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COMMUNICATION

An antimony(V) dication as a Z-type ligand: Turning on styrene activation at gold

Ying-Hao Lo and François P. Gabbaï *[a]

Dedication ((optional))

Abstract: With the intent to demonstrate that the charge of Z-type ligands can be used to modulate the electrophilic character and catalytic properties of coordinated transition metals, we are now targeting complexes bearing polycationic antimony-based Z-type ligands. Toward this end, the dangling phosphine arm of ((*o*-$(Ph_2P)C_6H_4)_3)SbCl_2AuCl$ (**1**) was oxidized with hydrogen peroxide to afford [((*o*-$(Ph_2P)C_6H_4)_2$(*o*-$Ph_2PO)C_6H_4)SbAuCl_2]^+$ ([**2**]$^+$) which was readily converted into the dicationic complex [((*o*-$(Ph_2P)C_6H_4)_2$(*o*-$Ph_2PO)C_6H_4)SbAuCl]^{2+}$ ([**3**]$^{2+}$) by treatment with 2 equiv. $AgNTf_2$. Both experimental and computational results show that [**3**]$^{2+}$ possess a strong Au→Sb interaction reinforced by the dicationic character of the antimony center. The gold-bound chloride anion of [**3**]$^{2+}$ is rather inert and necessitates the addition of excess $AgNTf_2$ to undergo activation. The activated complex, referred to as [**4**]$^{2+}$ [((*o*-$(Ph_2P)C_6H_4)_2$(*o*-$Ph_2PO)C_6H_4)SbAuNTf_2]^{2+}$ readily catalyzes both the polymerization and the hydroamination of styrene. This atypical reactivity underscores the strong σ-accepting properties of the dicationic antimony ligand and its activating impact on the gold center.

Although traditionally regarded as laboratory curiosities, Z-type, Lewis acidic ligands and the complexes they form with transition metals are now gaining increasing validation in the area of catalysis[1] where the electron accepting properties of the Lewis acidic center can be used to modulate the electron density and catalytic reactivity of the adjacent metal center.[2] The accepting properties of Z-type ligands can be influenced by a variety of factors including the nature of the atom acting as the Lewis acid,[3] its redox state or its coordination environment.[1i,1j] Examples that illustrate the tunability of these ligand systems include double-decker complexes of type **I** where variation of the group 13 element allows for a precise control of the Ni-E interaction[4] or complexes of type **II** where the redox state of the antimony center can be used to adjust the strength of the Au-Sb interaction (Figure 1).[5] Based on the principle that cationic main group compounds are more Lewis acidic than their neutral counterparts,[6] we have been interested in an approach whereby anion abstraction serves to enhance the σ-accepting properties of the Z-type ligand.[7] We demonstrated this idea in the case of complex **III** which, upon conversion into **IV** by fluoride anion abstraction, became catalytically active as a result of a stronger Pt→Sb interaction.[8] With the view of further augmenting the accumulation of positive charges on the Lewis acidic main group element, we are now investigating ligand platforms that would support the formation of antimony dications, within the coordination sphere of a late transition metal. It occurred to us that isolating such a complex may necessitate the use of auxiliary donor functionalities introduced to tame the high reactivity of the dicationic antimony moieties.[9] Inspired by the work of Burford on species such as **V** which shows that phosphine oxides are privileged ligands for antimony cations,[10] we have now decided to target complexes of type **VI** in which one of the phosphine oxide donors is replaced by a metalloligand. In this paper, we describe our first implementation of this idea and its application to gold mediated catalysis.

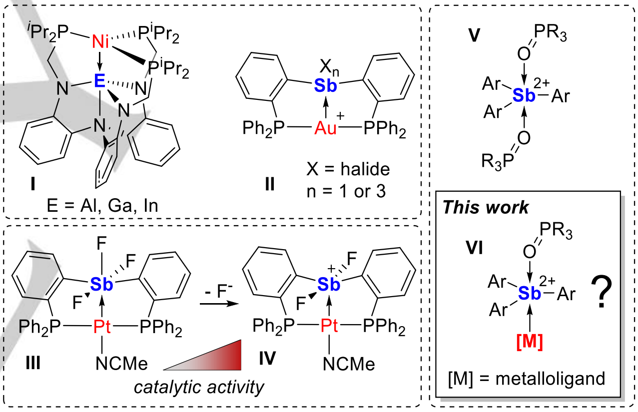

Figure 1. Examples of transition metal complexes that contain Z-type ligands (**I** to **IV**) and outline of work mentioned within (**V** and **VI**).

As an entry point for the synthesis of a complex of type **VI**, we considered **1**, a known gold complex which features a phosphino arm free of metal coordination.[11] To test if this unit could be converted into the corresponding phosphine oxide, complex **1** was combined with one equivalent of hydrogen peroxide (Scheme 1). This reaction afforded complex [**2a**][Cl] as an air stable solid, the crystal structure of which (*vide infra*) confirmed the successful conversion of one of the three phosphino arms of the ligand into a phosphine oxide. This complex has also been characterized by EA and ^{31}P MAS NMR spectroscopy. The latter shows two signals at 60.2 ppm and 41.6 ppm. The respective 2:1 intensity ratio measured for these two resonances indicates that they correspond to the gold-coordinated phosphine and the phosphine oxide units, respectively. When in solution, [**2a**][Cl] gives rise to a second isomer ([**2b**][Cl]) for which the ^{31}P nucleus of the

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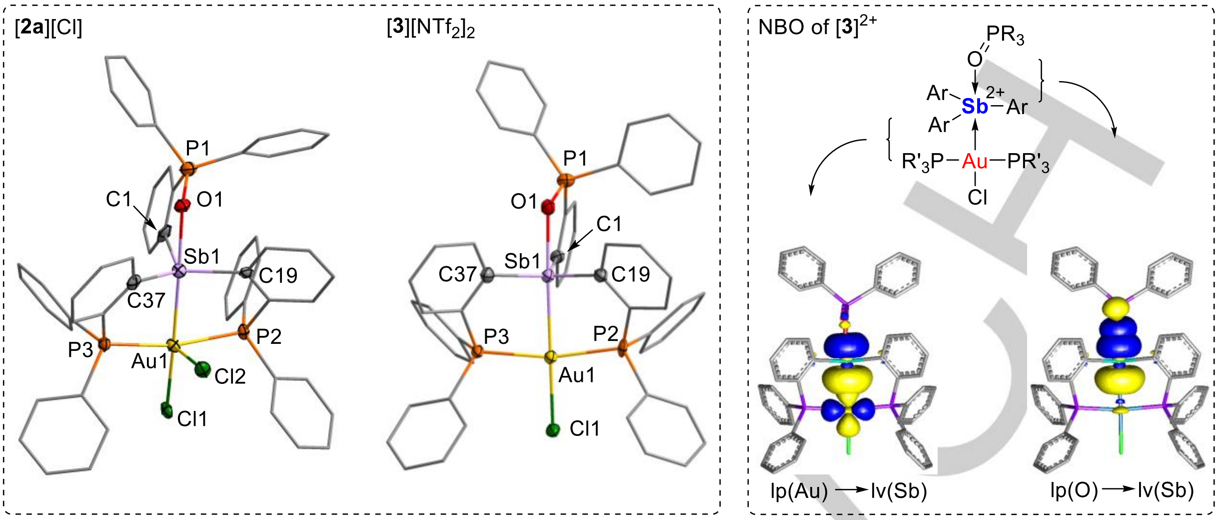
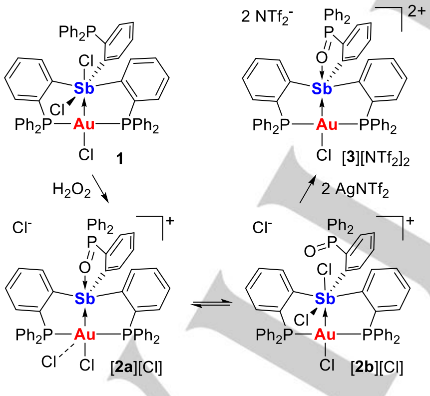


Figure 2. Left: Solid-state structure of [**2a**][Cl] and [**3**][NTf$_2$]$_2$. Thermal ellipsoids are drawn at the 50% probability level. The phenyl groups are drawn in wireframe, the. hydrogen atoms, interstitial solvent molecules, and counteranions are omitted for clarity. Relevant metrical parameters can be found in the text or in the Supporting Information. Right: NBO plots of the (a) Sb–Au and (b) O–Sb major bonding interactions in [**3**]$^{2+}$ (isodensity value 0.05). Hydrogen atoms are omitted.

phosphine and phosphine oxide units resonate at 96.1 ppm and 44.3 ppm, respectively. The structure of [**2b**][Cl] is proposed to be that depicted in Figure 2, based on the similarity of the phosphine chemical shift with that of ((*o*-(Ph$_2$P)C$_6$H$_4$)$_2$SbCl$_3$)AuCl (79.2 ppm).[5a] To confirm that these two isomers differ in the way they interact with the chloride counterions, we treated [**2a**][Cl]/[**2b**][Cl] with 2 equivalents of AgNTf$_2$. In situ ^{31}P NMR spectroscopy indicated the emergence of a new species, [**3**][NTf$_2$]$_2$, characterized by a single set of resonances at 68.7 ppm and 42.3 ppm (2:1 integration ratio).



Scheme 1. Synthesis of [**2a**][Cl] and [**3**][NTf$_2$]$_2$

The structures of [**2a**][Cl] and [**3**][NTf$_2$]$_2$ have been established in the solid-state.[12] The Au–Sb bond distances of 2.613(7) Å in [**2a**][Cl] and 2.6269(7) Å in [**3**][NTf$_2$]$_2$ are significantly shorter than in **1** (2.709(9) Å) thus indicating a strengthening of the Au–Sb interaction triggered by the increased Lewis acidity of the antimony center. In accordance with the bonding situation depicted for model complex **VI**, the coordination geometry of the antimony center in both complexes is distorted trigonal bipyramidal with the gold atom and the oxygen atom of the phosphine oxide occupying the apical sites. A further indicator of this coordination geometry comes from the sum of C–Sb–C angles which approaches the ideal value of 360° in both structures ($\Sigma_{(C\text{–}Sb\text{–}C)}$ = 356.1(4) for [**2a**][Cl] and 356.7(4)° for [**3**][NTf$_2$]$_2$). The values of the P–Au–P (167.30(9) for [**2a**][Cl] and 166.25(9)° for [**3**][NTf$_2$]$_2$) and Cl–Au–Sb (172.79(6) for [**2a**][Cl] and 176.39(6)° for [**3**][NTf$_2$]$_2$) angles indicates that the four primary ligands bound to gold are arranged in a square planar geometry, with the chloride ligand (Cl1) positioned trans from the antimony atom. This square planar geometry is consistent with the strong donation of a gold d-orbital electron pair to antimony, leading to an electronic configuration that approaches that of a classical d^8 metal center. In the case of [**2a**][Cl], the square planar gold atom is capped by a chloride ligand that forms a long Au–Cl interaction of 2.910(2) Å. A Natural Bond Orbital (NBO) analysis of [**3**]$^{2+}$ affords a bonding description in which a dicationic triarylantimony unit is stabilized intramolecularly by donation from the phosphine oxide functionality and from the metallobasic gold atom. Indeed, the NBO method describes the Sb–O interaction as a lp(O)→p(Sb) donor acceptor interaction which contributes to the stability of the complex by E$^{(2)}$ = 69.7 kcal/mol. The Sb-Au linkage is also donor acceptor in character and involves a $d_{x^2-y^2}$(Au)→p(Sb) and a d_{z^2}(Au)→p(Sb) interactions which stabilize the complex by E$^{(2)}$ = 39.3 kcal/mol and 10.5 kcal/mol, respectively. Taken together, the second order perturbation energies suggest that the dative bonds formed by the two donors have a similar strength. This bonding description supports the formulation of complex [**3**]$^{2+}$ as a stibonium dication stabilized intramolecularly by two Lewis bases.

With the view of activating the gold center,[5a] we treated [**3**]$^{2+}$ with an additional equivalent of AgNTf$_2$ in dichloromethane (Figure 3). ^{31}P NMR spectroscopy showed the emergence two new resonances at 67.9 ppm and 49.1 ppm (2:1 intensity) which we assign to the formation of [**4**][NTf$_2$]$_2$, a complex in which the gold-

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bound chloride anion is replaced by a triflimide anion. Formation of [**4**][NTf_2]$_2$ is however partial and only reaches 55% conversion after addition of 7 equivalents of $AgNTf_2$. The stability of the Au-Cl bond of [**3**]$^{2+}$ is assigned to the dicationic nature of the complex and its reluctance to acquire a greater positive character by replacement of the chloride by a more weakly coordinating triflimide counteranion. We note that the phosphine oxide resonance of [**3**]$^{2+}$ undergoes a small but noticeable upfield shift which might be explained by a change in the polarity of the medium as an excess of $AgNTf_2$ is added to the solution.

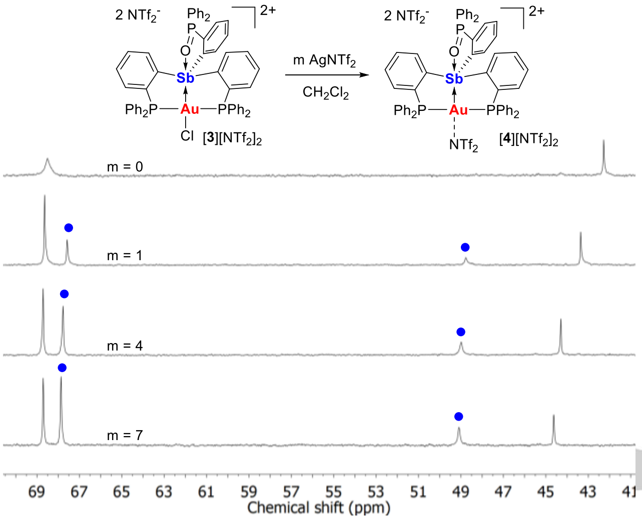
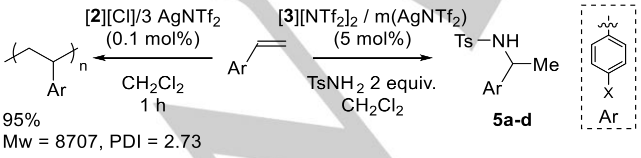


Figure 3. Chloride abstraction from [**3**][NTf_2]$_2$ by addition of equivalents of $AgNTf_2$. The resonances marked by a blue dot correspond to the [**4**][NTf_2]$_2$.

Given the weakly coordinating nature of the triflimide anion and its extensive use as a counteranion in gold mediated catalysis,[13] we became eager to test the catalytic properties of [**4**][NTf_2]$_2$. When [**4**][NTf_2]$_2$ was generated *in situ* by addition of 3 equivalents of $AgNTf_2$ to [**2**][Cl], we observed rapid styrene polymerization (Scheme 2).[14] The emergence of such a reactivity for a bis(phosphine)gold moiety such as that in [**4**][NTf_2]$_2$ is surprising and reflective of the reactivity enhancement achieved in the polycationic gold complex. A parallel can be drawn between this finding and the reactivity enhancement sometimes observed when cationic L-type ligands are coordinated to late transition metals.[15]



Scheme 2. Hydroamination of styrene catalyzed by [**3**]$^{2+}$/ $AgNTf_2$ and polymerization of styrene catalyzed by or [**2**]$^{+}$/ 3 $AgNTf_2$.

Next, we decided to test whether this catalyst could also promote hydroamination reactions. The reaction of styrene and *p*-toluenesulfonamide ($TsNH_2$) afforded the Markovnikov product which was obtained in high yield after 6 h (Scheme 2; Table 1, entry 1). Given the stoichiometry of the chloride abstraction reaction (Figure 3), we decided to vary the [**3**]$^{2+}$/$AgNTf_2$ ratio from 1/1 to 1/7 (entries 2-4). NMR monitoring indicates that additional equivalents of $AgNTf_2$ results in a higher yield of the product after the first hour. This result suggests that the putative triflimide complex acts as a catalyst, presumbaly via the electrophilic mechanism shown in Scheme 3.

Table 1. Hydroamination of styrene and substituted styrenes by $TsNH_2$.

Entry	precatalyst	X	m[a]	T (°C)	Time	Yield [b]	Product
1	[**3**][NTf_2]	H	1	35	6 h	94%	**5a**
2	[**3**][NTf_2]	H	1	35	1 h	20%	**5a**
3	[**3**][NTf_2]	H	4	35	1 h	29%	**5a**
4	[**3**][NTf_2]	H	7	35	1 h	44%	**5a**
5	[**2**][Cl]	H	3	35	6 h	93%	**5a**
6	[**2**][Cl]	H	3	35	1 h	19%	**5a**
7	[**2**][Cl]	H	6	35	1 h	29%	**5a**
8	[**2**][Cl]	H	9	35	1 h	46%	**5a**
9	[**3**][NTf_2]	F	1	35	6 h	96%	**5b**
10	[**3**][NTf_2]	Cl	1	35	6 h	42%	**5c**
11	[**3**][NTf_2]	Me	1	25	20 min	32%	**5d**

[a] m refers to the number of equivalents of $AgNTf_2$. [b] The yield was measured by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard

We were also eager to test whether [**4**][NTf_2]$_2$ could be generated in situ, starting from [**2**][Cl]. We found that when generated in this way, [**4**][NTf_2]$_2$ showed a catalytic activity in the hydroamination of styrene that is almost identical to that obsvered when [**3**][NTf_2]$_2$ is used as a pre-catalyst (entries 5-8). This reaction is not activated by complex [**3**]$^{2+}$ or $AgNTf_2$ alone. When 5 mol% $HNTf_2$ was employed as a catalyst, only 16% of hydroamination product was formed, and formation of polystyrene was observed. This poor selectivity adds credence to the involvement of the gold-antimony complex as the active species. Complex [**4**][NTf_2]$_2$ appears significantly more active than other gold-based catalysts such as $Ph_3PAuCl/AgOTf$ or $(PhO)_3PAuCl/AgOTf$.[16] These two catalysts also promote the reaction of styrene with *p*-toluenesulfonamide but necessitate high temperatures (85°C) and extended reaction times (14 h) to afford the hydroamination product in only moderate yields (50-60%). 4-Fluorostyrene is also efficiently hydroaminated, a results expected based on the similar Hammet parameters[17] of hydrogen ($\sigma_p = 0$) and fluorine ($\sigma_p = 0.06$) (entry 9). Reaction of the more electron-poor 4-chlorostyrene ($\sigma_p = 0.23$) is distinctly slower in agreement with the proposed electrophilic mechanism (entry 10). Further support for this electrophilic mechanism is provided by the behavior of 4-methylstyrene which is fully consumed after 20 mins at room temperature. In this case, however, only about 32% of the hydroamination product is formed along with unidentified products and oligomers (entry 11).

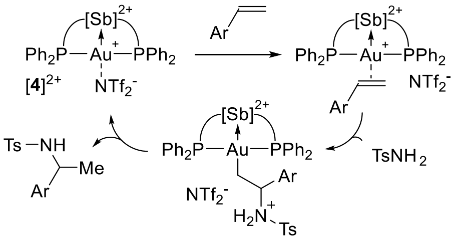


Figure 4. Proposed mechanism for hydroamination catalyzed by [**4**]$^{2+}$.

In conclusion, we describe the synthesis and characterization of a gold chloride complex, [**3**][NTf$_2$]$_2$, featuring a dicationic Z-type antimony ligand. Formation of this complex is made possible by the coordination of a neutral phosphine oxide donor that attenuates the reactivity of the dicationic antimony center. Despite its electron-deficient nature, the gold center of [**3**]$^{2+}$ can be activated by conversion into the proposed triflimide complex [**4**]$^{2+}$. Generation of this complex is accompanied by the emergence of atypical reactivity[18] toward styrene which is readily polymerized or converted into the hydroamination Markovnikov product when in the presence of *p*-toluenesulfonamide. These unusual reactions highlight the unique activation resulting from the coordination of the dicationic antimony Z-type ligand to the gold center.

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Conflict of interest

The authors declare no conflictof interest.

Keywords: antimony • gold • ligand design • olefin • hydroamination

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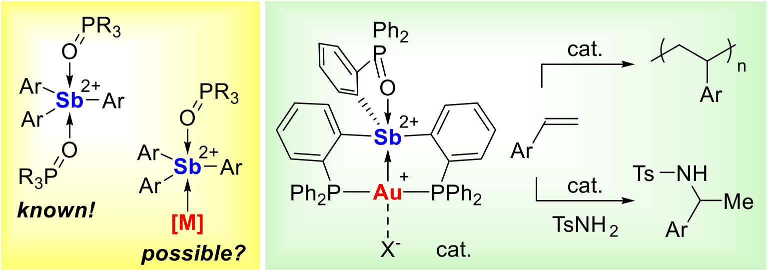

Very positive is the influence played by a doubly charged antimony Z-type ligand on the electrophilic properties of the corresponding gold complex. The accentuated σ-accepting properties of this new antimony ligand impart atypical reactivity to the gold center which readily promotes the polymerization and hydroamination of styrene.

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