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**Prying open a reactive site for allylic
arylation by phosphine ligated
geminally-diaurated aryl complexes.**

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ABSTRACT:

Gas-phase ion-molecule reaction experiments, theoretical kinetic modelling and computational chemistry were used to examine the role of a second gold center in promoting allylic arylation. Geminally di-aurated complexes, $[(L)_nAu_2Ph]^+$ are demonstrated to participate in C-C bond formation reactions with allyl halides, $CH_2=CHCH_2X$ ($X = Cl, Br$ and I) given a favorable phosphine ligand architecture. Thus while $[(Ph_3P)_2Au_2Ph]^+$, **1** is unreactive towards the allyl halides, $[(dppm)Au_2Ph]^+$, **2** (where $dppm =$ bis(diphenylphosphino)methane, $(Ph_2P)_2CH_2$) reacts via C-C bond coupling to produce $[(dppm)Au_2X]^+$. The reaction kinetics (efficiencies) follows the expected leaving group ability, $X = I (58\%) > Br (2\%) > Cl (0.02\%)$.

DFT calculations were carried out to examine potential mechanism for the C-C bond coupling reactions of **2** with each of the three allyl halides. The most favorable mechanism for C-C bond coupling of **2** requires the active participation of both gold centres in a redox couple mechanism wherein the allylic halide oxidatively adds across the gold centres to form a Au^IAu^{III} complex lacking a $Au\cdots Au$ interaction, followed by intramolecular reductive elimination of allyl benzene from the Au^{III} centre.

TITLE RUNNING HEAD: Gold promoted allylic arylation

KEYWORDS: geminally-diaurated aryl gold complex, bisphosphine ligand, metal carboxylates, mass spectrometry, decarboxylation, ion-molecule reactions, allyl halides, DFT calculation.

Introduction:

There has been a flurry of interest in developing homogeneous gold-catalyzed carbon-carbon bond forming reactions. This interest arises from the fact that gold(I) complexes have a number of synthetically useful modes of reactivity including oxidation/reduction chemistry, significant π Lewis acid character, and the ability to insert into C-H bonds.^[1] In addition to the chemistry available at a single gold center new modes of reactivity are now being uncovered by employing digold catalysts.^[2,3] A recent example is the gold-catalyzed allylation of arylboronic acids (Scheme 1 A) for which Levin and Toste have suggested a mechanism involving oxidative addition across both gold atoms of a digold complex to form a Au(II)-Au(II) intermediate.^[2g]

Scheme 1. Examples of di-gold complexes: (A) proposed mechanism for allylic arylation involving digold intermediates;^[2g] (B) *gem*-diaurated complexes (IPr = 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene).

Historically, bimetallic catalysis has been a particularly fruitful area of research, albeit not often well understood.^[4] Thus we were interested in further exploring the reactivity of digold systems. Based on our earlier observation of allylic alkylation reactions promoted by cationic coinage metal clusters,^[5] we speculated that cationic *geminally*-diaurated complexes similar to the ones shown in (Scheme 1B)^[6] might be capable of promoting allylic arylation reactions. We were further encouraged by the fact that in recent years cationic gold complexes supported by phosphine or N-heterocyclic carbene ligands have gained attention as potential catalytic intermediates in the functionalization of C-C multiple bonds.^[7]

Nesmeyanov et al. reported the synthesis, structural characterization and limited reactivity of *gem*-diaurated complexes,^[6a] but these fascinating species were largely ignored for 30 years until similar intermediates were detected in homogeneous gold-catalyzed reactions. Since then, several *gem*-diaurated aryls have been isolated and structurally characterized.^[8] While *gem*-diaurated aryl and vinyl species have been implicated repeatedly as off-cycle reservoirs in gold catalyzed C-C bond-forming reactions,^[6b,9] almost nothing is known about the inherent reactivity of *gem*-diaurated complexes towards organic substrates. Indeed, the only mode of reactivity that has been reported is the “S_N2 like” ligand exchange at gold (eq. 1).^[6a,10] Here we use multistage mass spectrometry (MSⁿ) techniques to examine whether cationic *gem*-diaurated complexes themselves can directly facilitate C-C bond forming reactions in the gas-phase. Ion-molecule reactions of the *gem*-diaurated complexes [(L)_nAu₂Ph]⁺ **1** (n = 2, L = Ph₃P) and **2** (n = 1, L = dppm = bis(diphenylphosphino)methane, (Ph₂P)₂CH₂) with allyl halides, CH₂=CHCH₂X (X = Cl, Br and I) were examined.^[11] A key finding is that the ligand plays a pivotal role in promoting C-C bond coupling. Thus while **1** does not undergo C-C bond coupling with the allyl halides, **2** does. The origin of this ligand effect is examined through computational chemistry methods.

Experimental:

Reagents

Reagents were purchased from Aldrich and used without further purification. Methanol and chloroform were purchased from RCI Labscan. Chloro(triphenylphosphine)gold(I) was purchased from STREM. Triphenylphosphine was purchased from Riedel-de Haën. Silver(I) benzenesulfinate was prepared by a literature method.^[12]

Mass spectrometry experiments

All mass spectrometry experiments were carried out using a Finnigan LTQ FT hybrid linear ion trap (Finnigan, Bremen, Germany) fitted with the standard factory electrospray ionization source and modified as described previously to allow the introduction of gaseous neutral reagents into the ion trap.^[13] A previous study has demonstrated that ions in the linear ion trap are essentially quasi-thermalized to room temperature.^[14] Accurate mass measurements using the FT-ICR allowed unambiguous assignment of the observed signals.

Preparation and isolation of complexes 1 and 3: $[(\text{Ph}_3\text{P})_2\text{Au}_2\text{Ph}]^+$ and $[(\text{Ph}_3\text{P})_2\text{Au}_2(\text{O}_2\text{SPh})]^+$.

Silver(I) benzenesulfinate (50 μmol in 5 mL 1:1 MeOH/ CHCl_3) was added to a solution of chloro(triphenylphosphine)gold(I) (10 μmol in 5 mL 1:1 MeOH/ CHCl_3) and the solution was made up to 20 mL with 1:1 MeOH/ CHCl_3 (v/v). The solution was stirred for 5 minutes before being transferred via syringe to the electrospray source at 3 $\mu\text{L min}^{-1}$. Typical electrospray source conditions were: Positive ion mode, Sheath Gas = 5 arbitrary units, Auxiliary Gas = 0 arbitrary units, Sweep Gas = 0 arbitrary units, Spray Voltage = 4.5 kV, Capillary Temp. = 300 $^\circ\text{C}$, Capillary Voltage = 15 V, Tube Lens Voltage = 65 V. The most abundant peak of the

isotope pattern (m/z 995 for **1** and m/z 1059 for **3**) was isolated within the ion trap for further investigation.

Preparation and isolation of complexes **2 and **4**: [(dppm)Au₂Ph]⁺ and [(dppm)Au₂(O₂CPh)]⁺.**

Dppm (10 μ mol in 3 mL 1:1 MeOH/CHCl₃) was added to a mixture of benzoic acid (0.2 mmol in 2 mL MeOH) and chloro(triphenylphosphine)gold(I) (10 μ mol in 3 mL 1:1 MeOH/CHCl₃) and the solution was made up to 20 mL with 1:1 MeOH/CHCl₃ (v/v). The solutions were allowed to sit for at least 15 minutes before being transferred via syringe to the electrospray source at 5-10 μ L min⁻¹. Typical electrospray source conditions were: Positive ion mode, Sheath Gas = 10 arbitrary units, Auxiliary Gas = 5 arbitrary units, Sweep Gas = 0 arbitrary units, Spray Voltage = 6.00 kV, Capillary Temp. = 250 °C, Capillary Voltage = 49 V, Tube Lens Voltage = 205 V. The most abundant peak of the isotope pattern (m/z 855 for **2** and m/z 899 for **4**) was isolated within the ion trap for further investigation.

Preparation and isolation of complex **5: [Au(Ph)(TPPMS)]⁻**

Gold(III) acetate (5.7 μ mol; 2 mg) was added to [(Ph₃P)₂N][TPPMS] (TPPMS = triphenylphosphine monosulfonate; 0.5 μ mol; 0.5 mL, 1 mM in MeOH) and benzoic acid (10 μ mol; 0.5 mL, 20 mM in MeOH). The solution was transferred immediately via syringe to the electrospray source at 5-10 μ L min⁻¹. Typical electrospray source conditions were: Negative-ion mode, Sheath Gas = 10 arbitrary units, Auxiliary Gas = 0 arbitrary units, Sweep Gas = 0 arbitrary units, Spray Voltage = -4.00 kV, Capillary Temp. = 200°C, Capillary Voltage = -45 V, Tube Lens Voltage = -250 V. The most abundant peak of the isotope pattern (m/z 615) was isolated within the ion trap for further investigation.

Ion-molecule reactions and rate constant determinations

The neutral allyl halide reagent was infused at various concentrations into the ion trap via a heated modification in the helium inlet line.^[13] There, it was allowed to interact with the reactant ion. Rates of reaction between the neutral reagent and the reactant ion were measured by varying the time delay between isolation of the reactive ion within the ion trap containing the neutral reagent and mass analysis of the contents of the ion trap (referred to as 'reaction delay', RD). The decay of the reactant ion was monitored over at least 7 values of RD.

The intensity of the reactant ion at each RD was determined by integration of its ion count. Relative pseudo first-order rate constants were obtained from the slope of plots of $\ln_e(\text{signal intensity})$ vs. RD plot. Absolute pseudo first-order rate constants were estimated by dividing the relative rate constant by the calculated concentration of allyl halide in the ion trap. The rate constants reported are an average of three independent experiments conducted on separate days. Theoretical collision rates were calculated for each reaction via the Average Dipole Orientation theory of Su and Bowers using the COLRATE program^[15], and 'reaction efficiency' (ϕ) values are reported as: (experimental absolute rate)/(theoretical collision rate) $\times 100\%$.

Computational details.^[16-21] Gaussian 09^[16] was used to fully optimize all the structures reported in this paper at the M06 level of density functional theory (DFT).^[17] The effective-core potential of Hay and Wadt with a double- ξ valence basis set (LANL2DZ) was chosen to describe Au, Cl, Br, I, and P. The 6-31G(d) basis set was used for other atoms. Polarization functions were also added for Au ($\xi_f = 1.05$), Cl ($\xi_d = 0.64$), Br ($\xi_d = 0.428$), I ($\xi_d = 0.289$), and P ($\xi_d = 0.387$). This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural

optimization. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the M06/BS1 calculations, we carried out single-point energy calculations for all of the structures with a larger basis set (BS2) at the B3LYP-D3BJ level of theory. BS2 utilizes the def2-TZVP basis set on all atoms. Effective core potentials including scalar relativistic effects were used for gold and iodine atoms. The B3LYP-D3BJ calculations were used to overcome the deficiency of the M06 level in incorporating long-range correlation for dispersion forces. To estimate the corresponding enthalpy, ΔH , and Gibbs energies, ΔG , the corrections were calculated at the M06/BS1 level and finally added to the single-point energies. We have used the corrected enthalpy and Gibbs free energies obtained from the B3LYP-D3BJ/BS2//M06/BS1 calculations throughout the paper unless otherwise stated.

Results and Discussion

Gas-phase formation and DFT-calculated structures of phosphine-ligated *gem*-diaurated aryl complexes

1 (m/z 995) can be formed via desulfination of $[(\text{Ph}_3\text{P})_2\text{Au}_2(\text{O}_2\text{SPh})]^+$, **3** (eq. 2, X = S, $n = 2$, L = Ph_3P) under collision-induced dissociation (CID) conditions^[22] within the ion trap mass spectrometer (Supporting Information Figures S1 and S2). **2** (m/z 855) can be formed via decarboxylation of $[(\text{dppm})\text{Au}_2(\text{O}_2\text{CPh})]^+$, **4** (eq. 2, X = C, $n = 1$, L = dppm) under CID conditions^[23] within an ion trap mass spectrometer, or it can be isolated directly from electrospray ionization (ESI) of a solution containing AuClPPh_3 , dppm and benzoic acid in

methanol/chloroform (Supporting Information Figures S3 and S4). The latter method is most efficient. High resolution mass spectrometry experiments show that this is the monocation and not a macrocyclic dication, $\{[(\text{dppm})\text{Au}_2\text{Ph}]^+\}_2$, **6**.

DFT calculations were performed to determine the lowest energy isomers of the geminal digold complex in the gas phase. As depicted in Figure 1a, the geminal complex exists as two isomers **2** and **2'**, which differ in their coordination modes. The lower energy isomer (**2**) can be interpreted in terms closely related to that by Weber and Gagné in describing the bonding in a binuclear gold vinyl complex.^[24] Owing to the parallel orbitals at both gold centres, the orientations of the phenyl bridge in both **2** and **2'** are skewed.^[25] In **2'**(σ -diaurated isomer) the Au-C(Ph) σ orbital is involved in interaction with the second gold empty orbital, while in **2**(σ - π -diaurated isomer), both the Au-C(Ph) σ orbital and the phenyl π orbital interact simultaneously with the empty orbital (Figure 1b).^[7] The presence of interaction between the Au-C(Ph) σ orbital and the second gold empty orbital in **2** is indicated by NBO analysis. The second order perturbation energy, $E(2)$, for **2'** shows an energy of 33.5 kcal/mol for interaction of the Au-C(Ph) σ bond with the second gold empty orbital. This interaction becomes weaker in **2** with an $E(2)$ value of 20.0 kcal/mol due to the

contribution of the π bond in the structure of **2**. The weaker interaction between the Au-C(Ph) σ orbital and the second gold orbital in **2** results in a longer Au-Au distance of 2.925 Å with a smaller Wiberg bond index of 0.169. The Au-Au distance in **2'** is calculated to be shorter (2.756 Å) with a larger Wiberg bond index (0.205). As shown in Figure 1b, the geometry of dppm results in a larger orbital overlap for **A** and a smaller orbital overlap for **B**. The lower stability of isomer **2'** compared to **2** can be attributed to the smaller orbital overlap between the Au-C(Ph) σ orbital and the second gold empty orbital.

Figure 1. Schematics showing (a) the equilibrium between two isomers **2** and **2'** for the geminal digold complex (the relative energies ΔG (ΔH) in kcal/mol were obtained from B3LYP-D3BJ/def2-TZVP//M06/LANL2DZ*-6-31G* calculations), and (b) orbital representations depicting the interaction of the second gold empty orbital with a π orbital of the phenyl ring (**A**) and with the Au-C(Ph) σ orbital (**B**).

The CID fragmentation patterns of the geminal digold complexes are entirely consistent with their calculated structures (see Supporting Information Figures S5-7 for the accurate mass analysis, CID spectra of **1** and **2**, and associated reaction equations).

Gas-phase ion-molecule reactions of allyl halides with phosphine ligated *gem*-diaurated aryl complexes

To investigate the inherent reactivity of the geminal digold complexes **1** and **2** in allylic arylation, we examined their gas-phase reactivity towards the allyl halides, C_3H_5X ($X = Cl, Br$ and I). In these experiments, **1** and **2** were generated in a linear ion trap by one of the

two methods described above, purified in the gas phase via mass selection and then allowed to interact with a known concentration of gaseous allyl halide introduced into the ion trap^[10] for a specified length of time (the reaction delay, RD), after which any resulting products or remaining reactant were ejected from the ion trap, detected and quantified.

These experiments highlight that both the ligand and the substrate play a role in the reactions of ligated *gem*-diaurated aryls with allyl halides. $[(\text{Ph}_3\text{P})_2\text{Au}_2\text{Ph}]^+$ m/z 995 (**1**) is completely unreactive towards all allyl halides $\text{C}_3\text{H}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$, eq. 3), even at 10 seconds, which is the longest reaction time we can probe (data not shown). In contrast, an examination of Figure 2 shows that ion-molecule reactions (IMRs) between mass selected $[(\text{dppm})\text{Au}_2\text{Ph}]^+$ (**2**, m/z 855) and allyl halides results in allylic alkylation to yield the ionic product, $[(\text{dppm})\text{Au}_2\text{X}]^+$ (eq. 4).

Figure 2. MS² spectra showing IMRs between **2** and C₃H₅X, for X =: (a) Cl (concentration of 9×10^9 molecules/cm³, RD = 10,000 ms), (b) Br (concentration of 6×10^9 molecules/cm³, RD = 10,000 ms), (c) I (concentration of 6×10^9 molecules/cm³, RD = 1,000 ms). The mass-selected ion is marked with an asterisk.

To quantify the kinetic order of reactivity, rate measurements were carried out and a comparison of the rate constants and reaction efficiencies (Table 1) highlights that the reactivity of the substrates follow their expected leaving group ability, X = : I (58%) > Br (2%) > Cl (0.02%).

Table 1. Gas-phase kinetics associated with the ion-molecule reactions of mono- and bi-nuclear gold ions with C₃H₅X, X = Cl, Br, I.

Ion	Molecule	$k_{\text{exptl}}^{[a][b]}$	$\phi^{[c]}$
[(dppm)Au ₂ Ph] ⁺	C ₃ H ₅ Cl ^[d,e]	2.1×10^{-13}	0.02
[(dppm)Au ₂ Ph] ⁺	C ₃ H ₅ Br	1.9×10^{-11}	2.0
[(dppm)Au ₂ Ph] ⁺	C ₃ H ₅ I	5.0×10^{-10}	58
[(TPPMS)AuPh] ⁻	C ₃ H ₅ I ^[d,f]	2.2×10^{-14}	<0.001
[(Ph ₃ P) ₂ Au ₂ Ph] ⁺	C ₃ H ₅ I	No reaction	0

[a] In units of cm³ molecule⁻¹ s⁻¹. [b] Experimental rates for consumption of reactant ion. [c] Reaction efficiency (ϕ) = ($k_{\text{exptl}}/k_{\text{theor}}$) × 100%. The theoretical ion-molecule collision rate was obtained from average-dipole orientation (ADO) theory, calculated using the Colrate program.^[15b] [d] Reaction rate too slow to measure accurately. A maximum possible rate was calculated by estimating no more than: [e] 2% product formation under the reaction conditions; [f] 1% product formation under the reaction conditions.

Previous experiments have shown that the mononuclear organo gold(I) anion [CH₃AuCH₃]⁻ reacts only sluggishly with allyl iodide (eq. 5, reaction efficiency of 0.07%)^[11c] but that the monoligated gold cation, [Ph₃PAu]⁺, reversibly binds allyliodide (eq. 6).^[26] Thus, both the second gold centre and the nature of the ligand in **2** play a crucial role in C-C bond coupling reactions with the allyl halides. To test the role of a single gold centre with a more relevant mononuclear phenyl gold-phosphine complex, the fixed charge phosphine complex [(TPPMS)AuPh]⁻ (**5**) was “synthesized” in the gas-phase as reported previously,^[11e] mass selected, and exposed to allyl iodide. While a very small signal of the ionic product [(TPPMS)AuI]⁻ consistent with C-C bond coupling (eq. 7) is observed (Supporting Information, Figure S8) this is an extremely slow reaction (reaction efficiency <0.001%, Table 1); hence, the presence of a second gold centre plays a key role in promoting C-C bond-formation.

Mechanism of allylic arylation

Having established the inherent reactivity of the geminal digold complex towards the allyl halides we next turned to DFT calculations to provide a feasible mechanism of this allylic arylation reaction. Two different classes of mechanisms were considered: reactions which are isohypsic with respect to the oxidation state of gold;^[27] and reactions that involve redox changes to one of the gold atoms. Based on a comprehensive DFT survey of possible C-C bond forming pathways, four key potential mechanisms emerged, and these are illustrated in Figure 3 for allyliodide and depicted for the other allylic substrates in the SI (Figures S9, S10).

Figure 3. Four competing mechanisms for C-C bond coupling between **2** and allyl iodide to yield allyl benzene and $[(\text{dppm}) \text{Au}_2\text{I}]^+$ calculated at the B3LYP-D3BJ/def2-TZVP//M06/LANL2DZ*-6-31G* level of theory, shown as diagrams comparing the energetics of the various mechanism. (a) illustrates concerted isohypsic reactions involving C-C bond formation (i) at the α carbon via TS'_{7-8_I} , and (ii) at the γ carbon via TS_{7-8_I} . (b) shows the redox couple pathways involving allyl iodide oxidative addition (iii) at one gold center, and (iv) across both gold centers as the preferred mechanism. The relative Gibbs and enthalpy energies (in parentheses) are given in kcal/mol.

In the higher energy concerted isohypsic mechanisms in which the gold core remains in the Au^IAu^I state throughout, (i) and (ii), C-C bond formation occurs at the α and γ carbon atoms by S_N2 and S_N2' processes,^[28] respectively. As shown in Figure 3, the reaction begins with the coordination of allyl iodide to **2** to yield **7_I** in which the phenyl group is no longer a bridging ligand. We were unable to find a transition state between **2** and **7_I** and a relaxed PES scan between the two structures shows that it is an entirely exothermic pathway (see SI Figure S11). From **7_I**, formation of allyl benzene is achieved through **TS_{7-8_I}** (pathway (ii)), which involves a rocking motion of the allyl fragment between the iodide and the *ipso* carbon of the phenyl group. This forms the product complex, **8_I**, in which allyl benzene is coordinated to a single gold atom through a phenyl π -bond. A related concerted isohypsic mechanism in which C-C bond formation occurs at the α carbon of the allyl halide has a higher barrier via transition structure **TS'_{7-8_I}**.

The lowest energy pathway for all of the allylic substrates is the redox couple mechanism (pathway (iv)). In this mechanism, the reaction starts with direct oxidative addition of allyl iodide across the gold(I) centres via transition structure **TS_{7-12_I}** to give a Au^IAu^{III} complex (**12_I**) followed by reductive elimination at the Au^{III} centre leading directly to the products. An alternative higher energy redox couple mechanism (iii) involves intramolecular oxidative addition at one Au^I center in **7_I** to give **10_I** followed by reductive elimination across both gold centres. Oxidative addition through **TS_{7-12_I}** is an easier process due to the electron-donating phenyl group which makes gold more prone to oxidation. This interpretation is further supported by the higher stability of the Au^IAu^{III} complex **12_I** compared to **10_I** (~7.0 kcal/mol).

As mentioned above, for all of the allylic substrates, the pathway involving C-C bond formation via transition structure **TS_{12-8_X}** is the most favourable (mechanism (iv) in Figure 3). The relative energies of all the stationary points on this pathway are summarized in Table

2. We note that in comparing the reactivity of allyl-X (X = Cl, Br, I) (Table 2), the reaction energies for coordination of allyl-X to form **7_X** follow the order I > Br > Cl, i.e. -12.6, -8.5, -5.1 kcal/mol, respectively. This is consistent with the greater ability of iodine as an electron donor, resulting from the higher energy of iodine lone pairs.^[29] Although the most favourable interaction in the initial adduct formation is that of the iodide with a gold centre, the reactivity trend observed results from energies of **TS_{12-8_X}** relative to **2**. Indeed, for the most reactive substrate (X= I), the DFT manifold lies entirely below **2**, in contrast to X = Cl where **TS_{12-8_Cl}** lies slightly above **2**, and for which there is negligible reaction detected by mass spectrometry. These results suggest that the higher reactivity of the adduct **7_I** compared to **7_Br** and **7_Cl** can be traced back to its higher stability.

Table 2. DFT-predicted Gibbs relative energies for the reaction of **2** with C₃H₅X (X=Cl, Br, I) to yield allyl benzene and [(dppm)Au₂X]⁺ via the redox couple mechanism reaction involving C-C bond formation at a Au^{III} centre via **TS_{12-8_X}** (mechanism (iv) in Figure 3).

Structure ^[a]	C ₃ H ₅ I	C ₃ H ₅ Br	C ₃ H ₅ Cl
2	0.0	0.0	0.0
7_X	-12.6	-8.5	-5.1
TS_{7-12_X}	-7.6	-4.1	0.0
12_X	-12.1	-10.2	-5.9
TS_{12-8_X}	-5.7	-2.3	0.7
9_X	-45.9	-39.4	-33.8

[a] Structures are calculated at B3LYP-D3BJ/def2-TZVP//M06/LANL2DZ*-6-31g* level. Energies are in kcal/mol relative to respective separated reactants.

As noted above, the related cation containing Ph₃P as a non-bridging ligand in [(Ph₃P)₂Au₂Ph]⁺ (**1**) is unreactive towards the allyl halides examined in mass spectrometric studies. Consistent with this observation, we find in DFT computation that the analogous reaction to that of [(dppm)Au₂Ph]⁺ (**2**) with allyl iodide is endergonic (eq. 8).

Conclusions

Mass spectrometry has emerged as an important tool in monitoring metal catalyzed reactions^[30], resolving mechanistic controversies in gold chemistry^[31] and directing the synthesis of new coinage metal compounds^[32]. Here we have shown that multistage mass spectrometry experiments can be used to discover new C-C bond forming reactions. In particular we have demonstrated that *gem*-diaurated aryls can participate in allylic arylation reactions in the gas-phase when the gold(I) centres are bridged by bis(diphenylphosphino)methane. While descriptors have been developed to better understand the role of chelating P,P-donor ligands in the reactivity of mononuclear metal complexes,^[33] a full understanding of how these ligands influence reactivity in binuclear complexes is a subject of ongoing research in the organometallic and catalysis community.^[34] Our DFT calculations show that the dppm ligand plays a key role in allowing the *gem*-diaurated aryl to act as a “molecular hinge”. Indeed the ring strain induced by the dppm partially “pries open” a reactive site, which further “opens” upon approach of the allyl halide (Figure S11). The dppm ligand also controls the lowest energy pathway, which involves regiospecific bond formation at the γ carbon of the allyl halide. Whether this effect can be translated to solution remains an open question. The ring strain induced by the dppm may cause the preferential

formation of a macrocyclic complex **6**, or alternatively a solvent molecule, S, might open up the *gem*-diaurate to form the binuclear complex **15**.

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Supporting Information

Additional supporting information, which includes: the Cartesian coordinates of all species examined; a full citation of reference 16; mass spectra showing the formation of **1** – **4** and the fragmentation reactions of **1** and **2**; formation and ion-molecule reaction of [(TPPMS)AuPh]⁺, **5**, with C₃H₅I; DFT-calculated potential energy diagrams for the reactions of **2** with C₃H₅Br and C₃H₅Cl; relaxed PES scan for reaction of allyl iodide with **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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