A cationic gold-fluorenyl complex with a dative Au→C+ bond: Synthesis, structure, and carbophilic reactivity.

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A cationic gold-fluorenyl complex with a dative Au→C$^+$ bond: Synthesis, structure, and carbophilic reactivity.

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Abstract: Aiming to study the interaction of gold with the highly Lewis acidic fluorenyl cation, we synthesized (*o*-[$Ph_2P(C_6H_4)$Flu)AuCl(tht)][BF_4] ([2][BF_4]) and (*o*-$Ph_2P(C_6H_4)$Flu)$AuCl_2$ (3) (Flu = 9-fluorenyl) and found that the latter could be converted into [(*o*-$Ph_2P(C_6H_4)$Flu)AuCl]$^+$ ([4]$^+$) upon treatment with $NaBArF_{24}$ ($BArF_{24}$ = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$). [4]$^+$, which has been isolated as a chloride-bridged dimer, readily catalyses the cycloisomerisation of 2-allyl-2-(2-propynyl)malonate. Computational results show that [4]$^+$ possesses a strong Au→C$^+$ bond and readily activates enynes.

The introduction of Z-type ligands in the coordination sphere of transition metals is increasingly being considered as a means to enhance catalysis.[1, 2] This area has been transformed by the use of ambiphilic, boron-based Z-type ligands[2] and their demonstrated ability to form M→B interactions as in the case of **A** (Figure 1),[3] one of the earliest examples of such a complex. Based on the isolobal relationship between boranes and carbocations, we decided to target a family of related complexes designed to possess a M→C$^+$ interaction.[4] We contended that the positive nature of the carbocation would stabilize the accepting orbital, leading to a stronger M→Z-type ligand interactions. While this assumption was validated by the synthesis of a series of group 10 complexes of type [**B**$_M$]$^+$,[5] our efforts to isolate complexes with genuine Au→C$^+$ dative interactions led to derivatives of type [**C**]$^+$ in which the interaction between the two centres is dominated by electrostatic forces.[6-8] Reasoning that a more Lewis acidic carbocationic unit would lead to stronger Au→C$^+$ bonding, we have decided to target a complex of type [**C**]$^+$ featuring an antiaromatic fluorenyl cation as the carbenium moiety (Figure 1).[9] In this paper, we show that the elevated Lewis acidity of the fluorenyl cation is such that it results in the formation of square planar gold derivatives, indicating at least partial oxidation of the gold centre. In addition to describing the structure of these complexes, we also document their potential as carbophilic catalysts.

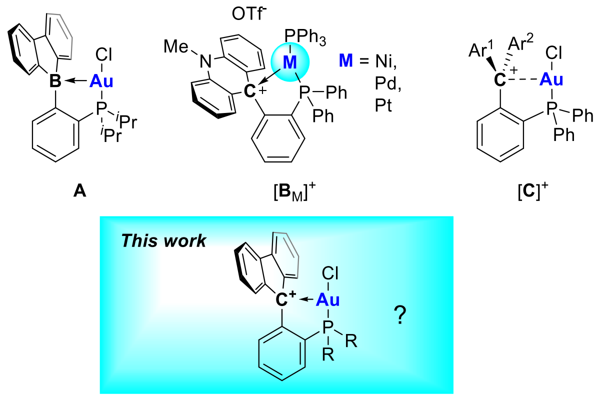

Figure 1. Structures of **A**, [**B**]$^+$ and [**C**]$^+$ and objective of the current study.

To access the targeted complexes, we first constructed the ligand by allowing 1-lithio-2-diphenylphosphino-benzene to react with fluorenone (Figure 2). This reaction led to the formation of the phosphinocarbinol **L**OH which was subsequently treated with (tht)AuCl (tht = tetrahydrothiophene) in CH_2Cl_2, leading to the precipitation of the phosphine gold complex **1** as a white powder. Direct addition of 1 equiv. of HBF_4 to this suspension led to the dissolution of the powder and an immediate colour change from colourless to yellow, affording [**2**][BF_4] in a 72% yield. The formation of [**2**][BF_4] can be followed by ^{1}H NMR spectroscopy which shows that the resonance of the OH proton in **1** at 4.62 ppm disappears upon addition of HBF_4. At the same time, the ^{31}P NMR resonance undergoes a shift from 38.5 ppm for **1** to

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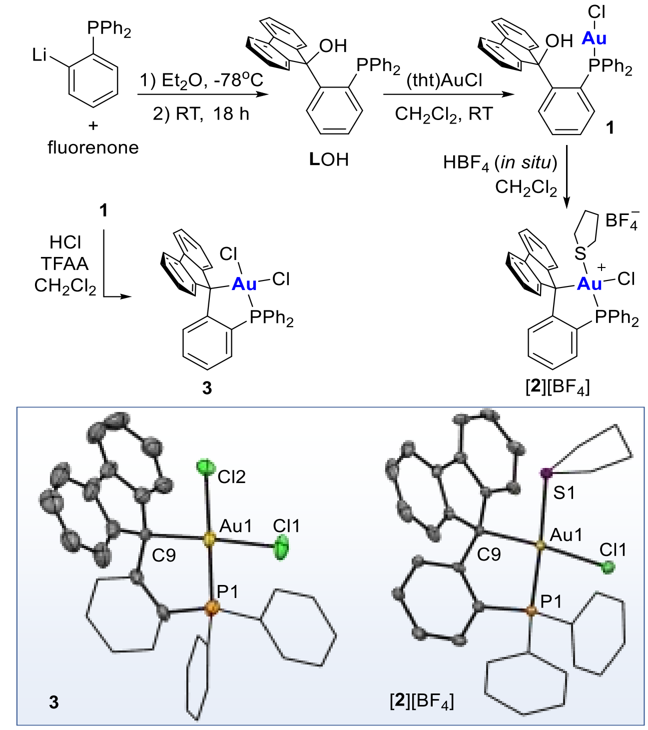
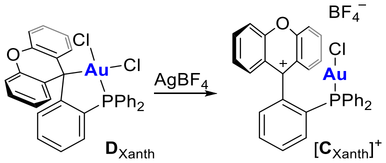


Figure 2. Synthesis of the carbinol ligand **L**OH and gold complexes **1**, [**2**][BF$_4$] and **3** with ORTEP drawings to the solid state structures of [**2**][BF$_4$] and **3**. The BF$_4^-$ counter anion of [**2**][BF$_4$] and all hydrogen atoms are omitted for clarity. Selected bond lengths for [**2**][BF$_4$]: Au1-C9, 2.106(2) Å; Au1-Cl1, 2.3562(5) Å; Au1-S1, 2.4137(5) Å; Au1-P1, 2.2776(5) Å. Selected bond lengths for **3**: Au1-C9, 2.131(8) Å; Au1-Cl1, 2.379(2) Å; Au1-Cl2, 2.336(2) Å; Au1-P1, 2.245(2) Å.

69.6 ppm for [**2**][BF$_4$]. For comparison, the ^{31}P NMR resonances of previously synthesized ortho-carbenium phosphine gold chloride complexes of type [**C**]$^+$ all range from 22.4 to 25.9 ppm.[6, 7] This difference suggested to us that [**2**][BF$_4$] is not a simple gold chloride complex of type [**C**]$^+$, but possibly a square planar gold derivative similar to the known complex **D**$_{xanth}$ (Scheme 1), characterized by a ^{31}P NMR resonance at 60.2 ppm.[6] We also tested the dihydroxylation of **1** by addition of HCl in the presence of trifluoroacetic anhydride (TFAA). This reaction afforded a new air-stable yellow complex, referred to as **3**, in a 59% yield (Figure 2). The ^{31}P NMR resonance of **3** at 62.2 ppm is close to that of [**2**][BF$_4$], suggesting a similar structure.

In accordance with the above-discussed NMR data, the crystal structures of [**2**][BF$_4$] and **3** indicate that these complexes are indeed square planar gold complexes (Figure 2). The gold atom and the C9 carbon of the fluorenyl unit are separated by relatively short interatomic distances of 2.106(2) Å in [**2**][BF$_4$] and 2.131(8) Å for **3**. It follows that these structures are the gold analogues of the palladium allyl complexes that have been isolated by Iwai and Sawamura using the same phosphino-fluorenyl ligand system.[10] Pyramidalization at the C9 carbon atom is in line with a covalent bond between an sp^3 carbon and a gold atom. Furthermore, the ^{13}C NMR signal of the fluorenyl C9 carbon atom at 88.2 (J_{CP} = 7.2 Hz) and 85.6 ppm (J_{CP} = 7.3 Hz) for [**2**][BF$_4$] and **3**, respectively, indicate a strong Au-C9 interaction signalling quenching of the carbenium centre. It is important to note that the chloride ligand of [**2**][BF$_4$] is trans to the C9 atom while the tht ligand is coordinated trans to the phosphine unit. In complex **3**, the two Au-Cl bonds have different lengths of 2.379(2) Å and 2.336(2) Å for Au1-Cl1 and Au1-Cl2, respectively, with the slightly longer Au1-Cl1 bond indicating a greater trans influence exhibited by the fluorenyl ligand. Similar observations were made in the previously synthesized complex **D**$_{xant}$ (Scheme 1).[6] Comparing the structure of complex [**2**][BF$_4$] with that of **A**[3] highlights the difference in the Lewis acidity and oxidizing properties between the isolobal borafluorene and cationic fluorenyl units.



Scheme 1. Conversion of **D**$_{xant}$ into [**C**$_{xanth}$]$^+$ via chloride abstraction

We had previously shown that **D** could be converted into [**C**$_{xanth}$]$^+$ upon chloride anion abstraction, indicating C9-Au bond heterolysis and formal reduction of the gold centre (Scheme 1).[6] To test the possibility of a similar reaction, **3** was treated with NaBArF$_{24}$ in difluorobenzene (DFB). Upon standing at -40 °C under a layer of hexanes, single crystals of [**4**$_2$][BArF$_{24}$]$_2$ formed over a few days (Figure 3). An X-ray analysis of these crystals reveals the formation of a centro-symmetrical dimer featuring a Au(μ-Cl)$_2$Au core (Figure 3), a motif that has been seen in a few other complexes.[11] Because the Cl and Au atoms are disordered over two positions, individual Au-Cl distances cannot be discussed. Yet, the average Au-Cl distance of 2.49 Å

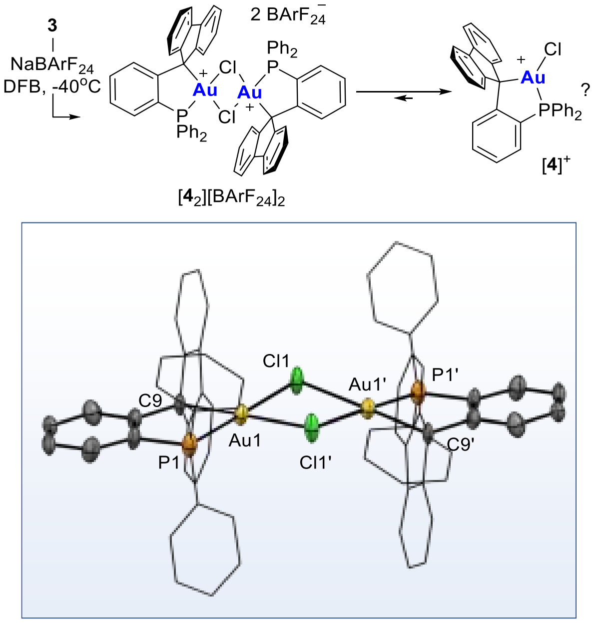


Figure 3. Synthesis of [**4**$_2$][BArF$_{24}$]$_2$ and ORTEP representation of the dimer with only one component of the disordered Au$_2$Cl$_2$ core shown. BArF$_{24}^-$ counter anions and hydrogen atoms omitted for clarity.

in [**4**$_2$][BArF$_{24}$]$_2$ suggests an elongation of the gold-chlorine bond when compared to those in [**2**][BF$_4$] and **3**. This elongation can be correlated to the bridging position of the chlorine atoms in [**4**$_2$][BArF$_{24}$]$_2$. The average Au1-C9 distance of 2.13 Å is similar to that in complexes [**2**][BF$_4$] and **3**, indicating the presence of a strong bond between these two centres. We also note the presence of an interstitial difluorobenzene molecule involved in a short Au-F contact (av. 2.97 Å), speaking to the electrophilic character of the core. Crystals of [**4**$_2$][BArF$_{24}$]$_2$ are very sensitive and readily decompose in air. In CD_2Cl_2, these crystals give rise to a ^{31}P NMR signal at 73.8 ppm which decoaleces into two resonances at ~0 °C, suggesting a rapid monomer-dimer equilibrium (Figure 3). Progressive cooling to -75 °C lead to the appearance of two peaks, which are tentatively assigned to the monomer [**4**]$^+$ (73.2 ppm) as the major species and the dimer [**4**$_2$]$^{2+}$ (74.1 ppm) as a minor species, as supported by DFT calculations and ESI mass spectrometry (see SI). The ^{13}C NMR spectrum at -40 °C displays a broad, unresolved resonance at 102.4 ppm assigned to the C9 carbon atom.

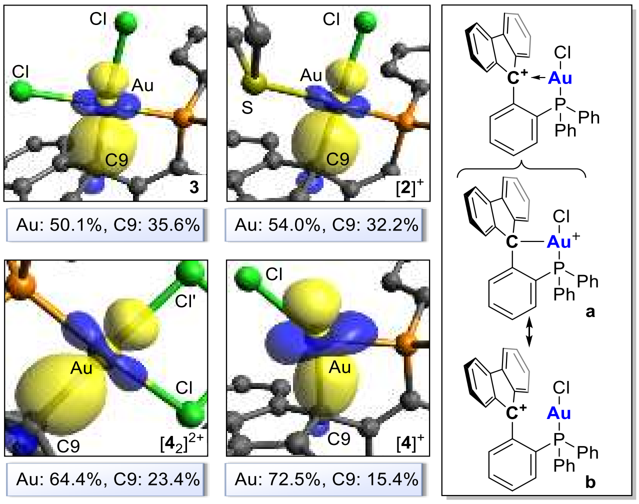
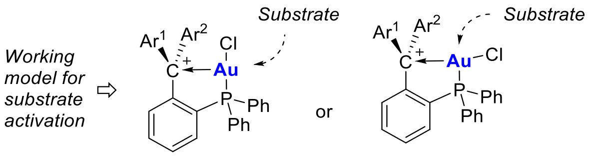


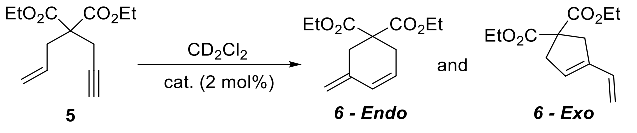
Figure 4. Top: Pipek-Mezey orbitals of complexes **3**, [**2**]$^+$ and [**4**$_2$]$^{2+}$ showing the Au1-C9 interaction. Bottom: Resonance structures accounting for the polarity of the Au-C9 bond in [**4**$_2$]$^{2+}$.

The Au-C9 interaction in [**2**]$^+$, **3**, [**4**]$^+$ and [**4**$_2$]$^{2+}$ was further studied using a Pipek-Mezey localization analysis (see SI for details). This computational analysis reveals that the Au-C9 interaction is polarized toward gold (Figure 4). These results indicate that the Au-C9 interaction acquires significant Au→C$^+$ dative character, especially in the case of [**4**]$^+$, which according to computations, adopts a distorted T-shaped structure. For comparison, we also computed the structure of $[Ph_3P(Me)AuCl]^+$ and inspected the polarity of the Au-C$_{Me}$ using the Pipek-Mezey localization method. A comparison of the Au/C orbital contribution ratio ($r_{Au/Coc}$) (4.71 for [**4**]$^+$ and 2.27 for $[Ph_3P(Me)AuCl]^+$) indicates that $[Ph_3P(Me)AuCl]^+$ features a significantly less polar Au-C interaction, speaking to the influence of the fluorenyl substituent in [**4**]$^+$ over the polarity and hence dative character of the Au→C$^+$ bond. These computational results indicate that the gold atom of cationic complexes tends to resist oxidation by full transfer of its valence electron to the ligands. It could also be stated that ligand field inversion becomes prevalent, especially in [**4**]$^+$.[12] It follows that [**4**]$^+$ is best described based on two extreme resonance structures (**a** and **b**), the overlay of which can also be depicted by acknowledging the dative character of the Au→C$^+$ interaction (Figure 4). The polarity of the Au-C9 interaction in [**4**]$^+$ is reminiscent of that in [**B**$_{Pd}$]$^+$, which could also be described on the basis of analogous resonance structures.[5] Because the adoption of the dative formalism sometimes leads to confusion,[13] we will remind ourselves that the gold atom in these complexes, including in [**4**]$^+$ is trivalent as it involves three of its valence electron in forming bonds with its ligands. One of these electrons is involved in a bond with the chlorine atom. Two other electrons are involved in a polar bond with the C9 atom of the fluorenyl cation. Our point of view may contrast with that of Manca and coworkers, who recently proposed that square planar gold complexes with inverted ligand fields should be assigned a d^{10} electronic configuration.[14] This proposal can be traced back to the case of $[Cu(CF_3)_4]^-$ which has been extensively discussed,[15] including by Hoffmann and co-workers who remain split on the d^8/d^{10} electronic configuration question for copper as highlighted in the "Oxidation State Wars?" section of their seminal contribution.[12] We will note in passing that similar debates have taken place in the context of Z-type ligand chemistry, an area in which assigning d electron configuration in complexes with metal⟶Lewis acid dative bonds remains a topic of discussion.[16]



Scheme 2. Working model for substate activation by complexes of type [**C**]$^+$.

In previous reports, we have shown that the carbenium ion of complexes of type [**C**]$^+$ influences the catalytic reactivity of the gold centre cyclization of propargyl amides.[6, 7] The working model ascribed to this catalysis involves coordination of the alkynyl functionality to the gold atom. At the same time, the carbocationic unit acts as a latent Z-type ligand and accepts electron density from the gold atom (Scheme 2). The reactivity of each gold chloride complex could be correlated to the Lewis acidity of the adjacent carbenium unit since a higher activity was observed for complexes with a more Lewis acidic carbenium unit.[6, 7] Isolation of complexes [**4**$_2$][BArF$_{24}$]$_2$ gives us a unique method to investigate our previously hypothesized working model. Given that prior benchmarking had involved the cyclization of propargyl amides as a test reaction, we first considered [**4**][BArF$_{24}$] as a catalyst for the cyclization of N-propargyl-4-fluorobenzamide in CD_2Cl_2. However, addition of the substrate resulted in immediate catalyst decomposition as indicated by a colour change of the solution, leaving the reaction substrate untouched as confirmed by ^1H NMR spectroscopy. Correlating this decomposition



Conversion after 10 min.: 0% for cat. = [**2**][BF$_4$]; 100% for cat. = [**4$_2$**][BArF$_{24}$]$_2$

Scheme 3. Cyclization of 2-allyl-2-(2-propynyl)malonate promoted by the gold complexes.

to the high acidity of the amide functionality, we decided to test the [**4**][BArF$_{24}$] as a catalyst for the cyclization of 2-allyl-2-(2-propynyl)malonate (Scheme 3). When the reaction was run at room temperature with a 2 mol% of the gold complex, complete conversion of the enyne substrate into its cyclized isomers **6a** and **6b** was observed after just 10 minutes. ^{1}H NMR analysis of the catalytic mixture showed formation of the exo and endo cyclized products in a 1:1.2 ratio. This reaction did not proceed to any measurable extent when [$\mathbf{C_{xant}}$][BF$_4$] and [**2**][BF$_4$] were employed as catalyst. The lack of activity [**2**][BF$_4$] indicates that the electrophilic gold centre is effectively poisoned by the tht ligand. The contrasting behaviour of [$\mathbf{C_{xant}}$][BF$_4$] and [**4**][BArF$_{24}$] illustrates the influence of interfacing the gold atom with a highly Lewis acidic fluorenyl cation and is reminiscent of gold catalysts activated via oxidation of the gold center.[17] The activity of [**4**][BArF$_{24}$] also suggest dissociation of the dimer into monomers, upon interaction with the reaction substrate. In support of this view, we note that [**4**][BArF$_{24}$] reacts with tetrahydrothiophene in CH$_2$Cl$_2$ to afford [**2**][BF$_4$].

In summary, our efforts to isolate a phosphine gold chloride complex flanked by an adjacent fluorenyl cation have led to the isolation of phosphino-fluorenyl-gold complexes, the formation of which reflects the high acidity of the antiaromatic fluorenyl cation. This behaviour contrasts with the results of prior efforts that had led to the successful isolation of complexes of type [**C**]$^+$ featuring a phosphine gold moiety flanked by a weakly Lewis acidic carbenium ions. Finally, bonding analyses show that the Au-C bond in these complexes has strong Au→C$^+$ dative character, especially in the case of [**4**]$^+$, which behaves as a particularly potent catalyst in enyne cyclization reactions.

Acknowledgements

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Conflicts of interest

There are no conflicts to declare.

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