

## Ion Pairing in Cationic Olefin–Gold(I) Complexes

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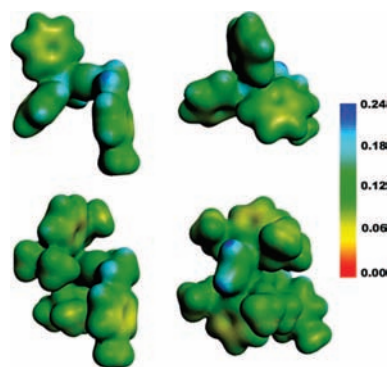
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Gold(I) cationic complexes of general formula  $[LAu^+...X^-]$  [ $L$  = phosphines<sup>1</sup> or NHCs<sup>2</sup> (N-Heterocyclic Carbenes),  $X^-$  = weakly coordinating anion] are successfully employed as catalysts in a large variety of organic reactions involving the activation of unsaturated carbon–carbon bonds.<sup>3</sup> A key role in such reactions is played by the counterion, which strongly affects activity,<sup>4,5</sup> regioselectivity,<sup>6</sup> and stereoselectivity.<sup>7</sup> Although ion pairing<sup>8</sup> is recognized to be responsible for the observed counterion effects, rather surprisingly the anion–cation interaction in Au(I) complexes has never been investigated from the experimental point of view and only very rarely from the theoretical one.<sup>9,10</sup>

Here we report preliminary results concerning the determination of the relative anion–cation orientation(s) in  $[(PPh_3)Au(4\text{-Me-styrene})]BF_4$  (**1BF<sub>4</sub>**)<sup>11</sup> and  $[(NHC)Au(4\text{-Me-styrene})]BF_4$  [**2BF<sub>4</sub>**;<sup>12</sup> NHC = 1,3-bis(di-iso-propylphenyl)-imidazol-2-ylidene], investigated by combining NMR spectroscopy and Density Functional Theory (DFT) calculations incorporating solvent and relativistic effects (see the Supporting Information, SI). We show, for the first time, that the counterion is not located near the gold atom formally having a positive charge. On the contrary, it preferentially stays in the periphery of the cation, its exact position being critically determined by the nature of the ancillary ligand. We also report a complete characterization of these olefin adducts that, to the best of our knowledge, is not present in the literature.<sup>13–18</sup>

**1BF<sub>4</sub>** has been generated *in situ* within an NMR tube at  $-20\text{ }^\circ\text{C}$  and completely characterized by 1D and 2D multinuclear NMR experiments in  $CD_2Cl_2$  (SI). The coordination of 4-Me-styrene at the **1<sup>+</sup>** cation causes a marked shielding of carbon 1 ( $\underline{C}H_2=CHAr$ ) whose chemical shift goes from 113.07 ppm in the uncoordinated olefin to 101.36 ppm. A much smaller variation of chemical shift is observed for carbon 2 ( $\underline{C}H=CHAr$ , from 138.36 to 137.31 ppm). This suggests that 4-Me-styrene coordinates unsymmetrically at gold(I). Indeed, our DFT calculations show the Au–C1 bond (2.27 Å) to be significantly shorter than the Au–C2 bond (2.55 Å). **2BF<sub>4</sub>** has been synthesized and isolated as a white powder at  $-20\text{ }^\circ\text{C}$ . It is much more stable than **1BF<sub>4</sub>**, surviving for days at room temperature in  $CD_2Cl_2$  solution. C1 exhibits a higher shielding as a consequence of coordination (from 113.07 to 84.73 ppm), while also C2 shows considerable shielding (from 138.36 to 129.37 ppm). Consistently, the computed Au–C bond distances are shorter than those in **1BF<sub>4</sub>** but remain significantly different (Au–C1, 2.25 Å; Au–C2, 2.42 Å).

A detailed analysis of the charge distribution on **1<sup>+</sup>** and **2<sup>+</sup>** cations, carried out using several methods (SI), indicates that the positive charge is significantly redistributed on the ligands. The gold atom actually carries a charge not larger than 0.21 and 0.26 in **1<sup>+</sup>** and **2<sup>+</sup>**, respectively.<sup>19</sup> A confirmation of this charge redistribution comes from analysis of the Coulomb potential of the cationic complexes mapped on an electronic isodensity surface (Figure 1). The isodensity value chosen is that approximately corresponding to tangent density surfaces for the isolated cation and anion placed at the optimized geometry of the ion pair (*vide*



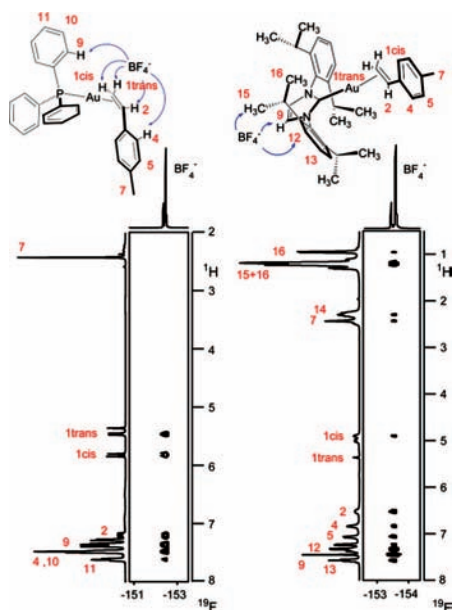
**Figure 1.** Lateral (left) and back (right) views of the Coulomb potential of **1<sup>+</sup>** (up) and **2<sup>+</sup>** (down) mapped on an electronic isodensity surface ( $\rho = 0.007\text{ e}/\text{Å}^3$ ). Coulomb potential in au.

*infra*). This surface thus roughly visualizes the steric dimension of the ions. Clearly, both complexes present a net attractive potential (positive on the whole isodensity surface), but the gold atom is not the most attractive site. The most attractive regions on the surface (blue-colored in Figure 1) are instead located at the olefin's hydrogen atoms and, in the case of **2BF<sub>4</sub>**, at the rather acidic protons of the imidazole ring.

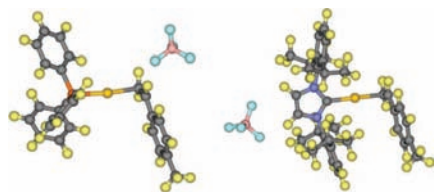
<sup>19</sup>F,<sup>1</sup>H-HOESY, low-temperature, NMR experiments<sup>20</sup> have been performed under conditions where diffusion NMR experiments indicate that self-aggregation is limited to ion pairing (SI).<sup>21</sup> The results are in excellent agreement with the charge distribution analysis. For **1BF<sub>4</sub>**, strong contacts are observed between the F-nuclei of the counterion and resonances 1*cis*, 1*trans*, and 2 of the 4-Me-styrene and resonance 9 of the phosphine ligand (Figure 2). Contacts of medium intensities are also observed between the counterion and resonances 4 and 10. A very weak contact is detected with the 11 resonance, while the anion does not show any interaction with protons 5 and 7. The <sup>19</sup>F,<sup>1</sup>H-HOESY NMR spectrum of **2BF<sub>4</sub>** shows a strong contact between the F atoms of the counterion and resonance 9 of the NHC ligand, contact of medium intensity with resonances 13 and 15, and very weak contacts with olefin resonances 1, 2, 4, and 5 (Figure 2).

A quantitative analysis of the interionic NOE intensities indicates that in complex **1BF<sub>4</sub>** the counterion is located on the side of 4-Me-styrene and, particularly, close to the olefin region that is opposite to the 4-Me-Ph moiety (Figure 2). In **2BF<sub>4</sub>**, the counterion approaches the cation from the side of the NHC ligand and is mainly located close to the imidazole ring (Figure 2).<sup>22,23</sup> The weak contacts with the olefinic protons originate from a small contribution of the arrangement where the anion is located on the side of 4-Me-styrene.

Several full geometry optimizations have been carried out, and the potential energy surfaces of the **1BF<sub>4</sub>** and **2BF<sub>4</sub>** ion pairs were thoroughly investigated (SI). No stable structures are obtained in



**Figure 2.** Low temperature  $^{19}\text{F},^1\text{H}$ -HOESY NMR spectra (376.65 MHz,  $\text{CD}_2\text{Cl}_2$ ) of complexes  $1\text{BF}_4$  (left) and  $2\text{BF}_4$  (right).



**Figure 3.** The most stable ion-pair configuration for  $1\text{BF}_4$  (left) and  $2\text{BF}_4$  (right).

which  $\text{BF}_4^-$  is positioned close to the metallic center. The most stable configurations for the  $1\text{BF}_4$  and  $2\text{BF}_4$  ion pairs are shown in Figure 3.

In these, as can be seen, the counterion is placed close to the styrene and on the side of the NHC ligand, respectively. The potential energy surfaces are found to be relatively flat, and additional minima were found. These minima lie very close in energy and are deemed to contribute at equilibrium (SI). All these structures are completely consistent with the observed  $^{19}\text{F},^1\text{H}$ -HOESY contacts.

In conclusion, by combining NOE NMR measurements and accurate theoretical modeling, we have discovered that the counterion in olefin–Au(I) catalysts resides mainly far away from the gold site, the latter carrying only a small fraction of the positive charge. The preferential position of the counterion is tunable through the choice of the ancillary ligand, and this opens the way to greater control over the properties and activity of these catalysts. In our specific case, an interesting structure/reactivity correlation can be sketched. The position of the counterion determined for  $1\text{BF}_4$  is apt to interfere with the nucleophile attacking the coordinated olefin. On the contrary, electronic (interactions with H9) and steric (hindered 2,6-diisopropyl aryls) confinement of the counterion make strong counterion effects in  $2\text{BF}_4$  unlikely. In nice agreement, counterion effects in Au(I) catalyzed activation of unsaturated substrates are much more frequent when phosphines<sup>4,6,7</sup> are used as ancillary ligands instead of NHCs.<sup>5</sup>

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**Supporting Information Available:** Details on the syntheses, NMR characterization, and computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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