *Surf. Sci.* **1988**, *207*, 1.
(595) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *Surf. Sci.* **1983**, *135*, 128.
(596) Powell, P. *Principles of Organometallic Chemistry,* 2nd ed.; Chapman and Hall: London, 1988.
(597) Elschenbroich, C.; Salzer, A. *Organometallics; A Concise Introduction,* 2nd ed.; VCH: Weinheim, 1992.
(598) Timms, P. L. *Adv. Inorg. Radiochem.* **1972**, *14*, 121.
(599) Pike, R. D. *Mech. Inorg. Organometal. Reac.* **1989**, *6*, 285.
(600) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843.
(601) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620.
(602) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(603) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13.
(604) Fujisawa, M.; Sekitani, T.; Morikawa, Y.; Nishijima, M. *J. Phys. Chem.* **1991**, *95*, 7415.
(605) *CRC Handbook of Chemistry and Physics*, 55th ed.; CRC Press: Cleveland, 1974.
(606) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736.
(607) Trost, B. M.; Strege, P. E.; Weker, L.; Fullerton, T. J.; Dietsch, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.
(608) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201.
(609) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 845.
(610) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847.
(611) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773.
(612) Gentle, T. M. Ph. D. Thesis, University of California, Berkeley, 1984.
(613) Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534.
(614) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067.
(615) Domagala, M. E.; Campbell, C. T. *Surf. Sci.* **1994**, *301*, 151.
(616) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.
(617) Ettore, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45.
(618) Hall, P. W.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organometal. Chem.* **1975**, *84*, 407.
(619) Lau, W.; Huffman, J. C.; Kochi, J. K. *Organometallics* **1982**, *1*, 155.
(620) DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601.
(621) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.
(622) Kuch, P. L.; Tobias, R. S. *J. Organometal. Chem.* **1976**, *122*, 429.
(623) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.
(624) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.
(625) Åkermark, B.; Johansen, H.; Roos, B.; Wahlgren, U. *J. Am. Chem. Soc.* **1979**, *101*, 5876.
(626) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.
(627) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.
(628) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321.
(629) Flood, T. C. In *Topics in Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: New York, 1981; Vol. 12 (Topics in Inorganic and Organometallic Stereochemistry), pp 37–117.
(630) Jarvis, J. A. J.; Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 373.
(631) Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 31.
(632) Tamaki, A.; Kochi, J. K. *J. Organometal. Chem.* **1973**, *61*, 441.
(633) Tamura, M.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1483.
(634) Tamura, M.; Kochi, J. K. *J. Organometal. Chem.* **1972**, *42*, 205.
(635) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.
(636) Tjandra, S.; Zaera, F. *J. Catal.* **1994**, *147*, 598.
(637) Berko, A.; Solymosi, F. *J. Phys. Chem.* **1989**, *93*, 12.
(638) Solymosi, F.; Károly, R. *J. Am. Chem. Soc.* **1991**, *113*, 9145.
(639) Jenks, C. J.; Lin, J.; Chiang, C.; Kang, L.; Leang, P. S.; Wentzlaff, T. H.; Bent, B. E. In *Structure-Activity and Selectivity in Heterogeneous Catalysis*; Grasselli, R. K., Sleight, A. W., Eds.; Elsevier: Amsterdam, 1991; pp 301–307.
(640) Squire, D. W.; Dulcey, C. S.; Lin, M. C. *J. Vac. Sci. Technol. B* **1985**, *3*, 1513.
(641) Tjandra, S.; Zaera, F. Unpublished results.
(642) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.
(643) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81.
(644) Nickias, P. N.; Selegue, J. P.; Young, B. A. *Organometallics* **1988**, *7*, 2248.
(645) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077.
(646) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.
(647) Werner, H. *J. Organometal. Chem.* **1994**, *475*, 45.
(648) Empsall, H. D.; Hyde, E. M.; Markham, M.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589.
(649) Lourdichi, M.; Mathieu, R. *Organometallics* **1986**, *5*, 2067.
(650) Duggan, T. P.; Golden, M. J.; Keister, J. B. *Organometallics* **1990**, *9*, 1656.
(651) Davis, S. M.; Zaera, F.; Gordon, B. E.; Somorjai, G. A. *J. Catal.* **1985**, *92*, 240.
(652) Koel, B. E.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1984**, *146*, 211.
(653) Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organometal. Chem.* **1983**, *258*, 217.
(654) Bruce, M. I.; Swincer, A. G. *Adv. Organometal. Chem.* **1983**, *22*, 59.
(655) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023.
(656) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.
(657) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.
(658) Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63.
(659) James, B. R. *Adv. Organometal. Chem.* **1979**, *17*, 319.
(660) James, B. R. *Homogeneous Hydrogenation*; Wiley-Interscience: New York, 1973.
(661) Birch, A. D.; Williamson, D. H. *Org. React.* **1976**, *24*, 1.
(662) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, *1711*,
(663) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.
(664) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331.
(665) Halpern, J. In *Organotransition Metal Chemistry*; Ishii, Y., Tsutsui, M., Eds.; Plenum: New York, 1975; pp 109–117.
(666) Dawans, F.; Morel, D. *J. Mol. Catal.* **1977–78**, *3*, 403.
(667) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 6.
(668) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.
(669) Halpern, J. *Science* **1982**, *217*, 401.
(670) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335.
(671) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.
(672) Zaera, F.; Somorjai, G. A. In *Hydrogen Effects in Catalysis: Fundamentals and Practical Applications*; Paál, Z., Menon, P. G., Eds.; Marcel Dekker: New York, 1988; pp 425–447.
(673) Thomson, S. J. In *Catalysis: A Specialist Periodical Report*; Kemball, C., Dowden, D. A., Eds.; The Chemical Society: London, 1980; Vol. 3, pp 1–38.
(674) Zaera, F. Ph. D. Thesis, University of California, Berkeley, 1984.
(675) Hasse, W.; Günter, H.-L.; Henzler, M. *Surf. Sci.* **1983**, *126*, 479.
(676) Godbey, D.; Zaera, F.; Yeates, R.; Somorjai, G. A. *Surf. Sci.* **1986**, *167*, 150.
(677) Marinova, T. S.; Chakarov, D. V. *Surf. Sci.* **1988**, *200*, 309.
(678) Zaera, F. *J. Catal.* **1990**, *121*, 318.
(679) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 5090.
(680) Bowker, M.; Gland, J. L.; Joyner, R. W.; Li, Y.; Slin'ko, M. M.; Whyman, R. *Catal. Lett.* **1994**, *25*, 293.
(681) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.
(682) Wieckowsky, A.; Rosasco, S. D.; Salaita, G. N.; Hubbard, A.; Bent, B. E.; Zaera, F.; Godbey, D.; Somorjai, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 5910.
(683) Rodriguez, J. A.; Goodman, D. W. *Surf. Sci. Rep.* **1991**, *14*, 1.
(684) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1995**, *117*, 1814.
(685) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3156.
(686) Stone, D.; Hemminger, J. C.; Janssens, T. V. W.; Zaera, F. To be published.
(687) Creighton, J. R.; Ogle, K. M.; White, J. M. *Surf. Sci.* **1984**, *138*, L137.
(688) Davidson, J. L.; Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J.; Woodward, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 714.
(689) Alt, H. G.; Schwärtzle, J. A. *J. Organometal. Chem.* **1978**, *155*, C65.
(690) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.
(691) Clark, H. C. *J. Organometal. Chem.* **1980**, *200*, 63.
(692) Otsuka, S.; Nakamura, A. *Adv. Organometal. Chem.* **1976**, *14*, 245.
(693) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 4107.
(694) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.
(695) Lobach, M. I.; Kormer, V. A. *Russ. Chem. Rev.* **1979**, *48*, 759.
(696) Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.
(697) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1980**, *102*, 5948.
(698) Wilczynski, R.; Fordyce, W. A.; Halpern, J. *J. Am. Chem. Soc.* **1983**, *105*, 2066.
(699) Bennett, M. A.; Huang, T.-N.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 312.
(700) Holy, N. L. *J. Org. Chem.* **1979**, *44*, 239.
(701) Johnson, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7395.
(702) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1970**, *12*, 324.
(703) Russell, M. J.; White, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1977**, 427.
(704) Stuhl, L. S.; Rakowski-DuBois, M.; Kirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405.
(705) Parmeter, J. E.; Hills, M. M.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 72.
(706) Gentle, T. M.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469.
(707) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Phys. Chem.* **1986**, *90*, 3188.
(708) Megiris, C. E.; Berlowitz, P.; Butt, J. B.; Kung, H. H. *Surf. Sci.* **1985**, *159*, 184.
(709) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(710) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793.
(711) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224.

(712) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1985; Vol. II (The Nature and Cleavage of Metal-Carbon Bonds), pp 625–787.
(713) Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* **1984**, 1260.
(714) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.
(715) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.
(716) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
(717) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.
(718) Ziegler, K.; Nagel, K.; Pfohl, W. *Justus Liebigs Ann. Chem.* **1960**, *629*, 210.
(719) Pfohl, W. *Justus Liebigs Ann. Chem.* **1960**, *629*, 207.
(720) Hérisson, J.-L.; Chauvin, Y. *Makromol. Chem.* **1970**, *141*, 161.
(721) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley: New York, 1986.
(722) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.
(723) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300.
(724) Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.
(725) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417.
(726) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 3754.
(727) Hoerlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Krueger, C.; Ziegler, M. L.; Zahn, T. *J. Organometal. Chem.* **1987**, *321*, 257.
(728) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Acta Crystallogr., Sect. B* **1978**, *34*, 3086.
(729) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.
(730) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619.
(731) Allison, N. T.; Fritch, J. R.; Volhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 1384.
(732) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.
(733) Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900.
(734) Wang, P.-K.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1990**, *94*, 1154.
(735) Hoffmann, R. In *Frontiers in Chemistry*; Laidler, J. K., Ed.; Pergamon Press: Oxford, 1982; pp 247–263.
(736) Whitesides, G. M. *Pure Appl. Chem.* **1981**, *53*, 287.
(737) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *101*, 4981.
(738) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003.
(739) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.
(740) Cairncross, A.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 247.
(741) Cohen, T.; Cristea, I. *J. Am. Chem. Soc.* **1976**, *98*, 748.
(742) Van Koten, G.; Noltes, J. G. *J. Chem. Soc., Chem. Commun.* **1974**, 575.
(743) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.
(744) Paul, A.; Bent, B. E. *J. Catal.* **1994**, *147*, 264.
(745) Xi, M.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 7426.
(746) Xi, M.; Bent, B. E. *Langmuir* **1994**, *10*, 505.
(747) Fairbrother, D. H.; Peng, X. D.; Viswanathan, R.; Stair, P. C.; Trenary, M.; Fan, J. *Surf. Sci.* **1993**, *285*, L455.
(748) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.
(749) Murahashi, S.-I.; Kitani, Y.; Uno, T.; Hosokawa, T.; Miki, K.; Yonezawa, T.; Kasai, N. *Organometallics* **1986**, *5*, 356.
(750) Nuel, D.; Dahan, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658.
(751) Chisholm, M. H.; Ho, D.; Huffman, J. C.; Marchant, N. S. *Organometallics* **1989**, *8*, 1626.
(752) Kim, H. P.; Angelici, R. J. *Adv. Organometal. Chem.* **1987**, *27*, 51.
(753) Dean, C. E.; Kemmit, R. D. W.; Russell, D. R.; Schilling, M. D. *J. Organometal. Chem.* **1980**, *187*, C1.
(754) Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.
(755) Yamazaki, H.; Hagihara, N. *J. Organometal. Chem.* **1967**, *7*, 22.
(756) Maitlis, P. M. *Pure Appl. Chem.* **1973**, *33*, 489.
(757) Sesselman, W.; Woratschek, B.; Ertl, G.; Küppers, J.; Haberland, H. *Surf. Sci.* **1983**, *130*, 245.
(758) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1421.
(759) Banks, R. L.; Bailey, G. C. *Ind. Eng. Chem., Prod. Res. Develop.* **1964**, *3*, 170.
(760) Tysoe, W. T.; Ramirez-Cuesta, H.; Zgrablich, G. A.; Hoffmann, H.; Zaera, F.; Ormerod, R. M.; Lambert, R. M. To be published.
(761) Gellman, A. J. *Langmuir* **1991**, *7*, 827.
(762) Ormerod, R. M.; Lambert, R. M. *Catal. Lett.* **1990**, *6*, 6971.
(763) Patterson, C. H.; Lambert, R. M. *J. Phys. Chem.* **1988**, *92*, 1266.
(764) Bertolini, J. C.; Massardier, J.; Dalmai-Imelik, G. *J. Chem. Soc., Faraday 1* **1978**, *74*, 1720.
(765) Avery, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 6711.
(766) Xu, C.; Peck, J. W.; Koel, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 751.
(767) Kleitzein, H.; Werner, H.; Serhadli, P.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46.
(768) Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026.
(769) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.
(770) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447.
(771) Biloen, P.; Sachtler, W. M. H. *Adv. Catal.* **1981**, *30*, 165.
(772) Vannice, M. A. In *Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1982; Vol. 3 pp 139–198.
(773) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.
(774) Cramer, R. *Acc. Chem. Res.* **1968**, *1*, 186.
(775) Cossee, P. *J. Catal.* **1964**, *3*, 80.
(776) Boor, J. *Ziegler-Natta Catalysis and Polymerizations*; Academic Press: New York, 1979.
(777) Sinn, H.; Kaminsky, W. *Adv. Organometal. Chem.* **1980**, *18*, 99.
(778) Pino, P.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857.
(779) Pardy, R. B. A. *J. Organometal. Chem.* **1981**, *216*, C29.
(780) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076.
(781) Klein, H.-F.; Hammer, R.; Gross, J.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 809.
(782) Stille, J. K.; Hines, L. F.; Fries, R. W.; Wong, P. K.; James, D. E.; Lau, K. *Adv. Chem. Ser.* **1974**, *132*, 90.
(783) Burgess, C.; Hartley, F. R.; Searle, G. W. *J. Organometal. Chem.* **1974**, *76*, 247.
(784) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532.
(785) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983.
(786) Schrock, R. R. *Science* **1983**, *219*, 13.
(787) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 803.
(788) Levisalles, J.; Rose-Munch, F.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1981**, 152.
(789) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252.
(790) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237.
(791) Tysoe, W. T. *Langmuir* **1995**, in press.
(792) Stair, P. C.; Somorjai, G. A. *J. Chem. Phys.* **1977**, *66*, 2036.
(793) Schaefer, H. F., III. *Acc. Chem. Res.* **1979**, *12*, 288.
(794) Liu, M. T. H. *Acc. Chem. Res.* **1994**, *27*, 287.
(795) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 414.
(796) Garcia Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406.
(797) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.
(798) Höhn, A.; Otto, H.; Dziallas, M.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1987**, 852.
(799) Sakai, S.; Morokuma, K. *J. Phys. Chem.* **1987**, *91*, 3661.
(800) Horton, A. D.; Kemball, A. C.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2953.
(801) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220.
(802) Xiao, J.; Cowie, M. *Organometallics* **1993**, *12*, 463.
(803) Field, J. S.; Haines, R. J.; Sundermeyer, J.; Woollam, S. F. *J. Chem. Soc., Dalton Trans.* **1993**, 3749.
(804) Al-Essa, R. J.; Puddephatt, R. *J. Chem. Soc., Chem. Commun.* **1980**, 45.
(805) Ling, S. S. M.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 412.
(806) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661.
(807) Green, M.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 37.
(808) Miller, G. A.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 709.
(809) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700.
(810) Green, M.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1333.
(811) Casey, C. P.; Meszaros, M. W.; Fagan, P. J.; Bly, R. K.; Colborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053.
(812) Klug, C. A.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1991**, *95*, 2119.
(813) Klug, C. A.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1991**, *95*, 7033.
(814) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388.
(815) Pearlstine, K. A.; Friend, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 5898.
(816) Cotton, F. A.; Musco, A. *J. Am. Chem. Soc.* **1968**, *90*, 1444.
(817) Brookhart, M.; Lippman, N. M.; Reardon, E. J., Jr. *J. Organometal. Chem.* **1973**, *54*, 247.
(818) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S.; Dubois, L. H. *J. Phys. Chem.* **1994**, *98*, 2952.
(819) Zaera, F.; Fischer, D. A.; Carr, R. G.; Kollin, E. B.; Gland, J. L. In *Electrochemical Surface Science: Molecular Phenomena at Electrode Surfaces*; Soriaga, M. P., Ed.; ACS Symp. Ser. 378; American Chemical Society: Washington, 1988; pp 131–140.
(820) Gland, J. L.; Zaera, F.; Fischer, D. A.; Carr, R. G.; Kollin, E. B. *Chem. Phys. Lett.* **1988**, *151*, 227.
(821) Ogle, K. M.; Creighton, J. R.; Akhter, S.; White, J. M. *Surf. Sci.* **1986**, *169*, 246.

(822) Moshin, S. B.; Trenary, M.; Robota, H. J. *Chem. Phys. Lett.* **1989**, *154*, 511.
(823) Greenlief, C. M.; Radloff, P. L.; Zhou, X. L.; White, J. M. *Surf. Sci.* **1987**, *191*, 93.
(824) Borg, H. J. Ph.D. Thesis, Technical University of Eindhoven, The Netherlands, 1995.
(825) Erley, W.; Li, Y.; Land, D. P.; Hemminger, J. C. *Surf. Sci.* **1994**, *103*, 177.
(826) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978**, *15*, 407.
(827) Baro, A. M.; Ibach, H. *Vide, Couches Minces, Suppl.* **1980**, *201*, 458.
(828) Kang, D. B.; Anderson, A. B. *Surf. Sci.* **1985**, *155*, 639.
(829) Somorjai, G. A.; Van Hove, M. A.; Bent, B. E. *J. Phys. Chem.* **1988**, *92*, 973.
(830) Demuth, J. E. *Surf. Sci.* **1978**, *76*, L603.
(831) Zhu, X.-Y.; White, J. M. *Surf. Sci.* **1989**, *214*, 240.
(832) Zhu, X.-Y.; Castro, M. E.; Akhter, S.; White, J. M. *J. Vac. Sci. Technol. A* **1989**, *7*, 1991.
(833) Sachtler, J. W. A. Ph.D. Thesis, University of Leiden, The Netherlands, 1982.
(834) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Phys. Chem.* **1984**, *88*, 1960.
(835) Nishijima, M.; Yoshinobu, J.; Sekitani, T.; Onchi, M. *Surf. Sci.* **1991**, *242*, 493.
(836) Tysoe, W. T. Ph.D. Thesis, Cambridge University, 1982.
(837) Marinova, T. S.; Chakarov, D. V. *Surf. Sci.* **1987**, *192*, 275.
(838) Glines, A. M.; Anton, A. B. *Surf. Sci.* **1993**, *286*, 122.
(839) Burke, M. L.; Madix, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 1475.
(840) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 623.
(841) Wang, L. P.; Tysoe, W. T.; Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F. *J. Phys. Chem.* **1990**, *94*, 4236.
(842) Davis, S. M.; Somorjai, G. A. *J. Catal.* **1980**, *64*, 60.
(843) Davis, S. M. Ph.D. Thesis, University of California, Berkeley, 1981.
(844) Davis, S. M.; Somorjai, G. A. *J. Catal.* **1980**, *65*, 78.
(845) Zax, D. B.; Klug, C. A.; Slichter, C. P.; Sinfelt, J. H. *J. Phys. Chem.* **1989**, *93*, 5009.
(846) Ogle, K. M.; White, J. M. *Surf. Sci.* **1986**, *165*, 234.
(847) Braterman, P. S.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 657.
(848) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E.; Lavington, S. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1613.
(849) Thomson, J.; Baird, M. C. *Can. J. Chem.* **1970**, *48*, 3443.
(850) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 24.
(851) Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232.
(852) Yamamoto, K.; Nakanishi, K.; Kumada, M. *J. Organometal. Chem.* **1967**, *7*, 197.
(853) Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 8967.
(854) Collman, J. P.; MacLaury, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 3019.
(855) Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1976**, *98*, 5832.
(856) Daub, G. W. *Prog. Inorg. Chem.* **1977**, *22*, 409.
(857) Whitesides, G. M.; Boschetto, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 1529.
(858) De Luca, N.; Wojcicki, A. *J. Organometal. Chem.* **1980**, *193*, 359.
(859) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.
(860) Rogers, W. N.; Baird, M. C. *J. Organometal. Chem.* **1979**, *182*, C65.
(861) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814.
(862) Kash, P.; Teplyakov, A.; Yang, M.; Sun, D.-H.; Flynn, G.; Bent, B. E. To be published.
(863) Campbell, C. T. *Annu. Rev. Phys. Chem.* **1990**, *40*, 775.
(864) Hugenschmidt, M. B.; Domagala, M. E.; Campbell, C. T. *J. Vac. Sci. Tecnol. A* **1992**, *10*, 2556.
(865) Tjandra, S.; Zaera, F. *J. Am. Chem. Soc.* **1992**, *114*, 10645.
(866) Herz, R. K.; Gillespie, W. D.; Petersen, E. E.; Somorjai, G. A. *J. Catal.* **1981**, *67*, 371.
(867) Peden, C. H. F.; Goodman, D. W. *J. Catal.* **1987**, *104*, 347.
(868) Sault, A.; Goodman, D. W. *J. Catal.* **1990**, *126*, 57.
(869) Sachtler, J. W. A.; Biberian, J. P.; Somorjai, G. A. *Surf. Sci.* **1981**, *110*, 43.
(870) Sachtler, J. W. A.; Somorjai, G. A. *J. Catal.* **1984**, *89*, 35.
(871) Davis, S. M.; Somorjai, G. A. In *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1982; Vol. 4 (Fundamental Studies of Heterogeneous Catalysis), pp 217–364.
(872) Davis, S. M.; Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 7453.
(873) Smith, C. E.; Biberian, J. P.; Somorjai, G. A. *J. Catal.* **1979**, *57*, 426.
(874) Davis, S. M.; Zaera, F.; Somorjai, G. A. *J. Catal.* **1982**, *77*, 439.
(875) Zaera, F.; Somorjai, G. A. *Langmuir* **1986**, *2*, 686.
(876) Dalmai-Imelik, G.; Massardier, J. In *6th Int. Congr. Catal.*; The Chemical Society: London, 1976; pp 90–100.
(877) Engstrom, J. R.; Goodman, D. W.; Weinberg, W. H. *J. Phys. Chem.* **1990**, *94*, 396.
(878) Oudar, J.; Pinol, S.; Pradier, C. M.; Berthier, Y. *J. Catal.* **1987**, *107*, 434.
(879) Pradier, C. M.; Margot, E.; Berthier, Y.; Oudar, J. *Appl. Catal.* **1988**, *43*, 177.
(880) Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 663.
(881) Davis, S. M.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 1545.
(882) Zaera, F.; Somorjai, G. A. *J. Phys. Chem.* **1985**, *89*, 3211.
(883) Brown, R.; Kemball, C.; Oliver, J. A.; Sadler, I. H. *J. Chem. Research [S]* **1985**, 274.
(884) Loaiza, A. J.; M., X.; Zaera, F. *J. Catal.* **1995**, submitted for publication.
(885) Goodman, D. W. *Surf. Sci.* **1982**, *123*, L679.
(886) Rodriguez, J. A.; Goodman, D. W. *J. Phys. Chem.* **1990**, *94*, 5342.
(887) Godbey, D.; Garin, F.; Somorjai, G. A. *J. Catal.* **1989**, *117*, 144.
(888) Engstrom, J. R.; Goodman, D. W.; Weinberg, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 8305.
(889) Egawa, C.; Iwasawa, Y. *Surf. Sci.* **1988**, *198*, L329.
(890) Wax, M. J.; Kelley, R. D.; Madey, T. E. *J. Catal.* **1986**, *98*, 487.
(891) Zaera, F.; Godbey, D.; Somorjai, G. A. *J. Catal.* **1986**, *101*, 73.
(892) Davis, S. M.; Zaera, F.; Somorjai, G. A. *J. Catal.* **1984**, *85*, 206.
(893) Rucker, T. G.; Logan, M. A.; Gentle, T. M.; Muetterties, E. L.; Somorjai, G. A. *J. Chem. Phys.* **1986**, *90*, 2703.
(894) Goodman, D. W. *Acc. Chem. Res.* **1984**, *17*, 194.
(895) Geerlings, J. C.; Zonnevylle, M. C.; De Groot, C. P. M. *Surf. Sci.* **1991**, *241*, 315.
(896) Castner, D. G.; Blackadar, R. L.; Somorjai, G. A. *J. Catal.* **1980**, *66*, 257.
(897) Dwyer, D. J.; Yoshida, K.; Somorjai, G. A. *Adv. Chem.* **1979**, *178*, 65.
(898) Logan, M.; Gellman, A.; Somorjai, G. A. *J. Catal.* **1985**, *94*, 60.
(899) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.

CR940453K