

# Mimicking Aspects of Heterogeneous Catalysis: Generating, Isolating, and Reacting Proposed Surface Intermediates on Single Crystals in Vacuum

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## I. Introduction

One of the more controversial issues in surface science concerns the relevance of studies on single-crystal surfaces under vacuum conditions for processes such as heterogeneous catalysis which occur over compositionally and structurally heterogeneous



Currently an Associate Professor of Chemistry at Columbia University, Brian Bent received a B.A. in chemistry from Carleton College in 1982 and a Ph.D. in physical chemistry from the University of California, Berkeley, in 1986. From 1986 to 1988, he was a postdoctoral research associate at AT&T Bell Laboratories. Since 1988, he has been on the faculty of Columbia University where his research group is studying the kinetics and mechanisms of surface reactions which are relevant for materials deposition and etching as well as for heterogeneous catalysis.

materials at much higher pressures. While there is little doubt that the basic principles of structure, bonding, and reactivity derived from studies in vacuum ambients also apply at high pressures, there is a legitimate concern that the key factors that make surfaces do remarkable catalysis at high pressures are missing in single-crystal, vacuum studies.

The basis for this concern is the finding that monolayer adsorption of catalytic reactants on single crystals often leads to stoichiometric reactions which are different from the catalytic processes observed at higher pressures. For example, in the catalytic Fischer–Tropsch synthesis reaction, carbon monoxide and hydrogen are reacted over transition metal surfaces to form hydrocarbons, but, to date, no study of *monolayers* of carbon monoxide and hydrogen on metal single crystals has documented the formation of any hydrocarbon product. Thus, while there are some beautiful examples where single crystals carry out catalytic processes in single monolayers and where surface analysis techniques have been extraordinarily successful in determining the catalytic mechanism,<sup>1</sup> there are also many examples where single crystals, single monolayers, and vacuum ambients do not adequately mimic all aspects of catalytic processes. A key question, therefore, with respect to the relevance of single-crystal, vacuum-based studies for heterogeneous catalysis concerns the extent to which these model systems are able to mimic the chemistry of catalytic processes.

The focus of the present review is an approach for inducing adsorbed monolayers to mimic aspects of heterogeneous catalytic processes which have proven difficult to study in vacuum. The two issues that will be addressed are catalytic reaction intermediates and elementary reaction steps. The difficulty in studying catalytic reaction intermediates is that these species are typically too short-lived and the surface concentrations too small for spectroscopic detection and study. The short lifetime of reaction intermediates also translates into problems for identifying and studying elementary reaction steps. But even more problematic are catalytic processes where the elementary reactions of interest do not occur at all under vacuum adsorption conditions. The most common examples in this regard are bond synthesis reactions, since the high reactivity of atomically clean surfaces favors bond dissociation over bond formation on these materials.

Many of these difficulties in mimicking catalytic reactions have been surmounted in the past 10 years. Experimental approaches have been developed which allow surface chemists to isolate catalytically relevant reaction intermediates and to study elementary surface reaction steps. A particularly fruitful approach has been to generate proposed reaction intermediates on surfaces at cryogenic temperatures. By generating these normally reactive species at low temperatures, subsequent thermal reactions can be prevented. Thus, species which are low-coverage, short-lived intermediates under catalytic reaction conditions become stable surface fragments which can be accumulated into high surface coverages. The long surface lifetimes make possible spectroscopic study of these normally transient species. The high surface coverages promote bimolecular surface reactions.

In essence, the types of studies described above are two-dimensional matrix isolation experiments<sup>2</sup> with the surface as the matrix. The experimental challenges are: (1) to generate the desired surface species at cryogenic temperatures, (2) to form adsorbed layers of sufficient coverage and purity for meaningful spectroscopic study, and (3) to identify and investigate elementary reaction steps as the 2D matrix is heated to induce reaction. These three topics are the focus of the current review. The scope of the review is further limited to hydrocarbon fragments on metal surfaces. Stable molecules are not considered. Reviews which cover the bonding and reactions of *stable* hydrocarbon molecules are given in refs 3–14. Reviews of heteroatom-containing organics are given in refs 12–15, and a review of organic reactions on oxide surfaces appears in this issue.<sup>16</sup> Also relevant to the current review are studies of hydrocarbon catalysis over metal single crystals at atmospheric pressure, and reviews of this work are given in refs 11 and 17–19. Particularly noteworthy in the context of the present work is the recent review by Zaera<sup>6</sup> which discusses the bonding and reactions of hydrocarbon molecules and fragments on metals in the context of what is known about the corresponding ligands in organometallic compounds. The current review differs from prior accounts in that it focuses on hydrocarbon fragments

that are of particular relevance to heterogeneous catalysis.

This review is organized into three sections. The first describes methods for generating hydrocarbon fragments which have been proposed as intermediates in heterogeneous catalysis. The second summarizes and evaluates the techniques most commonly applied for identifying hydrocarbon fragments, and the third section reviews what has been learned about the bonding and reactivity of these surface fragments, with particular emphasis on the species most often proposed as catalytic reaction intermediates.

## II. Methods for Generating and Isolating Surface Reaction Intermediates

The hydrocarbon fragments most frequently proposed as surface intermediates in heterogeneous catalysis and the catalytic processes for which they have been proposed as intermediates are summarized in Tables 1–3. (Leading references to the species and reactions listed in the tables are given as refs 20–27.) Several aspects of these tables deserve comment. First, the reactions shown are in many cases not elementary steps. In particular, since the focus of this review is reactive intermediates, reaction steps that produce stable molecules (e.g. alkenes and alkynes) as intermediates are not shown. For example, in the alkene and alkyne hydrogenations in Table 1, the steps involving the adsorption of the unsaturated hydrocarbon and hydrogen followed by addition of H to form the surface alkyl or vinyl species are not shown. Second, in the case of C–C double and triple bond coordination to the surface, the extent of C–C bond rehybridization (i.e.  $\pi$ -coordination vs.  $\alpha,\beta$ -di- $\sigma$  coordination) is not addressed by the structures shown. In other words, the structure



should be viewed as equivalent to



and the following structure



should be viewed as equivalent to



Third, the tables do not indicate which species/pathways are most prevalent (or most frequently proposed) for catalysis. Note, for example, that in Table 1 alkane H,D-exchange is shown to occur both via an alkene intermediate and via a carbene intermediate, yet the latter is only very infrequently proposed as a mechanism for exchange.

It is only within the last 10 years that significant numbers of the surface species indicated in Tables 1–3 have been isolated and studied on single-crystal surfaces. And it is interesting to note that there are still no single-crystal studies for many of these proposed intermediates. Part of the reason for this

**Table 1. Proposed Surface Reaction Intermediates in Heterogeneous Hydrocarbon Catalysis for which C–C Bonds Remain Intact**

Process	Proposed Mechanism(s)
Alkene Hydrogenation / Alkene H,D-Exchange / Alkene Isomerization / Alkane H,D-Exchange	
Diene Hydrogenation / Diene H,D-Exchange / Alkene H,D-Exchange	
Alkyne Hydrogenation / Alkyne H,D-Exchange / Alkene H,D-Exchange	
Alkane H,D-Exchange	
Aromatization	

Legend: = alkyl; metallacycle = carbene; allyl = carbyne; vinyl

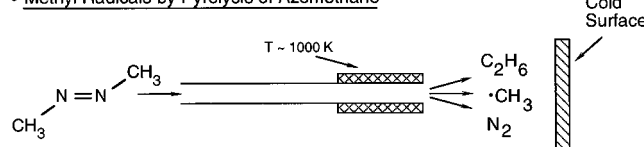
lack of study is that the low partial pressure of hydrogen in vacuum ambients favors dehydrogenation and formation of surface fragments with low H:C ratios (e.g. ethylidyne,  $CCH_3$ , where H:C = 1.5) and, until recently, species with high H:C ratios (e.g. methylene,  $CH_2$ , where H:C = 2) were not isolated. Yet while thermodynamics favors dehydrogenation on clean metal surfaces, quite a number of methods have now been demonstrated for generating and isolating more highly hydrogenated intermediates at low surface temperatures where they are kinetically stable.

This section reviews the approaches that have been developed for synthesizing high surface coverages of the hydrocarbon fragments indicated in Tables 1–3. These approaches can be subdivided into four categories: (1) trapping gas-phase ions and radicals on cold surfaces, (2) thermal dissociation of adsorbed molecular precursors, (3) photon-, electron-, and collision-induced dissociation of adsorbed molecular precursors, (4) coupling reactions in adsorbed monolayers. Each of these approaches is discussed in the subsections below using adsorbed alkyl groups to illustrate the methodology.

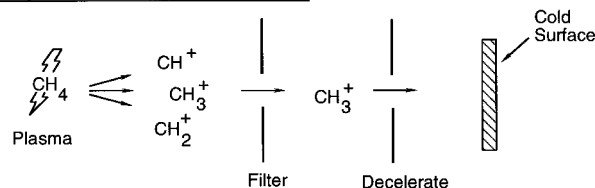
### A. Trapping Gas-Phase Ions and Radicals

All of the proposed catalytic reaction intermediates highlighted in Tables 1–3 correspond to highly reactive, open shell molecular fragments in the gas phase. These species cannot, therefore, be generated on surfaces simply by volatilizing and dosing com-

#### • Methyl Radicals by Pyrolysis of Azomethane



#### • Methyl Cations from Plasma Discharges



**Figure 1.** Schematic diagrams of sources for generating methyl groups on surfaces via the adsorption of radicals and ions. The methyl radical source shown was developed by Stair and co-workers as described in ref 28. The  $CH_3^+$  source was developed by Strongin and Mowlem as described in ref 53.

mercially available molecules. Conceptually, the most straightforward method for generating these surface fragments is to apply a gas phase radical or ion source for generating and dosing these reactive species onto surfaces which have been cooled sufficiently to prevent decomposition.

The primary technological challenges in dosing radicals and ions concern the intensity and purity of the sources. For radicals, source purity is particularly critical because of the difficulty in filtering neutral particles. In the case of methyl radicals, a simple and highly effective source based on the gas

**Table 2. Proposed Surface Reaction Intermediates in Heterogeneous Hydrocarbon Catalysis Involving C-C Bond Scission**

Process	Proposed Mechanism(s)
Hydrogenolysis	
Hydrogenolysis	
Hydrocracking	
Demethylation	
Alkane Isomerization	
Alkane Isomerization / Dehydrocyclization	

Legend: = alkyl; metallacycle = carbene; allyl = carbyne; vinyl

phase pyrolysis of azomethane has been developed<sup>28</sup> and is finding considerable application in surface studies.<sup>28-32</sup> The concept behind the azomethane source as developed by Stair and co-workers<sup>28</sup> is illustrated schematically in Figure 1. As shown, azomethane is passed into the vacuum system through a tube whose terminus is heated to ~1000 K. Gas-phase unimolecular decomposition produces methyl radicals and nitrogen.<sup>28</sup> Ethane and methane are secondary reaction products.<sup>28-31</sup> The significant aspect for most surface experiments is that the products besides methyl radicals are species which do not readily adsorb. Thus, when the flux from this source is impinged onto surfaces held at 100 K, methane, ethane, and nitrogen generally desorb while methyls are trapped intact. In the first surface application of this source, methyl radicals were adsorbed onto an oxygen-covered Mo(100) surface.<sup>29</sup> Subsequently, methyls have been adsorbed, isolated, and identified on Cu(111),<sup>30</sup> Cu(100),<sup>33</sup> Pt(111),<sup>31</sup> Ni(100),<sup>34</sup> and Rh(111).<sup>32</sup> It should also be noted that CH<sub>3</sub> radicals have been produced for surface studies by passing methane over a partial oxidation catalyst (Li<sub>x</sub>Mg<sub>x</sub>O).<sup>35,36</sup>

Azoalkyl sources incorporating ethyl and propyl groups have also been found to generate alkyl groups which have been trapped on a Cu(111) surface, but the pyrolysis chemistry generates other byproducts

which also adsorb and may affect the surface reaction kinetics.<sup>37</sup> To our knowledge, radical sources for other species (except atoms) have yet to be applied in surface studies. In this regard, however, it is noteworthy that the thermal<sup>38-52</sup> and photochemical (see Table 4) reactions of monolayers on metal surfaces have been reported to generate gas-phase radicals<sup>38-43</sup> and carbenes,<sup>44-52</sup> so one might envision designing sources where surface-generated radicals are captured by an adjacent clean surface.<sup>35,36</sup>

Ion sources are potentially of more general utility than radical sources since the desired species can be obtained at high purity by ion filtering. The technical challenge is to form ion beams with sufficient intensity at low enough velocity so that monolayer coverages can be obtained within minutes without fragmentation during adsorption. Typical sources generate high purity ion fluxes of 10<sup>12</sup> molecules cm<sup>-2</sup> s<sup>-1</sup> which means that for unit sticking probability monolayers can be formed within 10 min; typical kinetic energies of focused beams are, however, ~1 keV which means that surface fragmentation is probable unless the beam is decelerated—a process which often results in loss of intensity.

Figure 1 illustrates schematically the only example to our knowledge in which a source of low-energy ions has been used to generate a monolayer coverage of a hydrocarbon fragment on a metal surface. In this

**Table 3. Proposed Surface Reaction Intermediates in Heterogeneous Hydrocarbon Catalysis Involving C–C Bond Formation**

Process	Proposed Mechanism(s)
Dehydrocyclization	
Dehydrocyclization	
Fischer-Tropsch Synthesis	
Ziegler-Natta Polymerization	
Acetylene Trimerization	

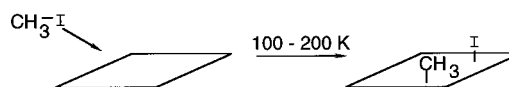
Legend: = alkyl; metallacycle = carbene; allyl = carbyne; vinyl

experiment by Strongin and Mowlem,<sup>53</sup> a methane plasma was used to generate  $\text{CH}_x^+$  ions from which  $\text{CH}_3^+$  was filtered and decelerated via magnetic fields to an energy of  $\sim 1$  eV prior to adsorption on a 140 K Pt(111) surface. The presence of methyl on the surface was indirectly inferred from the kinetics of methane evolution, which were similar to those reported for  $\text{CH}_3\text{I}$  decomposition on Pt(111), a system where the presence of methyl has been verified spectroscopically.<sup>54–59</sup>

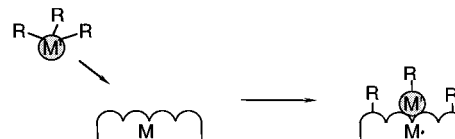
## B. Thermal Dissociation of Adsorbed Molecular Precursors

While the adsorption of radicals and ions generates, directly, catalytically relevant hydrocarbon fragments on surfaces, the gas-phase sources required are technologically challenging. A much simpler experimental approach is to adsorb molecular precursors which thermally dissociate on the surface to generate the desired fragment. The key issues with respect to the utility of this approach are the decomposition pathway, the decomposition kinetics, and the formation of coadsorbed species. Specifically, the surface must promote dissociation of specific bonds in the precursor in order to generate the desired fragment; the decomposition reaction must occur at sufficiently low temperature so that the

### • Oxidative Addition



### • Transmetalation



**Figure 2.** Two approaches for using molecular precursors to generate alkyl groups on metal surfaces.

fragment produced is stable; and it is desirable that coadsorbed fragments generated on the surface by the dissociation reaction be weakly interacting with the species of interest.

Examples of molecular precursors to generate alkyl groups on metals are shown schematically in Figure 2. Molecules which have received considerable attention are the alkyl halides. The unusually weak bond between carbon and halogens and the unusually strong bond between halogens and metals means that carbon-halogen (C–X) bond scission is thermodynamically favored over C–H bond scission. Numerous studies have also shown that C–X bond scission

**Table 4. Summary of Studies of Halohydrocarbon Adsorption on Metal Surfaces**

surface	molecule(s)	analysis technique(s) <sup>a</sup>	
Al(100)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> I (x = 1–6)	TPD, <sup>67,68,76</sup> HREELS, <sup>67</sup> RAIRS <sup>85</sup>	
	I(CH <sub>2</sub> ) <sub>x</sub> I, Br(CH <sub>2</sub> ) <sub>x</sub> Br (x = 2–6)	TPD, <sup>68,353</sup> H/TPD, <sup>353</sup> HREELS <sup>68,353</sup>	
	CH <sub>2</sub> =CHCH <sub>2</sub> Br, CH <sub>2</sub> =CHCH <sub>2</sub> I	TPD, <sup>353</sup> H/TPD, <sup>68,353</sup> HREELS <sup>353</sup>	
	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>x</sub> Br (x = 2, 4)	TPD <sup>68,353</sup>	
Al(111)	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> I, C <sub>6</sub> H <sub>5</sub> I	TPD <sup>68</sup>	
	CH <sub>3</sub> I, CH <sub>3</sub> Br, CH <sub>3</sub> Cl	AES, <sup>372</sup> HREELS <sup>372</sup>	
	CD <sub>3</sub> I	HREELS <sup>372</sup>	
Al film	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> I	TPD <sup>67</sup>	
	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>45,77,373</sup> AES <sup>77,373</sup>	
	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	TPD, <sup>287,288</sup> XPS, <sup>287</sup> <i>hν</i> , <sup>287,288</sup> TOF <sup>287,288</sup>	
Ag(111)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	GC, <sup>374</sup> MS <sup>374</sup>	
	CH <sub>3</sub> Cl, CH <sub>3</sub> Br, CH <sub>3</sub> I	TPD, <sup>256</sup> Si/TPD <sup>256</sup>	
	CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , CCl <sub>4</sub> , CCl <sub>3</sub> Br	TPD, <sup>145,149,150</sup> K/TPD, <sup>38</sup> C <sub>6</sub> H <sub>5</sub> /TPD, <sup>84</sup>	
	CF <sub>3</sub> I	CH <sub>2</sub> =CH/TPD, <sup>84</sup> XPS, <sup>145,149,150</sup> UPS, <sup>145</sup> LEED, <sup>145</sup> Δφ, <sup>145</sup> <i>hν</i> , <sup>147,149,150,375,376</sup> e <sup>115</sup> TPD, <sup>375</sup> <i>hν</i> , <sup>375,377</sup>	
Ag film	CH <sub>3</sub> CH <sub>2</sub> I	TPD, <sup>378,475</sup> I/TPD, <sup>378</sup> AES, <sup>378</sup> XPS, <sup>378</sup> UPS, <sup>378</sup> <i>hν</i> , <sup>41,379–381</sup> e <sup>380</sup>	
	CH <sub>3</sub> CH <sub>2</sub> Cl	TPD, <sup>113,146,246</sup> H/TPD, <sup>146</sup> XPS, <sup>146</sup> Δφ <sup>146</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> I, ClCH <sub>2</sub> I, Cl(CH <sub>2</sub> ) <sub>2</sub> I	TPD, <sup>148,382</sup> XPS, <sup>148</sup> UPS, <sup>148</sup> Δφ, <sup>148</sup> <i>hν</i> , <sup>147,148,382</sup> e <sup>7,116,382</sup>	
	CH <sub>2</sub> =CHI	TPD <sup>246</sup>	
	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	TPD, <sup>354</sup> HREELS <sup>354</sup>	
	C <sub>6</sub> H <sub>5</sub> I	TPD, <sup>83</sup> C <sub>6</sub> D <sub>5</sub> /TPD <sup>83</sup>	
	C <sub>6</sub> H <sub>5</sub> Cl	TPD, <sup>383,384</sup> XPS, <sup>114</sup> UPS, <sup>114</sup> HREELS, <sup>385</sup> IR, <sup>384</sup> Δφ, <sup>114</sup> <i>hν</i> , <sup>114,383–385</sup> e <sup>114</sup>	
	CH <sub>2</sub> I <sub>2</sub>	XPS, <sup>386</sup> <i>hν</i> , <sup>386,387</sup> TOF <sup>386,387</sup>	
	CH <sub>3</sub> I	TPD, <sup>234</sup> HREELS, <sup>234</sup> IR, <sup>234</sup> Δφ <sup>234</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> I (x = 1–3)	TPD, <sup>250</sup> AES, <sup>250</sup> LEED <sup>250</sup>	
Au(100)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	TPD, <sup>250</sup> <i>hν</i> , <sup>250</sup>	
	CH <sub>3</sub> I	TPD, <sup>225</sup> <i>hν</i> , <sup>225</sup>	
Au film	CH <sub>3</sub> Cl	MS <sup>388</sup>	
	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	XPS, <sup>389</sup> UPS <sup>389</sup>	
Cr, Mn, Co films	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl	MS, <sup>374,390,391</sup> GC <sup>374</sup>	
	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl		
Cu(111)	CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>30,39,40,69,70,141</sup> I/TPD, <sup>49</sup> HREELS, <sup>30,69,141,214</sup> Δφ <sup>66,69</sup>	
	CHD <sub>2</sub> I	HREELS <sup>141,214</sup>	
	CH <sub>3</sub> Br	TPD, <sup>235</sup> HREELS, <sup>235</sup> <i>hν</i> , <sup>235</sup>	
	CH <sub>3</sub> CH <sub>2</sub> I, CH <sub>3</sub> CD <sub>2</sub> I	TPD, <sup>66,69,70</sup> HREELS <sup>66,69,214</sup>	
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	TPD, <sup>66,69,70,245b</sup> HREELS, <sup>66,69,245b</sup> Δφ <sup>66,69</sup>	
	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I	TPD, <sup>245b</sup> HREELS <sup>245b</sup>	
	F-substituted propene	TPD, <sup>479</sup> HREELS <sup>479</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> I (x = 4–5)	TPD <sup>70</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> Br (x = 1–5)	TPD, <sup>66,69</sup> HREELS, <sup>66,214</sup> Δφ <sup>66,69</sup>	
	CH <sub>2</sub> ClCH <sub>2</sub> Cl	MS, <sup>392,393</sup> AES, <sup>79,392,393</sup> UPS, <sup>393</sup> ARUPS, <sup>392</sup> NEXAFS, <sup>394</sup> NISXW, <sup>394</sup> Δφ, <sup>392</sup> e <sup>392,393</sup>	
	CH <sub>2</sub> BrCH <sub>2</sub> Cl	UPS, <sup>395</sup> LEED, <sup>395</sup> Δφ, <sup>395</sup> e <sup>395</sup>	
	C <sub>6</sub> H <sub>5</sub> I	TPD, <sup>361,362</sup> H/TPD, <sup>361,362</sup> RI/TPD, <sup>71</sup> C <sub>6</sub> D <sub>5</sub> /TPD, <sup>362</sup> NEXAFS, <sup>195</sup> HREELS, <sup>361,362</sup> Δφ, <sup>361</sup> e <sup>71,362</sup>	
	F-substituted C <sub>6</sub> H <sub>5</sub> I	TPD <sup>363</sup>	
	C <sub>6</sub> H <sub>5</sub> Cl	NEXAFS <sup>195</sup>	
	Cu(100)	CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>132,396</sup> HREELS, <sup>132</sup> Δφ <sup>132</sup>
		CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>396</sup> CD <sub>2</sub> /TPD, <sup>132</sup> CD <sub>3</sub> /TPD, <sup>132</sup> C <sub>2</sub> D <sub>5</sub> /TPD, <sup>132</sup> Δφ, <sup>132</sup> HREELS <sup>132</sup>
		CH <sub>3</sub> CH <sub>2</sub> I	TPD <sup>396</sup>
		CH <sub>3</sub> CH <sub>2</sub> Br	TPD, <sup>132</sup> HREELS <sup>132</sup>
		CHD <sub>2</sub> CD <sub>2</sub> Br	TPD <sup>136</sup>
secondary bromoalkanes		TPD, <sup>82,137</sup> Δφ <sup>137</sup>	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> Cl (x = 2–6)		TPD, <sup>66</sup> AES <sup>66</sup>	
CH <sub>2</sub> =CHBr		TPD, <sup>194</sup> NEXAFS, <sup>194</sup> Δφ <sup>194</sup>	
CH <sub>2</sub> =CHI, CH <sub>2</sub> =CHCl		TPD, <sup>194</sup> NEXAFS <sup>194</sup>	
CHCl=CHCl, CHCl=CCl <sub>2</sub>		TPD, <sup>397</sup> NEXAFS <sup>397</sup>	
chloroethanes and -propanes		TPD, <sup>383</sup> Δφ <sup>383</sup>	
Cu(110)		CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>140,236,251</sup> H/TPD, <sup>140,236,251</sup> CH <sub>2</sub> /TPD, <sup>140,251</sup> I/TPD <sup>140</sup>
		CH <sub>3</sub> Cl	TPD, <sup>398</sup> UPS, <sup>398</sup> HREELS <sup>398</sup>
	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>140,236</sup> H/TPD, <sup>140</sup> CD <sub>3</sub> /TPD <sup>140,236,251</sup>	
	CH <sub>3</sub> CH <sub>2</sub> I	TPD, <sup>75,251</sup>	
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> I, CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> I	TPD, <sup>75,236,245a</sup> IR <sup>245a</sup>	
	CH <sub>3</sub> CHICH <sub>3</sub>	IR <sup>245a</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> I	TPD, <sup>75,399</sup> I/TPD, <sup>75</sup> LEED <sup>75</sup>	
Cu(111)/Br	CH <sub>3</sub> Br	TPD, <sup>400</sup> LEED, <sup>400</sup> <i>hν</i> , <sup>400</sup> e <sup>400</sup>	
	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	MS, <sup>374,388</sup> GC <sup>374</sup>	
Cu film	CH <sub>3</sub> Br	TPD, <sup>78</sup> HREELS, <sup>78</sup> <i>hν</i> , <sup>78</sup>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl, (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl	MS <sup>390</sup>	
Cu catalyst	CH <sub>2</sub> ClCH <sub>2</sub> Cl	MS <sup>401</sup>	
Cu/SiO <sub>2</sub>	CH <sub>3</sub> I	IR <sup>402,403</sup>	
Fe(110)	CCl <sub>2</sub> F <sub>2</sub>	TPD <sup>46,47,50</sup>	

Table 4. (Continued)

surface	molecule(s)	analysis technique(s) <sup>a</sup>
Fe(100)	CCl <sub>4</sub>	TPD, <sup>48-50</sup> O/TPD, <sup>49</sup> AES <sup>48</sup>
Fe film	CH <sub>3</sub> Cl	TPD, <sup>404</sup> XPS <sup>404</sup>
	CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br	catalytic hydrogenolysis <sup>405</sup>
	CH <sub>3</sub> Cl	MS <sup>388</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl, (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl	MS <sup>390</sup>
K film	CH <sub>3</sub> Br	TPD, <sup>38</sup> MS, <sup>38</sup> XPS, <sup>38</sup> UPS, <sup>38</sup> Δφ <sup>38</sup>
Mg(0001)	CH <sub>3</sub> Br	TPD, <sup>406</sup> (CH <sub>3</sub> ) <sub>2</sub> O/TPD, <sup>406</sup> AES, <sup>406</sup> XPS, <sup>406</sup> HREELS <sup>406</sup>
Mo(110)	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>280</sup> HREELS <sup>280</sup>
	CH <sub>3</sub> I	TPD, <sup>407</sup> HREELS <sup>407</sup>
Mo film	CH <sub>3</sub> Cl	MS <sup>408</sup>
Na film	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	GC, <sup>409</sup> MS, <sup>409</sup> hν <sup>409</sup>
Ni(100)	CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>142,143,410,411</sup> H/TPD, <sup>142,143</sup> AES, <sup>143</sup> XPS, <sup>253,410,411,476</sup> SSIMS, <sup>143,410</sup> TPSIMS <sup>143,412</sup>
	CH <sub>3</sub> Cl, CH <sub>3</sub> Br	TPD, <sup>143</sup> AES, <sup>143</sup> SSIMS <sup>143</sup>
	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>142</sup> H/TPD <sup>142</sup>
	CH <sub>3</sub> CH <sub>2</sub> I, CD <sub>3</sub> CD <sub>2</sub> I	TPD, <sup>229b</sup> H/TPD, <sup>230</sup> XPS, <sup>229b,253</sup> SSIMS <sup>229b</sup>
	CD <sub>3</sub> CH <sub>2</sub> I, CH <sub>3</sub> CD <sub>2</sub> I	TPD, <sup>229b,230</sup> H/TPD <sup>229b,230</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> I, CD <sub>3</sub> (CD <sub>2</sub> ) <sub>2</sub> I	TPD, <sup>72,247,253</sup> H/TPD, <sup>72,253</sup> XPS, <sup>72,253</sup> SSIMS <sup>247</sup>
	CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> I, CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> I	TPD, <sup>72,253</sup> H/TPD, <sup>72,253</sup> CH <sub>3</sub> I/TPD <sup>72</sup>
	(CD <sub>3</sub> ) <sub>2</sub> CDI, (CH <sub>3</sub> ) <sub>2</sub> CHI, (CD <sub>3</sub> ) <sub>2</sub> CHI	TPD, <sup>72,247</sup> H/TPD, <sup>72</sup> XPS, <sup>247</sup> SSIMS <sup>247</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>x</sub> I (x = 3-5)	TPD, <sup>72,253</sup> XPS <sup>253</sup>
	CH <sub>3</sub> CHICH <sub>2</sub> CH <sub>3</sub>	TPD, <sup>72,253</sup> H/TPD <sup>253</sup>
	(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> I	TPD <sup>263</sup>
	(CH <sub>3</sub> ) <sub>3</sub> CI, (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> I	TPD, <sup>253</sup> H/TPD <sup>253</sup>
	C <sub>6</sub> H <sub>5</sub> I, C <sub>6</sub> H <sub>11</sub> I, C <sub>6</sub> H <sub>9</sub> Br, I(CH <sub>2</sub> ) <sub>x</sub> I (x = 3-6)	TPD, <sup>357</sup> XPS <sup>357</sup>
Ni(111)	CF <sub>3</sub> I	TPD, <sup>413</sup> AES, <sup>413,478</sup> IR <sup>413</sup>
	CH <sub>3</sub> I	TPD, <sup>144</sup> H/TPD <sup>144</sup>
	CH <sub>3</sub> Cl	TPD, <sup>414</sup> AES, <sup>414</sup> hν, <sup>414,415</sup> TOF <sup>414</sup>
	CH <sub>3</sub> Br	TPD, <sup>416</sup> Br/TPD, <sup>416</sup> hν, <sup>416,417</sup> TOF <sup>416,417</sup>
	CF <sub>3</sub> I	TPD, <sup>418,419</sup> H/TPD, <sup>418</sup> AES, <sup>418,419</sup> IR, <sup>418</sup> e <sup>419</sup>
Ni film	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	MS, <sup>374,388</sup> GC, <sup>374</sup> XPS, <sup>389</sup> UPS <sup>389</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl, (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl	MS <sup>390</sup>
	CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br	catalytic hydrogenolysis <sup>405</sup>
Pb film	CH <sub>3</sub> Cl	MS <sup>388</sup>
Pd(100)	CH <sub>3</sub> I	TPD, <sup>235-237</sup> H/TPD, <sup>236</sup> O/TPD, <sup>237</sup> AES, <sup>235</sup> XPS, <sup>236,237,420</sup> UPS, <sup>235-237,420</sup> Δφ, <sup>235,236</sup> hν <sup>236,420</sup>
	CH <sub>3</sub> Cl	TPD, <sup>421-424</sup> K/TPD, <sup>421,422,424,425</sup> Cl/TPD, <sup>423</sup> AES, <sup>424</sup> UPS, <sup>423</sup> EELS, <sup>423</sup> Δφ, <sup>422,423</sup> hν <sup>425</sup>
	CH <sub>3</sub> CH <sub>2</sub> I	TPD, <sup>248</sup> AES, <sup>248</sup> XPS, <sup>248,420</sup> UPS, <sup>248,420</sup> Δφ, <sup>248</sup> hν <sup>248,420</sup>
	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>190,237</sup> O/TPD, <sup>237</sup> I/TPD, <sup>190</sup> AES, <sup>190</sup> XPS, <sup>190,237,420</sup> UPS, <sup>190,237,420</sup> Δφ, <sup>190</sup> hν <sup>190,420</sup>
Pd(111)	CH <sub>3</sub> I	TPD, <sup>426</sup> CO/TPD, <sup>426</sup> I/TPD, <sup>426</sup> XPS <sup>426</sup>
Pd film	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	GC, <sup>374</sup> MS <sup>374,388</sup>
	CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br, (CH <sub>3</sub> ) <sub>3</sub> CCl	catalytic hydrogenolysis <sup>405,427</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl, (CH <sub>3</sub> ) <sub>2</sub> CHCl	MS <sup>390</sup>
Pd catalyst	CH <sub>3</sub> Cl, CH <sub>3</sub> I	IR <sup>428</sup>
Pt(111)	CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>54,55,151,216,231-233</sup> H/TPD, <sup>151,231-233,430</sup> CO/TPD, <sup>55</sup> I/TPD, <sup>431</sup> BPTDS, <sup>233,430</sup> POTPD, <sup>151</sup> AES, <sup>55</sup> XPS, <sup>432</sup> HREELS, <sup>54,55</sup> IR, <sup>57,59,216</sup> TPSIMS, <sup>55</sup> hν <sup>431,432</sup>
	CH <sub>3</sub> Br, CD <sub>3</sub> Br	TPD, <sup>54,215,433-435</sup> I/TPD, <sup>431</sup> AES, <sup>434,435</sup> UPS, <sup>215</sup> XPS, <sup>433</sup> HREELS, <sup>54,215,434,436</sup> hν, <sup>215,431,433-442</sup> TOF <sup>438,439,441</sup>
	CH <sub>3</sub> Cl, CD <sub>3</sub> Cl	TPD, <sup>54,434,435,443,444</sup> I/TPD, <sup>431</sup> C/TPD, <sup>443</sup> H <sub>2</sub> O/TPD, <sup>444</sup> HREELS, <sup>54,434</sup> IR, <sup>57</sup> Δφ, <sup>443</sup> hν <sup>431,434,435,443-449</sup>
	CH <sub>2</sub> I <sub>2</sub> , CD <sub>2</sub> I <sub>2</sub>	TPD, <sup>151</sup> POTPD <sup>151</sup>
	ClCH <sub>2</sub> I	TPD, <sup>278</sup> XPS, <sup>278</sup> HREELS <sup>278</sup>
	CH <sub>3</sub> CH <sub>2</sub> I	TPD, <sup>56,249,450</sup> XPS, <sup>56,249,450</sup> IR <sup>56,57,451</sup>
	CD <sub>3</sub> CD <sub>2</sub> I, CD <sub>3</sub> CH <sub>2</sub> I, CH <sub>3</sub> CD <sub>2</sub> I	TPD, <sup>227,474</sup> H/TPD, <sup>227</sup> IR <sup>451</sup>
	CH <sub>3</sub> CH <sub>2</sub> Br	IR <sup>57</sup>
	CH <sub>3</sub> CH <sub>2</sub> Cl, CD <sub>3</sub> CD <sub>2</sub> Cl	TPD, <sup>242,452</sup> H <sub>2</sub> O/TPD, <sup>452</sup> XPS, <sup>299</sup> HREELS, <sup>242,243</sup> hν <sup>242,243,452</sup>
	CH <sub>2</sub> =CHI	TPD, <sup>320-322,350</sup> H/TPD, <sup>320,322,350</sup> POTPD, <sup>151,322,350</sup> XPS, <sup>320,322</sup> HREELS, <sup>320,322</sup> IR, <sup>321</sup> TPSIMS <sup>320,322</sup>
	CH <sub>2</sub> =CHBr, CH <sub>2</sub> =CHCl	IR, <sup>57</sup> XPS <sup>299</sup>
	CHCl-CHCl- <i>cis</i> , - <i>trans</i>	TPD, <sup>453</sup> HREELS, <sup>453,454</sup> hν <sup>454</sup>
	ClCH <sub>2</sub> CH <sub>2</sub> Br	TPD, <sup>455</sup> XPS, <sup>455</sup> hν <sup>455</sup>
	CF <sub>3</sub> Cl	TPD, <sup>456</sup> XPS, <sup>456</sup> UPS, <sup>456</sup> Δφ, <sup>456</sup> hν, <sup>456</sup> e <sup>456</sup>
	CF <sub>3</sub> I	TPD, <sup>44,473</sup> H/TPD, <sup>44</sup> XPS, <sup>44</sup> HREELS, <sup>44,473</sup> Δφ <sup>44</sup> , hν <sup>473</sup>
Pt(100)	C <sub>6</sub> H <sub>5</sub> Cl	UPS <sup>457</sup>
Pt/SiO <sub>2</sub>	CH <sub>3</sub> I, CH <sub>3</sub> Cl	IR <sup>458</sup>
	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	MS, <sup>374</sup> GC <sup>374</sup>
Pt/SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> Cl	IR, <sup>429,459</sup> hν <sup>459</sup>
Pt film	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br, (CH <sub>3</sub> ) <sub>3</sub> CCl	catalytic hydrogenolysis <sup>405</sup>
Rh(111)	CH <sub>3</sub> I	TPD, <sup>73,460</sup> O/TPD, <sup>73</sup> HREELS, <sup>73,460</sup> hν <sup>460</sup>
	CH <sub>2</sub> I <sub>2</sub>	TPD, <sup>73,74,254</sup> O/TPD, <sup>73,74</sup> AES, <sup>254</sup> XPS, <sup>254</sup> HREELS, <sup>73,74,254</sup> Δφ, <sup>254</sup> hν <sup>254</sup>

**Table 4. (Continued)**

surface	molecule(s)	analysis technique(s) <sup>a</sup>
Rh film	CH <sub>3</sub> CH <sub>2</sub> I, (CH <sub>3</sub> ) <sub>2</sub> CHI	TPD, <sup>244</sup> O/TPD, <sup>244</sup> HREELS <sup>244</sup>
	C <sub>6</sub> H <sub>5</sub> F	HREELS <sup>461,462</sup>
	XCH <sub>2</sub> CH <sub>2</sub> OH (X = F, Cl, Br, I)	TPD, <sup>480</sup> HREELA <sup>480</sup>
	CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br	catalytic hydrogenolysis <sup>405</sup>
Ru(001)	C <sub>2</sub> Cl <sub>4</sub>	TPD <sup>51</sup>
	CH <sub>3</sub> I, CD <sub>3</sub> I	TPD, <sup>213</sup> H/TPD, <sup>213</sup> AES, <sup>213</sup> HREELS <sup>213</sup>
Ti film	CF <sub>3</sub> I	TPD, <sup>379,477</sup> H/TPD, <sup>379</sup> AES, <sup>379,477</sup> HREELS, <sup>379</sup> ESDIAD <sup>379</sup>
	<i>n</i> -alkyl halides	MS <sup>390,391,463</sup>
	branched alkyl chlorides	MS <sup>390,464</sup>
	alkyl dichlorides	MS <sup>465a</sup>
W foil	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	MS, <sup>374</sup> GC <sup>374</sup>
	CH <sub>3</sub> Cl, CH <sub>3</sub> Br, CH <sub>3</sub> I	AES, <sup>465b</sup> TPD <sup>465b</sup>
W filament	CH <sub>3</sub> Br	gas IR <sup>466</sup>
W film	CH <sub>3</sub> CH <sub>2</sub> Cl, CH <sub>3</sub> CH <sub>2</sub> Br	catalytic hydrogenolysis <sup>405</sup>
	CH <sub>3</sub> Cl, CH <sub>2</sub> Cl <sub>2</sub>	GC, <sup>374</sup> MS <sup>374,408</sup>
Fischer–Tropsch catalysts	CH <sub>3</sub> I	GC <sup>62,63</sup>
	CH <sub>x</sub> Cl <sub>4-x</sub>	GC <sup>64</sup>
	CH <sub>2</sub> =CHBr	MS <sup>65</sup>

<sup>a</sup> Legend: AES = Auger electron spectroscopy; MS = mass spectrometry; GC = gas chromatography; TPD = temperature-programmed desorption or reaction, X/TPD = temperature-programmed desorption or reaction with X coadsorbed on the surface; BPTDS = bismuth postdosing mass spectrometry; POTPD = predosed oxygen temperature-programmed desorption; XPS = X-ray photoelectron spectroscopy; UPS = ultraviolet photoelectron spectroscopy; NEXAFS = near-edge X-ray absorption fine structure; HREELS = high-resolution electron energy loss spectroscopy; IR = infrared spectroscopy; TPSIMS = temperature-programmed secondary ion mass spectrometry; SSIMS = static secondary ion mass spectrometry; ESDIAD = electron-stimulated desorption ion angular distribution;  $\Delta\phi$  = measurements of the change in surface work function;  $h\nu$  = surface photochemistry studies;  $e =$  electron-induced dissociation and desorption studies.

is kinetically favored over C–H bond scission (see Table 4). In almost every case, carbon–iodine bond scission occurs at or below 200 K, while C–H bond scission in alkyl groups occurs above 200 K. The net result is selective cleavage of the C–X bond to generate the desired fragment. This process of dissociative adsorption by carbon–halogen bond scission is what is known in organometallic chemistry as an oxidative addition, and the oxidative addition of alkyl halides is a common route to metal alkyl compounds.<sup>60</sup>

Quite a variety of hydrocarbon fragments have been generated on metal surfaces by oxidative addition—most within the last three years. (For a review of work prior to this time, see ref 61.) Table 4 summarizes the studies in the literature and indicates the experimental techniques that have been applied. (It is important to note, however, that the hydrocarbon halides do not dissociate for all systems listed—especially the chlorides and bromides which desorb from most transition metals without measurable dissociation.) Also included in Table 4 are results for metal films and catalysts at higher pressures and under catalytic reaction conditions. (Studies of adsorption on nonmetallic surfaces are not included.) Particularly noteworthy in this latter regard are studies of alkyl halide reactions with Fischer–Tropsch catalysts as a means to generate and assess the role of postulated reaction intermediates.<sup>62–65</sup>

As is evident from Table 4, fragments besides alkyls have been generated by the thermal dissociation of haloalkanes, and these include methylene (CH<sub>2</sub>), vinyl (CH=CH<sub>2</sub>), phenyl (C<sub>6</sub>H<sub>5</sub>), allyl (CH<sub>2</sub>CHCH<sub>2</sub>), and metallacycles (MC<sub>n</sub>H<sub>y</sub>M). The identification, bonding, and reactivity of these species are discussed in sections III and IV.

The commercial availability, ease of handling, and the simplicity of their surface reactivity have made

hydrocarbon halides the most extensively applied precursors for generating hydrocarbon fragments on metal surfaces. There are, however, several issues with respect to the use of these compounds as precursors which deserve mention. First, the extent of hydrocarbon fragment formation depends both on the activation energy for C–X bond dissociation (generally 10–20% of the gas-phase bond dissociation energy<sup>66</sup>) and on the activation energy for molecular desorption of the haloalkane. The latter value is important since it is the rate of dissociation relative to desorption which determines the dissociation yield. Striking examples of the effect of this competition between desorption and dissociation are seen in the variation of the alkyl halide dissociation yield as a function of alkyl chain length on aluminum<sup>67,68</sup> and copper<sup>66,69</sup> surfaces. Bromoethane, for example, has a negligible dissociation yield on Cu(111), but bromopropane dissociates with near-monolayer yield—not because the activation energy for dissociation is lowered upon increasing the alkyl chain from two to three carbons, but because activation energy for desorption increases so that the rate of desorption decreases.<sup>66</sup>

A second noteworthy aspect of using haloalkanes as molecular precursors for adsorbed hydrocarbon fragments is that in some, and possibly all, of these dissociative adsorption reactions, hydrocarbon radicals are produced. Gas-phase methyl radicals have been detected for CH<sub>3</sub>Br dissociation on potassium films,<sup>38</sup> CH<sub>3</sub>I dissociation on Cu(111),<sup>39,40</sup> and CF<sub>3</sub>I dissociation on Ag(111).<sup>41</sup> Similarly, CH<sub>2</sub> ejection is observed for CH<sub>2</sub>I<sub>2</sub> dissociation on Al(111),<sup>45</sup> CF<sub>2</sub> ejection for CF<sub>2</sub>Cl<sub>2</sub> dissociation on Fe(110),<sup>46,47,50</sup> and CCl<sub>2</sub> ejection for CCl<sub>4</sub> dissociation on Fe(110).<sup>48,49,51</sup> In each of these systems, some of the radicals and carbenes are ejected to the gas phase and some are trapped on the surface. There have also been reports of radical<sup>33,70–73</sup> and carbene<sup>45,74</sup> reaction prior to



adsorption on the surface. Thus, one must use caution in studies applying halohydrocarbon precursors (particularly studies under catalytic reaction conditions where gas phase free radical reactions can occur) to establish that the desired hydrocarbon fragment is generated and thermally accommodated with the surface prior to reaction. General rules for predicting which metal surfaces will produce radicals in halohydrocarbon adsorption have yet to be established, but one would expect metals whose halide compounds have the most negative heats of formation (per mole of metal-halogen bonds) to be likely candidates for halogen abstraction and radical formation. On this basis, one would predict that in addition to the metals mentioned above, Cr, Mn, and Cd would be particularly likely candidates for radical formation, while at the other extreme, Pt and Au would be least likely.

A final, and most significant, issue of note with respect to halohydrocarbon precursors is that the strong metal-halogen bond which makes radical and carbene ejection thermodynamically favorable also binds the halogen strongly to the metal surface. In most cases, these metal halides are stable throughout the temperature range where the surface hydrocarbon fragments react, so effects of the coadsorbed surface halide on the bonding and reactions of the hydrocarbon fragment must be considered. Interestingly, the effects have proven to be surprising small. Except for near saturation coverage where dramatic caging effects have been reported,<sup>75</sup> the surface reaction pathways for alkyls,<sup>30,67,76-79,80-82</sup> phenyls,<sup>83</sup> and vinyls<sup>84</sup> in the presence and absence of halogens are unchanged, and the reaction peak temperatures in TPD experiments are always perturbed by less than 50 K<sup>84</sup>—often by less than 10 K.<sup>30,76,80-83</sup> The reason the effect of the halogen is small is still not yet fully understood, but in comparing adsorbed halogens with adsorbed alkali metal atoms (adsorbates where dramatic effects of coadsorption are often observed) two differences are particularly noteworthy: (1) the surface work function change is generally only several hundred millielectronvolts for halogens compared with 2–3 eV for alkali metals, and (2) the tendency for compound formation between adsorbed halogens and coadsorbates is less than for adsorbed alkali metals which are, for example, readily oxidized by coadsorbed carbon monoxide in some systems.

Molecular precursors which can avoid the issue of coadsorbed surface species are organometallic compounds. Specifically, in the case of homoleptic alkyls (i.e. organometallics in which all ligands are the same alkyl group), if the metal atom is chosen to be the same as those in the metal surface of interest, then dissociative adsorption as shown schematically in Figure 2 leads to a pure monolayer of the desired hydrocarbon fragment. This approach has been applied to generate alkyl groups via the dissociative adsorption of trialkyl aluminum compounds on aluminum surfaces.<sup>76,85</sup> Other organometallics which have been used to generate alkyls on metal surfaces include:  $\text{CH}_3\text{AuP}(\text{CH}_3)_3$  on Au(100);<sup>86</sup> (diolefin)di-alkylplatinum(II) complexes on Pt films;<sup>87</sup> bismuth trialkyls on Pt(111),<sup>88</sup> and  $(\text{CH}_3\text{CH}_2)_2\text{Zn}$  on Pd(100).<sup>89</sup>

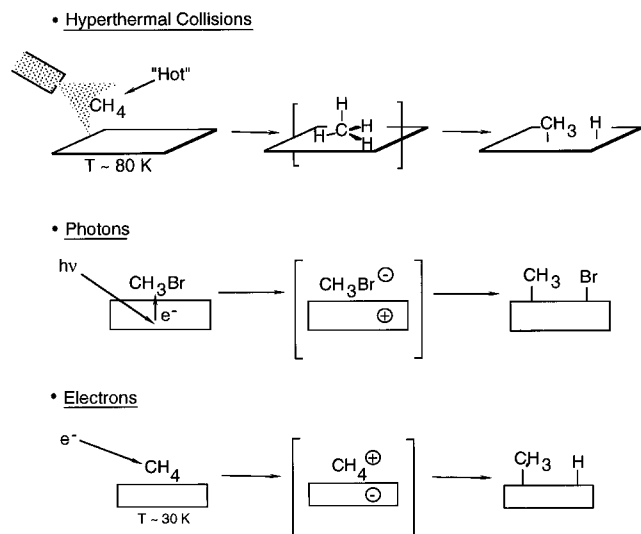
In the case of the aluminum alkyl system, infrared spectroscopy studies indicate that alkyl ligands migrate away from the central aluminum atom by 200 K.<sup>85</sup> Such a finding is not surprising given that activation energies for diffusion of adsorbates on metals are typically only 20% of the surface binding energy, and the binding energy of alkyls on aluminum is  $\sim 46$  kcal/mol.<sup>76</sup>

As a final class of molecular precursors, we consider hydrocarbons. While selective decomposition is not inherent for these molecules in which all C–H bonds are of approximately the same strength, it is well-established<sup>11</sup> that the kinetics for C–H bond scission depend strongly on the identity of the hydrocarbon fragment, and it is frequently found that the more dehydrogenated the fragment the slower the rate of C–H bond scission. Thus, a single C–H bond dissociates in ethylene on a Ni(100) surface to generate vinyl species which are thermally stable from  $\sim 175$  to 220 K.<sup>90-93</sup> Similarly, phenyl ( $\text{C}_6\text{H}_5$ ) has been reported as a stable intermediate in the decomposition of benzene on Os(0001)<sup>94</sup> and Ni(110).<sup>95</sup> Other fragments formed by simple C–H bond scission reactions and the hydrocarbon precursors from which they have been derived include: benzyne ( $\text{C}_6\text{H}_4$ ) from benzene and benzene thiol on Mo(110)<sup>96,97</sup> and from benzene on Os(0001);<sup>94</sup> and benzyl from toluene on Pt(111)<sup>98-100</sup> and Ru(001).<sup>101,102</sup> Other systems in which the hydrocarbon precursor is more extensively dehydrogenated to generate species such as CCH,  $\text{CCH}_2$ ,  $\text{HCCH}_2$ ,  $\text{CCH}_3$ , and CH are discussed in sections III and IV.

In general, the fragments isolated from hydrocarbon precursors tend to be highly dehydrogenated and less reactive toward the addition of hydrogen. In some cases, these more highly dehydrogenated fragments have been found to exist as stable monolayers on the surfaces of single-crystal samples which are active catalysts for hydrocarbon reactions such as hydrogenation<sup>103</sup> and re-forming.<sup>104,105</sup> While these fragments are largely inactive as intermediates in the catalytic process, they are an unavoidable and integral part of the active catalyst. For example, the identity and structure of these species affects the catalytic reaction rate.<sup>10,104,106</sup> In the case of ethylene hydrogenation the rate actually decreases with increasing temperature above 430 K on a Rh(111) surface as the stable adsorbed monolayer converts from ethylidyne to vinylidene ( $\text{CCH}_2$ ) and acetylide ( $\text{CCH}$ ).<sup>106</sup> In general, it appears that as the hydrocarbon fragments on the surfaces of catalysts dehydrogenate, the catalyst deactivates.<sup>104</sup>

### C. Photon-, Electron-, and Collision-Induced Dissociation of Molecular Precursors

A key requirement in the thermal dissociation of molecular precursors to generate adsorbed hydrocarbon fragments is that the dissociation must occur at sufficiently low temperature for the hydrocarbon fragment to be stable on the surface. The precursor must therefore be quite labile. This issue can be circumvented by using nonthermal methods of molecular excitation to induce precursor dissociation at temperatures far below those at which most chemical bonds thermally dissociate at a measurable rate. The



**Figure 3.** Three types of surface/molecule excitation for inducing dissociation of molecular precursors to form adsorbed methyl groups.

issues with respect to the effectiveness of these excitation schemes are the reaction selectivity and the product yield. Given the substantial amounts of internal energy introduced into molecules by most excitation methods, one might expect multiple dissociation pathways or scission of multiple bonds to be an issue; on the other hand, the rapid rates of energy transfer and quenching for molecules on metal surfaces decrease the probability that dissociation will be observed at all. The interesting, and initially somewhat surprising, finding for adsorbate excitation using photons, electrons, and hyperthermal collisions was that each of these approaches leads to quite selective bond scission and produces adsorbed fragments with remarkably high yields. The activity and selectivity for each of these different types of excitation (which are illustrated schematically in Figure 3) are discussed separately below.

The application of hyperthermal gas/surface collisions to induce precursor decomposition to generate adsorbed fragments is illustrated for methyl formation from methane at the top of Figure 3. This approach has been utilized by Ceyer et al. in an elegant series of studies on Ni(111).<sup>107–112</sup> They have shown that two types of collision are effective.<sup>107–112</sup> In one approach, as shown in the top of Figure 3, a seeded supersonic molecular beam of translationally hot methane is impinged onto a Ni(111) surface held at 80 K. For kinetic energies above  $\sim 12$  kcal/mol, there is measurable dissociation of methane to produce adsorbed  $\text{CH}_3$  and H, and the cold surface quenches the initially hot  $\text{CH}_3$  before it can decompose further. In a variation of these studies, Ceyer et al. have shown that methyl can also be produced by colliding translationally hot inert gas atoms with a methane monolayer physisorbed on Ni(111) at 46 K.<sup>109,110</sup> The beauty of these approaches is that the same C–H bond dissociation reaction which presumably occurs in the dissociative adsorption of alkanes during hydrocarbon catalysis is induced to occur on a single-crystal surface under low flux conditions; also, by carrying out the process under nonequilibrium conditions (i.e. hot molecule/cold surface) the nascent products of the dissociative adsorption reac-

tion are trapped and isolated. The key to this selectivity is carrying out the process at temperatures  $\sim 100$  K below where the nascent methyl groups react by thermal pathways. Also, the amounts of energy in excess of the reaction barrier (which is  $\sim 12$  kcal/mol) that are achievable with neutral beams is generally rather limited, so multiple bond scission reactions are not observed.

An experimentally less-involved method of molecular excitation, which is amenable to vacuum experiments, is electron impact. It is well-known that electron-induced bond scission can be quite facile in adsorbed monolayers, and this phenomenon has been exploited by White, Koel, and co-workers<sup>7,84,113–117</sup> to generate a wide range of adsorbed hydrocarbon fragments on metal surfaces. An interesting finding from these studies is that the electron-induced dissociation process, which is illustrated schematically in Figure 3 for methane, generally dissociates a single C–H bond for electron energies near the onset of dissociation. The explanation offered<sup>7</sup> for this selectivity is as follows. The incident electron impacts the physisorbed molecular precursor and is either captured to form an anion or ejects an electron to form a cation. The ion, if not quenched or desorbed, then dissociates, and dissociation of the first bond in the molecule produces a surface fragment which is much more strongly bonded to the surface. This strong coupling greatly increases the rate of quenching which in turn decreases the probability of bond scission during subsequent excitation.

By using this electron-induced dissociation approach, the following hydrocarbon fragment syntheses have been demonstrated using hydrocarbon precursors: methane  $\rightarrow$  methyl on Pt(111)<sup>7</sup> and Pt(111)/carbon,<sup>119</sup> cyclohexane  $\rightarrow$  cyclohexyl on Pt(111),<sup>117</sup> cyclopropane  $\rightarrow$  cyclopropyl on Cu(111),<sup>120</sup> benzene  $\rightarrow$  phenyl on Ag(111),<sup>83,84</sup> and ethylene  $\rightarrow$  vinyl on Ag(111).<sup>84,113</sup> There are also examples in the literature where electrons have been used to selectively dissociate carbon-halogen bonds in halohydrocarbons (see “e” under techniques in Table 4). With respect to spectroscopic identification of these fragments it is desirable (for avoiding spectral interference) that the molecular precursor be chosen so that it may be thermally desorbed from the surface at temperatures below where the fragment of interest decomposes. Similar considerations also pertain to the photochemical dissociation of molecular precursors (see below). Also, since large electron impact energies are readily achieved, it is important that the electron energy be kept near the onset of dissociation to achieve some selectivity in the bond scission and avoid multiple bond dissociation events.<sup>114</sup>

In comparison with electron-induced decomposition, surface photodissociation is of more limited scope, but there are some similarities between the two approaches. In particular, it appears that the majority of monolayer photodissociation reported for metals is attributable to ionic species produced by photoinduced electron transfer from the metal to the adsorbate.<sup>121–124</sup> This phenomenon at least partially accounts for the fact that even though excited-state relaxation is greatly enhanced for adsorbates on metal surfaces in comparison with gas-phase species,

photodissociation cross sections are sometimes larger on surfaces than in the gas (charge transfer across the interface being responsible for the enhancement) and thresholds for photodissociation are often significantly red-shifted (electrons in the metal requiring lower energy excitations than electrons in the molecule to induce dissociation).<sup>121–124</sup> The anion generated in this electron-transfer process is analogous to that which can be formed by external electron attachment. The dissociation yield from these surface anions is a sensitive function of the anionic dissociation potential, and it has been suggested that the highly repulsive curves for halohydrocarbon anions accounts for the high dissociation efficiency observed for these molecular species.<sup>121–124</sup> Table 4 summarizes (see “*hν*” under techniques) the halohydrocarbon systems whose surface photochemistry has been investigated.

#### D. Synthesis Reactions in Adsorbed Monolayers

All the approaches described above for generating hydrocarbon fragments on metal surfaces rely on either direct adsorption of the fragment or some means of decomposing a molecular precursor. There are, in addition, a few reports in which hydrocarbon fragments have been synthesized via bimolecular combination reactions in adsorbed monolayers. In the case of alkyl formation, three approaches have been demonstrated, as illustrated schematically in Figure 4. Two of these involve hydrogen atom addition to ethylene, but the approaches differ in the method by which hydrogen is added. In the Fe(100) studies by Burke and Madix,<sup>125,126</sup> a hydrogen-precovered surface was treated with ethylene and the H addition reaction occurred by a Langmuir–Hinshelwood mechanism (i.e. bimolecular reaction between adsorbed species which are thermally accommodated with the surface). There are also other examples where ethylene hydrogenates to ethane but no intermediates are detected. An exception is Ni(111) where subsurface hydrogen reacts with adsorbed ethylene<sup>127</sup> and cyclohexene<sup>128</sup> to generate intermediates which are still under study. In the Ni(111) system, reaction intermediates can be isolated because subsurface hydrogen is metastable with

respect to surface H,<sup>129</sup> so the reaction between subsurface H and alkenes is unusually exothermic and can be carried out at low temperatures. In this regard, the subsurface H + alkene reactions on Ni(111) are analogous to the Eley–Rideal hydrogen-addition processes which have been observed for H atom impingement onto ethylene-precovered surfaces as described below.

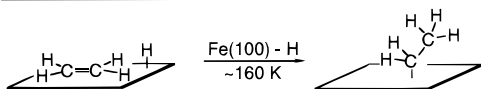
In studies of H + ethylene on Cu(100), no Langmuir–Hinshelwood hydrogenation reaction is observed when a partial monolayer of adsorbed H is reacted with ethylene. On the other hand, H addition does occur by an Eley–Rideal mechanism (i.e. a direct process) when hydrogen atoms are impinged onto a surface precovered with ethylene.<sup>80,82</sup> Since this Eley–Rideal approach utilizes the 52 kcal of potential energy per mole of H atoms (relative to half a mole of H<sub>2</sub>) to induce reaction along with the 5–6 kcal/mol of kinetic energy from the hot filament source used to generate the H atoms, this type of process can be induced at cryogenic temperatures where the desired H addition product can be isolated.

Low-temperature, Eley–Rideal pathways have also been demonstrated for atomic H addition (using a variety of H atom sources) to cyclohexene<sup>82</sup> and for H abstraction from cyclohexane<sup>81</sup> to generate cyclohexyl on copper surfaces, for H addition to cyclohexene on Ni(111),<sup>128</sup> and for H addition to CO on Ru(001) to produce formyl.<sup>130</sup> Studies of H atom reaction with alkenes, alkanes, and aromatics on graphite surfaces have also been reported by Küppers and co-workers.<sup>131</sup>

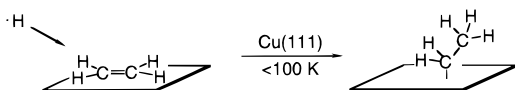
While one might imagine forming hydrocarbon fragments from a range of synthesis reactions besides H addition, the coupling of hydrocarbon fragments on metals (aside from the coinage metals—copper, silver, and gold) does not generally compete favorably with fragment decomposition pathways. On the coinage metals, however, coupling is quite facile. The CH<sub>2</sub> + CD<sub>3</sub> reaction illustrated in Figure 4 has recently been demonstrated on Cu(100) via isotope labeling, but the partially deuterated ethyl intermediate shown was not isolatable.<sup>132</sup> Recent studies suggest that vinyl + CH<sub>2</sub> coupling occurs on Cu(100) to produce a stable surface allyl.<sup>133</sup> It has also been shown that methyl groups react to produce some CCH<sub>3</sub> (ethylidyne) on Pt(111),<sup>31</sup> and a C<sub>4</sub> intermediate is produced during acetylene trimerization to benzene on Pd(111).<sup>134,135</sup>

There appears to be potential for using fragment coupling reactions to synthesize desired surface intermediates, particularly on the coinage metals, but relatively few systems have been investigated. The generality of this approach is probably limited by the difficulty in finding reaction kinetics which are sufficiently facile for the necessary bimolecular reactions to occur in preference to decomposition processes while still being able to isolate the nascent product. In this regard, the addition of gas-phase atoms and radicals to adsorbates via Eley–Rideal pathways offers particular promise, especially since selectively labeled species can be formed quite readily through isotope labeling of either the incident atom/radical or the surface-adsorbed species.<sup>80,82,136</sup>

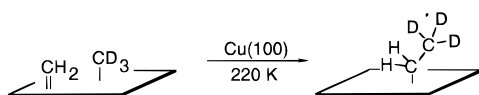
##### • Langmuir-Hinshelwood Mechanism



##### • Eley-Rideal Mechanism



##### • Hydrocarbon Fragment Coupling



**Figure 4.** Generation of surface ethyl groups via coupling reactions in adsorbed monolayers.

### III. Identifying Hydrocarbon Fragments on Metal Surfaces

Spectroscopic identification of hydrocarbon fragments on metal surfaces is still far from routine, but in many cases the obstacle to a convincing identification has been the inability to prepare monolayers of a single adsorbed species rather than deficiencies in the spectroscopic methods applied. Despite problems of monolayer purity, there are now a number of examples of hydrocarbon fragments whose identity is well-established, and with the development of the techniques described above for generating pure monolayers of targeted surface fragments, much more rapid identification of other catalytically relevant surface species can be anticipated.

In this section, the techniques most frequently applied to make these identifications are briefly reviewed in the context of their utility for surface hydrocarbon fragments. These include high-resolution electron energy loss spectroscopy (HREELS), reflection absorption infrared spectroscopy (RAIRS), low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), secondary ion mass spectrometry (SIMS), laser-induced thermal desorption (LITD), work function change measurements ( $\Delta\phi$ ), and temperature-programmed desorption (TPD). Special emphasis is given to chemical methods of identification—a topic not extensively discussed in prior reviews. Note that throughout this review the term “identification” refers only to the connectivity of the carbon and hydrogen atoms (i.e. HCCH vs CCH<sub>2</sub>) and does not imply anything about the surface bonding or adsorption site.

#### A. Chemical Identification

One of the most powerful, and yet often overlooked, approaches for identifying surface fragments is via studies of the surface reaction chemistry. These types of studies are particularly useful in systems where the hydrocarbon fragment of interest is stable to temperatures above where surface hydrogen atoms recombine and desorb. In this case, mass spectrometry of the hydrogen-containing products can be used to deduce the *average* C:H stoichiometry of the surface species.

As examples, we consider ethynylidyne (CCH<sub>3</sub>) on Pt(111),<sup>138,139</sup> alkyls on aluminum surfaces,<sup>67,68</sup> and CH<sub>3</sub> on copper surfaces.<sup>30,140,141</sup> On Pt(111), ethylene converts to CCH<sub>3</sub> which is stable to above 400 K while surface H recombines and desorbs as H<sub>2</sub> at ~300 K. As a result, the 1:3 ratio of hydrogen desorbing below and above the temperature where CCH<sub>3</sub> exists on the surface (there are no hydrocarbon desorption products at low coverages, so all hydrogen leaves the surface as H<sub>2</sub>) establishes the C<sub>2</sub>H<sub>3</sub> stoichiometry for ethynylidyne. This simple observation rules out species such as CHCH<sub>3</sub> which was originally proposed as the ethylene decomposition product. (It should be emphasized that when using a hydrogen mass balance, *all* gas-phase hydrocarbon products must also be accounted for. For example, in the case of C<sub>2</sub>H<sub>4</sub> decomposition on Pt(111), formation of C<sub>2</sub>H<sub>6</sub>(g) in addition to CCH<sub>3</sub>(ads) occurs at high surface

coverage, and this additional reaction channel removes surface hydrogen.)

Other systems where surface chemistry studies are particularly definitive for identification of surface hydrocarbon fragments include the decomposition of alkyl iodides on aluminum<sup>67,68</sup> and of methyl iodide on copper.<sup>30,140,141</sup> In both of these systems, no volatile hydrogen-containing products are evolved below 400 K. Yet on both metals, any hydrogen bonded directly to the metal desorbs at ~300 K, and saturated hydrocarbons as well as the precursor alkyl halides (in cases where they remain intact) desorb below 200 K. The absence of these products for submonolayer coverages cannot be explained if the alkyl halide decomposes by C–H bond scission (assuming carbon maintains a valence of four). If C–H bond scission occurs, either hydrogen is deposited on the surface, or some saturated hydrocarbon must form. Neither is detected, so it can be concluded that subsequent to carbon–iodine bond scission, the alkyls generated are stable to > 400 K in these systems (~450 K for CH<sub>3</sub>/Cu and ~520 K for alkyls/Al).

The possibility of C–C bond scission by alkyls on aluminum as well as the possibility of reversible C–H bond scission in the methyl/copper system can be ruled out on the basis of deuterium isotope labeling studies and mass spectrometry since hydrocarbons (as opposed to only H<sub>2</sub>) are evolved as hydrogen-containing products in both systems. In the case of the CH<sub>3</sub>/Cu(110) system, CH<sub>3</sub> ↔ CH<sub>2</sub> + H equilibration is ruled out by the absence of CH<sub>2</sub>D<sub>2</sub> evolution when CH<sub>3</sub> is coadsorbed with D.<sup>140</sup> Reversible dehydrogenation of CH<sub>3</sub> in the presence of surface D would presumably produce CH<sub>2</sub>D<sub>2</sub>, yet only CH<sub>3</sub>D is detected. Similar findings provide conclusive evidence for formation of methyl from CH<sub>3</sub>I on Ni(100)<sup>142,143</sup> and Ni(111).<sup>144</sup> In the case of alkyls on aluminum, an isotope cross-over experiment rules out reversible CH and CC bond scission. In this type of experiment, a 50:50 mixture of fully hydrogenated and fully deuterated species are coadsorbed. The observation that the resulting alkene products are also either fully hydrogenated or fully deuterated rules out reversible bond-breaking processes and confirms the presence and stability of the alkyl group.

As an example of a system where the products themselves are highly informative, we consider the reaction of alkyl iodides with Ag(111).<sup>184,145–150</sup> In this system, alkanes of twice the alkyl iodide chain length are produced, which is suggestive of coupling by surface alkyls. To establish that carbon–iodine bonds are dissociated prior to formation of the coupling product (i.e. that there is a regime where the hydrocarbon fragment is a stable intermediate on the surface and that a concerted alkyl halide coupling reaction is not involved), White and co-workers have employed a clever series of surface photochemistry studies.<sup>149</sup> This work utilized methyl bromide, which does not thermally dissociate on Ag(111). The finding that ethane is evolved at 200–300 K upon heating the surface after irradiation was performed only at 100 K establishes that C–Br bond scission must occur prior to methyl coupling. (Note that ethane desorption cannot be the rate-determining

ing step since ethane desorbs from Ag(111) below 100 K.)

Another particularly useful approach for chemical identification is coadsorption, and the hydrogen/deuterium studies described above are one example. In a similar vein, White et al. have proposed coadsorption of oxygen<sup>151</sup> to scavenge surface hydrogen from platinum as water, although care must be taken in these types of studies to assure that the scavenging agent does not promote bond scission as well. In a different approach, Campbell,<sup>152-157</sup> Muettterties,<sup>158-162</sup> Yates and Goodman,<sup>163</sup> Tamaru,<sup>164</sup> Friend,<sup>165</sup> Thiel,<sup>166</sup> and others<sup>167</sup> have demonstrated the utility of coadsorbing unreactive but strongly binding "displacing agents" to displace adsorbates from monolayers to the gas phase where they can be detected and identified by mass spectrometry. It should be noted, however, that in some cases, these displacing agents can also induce coupling reactions of adsorbed fragments. Campbell and co-workers have utilized this phenomenon in the case of displacement by bismuth to couple adsorbed fragments with coadsorbed deuterium in a technique they call D<sub>2</sub>-bismuth post dosing mass spectrometry (D<sub>2</sub>-BPTDS).<sup>157</sup>

These approaches illustrate the types of definitive chemical identification that are possible. In general, a chemical approach is most effective when hydrocarbon products are evolved from the surface so that mass spectrometry can be applied to monitor the reaction kinetics and to identify isotopic composition.

## B. HREELS and RAIRS

Surface vibrational spectroscopy is among the most widely used diagnostic technique for identifying hydrocarbon fragments because of the sensitivity to the type and coupling of C-H bonds and because of the power of isotope labeling for identifying and assigning the vibrational transitions. The functional group modes and fingerprinting of molecules, which have been well-established for species in bulk gases, liquids, and solids, is also applicable at surfaces for adsorbed species (or portions of adsorbed species) where the bonding is not strongly perturbed by the presence of the surface. On the other hand, for small and/or unsaturated hydrocarbon species where the bonding (and vibrations) are sensitive to the details of the surface, spectroscopic signatures have so far been established for only a few species. These include ethynylidyne (CCH<sub>3</sub>) where the intense symmetric methyl deformation and C-C stretching modes are diagnostic for a wide range of systems (see section IV.C.1) and benzene where an intense out-of-plane C-H bending mode is characteristic.<sup>3</sup> Also, in the case of ethylene and acetylene adsorption, Sheppard has proposed that the spectral frequencies and intensity profiles fall into a small number of classes which are indicative of different modes of coordination to the surface.<sup>4</sup>

Characteristic spectral features are probably present in other strongly interacting and surface-perturbed adsorbate systems, but the careful and extensive study required to establish them has still to be performed. As an example of the difficulties, it is worth noting that there are numerous reports in the literature in which surface CH species have been

identified largely on the basis of a mode near 800 cm<sup>-1</sup> in the surface vibrational spectrum which is attributed to a C-H bending frequency by analogy to frequencies reported for CH ligands in organometallic clusters. However, a recent extensive and convincing study of CH on Ni(111) by Ceyer and co-workers<sup>168</sup> indicates that the C-H bending frequency in this system is at 1275 cm<sup>-1</sup>—a result which suggests that either the surface bonding of CH is highly metal dependent or that prior vibrational assignments and species identification should be reexamined.

In summary, surface vibrational spectroscopy is powerful for identifying hydrocarbon fragments provided that spectroscopic signatures have been established or that extensive isotope-labeling studies are performed to establish precedent. Once fragments have been properly identified, the frequencies and intensities in HREELS and IR provide a wealth of information as a result of their sensitivity to the bonding and orientation of adsorbates.<sup>169-173</sup> With recent advances in methods for preparing high purity monolayers of a single hydrocarbon fragment, with the advent of a new generation of high-resolution and high-sensitivity HREELS spectrometers,<sup>174</sup> and with the improvements that continue to be made in infrared spectrometers, vibrational spectroscopy holds great promise for future studies of hydrocarbon fragments.

## C. LEED

For ordered overlayers, and recently even for some overlayers without long-range order, dynamical tensor LEED is a powerful technique for studying the bonding of hydrocarbon fragments, even though the position of the hydrogen atoms is difficult to determine. The challenge is to obtain data with sufficiently low electron exposures so that the adsorbate is not damaged and to calculate a structure which is consistent with the diffraction data. Great strides have been made in both areas,<sup>175-178</sup> so new insights into hydrocarbon fragments previously unstudied by LEED can be anticipated. To date the only hydrocarbon *fragment* to our knowledge whose structure has been solved by LEED crystallography is ethynylidyne,<sup>179-181</sup> although a number of molecular systems such as benzene<sup>182-184</sup> and acetylene<sup>185-186</sup> have been studied.

## D. XPS, UPS, and Photoelectron Diffraction

Surface photoemission techniques are particularly effective for identifying hydrocarbon fragments which have inequivalent carbon atoms that can be discriminated and quantified by XPS (e.g. benzyne (C<sub>4</sub>H<sub>6</sub>) on Mo(110)<sup>96</sup>) or which have  $\pi$ -bonds for which changes in valence electronic structure upon coordination to a surface can be quantified by UPS (e.g. acetylene on Ni(110)<sup>187</sup>). Angle-resolved UPS is important for determining adsorption symmetries, which are particularly informative in high-symmetry systems (e.g. acetylene<sup>188</sup> and benzene<sup>3</sup>). The power of photoelectron diffraction for determining atomic positions is also just beginning to be applied to hydrocarbon monolayers.<sup>189</sup> It is not yet clear to what extent

carbon 1s binding energies in XPS are diagnostic for C<sub>1</sub> hydrocarbon fragments such as CH<sub>2</sub> and CH<sub>3</sub>,<sup>190</sup> although XPS is clearly quite effective for detecting carbon–halogen bond scission in halohydrocarbons which are common precursors to adsorbed hydrocarbon fragments.

## E. NEXAFS

The bond specificity of NEXAFS makes it particularly useful for identifying certain types of surface species and reactions. For example, the commonly used halohydrocarbon precursors have carbon–halogen  $\sigma^*$  transitions which are often readily identifiable in NEXAFS<sup>191</sup> and which can be used as a measure of precursor dissociation. However the real power of NEXAFS lies in the ability to use the polarization dependence of the absorption resonances and the selection rules for photoabsorption to quantify the average orientation of chromophores in an adsorbed layer.<sup>191</sup> The difficulties are to properly assign the observed transitions (often done with the aid of gas-phase spectra), to determine the direction of the transition dipole for the resonance of interest, and to account for possible effects of changes in molecular structure (e.g. rehybridization) upon adsorption. The hydrocarbon systems which have been most effectively studied with NEXAFS are those involving unsaturated  $\pi$ -systems which give intense and diagnostic  $\pi^*$  resonances below the absorption edge. The polarization dependences of these transitions have been used to show that species like ethylene, acetylene, and benzene bond with their  $\pi$ -bonds approximately parallel to the surface<sup>191,192</sup> and that fragments such as vinyl (CHCH<sub>2</sub>) on Ni(100)<sup>193</sup> and Cu(100),<sup>194</sup> C<sub>4</sub>H<sub>4</sub> on Pd(111),<sup>135</sup> and phenyl on Cu(111)<sup>195</sup> bond with their  $\pi$ -bonds tilted by 20–50° away from the surface plane. Tetracene on Cu(100)<sup>196</sup> and benzyne (C<sub>6</sub>H<sub>4</sub>) on Mo(110)<sup>96</sup> are two examples where NEXAFS has shown that unsaturated hydrocarbons are oriented with their molecular planes approximately along the surface normal. In addition to the use of peak intensities to determine molecular orientation, it has been suggested that the position of the  $\sigma^*$  C–C resonance in NEXAFS spectra can be used as a measure of the C–C bond length in adsorbates.<sup>197–201</sup>

## F. SIMS and LITD

These techniques are particularly helpful in determining the stoichiometry and identity of surface fragments which are strongly bound and do not desorb in a TPD experiment. Examples of particularly effective and diagnostic applications include the identification of alkylidyne fragments in the decomposition of alkenes on Pt(111),<sup>202,203</sup> the identification of a C<sub>6</sub>H<sub>9</sub> intermediate in the decomposition of cyclohexane to benzene on Pt(111),<sup>204</sup> measurements of the kinetics for ethylene conversion to ethylidyne on Pt(111)<sup>205</sup> and Rh(111),<sup>206</sup> and kinetic studies of ethylene conversion to vinyl on Ni(100).<sup>92</sup> The disadvantage of these techniques with respect to systems in which halohydrocarbon precursors are employed is that the structural differences between the molecular precursor and the hydrocarbon fragment

are generally small which makes discrimination difficult; the kinetics of fragment decomposition are, however, readily monitored.

## G. Surface Work Function Measurements

While changes in the surface work function do not provide spectroscopic identification of surface hydrocarbon fragments, they are a sensitive function of changes in the composition and structure of adsorbed layers. The sensitivity and simplicity of this method makes it valuable for determining the temperature ranges over which surface fragments are stable.

## IV. Bonding and Reactions of Species Proposed as Intermediates in Hydrocarbon Catalysis

As indicated in Tables 1–3 there are six classes of surface fragments frequently proposed as intermediates in heterogeneous hydrocarbon catalysis: alkyls, carbenes, carbynes, allyls, vinyls, and metallacycles. The following six subsections review the current understanding of the bonding and reactivity of these species. A seventh subsection is also included to discuss phenyl, benzyne, cyclopentadienyl, vinylidene, and acetylide–species which, although less frequently proposed as reactive intermediates in heterogeneous catalysis, may also be present as stable monolayers during catalysis and which have been studied on single crystals in vacuum. Special emphasis is given to alkyls–species which are probably the most common of all proposed catalytic intermediates.

### A. Alkyls (C<sub>n</sub>H<sub>2n+1</sub>)

#### 1. Methyl

In heterogeneous catalysis, surface methyls are formed in such reactions as the oxidative coupling of methane, methane H–D exchange, and the Fischer–Tropsch synthesis (see Table 1), but directly analogous processes have yet to be observed on single crystals in vacuum. (The notable exception in this regard is the dissociative adsorption of methane using seeded molecular beam techniques.<sup>107,108</sup>) In most cases where methyls have been isolated and identified on single crystals, they have been generated via the dissociative adsorption of methyl halides, but other approaches have also been applied. Studies providing evidence for isolation of CH<sub>3</sub> on metal surfaces are summarized in Table 5. Also important (and not listed in Table 5) are the studies of systems where it has been demonstrated that azomethane (CH<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>), a potentially promising methyl precursor, does *not* decompose on the surface to produce CH<sub>3</sub>. These include studies of azomethane on Mo(110),<sup>207</sup> Ni(100),<sup>208</sup> Ni(111),<sup>208</sup> Cr(100),<sup>208</sup> Cr(111),<sup>208</sup> Pd(111),<sup>209</sup> Pt(111),<sup>210,211</sup> Ag(111),<sup>212</sup> and Cu(111).<sup>30</sup>

**a. Bonding.** Most of what is known about the surface bonding of CH<sub>3</sub> comes from vibrational spectroscopy. HREELS studies of methyl on Ni(111),<sup>168</sup> Ru(001),<sup>213</sup> Cu(111),<sup>141,214</sup> and Pt(111),<sup>215</sup> as well as IR studies on Pt(111)<sup>31,56,216</sup> suggest C<sub>3v</sub> adsorption symmetry. There is also HREELS evidence for C<sub>s</sub> adsorption symmetry on Cu(111),<sup>30</sup> Cu(100),<sup>132</sup> and

**Table 5. Metal Surface/Adsorbate Systems for Which Formation and Isolation of Surface-Bound CH<sub>3</sub> Has Been Proposed**

surface	precursor(s)	activation <sup>a</sup>	analysis technique(s) <sup>b</sup>	ref(s)
Ag(111)	CH <sub>3</sub> I	Δ	XPS, UPS, Δφ, TPD	145
	CH <sub>3</sub> Br	<i>hν</i>	TPD	149,150
	CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub>	<i>e</i>	TPD	467
Al(111)	CH <sub>3</sub> I	Δ	HREELS, AES, TPD	372
Au(111)	CH <sub>3</sub> I	<i>hν</i>	TPD	225
Au(100)	CH <sub>3</sub> I	Δ	TPD	234
	CH <sub>3</sub> AuP(CH <sub>3</sub> ) <sub>3</sub>	Δ	TPD	86,225
Cu(111)	CH <sub>3</sub> I, CHD <sub>2</sub> I, CD <sub>3</sub> I	Δ	HREELS, Δφ, D/TPD	66,69,141,214
	CH <sub>3</sub> Br	<i>hν</i>	HREELS, TPD	235
	·CH <sub>3</sub>		HREELS, TPD	30
Cu(110)	CH <sub>3</sub> I, CD <sub>3</sub> I	Δ	D/TPD	236,140,251
Cu(100)	CH <sub>3</sub> I, CD <sub>3</sub> I	Δ	HREELS, Δφ, TPD	132
Cu film	CH <sub>3</sub> Br	<i>hν</i>	HREELS, TPD	78
Fe(100)	CH <sub>3</sub> Cl	Δ	XPS, TPD	404
Mo(110)	CH <sub>3</sub> I	Δ	TPD, HREELS	407
Ni(100)	CH <sub>3</sub> I, CD <sub>3</sub> I	Δ	XPS, TPSIMS, D/TPD	142–144
Ni(111)	CH <sub>4</sub> , CH <sub>3</sub> D, CD <sub>4</sub>	<i>v</i>	HREELS, TPD	107,108,168
Pd(111)	CH <sub>3</sub> OH	Δ	XPS, SSIMS, TPD	468–471
	CH <sub>3</sub> I	Δ	XPS, TPD	426
Pd(100)	CH <sub>3</sub> I	Δ, <i>hν</i>	XPS, UPS, EELS, Δφ, TPD	235–237,420
	CH <sub>3</sub> Cl	<i>hν</i>	UPS, EELS, TPD	423,425
Pd(100)/K	CH <sub>3</sub> Cl		XPS, UPS, EELS, TPD	421,422,424
Pt(111)	·CH <sub>3</sub>		IR, TPD	31
	CH <sub>3</sub> I, CD <sub>3</sub> I	Δ	HREELS, IR, XPS, TPSIMS, D/TPD, BPTDS	54–58,216,430
	CH <sub>3</sub> Br, CD <sub>3</sub> Br	<i>hν</i>	HREELS, TPD	151,231–233
	CH <sub>3</sub> Cl, CD <sub>3</sub> Cl	<i>hν</i>	TPD, HREELS	434
	CH <sub>3</sub> <sup>+</sup>		TPD	53
	CH <sub>4</sub>	<i>e</i> <sup>-</sup>	TPD	7,118
Pt/SiO <sub>2</sub>	CH <sub>3</sub> Cl, CH <sub>3</sub> I	Δ	IR	429
Rh(111)	CH <sub>3</sub> I	Δ	HREELS, TPD	73,460
	·CH <sub>3</sub>		HREELS	32, 472
Rh(111)/O	·CH <sub>3</sub>		HREELS	32, 472
Ru(001)	CH <sub>3</sub> I, CD <sub>3</sub> I	Δ	HREELS, D/TPD	213
W foil	CH <sub>3</sub> I	Δ	AES, TPD	465

<sup>a</sup> Δ = heat; *hν* = photons, *e*<sup>-</sup> = electrons, *v* = velocity. <sup>b</sup> HREELS = high-resolution electron energy loss spectroscopy, IR = infrared spectroscopy; XPS = X-ray photoelectron spectroscopy; UPS = ultraviolet photoelectron spectroscopy; TPD = temperature-programmed desorption; D/TPD = TPD with deuterium isotope labeling; Δφ = surface work function change measurements; AES = Auger electron spectroscopy; SSIMS = static secondary ion mass spectrometry; TPSIMS = temperature-programmed secondary ion mass spectrometry.

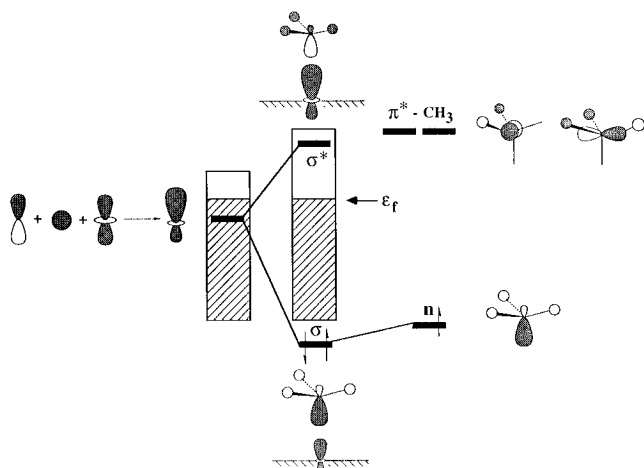
Pt(111),<sup>54,55</sup> but more extensive studies are needed to verify this lower site symmetry. In particular, these determinations of C<sub>s</sub> site symmetry by electron energy loss measurements rely on the applications of the selection rules for electron scattering, and more extensive measurements of the angular distribution of the scattered electrons are needed to fully assess the extent to which the scattering is dipolar in character as has been generally presumed in these analyses. It has also been suggested that the coadsorbed halogen in these systems (except for Ni(111) where H is coadsorbed) may have an effect on the surface bonding,<sup>54</sup> but studies comparing methyl radical and CH<sub>3</sub>I adsorption on Cu(111)<sup>30</sup> show little effect of coadsorbed iodine in this system.

The C<sub>3v</sub> site symmetry for methyl on these 3-fold symmetric surfaces implies adsorption in a top-site or a 3-fold hollow site. The metal–methyl stretching frequencies of 385 cm<sup>-1</sup> on Ni(111),<sup>168</sup> 370 cm<sup>-1</sup> on Cu(111),<sup>214</sup> and 492 cm<sup>-1</sup> on Pt(111) suggest, by comparison with organometallic compounds,<sup>168</sup> bonding in a 3-fold hollow site (see also section IV.A.2 and Figure 8). In the case of Ni(111), this assignment is corroborated by theoretical calculations which indicate bonding in a 3-fold hollow site and which predict metal–methyl vibrational frequencies of 369 cm<sup>-1</sup><sup>217</sup> and 308 cm<sup>-1</sup><sup>218</sup>—close to the measured value. Bind-

ing energy differences between sites are not large, however, and predictions of top site bonding have also been reported.<sup>219</sup>

On Ni(111),<sup>168</sup> Cu(111),<sup>30,141,214</sup> and Cu(100)<sup>132</sup> (but not on Pt(111)<sup>31,54–56,215,216</sup> or Ru(001)<sup>213</sup>) significant mode softening has been reported for the methyl C–H vibrations. In a molecular orbital picture of the methyl/surface bonding, there are two possibilities for the observed effect: methyl-to-metal charge donation from a C–H bond (giving rise to what is known in organometallic chemistry as agostic bonding<sup>220–222</sup>) or metal-to-methyl charge donation into a C–H antibonding orbital. Calculations for methyl on Ni(111)<sup>223,224</sup> support the latter interpretation, and Hoffmann and co-workers<sup>224</sup> use the molecular orbital interaction diagram shown in Figure 5 to account for this back-donation. Note in particular that the singly occupied methyl orbital lies lower in energy than the metal orbitals with which it interacts. The methyl–metal bonding orbital is thus methyl-like, corresponding to metal-to-methyl charge transfer. The methyl orbital into which charge is transferred is antibonding between the carbon and hydrogens, and thus C–H mode softening results.

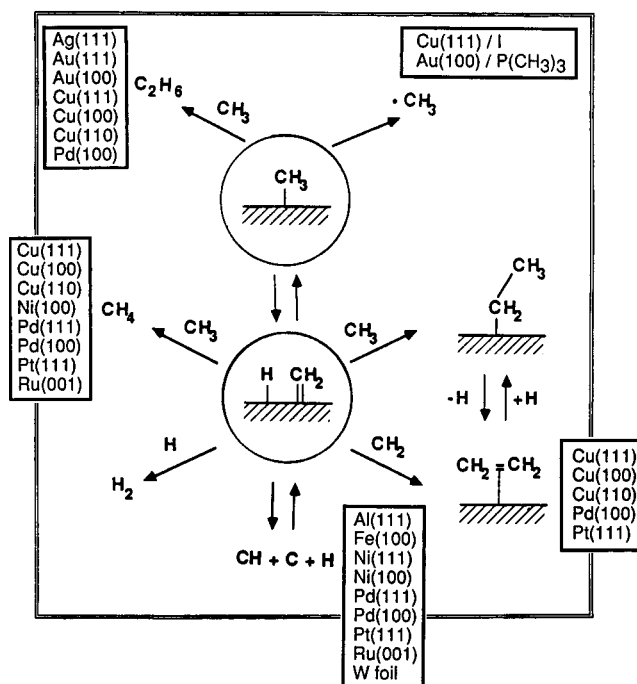
In two systems, the metal–methyl bond energy has been determined directly via desorption of the surface methyl groups. These systems are Au(100)/CH<sub>3</sub> with



**Figure 5.** Molecular orbital interaction diagram after Zheng, Apeloig, and Hoffmann<sup>224</sup> for methyl bonding to transition metal surfaces. The left-hand portion of the figure shows the metal hybrid generated by a combination of atomic orbitals and its approximate energy in the d-band relative to the Fermi level,  $\epsilon_f$ . The right-hand portion of the figure shows the shape and energy of the methyl fragment's highest occupied molecular orbital ( $n$ ) and lowest unoccupied orbital ( $\pi^*$ ). The center panel shows the interaction between the metal and methyl orbitals. Note that the bonding  $\sigma$ -orbital has larger lobes on the methyl than the metal (conversely for the  $\sigma^*$ -orbital) and that the metal–methyl bonding orbital is antibonding between the carbon and hydrogens in the  $\text{CH}_3$  group.

coadsorbed  $\text{P}(\text{CH}_3)_3$  where the  $\text{CH}_3\text{--Au}$  bond energy is  $25 \pm 2$  kcal/mol<sup>225</sup> and  $\text{Cu}(111)/\text{CH}_3$  with coadsorbed iodine where the  $\text{Cu--CH}_3$  bond energy is  $29 \pm 2$  kcal/mol.<sup>40</sup> While the effects of the coadsorbed  $\text{P}(\text{CH}_3)_3$  and iodine on the bond energy are unknown, these values are quite similar to those determined for ethyl groups on  $\text{Cu}(100)$ ,<sup>226</sup>  $\text{Pt}(111)$ ,<sup>227</sup>  $\text{Fe}(100)\text{--H}$ ,<sup>125,228</sup> and  $\text{Ni}(100)$ <sup>229b,230a</sup> (See Table 6). Also, estimates for the methyl–metal bond strength on  $\text{Ni}(100)$  have been obtained from TPD studies.<sup>162</sup> All of these values are also similar to those for alkyl ligands in organometallic compounds (see section IV.A.2). On the other hand, the calculated bond energies for  $\text{CH}_3/\text{Ni}(111)$  and  $\text{CH}_3/\text{Pt}(111)$  are significantly larger at 49 kcal/mol<sup>218</sup> and 50–53 kcal/mol,<sup>229a</sup> respectively, and the average energy of the three Pt–carbon bonds for ethylidyne ( $\text{CCH}_3$ ) on a reconstructed  $\text{Pt}(110)$  surface as determined by calorimetric measurements is 50 kcal/mol.<sup>230b</sup>

**b. Reactivity.** As indicated by the processes in Tables 1–3, heterogeneous hydrocarbon catalysis suggests the following elementary reactions for adsorbed methyl (see Figure 6): (1) loss of H to form  $\text{CH}_2$ , (2) addition of H to form methane, (3) methyl coupling to evolve ethane, (4) coupling with  $\text{CH}_2$  to form ethyl, and (5) reaction with alkenes to form



**Figure 6.** Potential reaction pathways for methyl groups on metal surfaces on the basis of surface reactions proposed in heterogeneous catalysis. The boxes indicate the surfaces on which these various pathways have been reported. Not shown is CH coupling to form acetylene (a reaction observed on  $\text{Ni}(111)$ <sup>168</sup>), and  $\text{CH}_2$  reaction with  $\text{CH}_2\text{CH}_3$  to form propyl and propylene (reactions observed on  $\text{Cu}(100)$ <sup>132</sup>).

longer chain alkyls. In vacuum single-crystal studies, methyls have generally been studied in the absence of coadsorbed species, in which case the surface reaction possibilities are loss of H to form  $\text{CH}_2$ , methyl coupling to form ethane, and bond homolysis to form gas-phase methyl radicals. Note, however, that loss of H produces surface  $\text{CH}_2$  and H, both of which can then react with the remaining methyls. Thus, as shown in Figure 6, all of the processes listed above for heterogeneous catalysts are theoretically possible for methyls adsorbed alone on metal surfaces.

In actuality, most of the pathways shown in Figure 6 are not generally observed on single crystals. As indicated, the most common reaction pathways to date for methyls on metals are hydrogenation to evolve methane and decomposition to produce surface carbon. Isotope-labeling studies have established that for comparable surface coverages of  $\text{CH}_3$  and H, methyl hydrogenation to methane is more facile than methyl decomposition on  $\text{Ni}(100)$ ,<sup>142,143</sup>  $\text{Ni}(111)$ ,<sup>144</sup> and  $\text{Cu}(110)$ ,<sup>140</sup> but these two processes have comparable rates on  $\text{Pt}(111)$ .<sup>151,231–233</sup>

**Table 6. Comparison of the Energetics and Kinetics of  $\beta$ -Hydride Elimination by Alkyl Groups on Metal Surfaces<sup>a</sup>**

surface/alkyl	ref(s)	$\beta$ -hydride elimination		olefin $\Delta H_{\text{ads}}$	metal–H bond $E$	metal–Alkyl bond $E$
		$E_a$	$\Delta H$			
$\text{Ni}(100)/\text{ethyl}$	229b, 230a	$6 \pm 1$	$\sim -4$	$\sim 12$	$\sim 64$	$\sim 31 \pm 3$
$\text{Cu}(100)/\text{ethyl}$	226	$14.5 \pm 2$	$6.5 \pm 4$	$8 \pm 2$	$55 \pm 4$	$33 \pm 6$
$\text{Fe}(100)\text{--H}/\text{ethyl}$	125, 228	31.2	$7 \pm 2$	$8 \pm 2$	$\sim 60$	$\sim 38$
$\text{Pt}(111)/\text{ethyl}$	227	6	$-7$	11	$\sim 60$	$\sim 38$
$\text{Al}(111), (100)/\text{isobutyl}$	76	$\sim 30$	$\sim 19$	$\sim 7$	$\sim 57$	$\sim 46$

<sup>a</sup> All values are in kcal/mol.



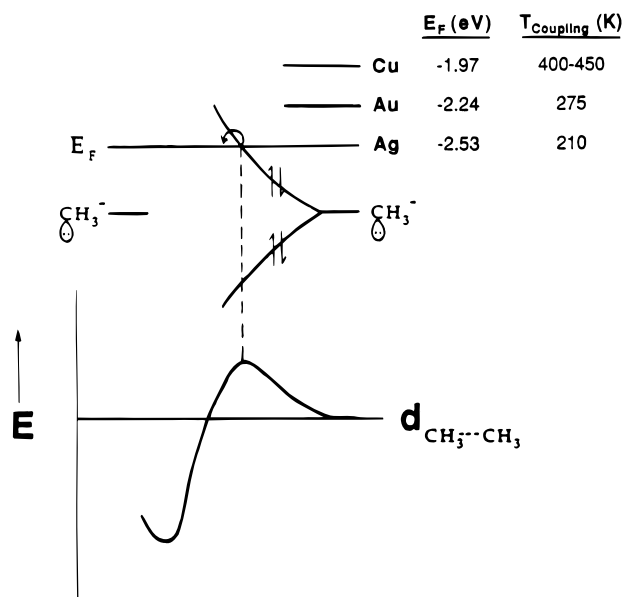
In contrast to the methyl decomposition discussed above, coupling to produce ethane is the only reaction observed for methyls on silver<sup>145,147,149,150</sup> and gold<sup>225,234</sup> surfaces. Carbon-carbon bond formation is also a primary reaction channel on copper surfaces with both ethane and ethylene being formed.<sup>132,140,141,235,236a</sup> Interestingly, mechanistic studies on Cu(110) suggest that the majority of the ethylene is formed by the  $\text{CH}_2 + \text{CH}_3 \rightarrow \text{CH}_2\text{CH}_3 \rightarrow \text{CH}_2\text{CH}_2 + \text{H}$  pathway shown in Figure 6;<sup>140</sup> although, the  $\text{CH}_2 + \text{CH}_2$  coupling reaction was also found to be kinetically facile.<sup>140</sup> Small amounts of ethylene and ethane have been reported for Pd(100),<sup>236b,236c,237</sup> and a small yield of surface ethylidyne ( $\text{CCH}_3$ ) is found for methyl radical adsorption on Pt(111).<sup>31</sup> Finally, for high surface coverages of methyl formed by methane dissociation on Ni(111), it has been demonstrated that methyls dehydrogenate to CH species which subsequently couple to form acetylene and benzene.<sup>168,238</sup>

The absence of these coupling reactions on other metals may be partly explained by the fact that these studies have generally been carried out with methyl halides for which the surface methyl coverage is limited by the presence of the coadsorbed halogen. It is possible that for higher methyl coverages C-C bond formation would be observed as is the case with methyl radical adsorption on Pt(111).<sup>31</sup> The importance of high coverages of surface fragments for promoting coupling reactions has been emphasized previously by Ceyer<sup>238</sup> and Ho.<sup>239</sup> Methyl coupling with surface oxygen is discussed in the review by Friend.<sup>14</sup>

Extended Hückel calculations by Zheng, Apeloig, and Hoffmann<sup>224</sup> indicate that, in the absence of dominant steric or diffusional energy barriers for methyl coupling, the methyl coupling rate is related to the position of the Fermi level of the metal relative to the metal-methyl bonding orbital. Provided the energy of the metal-carbon bonding orbital is approximately invariant with metal, the methyl coupling rates on Cu(111), Ag(111), and Au(111) are consistent with this theoretical prediction. This correlation is illustrated in Figure 7. As shown, the methyl-metal bonding orbital is initially doubly occupied and the methyl group can be viewed as  $\text{CH}_3^-$  due to charge transfer from the metal.<sup>224,240</sup> As the methyl groups approach each other, the potential energy of the system initially increases as the C-C bonding and antibonding orbitals, both doubly occupied, begin to form. The potential energy continues to increase until the C-C bonding orbital rises above the Fermi level. At this point, the antibonding electrons can transfer into the metal, and further C-C bond formation is attractive.<sup>224,240</sup> Since the calculated Fermi levels<sup>241</sup> for the coinage metals increase (i.e., move to less negative values) on going from silver to gold to copper, as shown in Figure 7, this theoretical picture predicts that the coupling rate should follow the trend observed.

## 2. Alkyls with $\beta$ -Hydrogens

**a. Identification.** Alkyls with  $\beta$ -hydrogens are more difficult to isolate and identify than surface methyls; not only are these species larger and spec-

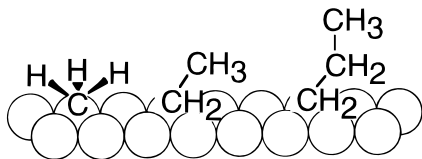


**Figure 7.** Molecular orbital picture after Zheng, Apeloig, and Hoffman<sup>224</sup> for methyl coupling to form ethane on metal surfaces. The 2-center, 4-electron interaction as two methyls (formally anions) approach is repulsive until the C-C antibonding orbital rises above the Fermi level so that the antibonding electrons can transfer to the metal. This picture suggests that activation energy for methyl coupling is related to the position of the methyl-metal bonding orbital relative to the Fermi level ( $E_F$ ) of the metal. The upper right indicates that such a correlation exists between the calculated metal Fermi levels<sup>241</sup> and the measured methyl coupling temperatures for the (111) surfaces of copper, silver, and gold.<sup>225</sup>

troscopically more complex, but they also are less stable and the decomposition products tend to be more difficult to isolate and characterize than those for methyl. Nonetheless, there is now good evidence for these species on single-crystal surfaces.

In the case of the aluminum/alkyl halide system, alkyl groups are stable to above 500 K, and the surface chemistry can be used to identify these species as described previously in section 3.<sup>67</sup> On other metals, surface alkyls decompose below room temperature which complicates the identification, but there is still good evidence for their formation from alkyl halides including: HREELS results for ethyl on Pt(111),<sup>242,243</sup> Cu(111),<sup>66,69,214</sup> Cu(100),<sup>132</sup> and Rh(111);<sup>244</sup> HREELS spectra of propyl on Cu(111)<sup>66,69,214,243</sup> and Al(100);<sup>67</sup> HREELS spectra for butyl and pentyl groups on Cu(111);<sup>66</sup> HREELS studies of 2-propyl on Rh(111);<sup>244</sup> IR studies of ethyl on Pt(111);<sup>56,57</sup> and IR studies of 1- and 2-propyl on Cu(110).<sup>245a</sup> In each of these systems, the alkyl vibrational spectra are significantly different than those for either the alkyl halide reactant or the alkene reaction product. On Ag(111), HREEL spectra have not been reported, but coupling of the surface alkyl groups at temperatures above where the C-X bonds dissociate (as determined by XPS) provides strong evidence for surface alkyl species.<sup>246</sup> On Ni(100), there is SIMS as well as XPS evidence for alkyl formation,<sup>229,247</sup> and on Pd(100) there is XPS, UPS, and  $\Delta\phi$  evidence for ethyl chloride photodissociation to form surface ethyl groups.<sup>248</sup>

In all of the studies above, alkyls with  $\beta$ -hydrogens have been generated on the surfaces using alkyl

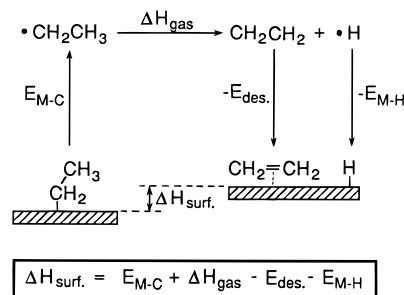


**Figure 8.** Schematic diagrams of the bonding geometries proposed for alkyls on a number of metal surfaces. The 3-fold hollow bonding geometry and  $C_{3v}$  symmetry for methyl are based on HREELS results as well as calculations for Ni(111).<sup>168</sup> The 3-fold hollow sites for ethyl and propyl are presumed by analogy to the methyl results. The tilted orientation for ethyl is consistent with HREELS results for a number of surfaces, and the upright methyl orientation for propyl is based on HREELS results for Cu(111)<sup>66,69,214,245b</sup> and IR results for Cu(110).<sup>245a</sup>

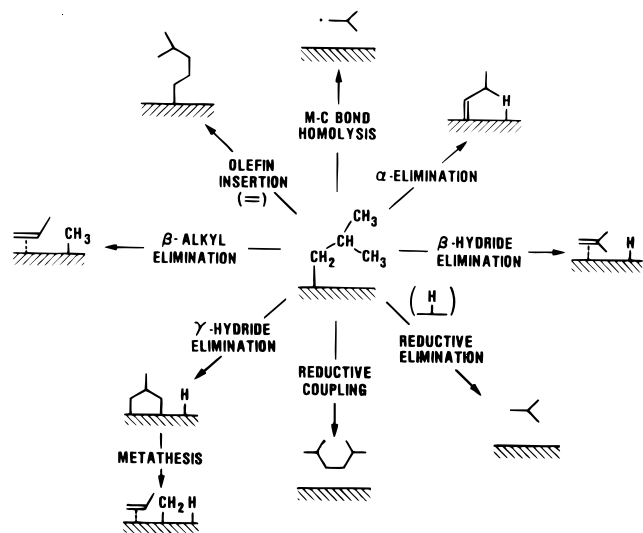
halides as precursors. As discussed previously in connection with Figures 2–4, convincing chemical evidence has also been provided for alkyl formation by other routes, including ethyl formation from H + ethylene on Cu(100)<sup>80,82</sup> and Fe(100)–H.<sup>126,228</sup> ethyl formation from Zn(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> on Pd(100),<sup>89</sup> methyl and ethyl formation from Bi(R)<sub>3</sub> on Pt(111),<sup>88</sup> cyclohexyl formation from H + cyclohexene on Cu(100),<sup>82</sup> and isobutyl formation on Al(111) and Al(100) from the dissociative adsorption of triisobutyl aluminum.<sup>76</sup>

**b. Bonding.** (See Figure 8.) The main findings from vibrational spectroscopy studies of alkyl bonding on metals are that (1) ethyl groups bond with the  $C_{3v}$  axis of the methyl group tilted from the surface normal on the Pt(111),<sup>242,243</sup> Cu(111),<sup>66,69,214</sup> Cu(100),<sup>132</sup> and Rh(111),<sup>244</sup> (2) propyl groups bond with the methyl  $C_{3v}$  axes oriented close to the surface normal on Cu(111)<sup>66,69,214,245</sup> and Cu(110),<sup>245a</sup> but with significant tilt on Al(100),<sup>67</sup> and (3) as for methyls, longer chain alkyls show mode softening of C–H stretch modes on copper surfaces.<sup>66,69,214</sup> Isotope-labeling studies establish that this mode softening is limited to C–H bonds at the  $\alpha$ -carbon (the point of attachment to the surface).<sup>214</sup> The fact that both C–H bonds at the  $\alpha$ -carbon show this effect is consistent with the molecular orbital picture of charge donation to a CH antibonding orbital as shown for methyl in Figure 5. The dependence of this interaction and of the alkyl bonding orientation on the surface coverage have yet to be extensively studied.

Finally, for aluminum, copper, platinum, nickel, and iron surfaces, the metal–alkyl bond strength has been determined from thermochemical cycles such as that shown in Figure 9. Since alkyl radical desorption is not observed for these systems, the bond strengths have been determined indirectly by using the measured activation energies for  $\beta$ -hydride elimination and its reverse (reductive elimination) to determine  $\Delta H$  for this surface process. These values are then combined with known heats of adsorption and gas-phase heats of formation to extract the alkyl–metal bond energy. The results, which are summarized in Table 6, are similar to those determined from desorption measurements for methyl on Cu(111)/I and Au(100)/P(CH<sub>3</sub>)<sub>3</sub> (see section IV.A.1). Note, however, that the Al–isobutyl bond energy of  $\sim 46$  kcal/mol is significantly larger than for alkyls on transition metals. This difference correlates with the surface reaction enthalpies for  $\beta$ -hydride elimina-



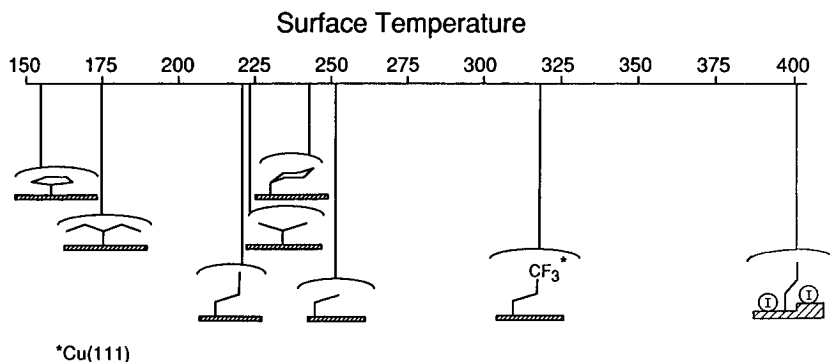
**Figure 9.** Illustration of the type of thermodynamic cycle used to establish the metal–carbon bond strength ( $E_{M-C}$ ) for ethyl groups on metal surfaces (from ref 75). The enthalpy change for the surface  $\beta$ -hydride elimination reaction ( $\Delta H_{\text{surf}}$ ) is established from the difference in the activation energies for the reaction run in both directions. The other quantities are either readily measurable or available in the literature.



**Figure 10.** Potential reaction pathways for an isobutyl group on a metal surface on the basis of what is known about the reactivity of alkyls from heterogeneous catalysis and organometallic chemistry.

tion; a similar correlation is also observed for metal-alkyl compounds in solution where  $\beta$ -hydride elimination by aluminum alkyls is endothermic by 20–25 kcal/mol and has an activation energy of 25–30 kcal/mol, compared with transition metal–alkyls where  $\beta$ -elimination is close to thermoneutral and activation energies are in the range of 10–20 kcal/mol. Further discussion of correlations between metal–alkyl bond strengths on metal surfaces and in organometallic compounds is given in refs 226 and 228.

**c. Reactivity.** On the basis of the catalytic chemistry summarized in Tables 1–3 as well as the known reactivity of alkyl ligands in metal–alkyl compounds, potential surface reaction pathways for  $\beta$ -hydrogen-containing alkyls are shown in Figure 10. While many reaction channels are possible, the dominant reaction channel on single crystals is  $\beta$ -hydride elimination. With the exception of aluminum,  $\beta$ -hydride elimination is surprisingly insensitive to the atomic identity of the metal surface, and  $\beta$ -hydride elimination from ethyl groups occurs at 200–230 K for ethyl groups on Pt(111),<sup>227,242,249</sup> 120–140 K on Ni(100),<sup>229b,230a</sup> 160–230 K on Pd(100),<sup>248</sup> 265 K on Au(111),<sup>250</sup> 230–250 K on copper,<sup>66,69,70,75,251</sup>

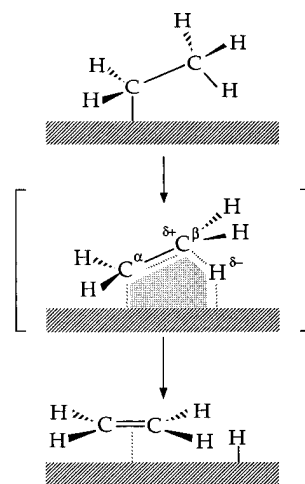


**Figure 11.** Temperature axis indicating the peak temperature for  $\beta$ -hydride elimination by the indicated alkyl groups on Cu(100) as measured in a temperature-programmed reaction-type experiment. For reference, a 3–5 K difference in peak temperature in this type of experiment corresponds to a factor of 2 in rate if the processes are carried out at a common reaction temperature. The Cu(111) result is from ref 245b. The Cu(100) results are from ref 137.

and 580 K on Al(100).<sup>67</sup> The similarities in the  $\beta$ -elimination kinetics between Ni, Pt, Pd, Cu, and Au (metals which show dramatically different behavior as catalysts for C–H bond scission processes) have been attributed to compensating changes in the reactant and product bond strengths on these metals.<sup>140,226</sup> In other words, while Pt binds the reactant alkyl more strongly than copper, it also binds the product olefin and hydrogen more strongly, so that the surface reaction enthalpy change is surprisingly similar to copper (see Table 6). In turn, the kinetics of  $\beta$ -hydride elimination appear to mirror the reaction thermodynamics.

In contrast to the surprisingly small effects of the nature of the metal on the rate of  $\beta$ -hydride elimination, studies on copper surfaces have shown that at least for this metal, alkyl structure and substituents have a remarkably large effect on reactivity.<sup>137,245b</sup> This variation in  $\beta$ -elimination rate with structure has provided important insights into the transition state for reaction. Selected results from these studies are summarized in Figure 11 which plots the peak temperatures determined by TPD studies for  $\beta$ -hydride elimination in a series of alkyls on copper. As shown, the reaction peak temperature varies from 155 K in the case of cyclopentyl to 320 K for trifluoropropyl groups. Since a 3–5 K change in peak temperature corresponds to a factor of 2 in rate, this 165 K temperature difference corresponds to more than 9 orders of magnitude in rate if the reactions are carried out at a common temperature near 200 K. Gellman and co-workers have demonstrated that the dramatic effects of fluorination at the alkyl  $\gamma$ -carbon are due to a destabilization of partial positive charge on the  $\beta$ -carbon in a hydride-like transition state.<sup>245b</sup> In contrast to this electronic effect, the 90 K difference in peak temperature between cyclopentyl and cyclohexyl groups appears to be attributable primarily to conformational effects.<sup>137</sup>

The picture that emerges for the  $\beta$ -hydride elimination transition state on copper is shown in schematically in Figure 12. Two key elements are a  $C^{\delta+}-H^{\delta-}$  charge separation and a dihedral angle of near 0 degrees between the substituents on the  $\alpha$ - and  $\beta$ -carbons. The former characteristic accounts for the effects of electron-donating  $CH_3$  groups and electron-withdrawing  $CF_3$  groups on the ethyl  $\beta$ -elimination rate (see Figure 11).<sup>245b</sup> The latter accounts for the



**Figure 12.** Schematic diagram of the key features of the transition state for  $\beta$ -hydride elimination by alkyl groups on copper surfaces. The inductive effects of substituents at the  $\beta$ -carbon were used to establish the  $C^{\delta+}-H^{\delta-}$  charge separation at the  $\beta$ -carbon<sup>245b</sup> while the planarity of the transition state as indicated by the shaded region was determined via studies with conformationally constrained alkyls.<sup>137</sup>

large variations in rate between cyclohexyl and cyclopentyl groups.<sup>137</sup> Note that a dihedral angle of zero between the substituents on the  $\alpha$ - and  $\beta$ -carbons maximizes overlap between the p-orbitals of the incipient  $\pi$ -bond of the product alkene. Theoretical calculations support these ideas.<sup>252</sup> It should also be noted that the  $\beta$ -elimination pathway shown in Figure 11 corresponds to a syn elimination, i.e. elimination of the hydrogen and the metal from the same side of the alkyl group. The syn nature of the elimination is confirmed by studies of  $\beta$ -elimination from stereoselectively deuterated cyclohexyl groups on Cu(100).<sup>82</sup>

It should be emphasized that the nature of the alkyl  $\beta$ -hydrogen elimination transition state may be metal specific. For example, recent studies of alkyl  $\beta$ -elimination on Ni(100) surfaces indicate that the elimination rate is slowed rather than enhanced by addition of electron-donating methyl groups to the  $\beta$ -carbon.<sup>253</sup> Further studies are warranted to address these significant differences.

Also of interest for future study are reactions of alkyls with coadsorbates. Relatively few studies of these processes have been investigated, but there are

reports of alkyl + H reactions to form alkanes on Pd(100),<sup>248</sup> Ni(100),<sup>229,230</sup> Cu(110),<sup>245a</sup> Al(100),<sup>67</sup> Pt(111),<sup>227,242,249</sup> and Ag(111).<sup>146</sup> In addition, recent experiments by Klivenyi and Solymosi<sup>254</sup> and by Bol and Friend<sup>73,74</sup> have shown that alkyls and carbenes, respectively, react with surface oxygen on Rh(111) to produce partial oxidation products; similar reactivity has been shown by Gleason and Zaera for alkyls on Ni(100).<sup>255</sup> It has also been demonstrated that alkyl groups react with silicon atoms and hydrogen on aluminum surfaces to form alkyl silanes<sup>256</sup> and that ethyl groups undergo a migratory insertion with coadsorbed CH<sub>2</sub> on Cu(100) to form propyl groups.<sup>132</sup> The yield for this latter coupling reaction is determined by the relative rates of  $\beta$ -hydride elimination and coupling, and it is found that the yield is about a factor of 40 larger for CD<sub>2</sub>CD<sub>3</sub> groups vs CH<sub>2</sub>CH<sub>3</sub> groups.<sup>132</sup>

This difference in yield may be attributed to the kinetic isotope effect for  $\beta$ -hydride elimination on copper. Competition studies of  $\beta$ -H and  $\beta$ -D elimination from -CD<sub>2</sub>CD<sub>2</sub>H groups on Cu(100) have demonstrated that the H:D elimination rate ratio is  $9.5 \pm 0.4$  at 260 K.<sup>136,226</sup> While this value is quite large, it is within the regime expected for a semiclassical kinetic isotope effect in the absence of tunneling. Thus, while it is possible that tunneling does play a role in  $\beta$ -hydride elimination on copper, tunneling is not required in order to account for the deuterium kinetic isotope effect. Similar conclusions have been reached previously by Madix and co-workers for C-H bond scission in ethylidyne on Pt(111),<sup>257</sup> C-H bond scission in methoxy groups on Cu(110),<sup>258</sup> and C-H bond scission in formate on Cu(110).<sup>259</sup>

As a final example of surface alkyl reactions, we consider the alkyl coupling reported for silver,<sup>246</sup> gold,<sup>250</sup> copper,<sup>70,140,141</sup> and nickel.<sup>72</sup> In the case of the silver, gold, and high-temperature copper coupling channels, there is good evidence for formation of stable surface alkyls prior to coupling, although the possibility of a direct reaction between surface ethyls and ethyl iodide has also been suggested for Ag(111).<sup>146</sup> On copper,<sup>70</sup> however, coupling products detected at temperatures below 200 K appear to result from alkyl free radicals produced during carbon-halogen bond scission, and these radical coupling products are also accompanied by alkyl disproportionation. Similar low-temperature alkyl disproportionation has been observed on Ni(100),<sup>144</sup> but no coupling products are detected in this system. In the Cu(111) studies,<sup>70</sup> the detection of coupling and disproportionation products in a ratio analogous to that reported for alkyl radicals in gas phase and solution environments was the primary evidence for radicals. On Ni(100),<sup>144</sup> the surface reaction kinetics and the results of isotope labeling studies suggest a radical mechanism. Given the recent reports of radical ejection during carbon-halogen bond scission on metal single crystals,<sup>38-40</sup> these conclusions seem reasonable. It should also be noted that radical formation during carbon-halogen bond scission at metal surfaces in solution phase processes has been a point of extensive debate in the literature.<sup>260-262</sup>

### 3. Other Alkyls

Neopentyl groups [(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>], which lack  $\beta$ -hydrogens, have been generated on Ni(100)<sup>263,264</sup> and Al(100)<sup>68</sup> surfaces via the dissociative adsorption of neopentyl iodide. On Ni(100), C-C bond scission occurs with an activation energy of  $\sim 22$  kcal/mol to produce butene,<sup>263</sup> while on Al(100) there is evidence for neopentyl radical desorption with an activation energy of  $\sim 40$  kcal/mol.<sup>68</sup> Recent isotope-labeling studies of the Ni(100) reaction indicate that the butene is formed by  $\alpha$ -C-C bond scission as opposed to  $\beta$ -methyl elimination which one would have expected on the basis of known reactions in organometallic chemistry.<sup>264</sup> These C-C and M-C bond scission reactions are to be contrasted with the  $\beta$ -C-H bond scission and alkyl coupling reactions generally observed for alkyls containing  $\beta$ -hydrogens (see section III.A.2). The other  $\beta$ -hydrogen-deficient alkyl studied on single crystals is benzyl (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-) which has been generated on Pt(111)<sup>98-100</sup> and Ru(001)<sup>101,102</sup> by the dissociative adsorption of toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>). Vibrational spectroscopy studies<sup>98,101,102</sup> indicate that the benzyls in these systems bind to the surface as  $\eta^7$  ( $\pi+\sigma$ )-bonded species. On both Pt(111) and Ru(001), benzyl decomposes to surface carbon and hydrogen, but on Pt(111), some of the benzyl also couples to form bibenzyl (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) and some undergoes hydrogenolysis to produce benzene.<sup>100</sup> There is also circumstantial evidence that benzyl forms from toluene decomposition on nickel surfaces on the basis of TPD studies employing isotope labeling.<sup>158-160</sup>

### B. Carbenes

Carbenes are common intermediates in both catalytic hydrocarbon synthesis and hydrogenolysis reactions (see Tables 1-3). While there have been numerous attempts to isolate and identify these species on metal single crystals, definitive spectroscopic and chemical evidence for surface CH<sub>2</sub> has been difficult to obtain. Quite a range of precursors have been investigated including the dihaloalkanes as summarized in Table 4, as well as diazarene (c-CH<sub>2</sub>N<sub>2</sub>) on Pd(110);<sup>265</sup> diazomethane (CH<sub>2</sub>N<sub>2</sub>) on Pt(111),<sup>266</sup> Ru(001),<sup>267</sup> polycrystalline Fe,<sup>268</sup> and Fischer-Tropsch catalysts;<sup>269</sup> and ketene (CH<sub>2</sub>CO) on Pt(111),<sup>270-272</sup> Fe(110),<sup>273</sup> and Ru(001).<sup>274-277</sup> Surface IR spectra provide evidence for CD<sub>2</sub> on Pt(111),<sup>56</sup> while XPS results are consistent with CH<sub>2</sub> formation from diazarene on Pd(110)<sup>265</sup> and from CH<sub>2</sub>I<sub>2</sub> on Pd(100).<sup>190</sup> The surface reactions of CH<sub>2</sub>I<sub>2</sub> on Pt(111),<sup>278,279</sup> Ni(100),<sup>142</sup> Cu(100),<sup>140</sup> and Cu(110)<sup>132</sup> are also suggestive of formation of adsorbed CH<sub>2</sub>. Diagnostic HREELS spectra for surface CH<sub>2</sub> have been difficult to obtain, largely because most HREELS studies may have been carried out on monolayers which were not pure CH<sub>2</sub>. The recent HREELS and TPD results for CH<sub>2</sub>I<sub>2</sub> dissociation on Mo(110) by Weldon and Friend<sup>280</sup> are an exception. The formation of almost pure CH<sub>2</sub>D<sub>2</sub> in coadsorption experiments with deuterium provides chemical evidence for surface CH<sub>2</sub> and the vibrational spectrum is consistent with this species. Comparison of the surface vibrational frequencies with those for organometallic

carbene complexes suggest that  $\text{CH}_2$  bonds in a bridge site on  $\text{Mo}(110)$ .<sup>280</sup>

Carbenes other than  $\text{CH}_2$  are relatively unstudied. There are, however, HREELS reports of  $=\text{CHCH}_3$  formation during ethylene decomposition on K-covered  $\text{Pt}(111)$  surfaces,<sup>281,282</sup> and recent studies of  $\text{BrClCHCH}_3$  and  $\text{CH}_3\text{CCl}_2\text{CH}_3$  dissociation on  $\text{Cu}(100)$ <sup>283</sup> and for of  $\text{I}_2\text{CHCH}_3$  on  $\text{Pt}(111)$ <sup>284</sup> indicate formation of the corresponding methyl-substituted carbenes.

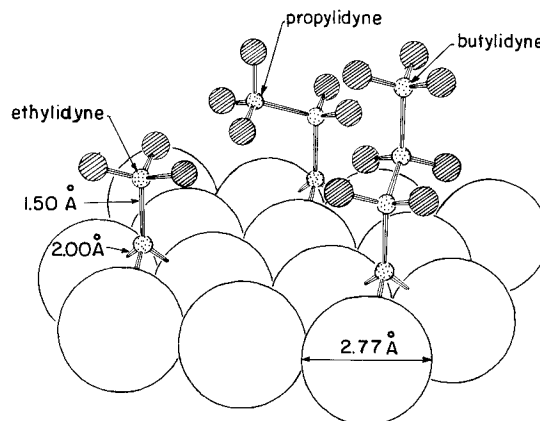
As with methyl,  $\text{CH}_2$  decomposition to surface carbon is the dominant reaction pathway on most transition metals in the absence of coadsorbed species.  $\text{CH}_2$  hydrogenation to methane has been reported for  $\text{Pt}(111)$ ,<sup>266,278,279</sup>  $\text{Ni}(100)$ ,<sup>142</sup>  $\text{Pd}(110)$ ,<sup>265</sup>  $\text{Pd}(100)$ ,<sup>190</sup>  $\text{Mo}(110)$ <sup>280</sup> and  $\text{Cu}(110)$ ,<sup>140</sup> and  $\text{CH}_2 + \text{CH}_2$  coupling to form ethylene as well as  $\text{CH}_2 + \text{CD}_3$  coupling to form surface ethyls are observed on  $\text{Cu}(100)$ <sup>132</sup> and  $\text{Cu}(110)$ .<sup>140</sup> An interesting finding from these copper studies was that the rates of  $\text{CH}_2 + \text{CH}_2$  coupling and  $\text{CH}_2 + \text{CD}_3$  coupling are similar, and both rates are factors of 50–100 faster on  $\text{Cu}(100)$  than on the more corrugated  $\text{Cu}(110)$  surface.<sup>132</sup> A possible explanation is that the rate of coupling is controlled by the rate of  $\text{CH}_2$  diffusion on these surfaces, and thus the reason for the similarities between  $\text{CH}_2/\text{CH}_2$  and  $\text{CH}_2/\text{CD}_3$  coupling rates on both surfaces. Rate-limiting diffusion is consistent with the bond-order/Morse-potential calculations of Shustorovich and Bell which predict near zero activation energy for  $\text{CH}_2$  coupling reactions on a  $\text{Cu}(111)$  surface,<sup>285,286</sup> with the implication that the measured activation energy for reaction is entirely attributable to diffusion. Similarities in alkyl/H coupling rates have also been previously noted on  $\text{Cu}(110)$ <sup>140</sup> and the possible diffusion of a  $\text{Cu-H}$  complex in the reaction has been suggested.<sup>140</sup>

As with radical formation reported for monohaloalkanes, there are reports of carbene generation and coupling during the dissociation of carbene precursors, including  $\text{CH}_2\text{I}_2$  dissociation on  $\text{Al}(111)$ <sup>45,287,288</sup> and  $\text{CCl}_4/\text{CCl}_2\text{F}_2$  dissociation on  $\text{Fe}(110)$ .<sup>46–51</sup> McBreen and co-workers have also nicely demonstrated  $\text{CH}_2$  ejection and adsorption for diazarene ( $c\text{-CH}_2\text{N}_2$ ) on  $\text{Pd}(110)$ .<sup>52,265</sup> Oxidation of carbene intermediates prior to bonding with the metal surface has been reported on  $\text{Rh}(111)$ .<sup>73,74</sup>

## C. Carbynes ( $\text{C}_n\text{H}_{2n-1}$ )

### 1. Ethylidyne ( $\text{CCH}_3$ )

**a. Identification.** Ethylidyne is the most extensively studied surface hydrocarbon fragment, and its identification as the highly stable, room temperature, decomposition product for ethylene on many metal surfaces is one of the early triumphs of UHV surface studies. The evidence for formation of ethylidyne has been extensively reviewed previously.<sup>6,15</sup> In the case of platinum, numerous techniques including TPD,<sup>139,289–291</sup> HREELS,<sup>292</sup> LEED,<sup>179,181</sup> RAIRS,<sup>293–296</sup> transmission IR,<sup>297,298</sup> SIMS,<sup>202</sup> XPS,<sup>299</sup> UPS,<sup>188</sup> NEX-AFS,<sup>198</sup> NMR,<sup>300</sup> sum frequency generation,<sup>301</sup> LITD,<sup>302</sup> and scanning tunneling microscopy<sup>303</sup> have been applied to study adsorbed  $\text{CCH}_3$ . The surfaces on which ethylidyne formation has been documented



**Figure 13.** Structures of ethylidyne ( $\text{CCH}_3$ ), propylidyne ( $\text{CCH}_2\text{CH}_3$ ), and butylidyne ( $\text{CCH}_2\text{CH}_2\text{CH}_3$ ) on a  $\text{Pt}(111)$  surface as determined by LEED crystallography (from ref 343). The significant restructuring of the surface metal atoms that occurs in these systems is not shown.

include:  $\text{Pt}(111)$ ,<sup>179,181,291–295,297,298</sup>  $\text{Rh}(111)$ ,<sup>180,304,305</sup>  $\text{Pd}(111)$ ,<sup>306,307</sup>  $\text{Ru}(001)$ ,<sup>308–310</sup>  $\text{Pt}(100)$  ( $5 \times 20$ ),<sup>311,312</sup>  $\text{Rh}(100)$ ,<sup>313</sup>  $\text{Ir}(111)$ ,<sup>314</sup>  $\text{V}(110)/\text{C}$ ,<sup>315</sup>  $\text{Mo}(110)/\text{C}$ ,<sup>316</sup>  $\text{Ni}(111)$ ,<sup>317</sup>  $\text{Pt}(110)$  ( $2 \times 1$ ),<sup>318</sup> and supported  $\text{Pt}$ ,<sup>300</sup>  $\text{Pd}$ ,  $\text{Rh}$ ,  $\text{Ru}$ ,<sup>297,298</sup> and  $\text{Ni}$ .<sup>319</sup> In most of these systems, the presence of ethylidyne is inferred on the basis of the characteristic vibrational spectrum. While ethylidyne has been generated most often by the dissociative adsorption of ethylene, other precursors which have also been reported to form  $\text{CCH}_3$  include: ethyl halides,<sup>227,242,243,249</sup> vinyl iodide,<sup>320–322</sup> propene,<sup>323–325</sup> acetylene + H,<sup>326</sup> ketene,<sup>274</sup>  $\text{CH}_3$ ,<sup>31</sup> butadiene,<sup>327</sup> and acrolein.<sup>328</sup>

**b. Bonding.** The bonding geometry determined by LEED crystallography for ethylidyne on  $\text{Pt}(111)$ <sup>179,181</sup> is shown in Figure 13, and similar results have also been obtained for  $\text{Rh}(111)$ .<sup>180</sup> As shown, the basal carbon is located in a 3-fold site with the C–C bond oriented along the surface normal. The C–C bond length is approximately the same as that in ethane and the metal-carbon bond lengths are nearly equal to the sum of the carbon and metal covalent radii. LEED analyses also show that the metal surface restructures significantly in response to ethylidyne coordination.<sup>180,181</sup> The geometrical similarities between surface ethylidyne and ethylidyne in the tricobalt cluster ( $\text{CCH}_3$ ) $\text{Co}_3(\text{CO})_9$  have been extensively discussed.<sup>292</sup> Molecular orbital calculations suggest that on both the surface and in the cluster the  $\text{CCH}_3$  ligand coordinates via  $\sigma$ -donation of electrons from the A orbital and via  $\pi$ -back-donation of electrons from the metal to the E orbital.<sup>329a</sup> It is interesting to note that these bonding ideas pertain not only to the 3-fold symmetric bonding sites most commonly observed for  $\text{CCH}_3$  but also to ethylidyne bonding on  $\text{Rh}(100)$ <sup>329b</sup> where no 3-fold symmetry sites are present.

**c. Reactivity.** In catalysis, carbynes such as ethylidyne are generally proposed as intermediates in high-temperature hydrogenolysis reactions, and the catalytic fate of the carbyne is hydrogenation to the corresponding gas-phase alkane (see Table 2). Studies on single-crystal surfaces are consistent with this hydrogenation process being a demanding reaction that requires high temperatures and pressures of hydrogen. It is found that single monolayers of

ethylidyne are quite stable on Pt(111)<sup>103,330</sup> and Rh(111)<sup>305</sup> surfaces as well as on dispersed metal catalysts under atmospheric pressures of hydrogen.<sup>297,298</sup> <sup>14</sup>C-labeling studies, however, show that these species do hydrogenate at a significant rate above 400 K.<sup>104,105</sup> Interestingly, in ethylene hydrogenation over Pt(111) and Rh(111), processes which can be carried out near room temperature, catalytically inactive ethylidyne monolayers cover the active catalyst surface. Several possible roles of this ethylidyne monolayer have been suggested, including hydrogen transfer from the surface to second layer species<sup>103,331</sup> and protection of the catalyst surface from more detrimental poisons.<sup>10</sup>

The reactions of ethylidyne in vacuum in the absence of a high surface coverage of hydrogen are exclusively dehydrogenation. On most metals, ethylidyne decomposes between 350 and 450 K to generate mixtures of surface species which probably include CCH<sub>2</sub>,<sup>332,333</sup> CCH,<sup>334</sup> and possibly individual CH species.<sup>335</sup> These reactions have yet to be fully characterized, and their relevance for catalysis is probably with respect to catalyst deactivation. For example, the "optimum temperature" for ethylene hydrogenation over the platinum metals has been correlated with the temperature at which the stable monolayer on the catalyst surface converts from CCH<sub>3</sub> to species such as CCH<sub>2</sub> and CCH.<sup>106</sup>

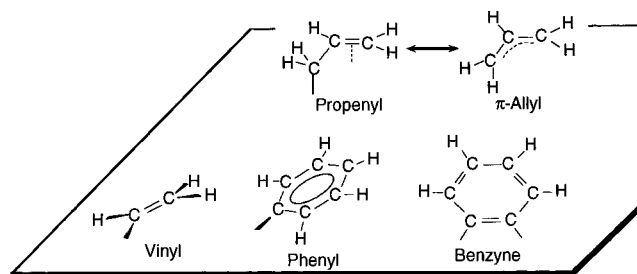
## 2. Methylidyne (CH)

Although much proposed as an intermediate in hydrocarbon decomposition reactions on metal surfaces in vacuum,<sup>6</sup> this species is often formed as part of a mixture of surface fragments, and a recent study of the surface vibrational spectrum for CH on Ni(111)<sup>168</sup> casts doubt on some prior assignments. In particular, most prior identifications of surface CH have been based on the observation of a CH bending vibration ( $\delta$ CH) at  $\sim 800$  cm<sup>-1</sup><sup>336</sup> (see ref 6 for a summary of this work). The work of Ceyer et al., however, provides evidence for a  $\delta$ CH mode for CH/Ni(111) at 1275 cm<sup>-1</sup>, so either the bonding of CH is strongly metal dependent or species previously identified as CH might instead be species such as C<sub>2</sub>H.

With respect to the reactivity of CH on single crystals, little is yet known, but on Ni(111), CH couples above 250 K to form acetylene which in turn couples above 300 K to form benzene.<sup>168</sup> On other metals dehydrogenation either with or without concurrent polymerization has been suggested.<sup>6</sup> Hydrogenation of various CH<sub>x</sub> species at atmospheric pressure of hydrogen has been reported on Fe(110).<sup>330</sup>

## 3. C<sub>3</sub>-C<sub>4</sub> Alkylidynes

Longer chain alkylidynes have been generated from 1-alkenes on Pt(111),<sup>4,203,289,337-339</sup> Rh(111),<sup>323,340</sup> Ru(001),<sup>324,325</sup> and Mo(110)/C<sup>341</sup> surfaces. Isobutylidyne has also been reported for isobutene decomposition on Pt(111)<sup>342</sup> and Mo(110)/C.<sup>341</sup> The evidence for these species is a combination of stoichiometry determinations from TPD measurement,<sup>289</sup> assignment of complex surface HREELS<sup>323,324,337,341,342</sup> and RAI-RS<sup>325,339</sup> spectra, LEED studies,<sup>340,343</sup> SIMS measurements,<sup>203</sup> and analogy to the formation of CCH<sub>3</sub> from



**Figure 14.** Schematic diagrams of the structures proposed for (a) vinyl on Ni(100)<sup>296</sup> and Cu(100),<sup>194</sup> (b) phenyl on Os(0001)<sup>94</sup> and Cu(100),<sup>195,361</sup> (c) benzyne on Mo(110),<sup>96</sup> and (d) propenyl/allyl on Al(100)<sup>353</sup> and Ag(111),<sup>354</sup> respectively.

ethylene. The results are consistent with the upright bonding geometries shown in Figure 13.

On Rh(111)<sup>323</sup> and Ru(001),<sup>324,325</sup> propylidyne decomposes via ethylidyne. These reactions are among the most clear-cut examples of C-C bond scission in adsorbed hydrocarbon fragments, and it is interesting that these processes occur at temperatures even below 300 K. Isotope-labeling studies on Rh(111),<sup>323</sup> while complicated by exchange, suggest that the C-C bond which cleaves in propylidyne is the one directly adjacent to the surface. No ethylidyne is observed during propylidyne decomposition on Pt(111),<sup>323</sup> and a possible difference between Rh/Ru and Pt with respect to C-C bond cleavage is the presence or absence of surface hydrogen at the propylidyne decomposition temperature on these metals,<sup>323,325</sup> with significant coverages of surface hydrogen being required to induce hydrogenolysis. In the case of butylidyne on Pt(111), TPD results indicate decomposition to a monolayer of average stoichiometry C<sub>4</sub>H<sub>2</sub>, for which Avery and Sheppard suggest the metallacycle di-carbyne ( $\equiv$ CCH=CHC $\equiv$ ) as a surface intermediate on the basis of HREELS results.<sup>337,338</sup> Such a species is somewhat analogous to those that have been proposed for catalytic hydrogenolysis (see Table 2).

## D. Vinyl ( $-\text{CH}=\text{CH}_2$ ) and $\eta^2\text{-CHCH}_2$ Species

As with other  $\pi$ -systems, the extent of  $\pi$ -bond interaction between CH=CH<sub>2</sub> fragments and metals can vary between weak  $\pi$ -coordination (vinyl coordination) and strong di- $\sigma$ -bonding ( $\eta^2$ -coordination). Surface vinyls have been proposed for ethylene decomposition on Ni(100),<sup>90-93,193</sup> acetylene hydrogenation on Ni[5(111) × (110)];<sup>344</sup> ethylene decomposition on Pt(100);<sup>345,346</sup> vinyl halide decomposition on Ag(111),<sup>246</sup> Cu(100),<sup>194</sup> and Pt(111),<sup>320-322</sup> and for the electron-induced decomposition of ethylene on Ag(111).<sup>84,113</sup> In the Ni(100) and Pt(111) studies, a weak  $\pi$ -surface interaction was concluded on the basis of HREELS results,<sup>90,91,322</sup> while on Ag(111) and Cu(100) weak  $\pi$ -coordination was presumed because these metals are known to interact weakly with the  $\pi$ -systems in ethylene and benzene. NEXAFS studies on Ni(100)<sup>193</sup> and Cu(100)<sup>194</sup> indicate a tilted adsorption geometry for vinyl as shown in Figure 14.

In contrast to these weakly  $\pi$ -interacting systems,  $\eta^2$ -coordination has been proposed for CHCH<sub>2</sub> species formed by ethylene decomposition on Pd(100),<sup>347</sup> and acetylene hydrogenation on Ru(001).<sup>348</sup> In both systems  $\eta^2$ -coordination was proposed because of the

absence of C=C stretching modes above 1500  $\text{cm}^{-1}$  in the HREELS spectra.  $\eta^2$ -Coordinated  $\text{HCCH}_2$  ligands with similar vibrational spectra are known from organometallic chemistry.<sup>349</sup>

The catalytic chemistry proposed for  $\text{CHCH}_2$  is dominated by coupling reactions with H and  $\text{CH}_2$ . In vacuum studies, coupling with H to evolve ethylene has been reported for Ag(111),<sup>82,113</sup> Ru(001),<sup>348</sup> and Ni[5(111) × (110)],<sup>344</sup> and coupling with  $\text{CH}_2$  has been found for Cu(100).<sup>133</sup> Also, in the absence of coadsorbates on Ag(111)<sup>246</sup> and Cu(100),<sup>194</sup> the sole reaction for vinyls is coupling to evolve butadiene. In other systems,  $\text{CHCH}_2$  species are reported to react by C-H and/or C-C bond scission: to form HCCH on Ni(100),<sup>90-93</sup> to form CH on Pd(100),<sup>347</sup> and to form species such as HCCH and  $\text{CCH}_2$  on Pt(111).<sup>320-322</sup>

## E. Allyl ( $\text{CH}_2\text{CHCH}_2$ )

Surface allyls are proposed as intermediates in catalytic hydrogenations as well as in skeletal isomerization reactions. They have also been proposed both in high-pressure catalysis<sup>20</sup> and in vacuum single-crystal studies<sup>204,351,352</sup> as intermediates in the aromatization of cyclohexane to benzene. Attempts to characterize these  $\text{C}_6\text{H}_9$  intermediates on Pt(111) are ongoing.<sup>204,351,352</sup>

Allyls have been generated on Al(100),<sup>353</sup> Ag(111),<sup>354</sup> and Cu(100)<sup>133</sup> surfaces by the dissociative adsorption of allyl halides, on Ag(110)/O by the deprotonation of isobutene,<sup>355</sup> and on Pt(111) by C-H bond scission in cyclohexene.<sup>351,352</sup> In both the Al(100) and Ag(111) systems the  $\text{CH}_2\text{CHCH}_2$  fragment was characterized by HREELS. The absence of modes above 1500  $\text{cm}^{-1}$  on Ag(111) led to the conclusion that  $\text{CH}_2\text{CHCH}_2$  coordinates as a flat-lying  $\pi$ -allyl, while the presence of a peak at 1655  $\text{cm}^{-1}$  indicative of a C=C double bond led to the proposal on Al(100) that at least some of the surface species were coordinated as alkenyls ( $-\text{CH}_2\text{CH}=\text{CH}_2$ ) (see Figure 14). Interestingly, these Al and Ag species also react differently. On Ag(111)<sup>354</sup> the sole reaction is coupling to form 1,5-hexadiene while on Al(100)<sup>353</sup> propylene and unidentified polymeric species are produced. Both the bonding and reactions in the Ag(111) system are supported by theoretical calculations.<sup>356</sup>

## F. Metallacycles

Although not much studied on single crystals, these species are frequently proposed as intermediates in catalytic skeletal isomerization and hydrogenolysis reactions. There are, however, several examples of metallacycles from the single-crystal literature, including saturated metallacycles generated from the adsorption of the corresponding dihaloalkanes on Al(100)<sup>353</sup> and Ni(100)<sup>357</sup> surfaces. In the aluminum studies, the presence of metallacycles was inferred on the basis of the well-established carbon-halogen dissociation chemistry on this metal,<sup>67</sup> and on the basis of alkene and diene evolution at temperatures above 500 K, which is the same temperature range where alkyls undergo  $\beta$ -elimination on aluminum.<sup>67</sup> Also, HREELS spectra are consistent with formation of the three-carbon metallacycle.<sup>353</sup> Unlike the longer chain metallacycles, this  $\text{C}_3$  species is quite unstable toward  $\beta$ -elimination—possibly because of the sig-

nificant stability of the resulting allyl. On Ni(100), formation of a three-carbon metallacycle was inferred on the basis of XPS results which showed dissociation of the C-I bond, and the thermal chemistry of this  $\text{C}_3$  species involves production of both propylene and cyclopentane.<sup>357</sup> For  $\text{I}(\text{CH}_2)_6\text{I}$  on Ni(100), the hydrocarbon products are cyclohexene and benzene.<sup>357</sup>

Recent studies by Lambert and co-workers have demonstrated the formation of an unsaturated  $\text{C}_4$  metallacycle on Pd(111)<sup>134,135</sup> and Cu(110)<sup>358</sup> via dissociative adsorption of the cyclic dichloride:  $\text{c-C}_4\text{H}_4\text{-Cl}_4$ . HREELS, TPD, and NEXAFS studies on Pd(111)<sup>134,135</sup> provide convincing evidence for formation of a  $-\text{CHCH}=\text{CHCH}-$  metallacycle which bonds with its  $\pi$ -system inclined by an angle of  $\sim 35^\circ$  from the surface plane.<sup>134,135</sup> Lambert et al. have also demonstrated that this  $\text{C}_4\text{H}_4$  metallacycle reacts with acetylene on Pd(111) and Cu(110) to produce benzene—an observation which supports its role as an intermediate in acetylene trimerization to benzene on this surface.<sup>134,135,358</sup>

In addition to these studies in which metallacycles have been generated via haloalkane precursors, metallacycles have also been proposed as intermediates in the decomposition of thiophene on Pt, Ni, Rh, Ru,<sup>6</sup> in the decomposition of 1-butene on Pt(111),<sup>337,338</sup> and in the aromatization of cyclohexane on Pt(111).<sup>359</sup>

## G. Other Hydrocarbon Fragments

While not as frequently proposed as catalytic reaction intermediates, phenyl, benzyne, cyclopentadienyl, vinylidene, and acetylide are hydrocarbon fragments for which there is extensive and/or particularly convincing evidence.

### 1. Phenyl

Phenyl groups were first isolated as reaction intermediates by Netzer and co-workers in HREELS studies of benzene decomposition on an Os(001) surface.<sup>94</sup> Phenyl groups have also been generated and isolated on Ag(111)<sup>83</sup> and Ni(100)<sup>360</sup> surfaces by the thermal dissociation of iodobenzene, and on Ag(111) by the electron-induced dissociation of benzene<sup>83,84</sup> and by the electron- and photon-induced dissociation of chlorobenzene.<sup>114</sup> More recently, phenyls have been isolated in the thermal and electron-induced dissociation of iodobenzene on Cu(111),<sup>195,361,362</sup> and they have been proposed as intermediates in the thermal decomposition of benzene on a Ni(110)<sup>95</sup> surface.

HREELS studies of phenyl bonding on Os(001)<sup>94</sup> and Cu(111)<sup>361</sup> suggest that the phenyl groups bond with their  $\pi$ -rings within  $30^\circ$  of parallel with the surface plane, while NEXAFS studies for near saturation coverages on Cu(111) indicate that the phenyl rings are, on average, inclined by  $43 \pm 5^\circ$  from the surface plane.<sup>195</sup> Neither system shows evidence from HREELS for substantial rehybridization of the aromatic ring. A tilted phenyl geometry, which is illustrated schematically in Figure 14, is analogous to the  $\eta^1$ -coordination geometry common for pyridine on metals, and it is interesting to note that if there is metal-to-phenyl electron transfer, then the resulting phenyl anion is isoelectronic with pyridine.<sup>361</sup>

Two types of reactions have been reported for adsorbed phenyl: coupling on Ag(111)<sup>83,84</sup> and Cu(111)<sup>361,362</sup> to produce and evolve biphenyl, and dehydrogenation on Ni(110),<sup>95</sup> Ni(100),<sup>360</sup> and Os(0001)<sup>94</sup> (in the osmium system there is evidence for phenyl dehydrogenation to a stable benzyne (C<sub>6</sub>H<sub>4</sub>) fragment<sup>94</sup>). Studies of the phenyl coupling reaction on Cu(111) in which selective fluorination of the phenyl groups was used to probe the nature of the transition state suggest that the transition state is electron rich with respect to the initial state.<sup>363</sup> It is also found that on both Cu(111)<sup>71</sup> and Ag(111),<sup>84</sup> phenyl groups couple with surface hydrogen and alkyls to form benzene and alkyl benzenes, and there is an unusually facile (~150 K) coupling reaction between phenyls and molecular alkyl iodides—a process for which there is evidence for a free radical mechanism.<sup>71</sup>

## 2. Benzyne

Reports of benzyne formation are limited to benzene thiol desulfurization on Mo(110)<sup>96</sup> and benzene decomposition on Os(0001).<sup>94</sup> Despite the small number of studies, the evidence is quite compelling. In the Mo(110) system, the XPS results indicate two chemically distinct forms of carbon in a ratio of 4:2, NEXAFS studies indicate an unusual upright orientation for the  $\pi$ -system, and the HREELS spectra can be reasonably assigned to a vertically adsorbed benzyne species as shown schematically in Figure 14.<sup>96</sup> In the Os studies, ARUPS studies indicate that benzyne is inclined at an angle of ~45° from the surface normal.<sup>94</sup> The only reactivity of benzyne that has been studied is its decomposition, which appears to occur via a mixture of surface fragments.

## 3. Cyclopentadienyl

This ligand, which is ubiquitous in organometallic chemistry, is relatively unstudied on surfaces. In the one published study to date, Avery has demonstrated via HREELS and TPD that cyclopentene dehydrogenates to cyclopentadienyl (Cp) on Pt(111).<sup>364</sup> The HREELS results indicate a flat-lying Cp ring. Recent studies have also shown that Cp groups formed by cyclopentadiene dissociative adsorption are stable to >500 K on Cu(100).<sup>365</sup>

## 4. Vinylidene

Identification of vinylidene (CCH<sub>2</sub>) has been hampered by mixtures of hydrocarbon fragments in the monolayers where it is proposed to form. A notable exception is ethylene decomposition on Ru(001) – p(2×2)O (i.e. a Ru(001) surface with a fractional oxygen coverage of 0.25 O/Ru). Weinberg and co-workers<sup>332</sup> have shown by TPD that the surface stoichiometry at 350 K is C:H = 1, and the HREELS spectrum at this temperature (which is quite sharp suggesting a single surface species) has a C–C stretching mode at 1435 cm<sup>-1</sup> indicative of a carbon–carbon double bond. Independent studies with acetylene rule out HCCH as the surface species, and the observed vibrational frequencies are consistent with those reported for a triosmium vinylidene cluster.<sup>332</sup> The X-ray crystal structure of this Os cluster shows that the vinylidene ligand, which is presumably

similar to vinylidene on Ru(001)/O, has a C–C bond length of 1.38 Å compared to a C=C bond length of 1.33 Å in ethylene.

Also definitive are studies on Pd(100) where both vibrational spectroscopy<sup>307</sup> and X-ray absorption measurements<sup>366</sup> are consistent with vinylidene. Vinylidene has also been reported on the basis of HREELS results as one of several species produced in ethylene decomposition on Pt(100)(1×1)<sup>312</sup> and Rh(100).<sup>333</sup> In studies of the Pt(100)(1×1) system by Hatzikos and Masel,<sup>312</sup> a vibrational mode at 1580 cm<sup>-1</sup> is attributed to vinylidene—indicating near sp<sup>2</sup> hybridization of the carbons analogous to the findings for Ru(001)/O.

## 5. Acetylide

There are numerous reports of acetylide (CCH) formation on metals during the decomposition of a wide range of hydrocarbons. Most identifications have been made on the basis of HREELS studies, and several reports are reasonably definitive including studies of C<sub>2</sub>H<sub>2</sub> decomposition on Ni(100);<sup>367</sup> C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> decomposition on Ni(110);<sup>368</sup> C<sub>2</sub>H<sub>4</sub> decomposition on Ru(001);<sup>308,369</sup> C<sub>2</sub>H<sub>4</sub> decomposition on Rh(100);<sup>333</sup> C<sub>2</sub>H<sub>4</sub> decomposition on Fe(100);<sup>370</sup> and C<sub>2</sub>H<sub>2</sub> deprotonation on Ag(110)/O.<sup>192</sup> In the Ag(110) system, it was suggested that acetylide coordination occurs via a  $\sigma$ -metal–carbon bond plus a weak  $\pi$ -interaction; in other systems, however, HREELS results indicate that the bonding is more analogous to that for acetylide in a triosmium cluster.<sup>371</sup> In this cluster, X-ray crystallography studies show a significantly lengthened C–C bond of 1.34 Å compared with 1.2 Å in acetylene, 1.33 Å in ethylene, and 1.54 Å in ethane.

## V. Summary and Outlook

Over the past five to 10 years, a large number of new approaches have been demonstrated for generating and isolating, at cryogenic temperatures, pure monolayers of hydrocarbon fragments which have been postulated as reaction intermediates in heterogeneous catalysis. Whereas early studies in the field focused on the highly dehydrogenated fragments formed when stable hydrocarbon molecules decompose on metal surfaces, more recent studies have focused on the formation of highly hydrogenated and reactive species such as surface alkyls. These alkyls, which are among the most frequently postulated intermediates in hydrocarbon catalysis, have now been generated on a wide range of metals using a variety of molecular precursors which are either dissociated in the gas phase or on the surface by thermal and nonthermal methods of excitation. By isolating high coverages of these species it has been possible to study their bonding and to identify elementary reaction steps such as  $\beta$ -hydride elimination which is one of the most frequently postulated reactions in heterogeneous catalysis. Physical organic studies of this particular reaction have provided considerable insight into the nature of the transition state for this process. It has also been found that whereas strongly bound alkylidyne species require high pressures of hydrogen in order for hydrogenation



tion to be observed, alkyls can be hydrogenated in single monolayer experiments on most metals in vacuum. And it has been demonstrated that high coverages of reactive surface fragments can induce carbon-carbon bond-forming reactions in single monolayers including: CH coupling to form acetylene on Ni(111), CH<sub>2</sub> + alkyl coupling to grow longer chain alkyls on Cu(100), and alkyl coupling to produce alkanes on copper, silver, and gold.

Given this progress, there are a number of directions ripe for future investigation. One is continued work on the generation of high purity monolayers of hydrocarbon fragments. Many of the fragments proposed as surface intermediates in hydrocarbon catalysis (see Tables 1-3) still have yet to be generated, isolated, identified, and studied on single-crystal surfaces. Most of these fragments should now be attainable using the methodologies described in this review.

In addition to the opportunities for generating and identifying new surface fragments, there are important opportunities for structural characterization of species already isolated such as alkyls, methylene, vinyls, and allyls. With the recent focus on generating these fragments and on identifying elementary reaction steps of catalytic relevance, there has been a lack of emphasis on structural determination via techniques such as LEED and photoelectron diffraction. These surface crystallographies as well as scanning tunneling microscopy will play an important role in taking our understanding of these reactive intermediates and their surface chemistry to the next level.

With respect to surface reactivity, three areas appear particularly promising. One is the application of physical organic methodologies such as inductive effects and conformational constraints to gain insights into the factors that control the rates of elementary reaction steps. A second is in the investigation of coupling reactions between coadsorbed species. Most studies to date have focused simply on the decomposition of hydrocarbon fragments. Of more catalytic relevance would be studies of reactions between hydrocarbon fragments as well as reactions of hydrocarbon fragments with coadsorbed species such as H, O, OH, and NH<sub>2</sub>, and also catalyst promoters and poisons. A third area of surface reactivity which appears particularly promising is the study of fragments and their reactions on a wider range of materials: stepped surfaces, alloys, oxides, metal particles on oxides, etc. There have been many advances in the preparation and characterization of these materials, and combining these new, more catalytically relevant materials with the approaches described here for generating more catalytically relevant surface fragments would appear particularly fruitful.

Finally, there are opportunities for drawing connections between monolayer results and catalytic studies that have yet to be fully exploited. For example, methods of fragment synthesis developed for vacuum studies could also be applied at higher pressures under catalytic reaction conditions to investigate mechanisms. Also, characteristic spectroscopic signatures from monolayer studies might be

used to interpret high-pressure infrared results. And the kinetic parameters that are being measured for elementary steps in monolayer reactions could be compared with and applied to kinetic models previously developed for high-pressure processes such as H,D exchange in alkenes and alkanes over metal films. These types of connections are particularly important for bridging the gaps that remain between monolayer surface chemistry studies and high-pressure catalysis.

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