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A Phosphine Gold(I) π -Alkyne Complex: Tuning the Metal–Alkyne Bond Character and Counterion Position by the Choice of the Ancillary Ligand

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The intra- and interionic structures of a mononuclear phosphine gold(I) alkyne complex $[(\text{PAr}^{\text{F}}_3)\text{Au}(2\text{-hexyne})]\text{BF}_4$ [1BF_4 ; $\text{Ar}^{\text{F}} = 3,5\text{-bis(trifluoromethyl)phenyl}$] and its analogous complex $[(\text{NHC})\text{Au}(2\text{-hexyne})]\text{BF}_4$ [2BF_4 ; $\text{NHC} = 1,3\text{-bis(diisopropylphenyl)imidazol-2-ylidene}$] have been investigated by combining 1D and 2D multinuclear NMR spectroscopy and density functional theory calculations. It has been found that alkyne in 1BF_4 is depleted of its electron density to a greater extent than that in 2BF_4 . This correlates with the $\Delta\delta(^{13}\text{C})$ NMR of the carbon–carbon triple bond. Instead, 2BF_4 is much more “kinetically stable” than 1BF_4 . ^{19}F – ^1H HOESY NMR experiments indicate that the counterion locates close to the gold atom in 1BF_4 (differently from that previously observed in the few other gold(I) ion pairs studied), exactly where the computed Coulomb potential indicates that partial positive charge accumulates.

Gold(I) cationic complexes $[\text{LAu}^+ \cdots \text{X}^-]$ [$\text{L} =$ phosphine,¹ N-heterocyclic carbene (NHC), and cyclic (alkyl)(amino)carbenes (CAAC);² $\text{X}^- =$ a weakly coordinating anion] are increasingly used as catalysts in a great variety of reactions involving the activation of carbon–carbon triple bonds.³ Despite this, π complexes $[\text{LAu}(\text{alkyne})]\text{X}$, through which the reaction

mechanism is generally thought to proceed,⁴ have been isolated in only a handful of cases⁵ and never with phosphine ligands,⁶ which are among the most widely used. At the same time, ion-pairing interactions in $[\text{LAu}(\text{alkyne})]\text{X}$ have never been investigated, although it is known that the counterion⁷ may have a significant role in affecting the activity^{8,9} and regio-¹⁰ and stereoselectivity.¹¹

Here we report on the synthesis and characterization of $[(\text{PAr}^{\text{F}}_3)\text{Au}(2\text{-hexyne})]\text{BF}_4$ [1BF_4 ; $\text{Ar}^{\text{F}} = 3,5\text{-bis(trifluoromethyl)phenyl}$; Scheme 1] and $[(\text{NHC})\text{Au}(2\text{-hexyne})]\text{BF}_4$ [2BF_4 ; $\text{NHC} = 1,3\text{-bis(diisopropylphenyl)imidazol-2-ylidene}$]. 1BF_4 represents the first example^{6b} of a mononuclear gold alkyne complex with a phosphine ancillary ligand.

An integrated experimental (NMR) and theoretical [density functional theory (DFT)]¹² investigation on the intra- and interionic structures of 1BF_4 and 2BF_4 has provided very useful information on the effect of the ancillary ligand on the Au–alkyne chemical bond and unprecedented indications on the relative anion–cation orientation.

1BF_4 was generated in situ within an NMR tube at 204 K and completely characterized by 1D and 2D multinuclear NMR experiments in rigorously anhydrous and deoxygenated CD_2Cl_2 (Scheme 1 and the Supporting Information, SI). Under such experimental conditions, 1BF_4 is stable for a few hours, but it quickly decomposes at higher temperature (> 223 K) (SI) yielding $[(\text{PAr}^{\text{F}}_3)_2\text{Au}]\text{BF}_4$ and colloidal gold.¹³

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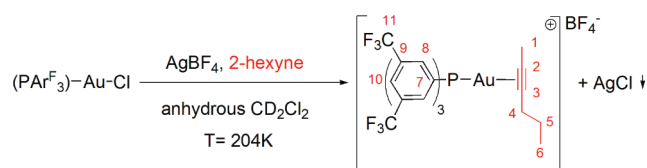
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Scheme 1



The coordination of 2-hexyne causes a deshielding of the PAr^{F_3} phosphorus resonance from 36.81 ppm in $\text{PAr}^{\text{F}_3}\text{AuCl}$ to 41.65 ppm. The chemical shifts of carbons 2 and 3 (Scheme 1) move from 78.75 and 80.81 ppm in the uncoordinated alkyne to 90.26 (doublet, $J_{\text{C}_2-\text{P}} = 8.06$ Hz, $\Delta\delta = 11.51$ ppm) and 91.79 ppm (doublet, $J_{\text{C}_1-\text{P}} = 8.18$ Hz, $\Delta\delta = 10.98$ ppm), respectively, in $\mathbf{1BF}_4$.^{6b} The very similar $\Delta\delta$ and $J_{\text{C}-\text{P}}$ values of C2 and C3 suggest that 2-hexyne coordinates symmetrically at gold. Indeed, the DFT-computed bond lengths are almost identical:^{6b} $\text{Au}-\text{C}_2 = 2.31$ Å and $\text{Au}-\text{C}_3 = 2.29$ Å (SI).

Deshielding values of the C2 and C3 quaternary carbons in $\mathbf{2BF}_4$ are 6.8 and 6.6 ppm, respectively, thus much smaller than those in $\mathbf{1BF}_4$ and in line with those found for similar complexes.^{5b,f} The DFT calculations (SI) show that 2-hexyne is coordinated symmetrically also in $\mathbf{2BF}_4$, with $\text{Au}-\text{C}$ distances ($\text{Au}-\text{C}_2 = 2.27$ Å and $\text{Au}-\text{C}_3 = 2.29$ Å) very similar to those in $\mathbf{1BF}_4$.

The computed $[\text{LAu}^+ \cdots \text{alkyne}]$ dissociation energies in $\mathbf{1BF}_4$ (37.4 kcal/mol) and $\mathbf{2BF}_4$ (38.1 kcal/mol) are also very close and are typical of other alkyne complexes.^{5f} Quite remarkably, by contrast, the alkyne ligand undergoes a significantly larger electron density depletion in $\mathbf{1}^+$ than in $\mathbf{2}^+$. In particular, charge transfer¹⁴ from the alkyne to LAu^+ is 0.25 electrons in $\mathbf{1}^+$ versus 0.15 electrons in $\mathbf{2}^+$, and this correlates very well with the carbon–carbon triple bond $\Delta\delta$ (SI). Consistently, $\Delta\delta$ in $\text{Cl}-\text{Au}-3\text{-hexyne}$ is only 5.3 ppm,^{5d} and our computed charge transfer is reduced to 0.07 electrons (SI). It appears evident that LAu^+ in $\mathbf{1}^+$ is globally more acidic than in $\mathbf{2}^+$. The very similar interaction energies and structured of $\mathbf{1}^+$ and $\mathbf{2}^+$ further suggest the presence, in the NHC complex, of a smaller alkyne $\rightarrow \text{AuL}^+ \sigma$ donation and a larger $\text{AuL}^+ \rightarrow \text{alkyne } \pi$ back-donation, producing the observed smaller net charge transfer. Decomposition of the computed electron density flux in terms of σ donation and π back-donation is of key interest,^{5d,f,6a} and we are currently investigating it in depth. The relative anion–cation position in $\mathbf{1BF}_4$ and $\mathbf{2BF}_4$ was investigated by performing $^{19}\text{F}-^1\text{H}$ HOESY NMR experiments¹⁵ in CD_2Cl_2 . $\mathbf{1BF}_4$ is particularly suitable for such studies because the intramolecular distances $\text{CF}_3 \cdots \text{H}_8$ or $\text{CF}_3 \cdots \text{H}_{10}$ can be used as references to quantify the average $\text{H} \cdots \text{F}$ interionic distances (SI).¹⁶

A strong contact is present between the fluorine atoms of the counterion and H8 of the phosphine ligand (Figure 1). Medium-strength contacts are observed between BF_4^- and H1, H4, and H10, whereas the anion does not show any interaction with H5 and H6. This nuclear Overhauser enhancement (NOE) pattern indicates that BF_4^- is

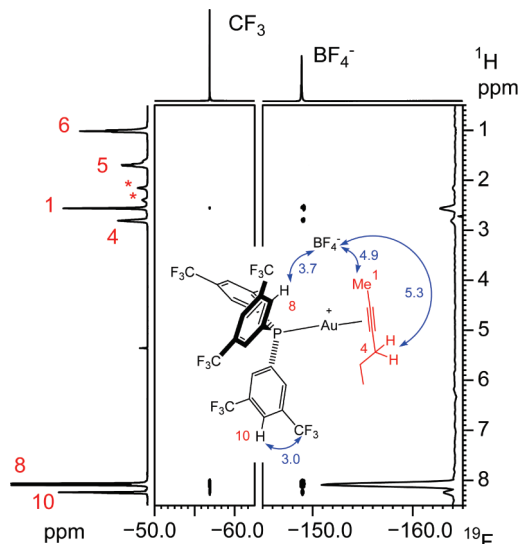


Figure 1. Two sections of the low-temperature $^{19}\text{F}-^1\text{H}$ HOESY NMR spectrum (376.65 MHz, 204 K, CD_2Cl_2) of $\mathbf{1BF}_4$. Asterisks denote the resonances of free 2-hexyne. Average interionic distances (Å) are shown in blue.

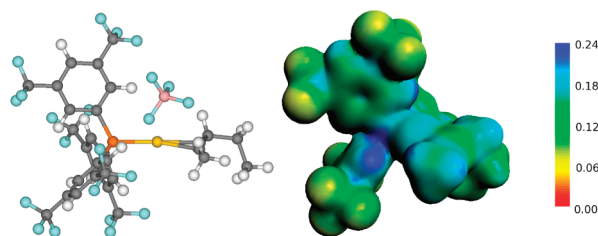


Figure 2. Left: Ball-and-stick representation of the most stable ion pair of $\mathbf{1BF}_4$. Right: Coulomb potential of $\mathbf{1}^+$ mapped on an electronic isodensity surface ($\rho = 0.007$ e/Å³; Coulomb potential in atomic units).

preferentially located in the space around the gold atom between the phosphine and alkyne ligands, closer to the phosphine, as depicted in Figures 1 and 2 (left). This relative anion–cation orientation is similar to that found, very recently, in the solid-state structure of the $[\text{P}(t\text{-Bu})_3\text{Au}(\text{4,4-dimethylpent-2-yne})]\text{SbF}_6$ complex.^{6b} The computed Coulomb potential of $\mathbf{1}^+$, mapped on an electronic isodensity surface (Figure 2, right), neatly confirms these conclusions, showing that the most attractive regions in $\mathbf{1}^+$ are the phosphorus atom and H8 of the aryl substituent close to the gold site (blue color in Figure 2). The average $\text{H} \cdots \text{F}_4\text{B}^-$ distances for H1, H4, and H8 resulting from NOE measurements (4.9, 5.3, and 3.7 Å, respectively; Figure 1) are in good agreement with those calculated,¹⁷ considering the energy of the most stable relative anion–cation configurations of the $\mathbf{1BF}_4$ ion pair (4.5, 5.6, and 4.1 Å; SI).

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of olefin ($L = PPh_3$) or the L ligand ($L = NHC$).¹⁸ ^{19}F – 1H HOESY NMR spectroscopy and DFT calculations show that the latter orientation is indeed predominant also in $2BF_4$ (SI).

Two distinct sets of resonances were visible in the 1H and ^{13}C NMR spectra for free and bound 2-hexyne when a slight excess of 2-hexyne was used for generating $1BF_4$; this indicates that the exchange process is slow in the $\Delta\delta$ time scale. 1H EXSY NMR (exchange spectroscopy) experiments¹⁹ were performed in order to derive kinetic parameters of the exchange process. An exchange rate constant $k_{obs} = 7.9 \pm 0.8 \text{ s}^{-1}$ and a second-order constant $k_2 = k_{obs}/[2\text{-hexyne}] = 158 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$ at 204 K were obtained. For $2BF_4$, line-shape analysis and 1H EXSY NMR (SI) indicate a k_{obs} that increases with the 2-hexyne concentration (SI), thus suggesting an associative exchange mechanism with $k_2 = 26 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ at 298 K. If an associative mechanism²⁰ is also operative in $1BF_4$, its alkyne exchange is clearly much faster than that of $2BF_4$ (by 2–3 orders of magnitude, assuming an activation energy comparable to that of alkene exchange^{20,21}).

In conclusion, the synthesis and characterization of a mononuclear phosphine gold(I) alkyne complex ($1BF_4$) and a comparison with its analogous NHC complex ($2BF_4$) have

allowed us to shed some light on the role played by the L ancillary ligand in modulating Au–alkyne and ion-pair interaction patterns. More pronounced electron density depletion occurs at the alkyne in $1BF_4$ than in $2BF_4$ because of the higher acidity of LAu^+ in 1^+ compared to that in 2^+ .²² This makes alkyne coordinated at the $PArF_3Au^+$ moiety more susceptible to nucleophilic attack. Instead, $2BF_4$ is much more “kinetically stable” than $1BF_4$, probably because of the steric protection exerted by the isopropyl groups of NHC that inhibit associative decomposition pathways. All of these findings support the view that catalysts with phosphine ancillary ligands are more effective in activating alkyne substrates (higher TOF), while NHC catalysts are more robust (higher TON), as found, for example, in the hydration of alkynes to ketones.^{23,24} Finally, the presence of CF_3 electron-withdrawing groups in $1BF_4$ causes a shift of the counterion, which tends to locate close to the gold atom in a position different from those previously observed in the few other gold(I) ion pairs studied.¹⁸ This illustrates how the relative anion–cation position, an important factor in determining the catalytic activity and selectivity, can be finely modulated by the proper selection of the ancillary ligand.

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Supporting Information Available: Details of 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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