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 [(PArF$_3$)$_2$Au(2-hexyne)]BF$_4$ (1BF$_4$; ArF = 3,5-bis(trifluoromethyl)phenyl) and its analogous complex [(NHC)Au(2-hexyne)]BF$_4$ (2BF$_4$; NHC = 1,3-bis(diisopropylphosphanyl)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 Δδ(13C) NMR of the carbon—carbon triple bond. Instead, 2BF$_4$ is much more “kinetically stable” than 1BF$_4$. 1H–1H HOESY NMR experiments indicate that the counterion locates close to the gold atom in 1BF$_4$ (different 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 [LAu+·⋯·X-] [L = phosphine; N-heterocyclic carbene (NHC), and cyclic (alkyl)(amino)carbenes (CAAC); X- = a weakly coordinating anion] are increasingly used as catalysts in a great variety of reactions involving the activation of carbon—carbon triple bonds. Despite this, π complexes [LAu(alkyne)]X, through which the reaction mechanism is generally thought to proceed, have been isolated in only a handful of cases and never with phosphine ligands, which are among the most widely used. At the same time, ion-pairing interactions in [LAu(alkyne)]X have never been investigated, although it is known that the counterion may have a significant role in affecting the activity and regio- and stereoselectivity.

Here we report on the synthesis and characterization of [(PArF$_3$)$_2$Au(2-hexyne)]BF$_4$ (1BF$_4$; ArF = 3,5-bis(trifluoromethyl)phenyl) (Scheme 1) and [(NHC)Au(2-hexyne)]BF$_4$ (2BF$_4$; NHC = 1,3-bis(diisopropylphosphanyl)imidazol-2-ylidene). 1BF$_4$ represents the first example of a mononuclear gold alkyne complex with a phosphine ancillary ligand.

An integrated experimental (NMR) and theoretical (density functional theory (DFT)) 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$_2$Cl$_2$ (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 [(PArF$_3$)$_2$Au]BF$_4$ and colloidal gold.


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The coordination of 2-hexyne causes a deshielding of the PAuF₃ phosphorus resonance from 36.81 ppm in PAuF₃AuCl 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, $\delta_{C-2} = 8.06$ Hz, $\Delta$ = 11.51 ppm) and 91.79 ppm (doublet, $\delta_{C-1} = 8.18$ Hz, $\Delta$ = 10.98 ppm), respectively, in 1BF₄.⁶b The very similar $\Delta$ and $\delta_{C-2}$ values of C2 and C3 suggest that 2-hexyne coordinates symmetrically at gold. Indeed, the DFT-computed bond lengths are almost identical:⁶b Au–C2 = 2.31 Å and Au–C3 = 2.29 Å (SI).

Deshielding values of the C2 and C3 quaternary carbons in 2BF₄ are 6.8 and 6.6 ppm, respectively, thus much smaller than those in 1BF₄ and in line with those found for similar complexes.⁵b,f The DFT calculations (SI) show that 2-hexyne is coordinated symmetrically as well in 2BF₄, with Au–C distances (Au–C2 = 2.27 Å and Au–C3 = 2.29 Å) very similar to those in 1BF₄.

The computed [LAu⁺···alkyne] dissociation energies in 1BF₄ (37.4 kcal/mol) and 2BF₄ (38.1 kcal/mol) are also very close and are typical of other alkyne complexes.⁵d Quite remarkably, by contrast, the alkyne ligand undergoes a significantly larger electron density depletion in 1⁺ than in 2⁺. In particular, charge transfer from the alkyne to LAu⁺ is 0.25 electrons in 1⁺ versus 0.15 electrons in 2⁺, and this correlates very well with the carbon–carbon triple bond $\Delta$δ (SI). Consistently, $\Delta$δ in Cl−Au−3-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 1⁺ is globally more acidic than in 2⁺. The very similar interaction energies and structured of 1⁺ and 2⁺ further suggest the presence, in the NHC complex, of a smaller alkyne → AuL⁺ σ donation and a larger AuL⁺ → alkyne π back-donation, producing the observed smaller net charge donation. 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 1BF₄ and 2BF₄ was investigated by performing $^{19}$F−$^1$H HOESY NMR experiments in CD$_2$Cl$_2$. 1BF₄ is particularly suitable for such studies because the intramolecular distances CF₃···H8 or CF₃···H10 can be used as references to quantify the average H···F interionic distances (SI).⁶b

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 BF₄⁻ 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 BF₄⁻ is 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 [P(t-Bu)₃Au(4,4-dimethylpent-2-yne)]SbF₆ complex.⁶b The computed Coulomb potential of 1⁺, mapped on an electronic isodensity surface (Figure 2, right), neatly confirms these conclusions, showing that the most attractive regions in 1⁺ are the phosphorus atom and H8 of the aryl substituent close to the gold site (blue color in Figure 2). The average H···F$_i$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 1BF₄ ion pair (4.5, 5.6, and 4.1 Å; SI).

The relative anion–cation orientation in 1BF₄ is significantly different from those found in [LAu(4-Me-styrene)]BF₄ complexes, where the anion preferentially locates on the side

(17) The (r) distances are computed considering that free rotation of the methyl and methylene groups is faster than the overall molecular correlation time (r⁻³ average), while the restricted rotation of the phenyl ring is slower than the overall ion-pair correlation time (r⁻⁵ average); Neuhaus, D.; Williamson, M. The Nuclear Overhauser Effect in Structural and Conformational Analysis; VCH Publishers: New York, 1989.
of olefin (L = PPh₃) or the L ligand (L = NHC). HESY NMR spectroscopy and DFT calculations show that the latter orientation is indeed predominant also in 2BF₄ (SI).

Two distinct sets of resonances were visible in the ¹H and ¹³C NMR spectra for free and bound 2-hexyne when a slight excess of 2-hexyne was used for generating 1BF₄; this indicates that the exchange process is slow in the Δδ time scale. ¹H EXSY NMR (exchange spectroscopy) experiments were performed in order to derive kinetic parameters of the exchange process. An exchange rate constant kₖₑₒₛ = 7.9 ± 0.8 s⁻¹ and a second-order constant k₂ = kₖₑₒₛ/[2-hexyne] = 158 ± 20 M⁻¹ s⁻¹ at 204 K were obtained. For 2BF₄, line-shape analysis and ¹H EXSY NMR (SI) indicate a kₖₑₒₛ that increases with the 2-hexyne concentration (SI), thus suggesting an associative exchange mechanism with k₂ = 26 ± 2 M⁻¹ s⁻¹ at 298 K. If an associative mechanism is also operative in 1BF₄, its alkyn exchange is clearly much faster than that of 2BF₄ (by 2–3 orders of magnitude, assuming an activation energy comparable to that of alkene exchange).

In conclusion, the synthesis and characterization of a mononuclear phosphine gold(I) alkyne complex (1BF₄) and a comparison with its analogous NHC complex (2BF₄) 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 alkyn in 1BF₄ than in 2BF₄ because of the higher acidity of LAu⁺ in 1⁺ compared to that in 2⁺. This makes alkyn coordinated at the PAr₃Au⁺ moiety more susceptible to nucleophilic attack. Instead, 2BF₄ is much more “kinetically stable” than 1BF₄, 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 alkyn substrates (higher TOF), while NHC catalysts are more robust (higher TON), as found, for example, in the hydration of alkynes to ketones. Finally, the presence of CF₃ electron-withdrawing groups in 1BF₄ 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. 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.

(21) Note that, if the exchange mechanisms were dissociative, different rates would likely imply different interaction energies, in contrast with our calculations.
(22) The computed alkyn→LAu⁺ charge transfer in (PPh₃)Au(2-hexyne)⁺ is very similar (0.21 electrons; SI) to that in 1BF₄.