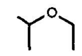
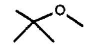
Table II. Diastereoselective Reaction with Cyclopentene-1,3-diol[a]

Entry	3 (R)	Yield, 6	6a : 6b [b]	($4a^2$: $4b^2$) [c]
1		71	86 : 14	(90 : 10)
2		83	98 : 2	(97 : 3)
3 [d]		42	99 : 1	(99 : 1)
4 [e]		41	>99 : 1	

[a] Conditions: $Pd(OAc)_2$ (0.1 equiv), Na_2CO_3 (1.5 equiv), MeCN at reflux for 24 h. [b] After deprotection with acid, isomers were separated by column chromatography. [c] See Table I. [d] The dehydrated enone was isolated in 10% yield. [e] $PdCl_2$ (0.05 equiv), AcONa (1.25 equiv), Bu_3N (0.3 equiv), DMF at 30 °C for 100 h.

methodology consists of a combination of diastereoselection and differentiation of a meso substrate. This combination resulting in high stereoselectivity may offer another highly efficient strategy for organic synthesis. The recognition of the prochiralities of meso substrates is a current topic of synthetic methodology for asymmetric reactions, wherein only differentiation of the enantiotopic groups is attempted.[15] Our result is the first example of the incorporation of new chiralities with differentiation of the prochirality in a meso structure.[16]

Acknowledgment. We thank the SC-NMR Laboratory of Okayama University for obtaining 500-MHz NMR spectra, and we are grateful for partial financial support by a Teijin Award in Synthetic Organic Chemistry, Japan, and a Grant-in-Aid for Scientific Research (No. 01649512) from the Ministry of Education, Science and Culture.

Supplementary Material Available: Experimental procedures and characterization data (IR, ^1H NMR, ^{13}C NMR, copies of 2D NMR spectra, HRMS, and COSY pulse sequence spectra) for **4** and **6** (22 pages). Ordering information is given on any current masthead page.

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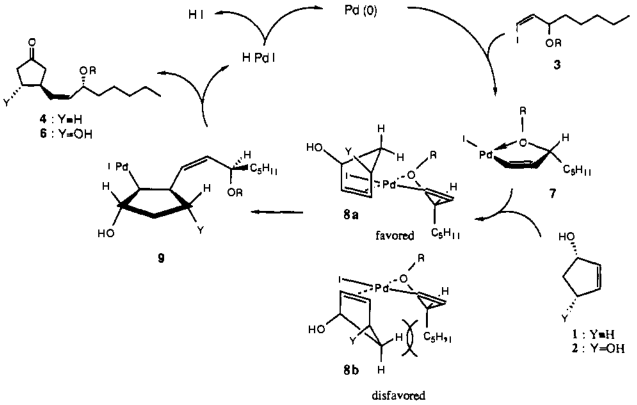
(16) Further investigations along this methodology are in progress. The following mechanism is plausible. In principle, insertion of olefin to alkenylpalladium takes place in cis fashion, and β-elimination of palladium hydride also proceeds by abstraction of the syn proton.[2-5] Thus, the alkenylpalladium species **7** generated by the oxidative addition of the alkenyl iodide **3** to Pd(0) undergoes insertion via the coordination from the less crowded face of the olefin of **1** and **2**. Therefore, the intermediate **8a** is favored for steric reasons. The alkylpalladium **9** collapses into **4** and **6** by picking up the syn proton.



Pulsed-Laser-Ionization High-Pressure Mass Spectrometry: A New Route to Gas-Phase Metal Ion-Ligand Thermochemistry

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Received July 31, 1989

The chemistry of bare metal ions and metal clusters has been the subject of extensive study with the advent of pulsed-laser ablation to generate gas-phase metal species. Using techniques of ion cyclotron resonance,[1,2] flowing afterglow,[3] and pulsed molecular beams,[4] many valuable insights into the dynamics of metal ion binding with neutral substrates has been realized. Despite these valuable efforts, relatively little absolute quantitative experimental data for metal ion-substrate binding energies has been obtained.

High-pressure mass spectrometry has previously been demonstrated as a precise method for obtaining ion-neutral clustering energetics.[5] In the present communication, we report the adaptation of pulsed-laser metal ion ablation to high-pressure mass spectrometry as a means of obtaining metal ion-ligand thermochemical data.

The modifications of a conventional high-pressure mass spectrometer system[6] to permit laser ionization experiments are shown in Figure 1. A Lumonics HyperEX 400 excimer laser operated at 308 nm (XeCl) was used to generate ions. Approximately 5 mJ of laser light (10-ns pulse width) was focused on a metal target mounted inside the gas-tight high-pressure region by a 5-cm lens mounted on the source housing. Metal ions generated by the laser pulse are rapidly thermalized by collisions (over 10^8 s^{-1}) with the flowing 5 Torr of buffer gas (typically Ar or N_2) present in the source. Ions diffuse slowly throughout the source under electric field free conditions until they either are discharged at the walls or exit through a 150-μm aperture into the main vacuum housing. The small fraction of ions that exit the ion source are focused, accelerated to 2 kV, and mass analyzed with a magnetic sector mass spectrometer. The laser pulse is also used to gate a multichannel analyzer, which then monitors the mass selected ion beam intensity as a function of ion residence time in the ion source. Intensities can be monitored for as long as 20 ms following the laser pulse before the ion signal decays to 0 as a result of diffusion to the walls. This time is sufficient for $>10^6$ collisions of ions with the bath gas to occur and ensures that the ions have reached thermal equilibrium with the bath gas. If small amounts of substrate with which the metal ions can either react or associate are added, the time evolution of these reaction products can also be readily monitored. If, at sufficiently long times, the time intensity profile of an ion and its association product become parallel, this is an indication that ion-molecule equilibrium has been established. From the steady state ion intensity ratio and the known substrate partial pressure, the clustering equilibrium constant may be calculated. A typical example of the establishment of metal ion-substrate clustering equilibrium is shown in Figure 2a for aluminum ions generated in a 150 °C bath of N_2 to which a small amount of acetone is added. After <1 ms, the intensities of $[Al(CH_3COCH_3)]^+$ and $[Al(CH_3COCH_3)_2]^+$ become parallel. The intensity of Al^+ has decayed rapidly to 0

[†] A. P. Sloan Foundation Fellow, 1988-1990.

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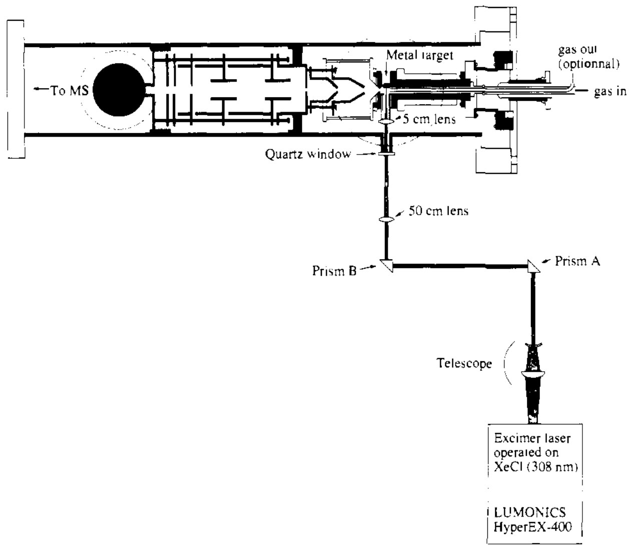


Figure 1. Schematic diagram of the laser-ablation/ionization high-pressure mass spectrometer.

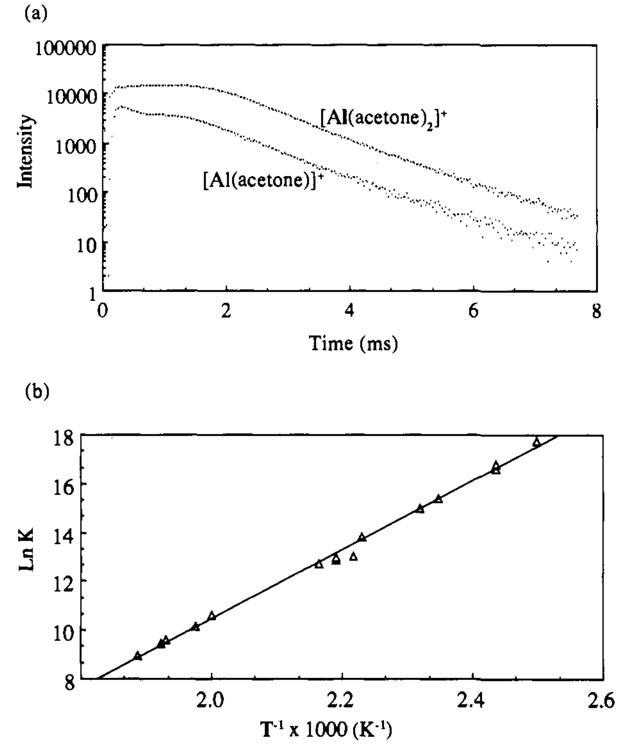
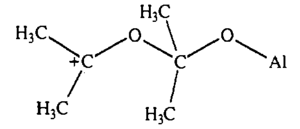


Figure 2. (a) Ion intensity profiles as a function of time after a 5-ns laser pulse. Data shown is the result of 300 laser pulses. (b) Van't Hoff plot of ln K vs $1/T$ used to obtain $\Delta H°$ and $\Delta S°$ for the clustering of Al$^+$ on to acetone.

since the binding of Al$^+$ to the first acetone is too strong to allow back dissociation to occur rapidly enough for equilibrium to be established at this temperature. However, the addition of the second acetone can be readily observed to achieve equilibrium. If this equilibrium is examined as a function of the ion source temperature, a plot of ln K_{eq} vs $1/T$ (van't Hoff plot) yields a slope of $-\Delta H°/R$ and intercept $\Delta S°/R$. In this way, the binding enthalpy of the second acetone to Al$^+$ is determined to be −26 ± 1 kcal/mol and the entropy of association is −45 ± 3 cal mol^{-1} K^{-1} (Figure 2b). The magnitude of this entropy change provides direct information concerning the nature of the bonding in the ion. For most simple clustering reactions, entropy changes of −25 ± 2 cal mol^{-1} K^{-1} are observed;[7] the value obtained here indicates that the cluster ion produced is of considerably lower entropy than expected. This is a result of restrictions of internal rotations of the complex. A logical conclusion is that an ion of structure I is being produced rather than one of structure II, which should have considerably greater freedom of internal rotation.[8] A similar phenomenon has been observed in the clustering of methylated acetone onto acetone. Future work will exploit the generality of metal ion production by laser ablation to carry out systematic studies of metal ion–substrate thermochemistry.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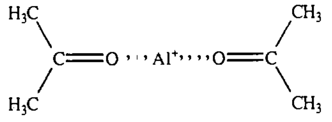
II

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[8] Models indicate that structure I will have considerable steric hindrance to internal rotation whereas structure II will have virtually free rotation.

Stereogenic (Chiral) Methyl Groups: Determination of Configuration by Direct Tritium Nuclear Magnetic Resonance Spectroscopy

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Received August 7, 1989

Since the original demonstration by Cornforth, Arigoni, and their co-workers,[1–3] compounds containing stereogenic[4] (so-called chiral) methyl groups, i.e., CHDT groups, have been used to study the stereochemistry of numerous biochemical (enzymatic) reactions.[5–12] The present methods for determining the configuration and enantiomeric excess of stereogenic methyl groups all involve processes in which one hydrogen is removed from the methyl group, generally by an enzymatic reaction. These methods usually depend on a kinetic isotope effect that results in the slower breaking of a C–D than a C–H bond[5,6] with the consequent formation of a tritium-labeled methylene group whose configuration can then be determined either by radioactive assays in conjunction with enzymatic or chemical techniques or, alterna-

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