NHC-Gold-Alkyne Complexes: Influence of the Carbene Backbone on the Ion Pair Structure

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Supporting Information

ABSTRACT: We have studied the ion pair structure of [NHC-Au(Cl)][BF₄] (NHC = nitrogen-heterocyclic carbene) by solution NOE NMR spectroscopy and relativistic DFT calculation. The neutral complexes [NHC-AuCl] have been synthesized through an improved, silver-free one-pot synthesis, by reaction (in air and using solvents and substrates without any previous purification) of the appropriate [NHC(H)]Cl, gold precursor, and KHCO₃. Ion pairs were generated in situ in NMR tubes. In our previous work, two main ion pair orientations were observed for unsaturated NHC ligands: one with the anion close to the carbene backbone (A, most populated) and another with the anion close to the alkyne (B). Here we focus on the effect of the carbene backbone on the ion pair structure, comparing the unsaturated NHC (1BF₄) with two different variants: a saturated NHC (2BF₄) and a polycyclic ligand with an extended aromatic system (3BF₄). For 2BF₄, the A:B ratio remains almost the same as for 1BF₄, while the ion pair structure of 3BF₄ becomes almost nonspecific, with a slight preference for the orientation B. Both cases can be explained analyzing the DFT Coulomb potential map, which shows an attractive region on the backbone of 2BF₄ and a flat weak potential around the whole 3BF₄.

Carbene ligands are commonly used in organometallic chemistry, and interest in their properties is continuously increasing in many fields. In particular, Arduengo-type N-heterocyclic carbene (NHC) show a great affinity toward gold(I), allowing chemists to isolate and study species such as gold carbonyls, multimetallic complexes, and linear [(NHC)-Au(UHC)][X] complexes (UHC = unsaturated hydrocarbon). The driving force of this research field, besides the natural curiosity of organometallic chemists, is the high potential of carbene gold complexes as catalysts. In fact, nowadays most gold(I) catalysts bear carbene or phosphine molecules as ligands, with a plethora of “variations on a theme”. Such variations are very important in order to direct the outcome of the catalysis, but finding a rationale for the results is not always easy. Among the factors influencing the product distribution, the anion can be crucial to tune the performance of a catalyst. Recent papers show that the anion can influence the yield and the regio- and stereoselectivity of a catalyst. It is also observed that the anion influences the structure of the catalyst and important intermediates of the catalytic cycle. Unfortunately, explaining the details of the anion effect is complicated, and, at the same time, its role is very difficult to study. One of the few pieces of experimentally accessible information is the most favored position of the anion in solution and its dependence on the ligand properties. For this reason, in the last years our group has been carrying out a systematic NMR/DFT study on one of the key intermediates in the functionalization of double and triple C–C bonds, the linear bis-coordinated [L-Au(UHC)][BF₄] ion pair. We have demonstrated how the anion position can be finely tuned by the choice of the ligand and how the ion pair structure can be related to the electronic properties of the phosphorus-based ligand. The results show that the anion is mainly located on the ligand side when carbene ligands are used and on the UHC side in phosphine-gold complexes. This is due to the charge distribution throughout the complex, which can be effectively rationalized by relativistic density functional theory (DFT) calculations and, in particular, maps of the Coulomb potential around the cation, useful to locate the most attractive regions.

In this contribution, we continue exploring the relation between ligand properties and anion/cation relative position, focusing on NHC carbene ligands. We heavily modified the ligand structure with the aim to produce a different charge...
distribution and, consequently, different ion pair structures. We already know that for the “classical” unsaturated [(IPr)-Au(η²-2-hexyne)][BF₄] [IPr = (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)] the anion is strongly attracted by the hydrogen atoms on the imidazole ring. The substitution of such hydrogen atoms with methyl groups only moderately reduces this interaction in [NHC-Au-(η²-alkene)][BF₄] related complexes. Here we study the influence of eliminating the unsaturation using the saturated heterocyclic carbene [(SIPr)-Au(η²-3-hexyne)][BF₄] [SIPr = 1,3-bis(2,6-di-isopropylphenyl)dihydromimidazol-2-ylidene] (Chart 1, 2BF₄).

Chart 1. Structure and Numbering of NHC Gold Complexes

Subsequently, cationic bis-coordinate gold(I) complexes 1–3BF₄ were generated in an NMR tube by the reaction of the parent [NHC-AuCl] complexes with AgBF₄ in CD₂Cl₂, in the presence of 3-hexyne (see the Supporting Information for details). From ¹H, ¹³C, ¹H-COSY, ¹H-NOESY, ¹H,¹³C-HMQC, and ¹H,¹³C-HMBC NMR spectroscopies all proton and carbon resonances belonging to the different fragments were assigned (see the Supporting Information and Scheme 1 for the numbering of carbon and proton resonances).

The interionic structure has been studied combining the ¹⁹F,¹H-HOESY NMR (Figures 1 and 2) technique and

Figure 1. (Top) Coulomb potential map (in au) of 2⁺, mapped on an electronic isodensity surface (0.007 e/Å³) (Bottom) ¹⁹F,¹H-HOESY NMR spectrum (376.65 MHz, 297 K, CD₂Cl₂) of complex 2BF₄. For the numbering of protons see Chart 1. * denotes the resonances of free 3-hexyne.27

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relativistic DFT calculations. The latter were performed using the ADF (Amsterdam Density Functional) package, at the TZ2P/BLYP/ZORA\textsuperscript{25} level (see Computational Details in the Supporting Information), including explicitly the conductor-like screening model (COSMO\textsuperscript{26} with $\epsilon = 8.93$) to include solvent effects.

From previous studies\textsuperscript{28} on [NHC-Au-(UHC)][BF\textsubscript{4}] ion pairs we found that two important ion pair relative orientations are possible, A and B, in which the anion is located near NHC and UHC, respectively. Other orientations seem to be unfavored.\textsuperscript{29} Since the protons of the imidazole ring of the NHC backbone are slightly acidic, they carry some additional positive charge and may act as an anchoring point for the anion, thus favoring orientation A.

This is confirmed by analyzing\textsuperscript{30} the NOE contacts for BF\textsubscript{4} (Figure S8 in the Supporting Information). The most intense contact is with H8 (Table 1), and it is representative for orientation A, whereas the contact H2/F (representative for the orientation B) is weaker. The weakness of H6/F and H7/F contacts indicates that the ion pair structure can be well described by either orientation A or B. The ratio between H8/F and H2/F is 1.00:0.18, leading to an A:B ratio of 85:15. As expected, it is very similar to that measured for [(IPr)-Au(η\textsuperscript{2}-2-hexyne)][BF\textsubscript{4}]\textsuperscript{96}

Figure 1 shows the $^{19}$F,$^1$H-HOESY spectrum for 2BF\textsubscript{4}. The most intense interaction is H8/F, and the general pattern is very similar to that for 1BF\textsubscript{4}. Performing a $^{19}$F,$^1$H-HOESY NMR experiment on the isolated ion pairs 2BF\textsubscript{4} (Table 1 and Supporting Information) gives essentially the same results, within the experimental error. The A:B ratio is around 76:24. Mapping the Coulomb potential of the 2$^+$ cation shows that H2 and H8 are indeed the most attractive regions of the cation, with a slight predominance of H8 (Figure 1).\textsuperscript{51} This map is in qualitative agreement with the experimental A:B ratio, and comparison of the potential maps of 2$^+$ and 1$^+$ (see the Supporting Information) shows that the partial saturation of the NHC ring only slightly reduces the accumulation of positive charge on the ligand backbone, thus giving a similar A:B ratio (Table 1).

Figure 2 shows the $^{19}$F,$^1$H-HOESY spectrum for 3BF\textsubscript{4}. In this case all the interionic interactions are of comparable intensity. In fact the weakest is H8/F (H8 is the most “internal” proton of the BIAN system), with relative intensity 0.24. This means that there is no single favored conformation and many anion/cation relative orientations are possible. The most intense contact is with H2, and, among the carbene ligands we have studied up to now, this is the first time that the conformation B is favored, even if slightly, over the A one. This aspecific ion pair structure is a direct consequence of the extended aromaticity on the backbone of the carbene, which makes the Coulomb potential quite flat throughout the cation. This is seen in the Coulomb map of 3$^+$ (Figure 2), where the regions around the 3-hexyne, the carbene ring, and the aromatic fragment of NHC show essentially the same small potential value.

In conclusion, we have described the ion pair structure for different [(NHC)-Au(η\textsuperscript{2}-3-hexyne)][BF\textsubscript{4}] complexes, chosen with the aim of heavily altering the imidazole ring. We also successfully tested a simple one-pot procedure for the synthesis of [NHC-AuCl] neutral precursors, which is silver-free and moisture- and air-tolerant.

The NOE results on the saturated NHC show that the removal of the unsaturation is not enough to markedly influence the ion pair structure, and the anion still prefers to stay on the carbene side. On the other hand, the extended aromaticity of an acenaphthene-based NHC makes the ion pair structure aspecific, with only a small preference for the UHC side.

These results underline that the structure in solution of NHC gold(1)-UHC ion pairs cannot be easily tuned, and meaningful modifications can be achieved only through large alterations of the NHC backbone. Gold complexes containing phosphorus-based ligands show a more marked ligand influence on the ion pair structure in solution.\textsuperscript{9a,28}

Table 1. Relative NOE Intensities Determined by Arbitrarily Fixing the Largest Intensity of the NOE(s) between the Anion Fluorines and the Cation Protons to 1

<table>
<thead>
<tr>
<th></th>
<th>1BF\textsubscript{4}</th>
<th>2BF\textsubscript{4}</th>
<th>3BF\textsubscript{4}</th>
</tr>
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<tr>
<td>H1</td>
<td>0.13</td>
<td>0.10</td>
<td>0.17</td>
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<tr>
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<td>H3</td>
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<td>0.32</td>
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<tr>
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<tr>
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</table>

*Isolated ion pairs. \textsuperscript{b}H3/F and H5/F contacts partially overlap. \textsuperscript{c}H6/F and H9/F contacts partially overlap. \textsuperscript{4}In this conformation A and B are not enough to fully describe the ion pair structure; see text.
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NOTES

The authors declare no competing financial interest.

REFERENCES


