Other reagents such as zinc–silver couple[17] or magnesium (ether, THF) were ineffective. The overall yield of **9a** from **6a** was 79%.

Completion of the synthesis proceeded by tosylation (*p*-TsCl, C_5H_5N) of the diol **9a** (R = H) to yield the oily monotosyl derivative **9a** (R = Ts), which was converted to **2a** in 96% yield by treatment with aqueous potassium hydroxide in methanol. This racemic synthetic material gave NMR, MS, and IR spectra identical with those of a natural sample isolated from the red alga *Laurencia nipponica*.[8]

The synthesis of the Z isomer (±)-**2b** was accomplished starting from the diastereoisomeric β-hydroxy acid (±)-**3b**, following an identical sequence of reactions (64% overall yield).

Supplementary Material Available: Analytical data for **2a–4a**, **6a–9a**, **2b–4b**, and **6b–9b** (5 pages). Ordering information is given on any current mastehad page.

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Gas-Phase Platinum Cluster Reactions with Benzene and Several Hexanes: Evidence of Extensive Dehydrogenation and Size-Dependent Chemisorption

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Surface science, organometallic chemistry, and reaction kinetic studies on model systems have significantly improved our understanding of heterogeneous catalysis. We have initiated studies on the hopefully simpler system of unsupported platinum metal clusters to further our understanding of this chemistry. This work concentrates on two important steps, chemisorption of hydrocarbons under reaction conditions and their dehydrogenation.

We describe the first observation of reaction products of benzene, cyclohexane, 2,3-dimethylbutane, and *n*-hexane with gas-phase platinum clusters. Our major conclusions are that gas-phase platinum clusters dehydrogenate saturated hydrocarbons to a C/H ratio near 1 and exhibit a cluster-size-dependent extent of chemisorption.

These experiments were carried out on a pulsed molecular beam apparatus described elsewhere.[1] Metal clusters are produced by condensation of laser-vaporized (12-mJ doubled NdYAG) metal in a high-pressure helium flow. Reactions are carried out by pulsing reactant mixtures into the reactor to overlap the cluster pulse. The reaction conditions are estimated to be 0.1–1 atm of helium (0.2–0.4% reactant), 300–600 K[2], and a residence time of ~100 μs. Cluster reaction products are detected by photoionization (ArF 0.1–0.4 mJ/pulse) time-of-flight mass spectrometry. Low laser intensities were found necessary to minimize

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(2) The upper limit of 600 K was estimated from the fastest components' time-of-flight velocity distribution. This is in agreement with more accurate velocity measurements on iron clusters under similar conditions. Whetten, R. .; Cox, D. M.; Trevor, D. J.; Kaldor, A., submitted for publication in *J. Phys. Chem.*

(3) Dehydrogenation is defined as the observed mass loss with respect to $Pt_n(reactant)_m$. In support of this, deuterium chemisorption was not found to occur on these small platinum clusters, under our reaction conditions, and is not stable on the most tightly bound states of the platinum metal surface above 380 K as reported by: Christmann, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976,** *54,* 365–392.
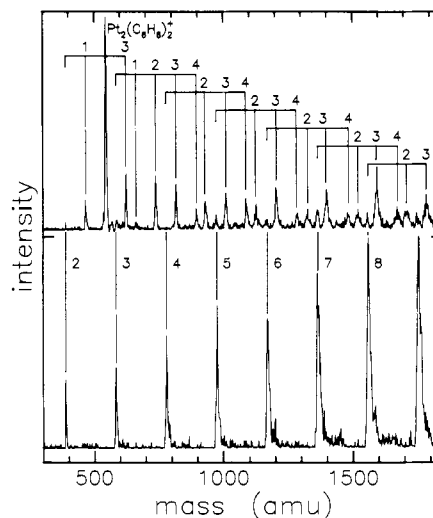
Figure 1. Time-of-flight mass spectra of platinum clusters after reactions with benzene. The lower trace is without reactant. The upper trace is with the pulsed addition of 0.21% benzene in helium. The notation indicates the number of adducts on each metal cluster. The metal clusters are all two-photon ionized, while the observed products are single-photon ionized: hence the enhancement of the product over metal signals.
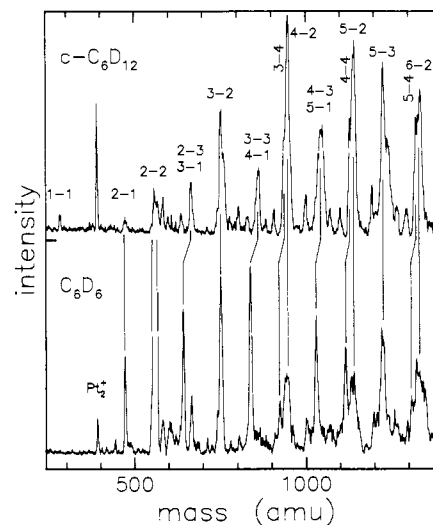

Figure 2. Time-of-flight mass spectra of platinum cluster reactions with benzene-d_6 (0.23% in helium) and with cyclohexane-d_{12} (0.25% in helium). The bis(benzene)diplatinum signal is off scale. The nomenclature used, *n–m*, stands for $Pt_n(adduct)_m$. Lines are drawn between the spectra to point out the similarities in mass of many of the products produced.

multiphoton dissociative ionization.

Figure 1 shows our results of reacting benzene with platinum clusters. The lower spectrum represents the clean metal without overlap of the cluster and reactant pulses. The following are our observations: (1) The platinum atom monoadduct ion and diadduct parent ion signals are very weak. (2) The largest peak is the bis(benzene)diplatinum parent ion. (3) The mono- and triadducts on Pt_2 are observed. The monoadduct appears with a small degree of dehydrogenation. The tetradduct parent ion is present but very weak. (4) For larger clusters, the di- and triadducts dominate, while the monoadduct decreases in intensity. Above Pt_3 the benzene adducts begin to dehydrogenate, more so with the number of metal atoms than with the number of adducts.

Figure 2 shows the spectra for cyclohexane-d_{12} addition, and Figure 3 gives the results with *n*-hexane and 2,3-dimethylbutane. The following are our observations: (1) The mono- and diadducts are dehydrogenated to nearly an aromatic C/H ratio. (2) For cyclohexane the triadducts on Pt_2–Pt_4 are not as dehydrogenated. The deuterium loss on the Pt_2 and Pt_3 triadduct of cyclohexane-d_{12} is consistent with dehydrogenated diadducts plus cyclohexane-d_{12}.
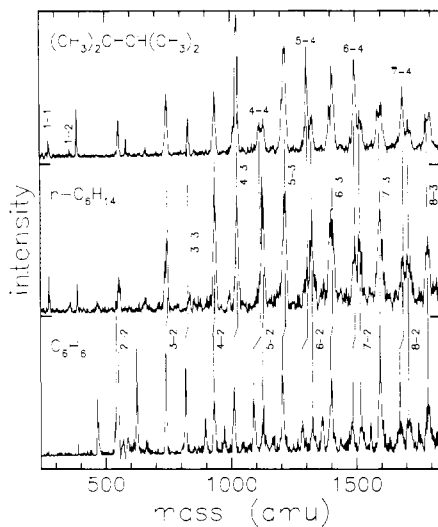
Figure 3. Time-of-flight mass spectra of platinum cluster reactions with benzene, *n*-hexane (0.22%), and 2,3-dimethylbutane (0.42%). The bis-(benzene)diplatinum peak is off scale. The nomenclature is the same as in Figure 2. The extensive degree of dehydrogenation is emphasized by the connecting lines between the similar cluster adducts in the three spectra.

(3) A dramatic increase in the extent of chemisorption occurs between Pt_3 and Pt_4 for *n*-hexane and 2,3-dimethylbutane, so that by Pt_4 the triadduct dominates and by Pt_5 the tetraadduct is of comparable intensity. (4) For Pt_2–Pt_8 with *n*-hexane and 2,3-dimethylbutane, the degree of dehydrogenation increases with cluster size. This is extensive, as evidenced by the similar mass of products for Pt_4–Pt_8 with *n*-hexane and with benzene. The branched hexane also dehydrogenates but retains on the average two–four more hydrogens. These highly dehydrogenated adduct peaks have widths that indicate a distribution of losses.

The platinum dimer favors the production of a bis(benzene) complex which most likely results from an enhanced stability, due to π-type bonding similar to bis(arene) complexes[4] and chemisorbed benzene.[5] However, at these temperatures (300–600 K), platinum insertion into C–H bonds cannot be ruled out.[6]

The propensity of cyclohexane chemisorption on platinum clusters is similar to benzene, except for the lack of an intense $Pt_2(C_6D_6)_2$ signal. This behavior and the extent of dehydrogenation suggest benzene formation and are seen even on the Pt atom. The distinct change in the multiple chemisorption behavior, as function of cluster size, for *n*-hexane and 2,3-dimethylbutane and the onset of benzene dehydrogenation we take as evidence of an enhanced reactivity for Pt_4 and larger clusters.

Benzene dehydrogenates on Pt_3 and larger, with a maximum hydrogen loss of eight atoms on $Pt_8(adduct)_3$. Reversible C–H bond breaking is observed above 370 K in benzene on the Pt(111) surface,[3] suggesting these small metal clusters have at least the same activity toward C–H. The similarity between *n*-hexane and 2,3-dimethylbutane dehydrogenation suggests that *n*-hexane does not produce aromatic species on these unsupported clusters. However, we note that the area occupied by three and four hexane or benzene molecules lying flat as found on surfaces, significantly exceeds the small-cluster surface area[7,8] requiring these species to be quite different from the surface chemistry analogues.

In conclusion, our observations are consistent with a qualitative model in which Pt clusters seek to become coordinatively saturated by activation of sufficient C–H bonds and subsequent loss of hydrogen.

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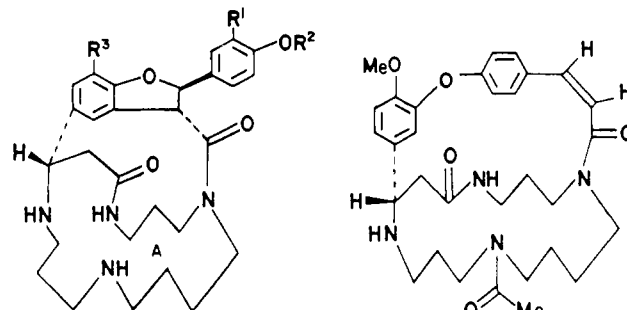
Total Synthesis of (±)-*O*-Methylorantine

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Among the most complex of the macrocyclic polyamine alkaloids are the ephedradines A (**1**), B (**2**), C (**3**), and D (**4**), hy-

1, $R^1 = R^2 = R^3 = H$ (ephedradine A, orantine)   **6**
2, $R^1 = OCH_3$; $R^2 = R^3 = H$ (ephedradine B)
3, $R^1 = OCH_3$; $R^2 = CH_3$; $R^3 = H$ (ephedradine C)
4, $R^1 = R^2 = H$; $R^3 = OCH_3$ (ephedradine D)
5, $R^1 = H$; $R^2 = CH_3$; $R^3 = H$ (*O*-methylorantine)

potensive components of the crude Chinese drug "mao-kon" prepared from the roots of *Ephedra* plants. The structures of these compounds, established by the X-ray crystallographic work of Hikino,[1–4] are characterized by the presence of a substituted dihydrobenzofuran grouping which bridges a 17-membered lactam ring (ring A) containing a spermine nucleus. The same dihydrobenzofuran system is found in the antifungal agent, hordatine A,[5] and in the closely related alkaloids, aphelandrine[6,7] and *O*-methylorantine (**5**),[7,8] isolated by Hesse from species of *Aphelandra* and *Chaenorhinum*, respectively.[9]

We now report the first total synthesis of (±)-*O*-methylorantine (**5**) by a convergent pathway paralleling routes previously employed in the formation of the spermine alkaloids chaenorhine (**6**)[10] and verbascenine.[11] The synthesis illustrates the generality of

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