

# Carbon–Hydrogen Bond Activation and Cyclodehydrogenation Reactions of Cyclic C<sub>8</sub> Hydrocarbons on Pt(111)

William L. Manner,<sup>†</sup> Lawrence H. Dubois,<sup>\*,‡</sup> Gregory S. Girolami,<sup>\*,†</sup> and Ralph G. Nuzzo<sup>\*,†</sup>

School of Chemical Sciences and the Frederick Seitz Materials Research Laboratory,  
University of Illinois at Urbana–Champaign, Urbana, Illinois 61801,  
and Defense Advanced Research Projects Agency, Arlington, Virginia 22203

Received: September 18, 1997; In Final Form: January 13, 1998

The mechanisms of the thermolytic decomposition of a series of unsaturated cyclic C<sub>8</sub> hydrocarbons adsorbed on a platinum(111) single crystal surface are described. This study both confirms and extends the results reported by Frei and Campbell which corrected errors in an earlier report from our laboratory on the mechanisms of thermal decomposition seen in this adsorbate system. We find that the dehydrocyclization of cyclooctene, cyclooctadiene (1,3 and 1,5 isomers), and cyclooctatetraene on Pt(111) proceeds through a related set of intermediates and ultimately yields a novel surface-bound bicyclic ring system. As noted by Frei et al., our earlier finding that benzene is produced in high yield is incorrect. The spectroscopic evidence reported here demonstrates that all four of the cyclic C<sub>8</sub> hydrocarbons form a bicyclo[3.3.0]octenyl (or, as more commonly named, a pentalenyl) intermediate of stoichiometry C<sub>8</sub>H<sub>6</sub>. This bicyclic ring system forms via a dehydrocyclization of cyclooctatetraene, which itself is formed in varying yields from each of the less-unsaturated *c*-C<sub>8</sub> adsorbates. The formation of the pentalenyl species proceeds at low temperatures (<375 K). Data from reflection–absorption infrared (RAIRS) and temperature-programmed reaction spectroscopies show that the pentalenyl intermediate is remarkably stable, persisting on the surface up to at least 450 K. At temperatures above 450 K, this intermediate fragments, liberating hydrogen, and leaving a carbonaceous overlayer. The formation of cyclooctatetraene, and thus the pentalenyl intermediate, proceeds with the highest efficiency for the two dienes and lowest for cyclooctane and *cis*-cyclooctene. RAIRS data further serve to identify several intermediates formed along the reaction pathway leading to the platinum-bound C<sub>8</sub>H<sub>6</sub> species.

## Introduction

The catalytic reforming of cyclic hydrocarbon adsorbates on transition metal surfaces has received considerable attention in research due in no small measure to the importance of such reactions in the industrial processes used for fuel production.<sup>1,2</sup> It is now known that the product distributions from these reactions depend sensitively on many factors involving both the catalyst and structural characteristics of the adsorbate. Important examples of the latter structural sensitivities include both the degree of unsaturation present in the ring and its size. For example, on Pt(111), cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene decompose to give benzene in high yields, while cyclohexane mostly desorbs molecularly upon heating.<sup>3–8</sup> In addition, the amount of benzene which desorbs from the Pt(111) surface varies sensitively with its coverage.<sup>9,10</sup> In contrast, volatile hydrocarbon products are not formed in any significant degree when unsaturated cyclic C<sub>5</sub> and C<sub>7</sub> hydrocarbons react on a Pt(111) surface. Both cyclic systems ultimately fragment to leave a carbonaceous overlayer on the surface.<sup>8,11–13</sup> Interestingly, the unsaturated cyclic C<sub>5</sub> and C<sub>7</sub> hydrocarbons both form stable planar intermediates which have now been identified spectroscopically and shown to be cyclopentadienyl (C<sub>5</sub>H<sub>5</sub>) and

cycloheptatrienyl (C<sub>7</sub>H<sub>7</sub>) surface complexes, respectively. The reactivity pattern of the bicyclic adsorbate, norbornadiene, is interesting and distinctive because an appreciable amount of benzene is formed on Pt(111) via a selective C–C bond scission process.<sup>14–16</sup>

This report reexamines the results presented in our earlier study of the reaction pathways followed by a related class of adsorbates, the saturated, and variously unsaturated cyclic C<sub>8</sub> hydrocarbons (including cyclooctane (COA), *cis*-cyclooctene (COE), 1,3-cyclooctadiene (1,3-COD), 1,5-cyclooctadiene (1,5-COD), and cyclooctatetraene (COT)).<sup>17,18</sup> Our interest in the mechanisms of the thermal decomposition of these hydrocarbons on Pt(111) stems partly from the importance of these molecules (especially 1,5-COD) as ligands in platinum CVD precursors and intermediates in their thermolysis.<sup>19,20</sup> In leading work, Muetterties and co-workers established that the various COD isomers and COE were converted, at least partially, to COT on Pt(111).<sup>15,16</sup> This product was detected by its displacement with P(CH<sub>3</sub>)<sub>3</sub> and was suggested to be a common intermediate in the decomposition of all the unsaturated C<sub>8</sub> cyclic hydrocarbons.<sup>21</sup>

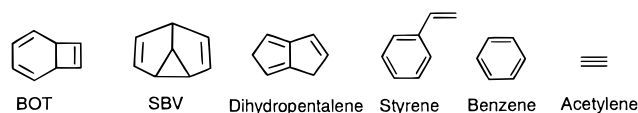
The non-surface-mediated reaction chemistry of COT is diverse, and its photochemical and thermolytic reactions give rise to a variety of different products. Among these are the isomeric molecules bicyclo[4.2.0]octa-2,4,7-triene (BOT), tricyclo[3.3.0.0]octa-3,6-diene (semibulvalene, SBV), 1,5-dihydropen-

<sup>†</sup> School of Chemical Sciences.

<sup>‡</sup> DARPA.

\* To whom correspondence should be addressed.

talene, styrene, and (the retrocyclization products) benzene and acetylene.<sup>22–26</sup>



In comparison, the reactivity of COT on transition metal surfaces (e.g., Pt(111)) is less well understood. An earlier report from our group presented data which suggested that cyclic  $C_8$  hydrocarbons dehydrogenate to COT on Pt(111).<sup>27</sup> It was proposed that this COT transformed further via ring contraction to form BOT, which in turn underwent a retro[2+2]cyclization to form benzene (which partially desorbed) and surface-bound acetylene.<sup>17,18</sup> A recent study performed on COE by Frei and Campbell demonstrated conclusively that COT is not converted to benzene on Pt(111) to any significant extent (<2% yield).<sup>28</sup> Their results revealed that the decomposition of COT (proposed to be a transient intermediate in the thermolysis of COE) proceeds to give a surface-bound intermediate with a stoichiometry of  $C_8H_6$ ; this species is reasonably stable in that it persists to temperatures as high as 560 K. These results (which emphasized reactions of COE) led us to carry out a series of detailed studies on an expanded series of cyclic- $C_8$  hydrocarbon adsorbates using a combination of reflection–absorption infrared (RAIRS), Auger electron (AES), high-resolution electron energy loss (HREELS), and temperature-programmed reaction (TPRS) spectroscopies. These results have allowed us to construct a corrected mechanistic scheme for the decomposition of these hydrocarbons on Pt(111). This report describes the mechanisms, energetics, and yields of the reactions which convert COE, 1,3-COD, and 1,5-COD to COT. With the new spectroscopies which are applied in the current work, we have been able to determine structures of several of the intermediates involved in the dehydrogenation of the cyclic  $C_8$  hydrocarbons on Pt(111) and to correct several adsorbate structural and organizational assignments made in previous studies (principally, on the basis of HREELS data).<sup>17,18</sup> We show that COT binds to Pt(111) at low temperatures as a (formal) planar  $\eta^8$  species (previous reports suggested a lower symmetry tublike structure for this molecule). At higher temperatures (325–375 K) the bound COT undergoes a dehydrocyclization reaction that affords the pentalenyl ( $C_8H_6$ ) ring system. This same intermediate is formed in the thermal decomposition of COE, 1,3-COD and 1,5-COD, and bicyclo[3.3.0]2-octene (tetrahydropentalene), albeit in varying yields. Above 500 K, the Pt-bound pentalenyl species decomposes to give hydrogen (which desorbs as  $H_2$ ) and a surface carbide layer. We confirm the results of Frei and Campbell: benzene is a desorbing species, but the yield of this product is extremely low.

## Experimental Section

Studies were carried out in a single ultra-high-vacuum chamber with a base pressure of less than  $4 \times 10^{-10}$  torr. The Pt(111) crystal was purchased from Cornell Laboratories and oriented to within  $0.5^\circ$  and polished to a fine mirror finish by standard metallographic techniques. The Pt(111) crystal was cleaned by heating at 950 K in the presence of  $1 \times 10^{-6}$  torr of  $O_2$  for three minutes followed by annealing in vacuum at 1000 K for 2 min. If this protocol did not clean the surface sufficiently, the crystal was sputtered with  $Ar^+$  ions (1 kV) at 950 K for approximately 15 min and subsequently annealed at 1050 K. Surface cleanliness was established by Auger electron

spectroscopy (detectable carbon  $\approx 0.5$  atomic %). Cooling was accomplished by connecting the crystal to a liquid nitrogen reservoir via a copper braid. Crystal heating was performed by mounting the crystal on a Varian-style button heater purchased from Spectra Mat. The crystal temperature was controlled over the temperature range of 95–1050 K ( $\pm 2$  K) using a Eurotherm 818P temperature programmer and a type K thermocouple spotwelded directly to the crystal.

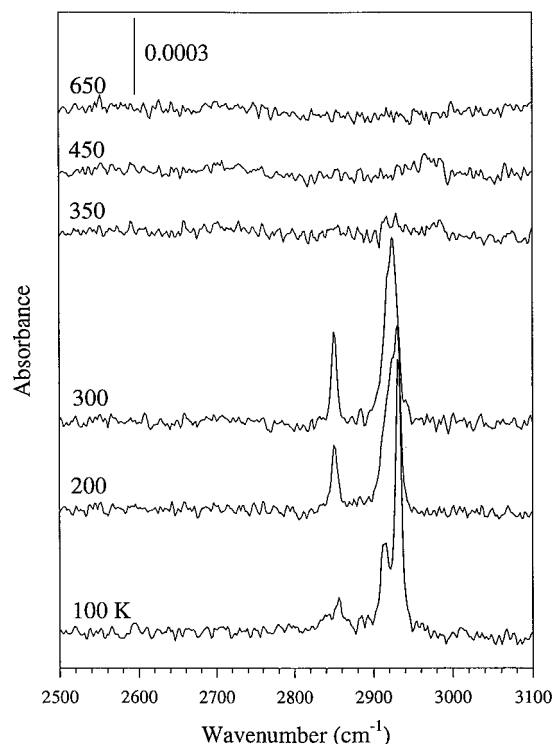
RAIR spectra were collected using a Digilab FTS 60A spectrometer equipped with a broad-band, liquid-nitrogen-cooled MCT detector. Reflection optics ( $\sim f/12$ ) were optimized at a near-grazing angle of incidence with respect to the crystal surface ( $\sim 84^\circ$ ).<sup>29</sup> The RAIR spectra, each of which represents 1024 scans taken at  $4\text{ cm}^{-1}$  resolution requiring a total collection time of approximately 6 min, are presented as absorbance plots ( $-\log R/R_0$ ).

TPRS were collected at a constant heating rate of 2 K/s. The spectra were recorded with a Vacuum Generators SXP 300 quadrupole mass spectrometer that was differentially pumped by a 45 L/s ion pump. The acceptance cone of the differentially pumped mass spectrometer was established using a 1 mm nickel enclosing aperture (Beam Dynamics, Minneapolis, MN); this skimmer assembly also served to shield the ionizer region of the mass spectrometer.

Cyclooctane, *cis*-cyclooctene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene were purchased from Aldrich. Bicyclo[3.3.0]2-octene was purchased from Wiley Organics. All samples were greater than 99% pure except for *cis*-cyclooctene which contained a  $\sim 5\%$  cyclooctane impurity. The samples were degassed thoroughly before being introduced into the chamber by a freeze–pump–thaw technique. Dosing was accomplished by backfilling the chamber through a Varian-style leak valve. Coverages are given relative to a saturation coverage of the adsorbate ( $\theta_{\text{sat}}$ ).

## Results

In this report, we describe the structures of a variety of hydrocarbon adsorbates (and the intermediates formed in the course of their decomposition) bound to Pt(111). These conclusions follow mainly from an analysis of the combined results of reflection–absorption infrared (RAIRS) and temperature-programmed reaction (TPRS) spectroscopies. Our earlier report described some aspects of the vibrational spectra of cyclic  $C_8$  hydrocarbons on Pt(111) obtained by high-resolution electron energy loss spectroscopy (HREELS).<sup>17,18</sup> In several important respects, however, reflection–absorption infrared (RAIR) spectroscopy is a complimentary technique that can provide additional information about adsorbate structure not available from HREELS.<sup>30–36</sup> First, RAIRS is a high-resolution technique: surface spectra are routinely obtained with resolutions of  $2\text{--}4\text{ cm}^{-1}$  vs  $\sim 50\text{ cm}^{-1}$  for a typical HREEL spectrometer.<sup>34,36</sup> The high resolution of RAIRS facilitates the interpretation of complex spectra which contain two or more vibrational modes in close proximity. Second, subtle changes in the vibrational spectra due either to chemical reactions or changes in the substrate binding can often be more readily deduced from RAIRS data. Third, for adsorbates on metallic surfaces, RAIRS is subject to a rigorous surface–dipole selection rule: a dynamic dipole moment with no component along the surface normal direction will have zero intensity.<sup>30,31,33,35</sup> The selection rules for HREELS are somewhat more complex since impact scattering frequently allows the observation of vibrational modes with no normal component; this scattering mechanism has a significant cross-section for the stretching motions of the C–H



**Figure 1.** Reflection-absorption infrared spectra for a submonolayer coverage ( $\theta_i \approx 0.8 \theta_{\text{sat}}$ ) of *cis*-cyclooctene adsorbed on Pt(111) after annealing at the following temperatures: 100, 200, 300, 350, 450, and 650 K.

bonds in most hydrocarbon adsorbates.<sup>34,36</sup> As a result, it is more difficult to deduce the orientations adopted by adsorbates from the HREEL spectra alone.

#### RAIR Spectra of C<sub>8</sub> Cyclic Hydrocarbons Adsorbed on Pt(111)

Unless otherwise noted, the RAIR spectra of submonolayer coverages of the specified C<sub>8</sub> cyclic hydrocarbon are shown. Exposures were made at 100 K; the substrate was flash annealed to the specified temperature and then cooled to 100 K before the spectrum was acquired. We present and discuss data obtained for each hydrocarbon adsorbate in turn.

***cis*-Cyclooctene (COE) on Pt(111).** Temperature-dependent RAIR spectra for submonolayer coverages ( $\theta_i \approx 0.8 \theta_{\text{sat}}$ ) of COE on Pt(111) are shown in Figure 1; mode assignments are presented in Table 1. The high-frequency region of the spectrum (2500–3100 cm<sup>-1</sup>) measured at 100 K shows three pronounced bands centered at 2857, 2914, and 2932 cm<sup>-1</sup>. We assign the band at 2857 cm<sup>-1</sup> to the symmetric stretching mode(s) of the methylene groups of molecularly bound COE. The bands at 2914 and 2932 cm<sup>-1</sup> are assigned to the antisymmetric stretches of the methylene groups. Although the olefinic C–H stretches of Pt-bound alkenes also occur in this frequency region, these bands should be weak because the olefinic C–H bonds should be nearly parallel with the surface.<sup>3,4,8,11,37</sup> We note that the methylene C–H stretching bands can be perturbed by C–H...M interactions<sup>38–41</sup> and by hyperconjugation effects,<sup>37,42–44</sup> both of which may be operative here.

The RAIR spectrum of COE changes considerably when the sample is heated to 200 K: the peak at 2857 cm<sup>-1</sup> (symmetric methylene stretch) sharpens and shifts to 2851 cm<sup>-1</sup>, and the two peaks at 2914 and 2932 cm<sup>-1</sup> collapse and form one broad band at 2931 cm<sup>-1</sup>. A further sharpening of these features occurs upon annealing the sample at 300 K. The spectrum at

this temperature is dominated by bands assignable to the  $\nu_{\text{sym}}$  (C–H) and  $\nu_{\text{anti}}$  (C–H) modes of methylene groups on adsorbate molecules which have undergone C–H bond activation. This result is supported by the TPD studies of Frei and Campbell and the data presented below, both of which suggest that C–H bond activation near 300 K proceeds to give a new intermediate of stoichiometry C<sub>8</sub>H<sub>12</sub>.

When the COE-dosed surface is heated to 350 K, the RAIR spectrum in the C–H region is essentially featureless; only weak absorption bands can be discerned between 2900 and 3000 cm<sup>-1</sup>. Upon annealing at 650 K, even these weak features are lost (there are also no bands evident in the low-frequency region at this temperature). Such changes mark a reaction pathway which proceeds via sequential C–H and C–C bond activation processes and which ultimately leads to the fragmentation of the alkene adsorbate.

**1,3-Cyclooctadiene (1,3-COD) on Pt(111).** The temperature-dependent RAIR spectra of 1,3-COD on Pt(111) are in many ways very similar to those obtained for COE (Figure 2; see Table 2 for mode assignments). The 100 K spectrum contains two broad bands at 2854 and 2930 cm<sup>-1</sup> which are assigned to the symmetric and antisymmetric stretching modes of the methylene groups, respectively. No vinylic stretches are discernible at this temperature, which suggests that all four vinylic C–H bonds lie essentially parallel to the surface. Such a structure would imply that the two C=C bonds are coplanar and conjugated. This latter finding is interesting in that the free molecule adopts a geometry in which the double bonds are not coplanar, but instead describe a dihedral as large as 57°.<sup>45,46</sup> The binding energy of 1,3-COD on the Pt(111) surface, therefore, must be larger than the strain that results from making the two C=C bonds coplanar.<sup>47</sup>

Annealing the sample at 200 or 300 K causes the bands in the RAIR spectrum of 1,3-COD to sharpen slightly and shift in frequency by a few wavenumbers. Again, the dominant bands at these temperatures appear to be  $\nu_{\text{sym}}$  (C–H) and  $\nu_{\text{anti}}$  (C–H) modes of methylene groups. The TPRS data presented below demonstrate that, at 300 K, some C–H bond activation has occurred. This bond cleavage process is correlated with the appearance of a broad, weak band in the RAIR spectrum near ~2880 cm<sup>-1</sup>.

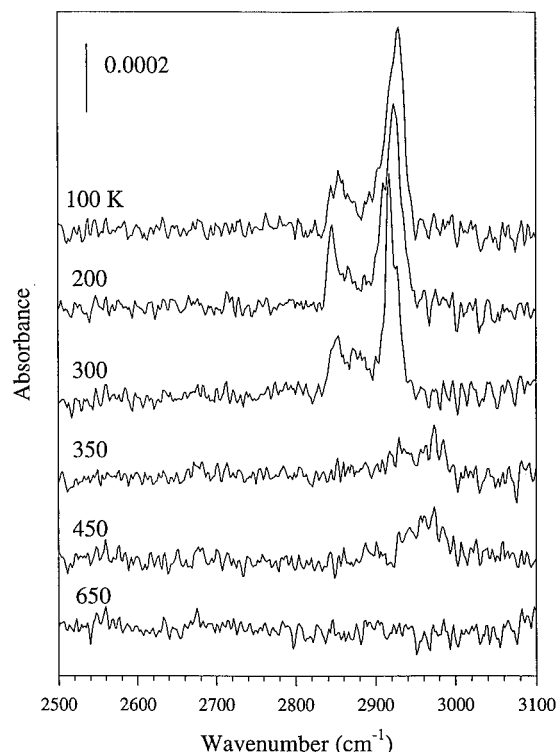
The RAIR spectrum of the 1,3-COD-dosed surface becomes essentially featureless after the sample is heated to 350 K; as before, weak features appear in the C–H stretching region between 2900 and 3000 cm<sup>-1</sup>. These latter bands increase in intensity after annealing to 450 K but then disappear upon heating to 650 K. These data suggest an intermediate containing a C–C and C–H framework, one stable to at least 450 K, is formed from the starting 1,3-COD.

**1,5-Cyclooctadiene (1,5-COD) on Pt(111).** A sub-monolayer of 1,5-COD adsorbed on Pt(111) at 100 K produces a relatively complex spectrum that features at least five bands in the C–H stretching frequency region (2804, 2845, 2872, 2900, and 3020 cm<sup>-1</sup>; see Figure 3, Table 3). The unperturbed vinylic stretch at 3020 cm<sup>-1</sup> present in the 100 K spectrum is significantly attenuated at 200 K. This result suggests that nonequilibrium 1,5-COD adsorption states are populated at low temperatures. The existence of this non-equilibrium population can be rationalized by considering the conformation of an unbound cyclooctadiene molecule. In the liquid and gas phases, 1,5-COD adopts a “tub” conformation possessing C<sub>2v</sub> symmetry,<sup>46,48,49</sup> a conformation that is conserved when 1,5-COD coordinates to a single transition metal center in a complex.<sup>49</sup> This geometry would create strong repulsions between the

**TABLE 1: Frequencies and Assignments for RAIR Spectra of *cis*-Cyclooctene on Pt(111) after Being Annealed at the Indicated Temperatures<sup>a</sup>**

assignment	100 K	200 K	300 K	350 K	450 K	650 K	neat IR spectrum <sup>b</sup>
CH $\nu(\text{C-H})^c$				~2920, 2982	~2969		
CH <sub>2</sub> $\nu_{\text{anti}}(\text{C-H})^d$	2914, 2932	2931	2926				2927 (broad)
CH <sub>2</sub> $\nu_{\text{sym}}(\text{C-H})^d$	2857	2851	2851				2851
C-H out-of-plane bend <sup>c</sup>				876	876		

<sup>a</sup> Frequencies in wavenumbers. <sup>b</sup> Assignments taken from the neat IR spectrum of *cis*-cyclooctene. <sup>c</sup> From the pentalenyl intermediate. <sup>d</sup> From adsorbed cyclooctene.



**Figure 2.** Reflection-absorption infrared spectra for a submonolayer coverage ( $\theta_i \cong 0.8 \theta_{\text{sat}}$ ) of 1,3-cyclooctadiene adsorbed on Pt(111) after annealing at the following temperatures: 100, 200, 300, 350, 450, and 650 K.

surface and the vinylic hydrogens and thus cannot constitute a suitable model for the binding of the nonconjugated C=C bonds to the (111) lattice plane.

Most of the multiple bands appearing between 2800 and 2900  $\text{cm}^{-1}$  likely reflect the effects of the chemically different environments on the vibrational modes of the methylene groups in the adsorbed 1,5-COD molecules. Tentative assignments for the 100 K spectrum are given in Table 3 and include both symmetric (the three bands at 2804, 2845, and 2872  $\text{cm}^{-1}$ ) and antisymmetric ( $\sim 2900 \text{ cm}^{-1}$ ) stretching combinations of the methylene groups. Annealing the sample at 200 K sharpens all the bands considerably relative to the line widths seen in the 100 K spectrum. At this temperature, the bands due to the C-H stretching modes of unbound vinylic groups also disappear.

Heating the sample to  $\sim 300 \text{ K}$  changes the spectra markedly. The modes from the molecularly bound 1,5-COD molecules decrease in intensity and new bands appear at 2782 and 2918  $\text{cm}^{-1}$ ; these latter bands signal the formation of a new intermediate that is generated by a C-H bond activation process. These new bands are not the possible dehydrogenation product, 1,3,5-cyclooctatriene, because the RAIR spectrum differs significantly from that obtained when the triene is directly adsorbed on the surface (data shown in the supplementary material). Thus,

the data suggest that the thermolysis (at 300 K) of 1,5-COD involves cleavage of only a single allylic C-H bond. As will be discussed in the TPRS section, however, this interpretation is overly simplistic.

When the sample is heated to 350 K, the vibrational modes for both 1,5-COD and the intermediate species formed at  $\sim 300 \text{ K}$  disappear. The spectra at 350 K show a broad, weak feature, similar to that described previously for 1,3-COD, centered between 2900 and 3000  $\text{cm}^{-1}$ . This intermediate is stable up to at least  $\sim 450 \text{ K}$ . Taken together, the data suggest that 1,5-COD is converted above 300 K to a planar  $\text{C}_8$  species via a series of sequential C-H bond activation steps. The logical inference, that COD is dehydrogenated to give COT, can be discounted on the basis of results reported by Frei and Campbell, which show that COT itself decomposes on Pt(111) at about 300 K. The data presented below suggest that if COT is formed, it is in turn transformed on Pt(111) into a new species near 300 K.

**1,3,5,7-Cyclooctatetraene (COT) on Pt(111).** Calculations suggest that COT assumes a boat conformation of  $D_{2d}$  symmetry in the gas phase (the four C=C bonds do not all reside in the same plane).<sup>50,51</sup> The 100 K RAIR spectrum of a submonolayer coverage of COT on Pt(111), however, clearly illustrates that the surface-bound adsorbate must be planar and must lie with its plane parallel with the surface (Figure 4; corresponding mode assignments are given in Table 4). At 100 K, only a weak band is seen in the C-H stretching region at 3009  $\text{cm}^{-1}$ , a region associated with vinylic groups. HREELS data previously reported suggested that COT is bound to Pt(111) at low temperatures in a "tub"-shaped geometry.<sup>17,18</sup> It is now clear that intensity due to impact scattering led to an incorrect model of the geometry and organization of the low-temperature bound state of COT. The 100 K RAIR spectrum shown here can only be rationalized by an essentially planar arrangement of the  $\text{C}_8$  framework.

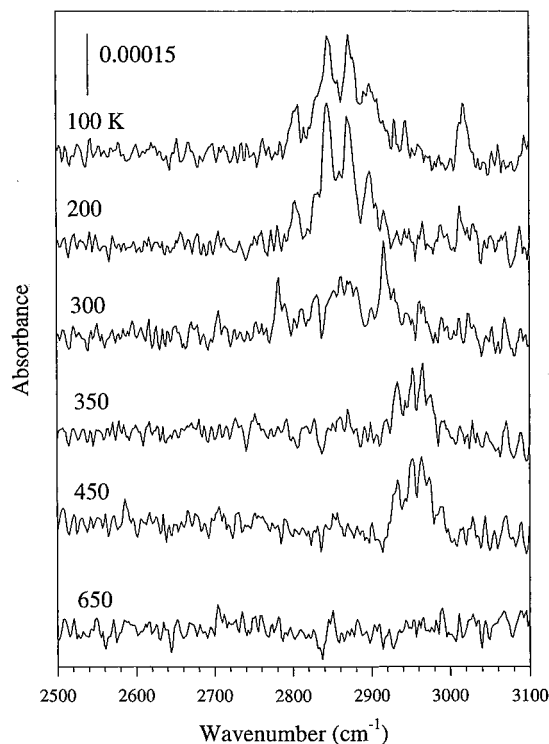
Confirming the results of Frei and Campbell, the RAIR spectra suggest that the thermolysis of COT commences at about 300 K. The RAIR spectra obtained above this temperature show the now familiar broad band centered at 2960  $\text{cm}^{-1}$ , one apparently due to a common thermolysis product of all the cyclic  $\text{C}_8$  molecules. As before, the decomposition of this intermediate ensues above 450 K, and by 650 K all modes in the C-H stretching region disappear.

**Bicyclo[3.3.0]2-octene.** In order to establish the identity of the reaction intermediate formed by the cyclic  $\text{C}_8$  adsorbates on Pt(111), we examined the thermolysis of a related  $\text{C}_8$  molecule, bicyclo[3.3.0]2-octene (BCE). At 100 K, the RAIR spectrum for a submonolayer of BCE shows three bands with significant intensity at 2868, 2924, and 2955  $\text{cm}^{-1}$  (Figure 5; mode assignments are given in Table 5). The bands at 2868  $\text{cm}^{-1}$  and 2955  $\text{cm}^{-1}$  are likely due to the symmetric and antisymmetric stretching modes of the methylene groups of BCE. The data suggest that BCE is bound with its C=C bond parallel to the surface. The weak band at 2924  $\text{cm}^{-1}$  is believed to be due to the C-H oscillators of the di- $\sigma$  bound olefin.<sup>11,52,53</sup>

**TABLE 2: Frequencies and Mode Assignments for RAIR Spectra of 1,3-Cyclooctadiene on Pt(111) after Being Annealed at the Indicated Temperatures<sup>a</sup>**

assignment	100 K	200 K	300 K	350 K	450 K	650 K	neat IR spectrum <sup>b</sup>
CH $\nu(\text{C-H})^c$				~2934, 2976	~2969		
CH <sub>2</sub> $\nu_{\text{anti}}(\text{C-H})^d$	2930	2924	2918				2926 (broad)
CH <sub>2</sub> $\nu(\text{C-H})^e$			~2880				
CH <sub>2</sub> $\nu_{\text{sym}}(\text{C-H})^d$	2854	2846	2846				2853
C-H out-of-plane bend <sup>c</sup>				881	887		

<sup>a</sup> Frequencies in wavenumbers. <sup>b</sup> Assignments taken from the neat IR spectrum of 1,3-cyclooctadiene. <sup>c</sup> From the pentalenyl intermediate. <sup>d</sup> From adsorbed 1,3-cyclooctadiene. <sup>e</sup> At least a partial contribution from an adsorbate resulting from the dehydrogenation of 1,3-cyclooctadiene.



**Figure 3.** Reflection-absorption infrared spectra for a submonolayer coverage ( $\theta_i \approx 0.8 \theta_{\text{sat}}$ ) of 1,5-cyclooctadiene adsorbed on Pt(111) after annealing at the following temperatures: 100, 200, 300, 350, 450, and 650 K.

The activation of the C-H bonds in BCE appears to occur at temperatures as low as 200 K. Perhaps the most intriguing feature seen in the latter data is the appearance of a new mode at  $\sim 2780 \text{ cm}^{-1}$ . The RAIR spectrum of cyclopentadiene adsorbed on Pt(111) also shows bands in this frequency region (at 2782 and 2831  $\text{cm}^{-1}$ ).<sup>8</sup> The data, therefore, suggest that the initial stages of the thermolysis are weakly activated and yield, via C-H bond activations, a more heavily dehydrogenated form of the [3.3.0]-C<sub>8</sub> ring system. It is interesting to note in this context that cyclopentene undergoes dehydrogenation to form Pt-bound cyclopentadiene at temperatures between 200 and 250 K.<sup>11</sup>

When the surface is heated to 300 K, the vibrational modes of BCE and its initial dehydrogenation product(s) are lost and are replaced by weak bands at  $\sim 2885$  and  $2960 \text{ cm}^{-1}$ ; only the latter broad feature remains after a 450 K anneal. As judged by RAIRS, all C-H containing species have decomposed after the sample is heated to 650 K.

**The Nature of the Planar C<sub>8</sub> Intermediate as Deduced from RAIRS.** The data presented above suggest that a variety of cyclic C<sub>8</sub> hydrocarbons decompose on Pt(111) to give a planar, surface-bound intermediate which is stable to  $\sim 450 \text{ K}$  or higher (although the yields of this intermediate depend on the precursor chosen). The structural characterization of this

intermediate is made somewhat difficult by the weak intensities of its infrared bands.

In order to improve the signal-to-noise ratio ( $S/N$ ) of the RAIRS data, we carried out the exposures of the Pt crystal to the series of unsaturated cyclic hydrocarbons at 450 K instead of 100 K. The RAIR spectra so obtained are presented in both the low- and high-frequency region in Figure 6. As is evident, dosing at a higher temperature affords spectra with substantially improved  $S/N$  values and band resolution. The RAIR spectra obtained for the five unsaturated cyclic C<sub>8</sub> hydrocarbons are indistinguishable within the noise and show only two sets of bands: a low-frequency mode at  $\sim 873 \text{ cm}^{-1}$  and two bands (where resolved) in the C-H stretching region at  $\sim 2932$  and  $2953 \text{ cm}^{-1}$ . We assign the band at  $873 \text{ cm}^{-1}$  to out-of-plane C-H bends of the planar intermediate. The low-intensity bands near  $2940 \text{ cm}^{-1}$  are assigned to the C-H stretching modes of this same intermediate (these modes are only visible due to the fact that the Pt interaction leads to some rehybridization of these centers). The close similarity seen between the 1,3-COD, 1,5-COD, and COT data and the spectrum taken of an intermediate derived from the bicyclic BCE ring system strongly suggests that the surface-bound product contains the fused C<sub>5</sub> ring architecture of a pentalenyl (C<sub>8</sub>H<sub>6</sub>) adduct.

### Temperature-Programmed Reaction Spectroscopy

The temperature-programmed reaction spectra shown below follow and extend those reported by Frei and Campbell. Their quantitative analysis serves to identify the stoichiometry of the species present on the Pt(111) surface at temperatures between 350 and 450 K. The following TPR spectra were collected after dosing the specified cyclic C<sub>8</sub> hydrocarbon at a temperature below 110 K, and in order to observe multilayer and monolayer desorption features, the exposures used corresponded to no more than twice that required for saturation ( $\theta_i \lesssim 2.0 \theta_{\text{sat}}$ ).

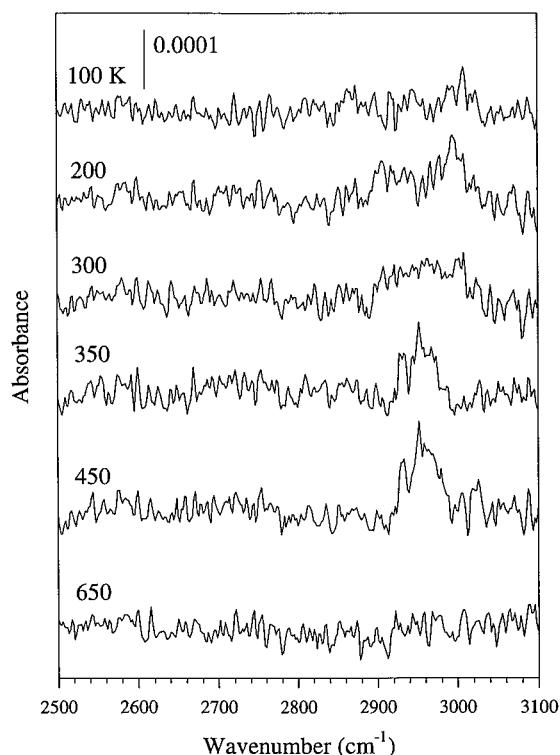
**Molecular Desorption from the Pt(111) Surface.** Figure 7 presents TPR spectra monitoring molecular desorption for the various hydrocarbons adsorbates (the  $m/e$  values are 110, 108, 108, 104, and 108 for COE, 1,3-COD, 1,5-COD, COT, and bicyclo[3.3.0]2-octene, respectively). The low-temperature desorption features seen below 210 K are characteristic of multilayer desorption. The only adsorbates that show measurable intensities for desorption from a more tightly bound "monolayer" are COE and bicyclo[3.3.0]2-octene. The quantity desorbing from the monolayer, however, is fairly small for each. The behaviors seen here are similar to the findings of numerous studies of cycloalkenes adsorbed on transition metal surfaces.<sup>3,7,10-14,16,18,54,55</sup>

**Dihydrogen Desorption.** The TPR data for the dihydrogen desorption obtained after dosing the specified cyclic C<sub>8</sub> hydrocarbon show many similarities: regions of significant intensity are found above and below 490 K (Figure 8). These results define a temperature range over which the planar intermediate is stable. Above 490 K, all the dihydrogen TPR spectra show a large maximum between 568 and 578 K with a broad shoulder

**TABLE 3: Frequencies and Mode Assignments for RAIR Spectra of 1,5-Cyclooctadiene on Pt(111) after Being Annealed at the Indicated Temperatures<sup>a</sup>**

assignment	100 K	200 K	300 K	350 K	450 K	650 K	neat IR spectrum <sup>b</sup>
CH $\nu(\text{C-H})$ (vinyl) <sup>c</sup>	3020						2995, 3012, 3070
CH $\nu(\text{C-H})$ <sup>d</sup>				~2955 (multiple bands)	~2955 (multiple bands)		
CH <sub>2</sub> $\nu(\text{C-H})$ <sup>e</sup>			2918				
CH <sub>2</sub> $\nu_{\text{anti}}(\text{C-H})$ <sup>c</sup>	2900	2900					2923, 2938, 2956
CH <sub>2</sub> $\nu_{\text{sym}}(\text{C-H})$ <sup>c</sup>	2804, 2845, 2872	2804, 2845, 2870	2862				2832, 2888
CH <sub>2</sub> $\nu(\text{C-H})$ <sup>e</sup>			2782				
C-H out-of-plane bend <sup>d</sup>				878	878		

<sup>a</sup> Frequencies in wavenumbers. <sup>b</sup> Assignments taken from the neat IR spectrum of 1,5-cyclooctadiene. <sup>c</sup> From adsorbed 1,5-cyclooctadiene. <sup>d</sup> From the pentalenyl intermediate. <sup>e</sup> An adsorbate resulting from the dehydrogenation of 1,5-cyclooctadiene (involving the loss of two hydrogens).



**Figure 4.** Reflection-absorption infrared spectra for a submonolayer coverage ( $\theta_i \approx 0.8 \theta_{\text{sat}}$ ) of 1,3,5,7-cyclooctatetraene adsorbed on Pt(111) after annealing at the following temperatures: 100, 200, 300, 350, 450, and 650 K.

extending to  $\sim 800$  K. The hydrogen desorption spectra below 500 K are different for each of the C<sub>8</sub> cyclic hydrocarbons and are discussed separately.

For COE, two dihydrogen desorption peaks are seen at 278 and 396 K. The lower temperature feature at 278 K is likely due to rate-limiting recombinative desorption of hydrogen on Pt(111).<sup>56</sup> This indicates that COE undergoes C-H bond activation on the Pt(111) surface below this temperature, a result consistent with earlier reports<sup>28</sup> and the spectroscopic observations presented above. The large feature centered at 396 K likely originates from reaction-limited H<sub>2</sub> desorption.

The dihydrogen desorption regions below 500 K for 1,3-COD and 1,5-COD are very similar, showing maxima consistent with reaction- and recombination-limited dihydrogen desorption processes. The latter appears as a poorly resolved shoulder ( $\sim 280$  K) while the reaction-limited dihydrogen desorption features exhibit maxima at 371 and 374 K for 1,3-COD and 1,5-COD, respectively.

The data shown in Figure 8 also reveal that a significant amount of dihydrogen desorption occurs below 490 K when COT is dosed on the Pt(111) surface. This result conflicts with

the findings reported in our previous study (which we now believe contained significant errors).<sup>17,18</sup> It appears that COT loses some fraction of its hydrogens below 337 K (as was also reported by Frei and Campbell).<sup>28</sup> Above 337 K, no significant dihydrogen desorption ensues until temperatures near 574 K are reached.

BCE exhibits two significant low-temperature dihydrogen desorption features at 297 and 342 K. These data support the interpretations deduced from the RAIR spectra, which suggested that BCE undergoes C-H bond activation at low temperatures and is converted to a stable intermediate at temperatures near 350 K.

**Temperature-Dependent Stoichiometries of the Surface-Bound Species as Deduced from TPRS.** The TPR data monitoring the desorption of dihydrogen ( $m/e = 2$ ), when interpreted using the protocol of Frei and Campbell,<sup>28</sup> allow us to estimate the stoichiometries of the surface-bound species formed upon dehydrogenation of most of the cyclic C<sub>8</sub> hydrocarbons. By integrating each TPD feature and comparing the integral with the integral for the entire spectrum, we can calculate the fraction of the total available hydrogen that is lost at each temperature. These fractions can be used to deduce stoichiometries for the thermolysis products provided that no hydrogen is lost in other ways (for example, as desorbing hydrocarbons). Control experiments show that this is a valid approximation for most of these adsorbates. It is also helpful if the TPD features are well resolved, a criterion that the thermal behaviors of most of the cyclic C<sub>8</sub> hydrocarbons meets.

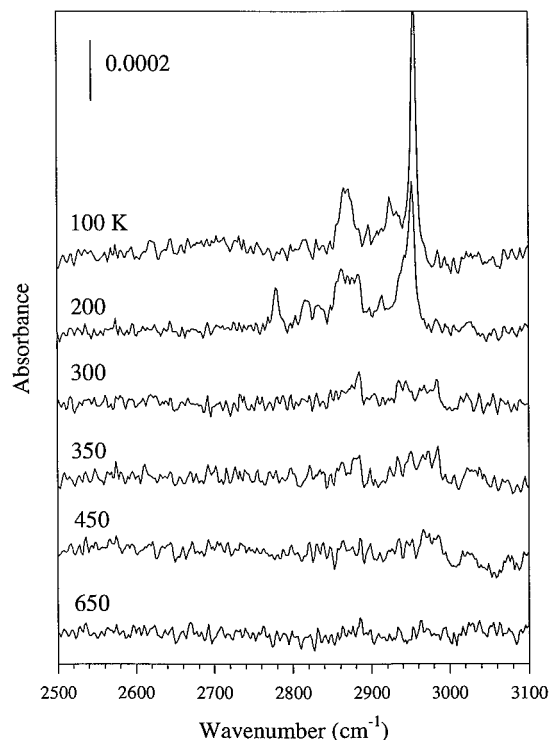
Of utmost interest is the stoichiometry of the common intermediate which RAIR spectroscopy suggests is present on the Pt(111) surface at 450 K. Integration of the region below 490 K shows that approximately  $60 \pm 2\%$ ,  $53 \pm 2\%$ ,  $54 \pm 2\%$ ,  $30 \pm 2\%$ , and  $54 \pm 2\%$  of the hydrogen atoms are lost below this temperature for COE, 1,3-COD, 1,5-COD, COT, and bicyclo[3.3.0]2-octene, respectively. This corresponds to an approximate C/H stoichiometry of C<sub>8</sub>H<sub>6</sub> for each of the C<sub>8</sub> cyclic hydrocarbons, assuming the ring is still intact. A TPD study performed by Frei and Campbell showed very similar results for COE on a Pt(111) surface, although the interpretations of the former are complicated somewhat by the molecular desorption which also occurs.<sup>28</sup> The structure of this intermediate is described in the Discussion section.

The TPR data for dihydrogen desorption also allows us to determine the stoichiometries of some of the intermediates formed on the surface via C-H bond activation at lower temperatures (100–350 K). For COE there is a low-temperature feature having a maximum ( $T_{\text{max}}$ ) at  $\sim 278$  K. Integration shows that approximately  $14 \pm 1\%$  of the 14 hydrogen atoms are lost below this temperature, which indicates that the initial thermolysis product has the approximate stoichiometry C<sub>8</sub>H<sub>12</sub>. Even though this intermediate has the correct stoichiometry for

**TABLE 4: Frequencies and Mode Assignments for RAIR Spectra of 1,3,5,7-Cyclooctatetraene on Pt(111) after Being Annealed at the Indicated Temperatures<sup>a</sup>**

assignment	100 K	200 K	300 K	350 K	450 K	650 K	neat IR spectrum <sup>b</sup>
CH $\nu$ (C–H) (vinyl) <sup>c</sup>	3009 (weak)	2995	2960 (broad)				2995, 3012, 3070
CH $\nu$ (C–H) <sup>d</sup>				2932, 2959	2932, 2959		
C–H out-of-plane bend <sup>d</sup>				881	878		

<sup>a</sup> Frequencies in wavenumbers. <sup>b</sup> Assignments taken from the neat IR spectrum of cyclooctatetraene. <sup>c</sup> From adsorbed cyclooctatetraene. <sup>d</sup> From the pentalenyl intermediate.



**Figure 5.** Reflection-absorption infrared spectra for a submonolayer coverage ( $\theta \approx 0.8 \theta_{\text{sat}}$ ) of bicyclo[3.3.0]2-octene adsorbed on Pt(111) after annealing at the following temperatures: 100, 200, 300, 350, 450, and 650 K.

cyclooctadiene, recent studies indicate that this is probably not the correct structure of the intermediate.<sup>28</sup> Frei and Campbell conclude that this intermediate is a cyclooctenediyl species generated via hydrogen abstractions from the  $\alpha$  and  $\gamma$  carbons of the COE ring. Recent studies performed in this laboratory revealed that cycloheptene decomposes on Pt(111) by a similar mechanism.<sup>37</sup>

1,5-Cyclooctadiene exhibits a low-temperature H<sub>2</sub> desorption feature with a maximum at 288 K which is unresolved from the larger feature at 374 K. It is difficult to deconvolute these two features owing to the asymmetry of the line shapes. We estimate by inspection, however, that the intensity of the low-temperature desorption feature is approximately one-half that of the larger one at 374 K. Since the two features together correspond to the loss of approximately six hydrogens (see above), the 1:2 ratio suggests that two hydrogens are lost from 1,5-COD at lower temperatures to give the new product observed in the RAIRS data (Figure 3). The RAIR spectra show, however, that this thermolysis product is not 1,3,5-cyclooctatriene. The data suggest, therefore, that the two hydrogens cannot be cleaved from adjacent carbons in the starting diene.<sup>57</sup> Instead, 1,5-COD must decompose to a cyclooctadienediyl (i.e., diallylic) species. Applying a similar line of analysis to the dihydrogen desorption trace for BCE, we estimate that the lower temperature feature (at 297 K) is approximately twice the intensity of the peak seen at

342 K. The lower temperature desorption peak, therefore, corresponds to the loss of approximately four hydrogens. This suggests, given the topology of this ring system, that the intermediate formed from BCE at 300 K is a bicyclo[3.3.0]-octatriene isomer. The most common isomeric structure reported is bicyclo[3.3.0]1,4,6-octatriene, a molecule more commonly referred to as 1,5-dihydropentalene. This assignment is consistent with the uncharacteristically low frequency of the C–H stretching bands observed in the RAIR spectrum taken at 300 K.

## Discussion

Taken together, the RAIRS and TPRS data presented above allow us to derive a detailed mechanistic scheme for the transformation of unsaturated cyclic C<sub>8</sub> hydrocarbons on Pt(111) (Scheme 1). To facilitate discussion, the mechanistic scheme previously reported by us (and now believed to constitute only a minor reaction pathway) is also shown (Scheme 2).<sup>17,18</sup>

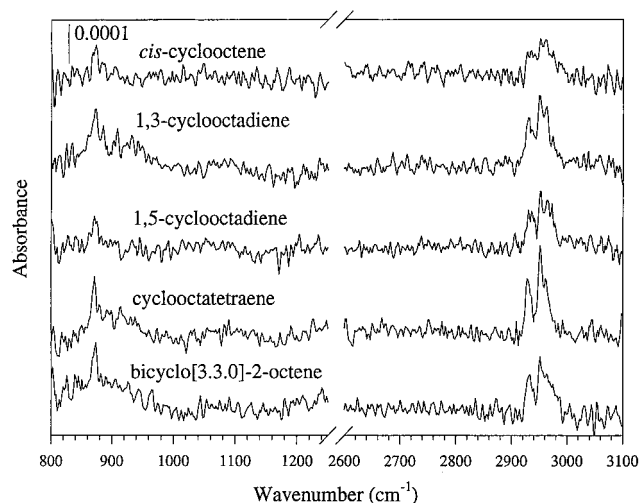
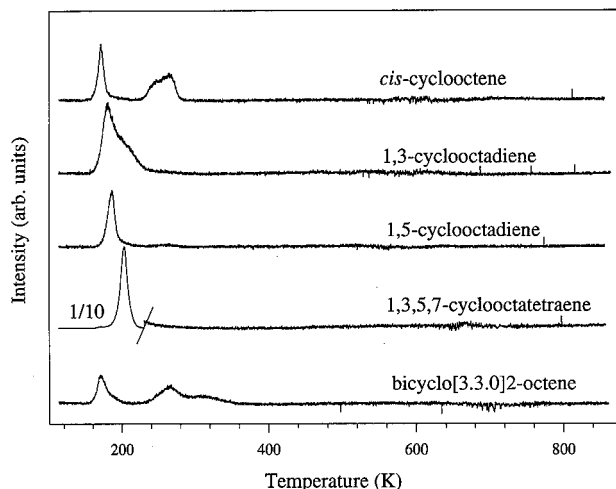
The two mechanistic schemes shown share several common features. In both, the decomposition of the unsaturated cyclic hydrocarbons proceeds via a series of sequential C–H bond activation steps, which in turn lead to the formation of a common intermediate at temperatures above 300 K. Our previously reported HREELS data strongly suggested that this intermediate was stable between 350 and 475 K and that it was a symmetric, planar species. At the time, we suggested that this intermediate was a planar cyclooctatetraene (C<sub>8</sub>H<sub>8</sub>) species. In subsequent work, however, Frei and Campbell convincingly demonstrated that the stable intermediate at 475 K has a stoichiometry of C<sub>8</sub>H<sub>6</sub> rather than the C<sub>8</sub>H<sub>8</sub>. Our current results confirm and extend this finding. As judged from the TPRS and RAIRS data, all of the monocyclic C<sub>8</sub> hydrocarbons studied here are converted (with varying efficiency) above 300 K to this C<sub>8</sub>H<sub>6</sub> species on Pt(111).

A simple mechanism closely related to gas-phase chemistry of COT explains the transformations involved in the Pt mediated chemistries. In the revised mechanism (shown in Scheme 1), decomposition is still thought to proceed for the monocyclic hydrocarbons through a series of sequential C–H bond cleavage steps to give COT, but now only as a transient intermediate. This COT is unstable at temperatures above ~300–350 K and is converted, via a ring-closure process, to the C<sub>8</sub>H<sub>6</sub> product. Although Frei and Campbell proposed that this C<sub>8</sub>H<sub>6</sub> product still possessed an intact monocyclic C<sub>8</sub> ring, the facile conversion of bicyclo[2.2.0]2-octene to this C<sub>8</sub>H<sub>6</sub> product strongly suggests that this latter species has a bicyclic framework. We thus propose that the highly symmetric pentalenyl intermediate (C<sub>8</sub>H<sub>6</sub>) is generated upon dehydrogenation of these cyclic C<sub>8</sub> hydrocarbons. This revised mechanism is fully consistent with our new data and the very important findings of Frei and Campbell. Our earlier work also grossly over-estimated the benzene yield. Whatever the nature of the decomposition pathways that are followed above 475 K, very little benzene is produced (<2% of a monolayer).

**TABLE 5: Frequencies and Mode Assignments for RAIR Spectra of Bicyclo[3.3.0]2-octene on Pt(111) after Being Annealed at the Indicated Temperatures<sup>a</sup>**

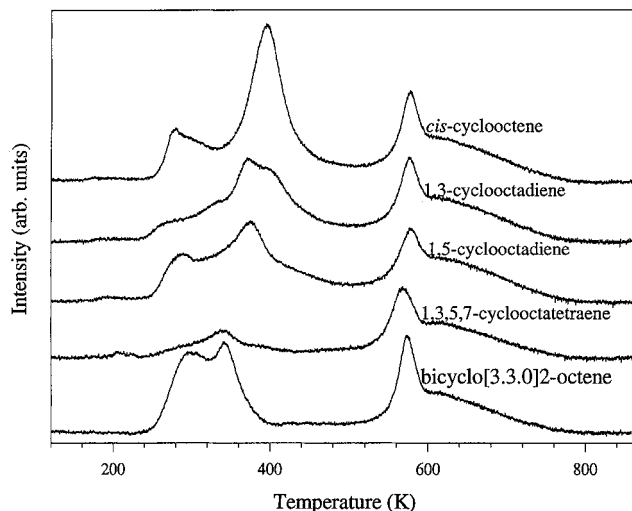
assignment	100 K	200 K	300 K	350 K	450 K	650 K	neat IR spectrum <sup>b</sup>
CH $\nu(\text{C-H})^c$			2885, ~2960 (weak bands)	2882, ~2960 (weak bands)	~2965 (weak)		
CH <sub>2</sub> $\nu_{\text{anti}}(\text{C-H})^d$	2955	2953					2942
$\nu(\text{C-H})$ di- $\sigma$ bonding <sup>d</sup>	2924						
CH <sub>2</sub> $\nu_{\text{sym}}(\text{C-H})^d$	2868	2872 (broad)					2846, 2861
CH <sub>2</sub> $\nu(\text{C-H})^e$		2780					
C-H out-of-plane bend <sup>e</sup>			880	880	877		

<sup>a</sup> Frequencies in wavenumbers. <sup>b</sup> Assignments taken from the neat IR spectrum of bicyclo[3.3.0]2-octene. <sup>c</sup> From the pentalenyl intermediate. <sup>d</sup> From adsorbed bicyclo[3.3.0]2-octene. <sup>e</sup> Largely from dihydropentalene, a dehydrogenation intermediate of bicyclo[3.3.0]2-octene (involving the loss of four hydrogens).

**Figure 6.** Reflection-absorption infrared spectra for high-temperature saturation exposures of *cis*-cyclooctene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, 1,3,5,7-cyclooctatetraene, and bicyclo[3.3.0]2-octene. The exposures were carried out at 450 K.**Figure 7.** Temperature-programmed reaction spectra for the specified C<sub>8</sub> cyclic hydrocarbon adsorbed on Pt(111). The exposures ( $\theta_i \approx 2.0 \theta_{\text{sat}}$ ) were made at <110 K. Ions followed correspond to the molecular ion for each of the specified cyclic hydrocarbons:  $m/e = 110$  (*cis*-cyclooctene); 108 (1,3-cyclooctadiene); 108 (1,5-cyclooctadiene); 104 (1,3,5,7-cyclooctatetraene); and 108 (bicyclo[3.3.0]2-octene).

We turn now to consideration of the various elementary steps of this mechanism, the intermediates involved and the energetics of the processes through which they are formed and further transformed.

**Structure of Cyclooctatetraene on Pt(111) at Low Temperatures.** An understanding of the structure of COT bound

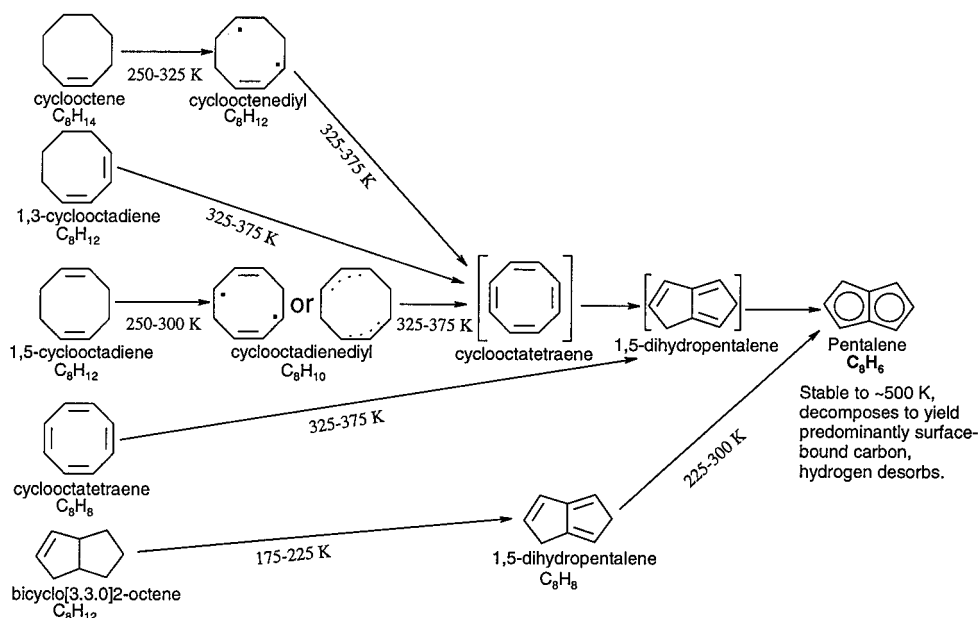
**Figure 8.** Temperature-programmed reaction spectra in the  $m/e = 2$  channel (dihydrogen desorption) for a coverage of  $\theta_i \approx 2.0 \theta_{\text{sat}}$  for each of the specified C<sub>8</sub> cyclic hydrocarbons.

to Pt(111) can be obtained from the HREEL and RAIR spectra. The former have been reported previously<sup>18</sup>, but in order to facilitate the present discussion and the reinterpretation of the structure of bound COT, a similar data set is presented in Figure 9. The HREEL spectrum of COT on Pt(111) measured at 170 K shows two bands in the C-H stretching region centered at ~2980 and 3030 cm<sup>-1</sup>.<sup>17,18</sup> From this observation, which suggested that both surface-bound and surface-remote C=C bonds were present, we concluded that COT adopts an  $\eta^4$  tub-shaped geometry in which two of the C=C double bonds are projected significantly upward away from the surface. This geometry, which is reminiscent of the conformation of the molecule in the gas phase, would give rise to C-H stretches with frequencies matching those seen experimentally. The RAIR spectra, however, clearly show that COT is bound on Pt(111) at low temperatures in a planar conformation. This finding suggests, therefore, that the high intensities of the C-H stretches seen in the HREEL spectra arise largely from an impact scattering mechanism.<sup>34,36</sup> What then explains the multiplicities of the C-H stretching bands seen in the low-temperature HREEL spectrum of COT adsorbed on Pt(111)?

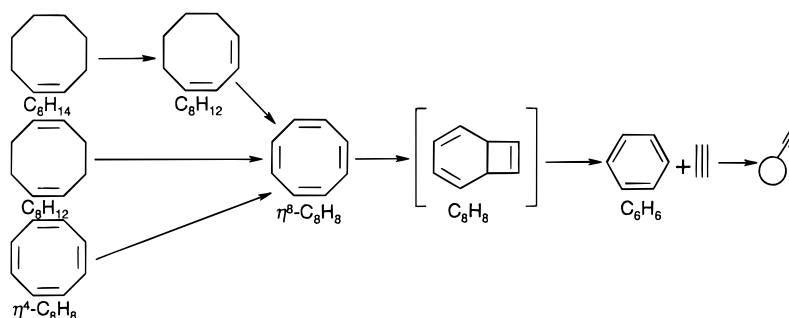
The data presented here and in the report of Frei and Campbell rule out interpretations which involve the activation of the C-H bonds of the COT ring at such low temperatures. The only prospect, in our view, is that the symmetry of the substrate interactions are involved in generating the band multiplicities and line shapes seen here. As shown in Scheme 3, a planar COT ring cannot form contacts to similar high-



## SCHEME 1



## SCHEME 2



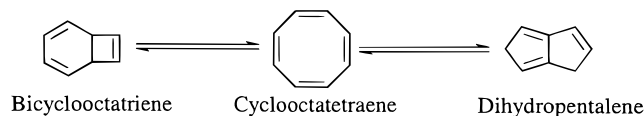
symmetry sites on the Pt(111) surface. The simple geometric model shown in the scheme suggests that the bonding of the ring system to the substrate must involve some heterogeneity in the registry between the carbon and surface atoms. The example showed in the scheme is but one of several possibilities that minimize the number of distinct environments for the C–H···M interactions in the bound form of the molecule. This result clearly suggests that such interactions, related as they are to the metal- $\pi$ -system bonding, are strong determinants of the frequencies of C–H stretching modes detected via impact scattering in the HREELS experiment. This conclusion is supported by the HREEL spectrum obtained for the pentalenyl intermediate, which, as we show, can be accommodated on Pt(111) with an organization that simplifies the nature and diversity of the C–H···M interactions.

**Structure of the Planar C<sub>8</sub>H<sub>6</sub> Intermediate.** The results of this study suggest that COE, 1,3-COD, 1,5-COD, and COT, are transformed on Pt(111) at temperatures near 350 K to a common intermediate (albeit in varying yields).<sup>17,18</sup> This species is relatively stable and persists unchanged on the surface up to temperatures as high as 500 K. When interpreted in the context provided by the data reported by Frei and Campbell, it is strongly argued that the intermediate is planar, retains a high-symmetry C<sub>8</sub> ring structure and that it has an average stoichiometry of C<sub>8</sub>H<sub>6</sub>.<sup>28</sup>

The representative HREEL spectra of COT (Figure 9) clearly show the progression of this transformation for a highly representative C<sub>8</sub> adsorbate. We know from RAIRS that the

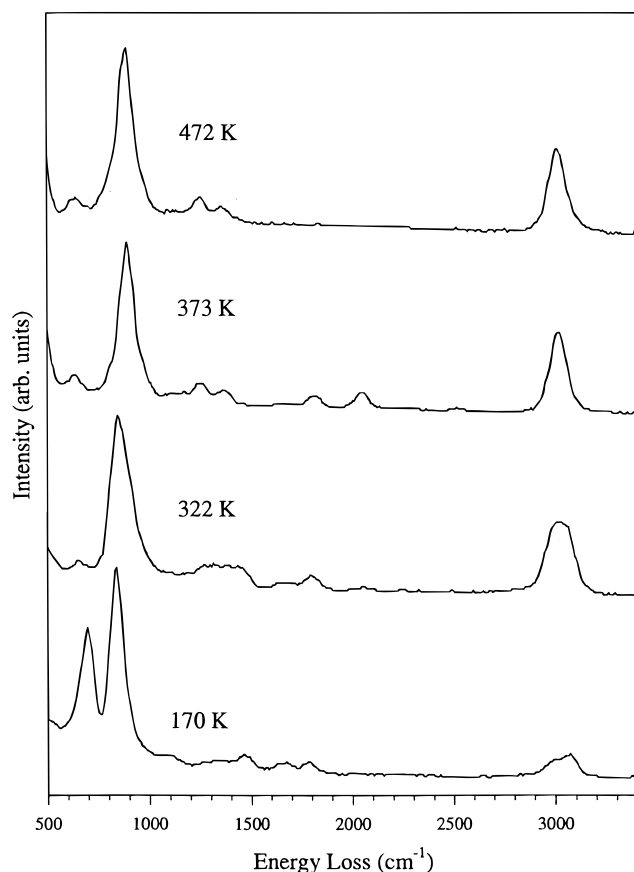
COT is initially bound in a planar conformation to the Pt(111) substrate. The HREEL spectra show that the COT decomposes to give a new planar species on the surface above 300 K (with concomitant loss of two hydrogens). This new intermediate is characterized in both the RAIRS and HREELS spectra by the dipole active out-of-plane C–H bending mode at ~880 cm<sup>-1</sup>.

What is the structure of this C<sub>8</sub>H<sub>6</sub> intermediate? In the gas phase, it is known that COT is converted thermally to a variety of different hydrocarbon products. The most important thermally activated conversions are shown below.



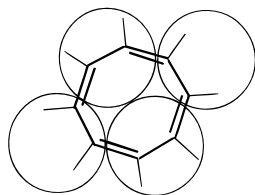
The equilibrium constants for these interconversions appear to favor the DHP ring system over the fused 6,4-ring architecture of BOT, an intriguing aspect given the likely involvement of radical pathways in the former's production. These reactions are all highly activated. We expect that the Pt substrate will greatly reduce the barriers for these cyclization reactions.

We previously suggested that cyclooctatetraene converts to BOT, while Frei and Campbell suggested that COT loses two hydrogen atoms but otherwise its structure is unchanged. The literature precedent described above and the report of Frei and Campbell led us to examine how a mechanism involving DHP could account for the experimental data. The best test of this



**Figure 9.** High-resolution electron energy loss spectra for a submonolayer of cyclooctatetraene on Pt(111) dosed at 100 K. The sample was heated to the indicated temperature before recording the spectrum at 100 K.<sup>17</sup>

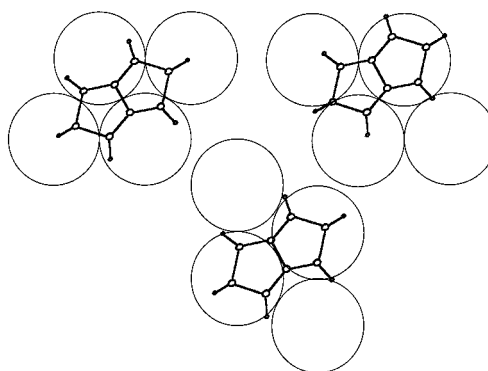
#### SCHEME 3



mechanism would be to carry out surface studies of DHP. This molecule, unfortunately, is very difficult to synthesize and purify. The related compound, tetrahydropentalene (THP), is commercially available, however. It is particularly significant to note that TPRS data show that this molecule decomposes above 300 K to give a stable surface-bound  $C_8H_6$  species, one whose RAIR spectrum is essentially indistinguishable from that measured for intermediates derived from the monocyclic  $C_8$  ring systems. The decomposition of the THP derived intermediate, as monitored by TPRS, also proceeds to give  $H_2$  desorption peaks (above 500 K) which are indistinguishable from those obtained using a monocyclic  $C_8$  adsorbate. It seems to us a very unlikely prospect that the energetics and kinetics of fragmentation and  $H_2$  extrusion from monocyclic and bicyclic  $C_8$  ring systems would be identical. The data therefore suggest that the pentalenyl ring system is a thermodynamic sink for the  $C_8$  ring systems, one which is accessed by the monocyclic adsorbates via the ring closure and subsequent dehydrogenation of COT.

The revised mechanism thus suggests that there are two common intermediates which lie along the reaction pathway

#### SCHEME 4



followed by the monocyclic  $C_8$  hydrocarbons: the (transient) planar COT complex and the (more thermally stable) bicyclic ring system. There do exist rate structure sensitivities in the conversions of COE, 1,3-COD, and 1,5-COD to this structure, however. With COE, for example, this conversion does not appear to be completely efficient and partitioning along other decomposition pathways is clearly suggested. The energetics of the C–H bond activation steps needed to convert these molecules to COT also appears to be sensitive to the structures of the adsorbates, albeit in ways which are not completely understood.

The pentalenyl intermediate is reminiscent of the cyclopentadienyl surface species formed by adsorbates such as cyclopentene and cyclopentadiene. As noted before, the cyclopentadienyl group and benzene, which contain only aromatic  $sp^2$  bonds, are characterized by very high decomposition temperatures on Pt(111). The high thermal stability of the  $C_8H_6$  intermediate is readily explained by the assignment of a pentalenyl structure, which also is aromatic and contains only  $sp^2$  bonds.

Theoretical calculations predict that the ground state of the neutral pentalene molecule should be antiaromatic and, as a result, is unstable.<sup>58</sup> It has been demonstrated, however, that the pentalenyl dianion is stable (the dianion is an aromatic ten- $\pi$ -electron system). Several examples of pentalenyl complexes of transition metals are known including some in which the pentalenyl group is bound to a trinuclear cluster.<sup>59–69</sup> Perhaps more interesting in the present context, though, are reports which describe discrete organometallic complexes which effect the conversion of various substituted cyclooctatetraenes to a bound pentalenyl ligand.<sup>59–63</sup> This, again, provides an excellent analogy supporting the reaction scheme proposed in this work.

The geometric models shown in Scheme 4 suggest that reasonably high-symmetry environments are accessible when this species is bound to the surface, some of which are similar to that proposed for the well-studied pentahaptocyclopentadienyl intermediate ( $\eta^5$ -Cp) and others analogous to those found for discrete metal–carbonyl clusters.<sup>11,12,61</sup> In the highest symmetry model of the structure, the pentalenyl species is adsorbed on the surface so as to place the center of the  $C_5$  rings directly over 3-fold-hollow sites. Before adsorption, the adsorbate possesses  $D_{2h}$  symmetry; after coordination on the hexagonal surface, the overall symmetry of the complex is reduced to  $C_{2v}$  symmetry.<sup>70</sup> Even so, the symmetry remains sufficiently high upon adsorption that only a small number of vibrational modes is allowed. The experimental data appear to be consistent (at least qualitatively) with this latter inference.

**Thermal Decomposition of the Pentalenyl Intermediate.** At temperatures significantly greater than 450 K (probably

above 500 K) the pentalenyl intermediate fragments leaving carbon on the surface which can be detected and quantified by Auger electron spectroscopy.<sup>71</sup> The hydrogen so generated combines to give dihydrogen which desorbs into the gas phase.

The pentalenyl framework does not appear to be an efficient pathway for forming stable hydrocarbon products which can be liberated into the gas phase via thermal activation. We concluded in our earlier study that COT underwent a ring contraction on Pt(111) to form bicyclo[4.2.0]-octa-1,3,5-triene (BOT), which in turn decomposed via a retro[2+2] cyclization to form benzene (which desorbed) and acetylene. This mechanism is now known to be a minor pathway in the product partitioning; the amount of benzene desorbing from the surface is extremely small (<2%).<sup>28,72</sup> The intriguing question remains, though, as to why cyclization to the pentalenyl bonding habit appears to be so strongly preferred. Several factors appear relevant here. First, the ring strain in this intermediate must be significantly lower than would be the case for an intermediate such as BOT. Second, the bonding interactions with the metal surface are likely to be exceptionally strong, involving as they likely do, a substantial charge transfer. Third, the pentalenyl architecture is formed from COT by a dissociative pathway. Thus, in the absence of background pressure of H<sub>2</sub>, entropy and the ligand energetics appear to strongly favor the selection of the pentalenyl structure. This preference appears to mirror aspects of the ring conversion phenomena seen in hydrocarbon reforming processes as well.

**Acknowledgment.** The support of the Department of Energy (Grant DEFG02-91-ER45439) through the Seitz Materials Research Laboratory of the University of Illinois at Urbana-Champaign is gratefully acknowledged.

**Supporting Information Available:** Reflection-absorption infrared spectrum for a submonolayer of 1,3,5-cyclooctatriene adsorbed on Pt(111) at 100 K (1 page). Ordering information is given on any current masthead page.

## References and Notes

- (1) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*, 2nd ed.; McGraw-Hill: New York, 1991.
- (2) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, 1981.
- (3) Henn, F. C.; Diaz, A. L.; Bussell, M. E.; Hugenschmidt, M. B.; Domagala, M. E.; Campbell, C. T. *J. Phys. Chem.* **1992**, *96*, 5965–5974.
- (4) Hugenschmidt, M. B.; Diaz, A. L.; Campbell, C. T. *J. Phys. Chem.* **1992**, *96*, 5974–5978.
- (5) Pettiette-Hall, C. L.; Land, D. P.; McIver, R. T., Jr.; Hemminger, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 2755–2756.
- (6) Rodriguez, J. A.; Campbell, C. T. *J. Catal.* **1989**, *115*, 500–520.
- (7) Tsai, M.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2539–2543.
- (8) Manner, W. L.; Nuzzo, R. G.; Girolami, G. S. 1997, in preparation.
- (9) Abon, M.; Bertolini, J. C.; Billy, J.; Massardier, J.; Tardy, B. *Surf. Sci.* **1985**, *162*, 395–401.
- (10) Tsai, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534–2539.
- (11) Avery, N. R. *Surf. Sci.* **1984**, *146*, 363–381.
- (12) Avery, N. R. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *39*, 1–9.
- (13) Henn, F. C.; Dalton, P. J.; Campbell, C. T. *J. Phys. Chem.* **1989**, *93*, 836–846.
- (14) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S.; Dubois, L. H. *Organometallics* **1995**, *14*, 3377–3384.
- (15) Muetterties, E. L. *Pure Appl. Chem.* **1982**, *54*, 83.
- (16) Tsai, M.-C.; Stein, J.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 3533–3534.
- (17) Hostetler, M. J.; Dubois, L. H.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 2044–2046.
- (18) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S.; Dubois, L. H. *J. Phys. Chem.* **1994**, *98*, 2952–2962.
- (19) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* **1991**, *3*, 677–685.
- (20) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 2576–2585.
- (21) , One likely reason that the desorption of COT is not quantitative is that it may only be present as a transient intermediate on the Pt(111) surface (see below).
- (22) Tanaka, I. *J. Chem. Soc. Jpn., Pure Chem. Soc.* **1954**, *75*, 212.
- (23) Tanaka, I. *Chem. Abstr.* **1954**, *48*, 4984b.
- (24) Jones Jr., M.; Schwab, L. O. *J. Am. Chem. Soc.* **1968**, *90*, 6549–6550.
- (25) Fonken, G. J. *Chem. Ind. (London)* **1963**, 1625–1626.
- (26) Dudek, D.; Glanger, K.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 788.
- (27) We performed analogous studies of cyclooctane on Pt(111). We found, as the literature suggests, that most of the cyclooctane layer desorbs molecularly upon heating the crystal.
- (28) Frei, N. A.; Campbell, C. T. *J. Phys. Chem.* **1996**, *100*, 8402–8407.
- (29) Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767–773.
- (30) Bradshaw, A. M.; Schweizer, E. *Infrared Reflection-Absorption Spectroscopy of Adsorbed Molecules*; Bradshaw, A. M., Schweizer, E., Ed.; Wiley: New York, 1988.
- (31) Chabal, Y. J. *Surf. Sci. Rep.* **1988**, *8*, 214.
- (32) Gadzuk, J. W. *Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces*; Gadzuk, J. W., Ed.; Plenum: New York, 1987; Vol. 1, pp 49–104.
- (33) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310–315.
- (34) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic: New York, 1982.
- (35) Francis, S. A.; Ellison, A. H. *J. Opt. Soc. Am.* **1959**, *49*, 131–138.
- (36) Sebastian, K. L. *J. Phys. C: Solid State. Phys.* **1980**, *13*, L115–L117.
- (37) Manner, W. L.; Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S., in preparation.
- (38) Hostetler, M. J.; Manner, W. L.; Nuzzo, R. G.; Girolami, G. S. *J. Phys. Chem.* **1995**, *99*, 15269–15278.
- (39) Manner, W. L.; Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S., in preparation.
- (40) Manner, W. L.; Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S., to be submitted for publication.
- (41) Raval, R.; Chesters, M. A. *Surf. Sci. Lett.* **1989**, *219*, L505–L514.
- (42) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024–2030.
- (43) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950–1955.
- (44) Manner, W. L.; Nuzzo, R. G.; Girolami, G. S., in preparation.
- (45) Baude, E. A. *Chem. Ind.* **1954**, 1557.
- (46) Allinger, N. L.; Viskocil, J. F.; Burkert, U.; Yuh, Y. *Tetrahedron* **1976**, *32*, 33–35.
- (47) Some rehybridization of the olefinic carbons probably occurs upon adsorption to the metal, which, in turn, could serve to lessen the ring strain.
- (48) Allinger, N. L.; Sprague, J. T. *Tetrahedron* **1975**, *31*, 21–24.
- (49) Barna, G. G.; Butler, I. S. *J. Raman Spectrosc.* **1978**, *7*, 168–172.
- (50) Traetteberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724–1726.
- (51) Brauer, D. J.; Krueger, C. J. *Organomet. Chem.* **1976**, *122*, 265–273.
- (52) Stuve, E. M.; Madix, R. J. *J. Phys. Chem. Lett.* **1985**, *89*, 3183–3185.
- (53) Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589–644.
- (54) Hostetler, M. J.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1995**, *117*, 1814–1827.
- (55) Pearlstine, K. A.; Friend, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 5898–5901.
- (56) Christmann, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976**, *54*, 365–392.
- (57) , Based on the poor resolution of the two desorption peaks below 490 K we cannot rule out the possibility that only one C–H bond is cleaved forming a  $\pi$ -allyl species of stoichiometry C<sub>8</sub>H<sub>11</sub>.
- (58) Baird, N. C.; West, R. M. *J. Amer. Chem. Soc.* **1971**, *93*, 3072.
- (59) Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 321–328.
- (60) Knox, S. A. R.; McKinney, R. J.; Riera, V.; Stone, F. G. A.; Szary, A. C. *J. Chem. Soc. Dalton Trans.* **1979**, 1801–1811 and references therein.
- (61) Howard, J. A. K.; Stansfield, R. F. D.; P., W. *J. Chem. Soc., Dalton Trans.* **1979**, 1812–1818.
- (62) Hunt, D. F.; Russell, J. W. *J. Organomet. Chem.* **1976**, *104*, 373–376.

- (63) Abbasali, Q. A.; Cloke, F. G. N.; Hitchcock, P. B.; Joseph, S. C. *P. J. Chem. Soc., Chem. Comm.* **1997**, 1541–1542.
- (64) Miyake, A.; Kanai, A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 801.
- (65) Kitano, Y.; Kashiwagi, M.; Kinoshita, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 723–727.
- (66) Manriques, J. M.; Ward, M. D.; Rieff, W. M.; Calabrese, J. C.; Jones, N. L.; Carroll, P. J.; Bunel, E. E.; Miller, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 6182–6193.
- (67) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 7899–7900.
- (68) Jonas, K.; Gabor, B.; Mynott, R.; Angermund, K.; Heinemann, O.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1712–1714.

(69) Jonas, K.; Kolb, P.; Kollbach, G.; Gabor, B.; Mynott, R.; Angermund, K.; Heinemann, O.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1997**, 1714–1716.

(70) Rehybridization may lower the symmetry of the pentalenyl intermediate on the Pt(111) surface.

(71) It is known that dihydropentalene decomposes to give benzene among other products upon pyrolysis. We do not observe benzene, however, by RAIRS or TPRS.

(72) The benzene could be produced at defects sites on the Pt(111) surface. Such sensitivities have been noted in the formation of benzene during the decomposition of cyclic C<sub>7</sub> hydrocarbons.