Gas-Phase Dehydrogenation of Saturated and Aromatic Cyclic Hydrocarbons by Pt$_n^+$ ($n = 1-4$)

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Abstract: Small platinum clusters are readily generated by electron ionization of Pt$_4$(PF$_3$)$_8$ in an FT-ICR mass spectrometer. Pt$_n^+$ ($n = 1-4$), cluster ions of a given n value may then be isolated and reacted with a variety of gaseous saturated and aromatic cyclic hydrocarbons. The present experiments thus illuminate catalytic dehydrogenation behavior intermediate between that of single-atom and bulk platinum. Extensive chemisorption (dehydrogenation of the hydrocarbon) and physisorption (nondissociative adsorption of intact neutral reagent molecule on the cluster) occur, depending on the particular reagent species. For example, each of the clusters exhibits chemisorption with at least one ligand for every neutral reactant species except for hexafluorobenzene. In general, the extent of chemisorption increases with cluster size. Also, some of the reactions do not proceed by a previously proposed C−H bond insertion mechanism. The detailed reaction pathways and product relative yields depend on the metal cluster ion, the reagent neutral species, and the stability of the final product.

Introduction

Metal clusters and transition metal ions have been the focus of intense research interest for many years. Metal clusters are of special importance because they provide a bridge between atoms and bulk materials.[1,2] Cluster reactions can help to elucidate the mechanisms of gas-phase reactions, provide insight into efficiencies of catalytic reactions, distinguish between possible cluster structures,[3−6] and provide a direct probe of the effect of cluster size on reactivity.[2,7] Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is especially valuable because it provides ultrahigh mass resolving power, wide mass range, simultaneous detection of all ions, and a long ion storage period to allow for extensive ion−molecule reaction chemistry.[7−15]

Of the transition metals, platinum is of particular interest because dehydrogenation reactions are important in petroleum processing. Specifically, cyclohexane can be dehydrogenated to benzene on the surface of bulk platinum.[16] Prior analysis of platinum cluster-catalyzed dehydrogenation has concentrated on neutral clusters. For example, there is an extended Hückel theory study of the stability of neutral Pt$_n$ ($n = 1-13$) clusters of various geometries.[17] High nuclearity platinum cluster carbonyl anions have been generated by [252]Cf-plasma desorption.[18] Neutral platinum clusters, Pt$_n$ ($n = 1-24$), have been used to activate methane, for which Pt$_n$ ($n = 2-5$) were more reactive than lone platinum or the bulk material.[19,20] Unsupported platinum metal clusters Pt$_n$ ($n = 2-8$) have also been reacted with benzene and hexanes; chemisorption (in this case, dehydrogenation of the benzene ligand) was observed for Pt$_3$ and larger clusters.[21]

In one of several studies on lone platinum and platinum cluster ions, Pt$^+$ and Pt$_2^+$ were found to dehydrogenate *n*-butane.[22] Pt$^+$ has also been used to catalyze the industrially important conversion of methane to methanol.[23] Finally, negative and positive atomic platinum ions have been reacted with several aromatic hydrocarbons, thiols, and H$_2$S.[24]

In this paper, we take advantage of a simple means for generating small platinum cluster ions, Pt$_n^+$ ($n = 1-4$), from Pt$_4$(PF$_3$)$_8$.[25] The platinum cluster ions are then trapped, isolated by mass selection, and allowed to react with various saturated

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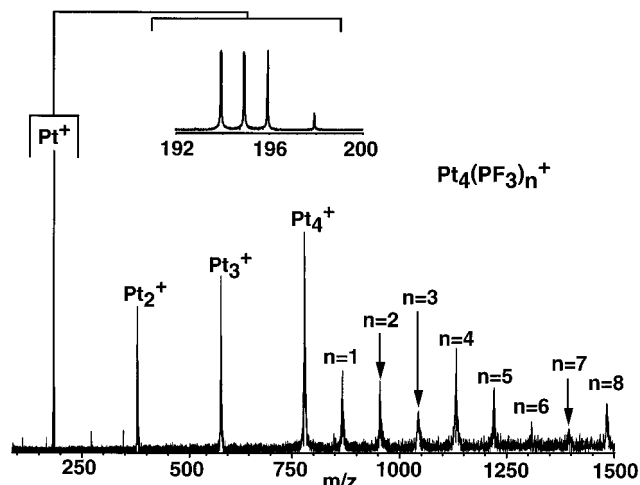
Figure 1. FT-ICR magnitude-mode mass spectrum of electron-ionized $Pt_4(PF_3)_8$. (inset) Mass scale expansion to show resolved isotopes of Pt^+.

and aromatic cyclic hydrocarbons in an FT-ICR mass spectrometer. Neutral reagents were chosen to assess the extent and mechanism of C–H bond activation. The nomenclature used in this paper follows that employed by Berg et al.[26] Ligands denote the number of hydrocarbon rings that exhibit chemisorption or physisorption with the metal cluster. Chemisorption is said to occur when the ligand has undergone a reaction (in this case, dehydrogenation), whereas physisorption describes nondissociative adsorption of an intact reagent molecule.

Experimental Section

All spectra were obtained from a standard FTMS-2000 FT-ICR mass spectrometer (Finnigan Corp., Madison, WI) equipped with dual 1.875 in. cubic source and analyzer ion traps centered in the bore of a superconducting magnet (3.0 T), an automatic solids insertion probe, and an Odyssey data station. The instrument was modified with CTI Corp. Helix CryoTorr 8 Cryopumps (1250 L s^{-1} pumping speed for N_2) rather than the usual diffusion pumps on both source and analyzer sides of the dual trap. Trapping potential was maintained at +2.0 V on each end-cap electrode.

Cyclic alkanes and aromatic hydrocarbons were obtained from Aldrich Chemical Co. (Milwaukee, WI). Platinum and platinum cluster ions were generated by electron ionization of a recently synthesized compound $Pt_4(PF_3)_8$.[25] A small amount of the parent compound was placed in a glass capillary vial and attached to the solids insertion probe. This arrangement yielded a constant sample pressure of 1.0×10^{-7} Torr in the source chamber and a measured background pressure of 1.0×10^{-9} Torr in the analyzer chamber. All FT-ICR measurements were performed in the analyzer trap. Ionization of the parent compound with an electron beam of 15 eV and 5.0 µA for 50 ms produced a spectrum including: molecular ion, subsequent loss of one to eight PF_3 units from the molecular ion, as well as the bare metal clusters Pt_n^+ ($n = 1-4$) (see Figure 1). No larger clusters are generated.

For the ion–molecule reactions, neutral reagent was introduced at a pressure of 1.0×10^{-6} Torr in the source chamber (2.0×10^{-9} Torr in the analyer chamber) through a leak valve (VLV variable leak valve with mini flange on inlet, Varian, Palo Alto, CA) from the sample reservoir after degassing by several freeze–pump–thaw cycles on the foreline vacuum chamber of the instrument. Following SWIFT[27,28] radial ejection[5] to isolate a given platinum or platinum cluster ionic species (including its entire isotopic distribution), the mass-selected ions were allowed to react for a set period before dipolar broad-band
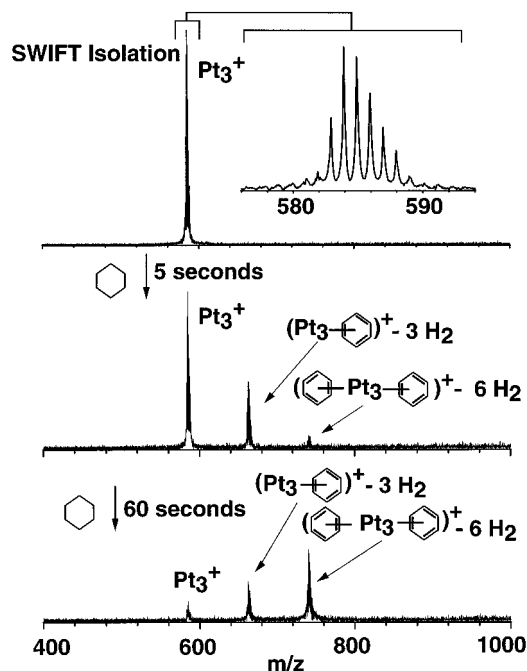
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Figure 2. FT-ICR mass spectra showing progressive reaction of SWIFT-isolated Pt_3^+ ions with cyclcohexane for 100 ms (top), 5 s (middle), and 60 s (bottom). The inset (top right) is mass scale expanded to show isotopic resolution for Pt_3^+.

excitation (frequency sweep at a rate of 1000 Hz µs^{-1}) and acquisition of a128K data point time-domain transient signal (direct mode at a Nyquist bandwidth of 1 MHz, padded with an additional 128K of zeroes) before discrete Fourier transformation (without prior apodization) and magnitude computation.

As a control experiment, argon was introduced through a series of pulsed valves at 1.0×10^{-4} Torr into the source chamber (5×10^{-7} Torr in the analyzer chamber), and the ions were allowed to cool by ion–neutral collisions for 10 s before the reactant was introduced. The product ion abundances from such experiments at each of several reaction periods were similar to those from direct introduction of reagent without prior argon collisional cooling. It is possible that the ions may not have been completely cooled by collisions. However, it is worth noting that we failed to observe any of the high-energy products featuring loss of one H seen by El-Nakat et al. when they reacted Pt^+ with benzene, toluene, *p*-xylene, and mesitylene.[24] We infer that the Pt_n^+ ions in our experiments are electronically and vibrationally thermalized before reaction.

Finally, in view of the many isotopic combinations for each cluster ion species, we analyzed the product ion isotopic multiplets with the modified polynomial method.[29]

Results and Discussion

Reactions of Pt_n^+ ($n = 1-4$) with Cyclic Alkanes, C_nH_{2n}. Ion–molecule reactions between platinum cluster ions and cyclic hydrocarbon neutrals were investigated after various reaction periods and the reaction products analyzed by FT-ICR MS. For example, the products observed after 100 ms, 5 s, and 60 s for the reaction of Pt_3^+ with cyclohexane are shown in Figure 2. The reactions were considered complete when further increase in reaction period did not generate any new products. The final reaction products were analyzed to determine both the extent of dehydrogenation and the number of ligands. Mass spectra of the reactions of pentane and cyclohexane with small platinum clusters are shown in Figures 3 and 4. On the left side of each figure are the products after 100 ms; note that little or no reaction has occurred. Following a

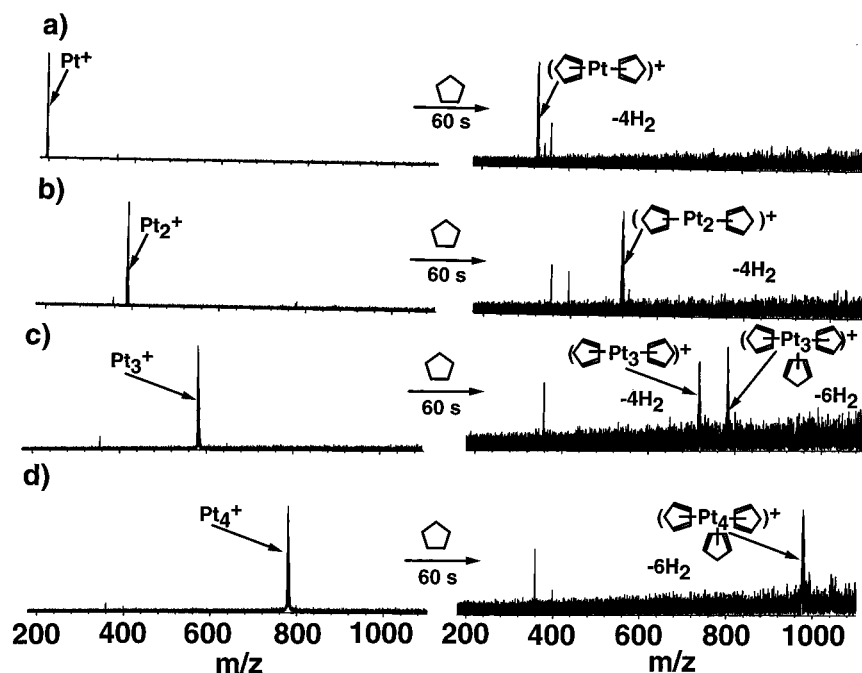(29) Yergey, J. *Int. J. Mass Spectrom. Ion Processes* **1983**, *52*, 337–349.

Figure 3. Reaction of (a) Pt$^+$, (b) Pt$_2^+$, (c) Pt$_3^+$, and (d) Pt$_4^+$ with cyclopentane. (left) FT-ICR mass spectra acquired after a 100 ms reaction period. (right) FT-ICR mass spectra acquired after the reaction was complete (60 s).

Figure 4. Reaction of (a) Pt$^+$, (b) Pt$_2^+$, (c) Pt$_3^+$, and (d) Pt$_4^+$ with cyclohexane. (left) FT-ICR mass spectra acquired after a 100 ms reaction period. (right) FT-ICR mass spectra acquired after the reaction was complete (60 or 120 s).
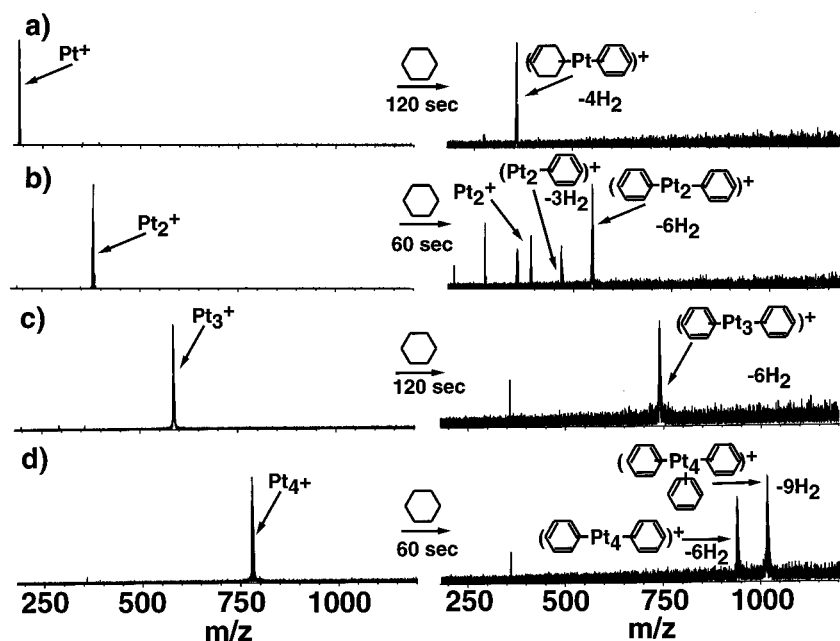
longer reaction period (60 or 120 s), the reaction was complete (right-hand spectra in Figures 3 and 4). Table 1 summarizes the results of each of these complete reactions.

The number of ligands and the total number of H$_2$ lost are compared for each of the final products. In the third and fourth columns of Table 1, the parentheses—( ), [ ], or none—denote the number of hydrogens lost for species with a given number of ligands. For instance, for the reaction of cyclohexane with Pt$_2^+$, there are three significant final products: unreacted Pt$_2^+$, Pt$_2$(C$_6$H$_6$)$^+$, and Pt$_2$(C$_6$H$_6$)$_2^+$. The designation "(major)" indicates that the product constituted at least 80% of the final products. Thus, for the reaction of Pt$_3^+$ with cyclohexane, two C$_6$ ligands have chemisorbed onto the metal cluster. However, there are two final products, one of which (by far the most abundant product) has lost six H$_2$'s, whereas the other has lost five H$_2$ groups. Dehydrogenation of each final major product

(as reflected by C/H ratio) as a function of Pt$_n^+$ cluster size is shown in the top of Figure 5. In cases for which there is no dominant product, the plotted data represent the one with the *most* ligands and *most* number of H$_2$ lost.

None of the reactions displays C–C bond cleavage. In prior studies, Co$^+$ and Ni$^+$ were found to cleave C–C bonds of cyclopentane and cyclohexane, whereas Fe$^+$ did not.[30] Fe$^+$ does cleave C$_7$ and C$_8$ rings.[7] Those cluster ions resemble the reactions of La$^+$[31] and Os$^+$[32] for which little C–C bond cleavage was observed. However, for Os$^+$, C–C bond cleavage becomes more prominent in the C$_7$ and C$_8$ cases.[32]

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Table 1.   Reactions of Pt_n^+ ($n = 1-4$) with Cyclic Alkanes, C_nH_{2n}

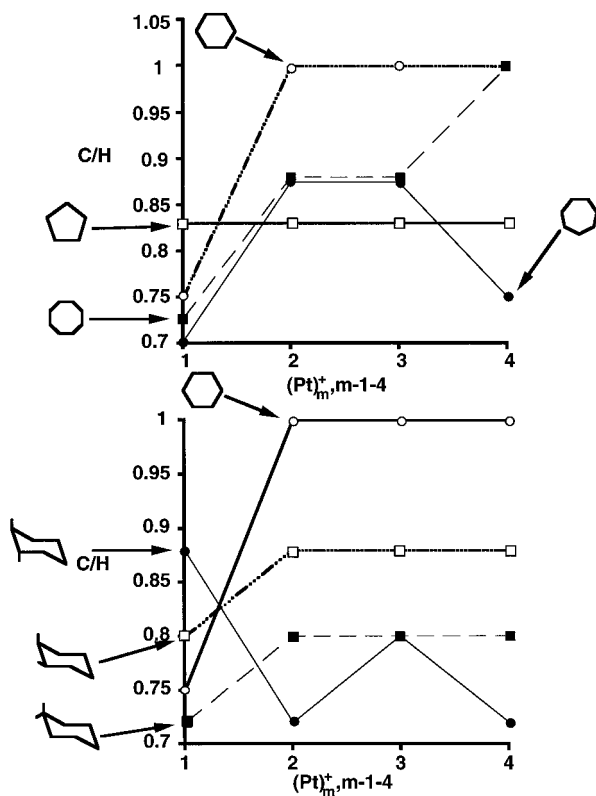| $(Pt_m)^+$	C_nH_{2n}	no. of ligands	total no. of H_2 lost
$m = 1$	$n = 5$	2	3; 4 (major)
$m = 1$	$n = 6$	2	4 (major); 5
$m = 1$	$n = 7$	2	4 (major); 5
$m = 1$	$n = 8$	2	4; 5
$m = 2$	$n = 5$	2	4
$m = 2$	$n = 6$	(0); [1]; 2	(0); [3]; 6
$m = 2$	$n = 7$	2	6
$m = 2$	$n = 8$	2	6; 7 (major)
$m = 3$	$n = 5$	(2); 3	(4); 6
$m = 3$	$n = 6$	2	5; 6 (major)
$m = 3$	$n = 7$	2	5; 6 (major)
$m = 3$	$n = 8$	2	6; 7 (major)
$m = 4$	$n = 5$	3	6
$m = 4$	$n = 6$	(2); 3	(6); 8; 9 (major)
$m = 4$	$n = 7$	3	7
$m = 4$	$n = 8$	2	8

Figure 5. Relative degree of dehydrogenation for various cyclic alkanes as a function of cluster size (see text). The higher the C/H ratio, the higher is the degree of dehydrogenation. The initial C/H ratios for the reactants are as follows: cyclopentane (0.5), cyclohexane (0.5), cycloheptane (0.5), cyclooctane (0.5), 1,2-*cis*-dimethylcyclohexane (0.57), 1,2-*trans*-dimethylcyclohexane (0.57), and 1,1-dimethylcyclohexane (0.5).

Each cyclopentane ligand chemisorbs to the metal cluster and loses two H_2, presumably to form cyclopentadiene. Each of the Pt_n^+ clusters except for Pt^+ dehydrogenates cyclohexane completely, presumably to produce benzene. Pt^+ dehydrogenates the first chemisorbed cyclohexane completely to yield C_6H_6; however, the second cyclohexane is left with either one double bond to yield C_6H_{10} or two double bonds to yield the much less abundant C_6H_8. The behavior of Pt^+ with cycloheptane is similar: the first cycloheptane loses three H_2 whereas the second cycloheptane does not. The larger Pt_n^+ clusters each eliminate three H_2 from each cycloheptane. An anomaly (see
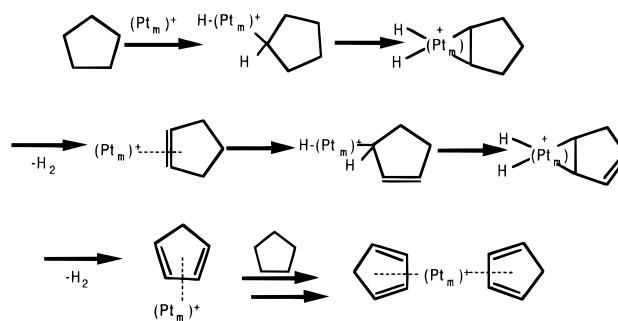
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Scheme 1

Figure 5) is Pt_4^+, which accepts one more C_7 ligand than any of the smaller Pt_n^+ clusters and eliminates only one H_2 from the third ligand. Therefore, the degree of dehydrogenation depends on the number of adsorbed ligands. Pt_4^+ is the only cluster cation that eliminates four H_2 from each of the chemisorbed C_8 ligands on reaction with cyclooctane. The other cluster cations do not readily dehydrogenate C_8H_{16} to C_8H_8, presumably due to the $4n$-electron antiaromatic character of the product.

In 1989, cyclohexene was detected as a reaction intermediate in the conversion of cyclohexane to benzene on the surface of solid Pt(111),[16] in support of the C−H bond insertion mechanism shown in Scheme 1 for the reaction of each of the small Pt_n^+ clusters with cyclopentane.

For Os^+, a different mechanism has been proposed for odd- and even-electron cases.[32] That behavior does not apply here because a ferrocene sandwich complex is most definitely not formed—only four H's, not the prerequisite five, are lost—since Pt^+ has two more electrons than Os^+. It is not so easy to conjecture about Pt_2^+, Pt_3^+, and Pt_4^+ without knowing their structures. Also, we cannot rule out other possible mechanisms (for example, allylic insertion followed by ring flip), until one face of each of the saturated cylic alkanes can be deuterated as Seemeyer et al. did with bare first-row transision metal ions (Sc^+−Zn^+).[33] Deuterating one side of each ring *all-cis*-cyclohexane-*1,2,3,4,5,6-d$_6$* proved to be a good probe for the presence of concerted syn elimination of H_2 (D_2).

Reactions of Pt_n^+ ($n = 1-4$) with Substituted Cyclohexanes. To demonstrate how ring substituents affect the Pt_n^+ chemistry, we reacted the platinum cluster ions with 1,2-*cis*-dimethylcyclohexane, 1,2-*trans*-dimethylcyclohexane, and 1,1-dimethylcyclohexane. The results of these complete reactions are listed in Table 2.

Once again, a C−H bond insertion mechanism is reasonable, as shown in Scheme 2 for the addition of the first 1,2-*cis*-dimethylcyclohexane ligand to Pt_4^+.

The reactivity of each of these substituted cyclohexanes as a function of degree of dehydrogenation is shown in the bottom of Figure 5. The degree of dehydrogenation increases from Pt^+ to Pt_2^+ and then levels off, except for 1,2-*trans*-dimethylcyclohexane, which exhibits minima for clusters with even numbers of platinums. Again, there is no sign of any C−C bond cleavage.
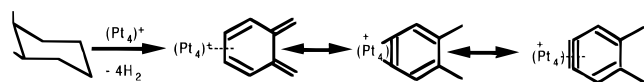
Reactions of Pt_n^+ ($n = 1-4$) with Benzene and Other Aromatic Hydrocarbons. The results of these complete reactions are summarized in Table 3 and Figure 6. The data for Figure 6 was generated using the same criteria as for the saturated cyclic hydrocarbons. The results of the reaction of benzene with each of the clusters are shown in Figure 7. Os^+,[32]

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Table 2. Reactions of Pt_n^+ ($n = 1-4$) with Substituted Cyclohexanes

$(Pt_m)^+$	reactant	no. of ligands	total no. of H_2 lost
$m = 1$	cyclohexane	2	4 (major); 5
$m = 1$	1,2-*cis*-dimethylcyclohexane	2	6
$m = 1$	1,2-*trans*-dimethylcyclohexane	2	6; 7
$m = 1$	1,1-dimethylcyclohexane	2	5
$m = 2$	cyclohexane	2	6
$m = 2$	1,2-*cis*-dimethylcyclohexane	2	6; 7
$m = 2$	1,2-*trans*-dimethylcyclohexane	2	5
$m = 2$	1,1-dimethylcyclohexane	2	6
$m = 3$	cyclohexane	2	5; 6 (major)
$m = 3$	1,2-*cis*-dimethylcyclohexane	2	6; 7
$m = 3$	1,2-*trans*-dimethylcyclohexane	2	6
$m = 3$	1,1-dimethylcyclohexane	2	5 (major); 6
$m = 4$	cyclohexane	3	8; 9
$m = 4$	1,2-*cis*-dimethylcyclohexane	2	7 (major); 8
$m = 4$	1,2-*trans*-dimethylcyclohexane	2	5 (major); 6
$m = 4$	1,1-dimethylcylohexane	2	5; 6 (major)

Scheme 2

Table 3. Reactions of Pt_n^+ ($n = 1-4$) with Benzene and Other Aromatic Hydrocarbons

$(Pt_m)^+$	reactant	no. of ligands	total no. of $H_2(F_2)$ lost
$m = 1$	benzene	(2); 3	(1); 2
$m = 1$	toluene	3	2
$m = 1$	*o*-xylene	2	2
$m = 1$	*m*-xylene	2	1; 2
$m = 1$	*p*-xylene	2	1; 2
$m = 1$	mesitylene	2	2
$m = 1$	hexafluorobenzene	2	0
$m = 2$	benzene	3	1
$m = 2$	toluene	3	3
$m = 2$	*o*-xylene	3	2
$m = 2$	*m*-xylene	3	3; 4
$m = 2$	*p*-xylene	3	3 (major); 4; 5
$m = 2$	mesitylene	1	2
$m = 2$	hexafluorobenzene	2	0
$m = 3$	benzene	4	2
$m = 3$	toluene	(3); 4	(3); 4 (major); 5
$m = 3$	*o*-xylene	3	3; 4 (major)
$m = 3$	*m*-xylene	2 (major); 3	1 (major); 3
$m = 3$	*p*-xylene	2 (major); 3	1 (major); 3
$m = 3$	mesitylene	2	2
$m = 3$	hexafluorobenzene	1	0
$m = 4$	benzene	5	3
$m = 4$	toluene	(1); [2]; 3	(2); [3]; 5
$m = 4$	*o*-xylene	3	3; 4 (major)
$m = 4$	*m*-xylene	4	5
$m = 4$	*p*-xylene	3	3; 4
$m = 4$	mesitylene	1	2
$m = 4$	hexafluorobenzene	0	0

Figure 6. Relative degree of dehydrogenation for various cyclic aromatic hydrocarbons as a function of cluster size (see text). The higher the C/H ratio, the higher the degree of dehydrogenation. The initial C/H ratios for the reactants are as follows: benzene (1.0), toluene (0.875), xylene (every isomer, 0.8), and mesitylene (0.75).

Sc^+,[10] Nb^+,[34,35] and Ta^+,[36,37] can each dehydrogenate benzene. Furthermore neutral niobium clusters,[38,39] niobium cluster ions,[40] and rhodium cluster ions, Rh_n^+ for $n < 19$,[26] also dehydrogenate benzene. Also, neutral platinum clusters, Pt_3-Pt_8, dehydrogenate benzene.[21] Here we see a trend similar to that for the niobium clusters. Neutral niobium clusters do not begin to dehydrogenate benzene until there are four niobium atoms in the cluster. Niobium cluster cations begin to dehydrogenate benzene when there are only three atoms in the cluster.[40] Similarly, lone platinum cations begin to dehydrogenate, whereas neutral platinum clusters do not begin to dehydrogenate benzene until there are three platinum atoms in the cluster.

Nothing in the reactions of the small platinum clusters with benzene, toluene, *p*-xylene, and *o*-xylene (see Table 3) suggests that anything other than the C−H bond insertion mechanism is occurring. The reaction of Pt^+ with benzene is shown in Scheme 3. From Figure 7a, the apparently stable product with two ligands and loss of one H_2 remains and the product with loss of two H_2 reacts further to physisorb another benzene ligand around the lone platinum cation. Fe^+ reacts with aromatic rings that have alkyl halide substituents to yield polyphenylene complexes[38,41,42] similar to those proposed in Scheme 3. However, that mechanistic picture does not hold up on examination of the reactions of the same Pt_n^+ clusters with *m*-xylene and mesitylene. For *m*-xylene, only one H_2 should be lost for each ligand chemisorbed—clearly not the case here for Pt_2^+ and Pt_4^+. Furthermore, it should be impossible for any H_2 to be lost from mesitylene. However, chemisorption for at least one of the ligands occurs for each of the clusters. Thus, these reactions clearly proceed by another mechanism. For example, the tropylium ion represents just one of many possible mechanistic routes. We propose to delineate the

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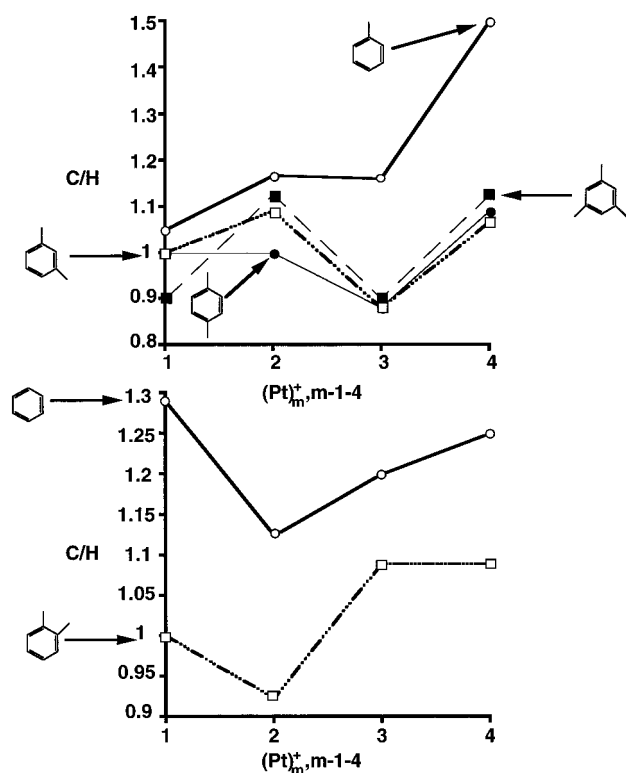(39) Zakin, M. R.; Cox, D. M.; Kaldor, A. *J. Phys. Chem.* **1987**, *91*, 5224−5228.

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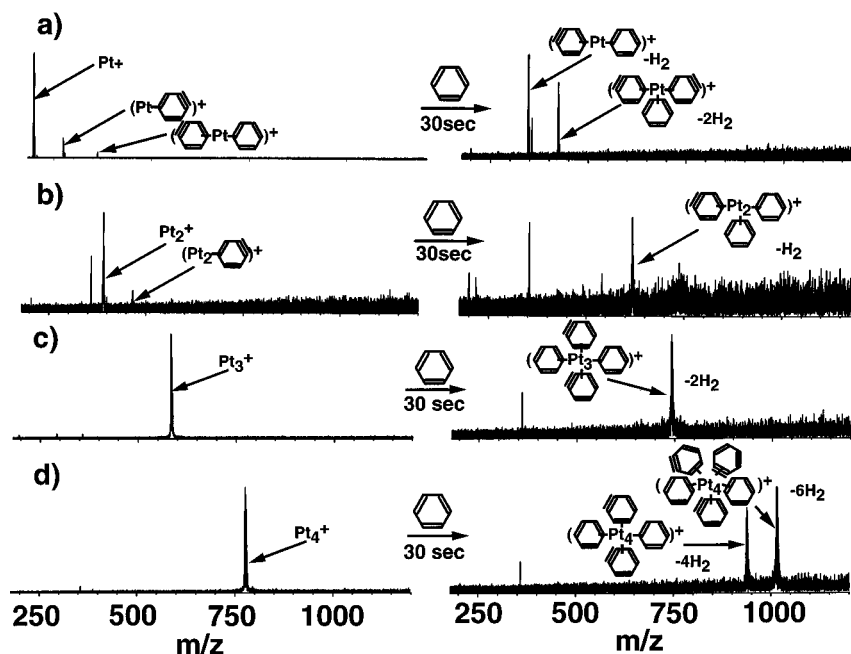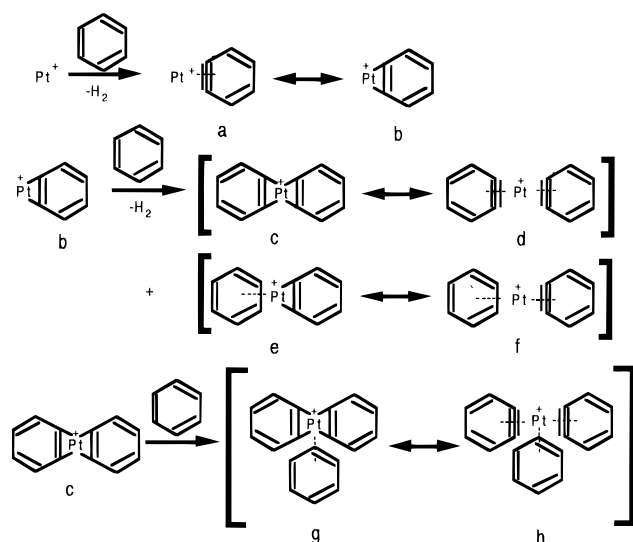(42) Bjarnason, A.; Taylor, J. W. *Organometallics* **1990**, *9*, 1493.

Figure 7. Reaction of (a) Pt$^+$, (b) Pt$_2^+$, (c) Pt$_3^+$, (d) Pt$_4^+$ with benzene. (left) FT-ICR mass spectra acquired after a 100 ms reaction period. (right) FT-ICR mass spectra acquired after the reaction was complete (30 s).

Scheme 3

mechanism in the future by deuterating these compounds at various sites to determine if ring or methyl hydrogens are lost.

In Figure 6, the reactivities of the Pt$_n^+$ cluster ions are again compared as a function of dehydrogenation of the final product. For toluene, *m*-xylene, *p*-xylene, and mesitylene (but not benzene or *o*-xylene), the even-platinum clusters are more efficient at dehydrogenation. For the reactions collected at the top of Figure 6, Pt$_4^+$ produces more complete dehydrogenation than does Pt$^+$. The final product of the reaction of benzene with Pt$^+$ (bottom of Figure 6) has a higher C/H ratio than the final product of the reaction of Pt$_4^+$ with benzene, in part because five benzene ligands are chemi- and physisorbed to the tetranuclear cluster cation, i.e., more than the number of ligands chemi- or physisorbed to any other cluster.

The hexafluorobenzene molecule offers a good example of physisorption. Due to the strength of the C–F bond, no loss of F$_2$ is found for any of the reactions. The only detected product results from physisorption of hexafluorobenzene to each of the small platinum clusters. Curiously, hexafluorobenzene does not physisorb to the Pt$_4^+$ cluster.

Reactions of gas-phase Pt$^+$ with benzene, toluene, *p*-xylene, and mesitylene[24] have previously been reported. El-Nakat et al. found different products for the reactions of the lone platinum cation after collisional cooling than when the ions were energetically "hot". In all cases, we observe essentially the same product ions that they found for their collisionally cooled ions. Our results may appear somewhat different because we let the reactions proceed more completely and we do not show the low-mass product ions (e.g., C$_6$H$_6^+$). A major difference between our results and those of El-Nakat et al. is that we never observe the small extent of lone H loss (e.g., PtC$_6$H$_5^+$ for the reaction with benzene) that they report for many of their reactions.

Conclusion

First, we have shown how to generate from Pt$_4$(PF$_3$)$_8$ small platinum cluster ions, Pt$_n^+$ ($n = 1–4$), under relatively gentle conditions. FT-ICR MS then provides for mass selection of a particular cluster for determination of pathways of ion–molecule reactions with saturated and unsaturated hydrocarbons. In preliminary work not shown here, we expect to be able to generate and isolate even larger clusters at higher magnetic field. Second, we find that not all of the gas-phase ion–molecule reactions of Pt$_n^+$ proceed by the C–H bond insertion mechanism. For the most part, the larger of the small Pt$_n^+$ clusters appear to more efficiently dehydrogenate cyclic hydrocarbons. However, the reactivity of a particular metal cluster is determined not only by the structure and stability of the cluster itself but by the structure and stability of the reagent molecule and the final product molecules. The extent of chemisorption and physisorption also appear to play a major role in the degree of dehydrogenation by these Pt$_n^+$ clusters. Future work will focus on site-specific deuterated reactant molecules as a probe of mechanistic pathways.