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Energetics and structures of adducts of JohnPhos(Au⁺), PPh₃(Au⁺) and IPr(Au⁺) with organic substrates. A mass spectrometry and DFT study

Claudio Iacobucci,^a Lionel Massi,^a Elisabet Duñach,^a Peeter Burk,^b and Jean-François Gal^{*a}

^a. Université Côte d'Azur, CNRS, Institut de Chimie de Nice, UMR 7272, 06108 Nice, France

^b. University of Tartu, Institute of Chemistry, Ravila 14a, 50411 Tartu, Estonia

Graphic for Table of Contents and Abstract

Abstract

We report a mass spectrometry study of the interaction between three representative Au(I) catalysts containing the ligands **L** = JohnPhos (2-biphenyl[bis(2-methyl-2-propanyl)]phosphine), TPP (PPh₃, triphenylphosphine), the *N*-heterocyclic carbene IPr (carbene form of 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazole), and 27 organic molecules **S** (substrates) bearing organic functionalities often present in reactants (alkenes, alkynes, allenes, enol ethers, aldehydes, ketones, epoxides). An experimental scale of gas-phase relative binding energy between three **L**(Au⁺) ions and the organic substrates was established by energy-resolved experiments of the 81 cationic two-coordinate gold adducts **L**(Au⁺)**S** using a quadrupole ion trap mass spectrometer. The experimental scale is expressed in units of normalized collision energy for 50% dissociation (NCE₅₀) of the precursor ion. In parallel, the gas-phase bond dissociation energetics and the structure of adducts were probed by DFT calculations. The experimental affinity order of each substrate for the three cationic gold complexes **L**(Au⁺), IPr(Au⁺) > TPP(Au⁺) > JohnPhos(Au⁺), is well reproduced by the calculated bond dissociation energies ΔE . At the computational level used in this study, the agreement between the calculated ΔE and the experimental NCE₅₀ values is limited to series of substrates with the same functionality, and reasonable correlations NCE₅₀ vs. ΔE are observed within series. The DFT-optimized structures are discussed and compared with available X-ray crystal structures. Although no general trend can be observed between bond lengths, or their changes upon coordination with the **L**(Au⁺) cations, and dissociation energies, a significant correlation between Au-O distance (**S** = O-bases) and ΔE is observed.

INTRODUCTION

In the last decade, Au(I) complexes have emerged as highly efficient tools in synthesis due to their ability to activate a wide range of chemical functions under mild and catalytic conditions.^{1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 1-17}

The gold atom in Au(I) complexes presents a remarkable carbophilic character, resulting in highly effective Lewis acids for the electrophilic activation of unsaturated hydrocarbons, often through a cationic two-coordinate gold π adducts.¹⁸ The Au(I) complexes are also referred as π acids, or Lewis acids with a distinctive “soft” character.¹⁹

The rationalization of the catalytic effects may benefit from quantitative measurements of the interactions of gold catalysts with organic ligands. The first efforts to establish quantitative Au(I) cation affinity scales for series of small Lewis bases started in 1990's in the Schwarz group in Berlin by Detlef Schröder et al.,^{20, 21} using Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The Au^+ ions were obtained by laser desorption from a solid target, and relative affinities were determined by ligand exchange at low pressure in the ICR trapping cell.

With the advent of electrospray ionization (ESI) as an ionization source in mass spectrometry, it was possible to produce more complex adduct ions by desolvation from solution containing metal salts and various neutral ligands. Applications of ESI-MS to studies on catalysis, using the additional possibility of dissociating ions by collision (collision induced dissociation, CID, or tandem MS, or MS/MS), and of ion/molecule reactions, were often advocated, in particular by Chen²², Plattner,^{23, 24} and O'Hair.²⁵

In the field of gold catalysis, a quantitative approach of $[\text{AuPMe}_3]^+$ /substrate bonding has been made by Jašíková and Roithová, by a careful treatment of the curves of the ion intensities (precursor and product ions) as a function of the collision energy.^{26, 27} This technique, usually called energy-resolved CID, or energy-resolved mass spectrometry (ERMS), provided gas-phase interaction energies between the $[\text{AuPMe}_3]^+$ cation and 9 unsaturated hydrocarbons.²⁶

In the Jašíková and Roithová work, the experimental bond dissociation energy (BDE) of the $[\text{AuPMe}_3]^+$ adducts with unsaturated hydrocarbons ranged from 162 to 186 kJ mol^{-1} , for benzene and 1,5-cyclooctadiene, respectively. The authors also reported calculated BDEs at density functional theory (DFT) level, which reproduced the general trend, although being systematically lower by 10 to 36 kJ mol^{-1} than the experimental values.

More recently, Gatineau et al. published experimental BDEs of the $\text{Au}^+ \text{--CO}$ bond for 16 adducts of general formula $\text{L}(\text{Au}^+)\text{CO}$, in which **L** are phosphines, phosphites or nitrogen-heterocyclic carbenes ligand frequently used in gold catalysis.²⁸

Experimental BDEs were established by a thorough analysis of the ERMS ion intensity curves. The BDE values for these $\text{L}(\text{Au}^+)\text{CO}$ systems were in the range 131 to 174 kJ mol^{-1} , showing a significant dependence on ligand **L** structure. DFT calculations reproduced the experimental BDEs with a fair precision.

In the present work, we also applied ERMS, using a quadrupole ion trap mass spectrometer, for the quantitative description of the $\text{Au}^+ \text{--} \text{S}$ bonding (S = substrate) in a series of 81 $[\text{L}(\text{Au}^+)\text{S}]$ adducts, L being one of the three ligands shown in adduct structures, Scheme 1: two phosphines: JohnPhos (2-biphenyl[bis(2-methyl-2-propanyl)]phosphine) and TPP (PPh_3 , triphenylphosphine), and the *N*-heterocyclic carbene (NHC) ligand IPr (carbene form of 1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazole). The 27 substrates S (Table 1) belong to seven families which may act as π -bases (alkenes, alkynes, allenes), O-bases (epoxides, aldehydes, ketones) or both (enol ethers). The functional groups of these 27 substrates are frequently involved in gold-catalyzed syntheses. We are not aware of quantitative mass spectrometry studies on such systems.

Scheme 1. The three series of adducts studied by mass spectrometry and DFT calculations.

An additional facet of the present work is that the observation of stable Au^+ adducts in solution, which can reveal reaction intermediates, bring relevant information as regard to the mechanistic aspect of catalysis.²⁹

In parallel, a quantum chemical study at the density functional theory (DFT) level was carried out for all adducts experimentally investigated, as well as for some adducts of the $[\text{PMe}_3\text{Au}]^+$ ion,²⁶ and for a few $\text{L}(\text{Au}^+)\text{CO}$ adducts,²⁸ for which experimental BDEs data are available. These calculated energetics and structural information on the adducts can be complementary indicators as regard to the activation of the substrates by the $\text{Au}(\text{I})$ catalysts.

Table 1. Substrates included in this work (usual names; IUPAC nomenclature given when necessary).

Alkenes		$R^1 = (\text{CH}_2)_3\text{Me}; R^2 = R^3 = \text{H}$ (1-Hexene) $R^1 = (\text{CH}_2)_5\text{Me}; R^2 = R^3 = \text{H}$ (1-Octene) $R^1 = \text{H}; R^2 = R^3 = (\text{CH}_2)_3\text{Me}$ (<i>trans</i> -5-Decene) $R^1 = R^2 = \text{Ph}; R^3 = \text{H}$ (1,1-Diphenylethylene) $R^1 = \text{H}; R^2 = R^3 = \text{Ph}$ (<i>trans</i> -Stilbene)
Alkynes	$R^1\text{-C}\equiv\text{C-R}^2$	$R^1 = R^2 = \text{Me}$ (2-Butyne) $R^1 = \text{CH}_3, R^2 = (\text{CH}_2)_3\text{Me}$ (2-Heptyne) $R^1 = R^2 = \text{PhCH}_3$ (Diphenylacetylene)
Allenes	$R^1\text{-CH=C=CH}_2$	$R^1 = (\text{CH}_2)_7\text{Me}$ (1,2-Undecadiene) $R^1 = \text{Cyclohexyl}$ (Cyclohexylallene) $R^1 = \text{Ph}$ (Phenylallene)
Enol ethers	$\text{H}_2\text{C=CH-O-R}^1$	$R^1 = \text{Et}$ (Ethyl vinyl ether) $R^1 = t\text{-Bu}$ (<i>tert</i> -Butyl vinyl ether) (2,3-Dihydrofuran = DHF) (2,3-Dihydropyran = DHP; IUPAC: 3,4-Dihydro-2H-pyran) (5-methyl-DHF; IUPAC: 5-Methyl-2,3-dihydrofuran) (2-methoxy-DHP; IUPAC: 2-Methoxy-3,4-dihydro-2H-pyran)
Ketones		$R^1\text{-R}^2 = (\text{CH}_2)_4$ (Cyclopentanone) $R^1 = R^2 = (\text{CH}_2)_2\text{Me}$ (4-Heptanone) $R^1 = \text{Me}, R^2 = 4\text{-Et-C}_6\text{H}_4$ (4-Ethylacetophenone) $R^1 = \text{Me}, R^2 = 4\text{-MeO-C}_6\text{H}_4$ (4-Methoxyacetophenone)
Aldehydes		$R^1 = (\text{CH}_2)_8\text{Me}$ (Decanal) $R^1 = \text{CH}(\text{Et})_2$ (2-Ethylbutanal) $R^1 = \text{Ph}$ (Benzaldehyde)
Epoxides		$R^1 = (\text{CH}_2)_5\text{Me}, R^2 = \text{H}$ (1,2-Epoxyoctane) $R^1\text{-R}^2 = (\text{CH}_2)_3$ (1,2-Epoxycyclopentane) $R^1\text{-R}^2 = (\text{CH}_2)_4$ (1,2-Epoxyoctane)

RESULTS AND DISCUSSION

Experimental binding energetics of organic substrates to L(Au⁺) ions by ERMS.

The applications of ERMS using quadrupole ion-trap (QIT) mass spectrometers for the examination of bonding in ions were reported as soon as the ion trap technique became available,^{30,31} and the technique was later refined by the Brodbelt group,³² and by Schröder and collaborators.³³ They

demonstrated the possibility of obtaining critical energies of dissociation after careful calibration, but different forms of bonding (covalent or hydrogen-bond) required different calibration schemes.

In QIT, CID is achieved by application of an excitation AC voltage resonant with the secular frequency of the ion to be dissociated. The energy deposited into the excited ion is dependent on its m/z and possibly on the instrument parameters. A standardization procedure for the excitation energy, leading to the so-called Normalized Collision Energy (NCE), allowed more straightforward comparisons of CID results.³⁴ The NCE values are reported as a percentage of the maximum resonant AC voltage, and will be called “NCE units” in the following.

In ERMS studies, the precursor or product ion intensities are usually plotted as a function of NCE, giving sigmoid curves. These plots contain the energetic information on the dissociation pathway(s) but need a specific treatment to extract quantitative data. In general, the ERMS sigmoid curves (generated by any MS technique) are modeled by a logistic function,^{35, 36, 37, 38, 39, 40} involving 4 or 5 parameters (depending of the symmetry of the sigmoid curve), as described in the Supporting Information.

In studies conducted with QIT instruments, for which the absolute collision energy cannot be established directly, a specific point of the sigmoid curve must be selected as a quantitative parameter related to the BDE. Essentially, two specific points of the sigmoid were used in ERMS studies using QIT: (i) the NCE value (or RF voltage) at which the relative intensity of the precursor ion is reduced by 50 %, ^{35-40, 41} called here NCE₅₀, and (ii) the so-called “Appearance Energy” (AE).^{33, 42}

For the ERMS experiments reported here, the ions corresponding to the two-coordinate cationic gold(I) complexes **L**(Au⁺)**S** are isolated in the gas phase and collided with the helium damping-gas of the ion trap. Under our experimental conditions, the loss of the substrate **S** is practically the only fragment-ion produced. We applied this method to establish a scale of relative gas-phase affinity of a series of organic substrates **S** containing different functional groups (alkenes, alkynes, allenes, enol-ethers, aldehydes, epoxides, ketones) with respect to three Au(I) complexes bearing different ligands. The ions **L**(Au⁺)**S** were generated by ESI of a dichloromethane solution of (JohnPhos)Au(OTf), TPP(NTf₂), or (IPr)Au(OTf) (OTf = CF₃SO₃; NTf₂ = (CF₃SO₂)₂N) and the substrate. We believe that the use of Au(I) salts involving a weakly coordinating anion (triflate or triflimide) ligands assisted the formation of adducts with neutral substrates of relatively weak Lewis basicity.⁴³

As expected, the CID experiments on the Au(I) adducts result in the dissociation along the weaker bond with **S** giving [**L**ⁿ(Au)]⁺ fragments (reaction 1).

Figure 1. Breakdown curve of the ion adduct at $m/z = 639$ $[\text{TPP}(\text{Au}^+)-\text{trans-stilbene}]$ as a function of the collision energy in units of Normalized Collision Energy (NCE, see text); ($\blacklozenge$) relative intensities of the precursor ion, $m/z = 639$, the red line corresponds to the ion intensity fitted to a sigmoid; NCE_{50} is defined as the NCE value for which the intensity of the precursor ion decreased by 50%, 20.2 NCE units in this case; ($\blacktriangle$) sum of the fragment $m/z = 459$ and its H_2O -adduct $m/z = 459$ (see text and Supporting Information); the tangent (green line) to the curve (not drawn) intersects the abscissa axis at a value taken as the Appearance Energy AE, 18.0 NCE units in this case.

The breakdown curves are constructed by plotting the relative intensity of the $\text{L}(\text{Au}^+)\text{S}$ ions as a function of the applied collision energy in the dimensionless NCE units (Figure 1, red curve). As seen in Figure 1, an ion attributed to the formation of the adduct $\text{L}(\text{Au}^+)\text{H}_2\text{O}$ during the trapping period is observed. Such ions were seen for almost all $\text{L}(\text{Au}^+)\text{S}$ dissociation experiments. Construction of the appearance curve for the fragment $\text{L}(\text{Au}^+)$ must consider the formation of the H_2O adduct. How the phenomenon was characterized and dealt with is described in detail, section S1 of the Supporting Information.

As stated above, two approaches are possible to deduce the relative bond strength from the breakdown curves, the appearance energy AE corresponding to the dissociation threshold; and the value that provides enough energy to induce 50% fragmentation NCE_{50} . In our study, we established that the two scales are precisely related (Supporting Information, Figure S2). All experimental and DFT-calculated data are gathered in a single Table S1 in the Supporting Information.

For benzene and toluene, the intensity of the $\text{L}(\text{Au}^+)\text{S}$ ions under our experimental conditions was low and difficult to stabilize, probably because they are weak Lewis bases to form in sufficient concentration an adduct in solution. Other substrates, tested and not reported here, gave rise to secondary reactions, in particular the terminal alkynes, which undergo metalation by proton transfer to form a neutral entity $\text{L}-\text{Au}-\text{C}\equiv\text{C}-\text{R}$, and may further add a second gold(I) ion to form a charged dinuclear species.⁴⁴

During the ERMS study of the adducts of *tert*-butyl vinyl ether, we observed a second dissociation channel, corresponding to the neutral loss of C_4H_8 , presumably methyl-2-propene. The corresponding

NCE₅₀ values are italicized in Table S1. For the TPP(Au⁺) and IPr(Au⁺) adducts, the dissociation occurred at significant lower NCE₅₀ (about 18 NCE units) than for the other vinyl ethers, with a shape of the ERMS sigmoid curves similar to those seen for the “normal” cases (reaction 1). We assume that the dissociation channel for the loss of C₄H₈ opens at about 18 NCE units, so that the higher collision energy necessary to **S** loss (1) cannot be reached. In the case of the JohnPhos(Au⁺) adducts, showing NCE₅₀ lower than 18 NCE units for the **S** dissociation channel, the loss of C₄H₈ was not observed. Anyway, all the NCE₅₀ values for *tert*-butyl vinyl ether were not included in the following discussions.

The AE scale is a slightly more subject to errors than the NCE₅₀ scale, because the uncertainty on the slope (see Figure 1) has a larger effect on the intercept than on the determination on the 50% dissociation. Therefore, only the NCE₅₀ values will be considered. Considering the short-term repeatability and the long-term reproducibility (see Supporting Information), the precision is about 1% in NCE units, with experimental NCE₅₀ values covering ranges of 12 to 26 NCE units. For comparison with two analogous studies, uncertainties of 2 to 4 kJ mol⁻¹ for a range of BDEs of 162-186 kJ mol⁻¹,²⁶ and of 4-8 kJ mol⁻¹ for a range of 131-175 kJ mol⁻¹,²⁸ were reported.

AE and NCE₅₀ are related to an experimental dissociation energy, actually the energy difference between the adduct ground state and the transition state for dissociation. If the dissociation process does not present a reverse activation barrier, as expected for a gas-phase cleavage, the observed dissociation energy can be considered equal the enthalpy of dissociation reaction at 0 K, when the translational and internal energy distributions and kinetic shifts are accounted for.^{28, 45}

In our case, we focus on the experimental relative affinity order for substrate **S** to **L**(Au⁺). Because of the lack of energetic data on similar systems, it was not possible to transform our NCE₅₀ or AE scale into BDEs using a calibration method. Experimental conditions being kept constant, the observed differences are quantitatively significant. Additional effects operating in ERMS studies of similar systems,²⁸ like size and mass, will be discussed in the section related to DFT results. For a comprehensive appraisal of the numerous NCE₅₀ values listed in Table S1, the relative affinity scale for the seven families of substrate toward the three **L**(Au⁺) ion is schematically represented in Figure 2.

Figure 2. Experimental ranges of substrate affinities for $L(Au^+)$ ions arranged by functional groups (data from Supporting Information, Table S1). The NCE_{50} units are defined in the text. The ligand L in $L(Au^+)S$ adducts are JohnPhos, triphenyl phosphine (TPP) and IPr, see Scheme 1.

The commonly accepted carbophilic character, and associated “softness”, of the Au^+ -based Lewis acids^{19,46} is not so clear-cut when looking at the NCE_{50} scales.

The bonding of substrates S with $IPr(Au^+)$ and $TPP(Au^+)$ shows some preference for carbon bases, but the some strong O-bases in the ketone series can rival in bond strength. For the $JohnPhos(Au^+)$ adducts, C- and O-bases are not clearly separated in term of NCE_{50} values, except epoxides which are weaker than the C-bases.

When looking at each family of substrates, it is immediately apparent that the affinities for $L(Au^+)$ are in the order $IPr(Au^+) > TPP(Au^+) > JohnPhos(Au^+)$. The stronger bonding of carbon monoxide with $L(Au^+)$ when L = carbene ligands was also observed by Gatineau et al.²⁸ On the other hand, they report relatively close BDEs of the CO adducts when L = phosphine and phosphite ligands, in particular for L = $JohnPhos(Au^+)$ and $TPP(Au^+)$. In contrast, we observe for all families a large difference in the NCE_{50} induced by the two phosphine ligands in $TPP(Au^+)$ and $JohnPhos(Au^+)$, in particular those involving π -bonding to substrates. For substrates acting as O-bases (aldehydes, ketones, epoxides), the adducts with $JohnPhos(Au^+)$ display a larger variation of NCE_{50} as compared to the adducts with $IPr(Au^+)$ and $TPP(Au^+)$. These observations suggest that the steric effect in our series of substrates is more important than for the carbon monoxide of small size, with also a larger differentiation between two phosphine ligands $TPP(Au^+)$ and $JohnPhos(Au^+)$, which have different steric requirement, the former showing a smaller Tolman cone angle.⁴⁷

More generally, the three $L(Au^+)$ exhibit variable discrimination for given structural variations in the substrates. For alkenes and alkynes, the affinity order for the substrates is the same for the three $L(Au^+)$ ions (see Table S1 in SI). For the other substrate families, the NCE_{50} ranges are rather limited and the affinity orders relative to the $L(Au^+)$ ions are not always maintained.

Calculated binding energies and geometries of substrates adducts $L(Au^+)S$, comparison with experiment.

Our experimental results establish relative affinities of substrates for the $L(Au^+)$ ions, so the aim of the calculations was to compare the affinity orders and achieve a reasonable assessment of the adduct structures. Considering the number and size of the structures to be examined, a relatively straightforward DFT level (PBE/def2-SVP, see description in the computational method subsection) was chosen.

In a first step, test results of our PBE/def2-SVP approach were compared to results using comparable DFT approaches. Jašíková and Roithová measured absolute BDEs for adducts $PMe_3(Au^+)/$ unsaturated hydrocarbons and compared the experimental values with the DFT-calculated data at the mPW1PW91/cc-pVTZ:LanL2DZ level of theory.²⁶ Our PBE/def2-SVP calculations on the systems studied by Jašíková and Roithová are reported in the Supporting Information (Table S2, Figure S3). Our calculated absolute BDEs and dissociation enthalpies are closer to the experimental results than the original calculation,²⁶ and the correlations $BDE(calc.)/BDE(exp.)$ display the same precision for the two DFT levels. Another basis for evaluating our calculated BDEs can be found in the combined experimental and DFT (PBE0-D3BJ/def2-TZVP level) theoretical study by Gatineau et al.²⁸ Among the 16 adducts $L(Au^+)CO$ we chose four ($L = PMe_3$, TPP, JohnPhos, IPr) to be recalculated at the level used in the present work, see Supporting Information (Table S3, Figure S4). For the limited set, the two theoretical levels agree quite well, and our less sophisticated DFT level reproduce satisfactorily the experimental data. These two tests indicate that our DFT approach is, at least, adequate for establishing an affinity order of the substrates for the $L(Au^+)$ ions.

We also verified that electronic energy ΔE , enthalpy ΔH and Gibbs energy ΔG for the dissociation process (reaction 1) are equivalent. The three thermochemical variables were calculated for the adducts of 13 model substrates with four $L(Au^+)$ ions ($L = PMe_3$, TPP, JohnPhos, IPr; Table S4, Supporting Information). As shown in Figure S5 (Supporting Information), these variables are strongly correlated. Therefore, we report only the ΔE values, calculated for all adducts for which NCE_{50} values were experimentally determined. These ΔE values are listed in Table S1 of the Supporting Information, along with the interatomic distances related to the effect of coordination: lengths of (i) $L-Au^+$ bonds, (ii) bonds formed in the adduct, (iii) bonds expected to be modified in the substrates at, or close to, the bonding site.

When applied to the whole set of data (3 $L(Au^+)$ ions x 26 substrates, *tert*-butyl vinyl ether excluded, *vide supra*) the relation between NCE_{50} and ΔE is not satisfactory ($R^2 = 0.65$; Figure S6 and comments in the Supporting Information). In ERMS experiments, the role of the size of the dissociating ion, in particular the number of degrees of freedom (DOF) of the dissociating ion, and possibly its mass, was advocated.^{28, 48, 49, 50}

For this reason, we tested the effect of introducing the DOF, as well as the mass, in the relationships between NCE_{50} and ΔE , but no improvement was observed (see comments to Figure S6 in Supporting Information).

Better correlations were observed between experimental and calculated dissociation energies when restricted to subsets of closely related series. Gatineau et al. observed an acceptable correlation ($R^2 = 0.81$) for binding of a single substrate (carbon monoxide) to 16 $L(Au^+)$ ions.²⁸ In the present work, only three $L(Au^+)$ ions are studied, nevertheless we examined these 3-points correlations. Table S1 shows that the order of calculated binding energy of each substrate, $IPr(Au^+) > TPP(Au^+) > JohnPhos(Au^+)$, reproduces well the experimental observations. In fact, the calculated ΔE values are fairly proportional to the experimental affinities of each substrate for the 3 $L(Au^+)$ ions. A typical plot is shown Figure 3, and similar plots can be observed for all substrates. The statistical parameters of the linear regressions for the data for seven substrates (one of each series) are given in the Supporting Information, Table S5.

Figure 3. Proportionality between NCE₅₀ (normalized units) and ΔE for the three $L(Au^+)$ adducts of 1-octene.

To further assess the range of applicability of such relationships, the precision of linear regressions for families of similar substrates bound to the three $L(Au^+)$ ions was examined. The whole series were separated according to more or less constraint on the functional criteria. The results on different subfamilies are detailed in the Supporting Information, Table S6. With the exception of aldehydes, all correlations are better than for the whole set of data ($R^2 > 0.65$). The separation into C-bases ($R^2 = 0.76$) and O-bases ($R^2 = 0.73$) improves the quality of the NCE₅₀ / ΔE relationship, and linearity is even better when separated into functional group for alkenes, alkynes, enol ethers, ketones and epoxides, but not for aldehydes. As illustrations, the best and the worst correlations are shown Figure 4. The poor correlation for aldehydes is due to an outlier (benzaldehyde) and to the small range of NCE₅₀ and ΔE . It is noteworthy that this outlier corresponds the lower-than-usual NCE₅₀ value of 12.37 for benzaldehyde, but no explanation was found for that.

Figure 4. Plots of the best and worst correlations for data treated by functional groups; for NCE_{50} units, see text. Removal of the outlier (red point) improves R^2 to 0.78. The regression equations $NCE_{50} = m \Delta E + b$, for tested subfamilies of substrates are listed in Table S6 of the Supporting Information.

To sum up the computational analysis of the energetics of the $L(Au^+)S$ adducts, it appears that the DFT approaches used in the literature^{26,28} and in this work, and considering the experimental uncertainties, are able to reproduce the experimental gas-phase binding energies with a reasonable precision within series of related adducts, either a single substrate with several $L(Au^+)$ ions, or a series of substrates pertaining to the same functionality coordinated to a few $L(Au^+)$.

It is interesting to examine the geometry of adducts obtained by the DFT calculations. Several crystal X-ray structures are known for π -adducts of the three $L(Au^+)$ ions, and also for some acetonitrile adducts. We are not aware of experimental structures for O-bases similar to those listed in Table 1. The data selected for comparison with the present DFT results are collected in Table S7 of the Supporting Information and are summarized in Table 2. The X-ray diffraction bond lengths and the calculated values are compared for similar structures. For acetonitrile adducts, we compare with decanal adducts, as aldehydes and nitriles exhibit similar Lewis basicities.⁵¹

In most cases, the calculated (gas-phase) bond lengths are systematically larger than the X-ray (solid state) values, about 0.05-0.10 Å for the bonds to Au^+ and about 0 to 0.05 Å for the ligand bonds. These differences are typically observed when DFT-calculated and X-ray structures are simultaneously published, for example in the case of metal complexes.^{52, 53, 54, 55}

Table 2. Experimental X-ray and DFT-calculated bond lengths in $L(Au^+)S$ relevant to adduct formation; all data in Å. Original data and references are compiled in Supporting Information (S7).

JohnPhos(Au ⁺)S					
Substrate S					
Alkenes (alkyl)	P-Au ⁺	Au-C1	Au-C2	C1=C2	
X-ray	2.29-2.31	2.21-2.29	2.29-2.37	1.33-1.37	
DFT	2.36-2.37	2.26-2.31	2.32-2.34	1.39	
Alkenes (aryl conjugated)					
X-ray	2.29	2.20	2.31	1.32	
DFT	2.35	2.31	2.34	1.39-1.41	
Allenes	P-Au ⁺	Au-C1	Au-C1	C1=C2 (coordinated C=C)	C2=C3 (non coordinated C=C)
X-ray	2.30-2.31	2.19-2.21	2.24-2.31	1.34-1.35	1.31
DFT	2.36-2.37	2.22	2.26-2.27	1.37	1.32
Enol ethers	P-Au ⁺	Au-C1	Au-C2	C1=C2 (coordinated C=C)	C(sp ²)-O
X-ray	2.28-2.29	2.17-2.18 ^a	2.55-2.58 ^a	1.37-1.41	1.28-1.33 ^a
DFT	2.35-2.36	2.20-2.21	2.56-2.69	1.40-1.41	1.32-1.33
N- or O-bases	P-Au ⁺	Au-N / Au-O			
X-ray ^b	2.25	2.03-2.05			
DFT ^c	2.28	2.16			
TPP(Au ⁺)S					
Substrate S					
Alkene (alkyl)	P-Au ⁺	Au-C1	Au-C2	C1=C2	
X-ray	2.27	2.27	2.29	1.35	
DFT	2.34	2.30	2.30	1.39	
Alkene (aryl conjugated)					
X-ray	2.28	2.23	2.32	1.36	
DFT	2.33	2.21	2.32	1.41	
IPr(Au ⁺)S					
Substrate S					
Alkenes	C ^{NHC} -Au ⁺	Au-C1	Au-C2	C1=C2	
X-ray	2.01-2.00	2.20-2.24	2.23-2.29	1.33-1.35	
DFT	2.04	2.22-2.28	2.28-2.33	1.39	
N- or O-bases	C ^{NHC} -Au ⁺	Au-N / Au-O			
X-ray ^b	1.95-1.97	2.02-2.01			
DFT ^c	1.98	2.12			

^a The X-ray value for bond lengths in 2,3-dihydrofuran appear to be anomalous as regard to those of the similar adducts (S = 2-methoxy-1-propene and 5-methyl-2,3-dihydrofuran), both experimentally and computationally, and are not considered, see Supporting Information.

^b Acetonitrile.

^c Decanal, for comparison (aldehydes and nitriles have similar Lewis basicities⁵¹).

The calculated structures of the JohnPhos(Au^+) adducts reproduce well the experimental geometry as regard to the interaction between the biphenyl moiety and the gold atom.^{54, 56, 57, 58, 59, 60}

The most stable DFT structures show the Au^+ /biphenyl interaction, in the free ion JohnPhos(Au^+) and in a typical adduct are shown in Figures 5 and 6 respectively.

Figure 5. Two conformations of the JohnPhos(Au⁺) ion at the DFT PBE/def2-SVP level (yellow: Au; orange: P; black: C; H atoms removed for clarity); (a) most stable form; the shortest distance (in Å) with one of the carbon atoms of the phenyl ring is shown as a dotted line. (b) the form with the second phenyl of the biphenyl away from the gold atom is less stable by 46 kJ mol⁻¹.

Figure 6. The most stable conformation of the JohnPhos(Au⁺) adduct with the enol ether 2,3-dihydrofuran at the DFT PBE/def2-SVP level; hydrogen atoms were removed for clarity (yellow: Au; orange: P; red: O; black: C; H atoms removed for clarity); The π -bonding between Au and the C=C bond is materialized by two bonds and the shortest distance with a carbon atom of the phenyl ring is shown as a dotted line (bond lengths in Å).

Figure 6 shows also that the enol ether is bound to Au through the C=C bond, and is a carbon base or π -base. The bonding through the oxygen atom leads to a less stable adduct, as for all other calculated enol-ether adducts, and in agreement with known experimental structures.⁵⁹ The difference in the bond lengths in the Au/C=C interaction of the enol ethers (**S** = 2,3-dihydrofuran in Figure 6) reflects the polarization of the π system by the resonance effect of the oxygen atom:

This dissymmetry of the Au-C bonding, observed in the solid-state structures published for the JohnPhos(Au⁺) adducts of a few enol ethers,⁵⁹ is clearly seen in the calculated values.

In the Au bonding to alkenes and alkynes, the two Au-C distances are very similar, but the presence of phenyl groups in 1,1-diphenylethylene, acting as π -electron donors, induces a large difference in Au-C bond lengths, like for enol ethers (Figure 7).

Figure 7. Difference in Au-C bond lengths (in Å) in the interaction with the ethylenic bond for the adduct TPP(Au⁺)1,1-diphenylethylene; π -bonding is materialized by two bonds (yellow: Au; orange: P; black: C; H atoms removed for clarity).

Allenes present two possible sites for π -bonding. For the unsymmetrically substituted alkyl-allenes ($R^1R^2C=C=CH_2$), the X-ray structures⁵⁸ show that the terminal double bond ($C=CH_2$) is the attachment site of Au. This feature is reproduced by the calculated structures of the alkyl- and phenyl-substituted allene adducts studied, with the exception of TPP(Au⁺)phenylallene. In the most stable structure of the later adduct, Au is bound to the double bond attached to the phenyl group, but the other isomer (Au bound to the terminal double bond) is only 2.5 kJ mol⁻¹ less stable. It is possible that in the solution submitted to ESI, a mixture of the two isomeric adducts is present, and consequently also present in the gas phase. At the current ERMS level of precision, we consider that the two isomeric adducts cannot be distinguished. The calculated most stable structures of the three phenylallene adducts are shown in the Supporting Information, section S9. Coordination modes of **L**(Au⁺) to allenes are known to be sensitive to substitution and to the nature of **L**.^{61, 62}

To the best of our knowledge, there is no experimental structure determined for carbonyl or ether adducts with the three **L**(Au⁺) of our study. For illustrating the bonding mode of **L**(Au⁺) to substrates acting as O-bases, we present two DFT-calculated adduct structures of cyclopentanone and cyclopentene oxide in Figure 8 (other structures are shown in the Supporting Information). The bond angles around the oxygen atoms reflect the direction of the electron lone pairs.

Figure 8. (a) Cyclopentanone adduct with TPP(Au⁺), showing the Au-O=C angle (130°) corresponding to the sp² hybridization of the oxygen atom; (b) Two views of the cyclopentene oxide adduct with JohnPhos(Au⁺), the right side view showing the angle between the Au-O bond and the plane of the oxirane ring (dihedral angle 113°), corresponding to the sp³ hybridization of the oxygen atom (yellow: Au; orange: P; red: O; black: C; H atoms removed for clarity).

The effect of coordination of substrates to L(Au⁺) on the lengths of (i) L-Au⁺ bonds, (ii) bonds formed in the adduct, (iii) bonds expected to be modified in the substrates at, or close to, the bonding site can be seen in Table S1 of the Supporting Information. How much the bond length alterations may be related to the bond energetics? A direct relation between the bond lengths to Au (Au-L or Au-S) and BDEs are not pertinent because they involve, on the one hand, bonding to phosphorus of phosphines or to carbon atom of NHC, and, on the other hand, bonding to π systems or to oxygen atoms, which are geometrically very different. The changes in bond lengths, organized by ligand and by family of substrates, are summarized in Table 3.

Table 3. Changes in bond lengths (BL, DFT-calculated, approximate ranges in Å) upon bonding of the substrate S with L(Au⁺) unit: $\Delta(X-Y) = [\text{BL}(\text{coordinated L(Au}^+) \text{ or coordinated S})] - [\text{BL}(\text{free L(Au}^+) \text{ or free S})]$; negative values correspond to a bond shortening.

Substrates	L = JohnPhos		L = TPP		L = IPr	
	$\Delta(\text{Au-P})$	$\Delta(\text{C=C})$ or $\Delta(\text{C}\equiv\text{C})$	$\Delta(\text{Au-P})$	$\Delta(\text{C=C})$ or $\Delta(\text{C}\equiv\text{C})$	$\Delta(\text{Au-C}_{\text{NHC}})$	$\Delta(\text{C=C})$ or $\Delta(\text{C}\equiv\text{C})$
Alkenes	0.04 to 0.06	0.04 to 0.05	0.04 to 0.06	0.04 to 0.05	0.06 to 0.08	0.04 to 0.05
Alkynes	0.04	0.03	0.05 to 0.06	0.03	0.06 to 0.07	0.03
Allenes ^a	0.06	0.05	0.05 to 0.07	0.04 to 0.05	0.07	0.05
Enol ethers ^b	0.04-0.05	0.05-0.06	0.06-0.07	0.05 to 0.06	0.06 to 0.07	0.05-0.06
		$\Delta(\text{C=O})$ or $\Delta(\text{C-O})$		$\Delta(\text{C=O})$ or $\Delta(\text{C-O})$		$\Delta(\text{C=O})$ or $\Delta(\text{C-O})$
Ketones	-0.02	0.03 to 0.04	-0.01	0.03 to 0.04	0.01	0.03 to 0.04
Aldehydes	-0.02 to -0.03	0.03	-0.01	0.03	0.01	0.03

Epoxides ^c	-0.03	0.04	-0.01	0.04 to 0.05	0.01	0.04
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^a coordinated C=C; the other C=C changes by less than 0.01 Å.
^b The C_{sp2}-O bonds in enol ethers are shortened (negative Δ(C_{sp2}-O) values) by about 0.03-0.05 Å for all adducts.
^c Changes in the two C-O bonds are very similar; mean values are listed.

The Δ(Au-P) and Δ(Au-C_{NHC}) values for the π-bases (alkenes, alkynes, allenes, enol ethers) are relatively homogeneous, i.e. all Au-ligand bonds are elongated by adduct formation. The behavior is different for O-bases, with negative Δ(Au-P) and Δ(Au-C_{NHC}) values (bond shortening) for **L** = JohnPhos and TPP, and small bond lengthening for **L** = IPr. On the other hand, substrate bonds involved in bonding with Au (double and triple bonds for π-bases, single and double bond for O-bases) are elongated by adduct formation in all cases. This is consistent with a weakening and a polarization of these bonds by the **L**(Au⁺) ions.

We examined the various changes in Au-**L** bond lengths (Δ(Au-P), Δ(Au-C_{NHC})), and in substrate bond lengths in detail, investigating potential relationships with the BDEs. In fact, global correlations between Δ(Au-P) and Δ(Au-C_{NHC}) and bond dissociation energies (experimental or calculated) are not observed (Figure 9(a)). Even within structurally similar families of substrates, linear trends do not lead to precise correlations, as shown in Figure 9(b) for ketones. More examples are given in the Supporting Information, section S8. Similarly, correlations between changes in C=C, C≡C or C=O bond lengths induced by coordination and the BDEs (not reported) are not significant.

Figure 9. (a) Plots of changes in Au-**L** bond lengths vs. calculated BDE for **L** = JohnPhos, TPP and IPr and all substrates included in this study. A plot vs NCE₅₀ shows a similar dispersion. The upper and lower data clusters correspond respectively to substrates acting as C-bases and O-bases. (b) Same plot restricted to the four ketones. The three clusters correspond to the three ligands, the changes in Δ(Au-P) and Δ(Au-C_{NHC}) being not significant for each ketone series. Similar plots for alkene and alkynes are shown in the Supporting Information.

The bonds formed in the adducts between Au and the substrates were examined from the same viewpoint. For substrates acting as C-bases, no correlation was observed between Au-C bond lengths and BDEs. The two Au-C bond lengths in the π -bonding are often very dissimilar, but even taking the mean value of the two bond lengths does not improve the linearity. On the contrary, significant correlations are found between Au-O bond lengths and BDEs; as shown in Figure 10. A more detailed analysis of these relations is given in the Supporting Information, section S8. For the Au-O bond (adducts of aldehydes, ketones, and epoxides), a shorter bond is associated with a stronger bonding, as expected.

Figure 10. Plots of bond lengths for Au-O formed in the coordination between $L(Au^+)$ and aldehydes, ketones and epoxide substrates, acting O-bases against the calculated BDE. If the plot is restricted to carbonyl substrates, the coefficient of determination is improved to $R^2 = 0.95$ (see Supporting Information, section S8.)

Consequently, these kinds of relationships do not provide a general vision of the deformation of the substrate bonds and their possible activation under the action of the $L(Au^+)$ ions. On the other hand, regularities between the calculated BDE and the Au-S bond lengths may be observed within specific families of substrates.

CONCLUSIONS

Using energy resolved mass spectrometry, we have established a scale of gas-phase binding energies for a series of 27 organic substrates with three typical Au(I) cations, JohnPhos(Au^+), $PPh_3(Au^+)$ and $IPr(Au^+)$, which are the active Lewis acidic part of common Au(I) catalysts. The active, electron-donating, centers of the substrates correspond to functional groups (carbon-carbon π -bonds including enol-ethers, carbonyls, epoxides) often encountered in reactants submitted to catalysis. The

experimental relative binding energies to the three cations can be considered as three Lewis basicity scales for the selected carbon and oxygen bases.

Gold(I) center in catalysts are consistently categorized as carbophilic, as a consequence of the “softness” of the Au(I)-based catalysts. In fact, the carbophilic vs. oxophilic distinction of the three $L(Au^+)$ cations examined is more subtle when looking at the experimental binding energies. Substrates bound to a given $L(Au^+)$ cation via carbon atoms (π bases) and via oxygen may present close NCE_{50} values, depending on substitution. On the other hand, each family of substrates present the same affinity order for the three cations: $IPr(Au^+) > TPP(Au^+) > JohnPhos(Au^+)$.

DFT calculations (PBE/def2-SVP level) were performed to refine our perception of the energetics and structural aspects of substrate bonding in $L(Au^+)S$ adducts. This level, which is compatible with a survey of a large number of relatively complex structures, was validated by comparing its performances with two other combined DFT/experimental studies.^{26,28} The calculated bond dissociation energies ΔE at the DFT level used in this work cannot precisely reproduce the variations of the entire set of our experimental NCE_{50} , but significant correlations are found within families with the same functional group. Comparison of the calculated gas-phase bond lengths and those obtained from X-ray diffraction studies (solid-state) show that the correct trends are obtained for a number of substrates acting as carbon bases.

The energetics and structural aspects of the interaction between Au(I) catalysts and substrates acting as oxygen bases appears to be largely ignored in the literature. We expect that our experimental and DFT-calculated data on $L(Au^+)(O\text{-bases})$ adducts can serve as a stimulus for more investigations in this field, and as a source of inspiration for the interpretation of catalytic mechanisms in polyfunctional substrates.

EXPERIMENTAL AND COMPUTATIONAL SECTIONS

Mass spectrometry and data treatment

Gas-phase adducts of the ligand-Au(I) ion with the organic substrates were obtained by electrospray ionization of a dichloromethane solution containing the one of the gold catalyst $L(Au^+)X^-$ [(JohnPhos)Au(OTf), $TPPAu(NTf_2)$, or $(IPr)Au(OTf)$] and the organic substrates **S**. The detailed mass spectrometry procedure, including the origin of chemicals, is provided in the Supporting Information. In summary, the breakdown curves were obtained by plotting the normalized intensity of the precursor ion ($I_{\text{precursor}}/\Sigma I$), as a function of collision energy, expressed as Normalized Collision Energy (NCE).³⁴ Fitting the breakdown curves by nonlinear regression to a 4-parameter logistic function, allowed the determination of the NCE_{50} , i.e. the NCE value needed to induce the fragmentation of 50% of the precursor ion. The data treatment is detailed in the Supporting Information. In similar experiments, it was noted that other parameters like ion mass, degrees of freedom and absolute AE, do not influence significantly the NCE_{50} values.³³ The determination of NCE_{50} for ionic species following the same fragmentation pattern, gives access to relative energy scales and therefore, quantitative data on the relative bond strength of the metal-ligand interaction or the relative reactivity of the adducts. The

NCE₅₀ values are repeatable to better than 0.1%, and display a long term reproducibility of about 0.2-0.4%.⁶³ Therefore, differences in NCE₅₀ larger than 1% are considered significant.

Computational method

All calculations were performed using the ORCA program package, versions 3.0.3 and 4.0.⁶⁴ The geometries of complexes and corresponding reagents were fully optimized using the 1996 correlational and exchange functionals of Perdew, Burke and Ernzerhof,⁶⁵ (PBE) and newer versions of Ahlrichs split-valence basis sets (def2-SVP).^{66, 67}

The resolution of identity method was used to speed up the calculations. Harmonic frequency analysis was used to confirm that the found structures correspond to minima (number of imaginary frequencies equals zero), and to calculate the thermodynamic parameters. It has been demonstrated that this model reproduces fairly well geometries and binding energies of different metal (Zn and coinage) complexes with organic ligands,^{68, 69} and represent an efficient good compromise between accuracy and efficacy. The BSSE correction was not considered useful in our context of assessment of relative affinities.

Electronic energies and optimized geometries for the DFT-calculated structures for the experimentally studied compounds are listed in Supporting Information-2.

Comparison with other computational results on the energetics of Au⁺ adducts,^{26,28} mentioned in the Result and Discussion section, are detailed in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Supporting Information-1 content: Mass spectrometry data acquisition and treatment; Experimental and calculated binding energies, calculated characteristic bond lengths; Experimental and calculated energetics for interaction between various substrates S and (Me)₃P(Au⁺); Experimental and calculated energetics for the interaction between CO and L(Au⁺); Calculated ΔE , ΔH , ΔG of adduct formation between model substrates S and L(Au⁺); Correlations of experimental NCE₅₀ and calculated ΔE ; Experimental and calculated bond lengths of L(Au⁺)S adducts; Correlations $\Delta(\text{Au-P})$, $\Delta(\text{Au-C}_{\text{NHC}})$ or various bond lengths with bond dissociation energies ΔE or NCE₅₀; Additional adduct structures. Supporting Information-2 contains the atomic coordinates and total (electronic) energies calculated at PBE/def2-SVP DFT level for the experimentally studied species.

AUTHOR INFORMATION

Corresponding Author

E-mail for J.-F. G.: Jean-Francois.GAL@univ-cotedazur.fr

Coauthors e-mails:

CB: iacobucci.claudio@gmail.com

LM: Lionel.MASSI@univ-cotedazur.fr

ED: Elisabet.DUNACH-CLINET@univ-cotedazur.fr

PB: peeter.burk@ut.ee

ORCID

Jean-François Gal: 0000-0002-5500-5461.

Elisabet Duñach: 0000-0002-9368-3378.

Peeter Burk: 0000-0001-5503-664X

Notes

The authors declare no competing financial interest.

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