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Stabilized carbenium ions as latent, Z-type ligands

Lewis C. Wilkins, Youngmin Kim, Elishua D. Litle and François P. Gabbaï*[a]

Abstract: Controlling the reactivity of transition metals using secondary, σ-accepting ligands is an active area of investigation that is impacting molecular catalysis. Here we describe the phosphine gold complexes [(*o*-$Ph_2P(C_6H_4)$Acr)AuCl]$^+$ ([**3**]$^+$, Acr = 9-*N*-methylacridinium) and [(*o*-$Ph_2P(C_6H_4)$Xan)AuCl]$^+$ ([**4**]$^+$, Xan = 9-xanthylium) where the electrophilic carbenium moiety is juxtaposed with the metal atom. While only weak interactions occur between the gold atom and the carbenium moiety of these complexes, the more Lewis acidic complex [**4**]$^+$ readily reacts with chloride to afford a trivalent phosphine gold dichloride derivative (**7**) in which the metal atom is covalently bound to the former carbocationic center. This anion-induced Au(I)/Au(III) oxidation is accompanied by a conversion of the Lewis acidic carbocationic center in [**4**]$^+$ into an X-type ligand in **7**. We conclude that the carbenium moiety of this complex acts as a latent Z-type ligand poised to increase the Lewis acidity of the gold center, a notion supported by the carbophilic reactivity of these complexes.

A new paradigm has emerged in catalysis whereby the positioning of an electron-deficient moiety next to a transition metal has led to remarkable changes in catalytic activity for a number of reactions.[1] This strategy has seen its most notable success in the chemistry of transition metal complexes bearing boron-containing Lewis acidic Z-type ligands[2] such as those in **I**, **II** and **III** (Figure 1A).[3] The boron atoms of such ligands directly interact with the transition metal center by drawing electron density from filled n d-orbitals. This interaction, which is accompanied by a lowering of the vacant n+1 p_x metal orbital, results in a more electron deficient and Lewis acidic transition metal center (Figure 1B).[4] Such effects, which have been observed with other σ-accepting ligands,[5] present substantial benefits in catalysis.[3b,3c] However, because the boron p_x orbitals are high in energy, the resulting orbital diagram resembles that of an inverted ligand field complex,[6] limiting the extent of stabilization provided to the metal orbitals. Carbenium ions are isolobal with boranes; yet, owing to nuclear and overall charge effects, their accepting orbitals are significantly lower leading to enhanced Lewis acidity[7] and oxidizing properties.[8] It follows that the accepting orbital of a carbocation should be better matched with those of the metal, decreasing the ligand field inversion and strengthening the M→Z interaction (Figure 1b). In other words, a carbenium ion should be more potent σ-acceptor ligands, leading to a greater enhancement in the hardness and Lewis acidity of the metal atom. Carbenium ions, which have already received interest as ligands for transition metals,[9] may also present a higher chemical resilience, in particular to oxidative conditions. With the view to capitalize on these attributes, we have thus decided to reengage in carbenium chemistry[10] and explore the synthesis and properties of carbenium-based analogs[11] of known L/Z ambiphilic boron-containing ligands (Figure 1C).[3a] The carbenium-based systems described herein bear similarities with phosphine ligands functionalized by carbon-based redox non-innocent moieties[12] while also adding to ongoing efforts in the chemistry of cationic phosphines as ligands for late transition metal catalysts.[13]

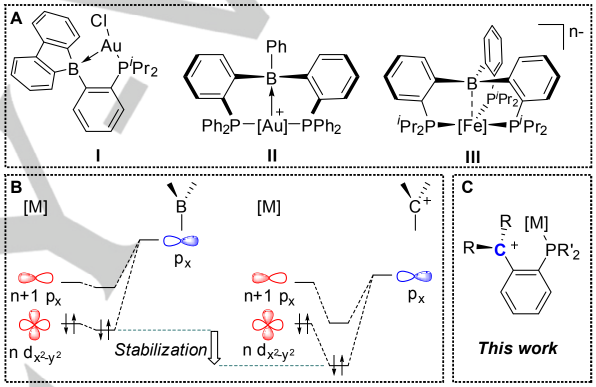

Figure 1. A) Selected examples of complexes featuring boron-based Lewis acidic Z-type ligands. B) Simplified metal-ligand molecular orbital diagram for the interaction of a metal with a boron-based or carbenium-based Z-type ligand. C) Graphical summary of the objective of this paper.

Bearing in mind that the high reactivity of carbenium ions may complicate these studies, we decided to focus on the incorporation of stabilized examples of such moieties. To this end, 1-lithio-2-diphenylphosphino-phenylene was quenched with *N*-methyl acridone or xanthone leading to the formation of the phosphinocarbinols **1** and **2**, respectively (Scheme 1).[14] Subsequently, the acridinium gold(I) chloride derivative [**3**]BF_4 was generated *via* the sequential addition of (tht)AuCl to the carbinol **1** in a 1:1 molar ratio followed by addition of 1 equiv. of HBF_4. This method afforded the target monocation as an air stable yellow/green solid in 97% yield. The analogous reaction was carried out with the xanthenol precursor **2**, generating the xanthylium product [**4**]BF_4 as an orange solid in equally good yield of 93% (Scheme 1). This transformation could be easily tracked using multinuclear NMR spectroscopy. The presence of the carbinol proton is diagnostic in the ^{1}H NMR spectrum giving a resonance at δ = 2.24 ppm for **1** and 2.49 ppm for **2** which disappears upon dehydration. Another prominent resonance that aids in identification is the *N*-methyl protons of **1** which appear at δ = 3.64 ppm which, upon treatment with HBF_4, undergo a down-field shift to δ = 4.90 ppm, concomitant with formation of the acridininium moiety.

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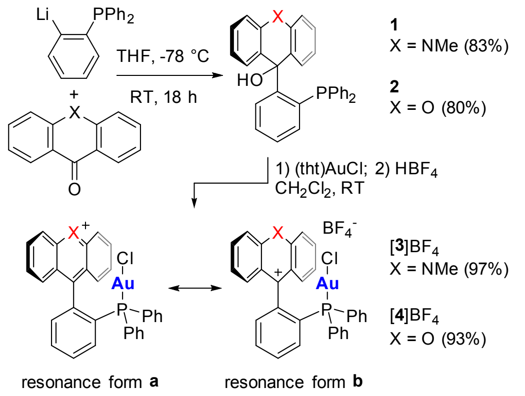


Scheme 1. Synthetic overview of carbinols **1** and **2** and monocations [**3**]BF_4 and [**4**]BF_4. Isolated yields shown.

Additionally, the ^{31}P NMR signals undergo a shift from δ ~ -19 ppm for both carbinol precursors **1** and **2**, to δ = 22.4 and 25.8 ppm for [**3**]BF_4 and [**4**]BF_4, respectively. While the central ring of the acridinium and xanthylium moieties are aromatic, their reactivity and the structure of their carbinol precursors show that the C9 position is electrophilic, as accounted by resonance structure **b**. In the case of xanthylium cations, the importance of this resonance structure was noted by Bayer in 1905 who proposed that such species should be considered as carbenium rather than oxonium ions.[15]

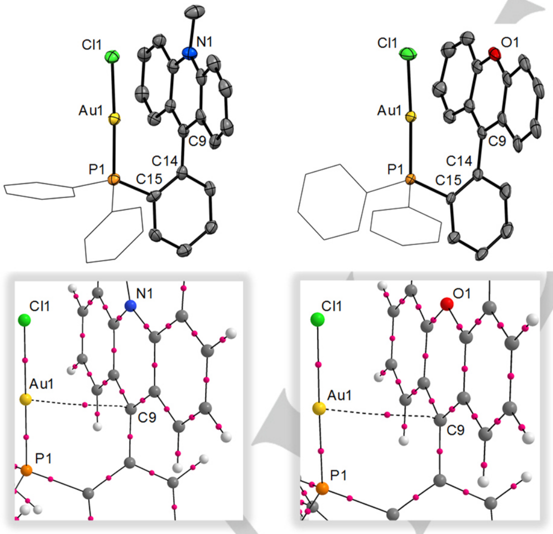
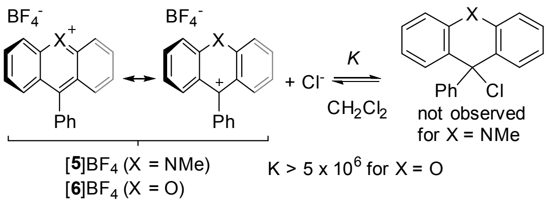


Figure 2. Structure of [**3**]BF_4 (left) and [**4**]BF_4 (right). BF_4 counterions and hydrogen atoms omitted for clarity. Thermal ellipsoids drawn at 50% probability. Result of AIM calculations showing gold-carbon bond path with BCPs (bottom).

The crystal structures of [**3**]BF_4 and [**4**]BF_4 are similar in terms of the eclipsing of the P(1)-Au(1)-Cl(1) motif with the C(9)-C(14)-C(15) plane showing an Au(1)-P(1)-C(14)-C(15) dihedral angle of only 10.0(9)° for [**3**]BF_4 and 1.36(18)° for [**4**]BF_4 (Figure 2).[16] Furthermore, a relatively short interatomic distance is noted between the gold atom and the carbenium center of 3.168(9) Å in [**3**]BF_4 and 3.131(3) Å for [**4**]BF_4, indicating the possibility of a weak interaction (Σ_{VDW}(Au-C) = 3.36 Å). In order to probe this interaction, an atoms-in-molecules (AIM) analysis[17] was implemented at the geometry optimized structures of [**3**]$^+$ and [**4**]$^+$. This analysis reveals that a bond path is indeed present between the C9 atom and the gold atom with electron density ρ(r) of 1.4 × 10^{-2} e/bohr^3 and 1.5 × 10^{-2} e/bohr^3 at the localized bond critical points (BCP) for [**3**]$^+$ and [**4**]$^+$ respectively (Figure 2). The low BCP ρ(r) values suggest that these contacts are extremely weak. This conclusion is supported by the results of Natural Bond Orbital calculations that show only weak donor-acceptor bonding between the gold atom and the adjacent acridinium or xanthylium units.

The weakness of the Au→C interaction in the structures of [**3**]BF_4 and [**4**]BF_4 is consistent with the observation of the ^{13}C NMR signals at δ = 159.7 and 173.8 ppm corresponding to the carbenium centers, respectively. These structural and spectroscopic findings indicate that the carbenium centers present in these complexes are uncompromised and thus potentially poised for engaging a Lewis basic partner. Intrigued by this possibility, we decided to interrogate the complexes with a simple Lewis base, a chloride anion. As a prelude to these studies, we first studied the interaction of *N*-methyl-phenyl-acridinium [**5**]$^+$ and phenyl-xanthylium [**6**]$^+$ with chloride anions. UV-vis. titration experiments carried out by addition of TBACl to solutions of the cation (10^{-4} M) in CH_2Cl_2 indicate that chloride anion binding by [**6**]$^+$ is essentially quantitative upon addition of 1 equivalent, even under dilute conditions ($K > 5 \times 10^6$ M^{-1}) (Scheme 2). By contrast, [**5**]$^+$ shows no affinity for chloride anions. We also tested the interaction of Ph_3PAuCl with chloride and confirmed by ^{31}P NMR the absence of any changes.



Scheme 2. Quenching of carbenium center by chloride with experimental rate constant

With this reactivity baseline established, we moved to studying the behavior of the gold(I) complexes upon addition of chloride, using UV-vis spectroscopy. While the spectrum of [**3**]BF_4 remained unchanged, addition of chloride to the more Lewis acidic xanthylium derivative [**4**]BF_4 led to the formation of a new species, referred to as **7**, characterized by a strong absorption band centered at 328 and 432 nm. The appearance of this atypical feature prompted us to also study the reaction by NMR spectroscopy. Addition of 1 equiv. of TBACl gave rise to a new

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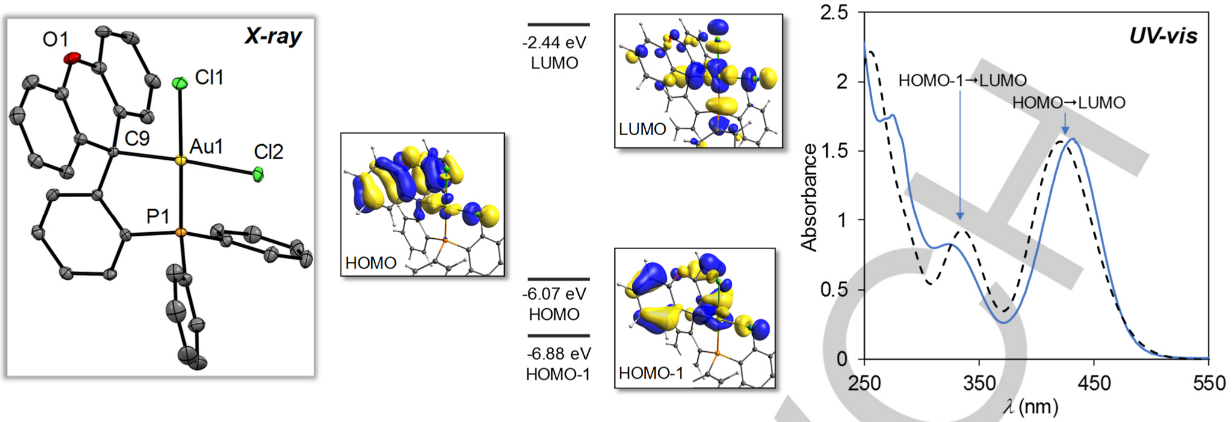
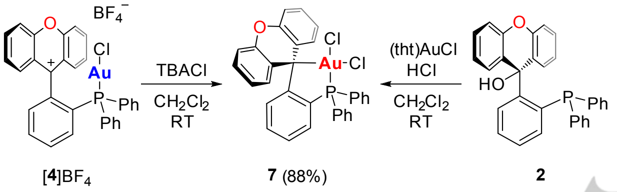


Figure 3. (Left) Solid-state structure of **7**. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms omitted for clarity. (Center) NBO depictions of the LUMO, HOMO and HOMO-1 orbitals. Isosurface value = 0.04. (Right) UV-vis. spectrum where solid trace = experimental, dashed trace = simulated.



Scheme 3. Oxidative addition of gold upon chloride coordination. Yield shown from alternative synthesis using HCl.

broad singlet resonance in the ^{31}P NMR spectrum at δ = 58.3 ppm which resolved upon cooling to -30 °C to a much sharper singlet centered at δ = 60.2 ppm. Furthermore, the resonance of the carbenium center was no longer present in the ^{13}C NMR spectrum with a quaternary carbon being observed at δ = 77.7 ppm.[18] Formation of **7** is also observed when the carbinol precursor (**2**) is combined with (tht)AuCl and ethereal HCl simultaneously. Finally, formation of **7** is reversible since treatment with $AgBF_4$ leads to regeneration of [**4**]$^+$.

We reasoned that **7** could be the results of chloride addition either to the carbenium ion or to the gold center. A structural assay showed that the latter had taken place, in concert with the formation of a covalent bond between the gold atom and the former carbenium ion (Scheme 3). Indeed the structure of **7** displays a square planar gold atom.[16] The two Au-Cl bonds have similar lengths (2.3746(2) Å for Au(1)-Cl(1) and 2.3943(3) Å for the Au(1)-Cl(2)) and the Au(1)-C(9) bond of 2.135(6) Å is in line with a covalent bond between an sp^3 carbon and gold atom.[18] TD-DFT calculations afford two dominant vertical excitations at 340 and 420 nm which satisfactorily coincided with those experimentally observed at 328 and 432 nm. Both absorptions, which have ligand to metal charge transfer character, involve the xanthene-based HOMO and HOMO-1 as the ligand-based orbitals, respectively. For both transitions, the metal-based orbital, which is the LUMO of the complex, has $d_{x^2-y^2}$ character as expected in the case of a d^8 electronic configuration (Figure 3). *In silico* comparison of **7** with its boron analog shows that the carbenium ion of **7** engages the gold atom more effectively (Figure 4). These computational results illustrate the greater σ-accepting properties of carbenium-based Z-type ligand as depicted in Figure 1B.

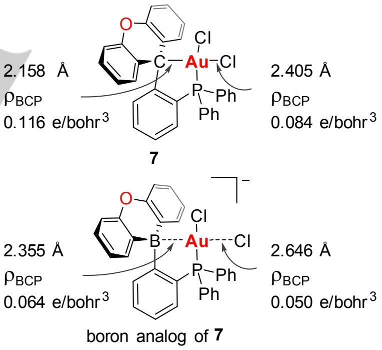
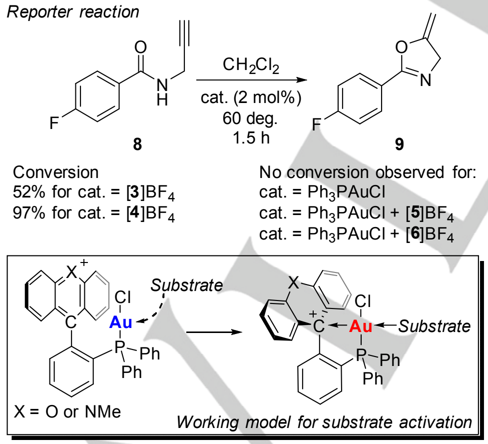


Figure 4. Comparison of **7** with its boron analogue showing selected interatomic separation obtained from DFT calculations. The corresponding bond critical points electron density (ρ_{BCP}) obtained from AIM calculations are also provided.

The structure of **7** shows that the arrested Au→C$_{carbenium}$ coordination seen in [**4**]BF_4 may be bolstered by the addition of a chloride anion which enhances the metallobasic character of the gold atom, promoting its coordination to the Lewis acidic carbenium ion. The result is a net anion-induced oxidation of the gold center which transitions from a d^{10} electronic configuration in [**4**]BF_4 into a d^8 electronic configuration in **7**. This anion induced oxidation bears a parallel with the susceptibility of aurates towards oxidation as documented in the seminal work of Kochi.[19] The reaction of [**4**]$^+$ with chloride could be viewed as providing a snapshot of a hypothetical, S$_N$1-like, C$_{sp^3}$-X bond activation reaction where halide dissociation from the carbon electrophile would have occurred first. Such a pathway has not been proposed for the insertion of gold(I) fragments into C$_{sp^3}$-X bonds which are generally assumed to occur via an S$_N$2 mechanism,[20] as typically seen in late transition metal chemistry.[21] The structure of the L/Z ligand in [**4**]BF_4 and its rigidity are certainly conducive of the formation of a d^8 gold center, an attribute that has been exploited to promote $C_{sp}{}^2$-X bond activation by gold using structurally related L_2-type ligands.[20a,22] Finally, we will note that the carbon ligand also changes from Z-type in [**4**]BF_4 to X-type in **7**. As a result, **7** resembles complexes obtained by intramolecular oxidative insertion of gold(I) halide moieties into C-X bonds.[23] A parallel must also be drawn with a series of recently reported Pd(II) and Rh(I) complexes featuring *o*-phosphino-triarylmethyl ligands.[24]

The conversion of [**4**]$^+$ into **7** is the result of a chloride push – carbenium pull effect. We reasoned that the pull exerted by the carbenium ion could also be assessed by probing the electrophilic reactivity of the gold center. Following up on this idea, we selected the cyclization of propargyl amide as a reporter reaction.[25] Using a 2 mol% catalyst loading, cyclization of **8** into **9** progressed swiftly at 60 °C in CH_2Cl_2 in the case of [**4**]BF_4 which proved to be markedly more active than [**3**]BF_4, in line with the higher Lewis acidity of the xanthylium unit (Scheme 4). Interestingly, no conversion was observed when Ph_3PAuCl was used in the presence or in the absence of either [**5**]BF_4 or [**6**]BF_4. These results underscore the importance of having the Lewis acidic carbenium ion integrated within the same molecular platform, leading us to propose that substrate activation by [**3**]BF_4 and [**4**]BF_4 is the result of a substrate-push/carbenium-pull effect as per the working model presented in Scheme 4. This working model is conceptually related to that proposed to explain the carbophilic reactivity of complexes of type **II** (Figure 1)[3b,26] whereby donation of electron density from the gold center to the Z-type ligand increases the electrophilic character of the former. A more acute version of these effects have been observed with more strongly Lewis acidic Z-type ligands,[5a] leading to reactivity patterns reminiscent of those of gold(III) compounds.[27]



Scheme 4. Cyclization of 4-fluoro-N-(prop-2-yn-1-yl)benzamide (**8**). Conversion derived from in situ ^{19}F NMR measurements of the ratio between starting material **8** and product **9**.

The synthesis and characterization of the cationic complexes [**3**]$^+$ and [**4**]$^+$ reported herein allow us to introduce the use of stabilized carbenium ions as latent Z-type ligands, poised to increase the Lewis acidity of the gold center, should a Lewis base become available. This possibility is illustrated by the reaction of [**4**]$^+$ with chloride which results in the formation of the trivalent gold derivative **7**. This anion-induced oxidation is also accompanied by a conversion of the carbenium Z-type ligand in [**4**]$^+$ into an X-type ligand in **7**. Finally, the carbenium moiety also influences the carbophilic reactivity of the gold center as illustrated by the activity of [**4**]$^+$ as a catalyst for the cyclization of propargyl amide **8**.

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Conflict of interest

The authors declare no conflictof interest.

Keywords: carbocation • gold • Z-type ligand • oxidative addition • alkynes

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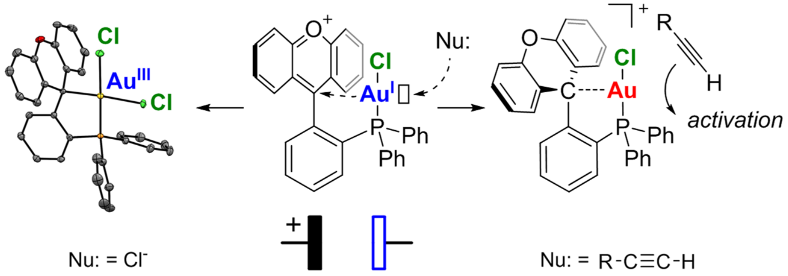

Like in a capacitor about to arc, the positive face of the xanthylium cation installed in a new ambiphilic ligand architecture stands set to engage the adjacent gold center in an Au→C$_{\text{carbenium}}$ interaction. The formation of this interaction shows that stabilized carbenium ions may act as latent Z-type ligands which, in the present case, can be used to increase the carbophilic reactivity of the gold center.

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