Cationic Gold(I) Complexes of Xenon and of Ligands Containing the Donor Atoms Oxygen, Nitrogen, Phosphorus, and Sulfur[†]

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Ligation of atomic gold(I) cation Au^+ by various inorganic and organic ligands containing heteroatoms has been examined by experimental and theoretical means. The $Au(Xe)^+$ complex has been studied comprehensively by CCSD(T) calculations in order to provide a benchmark for a gold(I) cation affinity scale. The best theoretical estimate of the binding energy is $D_0(Au^+{-}Xe) = 30.1$ kcal/mol. This value is used to relate calculated and experimentally bracketed binding energies of $Au(L)^+$ complexes with a relative gold(I) cation affinity scale for heteroatom ligands L, i.e., $Xe < C_6F_6 < H_2O < CO < H_2S < CH_3CN \approx C_2H_4 \approx NH_3 \approx CH_3NC < CH_3SCH_3 < PH_3$. In comparison to other transition metal cations, the gold(I) cation is unique in that the binding energies to several ligands are exceptionally large. Further, the covalent character of the $Au^+{-}L$ bonds as well as charge transfer from the ligand to gold are significant. Finally, the gas-phase behavior of Au^+ suggests some implications for possible new approaches to gold(I) chemistry in condensed matter.

Introduction

Probing the interactions between neutral or charged transition metals and organic or inorganic ligands at a molecular level is of fundamental interest in organometallic chemistry.[1] For a deeper understanding of the nature of these interactions, adequate theoretical approaches as well as experimental studies are desirable. In this respect gas-phase studies are particularly suited because they permit the exclusion of complicating effects which prevail in the condensed phase due to aggregation, solvation, or the presence of additional ligands or counterions. Accordingly, the gas phase can be used to combine experimental and theoretical efforts in order to provide simple mnemonics for bonding properties and possibly to propose new routes for condensed-phase chemistry.

The interactions of gold(I) cations with hydrocarbon ligands formed the subject of a series of recent experimental[2,3] and theoretical studies.[4,5] A particularly influential role is played by relativistic effects that are extremely large in gold compounds,[6,7] yet high levels of sophistication can be achieved in the theoretical treatment of gold(I) compounds.[4−13] Information about the gas-phase chemistry of Au^+ with inorganic ligands L is, however, limited to very few systems, i.e., L = halogens,[2b,8,14] water,[3,5b,9] ammonia,[3,5b,c] carbon monoxide,[3,5b,10] and some phosphines.[11,13c]

Here, we report a combined experimental and theoretical study of gold(I) complexes $Au(L)^+$ with ligands (L) containing the heteroatoms O, N, S, and P which are frequently used in gold chemistry. The gold−sulfur interaction is of particular interest due to the self-assembly of molecular monolayers of sulfur compounds on gold surfaces.[15] With regard to the thermochemistry of $Au(L)^+$ complexes, the previously com-

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puted[12] binding energy of the rare gas complex $Au(Xe)^+$ is evaluated by refined theoretical means. Treatment of $Au(Xe)^+$ as a benchmark can provide an absolute reference for a relative gold(I) cation affinity scale and may assist in the interpretation of the trends observed.

Experimental Methods

The experiments were performed with a Spectrospin CMS 47X FTICR mass spectrometer which has been described previously.[16] Au^+ cations were generated by laser-desorption/laser-ionization[17] of a gold target in the external ion source of the instrument. The ions were transferred to the analyzer cell which is located within a superconducting magnet (field strength 7.05 T). The first step in the generation of $Au(L)^+$ cations represents the reaction of mass-selected Au^+ with pulsed-in hexafluorobenzene which leads to the corresponding adduct complex $Au(C_6F_6)^+$. Even though association of Au^+ and C_6F_6 occurs quite fast,[3] the hexafluorobenzene ligand is not very strongly bound to Au^+ (see below) and can be exchanged by other ligands which were introduced at pressures between 10^{-9} and 10^{-7} mbar using leak valves. Subsequently, the ions of interest were mass-selected, typically thermalized by pulsed-in argon,[14] and mass-selected again prior to further ion/molecule reactions. All operations including data accumulation and processing were performed using an ASPECT 3000 minicomputer.

For the experimental evaluation of relative binding energies, three different methods were used: (i) If the disturbing associations of the monoligated gold(I) complexes $Au(L)^+$ with the neutral ligands L or L′ to form bisligand complexes $Au(L)_2{}^+$, $Au(L)(L')^+$, and $Au(L')_2{}^+$, respectively, were not too fast, the equilibria $Au(L)^+ + L' \rightleftarrows Au(L')^+ + L$ were studied by introducing both ligands simultaneously while monitoring the intensities of $Au(L)^+$ and $Au(L')^+$ at various reaction times until equilibria were established. The observed intensity ratios of $Au(L)^+$ and $Au(L')^+$ in conjunction with the ligands' partial pressures p(L) and p(L′) were then used to calculate the equilibrium constants (K_{eq}) from which the change in free energy can be deduced using the Gibbs−Helmholtz equation $\Delta\Delta G = -RT \ln K_{eq}$ assuming $T = 298$ K. (ii) Alternatively, $\Delta\Delta G$ was derived via a kinetic approach in which the rate constants of the forward (k_f) and backward (k_b) reactions $Au(L)^+ + L' \rightarrow Au(L')^+ + L$ and $Au(L')^+ + L \rightarrow Au(L)^+ + L'$, respectively, were measured and used to derive $\Delta\Delta G$ using $K_{eq} = k_f/k_b$. Note that in this approach the relatively large experimental uncertainty of the absolute rate constants[18] can be neglected because relative rate constants are considered. However, association reactions to form bisligated gold(I) complexes may disturb the evaluation in that these may compete with the ligand-exchange reactions. (iii) If the differences in relative gold affinities were large, the exchange reactions were studied only in one direction and the absence or occurrence of a certain ligand-exchange process was used to provide limits of the associated thermochemistry (bracketing method). This approach is less precise than the methods described in i and ii due to the fact that also slightly endothermic reactions can occur under FTICR conditions, though with significantly smaller rate constants.[19] To evaluate the range of the bracketing method in a more quantitative manner, the $Au(L')^+$ complexes were trapped with the more weakly bound ligand L at a pressure of ca. 10^{-7} mbar for 60 s. Hence, complete absence of $Au(L)^+$ (<1%) implies that $D(Au^+{-}L)$ is at least 6 kcal/mol lower than $D(Au^+{-}L')$, if kinetic barriers in excess of the endothermicity are neglected and association reactions do not perturb. Due to the unfavorable pumping characteristics of most of the neutral ligands used in this study, not all possible combinations of ligands have been examined experimentally.

Table 1. Calculated Properties of $Au(Xe)^+$ at the CCSD(T) Level[a] and with the B3LYP Hybrid Method[b]

method[c]	r_{Au-Xe}	ν	D_e	D_0
CCSD(T), A[d]	2.761	129	21.0	20.8
CCSD(T), B	2.681	140	25.7	25.5
CCSD(T), C	2.660	145	27.3	27.1
CCSD(T), D	2.574	149	30.3	30.1
B3LYP	2.845	116	22.2	22.0

[a] Counterpoise corrections are included. [b] Distances r_{Au-Xe} in Å, vibrational frequencies ν in cm^{-1}, and dissociation energies in kcal/mol. [c] A, B, C, and D refer to CCSD(T) calculations with different basis sets, for details see theoretical methods. [d] Taken from ref 12.

Theoretical Methods

To link the relative ligand binding energies determined with the FTICR technique to an absolute scale, a benchmark calculation was performed for the complex of gold(I) cation with xenon, $Au(Xe)^+$. Therefore, coupled cluster calculations with single and double excitations and a perturbative treatment of the triples (CCSD(T)) were performed using the programs Aces II[20] and Molpro.[21] The full counterpoise corrections for the basis-set superposition errors were included. Using the 19- and 8-valence-electron (VE) pseudopotentials of Andrae et al.[22] and Nicklass and Stoll,[23] respectively, four different basis sets (A−D) were applied: Basis A is that used previously,[12] i.e., (8s6p5d1f)/[7s3p4d1f] for Au and (5s5p2d)/[2s2p2d] for Xe, with a single *f* function ($\alpha = 0.2$) on gold. Basis B applies two *f* functions ($\alpha = 0.2$ and 1.19) for gold and the (8s8p6d6f)/[7s7p6d6f] basis of Runeberg for xenon.[24] Basis C equals B, with the exception of using five *f*-functions for gold ($\alpha = 0.067$, 0.2, 0.49, 1.19, 3.6). Basis D equals C, with one *g* function for gold ($\alpha = 1.1077$) added. The Xe basis set used in B−D gives polarizabilities of 27.43 and 27.62 au at MP2 and CCSD(T) levels, respectively, which match well with a previous theoretical estimate of 28.046 au[22] and the experimental values of 27.16[25] and 27.815 au,[26] respectively. In comparison, basis set A used in ref 12 gave a too small MP2 dipole polarizability of 21.025 au for Xe. This is of direct importance for the $Au(Xe)^+$ system whose bonding is both covalent as well as electrostatic with a $V(r) = -(\alpha z^2/2r^4)$ behavior.[12,27] The spectroscopic data in Table 1 are obtained from fits to the corresponding Morse potentials.

Additional theoretical studies were performed using density functional theory (DFT) with the B3LYP[28] hybrid functional. Harmonic frequencies were obtained with B3LYP in order to identify each structure as a genuine minimum and to estimate the zero-point vibrational energy (ZPVE) as well as thermal contributions. Relativity was also accounted for by using a pseudopotential, i.e., an energy-adjusted scalar RECP for gold which covers a $[Kr]4d^{10}4f^{14}$ core.[13] This basis set was augmented by two additional diffuse *d* function and one *f* polarization function resulting in [10s/8p/7d/1f]/(9s/5p/6d/1f) contraction. For the other atoms, standard TZ2P basis sets as implemented in

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Gaussian94[29] were used, except for the calculation of $Au(C_6F_6)^+$ in which the LANL2DZ basis set was applied.

Results and Discussion

In general, the experimental and theoretical techniques currently available permit the examination of a variety of substrates in their interaction with Au^+, and the unique properties in the Au^+ ligation to hydrocarbon molecules were demonstrated earlier to be caused by relativity.[3-5] However, both the experimental and theoretical methods involve costly machinery, and therefore, an obvious initial question deals with the adequate choice of the substrates. Further, heteroatom ligands often exhibit unfavorable pumping characteristics in high-vacuum devices and heavily contaminate the equipment.

To this end it appears appropriate to concentrate on the interaction of Au^+ with a few model substrates which may represent the wide spectrum of metal−ligand interactions in the condensed phase. With respect to the chemistry of gold(I), the heteroatoms O, N, S, and P are certainly among these ligands and within this context, Au−S interactions are of particular interest.[15,30] As a first approach, we have therefore chosen the element hydrides H_2O, NH_3, H_2S, and PH_3 as well as CH_3CN and CH_3NC (the latter were used for practical purposes instead of HCN and HNC) as representative substrates for the interaction of gold(I) with inorganic donor ligands.

$Au(Xe)^+$ and $Au(C_6F_6)^+$ Complexes. Before we address the donor ligands, it is indicated that we gain some further information about the $Au(C_6F_6)^+$ complex which is used as a versatile precursor for the generation of the gold(I) complexes in the gas phase.[3] According to earlier experimental findings, the dissociation energy $D(Au^+-C_6F_6)$ must be quite small as compared to the parent hydrocarbon, i.e., $D(Au^+-C_6H_6) \approx 70$ kcal/mol,[3,5c] yet only an upper limit of $D(Au^+-C_6F_6) < 38$ kcal/mol was determined so far.[3] Recently, the existence of $Au(Xe)^+$ was predicted theoretically, and an estimate of $D(Au^+-Xe) \approx 21$ kcal/mol was provided.[12] While the magnitude of the binding energy is substantial for the interaction of a rare gas with a singly charged metal cation,[31] it is rather low in comparison to other ligands. Thus, xenon may be adequate to obtain a lower limit for the $D(Au^+-C_6F_6)$ by the examination of ion/molecule reactions. Nevertheless, some improvement of the level of theory applied to predict $D(Au^+-Xe)$ was deemed indicated, and to this end the basis sets for Au and Xe were extended.

As seen from Table 1, improved basis sets increase the CCSD(T) dissociation energies $D_e(Au^+-Xe)$. With the larger Basis B the dissociation energy rises by almost 5 kcal/mol, while the saturation of the gold *f* subspace (between B to C) is less important. Notably, inclusion of an additional *g* function on gold (Basis D) has a sizable effect on the computed bond energy and also leads to a significant shrinking of r_{Au-Xe} by almost 0.1 Å. Although the trends from A−D show that the basis sets are far from saturation, for the time being we consider $D_0(Au^+-Xe) = 30.1$ kcal/mol as a benchmark in gold(I) cation chemistry and refer to it as an anchor point.

Table 2. Measured and Calculated[a] Intensities for the $Au(Xe)^+$ and $Au(Xe)_2^+$ Isotope Patterns[b,c]

$Au(Xe)^+$			$Au(Xe)_2^+$		
mass[d]	I_{exp}	I_{calc}	mass[d]	I_{exp}	I_{calc}
325	6.4	7.1	455	44.3	42.6
326	97.2	98.1	456	17.2	17.6
327	13.8	15.2	457	73.4	73.6
328	80.8	78.8	458	93.8	94.4
329	100.0	100.0	459	39.3	42.1
331	37.7	38.7	460	100.0	100.0
333	35.6	33.1	461	48.3	49.9
			462	53.8	53.9
			463	36.2	37.4
			464	20.4	22.3
			465	38.9	34.8
			467	15.6	11.0

[a] The isotope patterns were calculated using the Sheffield ChemPuter (Copyright Mark Winter, 1996) which is available via the Internet at http://www.shef.ac.uk/~chem/chemputer/isotopes.html. [b] Gold is a monoisotopic element, thus only ^{197}Au is considered. [c] The spectra were recorded in the broad-band mode with a mass window ranging from 140 to 1000 amu, a 64K data size for the transient, and zero-filling to 128K prior to Fourier transformation. For details of xenon isotope measurements with FTICR, see: De Koning, L. J. Proefschrift, Universiteit van Amsterdam, Amsterdam, 1989. [d] Nominal masses of $Au(Xe)^+$ and $Au(Xe)_2^+$ isotopomers in amu; only the major isotopomers are listed.

For comparison with the computational results for the other $Au(L)^+$ complexes (see below), we also performed B3LYP calculations on $Au(Xe)^+$. The basis sets used are comparable to Basis A in the CCSD(T) approach,[12] and $D_0(Au^+-Xe) = 22.0$ kcal/mol computed with B3LYP is qualitatively consistent with these results, justifying the use of this level of theory for larger $Au(L)^+$ complexes. A general reservation is, however, that for the time being supermolecular DFT calculations[32] do not describe the dispersion interactions well.

When Au^+ is reacted with pulsed-in C_6F_6 in the presence of xenon, besides $Au(C_6F_6)^+$ also $Au(C_6F_6)_2^+$, $Au(Xe)^+$, $Au(Xe)_2^+$, and $Au(C_6F_6)(Xe)^+$ are observed. The identity of these ions is confirmed by high-resolution mass analysis (e.g., $^{197}Au^{132}Xe^+$: $m_{exp} = 328.8702$ amu, $m_{calc} = 328.8707$ amu, $m/\Delta m > 600\,000$) as well as the typical isotope pattern (Table 2). The ions $Au(Xe)^+$ and $Au(Xe)_2^+$ represent two of the rare examples of reasonably bound xenon compounds with heavy elements.[31,33] Further, mass-selection and subsequent storage of $Au(C_6F_6)^+$ in the presence of xenon reveals that $Au(Xe)^+$ is indeed formed by ligand exchange according to reaction 1.

$$Au(C_6F_6)^+ + Xe \rightarrow Au(Xe)^+ + C_6F_6 \qquad (1)$$

$$Au(Xe)^+ + C_6F_6 \rightarrow Au(C_6F_6)^+ + Xe \qquad (2)$$

In the presence of hexafluorobenzene, the reverse reaction 2 also takes place with mass-selected $Au(Xe)^+$, suggesting that both $Au(L)^+$ species are in thermochemical equilibrium. Unfortunately, the equilibrium constant K_{eq} for the $Au(C_6F_6)^+/Au(Xe)^+$ couple could not be determined because both ions rapidly react with background water ($p < 1 \times 10^{-9}$ mbar) to yield $Au(H_2O)^+$ and also form the adducts $Au(C_6F_6)(Xe)^+$ and $Au(C_6F_6)_2^+$, respectively, as well as $Au(C_6F_6)(H_2O)^+$, $Au(H_2O)(Xe)^+$, and $Au(H_2O)_2^+$. Hence, the monoligated reactants $Au(C_6F_6)^+$ and $Au(Xe)^+$ disappear before the equilibration can be established. Note that the observation of $Au(C_6F_6)(Xe)^+$ also

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Table 3. Total Energies (E), Zero Point Vibrational Energies (ZPVE), Energies at 0 K (E_0), Thermal Corrections ($E_{298} - E_0$), and Gibbs Free Energies (E_{298})[a] (in hartree) and Energetics ΔE_R of the Ligand-Exchange Reaction $Au(C_6F_6)^+ + Xe \rightarrow Au(Xe)^+ + C_6F_6$ Calculated with B3LYP

	E	ZPVE	E_0	$E_{298} - E_0$	E_{298}
$Au(Xe)^+$	−150.598 740	0.000 265	−150.598 475	−0.027 464	−150.625 939
C_6F_6	−827.608 868	0.050 531	−827.558 337	−0.035 372	−827.593 709
$Au(C_6F_6)^+$ [b]	−962.733 180	0.050 321	−962.682 859	−0.040 557	−962.723 416
Xe	−15.469 884		−15.469 884	−0.016 903	−15.486 787
ΔE_R [kcal/mol]	−2.8	0.3	−2.5	−3.4	−5.9

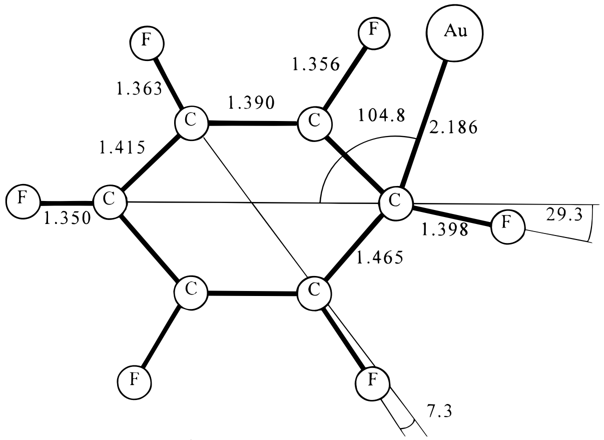
[a] Standard conditions: 298 K, 1 atm. [b] Data for isomer **I**, see Figure 1.

proposes a further route for the genesis of $Au(Xe)_2^+$ cation[12] via a second ligand-exchange reaction, instead of mere association of $Au(Xe)^+$ and xenon.

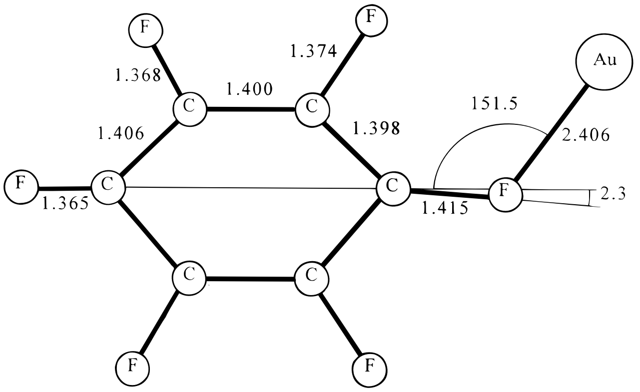
An estimate for $D(Au^+{-}C_6F_6)$ may be achieved by combination of the theoretical results with the measured relative rate constants of reactions 1 and 2. If we assume that the ions are equilibrated to room temperature,[3,18,19] we can convert the measured 1:3 ratio of the rate constants to $\Delta\Delta G(298) = 0.7 \pm 0.4$ kcal/mol in favor of the formation of $Au(C_6F_6)^+$. To relate this figure with the theoretical prediction for $D(Au^+{-}Xe)$, thermal contributions to $\Delta\Delta G$ must be considered. To this end, we examined $Au(C_6F_6)^+$ using the B3LYP approach. While we can certainly not expect that this level of theory would lead to an accuracy of better than ±10 kcal/mol for dissociation energies, it seems appropriate to achieve a reasonable estimate of the thermal contributions in order to compare $D(Au^+{-}L)$ with $\Delta\Delta G$ values.

Interestingly, the calculations predict two structural isomers for $Au(C_6F_6)^+$ (Figure 1). The most stable isomer **I** exhibits C_s symmetry with the gold(I) cation η^3-coordinated to hexafluorobenzene above the ring plane. In analogy to protonated fluoroarenes,[34] however, the η^1-end-on coordination of Au^+ to a fluorine atom is only 4.6 kcal/mol less stable (isomer **II**); a hypothetical C_{6v} symmetrical structure is 18.1 kcal/mol more energetic and bears two imaginary frequencies. At this level of theory, $\Delta\Delta H(0)$ of reaction 1 is calculated to be −2.5 kcal/mol. Not unexpected for an exchange reaction involving an atom,[35] formation of $Au(Xe)^+$ is significantly favored by thermal contributions (Table 3). With B3LYP, $\Delta\Delta G(298)$ for reaction 1 is computed as −5.9 kcal/mol. Adopting a thermal correction of about 3.4 kcal/mol in favor of $Au(Xe)^+$, we can use the experimentally measured $\Delta\Delta G$ of 0.7 kcal/mol in favor of $Au(C_6F_6)^+$ together with the benchmark $D_0(Au^+{-}Xe) = 30.1$ kcal/mol, to estimate $D_0(Au^+{-}C_6F_6) \approx 34$ kcal/mol. While limitations of the B3LYP approach are obvious, the direction of the thermal correction in favor of $Au(Xe)^+$ is distinct and needs to be considered in the evaluation of the relative gold(I) affinities. However, for the larger systems discussed further below, the thermal corrections can almost be neglected because these ligand-exchange reactions do not involve atoms, e.g. for the $Au(NH_3)^+/Au(C_2H_4)^+$ couple.[3]

The low binding energies for $Au(Xe)^+$ and $Au(C_6F_6)^+$ agree well with the finding that these ligands are rapidly exchanged by other ligands. Indeed, the water present in the background of the instrument ($p \approx 10^{-9}$ mbar) is already sufficient to convert $Au(C_6F_6)^+$ and $Au(Xe)^+$ into $Au(H_2O)^+$, which is consistent with $D(Au^+{-}OH_2) \approx 38$ kcal/mol,[3,5c,9] $D(Au^+{-}C_6F_6) \approx 34$ kcal/mol, and $D(Au^+{-}Xe) = 30$ kcal/mol, respectively. In fact, at longer reaction times the background water leads to the disappearance (<1%) of $Au(C_6F_6)^+$ even at $p(C_6F_6) = 2 \times 10^{-7}$ mbar in favor of $Au(H_2O)^+$; however, significant formation of the bisligand complexes $Au(C_6F_6)_2^+$, $Au(C_6F_6)(H_2O)^+$, and $Au(H_2O)_2^+$ prevents the determination of the corresponding equilibrium constant.



η^3-Complex **I**



η^1-end-on Complex **II**

Figure 1. Calculated structures of η^3-coordinated $Au(C_6F_6)^+$ (isomer I) and the η^1-end-on isomer II at the B3LYP level of theory (selected bond lengths in Å, and angles in degrees).

Other $Au(L)^+$ Complexes. The relative Au^+ cation affinities of some inorganic donor ligands can thus be assessed in a similar manner by sequential ligand substitution reactions of $Au(L)^+$ with more strongly bound ligands L′. In these experiments, the $Au(L)^+$ complexes of interest were reacted with other ligands L′ or mixtures of L and L′ in order to study ligand-exchange reactions in analogy to eqs 1 and 2. In almost all cases, the bisligated $Au(L')_2^+$ complexes of the more strongly bound ligand L′ were observed as the final reaction products at long reaction

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Table 4. Occurrence (+) and Nonoccurrence (−) of Ligand-Exchange Reactions $Au(L)^+ + L' \rightarrow Au(L')^+ + L$ for Various Ligands L and L′ [a]

L	Xe	C_6F_6	H_2O	CO	H_2S	L′ CH_3CN	C_2H_4	NH_3	CH_3NC	CH_3SCH_3	PH_3
Xe	○	+[b]	+	+	+[c]	+[c]	+[c]	+[c]	+[c]	+[c]	+[c]
C_6F_6	+[b]	○	+	+	+	+	+	+	+	+	+
H_2O	−	−	○	+	+	+	+	+	+	+	+
CO	−	−	−	○	+	+	+	+	+	+[c]	+
H_2S	−[c]	−	−	−	○	+	+	*d*	*d*	*d*	+
CH_3CN	−[c]	−	−	−	−	○	+[b]	*d*	*d*	*d*	*d*
C_2H_4	−[c]	−	−	−	−	+[b]	○	+[b]	+[b]	+	+
NH_3	−[c]	−	−	−	*d*	*d*	+[b]	○	*d*	*d*	*d*
CH_3NC	−[c]	−	−	−	*d*	*d*	+[b]	*d*	○	*d*	+
CH_3SCH_3	−[c]	−	−	−[c]	*d*	*d*	−	*d*	*d*	○	+
PH_3	−[c]	−	−	−	−	−	−	*d*	−	−	○

[a] The circles denote the degenerate ligand-exchange reactions $Au(L)^+ + L \rightarrow L + Au(L)^+$. For all ligand combinations, bisligated complex $Au(L)_n(L')_{2-n}{}^+$ ($n = 0-2$) formation was observed as secondary reactions (see text). [b] For these ligand combinations, forward and backward exchange reactions were observed if both ligands were leaked simultaneously into the mass spectrometer (see text). [c] These reactions were not studied explicitly, and the corresponding entries are extrapolated from the others. [d] These reactions were left out because they would require the leaking-in of two sticky reagents to the vacuum system.

times. More than 2-fold coordination of gold(I) can only be achieved at significantly higher pressures, probably involving van der Waals type binding.[36] Note that ligand exchange of $Au(C_6F_6)^+$ was observed neither for the inorganic molecules H_2, N_2, CO_2, and O_2 nor for the rare gases[12,27] krypton and argon. Further, except for association and ligand-exchange reactions, no particular gas-phase chemistry of gold cation has been observed for any of the substrates under study, which is in marked contrast to the broad variety of bond activations, coupling reactions, etc. prevailing in bare and ligated complexes of other transition metal ions[1] but in line with the classification of gold as a catalytically nonactive metal.[37]

Using this methodology (Table 4), an upper limit for $D(Au^+-OH_2)$ can be derived from the complete conversion of $Au(H_2O)^+$ into $Au(CO)^+$ in the presence of carbon monoxide and vice versa from the absence of $Au(H_2O)^+$ when $Au(CO)^+$ is reacted with water. Thus, $D(Au^+-OH_2)$ is at least 5 kcal/mol smaller than $D(Au^+-CO)$. The gold(I) carbonyl complex $Au(CO)^+$ has been studied computationally at various levels of theory which consistently suggest $D(Au^+-CO)$ to be in the order of 45 kcal/mol (B3LYP, 43.6;[3] CCSD(T), 44.1;[3] MP2, 45.1;[10a] 50.1[5b]), though also slightly higher values have been obtained with density functional methods.[5c] Recently, we learned about an extensive theoretical study which predicted $D_0(Au^+-CO) = 48 \pm 2$ kcal/mol,[38] and we adopt this value further below. In agreement with the large difference in relative gold(I) affinities for water and carbon monoxide, an equilibrium between $Au(H_2O)^+$ and $Au(CO)^+$ could not be established, and $Au(CO)^+$ evolves as the exclusive monoligated gold(I) complex whenever carbon monoxide was present as a neutral reagent in the FTICR mass spectrometer.

Hydrogen sulfide turns out to be more strongly bound to Au^+ than carbon monoxide, and B3LYP predicts $D(Au^+-SH_2) = 55.5$ kcal/mol. In accord with this result, $Au(H_2S)^+$ represents the exclusive monoligated gold(I) complex (>99.8%) when $Au(CO)^+$ is trapped for long reaction times in a 50:1 mixture of CO and H_2S, suggesting that $D(Au^+-SH_2)$ exceeds $D(Au^+-CO)$ by at least 6 kcal/mol. The calculated structure of $Au(H_2S)^+$ (Figure 2) deviates from the planar arrangement expected for a perfect alignment of the H_2S dipole with Au^+ due to some covalent character of the bond, in analogy to the previously described $Au(H_2O)^+$ cation.[9] Nevertheless, the local geometry of the H_2S moiety is hardly perturbed by the presence of gold cation, i.e., $r_{S-H} = 1.354$ Å and $\alpha_{HSH} = 94.3°$ in the complex as compared to $r_{S-H} = 1.344$ Å and $\alpha_{HSH} = 92.5°$ in free hydrogen sulfide. To obtain an upper limit for $D(Au^+-SH_2)$, the reactions of $Au(H_2S)^+$ with ammonia and ethene were examined. Complete replacement of H_2S by NH_3 and C_2H_4, respectively, was observed even for a 100-fold excess of H_2S, suggesting that $D(Au^+-NH_3)$ as well as $D(Au^+-C_2H_4)$ exceed $D(Au^+-SH_2)$ by at least 6 kcal/mol.

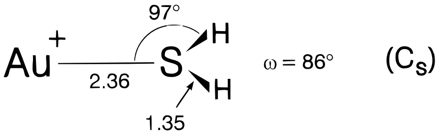

Figure 2. Calculated structure of $Au(H_2S)^+$ at the B3LYP level of theory (bond lengths in Å, and angles in degrees; ω defines the angle between the HSH plane and the Au−S axis).

The $Au(NH_3)^+$ and $Au(C_2H_4)^+$ complexes have been studied previously,[3,4a,5b−d] and B3LYP predicts $D(Au^+-NH_3)$ and $D(Au^+-C_2H_4)$ as 63.5 and 68.6 kcal/mol, respectively. In this case, however, equilibrium measurements gave a reverse order of relative stabilities, i.e., $\Delta\Delta G$ is 2.3 ± 0.5 kcal/mol in favor of $Au(NH_3)^+$ and thermal corrections are negligible.[3] This discrepancy demonstrates that the B3LYP approach is of limited accuracy, and in fact pure density functional methods, rather than the hybrid method B3LYP, predict $Au(NH_3)^+$ as the more stable complex[5c] in agreement with the experiments.[3] The current study provides a reasonable value for $D(Au^+-Xe)$, but this anchor point is much too far away to deduce the energetics for $Au(NH_3)^+$ and $Au(C_2H_4)^+$. Previously, a lower limit of $D(Au^+-C_2H_4) > 59$ kcal/mol was obtained experimentally from the replacement of the iodine ligand in AuI^+ by ethene.[3] Refinement of the latter value can be achieved by the observation that AuI^+ cation can inter alia be formed by reacting Au^+ cation with iodobenzene. Accordingly, $D(Au^+-I)$ must exceed $D(C_6H_5-I) = 64.7$ kcal/mol,[39] such that the replacement of iodine in AuI^+ by ethene to yield $Au(C_2H_4)^+$ raises the lower limit of $D(Au^+-C_2H_4) > 65$ kcal/mol. This result is in agreement with the calculated binding energies, but more precise

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values cannot be achieved for the time being and are in fact difficult to achieve with bracketing experiments.

The gold(I) affinities of CH_3CN and CH_3NC are of similar size to that of ethene, and fortunately, the associations to form the corresponding bisligated complexes are not too fast such that the equilibrium constants can be determined experimentally. Equilibration of $Au(L)^+$ ions in C_2H_4/CH_3CN mixtures implies that $D(Au^+{-}NCCH_3)$ is 1.0 ± 0.3 kcal/mol lower than $D(Au^+{-}C_2H_4)$. A similar value of 0.8 ± 0.4 kcal/mol in favor of $Au(C_2H_4)^+$ is derived from the kinetics of the forward and backward ligand exchange using $K_{eq} = k_f/k_b$. The reasonable agreement of the values derived from the equilibrium measurement and the kinetic approach also adds confidence to the inherent assumption that no kinetic barriers in excess of the reaction exothermicities are operative for ligand exchange in monoligated gold(I) complexes. Interestingly, despite the fact that $D(Au^+{-}C_2H_4)$ exceeds $D(Au^+{-}NCCH_3)$ for the monoligated complex, $Au(CH_3CN)_2^+$ rather than $Au(C_2H_4)_2^+$ is formed as the major bisligated complex at longer reaction times. This observation suggests that the binding energies do not strictly follow additivity,[40,41] i.e., $D(Au^+{-}C_2H_4) > D(Au^+{-}NCCH_3)$, but $D(LAu^+{-}C_2H_4) < D(LAu^+{-}NCCH_3)$ for L = C_2H_4 and CH_3CN. The observed preference for the formation of $Au(CH_3CN)_2^+$ in the gas phase is also consistent with the stability of this ion in solution.[42] Methyl isocyanide is, however, more strongly bound to gold(I) cation than ethene by 2.3 ± 0.5 and 2.6 ± 0.8 kcal/mol, using the equilibrium method and the kinetic approach, respectively. The bisligated complex of the stronger isonitrile ligand $Au(CH_3NC)_2^+$ appears as the exclusive final reaction product in this case.

Due to the particular relevance of gold−sulfur interactions for the formation of self-assembled monolayers,[15,30] we briefly examined the effect of alkylation of sulfur. Not surprisingly, methanethiol CH_3SH is more strongly bound to Au^+ than hydrogen sulfide, and dimethyl sulfide CH_3SCH_3 binds even better to Au^+ than ethene. The thermochemistry, could, however, not be assessed quantitatively for these two ligands, because the association reactions to form the corresponding bisligated complexes occurred too rapidly, and $Au(CH_3SH)_2^+$ and $Au(CH_3SCH_3)_2^+$, respectively, predominate at long reaction times. This failure is indeed somewhat expected, because alkylation increases the density of states and thereby facilitates association reactions.

Finally, ligation of phosphine to Au^+ was examined. In agreement with the widespread use of phosphines as ligands in gold(I) chemistry, PH_3 turns out to be the strongest ligand studied so far. In fact, even 1,3-butadiene[3] and dimethyl sulfide ligands are completely replaced in the presence of phosphine leading to $Au(PH_3)^+$ and subsequently $Au(PH_3)_2^+$. A substantial gold(I) cation affinity of phosphine has already been suggested in a comprehensive theoretical study by Häberlen and Rösch who predicted $D(Au^+{-}PH_3)$ to be as large as 95.9 kcal/mol.[11] Although we cannot provide a precise experimental value for $D(Au^+{-}PH_3)$, the observation of phosphine as a strong ligand suggests that the gold(I) cation affinity to phosphine is well above 80 kcal/mol which is consistent with the computational prediction.

Table 5. Bond Dissociation Energies *D* (kcal/mol) of $M(C_2H_4)^+$ Complexes for Transition Metals M (If Available, the Data Were Taken from Ref 31 and Otherwise Estimated)[a]

Sc	32	Y	33	La	46
Ti	31	Zr	35[b]	Hf	36[c]
V	28	Nb	37[b]	Ta	44[c]
Cr	30	Mo	25[b]	W	50[c,d]
Mn	20	Tc	26[e]	Re	30[c]
Fe	35	Ru	30[b]	Os	45[c,d]
Co	43	Rh	31	Ir	56[c,d]
Ni	42	Pd	28[c]	Pt	55[c,d]
Cu	45	Ag	34	Au	69[f]

[a] Estimates based on a comparison of $M(L)^+$ bond energies given in ref 31 within the corresponding transition metal series. [b] Estimate derived from the known $D(M^+{-}C_2H_2)$ values for this element and $D(M^+{-}C_2H_2)$ and $D(M^+{-}C_2H_4)$ of the corresponding 3d homolog. [c] Crude estimate derived from the known $D(M^+{-}CH_2)$ values for this element and its 3d and 4d homologs. [d] Consideration of 3d versus 4d elements in the estimation is divergent, indicating increased errors. [e] Estimated as: $D(Tc^+{-}C_2H_4) = D(Tc^+{-}CO) + [D(Mn^+{-}C_2H_4) - D(Mn^+{-}CO)]$; for consistency, in this case only theoretical values were considered. [f] This work.

Comparison of the $Au(L)^+$ Complexes. Ligation of gold(I) cation is remarkably different as compared to other transition metal cations. Let us illustrate this statement by referring to three examples. (i) While $D(Au^+{-}OH_2)$ is within the range of most $M^+{-}OH_2$ interactions in the gas phase,[31] hitherto $Au(H_2O)^+$ is the only water complex of a singly charged transition metal cation which deviates from C_{2v} symmetry due to pyramidalization.[9] In ionic solids, however, nonplanar geometries of $M^{n+}(OH_2)$ subunits are known for $n > 1$, and these deviations have been attributed to increasing sp-hybridization.[43] Similarly, the pyramidalized structures of $Au(H_2O)^+$ and $Au(H_2S)^+$ indicate significant covalent binding together with electron transfer from the ligand to gold cation. (ii) The strengths of several $Au^+{-}L$ bonds are exceptional as compared to other metal cations.[31] Due to the lack of comprehensive data sets for the heteroatom ligands under study, let us refer to the ethene complexes $M(C_2H_4)^+$ among which $D(Au^+{-}C_2H_4)$ significantly exceeds all other binding energies (Table 5). In the comparison of $D(M^+{-}C_2H_4)$, the data for first- and second-row transition metals appear quite reliable, but the comparison cannot be more than a guideline for the third-row transition metals, because with the exception of $D(La^+{-}C_2H_4)$[44] no data are available for these $M(C_2H_4)^+$ complexes, and some rough estimates had to be applied (see footnotes to Table 5). In particular, among the platinum group, for which relativistic effects are known to be significant, $M(C_2H_4)^+$ complexes of similar bond strengths as found for $Au(C_2H_4)^+$ may be expected. (iii) The gold(I) affinities of several ligands are sufficiently large that these can replace typical covalent ligands such as iodine in the AuI^+ cation.[3] The computed $D(Au^+{-}PH_3)$ = 96 kcal/mol[11] even exceeds the strength of the covalent P−H bond in phosphine (84 kcal/mol).[39] On the other hand, the gold(I) affinities of some open-shell ligands can be rather low. For example, $D(Au^+{-}F)$ = 18 kcal/mol[8,14] probably represents one of the weakest metal−fluorine bonds known, and its magnitude is similar to

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Table 6. Survey of the Calculated and Experimentally Bracketed Bond Dissociation Energies (*D*, kcal/mol) of $Au(L)^+$ Complexes

	MP2	CCSD(T)	B3LYP	ADF/BP[a]	BLYP[a]	experimental brackets
$Au(Xe)^+$		30.3[b]	22.2[b]			$D(Au^+{-}C_6F_6) - D(Au^+{-}Xe) = 3.8$ kcal/mol
$Au(C_6F_6)^+$			19.4[b]			$D(Au^+{-}OH_2) - D(Au^+{-}C_6F_6) > 6$ kcal/mol
$Au(H_2O)^+$	38.8[c]	35.9[c]	37.0[c]	41.2	38.1	$D(Au^+{-}CO) - D(Au^+{-}OH_2) > 5$ kcal/mol
$Au(CO)^+$	45.3,[d] 50.1[a]	44.1,[a] 48 ± 2[e]	43.6[a]	53.5	46.0	$D(Au^+{-}SH_2) - D(Au^+{-}CO) > 6$ kcal/mol
$Au(H_2S)^+$			55.5[b]			$D(Au^+{-}C_2H_4) - D(Au^+{-}SH_2) > 6$ kcal/mol
$Au(CH_3CN)^+$						$D(Au^+{-}C_2H_4) - D(Au^+{-}NCCH_3) = 1.0 \pm 0.3$ kcal/mol
$Au(C_2H_4)^+$	73.1[a]	68.8[a]	68.6[a]	70.0	63.8	$D(Au^+{-}C_2H_4) > D(Au^+{-}I) > D(C_6H_5{-}I) = 65$ kcal/mol
$Au(NH_3)^+$	68.6[a]	65.3[a]	63.5[a]	72.5	70.2	$D(Au^+{-}NH_3) - D(Au^+{-}C_2H_4) = 2.3 \pm 0.5$ kcal/mol
$Au(CH_3CN)^+$						$D(Au^+{-}CNCH_3) - D(Au^+{-}C_2H_4) = 2.3 \pm 0.5$ kcal/mol
$Au(CH_3SCH_3)^+$						$D(Au^+{-}S(CH_3)_2) > D(Au^+{-}C_2H_4)$
$Au(PH_3)^+$				95.9[f]		$D(Au^+{-}PH_3) - D(Au^+{-}C_2H_4) > 6$ kcal/mol

[a] References 5b,c. [b] This work. [c] Reference 9. [d] Reference 10a. [e] Theoretical evaluation, see ref 38. [f] Density functional theory, data taken from ref 11.

those of ionized alkali halides.[39] (iv) Ligation drastically reduces the ionization energy of gold atom (9.25 eV), thus strongly stabilizing gold(I) compounds. For example, combination of $D(Au^+{-}C_2H_4) = 69$ kcal/mol derived in this work with $D(Au{-}C_2H_4) < 12$ kcal/mol for the neutral complex[45] implies a lowering of the IE upon ligation with ethene by about 2.5 eV. The results of Häberlen and Rösch[11] suggest that for the phosphine ligand $IE(Au(PH_3))$ is even 2.9 eV lower than IE(Au). The trend of cation stabilization by ligation represents a general phenomenon,[1b,31] but the magnitude of this effect seems particularly large for gold.

The origin of the exceptional behavior of gold is due to relativity, and we would like to describe this in a simple chemical mnemonic for the coinage metals. Atomic Cu, Ag, and Au have s^1d^{10} ground states in the neutral and s^0d^{10} ground states in the monovalent cation states. Relativistic effects significantly stabilize the 6s orbital of the gold atom by about 2 eV, while these effects are almost negligible for copper and silver, being roughly proportional to the square of nuclear charge.[4,6,7,10b] As a consequence, not only does the ionization energy of atomic gold increase due to relativity but the 6s orbital also becomes much more electrophilic as compared to the 4s and 5s orbitals of Cu and Ag, respectively. Purely electrostatic interactions would suggest that the binding energies to a ligand L decrease from copper to gold. Due to the electrophilicity of the 6s orbital of Au^+, however, dative interactions involving partial electron transfer from the ligand to gold become significant resulting in an increase of covalent bonding in gold(I) complexes the lower is the ionization energy of the ligand.[3,46] With regard to the examples mentioned above, we can explain the binding situations as follows. (i) Like the oxonium and sulfonium ions H_3O^+ and H_3S^+, the $Au(H_2O)^+$ and $Au(H_2S)^+$ cations trade-off planarity because the ligands can act as σ donors.[9] In fact, the binding features of gold(I) show some distinct similarities to those of a proton.[47] (ii) The exceptionally large $D(Au^+{-}C_2H_4)$ can be traced back to the fact that ethene is a good π-donor and the difference of $IE(C_2H_4) = 10.5$ eV and $IE(Au) = 9.25$ eV[39] is not too large such that partial electron transfer can occur. In fact, the electronic structure of $Au(C_2H_4)^+$ is best described as that of a metallacyclopropane, rather than a Dewar−Chatt−Duncanson type π complex.[5d] Similarly, $D(Au^+{-}PH_3)$ is even larger than $D(Au^+{-}C_2H_4)$ because phosphine has better donor properties as well as a lower ionization energy (9.87 eV)[39] than ethene; moreover, relativistic effects are also quite large in the $Au(PH_3)^+$ complex.[13c] (iii) In view of the preceding arguments, the preference of gold(I) cation to attach dative ligands becomes clear. Thus, due to the high electrophilicity of the $6s^05d^{10}$ ground state of Au^+, its affinity to donor ligands is high, whereas covalent binding to an open-shell ligand $X^\bullet$ would involve excitation to an $6s^15d^9$ state formally leading to an unfavorable Au(II) compound. This way of reasoning also provides a rationale for the counterintuitive fact that $D(Au^+{-}X)$ increases from X = F to X = I. The $Au^+{-}X$ bond is best described in terms of an ion−dipole complex of gold cation with an $X^\bullet$ radical, rather than being of covalent nature. Hence, $D(Au^+{-}X)$ increases with the size of X because the polarizability increases and charge-transfer stabilization becomes more effective. Note that this argument does not contradict the covalent participation in the $Au(L)^+$ complexes with closed-shell ligands mentioned above because the latter would result in partial electron transfer to gold and thus a resonating binding of the type $Au^+{-}L \leftrightarrow Au{-}L^+$. Alternatively, the ligand may serve as a two-electron donor/acceptor as, for example, in the metallacyclopropane structure[5d] of $Au(C_2H_4)^+$ which formally corresponds to a favorable Au(III) compound. (iv) The unusually large decreases of the ionization energy upon ligation of gold(I) can also be rationalized by referring to the electronic situation. Due to the singly occupied 6s orbital in the neutral gold atom ($6s^15d^{10}$), the Au−L interactions are weak in the neutral complexes with closed-shell ligands L.[45] In contrast, strong electrostatic and covalent interactions along with charge-transfer arise for Au^+ ($6s^05d^{10}$). Precisely the opposite applies for the binding of gold to radicals $X^\bullet$ in that the neutral species involve coupling of the $6s^15d^{10}$ configuration of gold with the unpaired electron of $X^\bullet$ leading to a chemical bond with an appreciable binding energy. Upon cationization of AuX, however, one of the binding electrons is essentially removed. As a consequence, open-shell ligands lead to a drastic increase of IE(AuX) as compared to IE(Au) = 9.25 eV; e.g. IE(AuF) ≈ 11.5 eV.[48]

Finally, let us address the appealing question whether there exist some guidelines to *predict* gold(I) cation affinities in the gas phase using properties of the free ligands. To get a more concise picture of the bonding situations, let us therefore try to correlate the gold(I) cation affinities to some properties of the ligands L in $Au(L)^+$ complexes. For this purpose it is mandatory to obtain a reasonable compromise of the experimental brackets and the manifold of computational results obtained at various levels of theory (Table 6). The present results allow us to derive semiquantitative gold(I) cation

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(45) Nicholas, G.; Spiegelman, F. *J. Am. Chem. Soc.* **1990**, *112*, 5410.

(46) In this respect, the nature of the bond in $Au(C_6H_6)^+$ is particularly intriguing, because the IEs of gold and benzene are virtually identical.

(47) For a leading reference, see: Schmidbaur, H.; Hofreiter, S.; Paul, M. *Nature* **1995**, *377*, 502.

(48) The theoretical value given in ref 8b has been corrected for the reported underestimation of the calculated IE(Au).

Table 7. Best Estimates for the Dissociation Energies of Cationic Gold(I) Complexes (D(Au$^+$−L), kcal/mol) as Well as Ionization Energies (IE, eV)[a] and Proton Affinities (PA, kcal/mol)[b] of the Ligands L

	D(Au$^+$−L)[c,d]	IE(L)[e]	PA[e]
Au(Xe)$^+$	30 ± 3	12.13	118.6
Au(C_6F_6)$^+$	34 ± 3	9.91	177.7
Au(H_2O)$^+$	38 ± 4	12.62	166.5
Au(CO)$^+$	48 ± 2[f]	14.01	141.9
Au(H_2S)$^+$	55 ± 6	10.45	170.2
Au(CH_3CN)$^+$	68 ± 7	12.19	188.2
Au(C_6H_6)$^+$	69 ± 7	9.25	181.3
Au(C_2H_4)$^+$	69 ± 7	10.51	162.6
Au(C_3H_6)$^+$	70 ± 7	9.73	179.5
Au(NH_3)$^+$	71 ± 7	10.07	204.0
Au(CH_3NC)$^+$	71 ± 7	11.24	201.4
Au(CH_3SCH_3)$^+$	80 ± 8	8.69	200.6
Au(PH_3)$^+$	96 ± 8	9.87	188.6

[a] Reference 39. [b] Reference 49. [c] Evaluated from the theoretical and experimental data given in Table 6. [d] The absolute error of D(Au$^+$−L) is estimated as ±10% of the binding energy. Note, however, that the error in the relative affinities may be much smaller. [e] For errors, see refs 39 and 49. [f] Value derived from a detailed theoretical evaluation adopted from ref 38.

affinities (Table 7), but the evaluation must certainly neglect some minor inconsistencies, e.g. the divergent experimental and theoretical results for the Au(C_2H_4)$^+$/Au(NH_3)$^+$ couple.[3,5c] As a result of these disagreements and in particular due to the fact that we are dealing with theoretically predicted binding energies as references, an error estimate is rather difficult to achieve, though not impossible.[38] Nevertheless, we shall avoid the impression of an ultimate precision of the data given in Table 7 and assign an error of about 10% of the evaluated binding energies. Note that this restriction further accentuates the need for an absolute experimental anchor point for cationic gold complexes in the gas phase.

The nature of the bond of a ligand L to a transition metal cation can inter alia be influenced by two fundamental properties of L. The proton affinity (PA)[49] of L resembles the general preference of L to coordinate with cations and combines covalent as well as electrostatic interactions. The ionization energy (IE)[39] of the ligand may serve as a characteristic parameter for the amount of electron transfer from the ligand to the metal. Correlations of D(M$^+$−L) with the proton affinities of the ligands have been reported for a series of bare and ligated cationic transition metal ions M$^+$, and in some cases correlation coefficients close to unity have been obtained.[1b,50]

Figures 3a and 3b show that there exists some trends between the gold(I) cation affinities of the ligands and their proton affinities and ionization energies, respectively, but no direct correlations are apparent and the data are spread widely. For example, the proton affinities of water and ethene are quite similar (Table 7) while the binding of Au$^+$ to ethene is almost twice that of water. Similarly, the IEs of hexafluorobenzene, phosphine, and propene are quite close, but their gold(I) cation affinities differ largely. Thus, we conclude that despite some obvious trends, none of the correlations taken alone is satisfactory, and within a reasonable error margin not even a semiquantitative prediction of D(Au$^+$−L) is feasible. Hence, ligation of Au$^+$ is a result of the combination of electrostatic, dative, and charge-transfer interactions which are not at all additive and demand explicit consideration of each individual ligand.

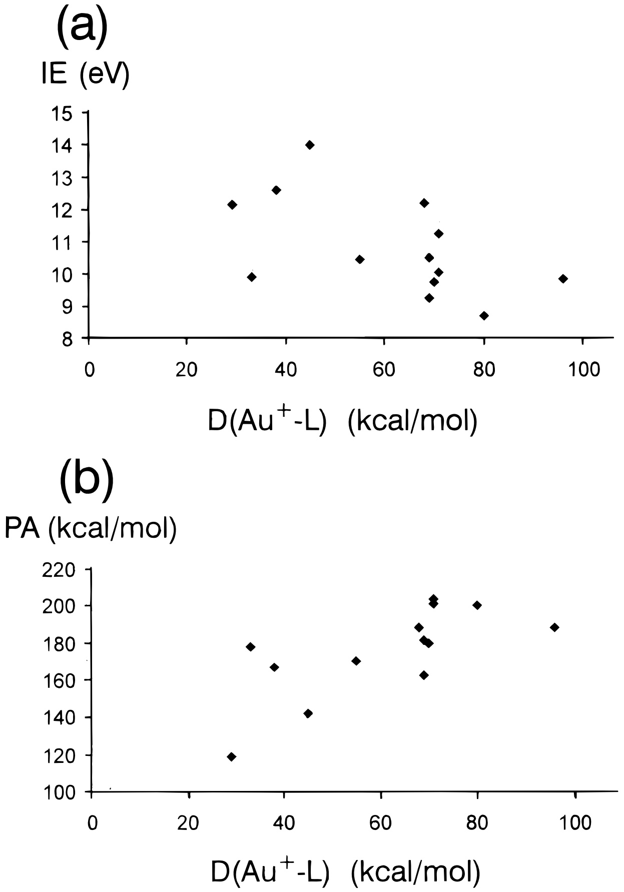

Figure 3. (a) Ionization energies (eV) of the ligands L versus the dissociation energies D(Au$^+$−L) (kcal/mol). (b) Proton affinities (kcal/mol) of the ligands L versus the dissociation energies D(Au$^+$−L) (kcal/mol). Thermochemical data of the free ligands are taken from ref 39.

This result emphasizes the value of theoretical calculations and moreover highlights the need for more concise bonding mnemonics for the correlation of microscopic properties with bulk quantities.

Conclusion

In the gas phase, Au$^+$ cation exhibits an exceptional ordering of ligand affinities as compared to other transition metals, by and large due to relativistic effects operative in gold(I) compounds. The theoretical prediction of D(Au$^+$−Xe) is among the most accurate energetic information on gaseous gold(I) complexes available today;[38] however, the variance of gold(I) cation affinities to closed-shell ligands is wide. In this respect, the bracketing range of the FTICR technique is not satisfactory, and association reactions to bisligand complexes may obstruct the equilibrium measurements. Further, these experiments are quite time-consuming because most of the donor ligands studied exhibit unfavorable characteristics in high-vacuum devices. Therefore, a more comprehensive evaluation of the gold(I) cation affinity scale by using other experimental techniques, such as Cooks' kinetic method[51] or threshold measurements,[1c] would be advantageous. A combination of the kinetic method with chemical ionization in a sector mass spectrometer would represent a convenient approach,[52] but it would require the availability of gold compounds which can be used as precursors.

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(49) Lias, S. G., Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695

(50) Operti, L.; Tews, E. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 5847 and references therein.

(51) Cooks, R. G.; Patrick, J. S.; Kotiqaho, T.; McLuckey, S. A. *Mass. Spectrom. Rev.* **1994**, *13*, 287.

Such compounds must, however, be sufficiently volatile at ambient temperatures *and* stable toward decomposition to metallic gold; unfortunately, all precursors we have examined so far do not meet these criteria.

More precise experimental determinations of the unusually large $Au^+-C_2H_4$ and Au^+-PH_3 binding energies[3,5d,11] are desirable and would in particular aid in the judgment of the various theoretical approaches. Spectroscopic characterization[53] of the $Au(Xe)^+$ cation would be particularly beneficial for the development of ab initio methods because the present results demonstrate that despite the theoretical effort applied even the inclusion of a single *g* function on gold still has significant effects on the structure and energetics of $Au(Xe)^+$.

With respect to gold chemistry in the condensed phase, most of the binding energies follow expectation, but the low value of $D(Au^+-C_6F_6)$ and the large size of $D(Au^+-C_2H_4)$ suggest further perspectives on gold(I) chemistry by using perfluorinated solvents on one hand and olefin ligands on the other hand. Further, the gas-phase behavior of Au^+ implies a viable route for the synthesis of the elusive gold(I) fluorides[8,10b,14] in condensed matter. While the interaction of neutral gold with xenon seems to be negligible, the considerable size of $D(Au^+-Xe)$ suggests that the fluorination of gold in liquid xenon using equimolar amounts of appropriate reagents (e.g. fluorine or XeF_2) may indeed lead to monovalent gold(I) fluorides which may be kinetically stabilized against disproportionation to Au(0) and Au(III) by the presence of xenon, for example, the yet unknown (Xe)AuF.

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