# Experimental and theoretical evidence of the first Au(I)···Bi(III) interaction†‡

**Eduardo J. Fernández,*[a] Antonio Laguna,*[b] José M. López-de-Luzuriaga,[a] Miguel Monge,[a] Mihai Nema,[ac] M. Elena Olmos,[a] Javier Pérez[a] and Cristian Silvestru[c]**

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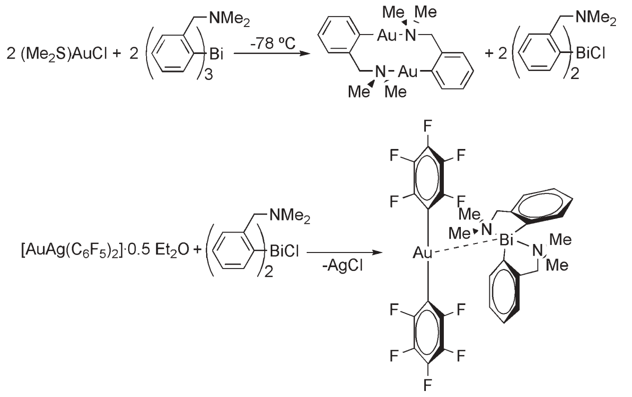
**Complex $[Au(C_6F_5)_2][Bi(C_6H_4CH_2NMe_2\text{-}2)_2]$ 1 displays the first example of an interaction between Au(I) and Bi(III), the nature of which is shown to be consistent with the presence of a high ionic contribution (79%) and a dispersion type (van der Waals) interaction (21%).**

Bonding interactions between Au(I) and other closed-shell metals like $Au^I$ itself (*i.e.* aurophilicity), Ag(I), Cu(I), Hg(I), Tl(I), Pb(II), *etc.* have been studied both from experimental[1] and theoretical[2] viewpoints with regard to the photophysical properties associated with them.[3] In this sense we have taken advantage of an acid–base strategy using basic aurates $[AuR_2]^-$ (R = perhalophenyl group) and Lewis acid metal salts that allows the isolation of unsupported Au(I)···M interactions (M = Ag(I),[4] Cu(I)[5] and Tl(I)[6]). These interactions have been studied by *ab initio* calculations at Hartree–Fock (HF) and at 2nd order Møller–Plesset perturbation theory (MP2) levels and showed a strong ionic character (*ca.* 80% of the interaction) and an additional dispersion-type component (*ca.* 20%). The strong stabilization obtained through the formation of these metallophilic interactions (around 250 kJ mol$^{-1}$) has allowed the stabilization of fairly uncommon structural situations such as, for instance, a $Au^I$–$Tl^I$ loosely bound butterfly cluster,[7] a Au(I)–$Ag_4$(I) square pyramidal disposition in which two anionic fragments attract each other,[8] and the first unsupported Au(I)···Cu(I) interaction.[5]

Although pnicogen N, P and, to a lesser extent, As and Sb-based ligands have been widely used in coordination chemistry, the corresponding bismuth ligands have received much less attention.[9] In this regard, Schmidbaur *et al.* recently reported that tertiary bismuthines ($R_3Bi$) ligands cannot be employed as donor ligands for Au(I) complexes due to rapid transorganylation processes that give rise to organogold compounds (see Scheme 1).[10] In addition, secondary interactions (van der Waals) between bismuth and other elements are known for Bi, C, N, O, S, Se, F, Cl, Br and I and covalent Bi–M bonds with M = Bi, Cr, Mo, W, Fe and Mn in organobismuth compounds.[9] To the best of our knowledge there are no metallophilic interactions of the type Bi(III)···M and, among all possible candidates Au(I) would be the metal of choice since it is able to induce large attractive relativistic effects. In addition, although Au(I) has a high tendency to form metal–metal interactions with other closed-shell metal centres, there have been no Au(I)···M(III) contacts (M = heterometal) described to date. Therefore, the preparation of a complex whose structure displays a Au(I)–Bi(III) bonding interaction would be an interesting challenge.



**Scheme 1** Transorganylation reaction between the tertiary bismuthine $Bi(C_6H_4CH_2NMe_2\text{-}2)_3$ and a Au(I) precursor (top) and transmetalation reaction between the $[AuAg(C_6F_5)_2]_n{\cdot}0.5OEt_2$ precursor and the diorganobismuth compound $[BiCl(C_6H_4CH_2NMe_2\text{-}2)_2]$ (bottom).

An emerging class of compounds is the diorganobismuth(III) halides $R_2BiX$ (R = aryl. X = halogen) since their structural chemistry reflects a Lewis amphoteric character in which there are Lewis acidic sites at the bismuth atoms and Lewis basic centers at the halogen atoms.[9] We wondered whether the $[AuR_2]^-$ Lewis base would play a similar role to the one observed for the halogen atoms, which would facilitate the formation of a Au(I)···Bi(III) bonding interaction. Thus, we have synthesized the complex $[Au(C_6F_5)_2][Bi(C_6H_4CH_2NMe_2\text{-}2)_2]$ **1** through a transmetalation reaction between the $[AuAg(C_6F_5)_2]_n{\cdot}0.5OEt_2$ precursor and the diorganobismuth compound $[BiCl(C_6H_4CH_2NMe_2\text{-}2)_2]$ (Scheme 1).

The crystal structure of **1** was determined by X-ray diffraction studies.§ It shows a gold atom linearly coordinated to two pentafluorophenyl groups with typical Au–C bond distances of 2.028(8) and 2.056(9) Å, while the bismuth center binds a carbon and a nitrogen atom of each $C_6H_4CH_2NMe_2$-2 ligand with Bi–C

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[a] *Departamento de Química, Universidad de La Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC. Complejo Científico-Tecnológico, 26004, Logroño, Spain. E-mail: eduardo.fernandez@dq.unirioja.es; Fax: +34 941 299 621; Tel: +34 941 299642*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009, Zaragoza, Spain. E-mail: alaguna@unizar.es; Fax: +34 976 761187; Tel: +34 976 761185*
[c] *Facultatea de Chimie si Inginerie Chimica, Universitatea Babes-Bolyai, RO-400028, Cluj-Napoca, Romania*

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‡ Dedicated to Professor Pekka Pyykko on the occasion of his 65th birthday.

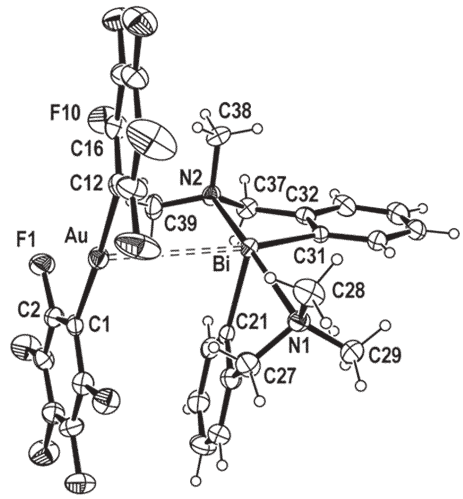

**Fig. 1** Crystal structure of complex **1**. Selected bond lengths and angles: Au–C(1) 2.028(8), Au–C(11) 2.056(9), Bi–C(21) 2.249(8), Bi–C(31) 2.243(8), Bi–N(1) 2.553(7), Bi–N(2) 2.477(7), Bi···Au 3.7284(5), Bi···F5$^{\#1}$ 3.4038 Å, C(1)–Au–C(11) 177.2(3), N(1)–Bi–N(2) 167.7(2), C(31)–Bi–Au 163.55(18), F5$^{\#1}$–Bi–N(1) 167.30(22)°. #1: $x + 1/2$, $y$, $-z + 1/2$.

bond distances (2.249(8) and 2.243(8) Å) of the same order as those in the starting material [BiCl($C_6H_4CH_2NMe_2$-2)$_2$] (2.258 and 2.264(5) Å) (Fig. 1).[11] Both amine groups are strongly coordinated to bismuth with Bi–N distances of 2.477(7) and 2.553(7) Å, the latter being very close to the Bi–N bond length found in the starting complex (Bi–N 2.570(5) Å), where only one of the amine arms is bound to Bi, while the second nitrogen displays only a weak interaction (Bi–N 3.047(5) Å). The most interesting feature of the structure of **1** is the presence of the first Au···Bi interaction described to date, with a Au–Bi distance of 3.7284(5) Å. Although this separation could in principle seem to be too long for a Au···Bi contact, it is worth mentioning that it is difficult to define a van der Waals radius for an element when taking into account the fact that formally E···E non-bonding distances vary a great deal. In the case of bismuth, Bi···M contacts leading to a variety of van der Waals radii for bismuth (including a Bi···Bi interaction as long as 4.8 Å) have been described.[9] It is also worth noting that the presence of additional Bi···F contacts of 3.4038(54) Å between adjacent molecules results in an octahedral environment for bismuth and leads to a monodimensional polymer as shown in Fig. 2. Residual C–H···F contacts between both ionic counterparts are also observed.

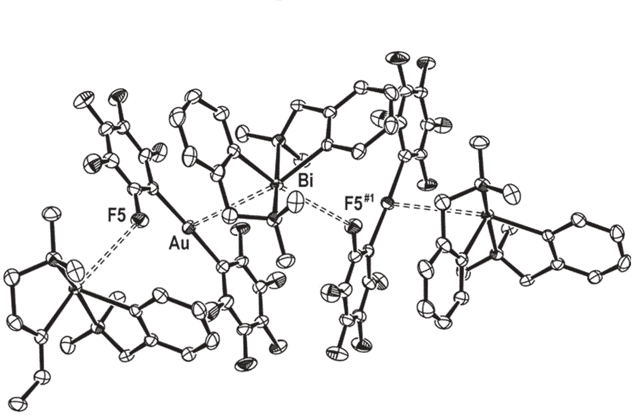

**Fig. 2** Part of the polymeric structure of complex **1**.

To study the experimental Au(I)···Bi(III) interaction we have carried out both DFT and *ab initio* calculations¶ on different models. Thus, in order to reduce computational costs we have carried out DFT-B3LYP calculations on model A [Au($C_6F_5$)$_2$][Bi($C_6H_4CH_2NMe_2$-2)$_2$] that analyze the complete molecular arrangement. This level of theory reproduces the ionic character of the interaction well and includes some of the correlation energy at low cost. Then, in order to analyze the effects governing the aggregation of Au$^{I}$ and Bi$^{III}$ counterparts separately, we have carried out *ab initio* calculations at HF and MP2 levels using two models. Model B consists of two ionic parts, [Au($C_6F_5$)$_2$]$^-$ and the simplified [Bi($CH_3$)$_2$($NH_3$)$_2$]$^+$ (both fully optimized at MP2 level), for which the BSSE-corrected interaction energy is analyzed at different Au···Bi distances at HF and MP2 levels. It is important to note that the only interaction studied between both ionic fragments for model B is the Au(I)···Bi(III) interaction since some weak $F_{ortho}$···H–C contacts observed experimentally have been avoided. Model C consists of the same anionic [Au($C_6F_5$)$_2$]$^-$ unit and the cationic [Bi($CH_3$)$_2$($NMe_2H$)$_2$]$^+$ unit, both optimized at MP2 level. In this model we have included the methyl groups on the amino ligands that represent the experimental situation of the pendant $NMe_2CH_2$ arm of the $C_6H_4CH_2NMe_2$-2 ligand. Thus, the interaction energy (BSSE corrected) is evaluated at different distances taking into account both the Au(I)···Bi(III) interaction and the weak $F_{ortho}$···H–C contacts observed at HF and MP2 levels of theory.

The full optimization of model A at the DFT-B3LYP level of theory leads to an attractive interaction between the ionic units with a Au(I)···Bi(III) distance of 3.57 Å, slightly shorter than the experimental one of 3.72 Å.

The analysis of the Au(I)···Bi(III) interaction at different distances has been carried out using the simplified model B, which only accounts for the metal–metal interaction. The results (the graph in Fig. 3) show that both the HF and MP2 curves are attractive with a minimum corresponding to the equilibrium distance at 3.60 Å (HF) or 3.15 Å (MP2) and a strongly attractive interaction energy of 226 kJ mol$^{-1}$ (HF) or 272 kJ mol$^{-1}$ (MP2). If we assume that the electrostatic component of the interaction is already obtained at HF level since dispersion-type (van der Waals) correlation effects are not included at this level, the dispersion-type component of the interaction can be obtained as the difference between the MP2 and HF interaction energies. Therefore, the Au(I)···Bi(III) interaction is about 83% ionic and 17% dispersion and both effects are attractive since when going from the HF to MP2 level the equilibrium distance is shortened and the interaction energy is strengthened.

For model C we consider both the weak $F_{ortho}$···H–C contacts and one Au···Bi interaction in the analysis. Thus, at HF level the interaction energy is also strongly attractive (240 kJ mol$^{-1}$) at an equilibrium distance of 3.77 Å, meanwhile an interaction energy of 303 kJ mol$^{-1}$ at 3.39 Å is obtained at MP2 level of theory (79% ionic and 21% dispersion interaction). It is noteworthy that although the equilibrium distances are larger for model C than for model B the interaction energies are also larger at both theoretical levels. This trend would be in accordance with the presence of two types of stabilizing interactions as the Au···Bi (ionic + dispersion) that represents around 90% of the whole attraction between ionic

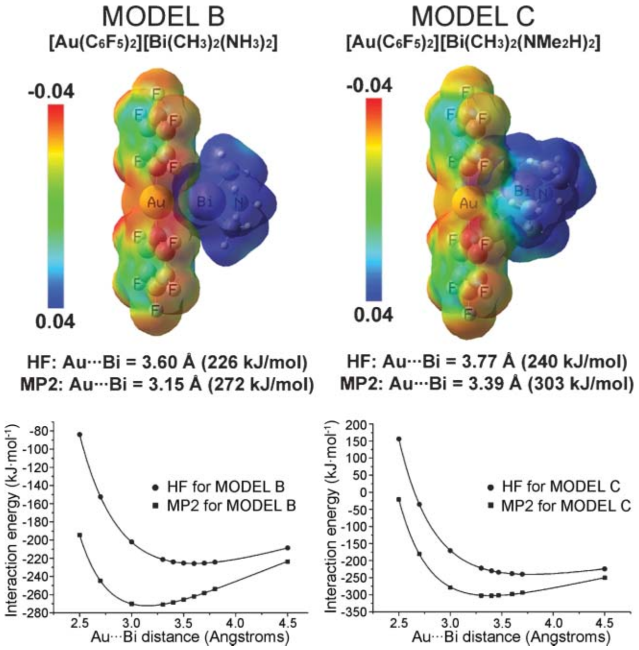

**Fig. 3** Electron density from the total MP2 density (isoval = 0.003) mapped with the electrostatic potential (ESP) for models B and C showing the acid–base ionic interaction nature and interaction energy curves for model B and C at the HF and MP2 levels of theory.

counterparts and the weak F···H–C contacts at 2.61–2.66 Å (ionic + dispersion) that could be considered as residual stabilizing interactions (10%).

Finally, in order to validate our results we have compared them to a purely ionic model. Thus, at first glance one may think that the experimental value of 3.72 Å for a Au(I)···Bi(III) bonding interaction would be quite large. Nevertheless, if one applies a pure Coulombic behavior for two opposite charges at a distance of 3.72 Å an interaction energy of 373.5 kJ mol$^{-1}$ is obtained (80% would be 298 kJ mol$^{-1}$). For model B we have obtained stabilization energies of similar magnitudes (226 (HF) and 272 (MP2) kJ mol$^{-1}$).

In summary, a strong interaction between Au(I) and Bi(III) centers has been characterized both experimental and theoretically. *Ab initio* calculations show that 90% of the interaction between ionic counterparts arises from a strong interaction between Au(I) and Bi(III), of which 79% is of ionic nature and 21% comes from dispersion-type interactions. As observed both experimentally and theoretically, the presence of weak F···H–C contacts also contributes to the stabilization of the structural arrangement. Changes to the perhalophenyl groups bonded to gold(I) and the aryl groups bonded to bismuth(III) are now in progress.

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## Notes and references

§ Crystal data for **1**: $C_{30}H_{24}AuBiF_{10}N_2{\cdot}0.5CH_2Cl_2$, $Mr$ = 1050.92, orthorhombic, *Pbca*, $a$ = 15.6334(2), $b$ = 18.3691(3), $c$ = 23.6070(3) Å, $V$ = 6779.3(2) Å$^3$, $Z$ = 8, $\lambda$ = 0.71073 Å, $\rho$ calcd = 2.059 g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 9.665 mm$^{-1}$, $R1$ = 0.0477, w$R2$ = 0.1097 for 8036 observed reflections ($I > 2\sigma(I)$). Data collection was performed at 223(2)K on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least squares on $F^2$.[12] CCDC 612507. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613365g

¶ Computational methods: All calculations were performed using the Gaussian 03 suite of programs.[13]

DFT-B3LYP calculations:[14] Density functional calculations using the B3LYP functional were carried out for the full optimization of model A. This model represents the complete structural arrangement of the complex $[Au(C_6F_5)_2][Bi(C_6H_4CH_2NMe_2\text{-}2)_2]$ **1**.

HF and MP2 calculations: Hartree–Fock and 2nd order Møller–Plesset perturbation theory[15] calculations were used for the analysis of the interaction energy for models B, $[Au(C_6F_5)_2][Bi(CH_3)_2(NH_3)_2]$ ($C_s$ symmetry) and C, $[Au(C_6F_5)_2][Bi(CH_3)_2(NMe_2H)_2]$ ($C_s$ symmetry). All ionic parts have been previously optimized at the MP2 level of theory: $[Au(C_6F_5)_2]^-$ ($D_{2h}$ symmetry), $[Bi(CH_3)_2(NH_3)_2]$ ($C_{2v}$ symmetry) and $[Bi(CH_3)_2(NMe_2H)_2]$ ($C_2$ symmetry). Thus, HF and MP2 single point calculations were carried out for models B and C at different Au–Bi distances. In the case of model B both the $CH_3$ and $NH_3$ ligands of the bismuth cation have been placed far away from the anionic part in order to evaluate only the Au(I)···Bi(III) interaction (see ESI†) It should be noted that the use of MP2 calculations exaggerates the attraction between interacting metals, leading to intermetallic equilibrium distances shorter than the experimental ones.

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