

Ion pairing in NHC gold(I) olefin complexes: A combined experimental/theoretical study

Nicola Salvi, Leonardo Belpassi, Daniele Zuccaccia, Francesco Tarantelli, Alceo Macchioni*

Dipartimento di Chimica, Università degli Studi di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

ARTICLE INFO

Article history:

Received 22 July 2010

Received in revised form

17 August 2010

Accepted 24 August 2010

Available online 1 October 2010

Keywords:

Ion pairing

NOE NMR

DFT

N-heterocyclic carbenes

Gold–alkene complexes

ABSTRACT

The relative anion–cation orientation in [(NHC)Au(alkene)]BF₄ ion pairs [NHC = N-Heterocyclic Carbene = 1,3-bis(di-iso-propylphenyl)-imidazol-2-ylidene (IPr) and 4,5-dimethyl-N,N'-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (^{Me}IPr); alkene = 4-methyl-1-pentene, 2,3-methyl-2-butene and 4-methylstyrene] has been investigated by combining ¹⁹F, ¹H-HOESY NMR spectroscopy in CD₂Cl₂ and a detailed analysis of the Coulomb potential of the cationic fragment through DFT calculations. Two main orientations have been found where the anion locates close to the imidazole ring (*NHC-side*) and close to the olefin (*olefin-side*). The *NHC-side* orientation is always predominant (65–83%) while the exact position of the anion in the *olefin-side* is finely tuned by the nature of olefin substituents. In all cases, the counterion resides far away from the gold site, the latter carrying only a small fraction of the positive charge.

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1. Introduction

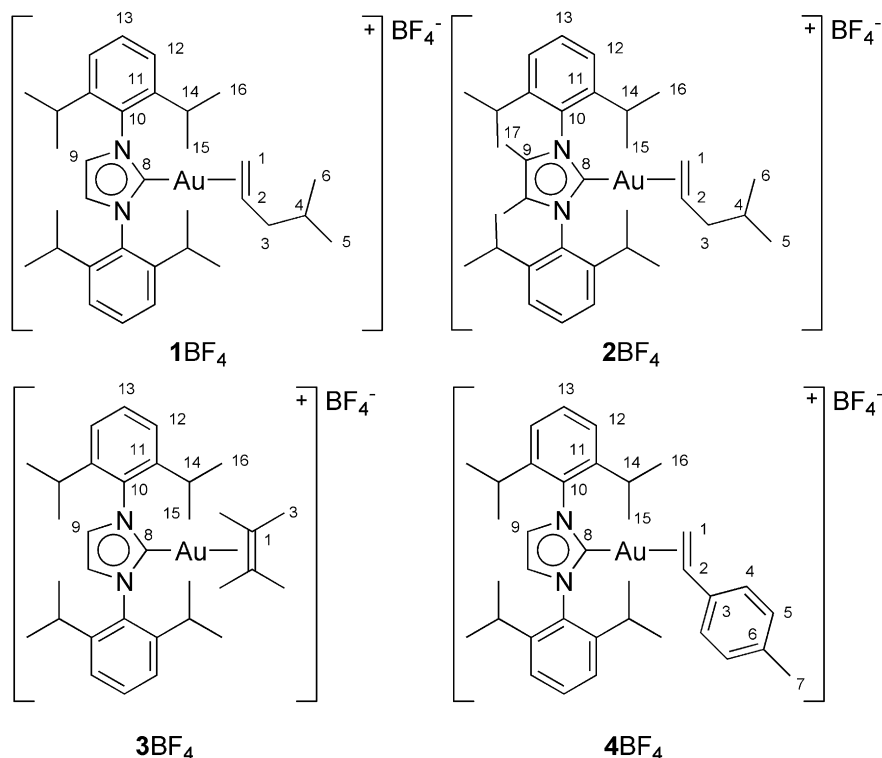
Au(I) compounds have been increasingly used as catalysts in a large variety of reactions [1] including additions of nucleophiles to alkenes, alkynes, allenes, dienes, and other unsaturated substrates [2]. The key intermediate of such catalytic reactions can be formulated as the ion pair [L–Au–S]X, where L is the ancillary ligand (usually a carbene or a phosphine), S is the substrate to be activated and X[−] is a weakly coordinating anion. It is now evident that a proper design of not only L but also the counterion X[−] is necessary in order to improve the catalytic activity [3,4], regioselectivity [5] and even stereo-selectivity [6–8]. A remarkable example of the latter concept has been reported by Toste and co-workers [7a]. By studying the asymmetric hydroalkoxylation of allenes, they found that the utilization of chiral counterions paired with achiral cationic catalysts led to higher *ees* than those obtained with chiral ancillary ligands and achiral counterions [7a].

Despite these well-recognized ion pairing effects [9], the relative anion–cation position(s), that is supposed to be critical in affecting catalytic performances, is often hypothesized basing on rather speculative and indirect arguments, while, in principle, it could be precisely determined basing on interionic NOE (Nuclear Overhauser Effect) NMR measurements [10,11,12,13] possibly integrated

with theoretical calculations [14]. This is partially due to the difficulties of isolating the key intermediates of the catalytic processes. Focusing on gold(I) catalysis, the isolation of [L–Au–S]X is not trivial [15] and has been achieved in a few cases using phosphines [16], N-heterocyclic carbenes (NHCs) [17] and cyclic (alkyl)(amino) carbenes (CAACs) [18] as ancillary ligands and alkenes [19] and alkynes [20] as substrates. Only very recently, some preliminary studies on the interionic structure of [L–Au–S]X have been reported [21,22]. They are based on NOE NMR and DFT investigations. The main result is that the gold center is not the preferred acidic-anchor point for the anion, despite its formal +1 charge, and the exact position of the anion is subtly dependent on the nature of L and S.

Since [L–Au–S]X species are known to be rather stable when L = NHC and S = alkenes, we decided to undertake a systematic investigation of the interionic structure of [(NHC)Au(alkene)]X ion pairs (**1**–4BF₄, Scheme 1) by combining NOE NMR spectroscopy and quantum chemical calculations [23] based on relativistic Density Functional Theory (DFT) and a detailed analysis of the Coulomb potential of the cationic fragment. The results are reported herein. The main goal of our studies is the understanding of how steric and electronic properties of the NHC-ligand and alkene substrate modulate the ion pair structure. This approach has been successfully applied to investigate Pt(II) [24], Pd(II)[25] and Ru(II)[26] ion pairs, revealing, in some cases, clear relationships between the interionic structure and the chemical reactivity and catalytic performance [27].

* Corresponding author. Tel.: +39 75 5855579; fax: +39 75 5855598.
E-mail address: alceo@unipg.it (A. Macchioni).



Scheme 1. NHC gold (I) olefin complexes.

2. Results and discussion

2.1. Synthesis and intramolecular characterization of the complexes

Complexes **1BF₄**, **2BF₄**, **3BF₄** [17b] and **4BF₄** [22] (Scheme 1) have been synthesized by the reaction of AgBF₄ with the neutral precursors [(IPr)Au–Cl] [28] (**5**) and [(^{Me}IPr)Au–Cl] [29] (**6**) and the appropriate alkene in CH₂Cl₂. They have been isolated as white powders, after the removal of AgCl from the reaction mixture (Experimental Section).

The assignment of all ¹H and ¹³C NMR resonances of complexes **1–4BF₄**, which is preliminary to the investigation of the relative anion–cation orientation in the ion pairs, has been carried out by crossing together the information coming from ¹H, ¹³C, ¹H–COSY, ¹H–NOESY, ¹H, ¹³C–HMOC, and ¹H, ¹³C–HMBC NMR experiments. Data are reported in the Experimental Section. **1–4** cations are particularly suitable to individuate preferential anion locations since they have magnetically inequivalent protons, which can be used as “reporters”, well-distributed in almost all the directions of the space. Even the two methyl groups of the isopropyl moieties are inequivalent and can be easily assigned by their selective NOE interactions with olefin and NHC protons (Fig. 1).

Experimental information on the olefin–gold interaction in complexes **1–4BF₄** has been obtained looking at the variation of the ¹H [$\Delta\delta^{1H} = \delta^{1H}(\text{complex}) - \delta^{1H}(\text{free or precursor})$] and, particularly, ¹³C [$\Delta\delta^{13C} = \delta^{13C}(\text{complex}) - \delta^{13C}(\text{free or precursor})$] chemical shifts taking free alkene and the starting neutral precursors **5** and **6** as references (Table 1). Olefin coordination causes a deshielding of the imidazol carbons that is more marked for C8 ($\Delta\delta^{13C} = 4.2/5.5$), directly bounded to gold, than for C9 ($\Delta\delta^{13C}$ about 1.5/2.3) in **1BF₄**, **2BF₄** and **4BF₄** complexes. In the case of **3BF₄** both carbon C8 and C9 are only slightly deshielded by the same value, ca. 1 ppm.

As a consequence of the coordination of the olefin to the metal center, carbons C1 and C2 of **1BF₄**, **2BF₄** and **4BF₄** complexes are

shielded; the effect is more pronounced for C1 ($\Delta\delta^{13C} = -19$ ppm for **1BF₄** and **2BF₄** while $\Delta\delta^{13C} = -28$ ppm for **4BF₄**) than for C2 ($\Delta\delta^{13C} = -4.8, -6.1$ and -9 ppm for **1BF₄**, **2BF₄** and **4BF₄** respectively) indicating an unsymmetrical coordination of the double bond with carbon C1 closer to the metal center [30]. In the case of **3BF₄** carbon C1 is only marginally shielded by about 1 ppm. The observed shifts are consistent with those reported in the literature [17b,17e].

In order to investigate in greater detail the structural aspects and the electronic structure of the complexes, we have carried out DFT calculations on **1⁺**, **2⁺**, **3⁺** and **4⁺**, performing geometry optimizations in CH₂Cl₂ solution (see Experimental Section for technical details). The principal geometrical parameters obtained for these complexes are reported in Table 2. The complete set of optimized coordinates for our complexes are given in the Supplementary information.

The data show, first of all, that the bond distance between Au and C8 is nearly constant (about 2.05 Å) along the series **1⁺–4⁺**, remaining essentially unaffected either by methyl substitution at position 9 of the carbene ring (compare, e.g., **1⁺** and **2⁺**) or by substitutions at the alkene (**1⁺** and **3⁺**). More significant geometrical modifications are found in the alkene moiety itself. In complex **1⁺**, the 4-methyl-1-pentene double bond C1–C2 is longer by about 0.04 Å than in the free system. The dihedral angle H1trans–C1–C2–C3 is reduced from 180° to 159° upon coordination, while H1cis–C1–C2–2 presents a smaller distortion (10°). In particular, our DFT calculations show the Au–C1 distance (2.27 Å) to be significantly shorter (by 0.13 Å) than Au–C2 (2.40 Å), confirming the unsymmetrical coordination of 4-methyl-1-pentene to the gold (I) site. This is consistent also with X-ray structures of similar complexes [17b]. For example, in [(NHC)Au(H₂C=CMe₂)]SbF₆ (**1a** in Table 2) the distance of the disubstituted carbon C2 from gold is about 0.09 Å longer than the Au–C1 distance.

The introduction of two methyl groups in position 9, leading from complex **1⁺** to complex **2⁺**, affects almost negligibly the

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