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Do Aurophilic Interactions Compete against Hydrogen Bonds? Experimental Evidence and Rationalization Based on ab Initio Calculations

Antonio Codina, Eduardo J. Fernández, Peter G. Jones, Antonio Laguna,* José M. López-de-Luzuriaga, Miguel Monge, M. Elena Olmos, Javier Pérez, and Miguel A. Rodríguez

Contribution from the Departamento de Química, Universidad de La Rioja Grupo de Síntesis Química de La Rioja, UA-CSIC, Madre de Dios 51, E-26004 Logroño, Spain, Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, D-38106 Braunschweig, Germany, and Departamento de Química Inorgánica-ICMA, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain

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Abstract: $[M(C_6F_5)\{N(H)=CPh_2\}]$ (M = Ag (**1**) and Au (**2**)) complexes have been synthesized and characterized by X-ray diffraction analysis. Complex **1** shows a ladder-type structure in which two $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ units are linked by a Ag(I)−Ag(I) interaction in an antiparallel disposition. The dimeric units are associated through hydrogen bonds of the type $N-H\cdots F_{ortho}$. On the other hand, gold(I) complex **2** displays discrete dimers also in an antiparallel conformation in which both Au(I)−Au(I) interactions and $N-H\cdots F_{ortho}$ hydrogen bonds appear within the dimeric units. The features of these coexisting interactions have been theoretically studied by ab initio calculations based on four different model systems in order to analyze them separately. The interactions have been analyzed at HF and MP2 levels of theory showing that, in this case, even at larger distances. The Au(I)−Au(I) interaction is stronger than Ag(I)−Ag(I) and that N−H···F hydrogen bonding and Au(I)−Au(I) contacts have a similar strength in the same molecule, which permits a competition between these two structural motifs giving rise to different structural arrangements.

Introduction

Aurophilicity is the tendency of closed-shell gold(I) atoms to aggregate at distances shorter than the sum of the van der Waals radii with an interaction energy that is comparable in strength to hydrogen bonds.[1] It is important to note that this aggregation is an intrinsic effect of the metal centers and is not imposed by the ligand architecture; this has been demonstrated in a large number of experimental and theoretical reported examples[2] and, in principle, gold−gold interactions could be used to control supramolecular structures and their dimensionality.[3]

This effect has prompted a number of research groups to seek similar situations in other closed-shell metal atoms of the same period or even the same group. Thus, *argentophilicity* or even *cuprophilicity* are terms coined to describe the analogous phenomena and have also been theoretically analyzed.[4] These metallophilic interactions are considered to be responsible for some physical properties.[5] Nevertheless, in most cases the formation of polymeric structures[6] or the ligand architecture plays a significant role in the aggregation of the metal centers and there are few examples of unsupported Ag(I)−Ag(I) or Cu(I)−Cu(I) interactions;[7] this may indicate that these are weaker than those of Au(I)−Au(I), leaving the *metallophilicity* concept as a matter for discussion.

In contrast, hydrogen bonds are well established as structural motifs for the construction of molecular networks. These interactions have been widely reviewed by Desiraju showing that several organometallic molecules bind into crystal architectures through intermolecular hydrogen bonds.[8] Indeed, hydrogen bonding is known as the master-key interaction in crystal engineering because it combines directionality with strength. On the other hand, hydrogen bonding has been extensively studied

* Corresponding author. E-mail: alaguna@posta.unizar.es.

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from a theoretical point of view giving a rich source of supplementary information concerning this phenomenon.[9]

Going further, self-assembled supramolecular architectures are currently of great interest. In this context, a number of gold(I)[10] and silver(I)[11] structures in which Au(I)−Au(I) or Ag(I)−Ag(I) interactions coexist with hydrogen bonds have been reported. Thus, the competition between hydrogen bonding and metallophilic interactions in the same crystal structure would lead to a delicate balance between both structural motifs.

Most of the literature regarding metallophilicity and hydrogen bonding has taken the crystallographic or spectroscopic point of view. Although metal−metal interactions and H-bonds have been separately studied by theoretical calculations, as far as we know, there is no report that emphasizes the theoretical comparison between gold−gold interactions and hydrogen bonds coexisting in the same molecule.

In this context, we now report the synthesis and structural characterization of the organometallic compounds $[M(C_6F_5)\{N(H)=CPh_2\}]$ (M = Ag (**1**), Au (**2**)) in which Ag(I)−Ag(I) or Au(I)−Au(I) intermetallic interactions coexist with hydrogen bonds. Ab initio calculations have been carried out in order to explain the role of these structural motifs in the formation of the crystal structures in the solid state.

Experimental Section

General. The reactions were carried out under an argon atmosphere and the solvents were dried by standard methods prior to use. Benzophenoneimine ligand and $AgClO_4$ are commercially available and were purchased from Aldrich. The rest of the starting materials, $NBu_4[Ag(C_6F_5)_2]$,[12] $[Ag(C_6F_5)]$,[12] and $[Au(C_6F_5)(tht)]$,[13] were prepared according to the literature.

Infrared spectra were recorded in the range of 4000−200 cm^{-1} on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer with Nujol mulls between polyethylene sheets. C, H, N analysis was carried out on a EA 1110 CHNS-O microanalyzer. Mass spectra were recorded on a HP59987 A ELECTROSPRAY spectrometer. ^1H and ^{19}F NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external) and $CFCl_3$ (^{19}F, external).

Syntheses. $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ (1): Method a. To a diethyl ether solution of $[Ag(C_6F_5)]$ prepared from $NBu_4[Ag(C_6F_5)_2]$ (0.274 g, 0.4 mmol) and $AgClO_4$ (0.082 g, 0.4 mmol) was added $N(H)=CPh_2$ (0.066 mL, 0.4 mmol). After 30 min of stirring the solvent was removed under reduced pressure and addition of *n*-hexane gave a white precipitate (**1**). The solid was filtered off and washed with *n*-hexane (3 × 5 mL). Yield 68%. **Method b.** To a dichloromethane solution of $NBu_4[Ag(C_6F_5)_2]$ (0.274 g, 0.4 mmol) was added complex $[Ag(N(H)=CPh_2)_2]ClO_4$[14] (0.228 g, 0.4 mmol). After 2 h of stirring the solvent was removed under vacuum and addition of diethyl ether led to the precipitation of a white solid identified as $[NBu_4][ClO_4]$, which was filtered off. The obtained diethyl ether solution was reduced under reduced pressure to ca. 5 mL and addition of *n*-hexane and subsequent filtration gave complex **1** as a white solid. Yield 79%. Anal. Calcd. for $C_{19}H_{11}AgF_5N$: C, 50.02; H, 2.43; N, 3.07. Found: C, 49.61; H, 2.24; N, 2.73. IR: $\nu(C_6F_5)$ at 1498, 943 and 791 cm^{-1}; ν(N−H) at 3308 cm^{-1}. ^{19}F NMR($(CD_3)_2CO$, room temperature, ppm): δ −106.40 (m, 2F, F_o); δ −160.71 (t, 1F, F_p, $^3J(F_p-F_m) = 19.5$ Hz); δ −162.68 (m, 2F, F_m). ^1H NMR($(CD_3)_2CO$, room temperature, ppm): δ 10.48 (s, 1H; N−H); δ 7.58−7.92 (m, 10H; Ph). ES(+) *m*/*z* (%): 288 (5) $[Ag(N(H)=CPh_2)]^+$, 441 (100) $[Ag(N(H)=CPh_2)_2]^+$. ES(−) *m*/*z* (%): 441 (100) $[Ag(C_6F_5)_2]^-$.

$[Au(C_6F_5)\{N(H)=CPh_2\}]$ (2): To a dichloromethane solution of $[Au(C_6F_5)(tht)]$ (0.181 g, 0.4 mmol) was added $N(H)=CPh_2$ (0.066 mL, 0.4 mmol). After 30 min of stirring the solvent was reduced under vacuum to ca. 3 mL and addition of *n*-hexane gave a white precipitate that was filtered off. Yield 86%. Anal. Calcd. for $C_{19}H_{11}AuF_5N$: C, 41.85; H, 2.03; N, 2.36. Found: C, 41.67; H, 2.10; N, 2.36. IR: $\nu(C_6F_5)$ at 1505, 955, and 790 cm^{-1}; ν(N−H) at 3276 cm^{-1}. ^{19}F NMR ($CDCl_3$, room temperature, ppm): δ −116.40 (m, 2F, F_o); δ −159.77 (t, 1F, F_p, $^3J(F_p-F_m) = 20.1$ Hz); δ −163.14 (m, 2F, F_m). ^1H NMR-($CDCl_3$, room temperature, ppm): δ 9.02 (s, 1H; N−H); δ 7.49−8.07 (m, 10H; Ph). ES(+): *m*/*z* (%): 469 (10) $[M - Ph]^+$. ES(−) *m*/*z* (%): 521 (100) $[Au(C_6F_5)_2]^-$.

Crystallography: X-ray Structure Analyses. Siemens P4 (**1**) or Nonius Kappa CCD (**2**) difractometers, ω and ϕ scans, Mo Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator. The structures were refined on F^2 with the program SHELXL-97[15] with anisotropic thermal parameters for all non-hydrogen atoms; the NH hydrogen atom was refined freely in **1**, all other H using a riding model.

Computational Details. The molecular geometries were initially optimized, keeping the intermolecular interactions frozen at large distances, at the DFT level of theory with the B3-LYP functional as implemented in the Gaussian 98 package program.[16] Electron correlation, keeping the core orbitals frozen, was included in further single point calculations at various metal−metal or H···F distances by using Møller−Plesset perturbation theory[17] with second-order corrections

Table 1. Details of Data Collection and Structure Refinement for Complexes **1** and **2**

compd.	**1**	**2**
formula	$C_{19}H_{11}AgF_5N$	$C_{19}H_{11}AuF_5N$
formula weight	456.16	545.25
T (K)	173(2)	293(2)
wavelength (Å)	0.71073	0.71073
crystal size (mm)	0.7 × 0.4 × 0.1	0.25 × 0.23 × 0.20
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	13.5320(16)	13.6780(4)
b (Å)	5.6217(8)	7.6814(3)
c (Å)	21.626(3)	17.4676(5)
β (deg)	95.168(9)	109.807(2)
V (Å^3)	1638.5(4)	1726.68(10)
Z	4	4
D_{calc} (mg/m^3)	1.849	2.097
μ(Mo Kα) (mm^{-1})	1.285	8.752
θ range for data collect. (deg)	3.02 to 25.00	2.93 to 20.81
no. of reflcns. collected	4295	4186
R(int)	0.0172	0.0599
no. of independent reflcns	2884	1806
absorption correction	Ψ-scans	multiscan
data/restraints/parameters	2884/0/239	1806/97/235
goodness-of-fit on F^2	1.032	1.084
final R indices [$I > 2\sigma(I)$] ($R1$, $wR2$)	0.0187, 0.0464	0.0339, 0.08
R indices (all data) ($R1$, $wR2$)	0.0233, 0.0476	0.0487, 0.0865
largest diff. peak and hole (e·Å^{-3})	0.300 and −0.330	0.964 and −1.854

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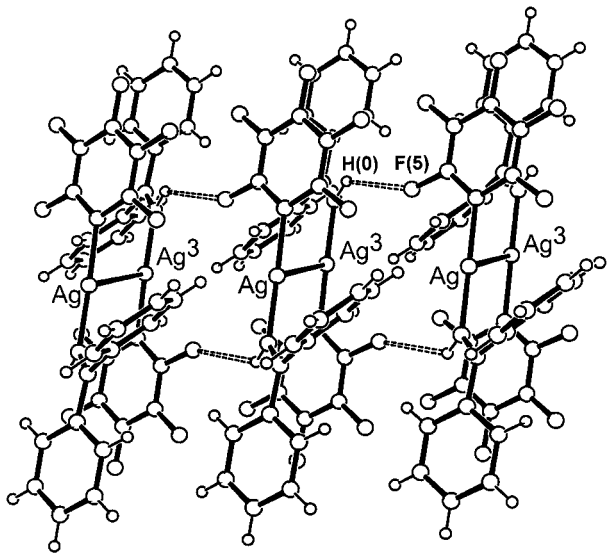

Figure 1. Crystal structure of complex **1**. Selected bond distances [Å] and angles [deg]: N···F(5) 3.186(2), H(0)···F(5) 2.53(2), N−H(0)···F(5) 130(2), Ag^3−Ag#1.

(MP2) using the Turbomole program.[18] The interaction energy at Hartree−Fock (HF) and MP2 levels of theory was obtained according to eq 1:

$$\Delta E = E_{AB}^{(AB)} - E_{A}^{(AB)} - E_{B}^{(AB)} = V(R)$$

a counterpoise correction for the basis-set superposition error (BSSE)[19] on ΔE was thereby performed.

The following basis set combination was employed: for H, C, N, and F, the standard split-valence 6-31G(d) basis set,[20,21] and for Ag and Au, the pseudorelativistic Hay−Wadt small-core effective core potential,[22] where the minimal basis set has been splitted to [341/3111/31] and [341/3111/21], respectively.[23]

Results and Discussion

Complex $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ (**1**) was prepared from $NBu_4[Ag(C_6F_5)_2]$[12] and $[Ag\{N(H)=CPh_2\}_2]ClO_4$[14] in dichloromethane at room temperature or by reacting a freshly prepared solution of "$Ag(C_6F_5)$" in diethyl ether, obtained by the reaction of $NBu_4[Ag(C_6F_5)_2]$ and $AgClO_4$,[12] with an equimolecular amount of the free ligand $N(H)=CPh_2$ (Scheme 1). Compound $[Au(C_6F_5)\{N(H)=CPh_2\}]$ (**2**) was obtained in the reaction between $[Au(C_6F_5)(tht)]$[13] and $N(H)=CPh_2$ in dichloromethane in a 1:1 molar ratio (see Scheme 1).

The crystal structure of complex **1** contains $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ molecules, which are involved in two types of intermolecular interactions (Figure 1). Thus, two $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ units display an Ag(I)−Ag(I) interaction of 3.0668(4) Å in an antiparallel conformation over an inversion center. These dimeric units are associated via four (but only one crystallographically independent) hydrogen bonds of the type N−H···F−C between the −NH groups of the imine ligands and the F_{ortho} of the pentafluorophenyl rings [H(0)···F(5) 2.53(2) Å; N−H(0)···F(5) 130(2)°] leading to a ladder-type structure (see Figure 1 and Table 2).

Scheme 1. Synthesis of $[M(C_6F_5)(N(H)=CPh_2)]$ (M = Ag(**1**), Au(**2**))

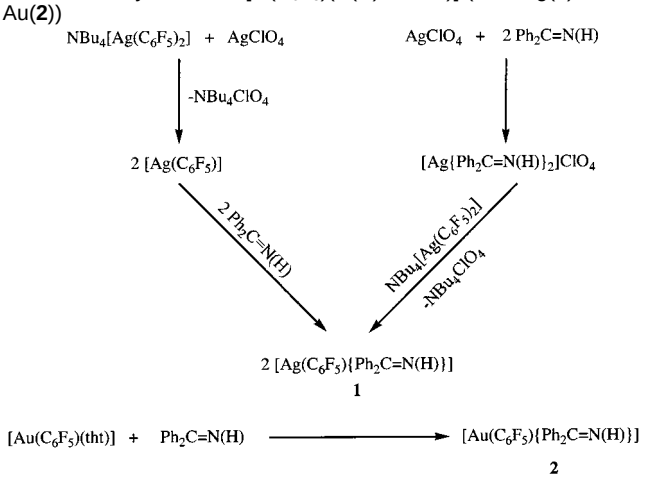

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**[a]

Ag−C(11)	2.091(2)	Ag−N	2.1315(17)
Ag−Ag#1	3.0668(4)	N−C(1)	1.287(3)
C(1)−C(31)	1.483(3)	C(1)−C(21)	1.494(3)
C(11)−Ag−N	171.23(7)	C(11)−Ag−Ag#1	74.68(5)
N−Ag−Ag#1	113.38(5)	C(1)−N-Ag	129.50(15)
N−C(1)−C(31)	118.85(18)	N−C(1)−C(21)	121.85(18)
C(31)−C(1)-C(21)	119.27(17)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x,-y+1,-z$.

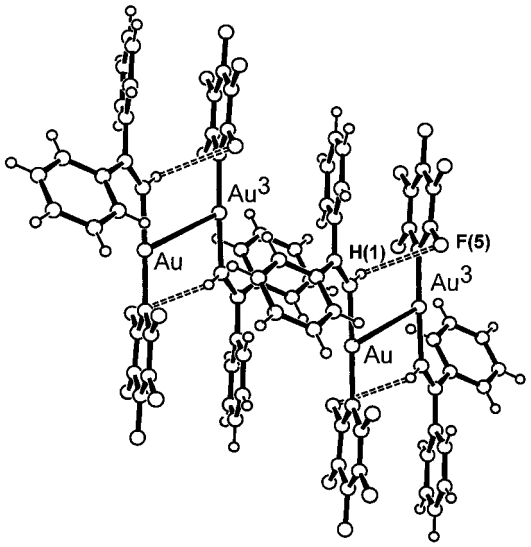

Figure 2. Crystal structure of complex **2**. Selected bond distances [Å] and angles [deg]: N(1)···F(5) 3.225(10), H1···F5 2.75(7), N(1)−H(1)···F(5) 116.1(1), Au^3−Au#1.

In contrast, for $[Au(C_6F_5)\{N(H)=CPh_2\}]$ (**2**) a different type of arrangement is observed (Figure 2). As in the silver compound, two molecules of **2** are associated in an antiparallel disposition. In this case, both the Au(I)−Au(I) interaction (3.5884(7) Å) and N−H···F hydrogen bonds (H(1)···F(5) 2.75 Å; N(1)−H(1)···F(5) 116°) are present within the dimeric units, which are not further associated, thus giving rise to a crystal

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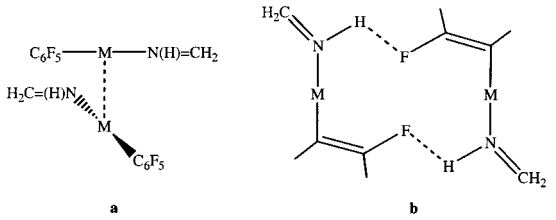
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**[a]

Au(1)−C(1)	2.002(10)	Au(1)−N(1)	2.044(8)
Au(1)−Au(1)#1	3.5884(7)	N(1)−C(7)	1.300(11)
C(7)−C(8)	1.470(13)	C(7)−C(14)	1.477(13)
C(1)−Au(1)−N(1)	178.0(3)	C(1)−Au(1)−Au(1)#1	110.1(2)
N(1)−Au(1)−Au(1)#1	71.9(2)	C(7)−N(1)−Au(1)	132.0(6)
N(1)−C(7)-C(8)	119.6(8)	N(1)−C(7)−C(14)	119.5(8)
C(8)−C(7)-C(14)	120.9(7)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1,-y+2,-z$.

Chart 1. Theoretical Model Systems $[M(C_6F_5)\{N(H)=CH_2\}]_2$ (M = Ag, Au)[a]



[a] In model **a** (perpendicular arrangement of the molecules) intermetallic interactions are analyzed. In model **b** (C_i symmetry) hydrogen bonding is studied.

lattice formed by noninteracting diauracycles (see Figure 2 and Table 3).

The only difference for these complexes arises from the change of the metal centers, with the stoichiometry and the type of ligands remaining unchanged. Thus, the drastic difference between these two crystal structures could be assigned to the different abilities of Ag(I) and Au(I) atoms to form intermetallic interactions.

Closer inspection of the structural parameters for **1** and **2** reveals that **1** displays short Ag(I)−Ag(I) distances and hydrogen bonds with a reasonable directionality while complex **2** shows long Au(I)−Au(I) distances and worse-based on both length and directionality-hydrogen bonds. This analysis would seem paradoxical since gold−gold interactions are expected to be stronger[24] and, in some cases, even shorter[25] than silver−silver ones.

To rationalize these unexpected results, we carried out ab initio calculations to investigate the intermolecular forces that govern these arrangements. First, to keep the computational costs feasible, we have carried out the geometry optimizations for the monomers with the DFT method, which includes some of the correlation energy at low cost. Next, we studied two different model systems (Chart 1) formed by two molecules of the type $[M(C_6F_5)\{N(H)=CH_2\}]$ (M = Ag, Au). The first studies were carried out on the perpendicular $[M(C_6F_5)\{N(H)=CH_2\}]_2$ (M = Ag, Au) dimers shown in Chart 1a. In these cases we studied the nature of Ag(I)−Ag(I) and Au(I)−Au(I) interactions, neglecting with these theoretical models the formation of hydrogen bonds. To account for the metal−metal interactions in dimer units, the DFT method is not the most appropriate and, consistently, MP2 calculations have been employed. The second type of model systems are also $[M(C_6F_5)\{N(H)=CH_2\}]_2$ (M = Ag, Au) dimers (Chart 1b) but in a C_i symmetry with an antiparallel orientation of the molecules. In these models the metals were at large distances, thereby permitting the study of hydrogen bonding interactions in both complexes. Finally, we performed MP2 single-point calculations (BSSE corrected) on the gold(I) model system but, in this case, with the crystal structure disposition studying the stabilization of the molecule when both Au(I)−Au(I) interactions and hydrogen bonds are present at the same time.

In Table 4 we summarize the interaction energies for the corresponding M−M equilibrium distances at HF and MP2 levels (see Figures 3 and 4). These data show some interesting features: (1) as in the experimental structural parameters, the theoretically obtained equilibrium distance for the Ag(I)−Ag(I) interaction is shorter than the Au(I)−Au(I) one; (2) surprisingly, even at larger distance, the gold−gold interaction is roughly twice as stable as silver−silver (20.8 vs 9.5 kJ/mol),

Table 4. Interaction Energies and Corresponding M−M Equilibrium Distances Obtained with the $[M(C_6F_5)\{N(H)=CH_2\}]_2$ Model System in a Perpendicular Disposition at HF and MP2 Levels of Theory

model system	R_e (M···M) (Å)	$V(R_e)$ (kJ/mol)
$[Ag(C_6F_5)\{N(H)=CH_2\}]$[a]		
HF level		
MP2 level	3.6	9.5
$[Au(C_6F_5)\{N(H)=CH_2\}]$[a]		
HF level	4.5	7.6
MP2 level	4.5	20.8

[a] Perpendicular.

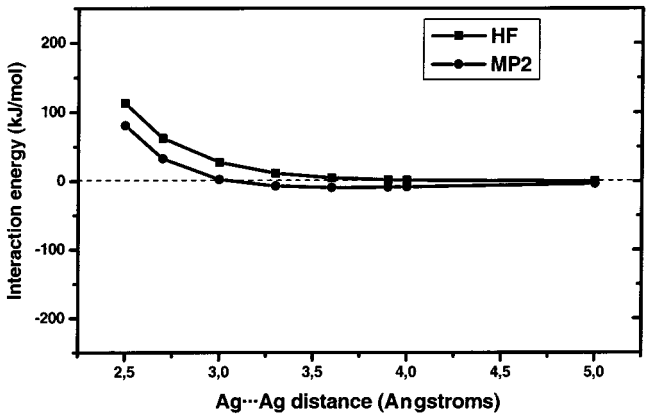


Figure 3. Interaction energy values for the Ag(I)···Ag(I) interaction in complex **1**.

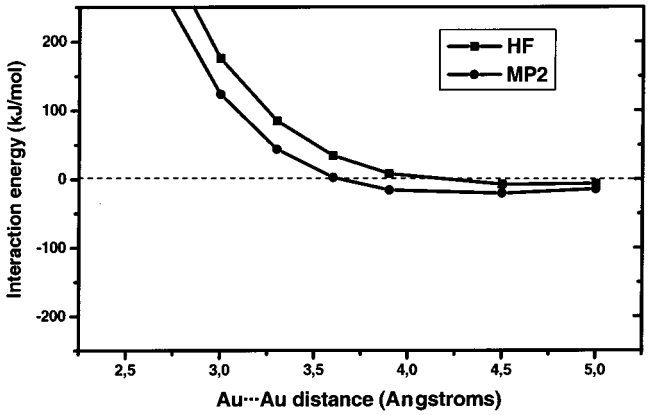


Figure 4. Interaction energy values for the Au(I)···Au(I) interaction in complex **2**.

(24) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3*, 1451.
(25) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 6002.

Table 5. Interaction Energies and Corresponding N−H···F Equilibrium Distances Obtained with the $[M(C_6F_5)\{N(H)=CH_2\}]_2$ Model System in C_i Symmetry at HF and MP2 Levels of Theory

model	R_e (N–H···F) (Å)	$V(R_e)$ (kJ/mol)
$[Ag(C_6F_5)\{N(H)=CH_2\}]$ C_i		
HF level	3.00	38.3
MP2 level	3.00	46.8
$[Au(C_6F_5)\{N(H)=CH_2\}]$ C_i		
HF level	2.50	39.6
MP2 level	2.25	49.6

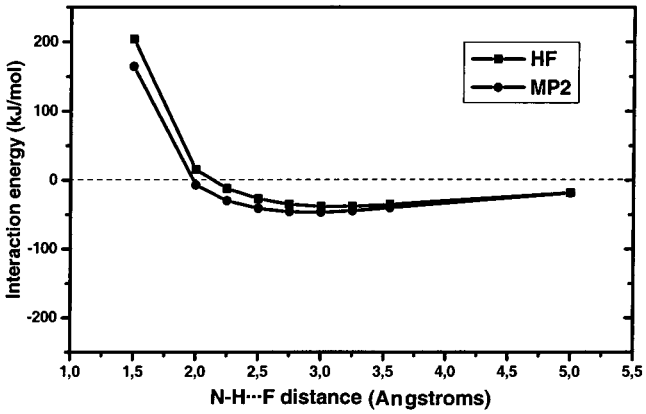


Figure 5. Interaction energy values for the N−H···F interaction in silver complex **1**.

suggesting that, in this case, *aurophilicity* is stronger than *argentophilicity*; (3) finally, it is important to note that correlation effects are responsible for the metallophilic interactions in the Ag complex since an energy minimum is obtained at the MP2 level and repulsion is found at the HF level of theory, where correlation effects are not included. The Au complex displays a stabilization energy of about −7.6 kJ/mol at the HF level that could be attributed to relativistic effects since dispersion-type correlation effects are not included at this level. The stabilization observed at the MP2 level (−20.8 kJ/mol) indicates, as has been previously described,[1c,d,2,4] that both relativistic and correlation effects are responsible for the Au(I)−Au(I) interaction.

The interaction energies for the corresponding hydrogen bonding equilibrium distances at HF and MP2 levels of theory for both silver and gold C_i models are given in Table 5 (see also Figures 5 and 6). It is noteworthy that at the HF level an interaction between H···F pairs appears, but,when correlation effects are included at MP2 level, larger stabilizations are observed, suggesting that hydrogen bonds have an important ionic contribution but that dispersion-type contributions should also be included in their description. Thus, assuming that HF covers mostly electrostatic interactions and the correlation energy (difference between HF and MP2) covers dispersion-type (van der Waals) contributions, for the Ag complex, we observe that 82% of the N−H···F interaction energy (−38.3 kJ/mol) is already obtained at the HF level. Nevertheless, the MP2 level of theory displays an extra stabilization of −8.5 kJ/mol (18%) due to correlation effects, giving rise to a total stabilization energy of −46.8 kJ/mol. A similar trend is obtained for gold complex **2** in which 80% (−39.6 kJ/mol) of the stabilization produced by the hydrogen bonds arises from an

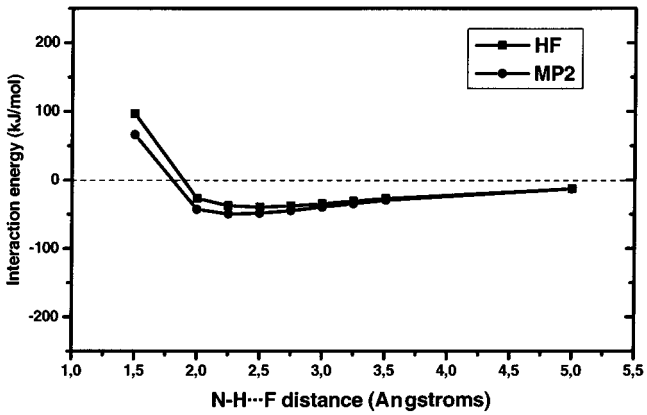


Figure 6. Interaction energy values for the N−H···F interaction in gold complex **2**.

ionic contribution while an extra stabilization from dispersion-type effects (20%, −10.0 kJ/mol) is observed at the MP2 level of theory.

As can be observed in Table 5 the hydrogen bond pairs in each model are energetically comparable at the MP2 level but the distance is shorter for the gold(I) system. However, looking at the experimental structural parameters, the F···H distances are shorter for silver complex **1**. These facts would indicate that in the absence of metallophilic interactions the theoretically predicted hydrogen bonds should be stronger and have a better directionality in the gold(I) compound.

At this point we can ask the following questions: (1) Are our calculations completely wrong? (2) If this is not the case, how can the experimental facts be explained? Regarding the first question, the level of calculation has proved its ability to model this kind of metallophilic interaction in good agreement with experimental results.[25,26] Thus, answering the second question, based on our calculations, the Au(I)−Au(I) interaction (20.8 kJ/mol) is energetically comparable with hydrogen bonding (49.6 kJ/mol calculated for two of them in the dimer model, one is 24.8 kJ/mol), as pointed out by Schmidbaur, but this is not the case for the silver complex (Ag(I)−Ag(I) interaction, 9.5 kJ/mol; single hydrogen bond, 23.4 kJ/mol; see Tables 4 and 5). As a result, *when the Au(I)−Au(I) interaction is present in the same dimeric unit, the hydrogen bonding loses strength and directionality in order to retain the gold−gold interaction*.

Finally, to check that our method is correct, we have tried to validate our theoretically studied model systems. To do this, we have carried out a single-point MP2 calculation (BSSE corrected) on the $[Au(C_6F_5)\{N(H)=CH_2\}]_2$ model system but taking the coordinates obtained in the X-ray crystal structure. This model includes the analysis of N−H···F hydrogen bonds and Au(I)−Au(I) interactions at the same time. We observe a stabilization energy of −42.6 kJ/mol (for the experimental Au−Au distance of 3.59 Å and N−H···F distance of 2.75 Å) when comparing with two free monomer units. On the other hand, a value of −42.2 kJ/mol is derived by adding the energies calculated at the MP2 level for the Au−Au interaction (perpendicular model at a distance of 3.6 Å, see Figure 4) and for the N−H···F hydrogen bonding (C_i antiparallel model at a

(26) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Chem. Eur. J.* **2000**, *6*, 636.

distance of 2.75 Å, see Figure 6). The excellent agreement between these values could validate our theoretical assumptions on the simplified model systems.

Conclusions

The present studies regarding structural parameter analysis and theoretical calculations provide further support for some ideas as conclusions:

(1) Our calculations show that *aurophilicity* should be comparable in strength with hydrogen bonding when both are present in the same system, thus, a competition between these two motifs is responsible for the observed structural arrangement in the crystal structure of $[Au(C_6F_5)(N(H)=CPh_2)]$ (**2**).

(2) *Argentophilicity* does appear, but as a weak interaction between silver(I) centers, so that, in this study, the crystal structure of $[Ag(C_6F_5)\{N(H)=CPh_2\}]$ (**1**) is governed by the presence of hydrogen bonding as a stronger structural motif.

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Supporting Information Available: X-ray crystallographic parameters (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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