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Experimental and Theoretical Studies of Gold(I) Complexes $Au(L)^+$ (L = H_2O, CO, NH_3, C_2H_4, C_3H_6, C_4H_6, C_6H_6, C_6F_6)

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Radiative association enhances the formation of $Au(C_6F_6)^+$ from bare Au^+ ions and hexafluorobenzene in the low-pressure regime of a Fourier transform ion cyclotron resonance mass spectrometer. Due to the relatively small bond dissociation energy (BDE) of $Au^+-C_6F_6$, this complex can be used as a versatile precursor for the generation of other $Au(L)^+$ complexes by ligand-exchange reactions. Ion/molecule reactions employing the bracketing technique provide a relative gold(I) cation affinity scheme for the various ligands L, i.e. $C_6F_6 < H_2O < CO < C_2H_4 < C_6H_6 < NH_3 < C_3H_6 < C_4H_6$. In addition, for some ligand pairs L/L′ both the forward and reverse ligand exchange reactions were observed from which equilibrium data at room temperature were derived. For $Au(H_2O)^+$, $Au(CO)^+$, $Au(NH_3)^+$, and $Au(C_2H_4)^+$ the absolute BDEs are evaluated by means of ab initio MO calculations at the MP2 level of theory, and the following gold(I) cation affinities are obtained: 39 kcal/mol (L = H_2O), 50 kcal/mol (CO), 69 kcal/mol (NH_3), and 73 kcal/mol (C_2H_4), respectively. On the basis of a comparison of the experimental and computational findings, the absolute error of the calculated BDEs is estimated to be ±5 kcal/mol. The unusually high BDE of $Au(C_2H_4)^+$ of ca. 70 kcal/mol is further confirmed by the observation that ethene can replace not only a benzene molecule in $Au(C_6H_6)^+$ in a slightly endothermic process but also the covalently bound iodine ligand in AuI^+ to yield $Au(C_2H_4)^+$, setting a lower limit of 59 kcal/mol for BDE($Au^+-C_2H_4$). Finally, the relative gold(I) cation affinity scale is compared to findings for $M(L)^+$ complexes of other transition metals.

Complexes of bare transition-metal cations with small ligands in the gas phase have attracted considerable interest within the last decade. Numerous experimental studies established accurate bond dissociation energies (BDEs) of $M(L)^+$ complexes for the first-row transition-metal cations with a large variety of ligands.[1] In addition, nowadays theoretical results on these systems are available and found to be in reasonable agreement with the experimental findings, provided the correlation energy is taken into account appropriately.[2] In fact, in some cases the computational results prompted a revision of experimental figures.[3] So far, not much experimental effort has been undertaken to evaluate the thermochemistry of second- and third-row transition-metal ions.[1] Previous studies by Wilkins and coworkers[4] addressed the chemistry of bare Au^+ with organic substrates, e.g. saturated and unsaturated hydrocarbons as well as monofunctionalized alkanes. A particular feature of Au^+ chemistry is due to the high ionization energy (IE) of the gold atom, which renders its chemistry quite different as compared to other transition-metal ions. For example, while most transition-metal cations dehydrate/dehydrohalogenate alkanols and haloalkanes, respectively, bare Au^+ preferentially undergoes hydride transfer to yield neutral AuH together with the corresponding α-cleavage products of the substrates, ie.. closed-shell organic ions.[4] In addition, heavy elements exhibit relativistic effects, which are most pronounced for gold.[5]

In this article we report combined experimental/computational studies of $Au(L)^+$ complexes with some inorganic and organic ligands L.[6] The relative gold cation affinities of the various ligands as derived from bracketing experiments are supplemented by ab initio MO computations and compared to previous findings for other ligated transition-metal ions.

Experimental and Computational Details

The experiments were performed with a Spectrospin CMS 47X Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, which has been described in detail elsewhere.[7] In brief, Au^+ ions were generated by laser desorption/laser

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ionization[8] by focusing a beam of a Nd:YAG laser onto a pure gold target. The ions were extracted from the source and transferred to the analyzer cell by a system of electric potentials and lenses. The isolation of $^{197}Au^+$ and all subsequent ion isolations were performed by using FERETS,[9] a computer-controlled ion ejection protocol which combines single-frequency pulses with frequency sweeps to optimize ion isolation. $Au(L)^+$ complexes were generated by reacting the ligands L with $Au(C_6F_6)^+$, which was produced from Au^+ and a pulsed-in C_6F_6/Ar mixture, and subsequently thermalized by collisions with argon.[10] It is borne out in the experiments that thermalization of atomic Au^+ is not as efficient as for other transition-metal cations,[10] and more than 1000 collisions with argon were necessary for effective thermalization. Organic substrates were introduced *via* leak valves at pressures ranging from 2×10^{-9} to 5×10^{-7} mbar. Branching ratios and rate constants were derived from the analysis of the reaction kinetics, and the pseudo-first-order rate constants were converted to absolute rate constants by calibrating the pressure measurements[11] using rates of well-known ion/molecule processes;[12] the error of the absolute rate constants is estimated to be ±25%.[10a] If forward and backward ligand-exchange reactions were observed, a ca. 1:1 mixture of the respective neutrals L and L′ was admitted to the FTICR cell. After the mass selection of $Au(L)^+$ and $Au(L')^+$ ions, generated as described above, the pressure and time dependence of the $Au(L)^+/Au(L')^+$ ratios was monitored. With the knowledge of absolute pressures, these ratios are then converted to thermal equilibrium constants, K_{eq}. As described in the following, the experimental error of K_{eq} amounts to ±20%; however, due to systematic errors which are associated with the pressure measurement,[10,11] the absolute errors may well be larger.

In the ab initio MO calculations we used the multielectron adjusted relativistic effective core potential (RECP),[13] augmented by additional diffuse and polarization functions, resulting in a [10s/8p/7d/1f]/(9s/5p/6d/1f) basis set for the gold atom.[6] For the other atoms we used the Dunning TZ2P basis sets with an additional f-polarization function ($\zeta = 1.85$) for the carbon, nitrogen, and oxygen atoms, i.e. the contraction [10s/6p/2d/1f]/(5s/3p/2d/1f) and the [5s/2p/1d]/(3s/2p/1d) basis set for hydrogen atoms.[14] Full geometry optimizations have been performed by using standard procedures at the SCF and MP2 levels of theory. As has been demonstrated previously,[6,15] simple Au^+ compounds are reasonably described by this theoretical approach, and a further increase of the inclusion of correlation energy does not result in substantial changes in geometry and/or energy. All valence electrons were correlated in the perturbational treatment, and these calculations were performed in appropriate symmetries using the GAUSSIAN92-DFT program package.[16] All computations were performed on either IBM/RS 6000 workstations or a CRAY-YMP computer. A complete theoretical treatment of basis set dependencies and relativistic effects, as well as various alternative computational approaches, will be published separately.[17]

Results and Discussion

Even at the low-pressure regime of the FTICR setup, thermalized Au^+ cations react with hexafluorobenzene (C_6F_6) to rapidly form the adduct complex $Au(C_6F_6)^+$, indicating that the rovibrationally excited encounter complex $Au(C_6F_6)^{+*}$ undergoes radiative stabilization.[18] Measurements of rate constants at different reactant pressures in the presence of argon as an additional third-body stabilization agent result in the following rate law for the association reaction of Au^+ with C_6F_6: $k(p) = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} + $(3 \times 10^{-20})p$ cm^6 molecule^{-2} s^{-1}. In a secondary reaction, association to yield the corresponding bisadduct complex $Au(C_6F_6)_2^+$ is observed (Scheme 1). For convenience, C_6F_6 was pulsed-in as a mixture with argon in order to allow rapid formation as well as thermalization of $Au(C_6F_6)^+$. Thus, when the reagents were pumped-off, they did not affect the subsequent measurements.

Scheme 1

$$Au^+ \xrightarrow{+C_6F_6} Au(C_6F_6)^+ \xrightarrow{+C_6F_6} Au(C_6F_6)_2^+$$

We were not able to determine the bond dissociation energy of the $Au(C_6F_6)^+$ so formed; however, as shown below, its BDE is relatively small. Therefore, this complex can be used as a suitable precursor for the generation of $Au(L)^+$ complexes with various other ligands by ligand-exchange reactions of the type

$$Au(C_6F_6)^+ + L \rightarrow Au(L)^+ + C_6F_6$$

In addition, association to yield $Au(C_6F_6)(L)^+$ as well as subsequently $Au(L)_2^+$ was also observed.

Assuming that multiple collisions with argon effectively thermalize the $Au(L)^+$ complexes so formed, the occurrence of ligand exchange indicates that the BDE(Au^+L) values or the particular ligands exceed BDE($Au^+-C_6F_6$). No exchange reactions were observed when $Au(C_6F_6)^+$ was reacted with N_2 and O_2. For those ligands which undergo ligand exchange with $Au(C_6F_6)^+$, the $Au(L)^+$ complexes so formed were subsequently mass-selected and reacted with other ligands L′ to probe relative gold cation affinities, e.g.

$$Au^+ + C_6F_6 \rightarrow Au(C_6F_6)^+ \quad \text{(i)}$$

$$Au(C_6F_6)^+ + H_2O \rightarrow Au(H_2O)^+ + C_6F_6 \quad \text{(ii)}$$

$$Au(H_2O)^+ + CO \rightarrow Au(CO)^+ + H_2O \quad \text{(iii)}$$

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Table 1. Occurrence (+) or Nonoccurrence (−) of Ligand-Exchange Reactions $Au(L)^+ + L' \rightarrow Au(L')^+ + L$ for Various Ligands L and L′[a]

	L′						
$Au(L)^+$	H_2O	CO	C_2H_4	C_6H_6	NH_3	C_3H_6	C_4H_6
$Au(C_6F_6)^+$	+	+	+	+	+	+	+
$Au(H_2O)^+$	○	+	+	+	+	+	+
$Au(CO)^+$	−	○	+	+	+	+	+
$Au(C_2H_4)^+$	−	−	○	+[b]	+[b]	+	+
$Au(C_6H_6)^+$	−	−	+[b]	○	+[b]	+	+
$Au(NH_3)^+$	−	−	+[b]	+[b]	○	+[b]	+
$Au(C_3H_6)^+$	−	−	−	−	+[b]	○	+
$Au(C_4H_6)^+$	−	−	−	−	−	−	○

[a] The circles denote the rapid degenerate exchange reactions $Au(L)^+ + L \rightarrow Au(L)^+ + L$. For all ligand combinations, formation of the bisadduct complexes $Au(L)_2^+$ was observed as a secondary reaction. [b] For these ligand pairs forward and backward ligand-exchange reactions between $Au(L)^+$ and $Au(L')^+$ were observed, if both neutral ligands were leaked simultaneously into the mass spectrometer. This observation indicates that for these ligands the difference of the gold(I) cation affinities of L and L′ is <4 kcal/mol (see text).

Scheme 2

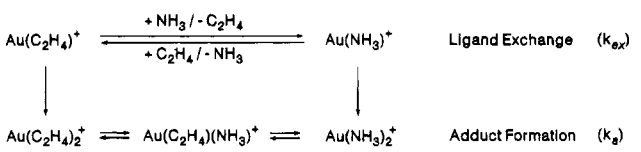

Table 2. Equilibrium Constants (K_{eq}) and Relative Abundances (%) of $Au(C_2H_4)^+$ and $Au(NH_3)^+$ as a Function of Partial Pressure *p* (mbar) and Reaction Time t_R (s)[a]

p			rel abund		
C_2H_4	NH_3	t_R	$Au(C_2H_4)^+$	$Au(NH_3)^+$	K_{eq}
2.1×10^{-8}	1.4×10^{-8}	10	3.2	100	0.021
2.1×10^{-8}	1.4×10^{-8}	20	2.9	100	0.019
7.1×10^{-8}	1.4×10^{-8}	5	8.0	100	0.016
7.1×10^{-8}	1.4×10^{-8}	10	8.3	100	0.017
2.9×10^{-7}	1.4×10^{-8}	5	48.5	100	0.023
2.9×10^{-7}	1.4×10^{-8}	10	49.0	100	0.024

[a] Prior to the reaction time a mixture of $Au(C_2H_4)^+$ and $Au(NH_3)^+$ was generated from Au^+ and C_6F_6 as described above, thermalized with pulsed-in argon, and preequilibrated for 15 s; then both ions were isolated in the FTICR cell. In terms of collision theory the ions undergo ca. 500 collisions with argon during thermalization and at least 15 collisions with ammonia and ethene, respectively. The intensities are normalized to $Au(NH_3)^+$ = 100%. Naturally, adduct formation increases with pressure and reaction time; for example, for the entry in the last row the ratio $Au(NH_3)^+$:$Au(NH_3)_2^+$ amounts to ca. 1:2.

This sequence of reactions enables us to determine a relative Au^+ affinity scheme for the various ligands, i.e. N_2, O_2 < C_6F_6 < H_2O < CO < C_2H_4 < C_6H_6 < NH_3 < C_3H_6 < C_4H_6 (Table 1). This ordering agrees well with the previous findings by Wilkins and co-workers,[4] who reported that benzene and also CH_3CN are more strongly bound to Au^+ than C_2H_4.

In the case of the ligand pair C_2H_4 and NH_3 (Scheme 2), the rates k_a for the competitive formation of the adduct complexes $Au(C_2H_4)_2^+$, $Au(C_2H_4)(NH_3)^+$, and $Au(NH_3)_2^+$, respectively, are much smaller than the rates of the ligand exchange reactions k_{ex}. Hence, it is possible to establish an equilibrium between $Au(C_2H_4)^+$ and $Au(NH_3)^+$ for certain C_2H_4/NH_3 ratios (Table 2), which in turn enables one to evaluate the equilibrium constant K_{eq}. As can be seen from the time independence of the $Au(C_2H_4)^+$:$Au(NH_3)^+$ ratios, the reaction time is sufficient to establish the equilibrium, and adduct formation does not affect the relative abundances. Furthermore, K_{eq} exhibits no distinct pressure dependence; rather, the small spread of the K_{eq} values reflects the experimental uncertainties, the pressure measurement in particular. Given a thermal equilibrium between the two gold(I) complexes and assuming room temperature for the reactants, K_{eq} can be converted to $\Delta\Delta G$ of the ligand-exchange reaction, leading to a value of -2.3 ± 0.5 kcal/mol[19] for the process

$$Au(C_2H_4)^+ + NH_3 \rightarrow Au(NH_3)^+ + C_2H_4$$

For the other ligand pairs studied, either the BDE differences were too large to attain equilibrium or rapid adduct formation obscures the otherwise straightforward conversion of ion signal intensities for the monoligand complexes to $\Delta\Delta G$. For example, if $Au(C_3H_6)^+$ is reacted with a 1:1 mixture of ammonia and propene, association to bisligated complexes is so rapid that ligand exchange to yield $Au(NH_3)^+$ amounts to only 5%. However, the occurrence of forward and backward ligand-exchange reactions was observed for the ligand pairs L/L′ = C_2H_4/C_6H_6, C_6H_6/NH_3, and NH_3/C_3H_6, with the formation of $Au(L')^+$ being favored when the partial pressures of L and L′ are identical.

A principal shortcoming of the bracketing technique is that absolute values for the ligand binding energies can usually not be obtained by using this approach.[20] Wilkins and co-workers derived lower limits for BDE(Au^+-H_2O) > 16 kcal/mol and BDE($Au^+-C_2H_4$) > 33 kcal/mol from the occurrence of ion/molecule reactions of Au^+ with alcohols and alkanes.[4] However, this information is not very conclusive in that upper bounds have not been determined yet. More recently it has been demonstrated that for closed-shell gold compounds ab initio MO calculations can be performed with reasonable accuracy.[6,15,21] Therefore, we calculated the BDEs of $Au(H_2O)^+$, $Au(CO)^+$, $Au(C_2H_4)^+$, and $Au(NH_3)^+$ at the MP2 level of theory using a relativistic effective core potential for the gold atom. In this article we refrain from a detailed discussion of the theoretical results with respect to basis set dependencies, different computational approaches, levels of correlation energy, and influences of relativistic effects;[17] rather, we will restrict the discussion to the structural and energetic aspects on the MP2 level of theory which will be compared with the experimental findings.

The optimized geometry of $Au(H_2O)^+$ (Figure 1) reveals a nonplanar structure, with the gold atom being located out of the H−O−H plane by 47°; the planar C_{2v}-symmetrical structure corresponds to a transition structure. BDE(Au^+-H_2O) has been calculated to be 38.8 kcal/mol with respect to isolated Au^+ and H_2O in their respective electronic ground states (Table 3).[6] The geometry-optimized structure of $Au(CO)^+$ and the BDE of 50.1 kcal/mol are in line with a recent computational

(19) The systematic errors are associated with the relative sensitivities of the ion gauge used (IMG 070, Balzers) for the various gases; for details, see ref 10a and 11.

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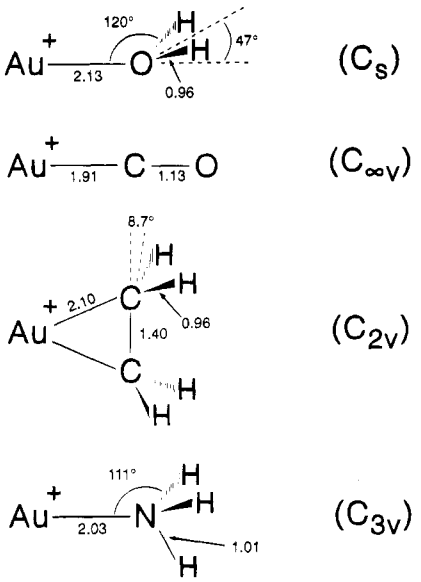


Figure 1. Optimized geometries of $Au(H_2O)^+$, $Au(CO)^+$, $Au(C_2H_4)^+$, and $Au(NH_3)^+$, at the MP2-TZ2P+f level of theory (bond lengths in Å and angles in degrees).

Table 3. Symmetries, Bond Distances (r_{Au-L} in Å), Mulliken Charges (q_{Au}) on the Gold Atom, and Bond Dissociation Energies (BDE in kcal/mol) for $Au(L)^+$ Complexes

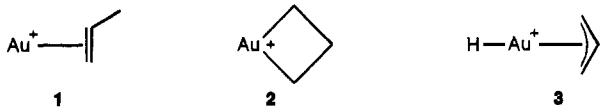
	sym	r_{Au-L}[a]	q_{Au}	BDE
$Au(H_2O)^+$ [b]	C_s	2.13	0.86	38.8
$Au(CO)^+$	$C_{\infty v}$	1.91	0.93	50.1
$Au(C_2H_4)^+$	C_{2v}	2.10	0.58	73.1
$Au(NH_3)^+$	C_{3v}	2.03	0.63	68.6

[a] The bond lengths refer to r_{Au-O}, r_{Au-C}, r_{Au-C}, and r_{Au-N}, respectively. [b] The fully geometry-optimized structure of $Au(H_2O)^+$ is nonplanar; for details, see ref 6.

study;[15] the somewhat smaller bond lengths in the present work, as compared to the previous study,[15] has to be ascribed to the different basis sets used, i.e. Hay/Wadt ECP and 6-31G** for the ligands versus TZ2P+f. The C_{2v}-symmetrical structure of $Au(C_2H_4)^+$ agrees well with its description as a π-complex of ethene with the Au^+ cation, in which the methylene groups are pyramidalized by 8.7°. Significant covalent contributions to the Au−C bonding are indicated by the lengthening of the C−C distance to 1.40 Å as compared to 1.33 Å in uncomplexed ethene. The computed BDE of $Au(C_2H_4)^+$ amounts to 73.1 kcal/mol. Finally, the optimized geometry of $Au(NH_3)^+$ exhibits C_{3v} symmetry with an almost unperturbed ammonia substrate and a BDE of 68.6 kcal/mol.

According to the computational results Au^+ binds ethene more strongly than ammonia (ΔE = 4.5 kcal/mol), whereas the equilibrium data imply the opposite ($\Delta\Delta G$ = −2.3 kcal/mol). A possible reason for the discrepancy between the theoretical and experimental results might be due to entropy effects. However, a frequency analysis and the subsequent computation of $\Delta\Delta G$ (298 K) do not resolve this discrepancy, since $\Delta\Delta H$ and $\Delta\Delta S$ precisely cancel each other, such that the computed $\Delta\Delta G$ (298 K) also amounts to 4.5 kcal/mol. While one might doubt the magnitude as well as the precision of the experimental figure, the relative order of stabilities of the two complexes is unambiguous. Consequently, we are left with the conclusion that the calculated BDEs are associated with an absolute error of at least 5 kcal/mol. With respect to the restricted basis set, and the limitations of the MP2 method in particular, an error of this magnitude is not unexpected at all.[2b,13,17]

Chart 1



Surprisingly, the BDEs of most ligands L to Au^+ are significantly larger than for other transition-metal cations M^+. For example, BDE($Au^+-C_2H_4$) is higher than those of most other known $M(C_2H_4)^+$ complexes. In particular, the electronically related $Cu(C_2H_4)^+$ and $Au(C_2H_4)^+$ complexes exhibit BDEs of only 36 and 34 kcal/mol, respectively,[3,22] i.e. less than half of the value for gold. Furthermore, the magnitude of BDE($Au^+-C_2H_4$) is on the order of that for cationic benzene complexes,[1a,23] which is in line with the experimental observation that the reaction of $Au(C_2H_4)^+$ with benzene to yield $Au(C_6H_6)^+$ and ethene is partially reversible.

The description of the structure of $Au(C_2H_4)^+$ as an intact olefin complex[24] is further supported by the occurrence of ligand exchange reactions; in particular, the rapid degenerate exchange with C_2D_4 to yield $Au(C_2D_4)^+$ takes place without any evidence for H/D exchange processes. Similarly, the structure of $Au(C_3H_6)^+$ should correspond to the genuine propene complex **1** (Chart 1). It is noteworthy that BDE($Au^+-C_3H_6$) exceeds BDE($Au^+-C_6H_6$), although benzene may potentially serve as a η^6 ligand. Chowdhury and Wilkins[4b] ascribed the absence of ligand exchange with benzene to an isomerization of the formal η^2 complex $Au(C_3H_6)^+$ (**1**), to yield the corresponding auracyclobutane **2**.[25] Furthermore, the absence of H/D exchange processes when $Au(C_3H_6)^+$ is reacted with either D_2 or C_2D_4 led these authors to conclude that structure **3** does not participate. In order to solve this structural problem, we examined the secondary reactions of $Au(C_3H_6)^+$. (i) Upon reaction of $CH_3CH_2CD_2OH$ with bare Au^+ the labeled complex $Au(CH_3CH{=}CD_2)^+$ is formed in reasonable yields.[4a] If this complex is reacted with unlabeled propene, besides adduct formation, rapid exchange to yield $Au(C_3H_6)^+$ is observed; again, there is no evidence supporting the occurrence of H/D exchange processes. (ii) Similarly, the C_3H_6 ligand in $Au(C_3H_6)^+$ can be replaced by NH_3 as well as butadiene to yield the corresponding $Au(L)^+$ complexes. These findings indicate that an intact propene substructure is present in $Au(C_3H_6)^+$; thus, we conclude that **1** is formed in the experiment. The absence of ligand exchange with benzene, which was interpreted previously[4b] in terms of structure **2**, can simply be accounted for by the unusually high BDE of the propene complex **1**. For the sake of completeness we wish to stress that our mass-

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spectrometric experiments cannot fully rule out that isomer **2** is also present. However, this would imply that structures **1** and **2** are in a rapid equilibrium. As a consequence, one would have to assume allylic C−H bond activation of **1** and subsequent H-transfer to the central carbon atom as well as formation of two Au−C bonds to yield **2**, with the allylic structure **3** as intermediate. Formation of **3** would imply not only that H/D exchange processes with labeled alkenes occur but also that dissociation to $C_3H_5^+$ and neutral AuH (IE = 10.6 eV) is expected to take place. From the absence of these features we conclude that, most likely, **1** is formed exclusively in the experiment.

In order to confirm the order of magnitude for the BDE of $Au(C_2H_4)^+$, we performed an additional bracketing experiment in which AuI^+ was reacted with ethene. AuI^+ has been generated by reacting Au^+ with CD_3I, indicating that BDE (Au^+−I) exceeds 59 kcal/mol. Interestingly, the covalent iodine ligand is replaced quite rapidly by ethene ($k_{ex} = 6.0 \cdot 10^{-10}$ cm^3 molecules^{-1} s^{-1}) with $Au(C_2H_4)^+$ as the exclusive ionic product (Scheme 3). To the best of our knowledge, this reaction represents the *first* example for the substitution of a covalent ligand by a π-bonded one.[26]

Scheme 3

$$Au^+ \xrightarrow{+CD_3I/-CD_3^\bullet} AuI^+ \xrightarrow{+C_2H_4/-I^\bullet} Au(C_2H_4)^+$$

As compared to the ligand binding energies of main-group as well as transition-metal cations, the ordering for Au^+ differs significantly from that described previously for Li^+,[27] Mg^+,[28] Al^+,[29] Mn^+,[30] Cu^+,[31] and $Ni(c\text{-}C_5H_5)^+$.[32] For example, the BDE(Au^+−L) values do not correlate with the corresponding proton affinities of the ligands,[33] as was observed for the other metal cations.[27−32] The most likely explanation for this deviation of Au^+ involves the high IE of gold as well as the effects of s → p and s → d excitations as compared to its first- and second-row transition-metal congeners. Particularly, for gold(I) complexes the high IE will lead to significant electron transfer from the ligand to the metal cation, resulting in a relatively large covalent contribution to the bonding. In contrast, the nature of the binding for other cationic transition-metal complexes has been described as primarily electrostatic.[2] For the gold(I) complexes studied here, the charge transfer from the ligand to the gold atom is also borne out in the charge distribution as derived from Mulliken population analysis (Table 3). Also, charge transfer causes the deviation from planarity in the case of $Au(H_2O)^+$, as analyzed in detail previously.[6] However, there exists no evident correlation between the IEs of the ligands and their corresponding gold cation affinity. Presumably, the unique feature of the gold(I) complexes is due to relativistic effects, which strengthen and shorten the bonds to the ligands. The precise nature and the origin of these effects are presently under investigation.[17]

Table 4. Calculated and Estimated Bond Dissociation Energies (BDEs in kcal/mol) for $Au(L)^+$ Complexes, Experimental Proton Affinities (PA in kcal/mol), and Ionization Energies (IE in eV) of the Ligands L

	BDE	PA(L)[a]	IE(L)[b]
$Au(H_2O)^+$ [c]	39	167	12.61
$Au(CO)^+$	50	142	14.01
$Au(C_2H_4)^+$	73	163	10.51
$Au(c\text{-}C_6H_6)^+$	≈70[c]	181	9.25
$Au(NH_3)^+$	69	204	10.16
$Au(C_3H_6)^+$	>75[c]	180	9.73
$Au(C_4H_6)^+$	>75[c]	193	9.08

[a] The experimental data were taken from ref 33. [b] For comparison: IE(Au) = 9.225 eV. [c] Estimate derived from ion/molecule bracketing (see text).

Finally, in our study of gold(I) chemistry in the gas phase we hardly observe processes in which typical metal-mediated bond-activation processes occur. For example almost all transition-metal cations undergo condensation reactions with two or more butadiene molecules to yield higher hydrocarbons.[1,34] Although the Au^+ cation clusters with butadiene to yield $Au(C_4H_6)_2^+$, the product appears to be a simple dimeric complex without any evidence for C−C bond formation, consecutive dehydrogenation, olefin losses, etc. Similarly, in contrast to most other transition-metal cations, no H/D exchange processes are associated with Au^+-mediated dehydration or dehydrohalogenation of labeled alkanols or haloalkanes, respectively, as are reported to occur for alkali-metal cations.[35] In fact, none of the other reactants under study underwent chemical activation processes except for obvious charge transfer or hydride abstraction when thermochemically feasible. Thus, while gold(I) chemistry deserves interest with respect to relativistic effects on bonding, as far as catalysis is concerned, in the gas phase atomic Au^+ seems to be quite inefficient.[36,37]

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