methylene group.[9] In contrast, in the $^2B_1$ state of TMM$^{\bullet+}$, to which the $\pi$ state of MCP$^{\bullet+}$ opens, the odd electron occupies the $2b_1$ nonbonding MO, which is largely localized on what was the exocyclic methylene group, and the positive charge is largely delocalized between C-2 and C-3. The necessity of moving the positive charge away from the diarylmethylene group in the ring opening of 6$^{\bullet+}$ would certainly tend to make the reaction less exothermic in this substituted radical cation than in the parent MCP$^{\bullet+}$.[32]

The aryl substituents in 6$^{\bullet+}$ should also tend to raise the activation energy for disrotatory ring opening. The existence of the $2b_1$ nonbonding MO in TMM$^{\bullet+}$ is what distinguishes the orbital symmetry allowed, disrotatory ring opening of the $\pi$ state of MCP$^{\bullet+}$ from the symmetry-forbidden, disrotatory ring opening of the cyclopropyl radical, where the $2b_1$ orbital of the reactant becomes the antibonding $2b_1$ MO of the allyl radical.[12,33] The availability of $2b_1$ in TMM$^{\bullet+}$ thus makes the disrotatory ring opening of the lowest $\pi$ state of MCP$^{\bullet+}$ very much like the analogous, orbital symmetry allowed reaction of the cyclopropyl cation.

To the extent that the aryl substituents in 6$^{\bullet+}$ cause the $\pi$ electron distribution in the lowest state of this radical cation to resemble that in the cyclopropyl radical more than that in the cyclopropyl cation, the activation energy for ring opening of 6$^{\bullet+}$ should be greater than that of the parent MCP$^{\bullet+}$.

## Conclusions

Our ab initio calculations on MCP$^{\bullet+}$ radical cation predict ring opening to TMM$^{\bullet+}$ to be exothermic from both the $^2B_1$ $\pi$ ground state and the $^2A_1$ $\sigma$ state of MCP$^{\bullet+}$. Disrotatory ring opening is computed to require an activation energy of about 2 kcal/mol from the $\pi$ state but to proceed without activation from the $\sigma$ state.

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(32) Of course, following disrotatory ring opening to $^2B_1$, pseudorotation of the TMM$^{\bullet+}$ to $^2A_2$ could occur. Pseudorotation from $^2B_1$ to $^2A_2$ should be thermodynamically favorable in the TMM$^{\bullet+}$ formed from 6$^{\bullet+}$, since the positive charge in $^2A_2$ is largely localized at the aryl-substituted methylene group.

(33) Longuet-Higgins, H. C. Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045.

Conrotatory ring opening of the $\pi$ state is forbidden by orbital symmetry and, hence, is expected to require a much larger activation energy. Conrotatory opening of the $\sigma$ state is allowed and is calculated to require an activation energy of about 4 kcal/mol. Therefore, ring opening is predicted to occur by a disrotatory pathway for both states.

ASSEFAPC CI calculations indicate that the $^2B_1$ and $^2A_2$ states of TMM$^{\bullet+}$ have nearly the same energy. Thus, pseudorotation in TMM$^{\bullet+}$ is predicted to be facile, and the EPR spectrum on TMM$^{\bullet+}$ should show all three methylene groups to be equivalent, except perhaps at very low temperatures. Rotation of one methylene group out of conjugation is computed to be unfavorable for both $^2B_1$ and $^2A_2$ but especially unfavorable for $^2A_2$.

Calculations have not been performed on the radical cations formed from 5 and 6, which have been studied experimentally.[8–10] Nevertheless, the ring opening observed in 5$^{\bullet+}$ is readily explicable if the aryl substituents on the ring confer a $\sigma$ ground state on this radical cation. The TMM$^{\bullet+}$ radical cation formed from 5$^{\bullet+}$ would not be expected to reclose to 6$^{\bullet+}$, and back electron transfer to form the lowest singlet state of the neutral TMM should afford 5 instead of 6, thus rationalizing the failure of 5 to form 6 after photoionization.

Finally, the failure of 6$^{\bullet+}$ to undergo ring opening may be understood on the basis of the experimentally observed localization of the positive charge in the diarylmethylene group.[9] This type of localization is expected to make ring opening in the $^2B_1$ state of the corresponding TMM$^{\bullet+}$ less thermodynamically favorable than in the parent system. Moreover, localization of the unpaired electron on the ring carbon is anticipated to result in a higher activation energy for disrotatory ring opening in 6$^{\bullet+}$ than in the parent MCP$^+$.

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# Reactions of Atomic Gold Ions with Aliphatic and Aromatic Hydrocarbons and Alkyl Halides

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**Abstract:** The reactions of gold cations with aliphatic and aromatic hydrocarbons have been studied by using Fourier transform mass spectrometry. Hydride abstraction is the major reaction channel with alkanes larger than ethane. With larger alkanes, hydride abstraction by Au$^+$ generates internally excited alkyl cations which fragment in competition with collisional stabilization. A minor pathway involving C–H insertion followed by $\beta$-hydrogen migration leads to dehydrogenation. Generation of reactive gold carbene (AuCH$_2^+$) from methyl halides and methide and hydride abstraction studies allows estimation of lower limits for Au$^+$–CH$_2$, Au–CH$_3$, and Au–H bond dissociation energies ($D$(Au$^+$–CH$_2$) $\geq$ 95.0 kcal/mol, $D$(Au–CH$_3$) $\geq$ 45.8 kcal/mol, and $D$(Au–H) > 67 kcal/mol). Au$^-$ undergoes slow $S_N2$ displacement reactions with methyl halides. With CCl$_4$ and CHCl$_3$, Au$^-$ yields AuCl$_2^-$ ion, allowing estimation of the lower limit of bond dissociation energy, $D°$(Au$^-$–2Cl) $\geq$ 162.6 kcal/mol. Generation of AuCBr$_2^-$ from CHBr$_3$ appears to be the first observation of a gas-phase anionic metal carbene.

The challenge of understanding C–H and C–C bond activation by transition metals has prompted a great deal of interest in such reactions over the past several years. Development of novel ion sources[1,2] and new mass spectrometric techniques[3–5] have yielded

a variety of fundamental thermodynamic, kinetic, and mechanistic information about gas-phase transition metal ion reactions.[7–11]

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(1) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235–1238.

Selective cleavage of C–H and C–C bonds in alkanes was demonstrated by Beauchamp and co-workers.[6] Dehydrogenation of linear alkanes is observed in reactions with $Sc^+$, $Ti^+$, and $V^+$, whereas $Fe^+$, $Co^+$, and $Ni^+$ demethanate these compounds. The simplest mechanism which has been suggested involves initial oxidative addition of a metal ion across a C–C or C–H bond, followed by $\beta$-hydrogen migration to the metal and reductive elimination of either an alkane or hydrogen. The concept of promotion energy was introduced by Armentrout and Beauchamp,[12] and Babinec and Allison[13] to explain the reactivity trends among first-row transition metal ions.

Although first-row transition metals have been studied extensively, third-row metals, particularly Au, have received little attention. Benninghoven and co-workers[14] observed incidental gold cationization [M + Au⁺] during secondary ion mass spectrometry (SIMS) using gold substrates. Employing gold electrodes,[15] ion-molecule reactions of Au⁺ are also reported to occur during spark source mass spectrometry. McLafferty and co-workers have reported observation of gold cluster ions during cesium SIMS studies by Fourier transform mass spectrometry (FTMS).[14b] In an earlier paper, the first systematic study of gas-phase reactions of gold, copper, and silver ions with alcohols was reported.[16a] In a low-pressure single-collision experiment, Cu⁺ was reported[16b,c] to be unreactive with alkanes. However, Tonkyn and Weisshaar[10b] recently observed a rapid reaction of Cu⁺ with ethane at 1 torr of He pressure in a fast flow reactor. Activation of allylic carbon–carbon bonds by Cu⁺ also was reported recently.[16d] Cassady and Freiser[16c] have demonstrated that copper and silver ions react with methyl nitrite by oxidative addition to the weak $CH_3O$–NO bond. Interestingly, one of the primary products of Cu⁺ reaction, $Cu(OCH_2)^+$, undergoes successive secondary, tertiary, and quaternary reactions with methyl nitrite producing an 18-electron $Cu(OCH_2)_4^+$ species as the final product.

Here, the gas-phase reactions of laser-desorbed gold cation with various aliphatic and aromatic hydrocarbons and alkyl halides
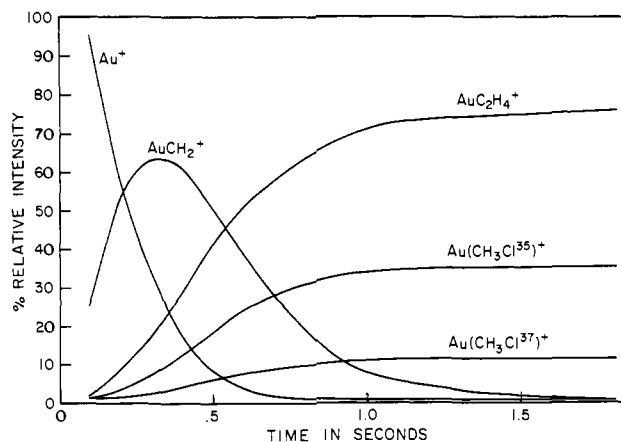


**Figure 1.** Ion intensities as percent of total ion current of gold cations and ionic reaction products as a function of time, with $CH_3Cl$, $P(CH_3Cl) = 1.0 \times 10^{-7}$ torr.

are examined. The lower limits of bond dissociation energies of Au–$CH_3$, Au–H, Au–Cl, Au–Br, Au⁺–$CH_2$, and other gold cation–ligands have been estimated from the observed reactions. In addition, reactions of the relatively inert anion, Au⁻, are reported.

## Experimental Section

The present studies were carried out using a Nicolet FTMS-1000 mass spectrometer and the technique of Fourier transform mass spectrometry which has been described in detail elsewhere.[17] The instrument is equipped with a 5.08-cm cubic trapping cell and a 3.0-T superconducting solenoid.[18] Positive or negative metal ions were generated by focusing the beam of a Tachisto 215 G pulsed TEA $CO_2$ laser through a zinc selenide lens onto a probe tip coated with metallic films or salts of interest. The laser delivered approximately 0.3–0.4 J per 40-ns pulse at 10.6 μm. Power density at the probe tip was in the range of $10^8$–$10^9$ W/cm². Positive or negative ions were retained in the cell by applying a potential of +1 or –1 V, respectively, to the trap plates.

In a typical experiment sequence, metal ions were formed by triggering the laser with the FTMS filament off. Following the ion formation laser pulse, typically after a 100-ms delay, all ions except for the metal cation or anion of interest were ejected from the cell by application of two radiofrequency ejection sweeps. Ions were then trapped in the cell for variable times (from a few milliseconds to several seconds) to allow ion-molecule reactions with the selected neutral reagent gas. Typical reagent pressure was ca. $10^{-7}$ torr. Ionic reaction products were detected and reaction pathways confirmed by standard double resonance methods.[19] Additional ejection sequences were also employed to isolate products of ion-molecule reactions for further study.

**Chemicals.** Gold film was made by depositing a few drops of "Liquid Bright Gold", a commercial solution distributed by Hanovia (East Hanover, NJ), on the probe tip. After the mixture was dried for 5–10 min, the probe tip was heated to 500 °C, resulting in formation of a gold film. Gas and liquid reagents used were purchased from commercial sources (Liquid Carbonics, Matheson, and Aldrich). Deuterated ethylbenzene ($C_6D_5CD_3$, 99.5%) was obtained from Aldrich. The reagents were used as supplied except for application of multiple freeze–pump–thaw cycles to remove noncondensable gases. Pressure measurements were made with an uncalibrated Granville-Phillips ion gauge.

## Results and Discussion

Ion–molecule reactions and product data for Au⁺ are summarized in Table I. A typical pseudo-first-order decay plot for reaction of Au⁺ with $CH_3Cl$ is shown in Figure 1. The branching

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**Table I.** Summary of Product Data for the Ion–Molecule Reactions of $Au^+$

| ion + neutral reactants | primary products [assumed neutral] | secondary[a] products | fraction of product ion signal | estimated bond energy limit (kcal/mol) |
|---|---|---|---|---|
| $Au^+ + CH_4$ | → no reaction | | | |
| $Au^+ + CH_3CH_3$ | → $AuC_2H_4^+$ [+ $H_2$] | | 1.00 | $D°(Au^+-C_2H_4) > 32.7$ |
| $Au^+ + CH_3CH_2CH_3$ | → $C_3H_7^+$ [+ AuH] | | 0.93 | $D°(Au-H) > 54.3$ |
|  | → $AuC_3H_6^+$ [+ $H_2$] | | 0.07 | |
| $Au^+ + (CH_3)_3CH$ | → $(CH_3)_3C^+$ [+ AuH] | | 0.99 | $D°(Au-H) > 56$ |
|  | → $AuC_4H_8^+$ [+ $H_2$] | | 0.01 | |
| $Au^+ + (CH_3)_4C$ | → $(CH_3)_3C^+$ [+ $AuCH_3$] | | 1.00 | $D°(Au-CH_3) > 31$ |
| $Au^+ + CH_3(CH_2)_3CH_3$ | → $C_5H_{11}^+$ [+ AuH] | $C_3H_7^{+*}$ | 0.99 | |
|  | → $AuC_5H_{10}^+$ [+ $H_2$] | | 0.01 | |
| $Au^+ + CH_3(CH_2)_4CH_3$ | → $C_6H_{13}^+$ [+ AuH] | $C_3H_7^{+*}$, $C_4H_9^{+*}$ | 0.99 | |
|  | → $AuC_6H_{12}^+$ [+ $H_2$] | | 0.01 | |
| $Au^+ + CH_3(CH_2)_5CH_3$ | → $C_7H_{15}^+$ [+ AuH] | $C_4H_9^{+*}$ | 0.99 | |
|  | → $AuC_7H_{14}^+$ [+ $H_2$] | | 0.01 | |
| $Au^+ + c\text{-}C_3H_6$ | → $C_3H_5^+$ [+ AuH] | $C_4H_7^{+*}$ | 0.73 | |
|  | → Au⁺ (cyclobutane structure) | | 0.27 | |
| $Au^+ + c\text{-}C_5H_{10}$ | → $C_5H_9^+$ [+ AuH] | | 0.98 | $D°(Au-H) > 61.7$ |
|  | → Au⁺ (cyclopentane structure) | | 0.01 | |
|  | → $Au^+$—(structure) [+ $H_2$] | | 0.01 | |
| $Au^+ +$ (benzene/cyclohexane ring) | → $C_6H_{11}^+$ [+ AuH] | | 0.99 | $D°(Au-H) > 60.4$ |
|  | → $Au^+$ [+ $H_2$] | | 0.01 | |
| $Au^+ + CH_2{=}CH_2$ | → $AuC_2H_4^+$ | $AuC_4H_8^+$ | 1.00 | |
| $Au^+ + CH_3CH{=}CH_2$ | → $C_3H_5^+$ [+ AuH] | $C_4H_7^+$ | 0.85 | $D°(Au-H) > 62.9$ |
|  | → $AuC_3H_6^+$ | $AuC_6H_{12}^+$ | 0.15 | |
| $Au^+ + C_6H_6$ | → $C_6H_6^+$ [+ Au] | | 0.06 | |
|  | → $AuC_6H_6^+$ | $Au^+(C_6H_6)_2^+$ | 0.94 | |
| $Au^+ + C_6H_5CH_3$ | → $C_{H5}CH_3^+$ | | 0.83 | |
|  | → $C_7H_7^+$ [+ AuH] | | 0.16 | $D°(Au-H) > 54.8$ |
|  | → $AuC_7H_8^+$ | | 0.01 | |
| $Au^+ + C_6H_5CH_2CH_3$ | → $C_6H_5CH_2^+$ [+ $AuCH_3$] | | 0.02 | $D°(Au-CH_3) > 38.6$ |
|  | → $C_6H_5C_2H_5^+$ [+ Au] | | 0.41 | |
|  | → $C_6H_5C_2H_4$ [+ AuH] | | 0.41 | |
|  | → $AuC_2H_4^+$ [+ $C_6H_6$] | | 0.08 | |
|  | → $AuC_6H_6^+$ [+ $AuC_2H_4$] | | 0.05 | |
|  | → $AuC_8H_{10}^+$ | | 0.03 | |
| $Au^+ + CH_3Cl$ | → $AuCH_2^+$ [+ HCl] | $AuC_2H_4^+$, $AuC_2H_4(CH_3Cl)^+$ | 0.94 | $D°(Au^+-CH_2) > 89.6$ |
|  | → $Au(CH_3Cl)^+$ | $Au(CH_3Cl)_2^+$ | 0.06 | |
| $Au^+ + CH_3Br$ | → $AuCH_2^+$ [+ HBr] | $AuC_2H_4^+$, $AuC_2H_4(CH_3Br)^+$ | 0.70 | $D°(Au^+-CH_2) > 92.4$ |
|  | → $Au(CH_3Br)^+$ | $Au(CH_3Br)_2^+$ | 0.29 | |
|  | → $H_2CBr^+$ [+ AuH] | | 0.01 | $D°(Au-H) > 66.8$ |
| $Au^+ + CH_3I$ | → $AuCH_2^+$ [+ HI] | | 0.06 | $D°(Au^+-CH_2) \geq 95.0$ |
|  | → $AuCH_3^+$ [+ I] | | 0.21 | $D°(Au^+-CH_3) > 56$ |
|  | → $Au(CH_3I)^+$ | | 0.11 | |
|  | → $AuI^+$ [+ $CH_3$] | | 0.52 | $D°(Au^+-I) > 56$ |
|  | → $CH_2I^+$ [+ AuH] | | 0.10 | $D°(Au-H) > 65.9$ |
| $Au^+ + CH_3CN$ | → $Au(CH_3CN)^+$ | $Au(CH_3CN)_2^+$ | 1.00 | |
| $Au^+ + CHBr_3$ | → $CHBr_2^+$ [+ AuBr] | | 1.00 | $D°(Au-Br) > 36.3$ |
| $Au^+ + CCl_4$ | → $CCl_3^+$ [+ AuCl] | | 1.00 | $D°(Au-Cl) > 60.2$ |

[a] Secondary products with asterisk are unimolecular decomposition products.

ratios for the product forming channels are obtained directly from the relative product ion signals measured by the mass spectrometer. Before dealing with any specific chemical reaction, a few general observations may be made about the overall reactivity of $Au^+$.

Two types of reaction products, hydride abstraction and dehydrogenation, predominate in the ion–molecule reactions of $Au^+$ with both linear and cyclic alkanes. Hydride abstraction is the primary reaction for alkanes other than methane and ethane. This requires that the enthalpy ($\Delta H = -D(Au-H) - IP(Au) + IP(R) + D(R-H)$) of reaction 1 be exothermic. The strong Au–H

$$Au^+ + RH \rightarrow AuH + R^+ \qquad (1)$$
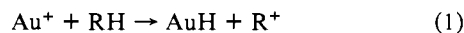
bond ($D(Au-H) = 71 \pm 3$ kcal/mol)[16,20] and high ionization potential of gold, $(IP(Au) = 212.7$ kcal/mol)[21] make hydride

(20) Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4385–4390.
(21) Levin, R. D.; Lias, S. G. NSRDS-NBS 71; National Bureau of Standards: Washington, D.C., 1982.

abstraction the dominant reaction process.

**Reactions of $Au^+$ with Linear Alkanes.** The simplest hydrocarbon, methane, is unreactive with $Au^+$. However, gold cations slowly dehydrogenate ethane and produce $AuC_2H_4^+$ with $m/z$ 225 (reaction 2). Hydride abstraction from ethane is endothermic by $\sim 4$ kcal/mol and is not observed.

$$Au^+ + CH_3CH_3 \begin{array}{l} \xrightarrow{1.00} AuC_2H_4^+ + H_2 \\ \xrightarrow{\times} C_2H_5^+ + AuH \quad \Delta H = +4 \text{ kcal/mol} \end{array} \qquad (2)$$

$AuC_2H_4^+$ may also be generated by the reaction of $Au^+$ with ethylene (reaction 3). The secondary reaction of $AuC_2H_4^+$ with ethylene produces $AuC_4H_8^+$ with $m/z$ 253 (eq 4).

$$Au^+ + CH_2{=}CH_2 \rightarrow AuC_2H_4^+ \qquad (3)$$

$$AuC_2H_4^+ + CH_2{=}CH_2 \rightarrow AuC_4H_8^+ \qquad (m/z\ 253) \quad (4)$$

**Scheme I**

$$Au^+ + CH_3\text{-}CH_3 \longrightarrow H\text{-}Au^+\text{-}CH_2CH_3 \longrightarrow$$

$$\left[\begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} Au^+\text{-}\begin{array}{c} CH_2 \\ || \\ CH_2 \end{array}\right] \xrightarrow{-H_2} Au^+\text{-}\begin{array}{c} CH_2 \\ || \\ CH_2 \end{array}$$

Specific ligand displacement reactions of $AuC_2H_4^+$ (reactions 5 and 6) suggest that $C_2H_4$ is a $\pi$-bonded ethylene ligand which

$$AuC_2H_4^+ + CH_3CN \rightarrow Au(CH_3CN)^+ + C_2H_4 \qquad (5)$$

$$AuC_2H_4^+ + C_6H_6 \rightarrow AuC_6H_6^+ + C_2H_4 \qquad (6)$$

can be displaced by more strongly bound ligands such as acetonitrile and benzene. This implies that $D°(Au^+\text{-}C_6H_6)$, $D°\text{-}(Au^+\text{-}(CH_3CN)) > D°(Au^+\text{-}C_2H_4)$. The occurrence of the exothermic reaction 2 to yield a gold–ethylene complex ion suggests that $D°(Au^+\text{-}C_2H_4) > 33$ kcal/mol.[22] This value can be compared to $D°(Co^+\text{-}C_2H_4) = 37 \pm 2$ kcal/mol determined by Armentrout and Beauchamp for the analogous cobalt complex.[23]

The initial step in the dehydrogenation of ethane appears to be metal insertion into a C–H bond, followed by a $\beta$-hydride shift and reductive elimination of $H_2$. This is illustrated in Scheme I and explains how gold–ethylene complex ion is produced from the reaction of $Au^+$ and ethane.
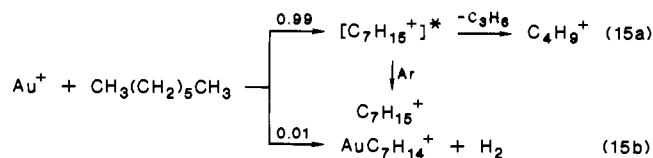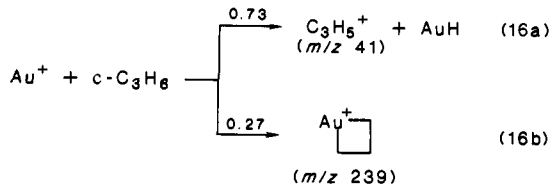
With propane, two reaction products, corresponding to hydride abstraction and dehydrogenation, are observed (reactions 7a and 7b). The major reaction product with $m/z$ 43 is probably an

$$Au^+ + CH_3CH_2CH_3 \longrightarrow \begin{cases} \xrightarrow{0.93} CH_3C^+HCH_3 + AuH \quad (7a) \\ \qquad\qquad (m/z\ 43) \\ \\ \xrightarrow{0.07} AuC_3H_6^+ + H_2 \qquad (7b) \\ \qquad\qquad (m/z\ 239) \end{cases}$$

isopropyl cation, since hydride transfer from the terminal methyl group of propane is endothermic by $\sim +2.2$ kcal/mol. $AuC_3H_6^+$ may also be generated from the reaction of $Au^+$ with propylene (reaction 8b). However, the major reaction channel of $Au^+$ with

$$Au^+ + CH_3CH=CH_2 \longrightarrow \begin{cases} \xrightarrow{0.85} {}^+CH_2CH=CH_2 + AuH \quad (8a) \\ \qquad\qquad \updownarrow \\ \qquad CH_2=CHCH_2^+ \\ \\ \xrightarrow{0.15} AuC_3H_6^+ \qquad\qquad (8b) \end{cases}$$

propylene is hydride abstraction, yielding allyl cation, $C_3H_5^+$, which undergoes a secondary reaction with propylene and produces $C_4H_7^+$ ion (reaction 9). $AuC_3H_6^+$, produced in reactions 7b and

$$C_3H_5^+ + CH_3CH=CH_2 \xrightarrow{-C_2H_4} C_4H_7^+ \qquad (9)$$

8b, might have one of several isomeric structures, including gold–propylene (a), allyl gold hydride cation (b), or the metallocyclobutane structure (c) Byrd and Freiser[9b] noted that ob-

$$Au^+\text{-}\!\!\parallel\!\!\diagdown \qquad Au^+\text{-}\!\!\overset{H}{\underset{\diagdown\!\!>}{|}} \qquad Au^+\!\!\overset{\square}{|}$$

      a            b             c

servation of H/D exchanges with $MC_3H_6^+$ in the presence of excess of $D_2$ is a characteristic of complexes possessing the allyl hydride structure. $AuC_3H_6^+$ is found to be unreactive with either $D_2$ or $CD_4$. Displacement of $C_3H_6$ by benzene is not observed under our experimental conditions (reaction 10). However,

$$AuC_3H_6^+ + C_6H_6 \rightarrow AuC_6H_6^+ + C_3H_6 \qquad (10)$$

propylene does react with the gold–benzene complex ion, formed directly from reaction of $Au^+$ with benzene, to yield $AuC_3H_6^+$ and $C_3H_6Au^+\text{-}C_6H_6$, reactions 11a and 11b, respectively.

$$AuC_6H_6^+ + CH_3CH=CH_2 \longrightarrow \begin{cases} \xrightarrow{} AuC_3H_6^+ + C_6H_6 \quad (11a) \\ \qquad\qquad (m/z\ 239) \\ \\ \xrightarrow{} C_3H_6AuC_6H_6^+ \qquad (11b) \\ \qquad\qquad (m/z\ 317) \end{cases}$$

$AuC_3H_6^+$ ions react rapidly with deuterated isopropyl alcohol to yield exclusively $((CD_3)_2CO)AuC_3H_6^+$ ion with $m/z$ 303, reaction 12. Since neither H/D exchanges nor HD loss are observed

$$AuC_3H_6^+ + DO\!-\!\overset{\displaystyle CD_3}{\underset{\displaystyle CD_3}{\overset{|}{\underset{|}{C}}}}\!-\!D \xrightarrow{-D_2} ((CD_3)_2CO)AuC_3H_6^+ \quad (12)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (m/z\ 303)$$

in reaction 12, it is unlikely that allyl hydride cation (b) is the structure of $AuC_3H_6^+$. This result, and the nonoccurrence of the ligand displacement reaction 10 suggests that $AuC_3H_6^+$ might possess the metallocyclobutane structure c.

Gold cation reacts with pentane according to reactions 13a, 13b, and 13c to produce primary reaction products $C_5H_{11}^+$ ($m/z$ 71) and $AuC_5H_{10}^+$ ($m/z$ 267) formed by hydride transfer and dehydrogenation. Hydride transfer (the major pathway) occurs in

$$Au^+ + CH_3(CH_2)_3CH_3 \longrightarrow \begin{cases} \xrightarrow{0.01} AuC_5H_{10}^+ + H_2 \qquad\qquad (13a) \\ \\ \xrightarrow{0.99} [C_5H_{11}^+]^* \longrightarrow C_3H_7^+ + C_2H_4 \ (13b) \\ \qquad\qquad\quad \downarrow M \\ \qquad\qquad\quad C_5H_{11}^+ \ (M = pentane) \ (13c) \end{cases}$$

many systems.[28] The initial pentyl cation in reactions 13b and 13c may have excess internal energy and could undergo either isomerization (1,2-hydrogen shift or skeletal rearrangement) or a number of collisions with neutral pentane to achieve collisional stabilization, prior to decomposition. Analogous processes were observed with higher alkanes such as hexane and heptane, and both were examined in the presence of excess argon.

Reaction of $Au^+$ ions with hexane occurs almost exclusively by hydride transfer and hydride transfer induced fragmentation, reaction 14a. No fragmentation products ($C_3H_7^+$ and $C_4H_9^+$)

$$Au^+ + C_6H_{14} \longrightarrow \begin{cases} \xrightarrow{0.99} [C_6H_{13}^+]^* \longrightarrow \begin{cases} \xrightarrow{-C_3H_6} C_3H_7^+ \qquad (14a) \\ \xrightarrow{M} C_6H_{13}^+ \ (M = hexane \\ \qquad\qquad\qquad and\ argon) \\ \xrightarrow{-C_2H_4} C_4H_9^+ \end{cases} \\ \\ \xrightarrow{0.01} AuC_6H_{12}^+ + H_2 \qquad\qquad (14b) \end{cases}$$

are observed when the pressure of the system is increased from $1 \times 10^{-7}$ to $2 \times 10^{-6}$ torr with argon. This significant pressure quenching might indicate the presence of internally excited $C_6H_{13}^+$ ions. Collision-induced dissociation of stabilized hexyl cation ($C_6H_{13}^+$) at $2 \times 10^{-6}$ torr argon pressure yielded the same two products $C_3H_7^+$ (major) and $C_4H_9^+$ (minor) observed in reaction 14a. Houriet et al.[24] also noted that hexyl cation formed by hydride abstraction decomposes to form fragment alkyl ions $C_3H_7^+$ and $C_4H_9^+$ by loss of the olefin molecules $C_3H_6$ and $C_2H_4$, respectively.

With $n$-heptane, heptyl cations are not observed under normal experimental conditions (pressure $\sim 10^{-7}$ torr of heptane). The major reaction product observed in this reaction is $C_4H_9^+$ (reaction 15a). When the pressure of the system is increased from $10^{-7}$ to $2 \times 10^{-6}$ torr with argon, heptyl cation, $C_7H_{15}^+$ (about 10%

(22) Calculations are based on heats of formation taken from ref 25a.

(23) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628–6632.

(24) (a) Houriet, R.; Parisod, G.; Gäumann, T. *J. Am. Chem. Soc.* **1977**, *99*, 3599–3602. (b) Houriet, R.; Gäumann, T. *Lecture Notes in Chemistry: Ion Cyclotron Resonance Spectrometry*; Hartman, H., Wanezek, K., Eds.; Springer-Verlag: Berlin, 1978; Vol. 7.

$$Au^+ + CH_3(CH_2)_5CH_3 \longrightarrow$$

$$\xrightarrow{0.99} [C_7H_{15}^+]^* \xrightarrow{-C_3H_6} C_4H_9^+ \quad (15a)$$

$$\downarrow Ar$$

$$C_7H_{15}^+$$
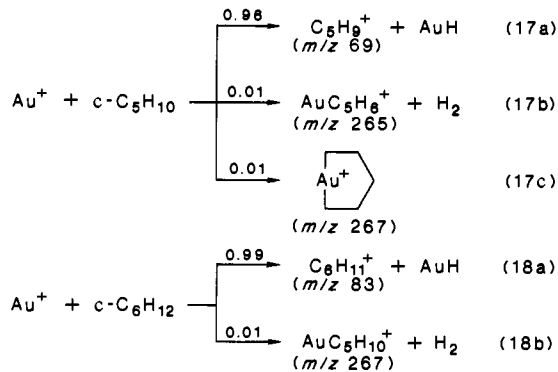
$$\xrightarrow{0.01} AuC_7H_{14}^+ + H_2 \quad (15b)$$

of the total reaction products), appears in the spectrum. All of the above observations suggest that hydride transfer induced fragmentation of internally excited larger alkyl cations occurs in competition with collisional stabilization.

**Reactions of Au$^+$ with Cyclic Alkanes.** Cyclopropane reacts with Au$^+$ according to reactions 16a and 16b. It appears that

$$Au^+ + c\text{-}C_3H_6 \longrightarrow$$

$$\xrightarrow{0.73} \begin{array}{c} C_3H_5^+ \\ (m/z\ 41) \end{array} + AuH \quad (16a)$$

$$\xrightarrow{0.27} \begin{array}{c} Au^+ \\ (m/z\ 239) \end{array} \quad (16b)$$

the $C_3H_5^+$ ion is the product of hydride transfer, followed by opening of the cyclopropane ring. $C_3H_5^+$ undergoes a secondary ion-molecule reaction with cyclopropane to yield an ion with $m/z$ 55 via elimination of ethylene. The product with $m/z$ 239 is apparently a metallocyclobutane cation formed by oxidative addition across a C–C bond of cyclopropane. This would be consistent with the fact that methane ($D°(\text{C–H}) = 104$ kcal/mol) does not react with Au$^+$ and with the relative bond dissociation energies for cyclopropane ($D°(\text{C–H}) = 106$ kcal/mol[25f] and $D°(\text{C–C}) = 54$ kcal/mol[25e]).

With cyclopentane and cyclohexane, hydride abstraction is the major reaction channel yielding cyclopentyl and cyclohexyl cations, reactions 17a and 18a, respectively. In contrast with linear alkane

$$Au^+ + c\text{-}C_5H_{10} \longrightarrow$$

$$\xrightarrow{0.98} \begin{array}{c} C_5H_9^+ \\ (m/z\ 69) \end{array} + AuH \quad (17a)$$

$$\xrightarrow{0.01} \begin{array}{c} AuC_5H_8^+ \\ (m/z\ 265) \end{array} + H_2 \quad (17b)$$

$$\xrightarrow{0.01} \begin{array}{c} Au^+ \\ (m/z\ 267) \end{array} \quad (17c)$$

$$Au^+ + c\text{-}C_6H_{12} \longrightarrow$$

$$\xrightarrow{0.99} \begin{array}{c} C_6H_{11}^+ \\ (m/z\ 83) \end{array} + AuH \quad (18a)$$

$$\xrightarrow{0.01} \begin{array}{c} AuC_6H_{10}^+ \\ (m/z\ 267) \end{array} + H_2 \quad (18b)$$

reactions, no hydride transfer induced fragmentations are observed, suggesting that the initial cations are reasonably stable. Products arising from the minor dehydrogenation channel, reactions 17b and 18b, forming gold–cyclopentene and gold–cyclohexene ions, are also observed. One additional minor product with $m/z$ 267, probably a metallocyclohexane ion, is observed with cyclopentane.

**Reactions of Au$^+$ with Aromatic Hydrocarbons.** Au$^+$ undergoes both charge transfer and complexation reactions with benzene (19a and 19b). The gold cation does not abstract hydride from benzene

$$Au^+ + C_6H_6 \longrightarrow$$

$$\xrightarrow{0.06} C_6H_6^+ + Au \quad (19a)$$

$$\xrightarrow{0.94} AuC_6H_6^+ \quad (19b)$$
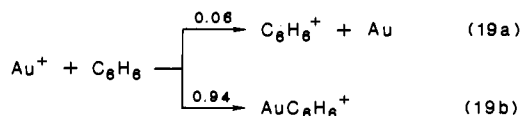
because this reaction is endothermic by 14 kcal/mol.[26]   The

**Scheme II**

$$Au^+ + CH_3CH_2\text{-}\langle\bigcirc\rangle \longrightarrow CH_3CH_2\text{-}Au^+\text{-}\langle\bigcirc\rangle \longrightarrow$$

$$AuC_2H_4^+ \longleftarrow \left[ \parallel\text{-}Au^+\text{-}\langle\bigcirc\rangle \right] \xrightarrow{-C_2H_4} Au^+\text{-}\langle\bigcirc\rangle$$
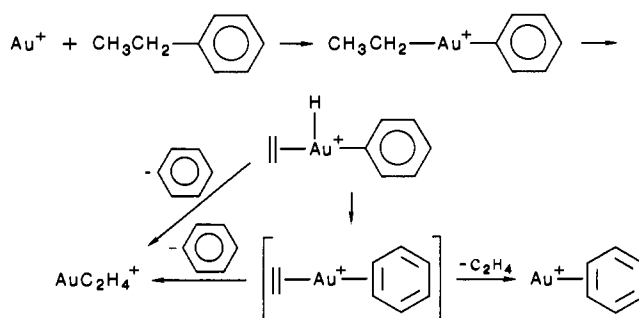
product of reaction 19, $AuC_6H_6^+$, undergoes a secondary reaction with another molecule of neutral benzene to yield $Au(C_6H_6)_2^+$.

Reactions of Au$^+$ with toluene are dominated by charge transfer and hydride abstraction, reactions 20a and 20b. A small amount

$$Au^+ + C_6H_5CH_3 \longrightarrow$$

$$\xrightarrow{0.83} C_7H_8^+ + Au \quad (20a)$$

$$\xrightarrow{0.16} C_7H_7^+ + AuH \quad (20b)$$

$$\xrightarrow{0.01} AuC_6H_5CH_3^+ \quad (20c)$$
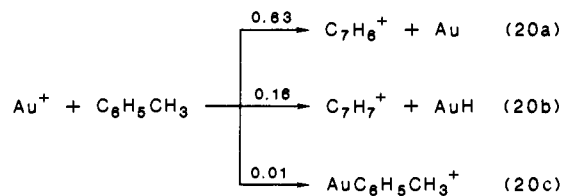
of complex formation, giving $AuC_6H_5CH_3^+$, which is probably a $\pi$-bonded complex ion, also occurs (reaction 20c). $C_7H_7^+$ ($m/z$ 91) produced from reaction 20b might possess either the benzyl or tropylium ion structure. Ausloos[27] noted that benzyl ions may be distinguished from the tropylium ions by their high reactivity with aromatic molecules and determined the relative ratios of benzyl/tropylium ion populations by measuring the reactivity of $C_7H_7^+$ ions with neutral toluene. In the present study, the same approach was applied to estimate the relative abundance of the two $C_7H_7^+$ ion structures. About 90% of the $C_7H_7^+$ ions react rapidly with toluene to yield $C_8H_9^+$ ion, indicating the occurrence of the benzyl ion reaction:

$$C_6H_5CH_2^+ + C_6H_5CH_3 \rightarrow C_8H_9^+ + C_6H_6 \quad (21)$$
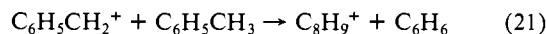
It is assumed that the unreactive $C_7H_7^+$ ions ($\sim 10\%$) are tropylium ions.

The gas-phase reaction of Au$^+$ with ethylbenzene yielded a variety of products, reactions 22a–f. The major reaction products

$$Au^+ + C_6H_5CH_2CH_3 \longrightarrow$$

$$\xrightarrow{0.02} C_7H_7^+ + AuCH_3 \quad (22a)$$

$$\xrightarrow{0.41} C_6H_5C_2H_5^+ + Au \quad (22b)$$

$$\xrightarrow{0.41} C_8H_9^+ + AuH \quad (22c)$$

$$\xrightarrow{0.03} AuC_8H_{10}^+ \quad (22d)$$

$$\xrightarrow{0.06} AuC_2H_4^+ + C_6H_6 \quad (22e)$$

$$\xrightarrow{0.05} AuC_6H_6^+ + C_2H_4 \quad (22f)$$
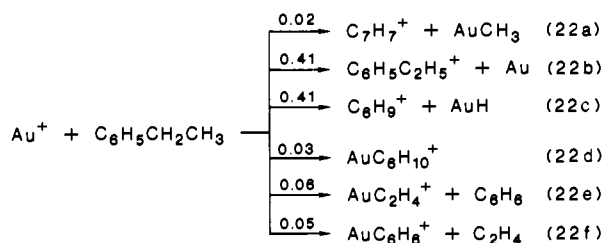
are dominated by charge transfer and hydride abstraction processes, reactions 22b and 22c. $AuC_8H_{10}^+$ is considered to be a $\pi$-bonded $Au^+\text{-}C_6H_5C_2H_5$ ion. The occurrence of reaction 22a implies $D°(\text{Au–CH}_3) > 38.65$ kcal/mol. In contrast to toluene, two additional ionic reaction products, with $m/z$ 225 and 275, are observed with ethylbenzene (reactions 22e and 22f). Specific ligand exchange reactions and studies using deuterated ethylbenzene indicate the formation of Au(ethylene)$^+$ and Au(benzene)$^+$, in reactions 22e and 22b, respectively. A proposed mechanism for formation of these two products is presented in
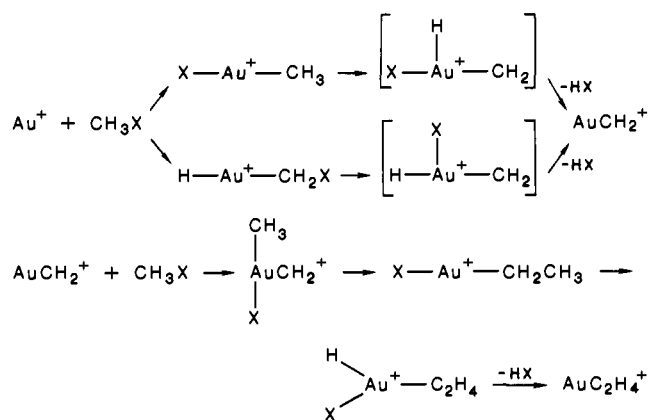
(25) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) Heat of formation of CHCl obtained from *JANAF Thermochemical Tables*, Natl. Stand. Ref. Data. Ser., No. 37, Natl. Bur. Stand, 1971. (c) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: 1980. (d) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*. (e) Bergman, R. G. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 191. (f) Baghal-Vayjooee, M. H.; Benson, S. *J. Am. Chem. Soc.* **1979**, *101*, 2838–2840.

(26) (a) Calculations are based on equation: $\Delta H_{rx} = -D(\text{Au–H}) + D°(\text{R–H}) + \text{IP}(\cdot\text{R}) - \text{IP}(\text{Au})$, or $\Delta H_{rx} = -D(\text{Au–H}) + \text{AP}(\text{R}^+) - \text{IP}(\text{Au})$. (b) $D(\text{Au–H}) = 70.6$ kcal/mol and $\text{IP}(\text{Au}) = 212.7$ kcal/mol,[16] $D(\text{C}_6\text{H}_5\text{–H}) = 110.5$ kcal/mol,[25a] $\text{IP}(\cdot\text{C}_6\text{H}_5) = 186.8$ kcal/mol.[25b] (c) Calculations are based on the equation $\Delta H_{rn} = D°(\text{CH}_3\text{–X}) - \text{EA}(\text{X}) - D(\text{Au–CH}_3) + \text{EA}(\text{Au})$.

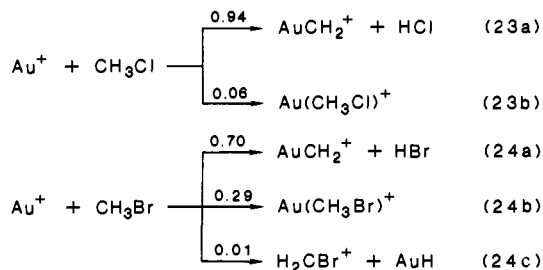(27) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259–5265.

(28) Lias, S. G.; Eyler, R. J.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *19*, 219–239.

*Reactions of Au⁺ with Hydrocarbons*

*J. Am. Chem. Soc., Vol. 109, No. 18, 1987* 5341
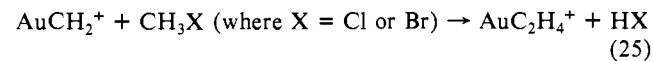
**Scheme III**



Scheme II and involves initial insertion across the ethyl-phenyl C-C bond, followed by a $\beta$-hydride transfer onto the gold. Subsequent migration of hydrogen to the phenyl ring and either concerted loss of benzene yields $AuC_2H_4^+$ or forms an activated complex, $C_2H_4-Au^+-C_6H_6$, with fragments, yielding $AuC_2H_4^+$ and $AuC_6H_6^+$.

**Reaction of Au⁺ with CH₃X (X = Cl, Br, I, and CN) and Other Halomethanes.** $Au^+$ reacts with $CH_3Cl$ and $CH_3Br$ according to reactions 23 and 24. Collision-induced dissociation studies and



$$Au^+ + CH_3Cl \quad \begin{array}{c} \xrightarrow{0.94} AuCH_2^+ + HCl \quad (23a) \\ \xrightarrow{0.06} Au(CH_3Cl)^+ \quad (23b) \end{array}$$

$$Au^+ + CH_3Br \quad \begin{array}{c} \xrightarrow{0.70} AuCH_2^+ + HBr \quad (24a) \\ \xrightarrow{0.29} Au(CH_3Br)^+ \quad (24b) \\ \xrightarrow{0.01} H_2CBr^+ + AuH \quad (24c) \end{array}$$

ligand exchange reactions (with benzene and acetonitrile) or $Au(CH_3Cl)^+$ and $Au(CH_3Br)^+$ indicate that they are loosely bonded $Au(CH_3X)^+$ complexes rather than $CH_3-Au^+-X$ cations (where X = Cl or Br). Both $Au(CH_3Cl)^+$ and $Au(CH_3Br)^+$ undergo secondary reactions with either $CH_3Cl$ or $CH_3Br$, forming the respective $Au(CH_3Cl)_2^+$ and $Au(CH_3Br)_2^+$ cations.

The dominant reaction of $Au^+$ with $CH_3Cl$ and $CH_3Br$ is formation of the reactive $AuCH_2^+$ ion which undergoes secondary

$$AuCH_2^+ + CH_3X \text{ (where X = Cl or Br)} \rightarrow AuC_2H_4^+ + HX \quad (25)$$

reaction with $CH_3Cl$ or $CH_3Br$ to yield $AuC_2H_4^+$. A mechanism for formation of the reactive carbene and its secondary product is outlined in Scheme III. $Au^+$ inserts across the weak C-X bond of $CH_3X$, followed by $\alpha$-hydrogen migration onto the metal and subsequent loss of HX giving $AuCH_2^+$ ions. Initial insertion of $Au^+$ into the C-H bonds of $CH_3X$, followed by $\alpha$-halogen migration and HX loss may also be envisaged as an alternative pathway. $AuCH_2^+$ also inserts into the C-X bond of methyl halides with subsequent methyl migration to the methylidene group to produce an $X-Au^+-CH_2CH_3$ intermediate. Such migratory insertion of an alkyl group into an alkylidene previously has been implicated for reactions of metal carbenes in both gas[29] and solution-phase reactions.[30] Rearrangement of the intermediate $X-Au^+-CH_2CH_3$ involving $\beta$-hydride migration onto the gold and subsequent loss of HX yields $AuC_2H_4^+$. Assuming that only exothermic reactions occur, $CH_3Cl$ and $CH_3Br$ reactions with $Au^+$

give lower limits for the bond dissociation energies, $D(Au^+-CH_2)$ > 89.6 and 92.4 kcal/mol,[31] respectively. The occurrence of a slow hydride abstraction reaction 24c also allows estimation of the lower limit for bond dissociation energy of gold hydride $D°(Au-H) \geq 67$ kcal/mol.[25a,d,26a]

The fast reaction of $Au^+$ with $CH_3I$ produced significant quantities of $AuCH_3^+$ and $AuI^+$ (reactions 26b and 26d) along

$$Au^+ + CH_3I \quad \begin{array}{c} \xrightarrow{0.06} AuCH_2^+ + HI \quad (26a) \\ \xrightarrow{0.21} AuCH_3^+ + I \quad (26b) \\ \xrightarrow{0.11} Au(CH_3I)^+ \quad (26c) \\ \xrightarrow{0.52} AuI^+ + CH_3 \quad (26d) \\ \xrightarrow{0.10} H_2CI^+ + AuH \quad (26e) \end{array}$$
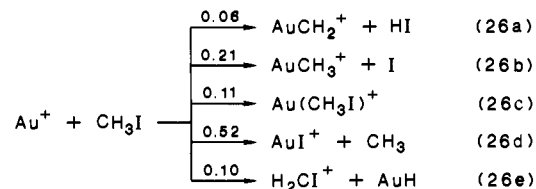
with lesser amounts of other products (reactions 26a, 26c, and 27e). The formation of both $AuCH_3^+$ and $AuI^+$ products in reactions of $CH_3I$ suggests formation of a $CH_3AuI^+$ intermediate via direct metal insertion across the carbon-halogen bond. However, $Au(CH_3I)^+$ appears to be a loosely bound methyl iodide complex rather than $CH_3AuI^+$ cation. Lower limits of bond dissociation energies of both $D°(Au^+-CH_3)$ and $D(Au^+-I)$ are estimated to be >56 kcal/mol. Formation of minor amounts of $AuCH_2^+$ also allows estimation of the lower limit of bond dissociation energy of gold carbene, $D°(Au^+-CH_2) \geq 95$ kcal/mol.[31]

$Au(CH_3CN)^+$ is the only primary reaction product observed when $Au^+$ reacts with $CH_3CN$. A secondary ion-molecule reaction with neutral $CH_3CN$ yields $Au(CH_3CN)_2^+$. In contrast to methyl halide reactions, the absence of gold carbene ion may be due to the high bond dissociation energy of $CH_3-CN$ ($D°-(CH_3-CN) = 123.9$ kcal/mol)[32] which makes metal insertion into the $CH_3-CN$ bond unfavorable.

The only product forming channels with $CHBr_3$ and $CCl_4$ are bromide and chloride abstraction reactions 27 and 28, forming

$$Au^+ + CHBr_3 \rightarrow CHBr_2^+ + AuBr \quad (27)$$

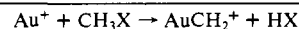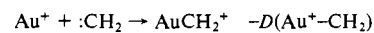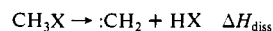$$Au^+ + CCl_4 \rightarrow CCl_3^+ + AuCl \quad (28)$$
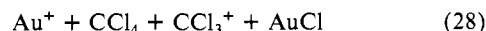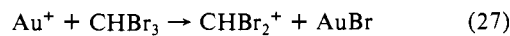
$CHBr_2^+$ and $CCl_3^+$ ions, respectively. Assuming that only exothermic ion-molecule reactions occur, the lower limit of bond dissociation energies of gold bromide and gold chloride are estimated as, $D(Au-Br) > 36.3$ kcal/mol and $D(Au-Cl) > 60.2$ kcal/mol, respectively.

**Ion-Molecule Reactions of Au⁻.** There have been only a few gas-phase studies involving the chemistry of bare metal anions to date.[16,33,34] However, most of these studies dealt with proton-transfer reactions, in order to determine the gas-phase acidities of metal hydrides. Recently, the chemistry of Fe⁻ and Co⁻ with organosulfur compounds has been reported.[34]

In contrast with the rich chemistry observed with gold cation, $Au^-$ is very unreactive with most of the organic compounds considered in this study, including alkanes, alkenes, and aromatic hydrocarbons. Except for a few proton-transfer reactions reported earlier,[16] the main reactions of $Au^-$ are limited to halide displacements and gold dihaloanion formation.

Ion-molecule reactions and product data for $Au^-$ are summarized in Table II. Gold anions are unreactive with $CH_3Cl$,

(29) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67–72.

(30) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (b) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43–51. (c) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650–2659. (d) Hayes, J. C.; Cooper, N. J. *Organometallics Compounds*; Shapiro, B. L., Ed.; Texas A&M:

(31) (a) Calculations are based on the following equations:

$$CH_3X \rightarrow :CH_2 + HX \quad \Delta H_{diss}$$

$$Au^+ + :CH_2 \rightarrow AuCH_2^+ \quad -D(Au^+-CH_2)$$

$$\overline{Au^+ + CH_3X \rightarrow AuCH_2^+ + HX}$$

$\Delta H_{diss} = \Delta H_f°(:CH_2) + \Delta H_f°(HX) - \Delta H_f°(CH_3X); \Delta H_{rx} = \Delta H_{diss} - D-(Au^+-CH_2)$. (b) Heats of formation are taken from ref 32 and 25a.

(32) *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983–84.

(33) (a) Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6352–6354. (b) Sallans, L.; Lane, K. R.; Squires, R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379–4385.
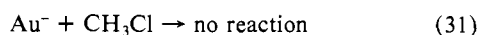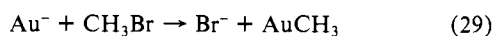
(34) Sallans, L.; Lane, K. R.; Freiser, B. S. 34th Annual Conference on Mass Spectrometry and Allied Topics, Cincinnati, Ohio, June 8–13, 1986.

**Table II.** Summary of Product Data for the Ion–Molecule Reactions of Au⁻

| reaction | ion + neutral reactants | primary products [assumed neutral] | fraction of product ion signal | estimated low bond energy limit (kcal/mol) |
|---|---|---|---|---|
| 1 | Au⁻ + CH₃Cl | → no reaction | | $D°(Au-CH_3) < 53$ |
| 2 | Au⁻ + CH₃Br | → Br⁻ [+ AuCH₃] | 1.00 | $D°(Au-CH_3) > 45.8$ |
| 3 | Au⁻ + CH₃I | → I⁻ [+ AuCH₃] | 1.00 | $D°(Au-CH_3) > 39.1$ |
| 4 | Au⁻ + CHCl₃ | → AuCl₂⁻ [+ :CHCl] | 1.00 | $D°(Au^--2Cl) \geq 162$ |
| 5a | Au⁻ + CHBr₃ | → AuBr₂⁻ [+ :CHBr] | 0.88 | |
| 5b | | → AuCBr₂⁻ [+ HBr] | 0.05 | |
| 5c | | → Br⁻ [+ AuCHBr₂] | 0.07 | |
| 6 | Au⁻ + CCl₄ | → AuCl₂⁻ [+ :CCl₂] | 1.00 | $D°(Au^--2Cl) > 128$ |
| 7 | Au⁻ + Cl₃CCH₂OH | → HAuCl⁻ [+ Cl₂C=CHOH] | 1.00 | |

**Scheme IV**

Au⁻ + CCl₃X (where X = Cl or H) ⟶ Cl—Au⁻—CCl₂X ⟶
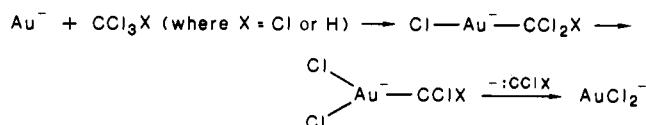


but undergo very slow S$_N$2 displacement reactions with CH₃Br and CH₃I forming Br⁻ and I⁻ anions, respectively, suggesting that

$$Au^- + CH_3Br \rightarrow Br^- + AuCH_3 \qquad (29)$$

$$Au^- + CH_3I \rightarrow I^- + AuCH_3 \qquad (30)$$

$$Au^- + CH_3Cl \rightarrow \text{no reaction} \qquad (31)$$

Au⁻ is kinetically a poor nucleophile.[35] The lower and upper limits of bond dissociation energies of gold-methide, $D°(Au-CH_3) >$ 39.1 and 45.8, and 53.1 kcal/mol, are estimated[26c] from reactions 30, 29, and 31, respectively.

Au⁻ reacts slowly with CHCl₃ and very rapidly with CCl₄ to yield AuCl₂⁻ anion. The much higher reaction rate of CCl₄ compared to CHCl₃ is probably due to the energy difference of the neutral carbene radicals $[\Delta H_f(CCl_2) - \Delta H_f(CCl_4)] - [\Delta H_f(CHCl) - \Delta H_f(CHCl_3)] = 34.7$ kcal/mol,[25a,b] assumed to be formed in reactions 32 and 33.

$$Au^- + CCl_4 \rightarrow Cl-Au-Cl^- + :CCl_2 \qquad (32)$$

$$Au^- + CHCl_3 \rightarrow Cl-Au-Cl^- + :CHCl \qquad (33)$$
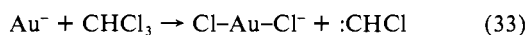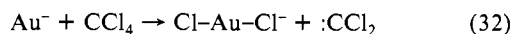
A possible mechanism for formation of AuCl₂⁻ is presented in Scheme IV. Au⁻ initially inserts into a weak C–Cl bond, α-Cl migration onto gold occurs, and subsequent decomposition of :CClX yields AuCl₂⁻ anion. The occurrence of slow reaction 33 yields $D°(Au^--2Cl) \geq 162$ kcal/mol.

AuBr₂⁻ is the major product of the reaction of Au⁻ with CHBr₃. The minor products are AuCBr₂⁻ and Br⁻ as shown in reactions 35 and 36, respectively. This observation of AuCBr₂⁻ may be the first report of an anionic metal carbene in the gas phase.



$$\text{Au}^- + \text{CHBr}_3 \qquad \xrightarrow{0.88} \text{AuBr}_2^- + \text{CHBr} \qquad (34)$$
$$\xrightarrow{0.05} \text{AuCBr}_2^- + \text{HBr} \qquad (35)$$
$$\xrightarrow{0.07} \text{Br}^- + \text{AuCHBr2} \qquad (36)$$
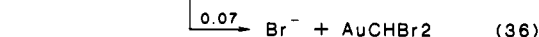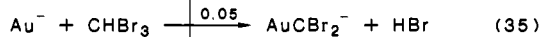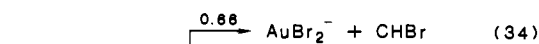
Au⁻ reacts rapidly with Cl₃CCH₂OH to produce HAuCl⁻ anion. The mechanism outlined in Scheme V may explain the formation of HAuCl⁻. Insertion of a gold anion into a carbon–halogen bond requires an electronic configuration (d¹⁰s¹p¹ or d⁹s²p¹) conducive to the formation of two bonds. The promotion energy required to achieve such a configuration is expected to be high. Thus, the formation of two bonds must provide sufficient energy to compensate for carbon–halogen bond dissociation and promotion energies. Although a lower limit estimate for $D(Au^--Cl)$ of > 81 kcal/mol can be inferred from reaction 4 (Table II), the bond energies for Au⁻–haloalkyl appear to be unknown. Thus, the

**Scheme V**

Au⁻ + Cl₃CCH₂OH ⟶ [Cl—Au⁻—C(Cl)(Cl)—CH₂OH] ⟶
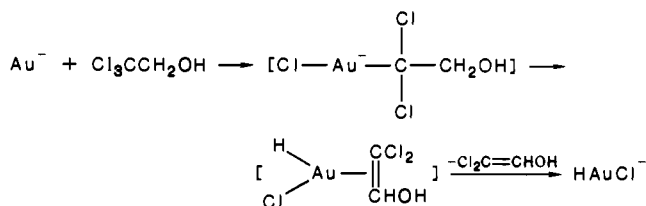


**Table III.** Thermochemical Data Evaluated in This Study[a]

| this study | previous value or comparable data with other transition metals |
|---|---|
| $D°(Au-H) > 67$ | $70.6 \pm 3$ kcal/mol[16,20] |
| $D°(Au-CH_3) \geq 45.8 < 53$ | $D°(CO-CH_3) = 41 \pm 10$ kcal/mol[8a] |
| $D°(Au-Cl) > 60.2$ | 82 kcal/mol[32] |
| $D°(Au-Br) > 36.3$ | |
| $D°(Au^+-CH_2) \geq 95.0$ | $D°(Fe^+-CH_2) = 95 \pm 5$ kcal/mol[12] |
| | $D°(Fe^+-CH_2) = 82 \pm 5$ kcal/mol[36b] |
| | $D°(Rh^+-CH_2) = 94 \pm 5$ kcal/mol[36a] |
| $D°(Au^+-C_2H_4) > 32.7$ | $D°(CO^+-C_2H_4) = 37 \pm 2$ kcal/mol[23] |
| $D°(Au^+-CH_3) > 56.0$ | $D°(CO^+-CH_3) = 57 \pm 7$ kcal/mol[36c] |
| $D°(Au^+-I) > 56.0$ | |
| $D°(Au^--2Cl) \geq 162.6$ | |

[a] Estimated lower limit bond dissociation energies in kcal/mol.

mechanisms implicated in Schemes IV and V should be considered tentative since the observed product anions may also form via a dissociative attachment mechanism. Initial insertion of Au⁻ into a C–Cl bond is followed by a β-hydride migration to the metal, and subsequent loss of Cl₂C=CHOH yields HAuCl⁻ anion. The inability of bare metal anions to hold π-bounded ligands has been reported.[34] No reactions of Au⁻ with F₃CCH₂OH were observed, probably owing to unfavorable energetics for initial insertion into the strong C–F bonds. The apparent unreactivity of Au⁻ with most organic compounds may be due to its stable d¹⁰s² electronic configuration.

**Thermochemical Data.** Table III lists the thermochemical data evaluated in this study. The bond dissociation energy of gold hydride determined from the present hydride transfer reactions compares well with literature values.[16,20] The minimum gold methide bond dissociation energy, $D°(Au-CH_3) \geq 45.8$ kcal/mol determined here for the first time, can be compared to $D°(CO-CH_3) = 41 \pm 10$ kcal/mol determined by Armentrout and Beauchamp.[8a] The bond dissociation energy of gold carbene, $D°(Au^+-CH_2) \geq 95$ kcal/mol falls within the general range (82–95 kcal/mol) of other transition metal carbenes determined by ion beam techniques[4,12] and photodissociation methods.[36b]

**Conclusion**

Au⁺ undergoes exothermic reactions with all of the hydrocarbons, except methane, examined in this study. Reactions with alkanes other than methane or ethane predominantly exhibit

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hydride abstraction, in competition with dehydrogenation. For higher alkanes, it is demonstrated that hydride abstraction by Au$^+$ generates internally excited alkyl cations which fragment in competition with collisional stabilization. Generation of the reactive gold carbene, AuCH$_2^+$, from methyl halides, methide, and hydride abstraction studies allows estimation of lower limits for Au$^+$–CH$_2$, Au–CH$_3$, and Au–H bond dissociation energies (*D*-(Au$^+$–CH$_2$) $\geq$95.0 kcal/mol, *D*(Au–CH$_3$) $\geq$ 45.8 kcal/mol, and *D*(Au–H) > 67 kcal/mol). In contrast to gold cation, Au$^-$ is relatively inert and in the present study its reactions have been limited to halide displacement and gold–dihalide anion formation. Generation of AuCBr$_2^-$ from CHBr$_3$ appears to be the first reported gas-phase anionic metal carbene. The apparent unreactivity

of Au$^-$ may be due to its stable d$^{10}$s$^2$ electronic configuration.

# Liquid Secondary Ionization Mass Spectrometric Characterization of Two Synthetic Phosphotyrosine-Containing Peptides

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**Abstract:** *N*-(*tert*-Butoxycarbonyl)-*O*-(dibenzylphosphono)-L-tyrosine (1), a suitably protected phosphotyrosine, has been prepared for peptide synthesis. Compound 1 and its intermediate precursors were characterized by elemental analyses, liquid secondary ion mass spectrometry (LSIMS), and NMR spectral data. With use of 1, both a tri- and a tetrapeptide, Val-Tyr(PO$_3$H$_2$)-Phe and Arg-Tyr(PO$_3$H$_2$)-Val-Phe, were prepared via solid-phase synthesis and fully characterized by LSIMS. LSIMS spectra were taken in both positive and negative ion modes as well as metastable decomposition spectra of the molecular ions of the two peptides with a B/E linked scan. For comparison, similar LSIMS spectra were acquired for peptides containing a phosphoserine (kemptide) and sulfated tyrosine (caerulein and cholecystokinin-8). The most significant features of the mass spectra of the phosphotyrosine-containing peptides are abundant molecular ions in both the positive and negative ion mode and peaks corresponding to losses of HPO$_3$ (−80 mu) and HPO$_4$ (−96 mu) from the parent molecules. Peaks for HPO$_3$ and HPO$_4$ loss are of very low abundances in peptides containing phosphoserine. The elemental compositions of the peaks corresponding to the losses of HPO$_3$ and HPO$_4$ from the parent molecular ions were confirmed by accurate mass measurements. The losses of HPO$_3$ and HPO$_4$ from the parent molecules of these two phosphotyrosine-containing peptides are important because they allow a distinction to be made between them and peptides containing phosphoserine or sulfated tyrosine (e.g., caerulein and cholecystokinin-8), the latter of which undergo much more extensive SO$_3$ loss (−80 mu) in the positive ion mode than the HPO$_3$ loss observed for the two phosphotyrosine-containing peptides.

Recently, a number of transforming proteins originating from the oncogenes of avian and mammalian tumor viruses have been characterized and shown to possess tyrosine-specific protein kinase activity.[1] Tyrosine kinase activity is also present in the receptors for epidermal growth factor (EGF)[2] insulin[3] and platelet derived growth factor[4] as well as in a number of proto-oncogenes.[5] In fact, it appears that several of these retroviral transforming proteins are related in structure to the growth factor receptors. In the case of the viral erb-B oncogene product, a high degree of homology

is found with the intracellular kinase domain of the EGF receptor, while a corresponding extracellular domain appears to be absent.[6,7]

Although these enzymes are known to mediate phosphoryl transfer between ATP and tyrosine residues in endogenous cytoplasmic proteins, their mechanism of action is not clearly understood. Neither are the consequences of the enzymatic phosphorylation of these proteins known or the effect, if any, that peptides resulting from proteolytic degradation of these phosphorylated proteins have on cellular processes. However, phosphorylations of specific amino acids in numerous enzymes, receptors, and ion channels are known to be important regulators of their respective functions. In this respect, it is essential to determine the substrate specificity for phosphorylation, which first requires the isolation and analysis of phosphopeptides. Although our understanding of the substrate specificity for tyrosine kinases is lacking, inhibitors based on the enzyme substrates would also be desirable, as tyrosine-specific protein kinases are enzymes that

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