

Gas-phase synthesis and reactivity of binuclear gold hydride cations, $(R_3PAu)_2H^+$ ($R = Me$ and Ph)[†]

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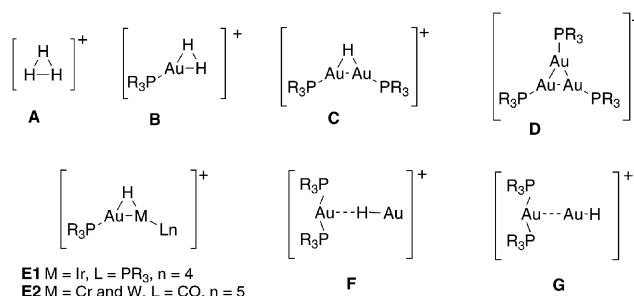
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Electrospray ionization of a mixture of the two gold phosphine chlorides, R_3PAuCl ($R = Ph$ and Me), silver nitrate and the amino acid *N,N*-dimethylglycine (DMG) yields a range of gold containing cluster ions including: $(R_3P)Au(PR'_3)^+$; $(R_3PAu)(R'_3PAu)Cl^+$ and $(R_3PAu)(R'_3PAu)(DMG-H)^+$ (where $R = R' = Ph$; $R = R' = Me$; $R = Me$ and $R' = Ph$). Collision induced dissociation (CID) of the $(R_3PAu)(R'_3PAu)(DMG-H)^+$ precursor ions yielded the hitherto unknown gold hydride dimers $(R_3PAu)(R'_3PAu)H^+$. The gas-phase chemistry of these dimers was studied using ion–molecule reactions, collision induced dissociation, electronic excitation dissociation (EED) and DFT calculations on the $(H_3PAu)_2H^+$ model system. A novel phosphine ligand migration was found to occur prior to fragmentation under CID conditions and this was supported by DFT calculations, which revealed a transition state with a bridging phosphine ligand.

Introduction

Metal hydrides are widely used as synthetic reagents and play roles as intermediates in catalytic hydrogenation and in other types of reactions including oxidation and C–H bond activation.^{1,2} Although gold hydrides have attracted attention as possible intermediates in catalytic processes,³ relatively few molecular gold hydrides have been characterised.⁴ Apart from a number of theoretical studies on various gold hydride systems,⁵ the mononuclear gold hydrides AuH , AuH_2 , $(H_2)AuH$, $(H_2)AuH_3$, AuH_2^- and AuH_4^- have been identified using matrix IR spectroscopy.⁶ In addition, a number of gas-phase studies have identified a range of gold hydride anions, Au_nH^- ($n = 2-7$),⁷ and cations, $Au_nH_m^+$ ($n = 2-7$; $m = 2-6$).⁸ In some of these studies, it was noted that the replacement of a gold atom in a metallic cluster with a hydrogen may not significantly alter the structure of the cluster.^{7a,b} This is a manifestation of the “isolobal” analogy, which generally assumes that R_3PAu^+ is isolobal with H^+ and has been widely used to make connections between main group species and related gold clusters analogues.⁹ For example $(R_3PAu)_3O^+$ is an analog of H_3O^+ ,¹⁰ while H_2Cl^+ can be related to $(R_3PAu)_2Cl^+$.¹¹ Surprisingly, isolobal analogues of one of the most important main group ions, H_3^+ (**A** in Scheme 1), which also has a rich history in mass spectrometry,¹² have not been widely studied. Scheme 1 shows that the sequential replacement



Scheme 1

of each H in **A** yields the gold clusters **B**, **C** and **D**. Of these clusters, **B** appears to be totally unknown, the closest clusters to **C** are a number of heterobimetallic complexes, **E**, which have been characterised by X-ray crystallography,⁴ while there are examples of **D** being incorporated into the structures of larger metal clusters.¹³

We have been interested in using collision induced dissociation (CID) of metal complexes to trigger ligand fragmentation with concomitant migration of a component of the ligand onto the metal centre¹⁴ as a means of generating novel species such as organometallics¹⁵ and metal hydrides.¹⁶ Thus we recently described a gas-phase synthesis of silver hydride cations from $[(M + Ag-H)_x + Ag]^+$ precursor ions (where M = an amino acid such as glycine or *N,N*-dimethylglycine) generated via electrospray ionisation (ESI).¹⁶ For example, CID on $[(H_2NCH_2CO_2) + 2Ag]^+$ yields the Ag_2H^+ ion (eqn (1)).^{16b}



Here we report on a gas-phase synthesis of the gold hydride dimers, **C** and examine their chemistry using advanced mass spectrometry methods including ion–molecule¹⁷ and low energy CID reactions.¹⁸ We also examine their fragmentation reactions using the electronic excitation dissociation (EED) technique developed by Zubarev *et al.*¹⁹ In addition, DFT calculations²⁰ were carried out on the

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[†] Electronic supplementary information (ESI) available: Structures with key bond lengths for gold species **I–O**; list of the Cartesian coordinates of the structures presented in Fig. 3, 6 and S1; peak assignments for Fig. 1, 2 and 5; calculated B3LYP/6-31G(d) energies of the various structures; estimated thermochemistry for eqn (11)–(13). See DOI: 10.1039/b604404b

$(\text{H}_3\text{PAu})_2\text{H}^+$ model system in order to gain insights into a novel phosphine ligand migration reaction, which was observed to occur under low energy CID conditions.

Experimental

Materials

Ph_3PAuCl was prepared *via* a literature procedure,²¹ while Me_3PAuCl was obtained from Sigma-Aldrich and used as received. All other reagents were also used as supplied: AgNO_3 (ICN Biomedical Inc.) and *N,N*-dimethylglycine [DMG, $(\text{CH}_3)_2\text{NCH}_2\text{-COOH}$] (Aldrich Chemical Co.).

Mass spectrometry experiments

Preparation of ESI solution. The following stock solutions were prepared: (i) Me_3PAuCl in MeCN (10 mM); (ii) Ph_3PAuCl in MeCN (10 mM); (iii) AgNO_3 in 50 : 50 MeOH/ H_2O with 1% acetic acid (20 mM); (iv) *N,N*-dimethylglycine (DMG) in 50 : 50 MeOH/ H_2O with 1% acetic acid (20 mM). The $\text{Me}_3\text{PAuCl}/\text{Ph}_3\text{PAuCl}/\text{AgNO}_3/\text{DMG}$ stock solutions were mixed in ratios of *ca.* 2 : 1 : 1 : 1 and diluted with MeOH to a final concentration of Ph_3PAuCl of around 0.1 mM.

Ion–molecule reactions on a quadrupole ion trap mass spectrometer. All ion–molecule reactions were carried out using a modified commercial ion trap mass spectrometer equipped with electrospray ionisation (Finnigan-MAT LCQ classic, San Jose, CA) described in detail elsewhere.²² The ESI solution, prepared as described above, was introduced to the mass spectrometer *via* electrospray ionization using a flow rate of 3 $\mu\text{L min}^{-1}$. The sheath air, capillary voltage and temperature were adjusted to *ca.* 30–60, 4.2–4.8 kV and 150–200 °C respectively. The CID experiments were performed following standard procedures²³ by mass selecting the desired precursor ion, with a selection window of 1–10 Th (depending on the desired isotope distribution), and then subjecting it to a corresponding activation potential of 10–15% and an activation (Q) of 0.25 for a period of *ca.* 30 ms. The acquisition mass range was typically between 100 and 1200. Ion–molecule reactions were performed as described elsewhere,²² and the reaction times were varied between 30 and 10 000 ms. The pressure of the neutral reagents used (*i.e.*; 2-propanol, allyl iodide, pyridine, DMSO and CH_3NO_2) in the trap was $\sim 3 \times 10^{-7}$ Torr, the pressure of O_2 was 4.9×10^{-5} Torr and that of N_2O was 3×10^{-7} Torr.

Linear ion trap–Fourier transform ion–cyclotron resonance mass spectrometry experiments. All other CID and electronic excitation (EED) experiments were carried out on a Finnigan-MAT LTQ-FTMS instrument equipped with electrospray ionisation (ESI). The ESI solution, prepared as described above, was introduced to the mass spectrometer *via* electrospray ionisation using a flow rate of 4.0 $\mu\text{L min}^{-1}$. Typical ESI source conditions used were: spray voltage, 4–5 kV, capillary temperature, 275 °C, nitrogen sheath pressure, 10–50, and capillary voltage/tube lens offset adjusted to maximise the intensities of the desired peaks. The injection time was set using the AGC function. CID was carried out by mass selecting the desired ions with

a 1–4 Th window and subjecting them to the following typical conditions: activation energy 10–15%; activation (Q) 0.25 V, and activation time 30 ms for analysis in the ion-trap. For high-resolution mass spectrometry and EED experiments, the analyte was first selected in the LTQ and then transferred to the FTMS cell. The EED voltages used were 20–26 V. The use of ion–electron interactions in the instrument have been previously described.²⁴ The LTQ-FTMS was calibrated for exact mass measurements as recommended by the manufacturer using the supplied Finnigan calibration solution in the positive ion mode. This solution contains: caffeine; the peptide L-methionyl-arginyl-phenylalanyl-alanine acetate- H_2O (MRFA) and ultramark 1621.

DFT Calculations

The Gaussian 03 suite of programs²⁵ was used to examine the structures and energies of ions and neutrals of interest. Geometry optimisation and frequency calculations were carried out at the B3LYP level of theory using the following basis sets: 6-31G(d) for P and H and the LanL2DZ effective core potential (ECP) of Hay and Wadt for Au.^{26a} Relative energies were calculated by scaling the zero point energies (ZPEs) using the scaling factors recommended by Scott and Radom (*e.g.* 0.9806 for ZPEs calculated at the B3LYP/6-31G(d) level of theory).^{26b} All of the results (structures and energies) from the DFT calculations are collated in the ESI.†

Results and discussion

(1) Synthesis of C and DFT calculations on C and its isomers

Our approach to a gas-phase synthesis of C relies on our recent discovery that bare silver hydride clusters can be formed upon collision induced dissociation (CID) of silver amino acid cluster cations generated *via* electrospray ionization of a mixture of the amino acid and silver nitrate (ESI) (eqn (1)).¹⁶ Electrospray ionization of the gold(i) chlorides, R_3PAuCl (where R = Me or Ph), is known to be dependent on the solution conditions and yields a number of different ions.²⁷ Thus Colton *et al.* have shown that ESI of mixtures of Ph_3PAuCl and phosphine ligands gives rise to ligand substitution reactions.^{27a} When Ph_3P was used, the dominant ion was $(\text{Ph}_3\text{P})_2\text{Au}^+$, although $(\text{Ph}_3\text{P})_3\text{Au}^+$ was also observed with weak abundance. In fact, the third Ph_3P ligand appears to be weakly bound as it is readily lost under MS/MS conditions. Decker *et al.* have used the addition of Ar_3P to promote the ionisation of “neutral” transition metal complexes under ESI conditions.^{27b} They noted that such an approach yields $(\text{Ar}_3\text{P})_2\text{Au}^+$ ions in their ESI mass spectra of $(\text{R}_3\text{P})\text{AuCl}$. Finally, Roithová *et al.* have shown that direct electrospray of Me_3PAuCl in methanol yields $(\text{Me}_3\text{PAu})_2\text{Cl}^+$ as the dominant ion.^{27c} Note that this corresponds to a well-known class of gold chlorinium ion in the condensed phase.¹¹

Given our aim of trying to “synthesise” gold hydride cations, and the fact that gold(i) amino acid complexes have been previously prepared by reacting R_3PAuCl with silver amino acid salts,²⁸ we focussed on preparing solutions containing a mixture of the two gold phosphine chlorides, R_3PAuCl (R = Ph and Me), silver nitrate and the amino acid *N,N*-dimethylglycine (DMG). ESI-MS of this mixture yields a range of gold-containing cluster ions (Fig. 1, Table S1†) including: $(\text{R}_3\text{P})\text{Au}(\text{PR}'_3)^+$; $(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})\text{Cl}^+$; and

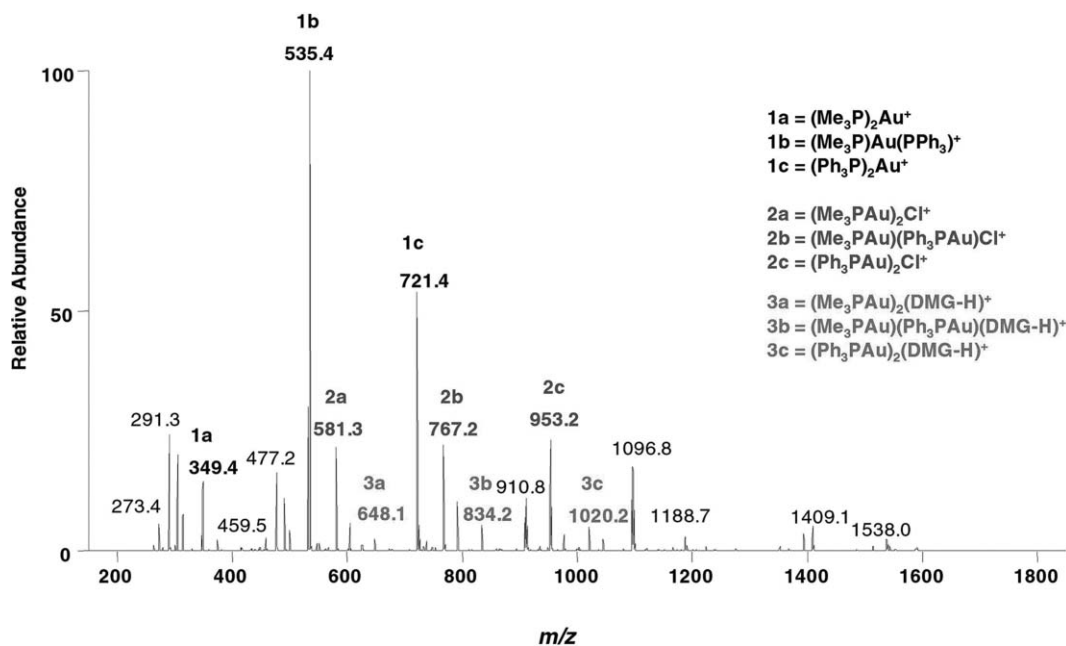
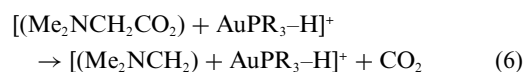
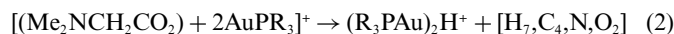


Fig. 1 ESI/MS of a mixture of gold phosphine chlorides (Me_3PAuCl and Ph_3PAuCl), silver nitrate and the amino acid *N,N*-dimethylglycine (DMG) in MeOH (see Experimental section for details). The three key series of ions discussed in the text are highlighted in bold. Other ions are identified in Table S1.†

$(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})(\text{DMG-H})^+$ (where $\text{R} = \text{R}' = \text{Ph}$; $\text{R} = \text{R}' = \text{Me}$; $\text{R} = \text{Me}$ and $\text{R}' = \text{Ph}$). These three main ion series are labeled in Fig. 1 and their assignments are facilitated by an examination of their isotope patterns as well as by accurate mass measurements using high resolution Fourier transform mass spectrometry (FTMS). For example, FTMS mass measurements of each of the $(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})(\text{DMG-H})^+$ ions yielded errors of less than 1 ppm (Table 1). Unlike, our previous silver studies,¹⁶ larger oligomeric $[(\text{DMG} + \text{Au-H})_x + \text{Au}]^+$ cluster ions were not observed. This is not surprising since the formation of such cluster ions would require the loss of the strongly coordinated phosphine ligand.

CID of the $(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})(\text{DMG-H})^+$ ions yields the desired gold hydride cations, $(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})\text{H}^+$ as the major fragment ions (eqn (2) and Fig. 2). The molecular formulas of each of these gold hydride cations was confirmed by using high resolution Fourier transform mass spectrometry, as shown in Table 1. The remaining fragmentation pathways consist of: loss of $\text{Me}_2\text{NCH}_2\text{CO}_2\text{Au}$ to yield the bis-ligated complex, $(\text{R}_3\text{P})_2\text{Au}^+$ (eqn (3)), and loss of the ligated gold hydride (eqn (4)). Interestingly, simple loss of R_3PAu^+ is barely observed (eqn (5)). The $[(\text{Me}_2\text{NCH}_2\text{CO}_2) + \text{AuPR}_3\text{-H}]^+$ ion, formed in eqn (4), appears to undergo subsequent decarboxylation (eqn (6)).



These gold hydride cations, formed in Fig. 2, may adopt other isomeric structures to **C**, such as **F** or **G**, which are related to the gold halides $(\text{R}_3\text{P})_2\text{AuX}$, composed of halide anions weakly coordinated to the $(\text{R}_3\text{P})_2\text{Au}^+$ ion.²⁹ In order to gain insights into the structures of these ions and their relative stabilities, we have turned to DFT calculations²⁵ using a model system ($\text{R} = \text{H}$),²⁰ and the resulting isomeric structures are shown in Fig. 3, while the full DFT details (energies and Cartesian coordinates) are given in the ESI.† A total of four different isomers were found including **C** (Fig. 3(a)), **F** (Fig. 3(b)), **G** (Fig. 3(c)) and **H** (Fig. 3(d)). The DFT calculations clearly favour a ground state structure of **C**, with **F**, **G** and **H** being less stable by 102.5, 116.3 and 105.5 kJ mol^{-1}

Table 1 Exact mass measurements supporting the assignments of the $(\text{R}_3\text{PAu})_2(\text{DMG-H})^+$ and $(\text{R}_3\text{PAu})_2\text{H}^+$ ions ($\text{R} = \text{Ph}$ and Me)

Ion	Formula	Predicted m/z	Measured m/z	Error (ppm)
$(\text{Ph}_3\text{PAu})_2(\text{DMG-H})^+$	$\text{Au}_2\text{P}_2\text{C}_{40}\text{H}_{38}\text{NO}_2$	1020.1703	1020.1712	0.88
$(\text{Me}_3\text{PAu})_2(\text{DMG-H})^+$	$\text{Au}_2\text{P}_2\text{C}_{10}\text{H}_{26}\text{NO}_2$	648.0764	648.0762	0.31
$(\text{Ph}_3\text{PAu})(\text{Me}_3\text{PAu})(\text{DMG-H})^+$	$\text{Au}_2\text{P}_2\text{C}_{25}\text{H}_{32}\text{NO}_2$	834.1234	834.1238	0.48
$(\text{Ph}_3\text{PAu})_2\text{H}^+$	$\text{Au}_2\text{P}_2\text{C}_{36}\text{H}_{31}$	919.1227	919.1224	0.33
$(\text{Me}_3\text{PAu})_2\text{H}^+$	$\text{Au}_2\text{P}_2\text{C}_6\text{H}_{19}$	547.0288	547.0284	0.73
$(\text{Ph}_3\text{PAu})(\text{Me}_3\text{PAu})\text{H}^+$	$\text{Au}_2\text{P}_2\text{C}_{21}\text{H}_{25}$	733.0757	733.0753	0.55

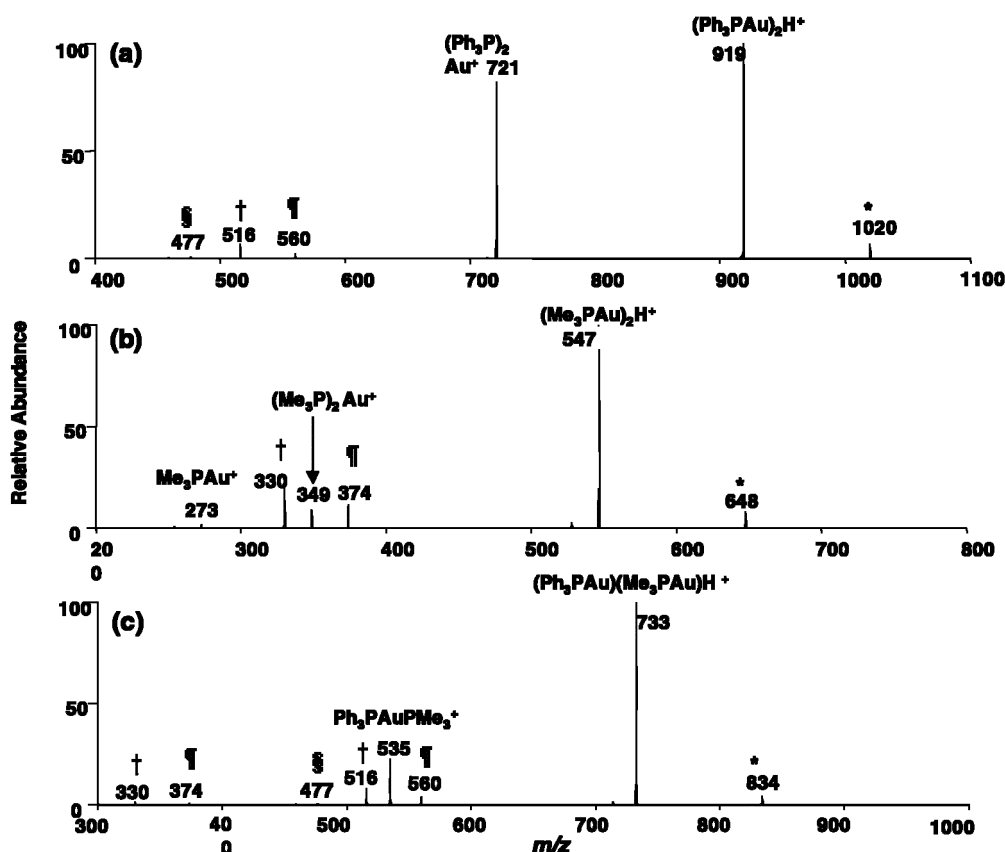
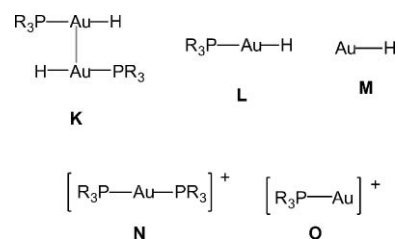


Fig. 2 LTQ CID MS/MS spectra showing the gas-phase synthesis of the gold hydride dimers: (a) $(\text{Ph}_3\text{PAu})_2\text{H}^+$; (b) $(\text{Me}_3\text{PAu})_2\text{H}^+$; (c) $(\text{Ph}_3\text{PAu})(\text{Me}_3\text{PAu})\text{H}^+$. A * represents the mass selected precursor ion. A ¶ represents the products formed *via* eqn (4). A † represents the products formed *via* eqn (6). A § represents $\text{Ph}_3\text{PAuOH}_2^+$, formed *via* an ion–molecule reaction of the product of eqn (5) with background water. Selection windows of 1–4 Th and normalised collision energies of 10–15% were used.

respectively. Isomer **C** is a symmetrical triangle structure. In order to examine how the bond lengths in the Au_2H^+ cluster vary as a function of ligation, we have also calculated the structures of the bare triangle, **I**, which is shown in Fig. S1(a)† and the mono-ligated species **J**, which is shown in Fig. S1(b).† Ligation has a significant effect on the Au–Au bond length, which changes from 2.713 Å to 2.775 Å and finally to 2.907 Å on moving through: **I** → **J** → **C**. While the Au–H bond lengths hardly vary in the symmetrical structures **I** and **C** (1.737 Å and 1.738 Å respectively), the mono-ligated species **J** is a significantly distorted triangle, with Au–H bond lengths of 1.648 Å and 1.890 Å. Finally, there is minor variation in the Au–PH₃ bond lengths, which are 2.352 Å for **J** and 2.358 Å for **C**. Interestingly, changes in the geometry of gold clusters upon binding thiols or thiolates have been noted in previous DFT studies.³⁰ For example, the symmetrical gold trimer cluster cation becomes distorted upon binding one H₂S ligand.^{30b}

In order to evaluate the structures of isomers **F**, **G** and **H** we also calculated the structures of the neutral dimer, **K**, and monomer, **L**, as well AuH (**M**) and the bis- and mono-ligated cations, **N** and **O**. The structures of each of these species are shown in Fig. S1(c)–(g).† A comparison of the Au–Au distances in the cluster cations **C**, **G** and **H** with the neutral dimer **K** reveals that **C** and **G** have the shortest distances (2.907 Å and 2.914 Å respectively), consistent with Au–Au bonding, while the Au–Au interactions are weaker in **H** and **K** due to the longer distances (3.321 Å and 3.414 Å

respectively). In fact the long Au–Au distance in **H** suggest that it can be regarded as a weakly bound cluster between the bis-ligated gold cation, **N**, and gold hydride, **M**, which is further borne out by the fact that the Au–PH₃ bond lengths are identical in **H** and **N** (2.378 Å), and there is only a minor lengthening of the Au–H bond in moving from **M** (1.559 Å) to **H** (1.565 Å).



(2) Structure/reactivity probes of **C**: ion–molecule reactions, low energy collision induced dissociation *versus* electron excitation dissociation (EED)

Although the DFT calculations support a ground state for structures **C**, we sought experimental probes of structure based on reactivity. We and others have previously shown that ion–molecule reactions can be used to probe the structures of inorganic species.¹⁷ In particular, they offer an opportunity to “titrate” vacant coordination sites in metal complexes.^{31,32} We previously

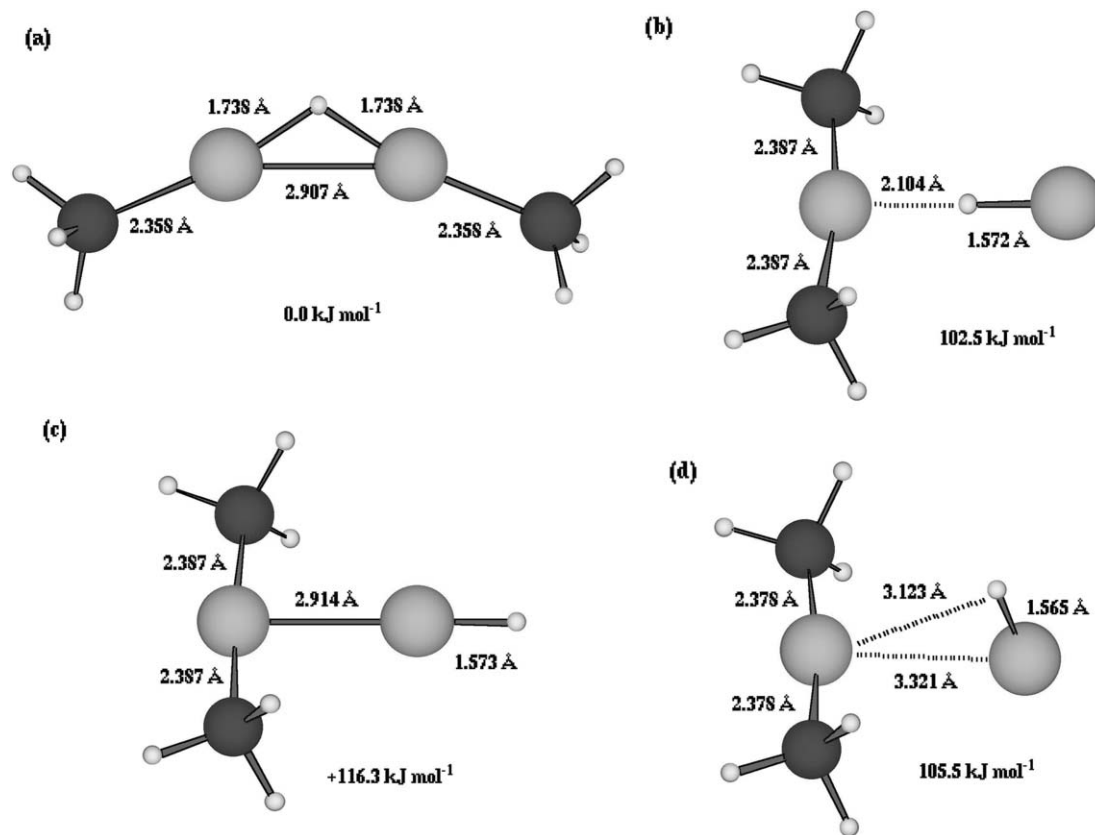
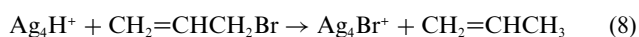


Fig. 3 DFT calculated structures (B3LYP/6-31G(d) level of theory with LanL2DZ ECP for Au) of: (a) C; (b) F; (c) G and (d) H. The relative stabilities of various isomers are in kJ mol^{-1} . Full details are given in the ESI.†

found that the “bare” silver hydride cations underwent a number of reactions including multiple ligation, as illustrated by Ag_2H^+ reacting with 2-propanol (eqn (7))^{16b} and a metathesis reaction, as illustrated by Ag_4H^+ reacting with allyl bromide (eqn (8)).^{16a} Although gold(I) complexes can adopt a range of coordination numbers,⁴ in the gas-phase coordination numbers of two tend to be favoured.^{27,33} Since E would be expected to react with ligands as the gold hydride moiety has a vacant coordination site, we decided to compare the reactivity of the gold hydride dimers with the mono coordinated gold ion, R_3PAu^+ . While the R_3PAu^+ ions were highly reactive to a range of neutral reagents such as H_2O and MeOH *via* ligand addition reactions (eqn (9) and Table 2), the gold hydride dimers ions were essentially unreactive, even to metathesis reactions with allyl iodide. These results are consistent with the R_3PAu^+ ions having a vacant coordination site,³² and rule out structure F for the gold hydride dimers.



Another structural probe widely used in the gas phase is CID. Our previous studies on silver hydride cluster cations have shown that they undergo a number of reactions, which depend on the size of the cluster, and whether it contains any extra ligands. The bare Ag_2H^+ cluster solely fragments *via* the loss of AgH

Table 2 Ion–molecule reactions between the gold cations R_3PAu^+ and $(\text{R}_3\text{PAu})_2\text{H}^+$ ($\text{R} = \text{Ph}$ and Me) and various neutral reagents^a

Neutral (L)	$\text{R}_3\text{PAu}^{+b}$		$(\text{R}_3\text{PAu})_2\text{H}^{+b}$	
	R = Me	R = Ph	R = Me	R = Ph
H_2O^c	+L	+L	NR	NR
MeOH^c	+L	+L	NR	NR
2-Propanol	+L	+L	NR	NR
MeCN^c	+L	+L	NR	NR
Pyridine	+L	+L	NR	NR
Allyl iodide	+L	+L	NR	NR
O_2	NR	NR	NR	NR
N_2O	NR	NR	NR	NR
CH_3NO_2	+L	+L	NR	NR
DMSO	+L	+L	NR	NR

^a The pressure of the helium bath gas in the trap is 1.75×10^{-3} Torr. The pressures of the other neutral reagents were as follows: 2-propanol *ca.* 1.7×10^{-7} Torr; pyridine *ca.* 1.9×10^{-7} Torr; allyl iodide *ca.* 2.4×10^{-7} Torr; CH_3NO_2 *ca.* 2.5×10^{-7} Torr; DMSO *ca.* 2.1×10^{-7} Torr; O_2 constituted 1% of the helium bath gas; N_2O constituted 54 ppm of the helium bath gas. ^b + L designates the addition of a ligand (see eqn (9)); while NR represents No Reaction under the experimental conditions used. ^c These neutral reagents were part of the background gases present in the trap (they were the ESI solvents used). No accurate pressure is known.

(eqn (10)).^{16b} Based on these previous studies, we anticipated that the phosphine ligated gold clusters, $(\text{R}_3\text{PAu})_2\text{H}^+$, would undergo either of two reactions: loss of the phosphine (eqn (11)) or cleavage of the cluster *via* loss of R_3PAuH (eqn (12)). An examination of Fig. 4 reveals that simple ligand loss (eqn (11)) does not occur for

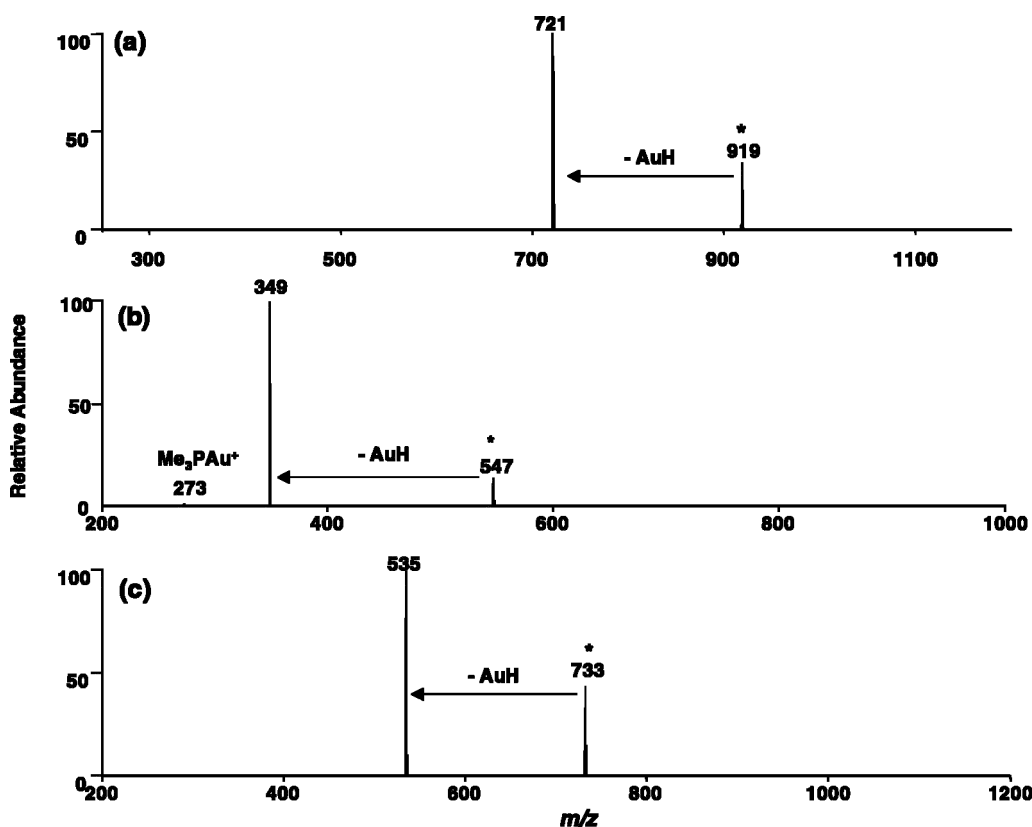
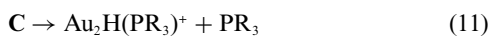


Fig. 4 LTQ CID MS³ spectra of the gold hydride dimers: (a) (Ph₃PAu)₂H⁺ (*m/z* 919); (b) (Me₃PAu)₂H⁺ (*m/z* 547); (c) (Ph₃PAu)(Me₃PAu)H⁺ (*m/z* 733). A * represents the mass selected precursor ion. Selection windows of 1–4 Th and normalised collision energies of 12–14% were used.

any of the systems studied. Moreover, an unanticipated reaction involving loss of AuH to yield the bis-ligated ion (R₃P)₂Au⁺ was observed to be the dominant fragmentation pathway in all cases (eqn (13)). Such a reaction is more consistent with isomers **F** or **G**, which DFT calculations predict to be less stable than **C**. Thus CID must involve an isomerisation reaction in which one of the phosphine ligands of **C** is relocated to the other gold site *prior* to fragmentation. While there appear to be no previous reports on gas-phase ligand migration reactions in gold cluster ions, isomerisation prior to fragmentation is a common process in low energy CID. For example intramolecular H/D exchange *precedes* fragmentation in protonated tryptophan.³⁴ Furthermore, there is precedence for phosphine migration reactions in other transition metal cluster systems in solution,³⁵ and there are also recent examples of phosphines acting as bridging ligands.³⁶



Since low energy CID is a slow heating process,¹⁸ and thus favours rearrangements with low barriers, we sought a high energy, prompt fragmentation technique to probe the structures of the (R₃PAu)(R'₃PAu)H⁺. Using the FT-ICR mass spectrometer, we examined the ion–electron induced dissociation reactions of these

cations. A number of ion–electron dissociation techniques have been developed, although work in this area has mainly focussed on analytical applications for biomolecule analysis³⁷ with the ion–electron interactions of ligated metal clusters being rarely studied.³⁸ The electronic excitation dissociation (EED) technique has its roots in the Electron Impact Excitation of Ions from Organics (EIEIO) technique pioneered by Freiser^{19a} and has been further developed by Zubarev *et al.*^{19b,c} It is suitable for singly charged cations and provides complimentary structural information to CID. Briefly, it involves allowing a singly charged cation to interact with a beam of electrons. At higher electron energies (>10 eV), these reactions appear to involve a two step process, in which the cation undergoes post-ionisation to form a transient doubly-charged radical cation, which then undergoes electron capture to reform the singly charged cation. The singly charged cation thus formed is in an electronically excited state and can undergo fragmentation. Applications of this technique have been limited to protonated peptides, where the fragmentation reactions observed *via* EED are similar to those occurring under UV photodissociation conditions. An examination of the EED spectra of the (R₃PAu)₂H⁺ ions (Fig. 5) reveals that the fragmentation reactions are no longer dominated by the rearrangement reaction (eqn (13)). Instead a major process involves simple loss of R₃PAuH (eqn (12)). In addition, a number of new reaction pathways are observed, including fragmentation of the phosphine ligands. For example, losses of Ph[•] (*m/z* 644 Th, Fig. 5a) and CH₄ (*m/z* 333 Th, Fig. 5b) from the coordinated ligands are observed, while dissociative fragmentation of the PPh₃ ligand yields an intense ion

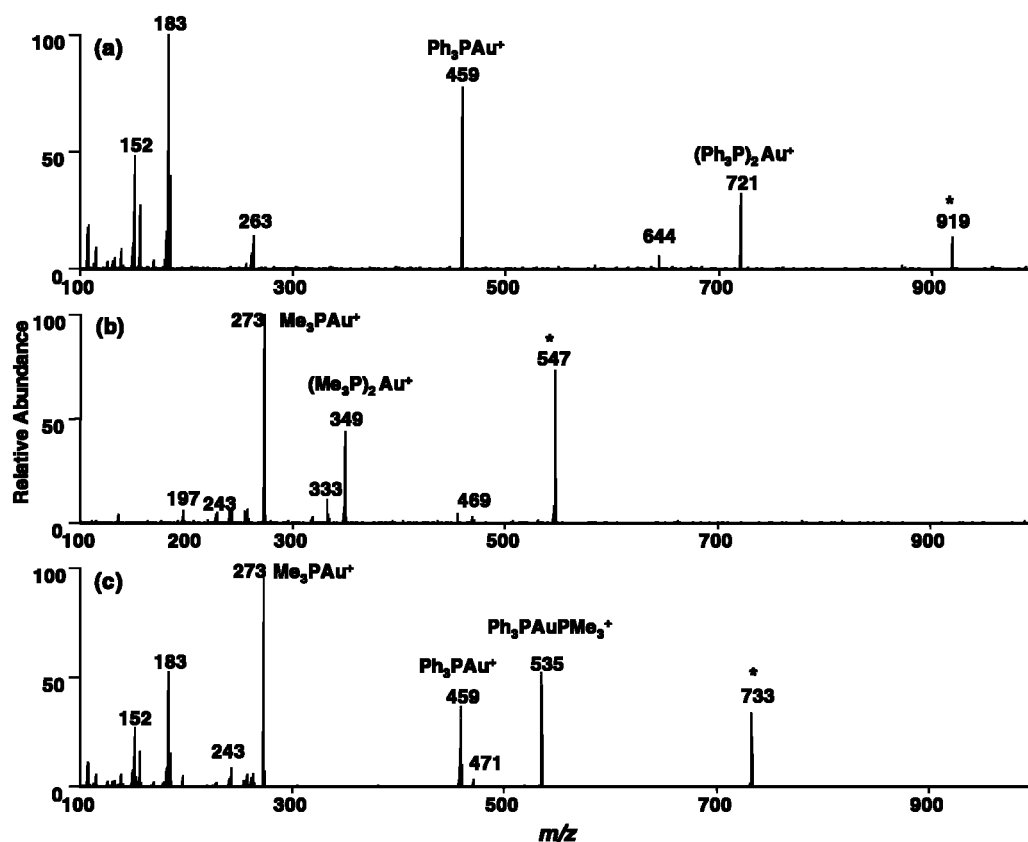


Fig. 5 LTQ FT EED spectra of the gold hydride dimers: (a) $(\text{Ph}_3\text{PAu})_2\text{H}^+$ (m/z 919); (b) $(\text{Me}_3\text{PAu})_2\text{H}^+$ (m/z 547); (c) $(\text{Ph}_3\text{PAu})(\text{Me}_3\text{PAu})\text{H}^+$ (m/z 733). An EED energy of 22–26 V was used. A * designates the mass selected precursor ion. See Table S1† for full assignment of fragment ions.

at 183 Th (Fig. 5b,c) consistent with the formation of $[\text{PPh}_2 - 2\text{H}]^+$. This ion is also observed in the EI/MS of PPh_3 .³⁹

(3) Insights into the phosphine ligand migration *via* DFT calculations

Since the ligand migration is most prominent in the low-energy CID spectra (Fig. 4) and could thus result in a mis-assignment of the structure of the cluster, we carried out further DFT calculations on the structures and energetics of transition states associated with the rearrangement of isomers **C** to **G** as well as the other species associated with eqn (11)–(13) using the $(\text{H}_3\text{PAu})_2\text{H}^+$ model system (Tables S2 and S3†). The results of these studies are shown in Fig. 6 and 7. The structure of the transition state for the migration of PH_3 from one gold atom to another, which connects isomers **C** and **G**, is shown in Fig. 6 and involves a bridging PH_3 . Similar transition states involving bridging PH_3 ligands have been calculated for PH_3 migrations in binuclear clusters of molybdenum^{40a} and tungsten.^{40b}

An examination of the energy diagram shown in Fig. 7, reveals why **C** prefers to undergo isomerisation to **G** rather than fragmentation *via* simple phosphine ligand loss (eqn (11)) or H_3PAuH loss (eqn (12)). Not only are the latter reactions more demanding energetically (eqn (11) and (12) are endothermic by 194.9 and 244.8 kJ mol^{-1} than AuH loss (eq (13)), but the transition state energy for the phosphine migration for this process is only 140.8 kJ mol^{-1} relative to the reactant **C**. Thus the driving

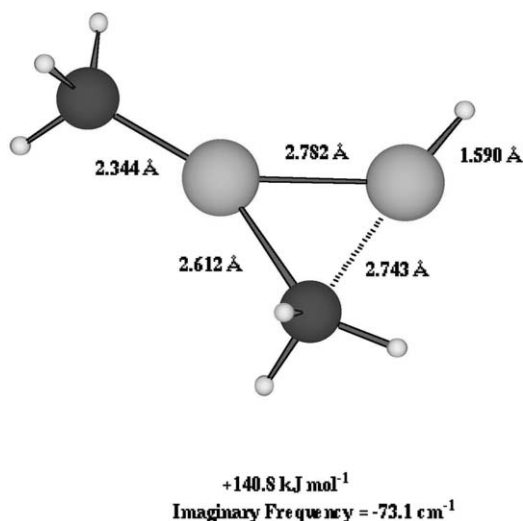


Fig. 6 DFT calculated (B3LYP/6-31G(d) level of theory with LanL2DZ ECP for Au) structure of the transition state for the phosphine migration of $(\text{H}_3\text{PAu})_2\text{H}^+$, which interconverts isomers **C** and **G**. The energy of this TS (in kJ mol^{-1}) is relative to the ground state structure **C**. Full details are given in the ESI.†

force for this rearrangement is the formation of the very stable $(\text{R}_3\text{P})_2\text{Au}^+$ ion, as experimentally observed in the CID spectra of each of the $(\text{R}_3\text{PAu})(\text{R}'_3\text{PAu})\text{H}^+$ species (Fig. 4).

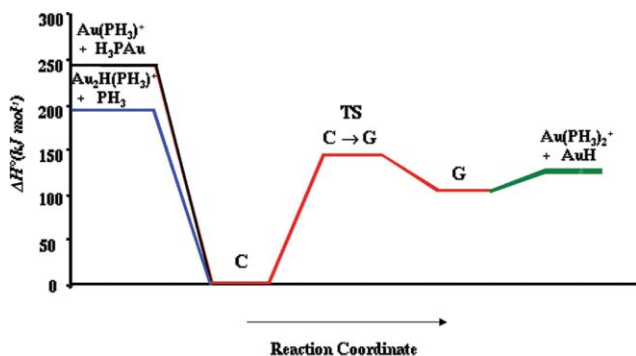


Fig. 7 DFT calculated (B3LYP/6-31G(d) level of theory with LanL2DZ ECP for Au) reaction energy profile for phosphine migration of the model $(\text{H}_3\text{PAu})_2\text{H}^+$ (C to G middle section) together with relative energies for eqn (3) (extreme left below), (4) (extreme left above) and (5) (extreme right). All energies are in kJ mol^{-1} . Full details are given in the ESI.†

Conclusions

Condensed phase studies of cluster compounds have established that: (i) addition of a ligand can bring about a fundamental change in cluster shape; (ii) clusters exhibit fluxionality *via* motion of the ligand shell and/or the metal shell.⁴¹ Less is known about the dynamic behaviour of clusters in the *gas phase*.⁴² Manard *et al.* have recently shown that ligation of alkenes can induce structural changes in gas-phase silver cluster cations,⁴³ while previous DFT studies have shown similar effects for the ligation of gold clusters by thiols and thiolates.³⁰ The results of the current study highlight the challenges in understanding the link between structure and reactivity of noble metal cluster ions in the gas phase and offer a rare glimpse into the role of the ligand. Thus ligand migration can precede cluster fragmentation under low-energy CID conditions, which may result in an incorrect structural assignment.⁴⁴ In these cases additional structural “tools” such as DFT calculations and ion–molecule reactions should be applied. EED appears to be a novel addition to the arsenal of tools for gas-phase structure determination of metal cluster ions.

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