T-Shaped Intermolecular CH···π (C≡C) Interactions in Chloroform Solvates of Gold(I) Ethyne Complexes

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The molecular structures of the chloroform solvates of the ethynediyl digold complexes NpPh₂P–Au–C≡C–Au–PNpPh₂·2CHCl₃ 1 (Np = naphthyl) and Np₂PhP–Au–C≡C–Au–PNp₂Ph·6CHCl₃ 2 have been determined by X-ray techniques; although none of the compounds have short Au···Au contacts compounds 1 and 2 do exhibit novel C–H···π interactions between the protons of CHCl₃ molecules and the π-electron system of the C≡C bond.

Interactions between acidic C–H groups and the π-system of C≡C bonds have been the subject of a number of theoretical calculations. It was concluded that the most favourable geometry is one in which there is an orthogonal approach of the C–H bond towards the centre of the triple bond,[1] producing a T-shaped geometry. Crystallographic evidence for O–H···π (C≡C) interactions, and in particular for one involving a platinum ethyne complex has recently been reported.[2] However, unambiguous experimental evidence for C–H···π (C≡C) interactions is scarce. Such weak interactions can contribute significantly to the conformation and packing modes of molecular systems and may be important in terms of molecular and chiral recognition.[3] Herein, we report what we believe to be the first examples of C–H···π interactions between chloroform solvate molecules and an ethynyl group. These have been observed in R₃P–Au–C≡C–Au–PR₃·nCHCl₃ and X-ray studies have confirmed the T-shaped geometric preference predicted theoretically for acetylenic systems.

The ethynylgold complexes NpPh₂P–Au–C≡C–Au–PNpPh₂·2CHCl₃ 1, (Np = naphthyl-) and Np₂PhP–Au–C≡C–Au–PNp₂Ph·6CHCl₃ 2 were made using modifications of the synthesis reported by Cross et al.[4] A colloidal suspension of [Au(PR₃)Cl] in ethanol, to which sodium ethoxide had been added was reacted with acetylene. The product is insoluble in ethanol and precipitates from the solution. Crystals were obtained by recrystallisation of the complexes from chloroform and the structures determined using X-ray diffraction.†

The geometry of these ethynylgold complexes resembles a dumbbell with the Au–C≡C–Au bond representing the bar between two large spherical triaryl phosphine end groups. The two halves of complex 1 are related by a crystallographic centre of symmetry at the centre of the ethyne bond. The central C≡C bond has a length of 1.222(16) Å and the Au–C bond 1.983(8) Å. These compare well with the values for Ph₃P–Au–C≡C–Au–PPh₃·2C₆H₆, [1.13(2) Å, 2.02(1) Å, respectively], (m-Tol)₃P–Au–C≡C–Au–P(m-Tol)₃ [1.19(2) Å, 2.002(9) Å, respectively] and (m-Tol)₃P–Au–C≡C–Au–P(m-

Tol)₃·C₆H₆ [1.19(2) Å, 2.00(1) Å, respectively].[5] The P–Au–C≡C unit deviates slightly from linearity with an angle at C(1) of 174(1)° and at Au(1) of 175.8(2)°.

In contrast to many gold(I) compounds, which frequently exhibit short Au–Au intermolecular contacts, the gold atom in 1 is linearly coordinated with no close approaches to the metal centres. However, centrosymmetrically related pairs of chloroform molecules are positioned with their C–H bonds directed orthogonally towards the centre of the ethyne C(1)≡C(1') bond (Fig. 1). The distance of H(41) to the bond centre of the triple bond is 2.42 Å. The H(41)–bond centre–H(41') vector is inclined by 85° to the triple bond and the C–H–centroid angle is 174.3°. The distances of H(41) to C(1) and C(1') are 2.45 and 2.55 Å, respectively. This arrangement is clearly indicative of pairs of C–H···π interactions which are favoured both by the acidic nature of the CHCl₃ protons and by the donation of electrons by the gold atoms into the triple bond. The geometry of the Cl₃CH–π(C≡C) interactions are very close to the optimal T-shaped geometry predicted theoretically. It is noteworthy that the CHCl₃ molecules 'dock' with C≡C in a pairwise fashion which utilises the same π-orbital rather than a pair of orthogonal π-orbitals.

Complex 2 also has a crystallographic symmetry centre which is located in the middle of the C≡C bond. Bond lengths for the Au–C≡C–Au chain are 1.225(34) Å for C≡C and 1.986(17) Å for Au–C; these are comparable to those in 1. The P–Au–C≡C unit is close to linear [178(2)° at C(1) and 176.6(6)° at Au(1)]. As in structure 1 there are no close approaches to the gold centres.

The structure is heavily solvated with six CHCl₃ molecules per gold dimer, four of which are positioned with their C–H bonds directed orthogonally towards the centre of the ethyne bond (Fig. 2). This arrangement is directly analogous to that observed in 1 except that in 2 two pairs of CHCl₃ molecules are

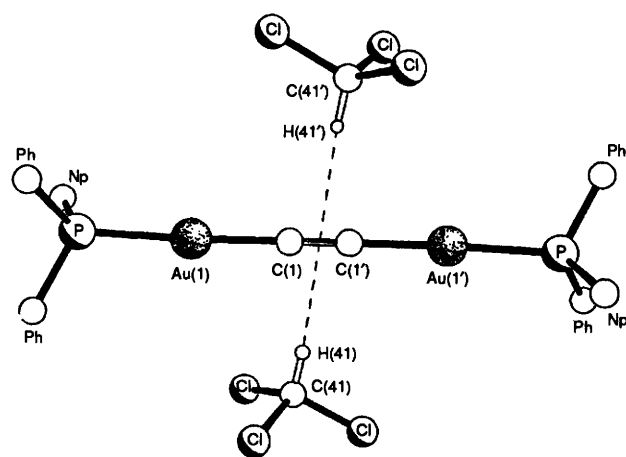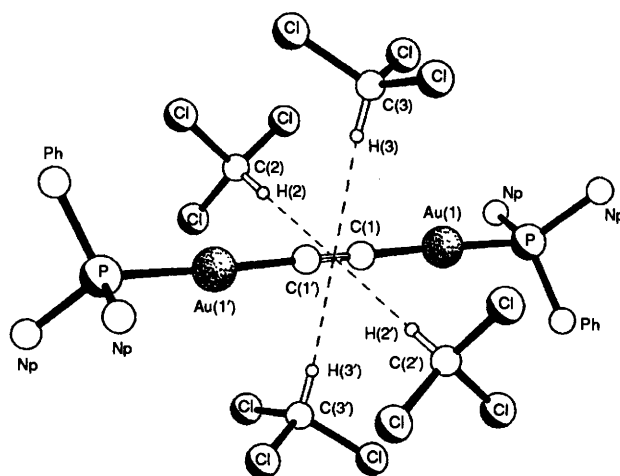Fig. 1 The C–H···π interactions in 1

Fig. 2 Pseudo-octahedral arrangement of CHCl₃ around the C(1)≡C(1') ethyne bond in 2, showing the C–H···π interactions

involved with their CH$\cdots\pi\cdots$HC axes oriented approximately orthogonally with respect to each other. The distances of H(2) and H(3) to the centre of the ethyne bond are 2.58 and 2.50 Å, respectively. The H(2)–H(2') and H(3)–H(3') vectors are inclined by 84.8° and 89.1° to the C(1)≡C(1') bond and by 89.1° to each other thus forming a pseudo-octahedral arrangement. The associated C–H–centroid angles are 166.6° at H(2) and 172.7° at H(3). Intermolecular distances of H(2) to C(1) and C(1') are 2.70 and 2.59 Å, of H(3) to C(1) and C(1') 2.59 and 2.57 Å, respectively. Although the C–H–centroid distances are slightly longer than those observed in 1 they still constitute significant C–H$\cdots\pi$ interactions. As in 1 these interactions are favoured by the acidity of the C–H proton in CHCl$_3$ and by the back donation of electron density from the gold into the C≡C bond. Clearly, the dumbbell shape of the R$_3$P–Au–C≡C–Au–PR$_3$ molecules provides an excellent sheltered cavity favourable for the 'docking' of small molecules with the ethyne bond.

A search of the Cambridge structural database[6] reveals nine other organometallic and organic compounds which display potential C–H$\cdots\pi$ (C≡C) interactions with similar dimensions.‡ However the majority (seven) are intramolecular[7–13] and probably a consequence of steric interactions between bulky ligands attached to the metal centres. In all of these examples the C–H–centroid angles are substantially less than 180° (mean 135°). Two compounds exhibit significant intermolecular C–H$\cdots\pi$ (C≡C) contacts though this was not commented on by the authors. One is a macrocyclic host–guest adduct[14] where there is a short contact between a proton of a pyridine ring and the centre of a triple bond in an adjacent molecule (distance X$\cdots$H = 2.45 Å, angle C–X$\cdots$H = 80.4° and X$\cdots$H–C = 153.9°, where X denotes the centroid of the triple bond). The other is the complex [W(C$_5$H$_5$)(CO)$_2$(C≡CC$_3$H$_5$)(PMe$_3$)]·CH$_2$Cl$_2$[15] which has four hydrogen atoms positioned around the C≡C bond in a pseudo-octahedral arrangement analogous to that in 2 with centroid–C–H angles between 79.4° and 84.8°. Two of the hydrogen atoms are from the methyl groups of the PMe$_3$, one is from the C$_5$H$_5$ ring and the fourth from a CH$_2$Cl$_2$ solvent molecule. The close approach from the proton of the CH$_2$Cl$_2$ to the centre of the C≡C bond (2.55 Å) is particularly noteworthy, but was not discussed in the original paper.

The above results have provided the first examples of C–H$\cdots\pi$ (C≡C) interactions which have the optimal theoretically predicted T-shaped geometry. However the H$\cdots\pi$ distances observed here (2.42–2.58 Å) are significantly shorter than those indicated by the theoretical calculations (>3.02 Å)[16,17] and must therefore be appreciably stronger.

Footnotes

† *Crystal data* for **1**: C$_{46}$H$_{34}$Au$_2$P$_2$·2CHCl$_3$, M = 1281.3, monoclinic, a = 12.241(2), b = 10.932(2), c = 18.100(3) Å, β = 100.21(2)°, U = 2383.7(7) Å^3, space group $P2_1/n$, Z = 2, D_c = 1.785 g cm^{-3}, μ(Cu-Kα) = 153.83 cm^{-1}, final R = 0.037, R_w = 0.041 for 3318 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 116°$].

For **2**: C$_{54}$H$_{38}$Au$_2$P$_2$·6CHCl$_3$, M = 1858.9, triclinic, a = 11.989(6), b = 12.597(4), c = 14.263(4) Å, α = 105.74(2), β = 98.94(2), γ = 75.31(4)°, U = 1731.4(12) Å^3, space group $P\bar{1}$, Z = 1, D_c = 1.783 g cm^{-3}, μ(Cu-Kα) = 149.76 cm^{-1}, final R = 0.061, R_w = 0.065 for 5119 independent observed reflections [$|F_o| > 4\sigma$ ($|F_o|$), $3° \leqslant 2\theta \leqslant 116°$].

Data were measured on a Siemens P4/PC diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structures were solved by the heavy-atom method and refined anisotropically using absorption-corrected data.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The data base search and comparisons between **1** and **2** and the literature structures are based on distances where the C–H bond lengths were normalised to 0.96 Å. The search limits were non-bonded distances C$\cdots$H $\leqslant$ 2.9 Å. Of the hits only entries with X$\cdots$H $\leqslant$ 2.50 Å for intramolecular interactions (X denotes the centre of the C≡C bond), X$\cdots$H $\leqslant$ 2.59 Å for intermolecular interactions, angle α(C–X$\cdots$H): 80° $\leqslant \alpha \leqslant$ 100° were considered to be significant.

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