COMMUNICATION

Isolation and reactivity of a gold(I) hydroxytrifluoroborate complex stabilized by anion-π⁺ interactions

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Jiliang Zhou,[a] Elishua D. Litle[a] and François P. Gabbaï*[a]

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A 9,9-dimethylxanthene-based ligand substituted at the 4- and 5-positions by a phosphine and a xanthylium unit, respectively, has been prepared and converted into an AuCl complex, the structure of which reveals an intramolecular Au-Cl···π⁺ interaction. This new ligand platform was also found to support the formation of an unprecedented hydroxytrifluoroborate derivative featuring a "hard/soft" mismatched Au-μ(OH)-BF_3 motif. Despite its surprising stability, this gold hydroxytrifluoroborate complex is a remarkably potent carbophilic catalyst which readily activates alkynes, without a co-catalyst.

The interaction of anions with electron-deficient π-systems is a carefully explored phenomenon[1, 2, 3] that has impacted the areas of molecular recognition,[4] catalysis,[5] and anion transport.[6] These interactions bear a large electrostatic component that scales with the quadrupole moment and polarizability of the p-acidic system involved (**A**, Figure 1). Because of additional Coulombic effects, positively charged π-acidic (π⁺) systems interact with anions even more favorably, leading to so-called anion-π⁺ contacts[7] whose stabilization energies can reach the 50-90 kcal/mol range (**B**).[2, 8] Intrigued by the considerable strength of these interactions, we have now decided to test whether π⁺ systems could be used to influence the reactivity of anion-ligated metal complexes or promote the stabilization of atypical metal-anion (MX) moieties. With this in mind, and drawing inspiration from recent advances in the chemistry of ambiphilic ligands,[9] we are now targeting phosphine ligands featuring a flanking π⁺ system,[10, 11] as illustrated by our recent work on γ-cationic phosphines of type **C**.[12-14] While the carbenium ion may be too far to strongly influence the electronic properties of the phosphorus atom as in α-cationic phosphines,[15] the formation of a direct Au–C interaction can be observed in the case of gold complexes of type $\mathbf{C_{[M]}}$. In the case of complex **D**, the Au→C bonding was correlated to an enhancement of the carbophilic reactivity of

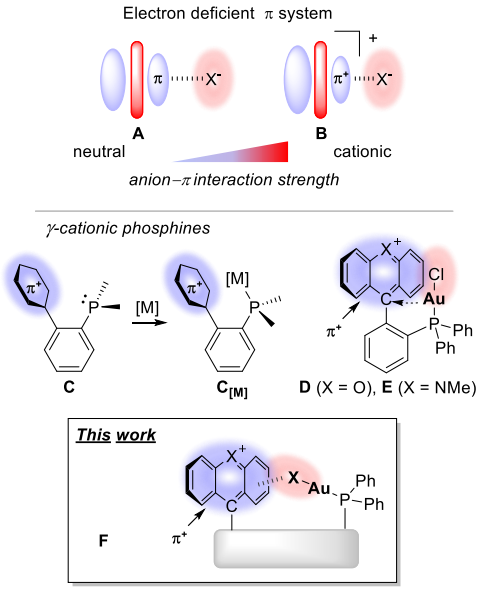

Figure 1. Top: Anion- π and anion-π⁺ interactions. The representation of the π systems accounts for their electrostatic potential profile and also schematically reflects their polarizability and positive quadrupole moment. Bottom: g-Cationic phosphines and their metal complexes along with the new systems targeted in this study.

the complex.[12] An analysis of this compound also shows that the gold-bound chloride anion is positioned 3.66 Å over the π⁺-face of the cationic unit, an indication of possible Coulombic stabilization. Combining this observation with our intent to test whether π⁺ systems could influence the reactivity of metal-bound anions, we have now decided to target related complexes of type **F** where the large separation between the cationic π system and the phosphine ligand would favor M-X···π⁺ interactions rather than direct M→C bonding. This article describes a study aimed at the synthesis and coordination chemistry of such a cationic phosphine, elaborated on a 9,9-dimethylxanthene backbone. The results of this study indicate that the amphiphilic pocket provided by this new platform allows for the isolation of an unprecedented Au-μ(OH)-BF_3 complex which behaves as a self-activating electrophilic catalyst.

As a starting point, phosphinocarbinol **1** was synthesized as depicted in Figure 2a. Treatment of a CH_2Cl_2 solution of **1** with 1 equiv. of aqueous HBF_4 in CH_2Cl_2 afforded the xanthylium/phosphine ligand [**2**]⁺ (also referred to as **L**⁺ or

[a] Department of Chemistry, Texas A&M University, College Station, TX 77843, USA. E-mail: francois@tamu.edu

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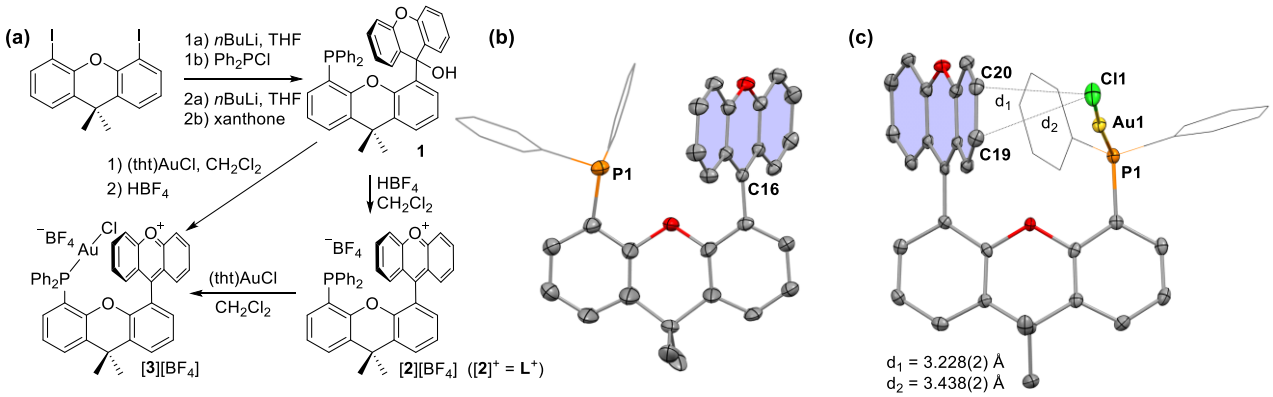


Figure 2. (a) Scheme showing the synthesis of **1**, its conversion into the cationic phosphine [**2**]$^+$ and the corresponding gold(I) complex [**3**]$^+$. (b and c) Structures of [**2**][BF_4] (b) and [**3**][BF_4] (c) as determined by X-ray crystallography. The BF_4^- anions, the interstitial solvent molecules and the hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level and the phenyl groups are drawn as thin lines.

JiPhos) as a BF_4^- salt ([**2**][BF_4]). This salt assumes a deep red color readily assigned to the presence of a xanthylium chromophore which also gives rise to low field ^{1}H NMR resonances in the 7.77-8.51 ppm range as well as a characteristic ^{13}C NMR resonance at 172.4 ppm corresponding to the carbenium center.[12] The ^{31}P NMR signal at -14.4 ppm is consistent with a free phosphino group as confirmed by X-ray diffraction (Figure 2b). The large P1···C16 separation of 4.297(2) Å shows that the rigidity of the backbone prevents a direct interaction between the phosphine and the xanthylium functionality.[13, 16]

Reaction of [**2**][BF_4] with (tht)AuCl (tht = tetrahydrothiophene) produces the phosphine xanthylium gold complex [**3**]$^+$ as a BF_4^- salt ([**3**][BF_4]) which can also be accessed by treatment of **1** with (tht)AuCl and HBF_4 in CH_2Cl_2. As for [**2**][BF_4], the ^{1}H NMR spectrum of [**3**][BF_4] shows low field ^{1}H NMR resonances in the 7.86-8.56 ppm range as well as a ^{13}C NMR resonance at 171.4 ppm. The ^{31}P NMR signal at 23.3 ppm is consistent with the coordination of gold to the phosphine ligand. Altogether, these spectroscopic features are reminiscent of those of [**D**][BF_4].[12] The crystal structure of [**3**][BF_4] confirms the formation of a gold chloride complex (Figure 2c). Although no short Au-C distances are observed as in the case of **D**$^+$, the Au-Cl moiety approaches the π^+ face of the xanthylium group leading to short Cl1-C19 and Cl1−C20 distances of 3.438(2) Å and 3.228(2) Å, respectively. This short distance indicates the formation of an intramolecular anion-π^+ interaction dominated by Coulombic terms. This view is consistent with the results of Atoms in Molecule and Natural Bond Orbital analyses which show that the charge transfer interactions between the chloride anion and the π^+ system are weak (see SI). An inspection of the electrostatic potential surface (ESP) map of the model compound 4-xanthylium-9,9-dimethylxanthene (**G**$^+$) at the geometry found in [**3**]$^+$ shows considerable positive character on the xanthylium unit, illustrating the π^+ characteristics of this cationic unit (Figure 3, left).[3] The ESP map of [**3**]$^+$ shows that the newly installed, electron-rich AuCl unit is positioned over the left quadrant of the π^+ xanthylium surface (Figure 3, right), consistent with an in intramolecular AuCl···π^+ interaction.

With [**3**][BF_4] in hand, we decided to compare its properties to those of [**D**][BF_4] which was reported to catalyze the cyclization of propargyl amides upon mild heating.[12] We had proposed that this activity was induced by the ability of the xanthylium unit to engage the gold center in an Au→$C_{carbenium}$ interaction along a direction perpendicular to the P-Au-Cl bond as depicted in Figure 1. Given the inability of the gold center to approach the xanthylium unit in [**3**]$^+$, we speculated that [**3**][BF_4] would be inactive. Indeed, when [**3**][BF_4] was tested as a catalyst for the cycloisomerization of *N*-ethynyl-4-fluorobenzamide, no conversion was observed at room temperature or at 60°C. This lack of activity is assigned to the rigidity of the 9,9-dimethylxanthene backbone which precludes direct Au→$C_{carbenium}$ bonding. This results also suggests that the xanthylium unit of [**3**]$^+$ is not sufficiently electrophilic to activate the gold center by Au—Cl bond cleavage.[17]

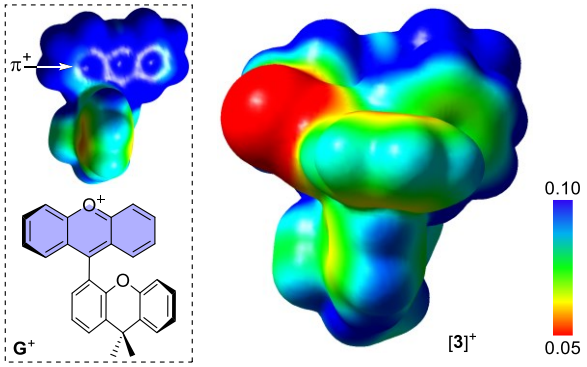


Figure 3. ESP maps of the model cation **G**$^+$ (left) and [**3**]$^+$ (right) obtained with a surface isovalue of 0.001 a.u. The gradient scale values are given in a.u.

The intimacy achieved between the π^+-surface[2, 3] of the xanthylium cation of [**3**]$^+$ and the gold-bound chloride anion led us to question whether the electrophilic properties of **L**$^+$ could be exploited for the stabilization of reputedly unstable gold species. For example, it is well known that [Ph_3PAu][BF_4] is too unstable to isolate[18] and is typically generated transiently *in situ* for synthetic purposes.[19] With this precedent as a backdrop, we decided to test the generation of gold BF_4^- species within the ambiphilic pocket of ligand **L**$^+$. To this end, [**3**][BF_4] was treated with $AgBF_4$ in dry CH_2Cl_2. The reaction proceeded smoothly to afford deep red solutions characterized by a single ^{31}P NMR

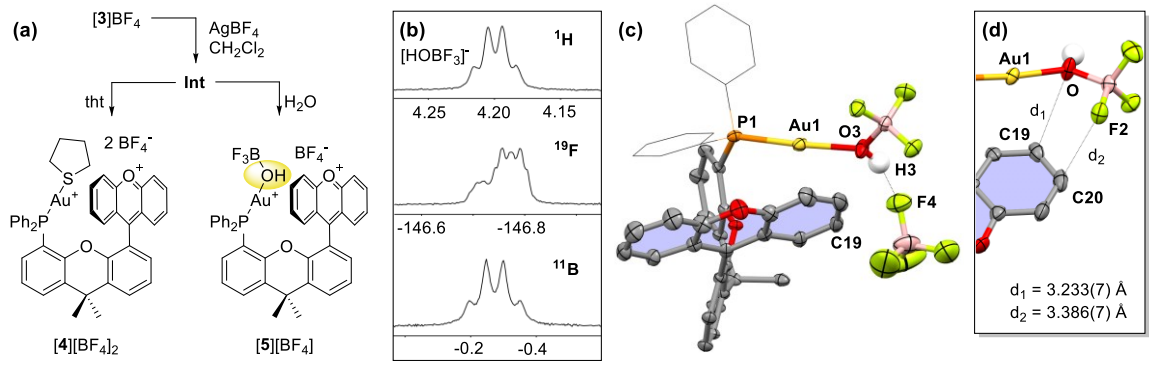
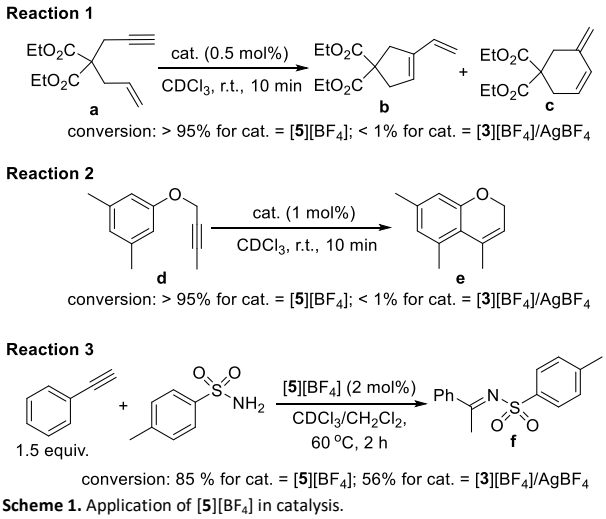


Figure 4. (a) Generation of the dicationic intermediate (**Int**) and its conversion into [**4**][BF_4]$_2$ and [**5**][BF_4]. (b) NMR spectroscopic characterization of the [BF_3OH]$^-$ anion in [**5**][BF_4]. (c) Structures of [**5**][BF_4]. Solvent residues and hydrogen atoms (except H3) omitted for clarity, thermal ellipsoids drawn at 50% probability, and phenyl groups drawn as thin lines. (d) Truncated view of the structure of [**5**][BF_4] showing short contacts between the [BF_3OH]$^-$ anion and the xanthylium π^+-system.

resonance at 20.2 ppm (Figure 4a). While the identity of intermediate (**Int**) as a gold BF_4^- species as not been unambiguously confirmed, it displayed sufficient longevity to cleanly react with tht, leading to the corresponding tht adduct [**4**][BF_4]$_2$ (Figure 4a, see SI).[13] Interestingly, when [**3**][BF_4] was treated with $AgBF_4$ in "as-provided" CH_2Cl_2, a new species was observed as indicated by the detection of a ^{31}P NMR resonance at 17.2 ppm. The same species could be generated by reaction of [**3**][BF_4] with $AgBF_4$ in dry CH_2Cl_2, followed by addition of 1 equiv. of water. This new species, referred to as [**5**][BF_4], was isolated and analyzed by NMR spectroscopy which revealed a set of atypical resonances, including a quartet in the ^{1}H NMR spectrum at 4.20 ppm ($^3J_{H\text{-}F}$ = 4.5 Hz), a quartet in the ^{11}B NMR spectrum at -0.3 ppm ($^1J_{B\text{-}F}$ = 6.7 Hz), and a quartet of doublets at -146.8 ppm flanked by a low field shoulder corresponding to the ^{10}B isotopomer (Figure 4b).[20] These spectroscopic features are consistent with the presence of a [BF_3OH]$^-$ (or trifluorohydroxyborate) anionic unit.[20, 21] This anion is occasionally found coordinated to transition metals[22, 23] as in $(OC)_5ReOHBF_3$, a complex that displays comparable ^{11}B and ^{19}F NMR spectroscopic features.[24] The presence of the OH group was further confirmed by the detection of a diagnostic O–H stretch at 3645 cm^{-1} in the IR spectrum of [**5**][BF_4]. Finally, [**5**][BF_4] also displays NMR resonances consistent with the presence of an intact [BF_4]$^-$ anion (see SI).

A subsequent structural assay indicated that [**5**][BF_4] indeed contains a [BF_3OH]$^-$ anion and is best formulated as [**L**Au-μ(OH)-BF_3][BF_4] (Figure 4c). The structure of [**5**]$^+$ resembles that of [**3**]$^+$ and features an intact xanthylium moiety flanking the phosphine-coordinated gold unit. The main difference pertains to the nature of the anion bound to the gold atom, which in the case of [**5**]$^+$ is a bridging hydroxide anion also connected to a BF_3 unit. The resulting Au-μ(OH)-B bridge is characterized by an Au-O-B angle of 123.1(4)º. The Au–O bond length (2.053(4) Å) of [**5**]$^+$ is comparable to those found in hydroxide-bridged gold complexes such as [(JohnPhosAu)$_2$(μ-OH)]$^+$ (av. Au–O: 2.07 Å) and [(IPrAu)$_2$(μ-OH)]$^+$ (av. Au–O: 2.04 Å).[25] The Au–O distance in [**5**]$^+$ is also comparable to that in [(*o*-tolyl)$_3$PAu(OH_2)]$^+$ (2.070(13) Å) which contains a water ligand.[26] The OH group is also hydrogen-bonded to the [BF_4]$^-$ counter anion as indicated by the O3 and F4 distance of 2.649(6) Å.[23] A review of the literature reveals that gold [BF_3OH]$^-$ species have not been previously described. As indicated by the O3–C19 and F2-C20 distances of 3.233(7) Å and 3.386(7) Å, respectively, the gold-bound [BF_3OH]$^-$ anion is engaged in anion-π^+ interactions with the xanthylium unit. We also attempted the generation of Ph_3PAu-μ(OH)-BF_3 by reaction of Ph_3PAuCl with $AgBF_4$ and water. This reaction afforded the [$Ph_3PAu(OH_2)$]$^+$ adduct as the major product and only traces of [BF_3OH]$^-$ anion. This contrasting behavior suggest that the intramolecular anion-π^+ interactions in [**5**]$^+$ may contribute to the stability of this complex.



Scheme 1. Application of [**5**][BF_4] in catalysis.

Salt [**5**][BF_4] is stable and can be kept in air for extended periods of time. Because of the predicted lability of the Au–O bond in this complex, we became eager to investigate its catalytic properties in reactions 1-3 shown in Scheme 1. Reaction 1 proceeded swiftly at room temperature, with a catalyst loading of 0.5 mol%. The reaction was essentially completed in 10 min., affording the five- and six-membered isomers **b** and **c** in a 22:78 ratio. The activity displayed by this new system is significantly higher than that reported for cationic gold(I)-catalysts such as $Ph_3PAuNTf_2$, [($Ph_3PAu)_3O$][[BF_4], or [JohnPhosAu(NCMe)][BF_4].[27] Similar observation was made for reaction 2 which produced **e** in less

that 10 min. at room temperature, with a catalyst loading of 1 mol%. Such a reaction has been described to proceed at comparable rates with cationic N-cyclopropenio-midazol-2-ylidene gold complexes, albeit in the presence of a silver activator.[11] Finally, we also tested reaction 3 which has been previously reported to necessitate heating to 100°C in THF for 9 hours when carried out with Ph_3AuCl as a precatalyst (2 mol%) and AgOTf as an activator (8 mol%).[28] By contrast, [**5**][BF_4] (2 mol%), without any activator, promoted the formation of imine **f**, reaching a conversion of 85% in just 2 hours at 60°C in $CDCl_3/CH_2Cl_2$. Reactions 1 and 2 were not promoted when [**3**][BF_4]/$AgBF_4$ was used as a catalyst, underscoring the favorable properties and greater stability of [**5**][BF_4]. Reaction 3 proceeded but in lower yields.

Altogether, we describe a new ambiphilic ligand platform $\mathbf{L}^+$ featuring a xanthylium unit and a diphenylphosphino group positioned at the upper rim of a 9,9-dimethylxanthene backbone. The resulting construct features a phosphine functionality available for metal coordination as well as a xanthylium unit with an exposed π^+ surface that becomes engaged in an AuCl$\cdots\pi^+$ interaction in the corresponding gold chloride complex. The unique properties of this ligand platform and its polar binding pocket are further highlighted by the isolation and full characterization of a gold $[BF_3OH]^-$ complex ([**5**]$^+$), an air stable derivative featuring an unprecedented and "hard/soft" mismatched[29] Au-μ(OH)-BF_3 motif. Despite its stability, [**5**]$^+$ is remarkably active as a carbophilic catalyst. Altogether, our results show that the M-X$\cdots\pi^+$ interaction may become a useful motif in the area of organometallic catalysis.

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Conflicts of interest

There are no conflicts to declare.

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