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Enhanced Metallophilicity in Metal–Carbene Systems: Stronger Character of Aurophilic Interactions in Solution

Alba Vellé,[a] Luis Rodríguez-Santiago,[b] Mariona Sodupe,[b] and Pablo J. Sanz Miguel*[a]

Abstract: Metallophilicity is an essential concept that builds upon the attraction between closed shell metal ions. We report on the $[M_2(bisNHC)_2]^{2+}$ (M = Au^I, Ag^I; NHC = N-Heterocyclic Carbene) systems, which display almost identical features in solid state. However, in solution the Au_2 cation exhibits a significant higher degree of rigidity owed to the stronger character of the aurophilic interactions. Both Au_2 and Ag_2 cationic constructs are able to accommodate Ag^+ ions via M-M interactions, despite their inherent Coulombic repulsion. When electrostatic repulsion between host and guest is partially diminished, M–M distances are substantially shortened. Quantum chemical calculations estimate intermetallic bond orders up to 0.2. Although at the limit of (or beyond) the van der Waals radii, metallophilic interactions are responsible for their behavior in solution.

The term aurophilicity was established by Schmidbaur to describe attractive interactions between Au^I centers, relying on earlier findings and empirical evidences.[1-6] Since then, substantial efforts have been made in order to understand the nature of such interactions,[7-12] further extended to other M⋯M contacts, such as argentophilicity.[13] In spite of the relatively low stabilization energy, in the rank of hydrogen bonds, numerous examples in which metallophilic interactions efficiently modify chemical and physical properties of metal-based compounds and materials have been described. Such interactions are strong enough to maintain aggregates and host-guest systems,[14-16] induce formation of nanoparticles,[17-20] cooperate in catalysis,[21-23] or to drive metal-directed self-assembly,[24-27] among others. Depending on the nature of solvents, ligands and counterions, binding energies between closed-shell metals have been estimated to be in the range 7–12 $kcalmol^{-1}$ for gold and 5–15 $kcalmol^{-1}$ for silver.[10,13,28,29] Although it could be assumed that aurophilic bonds are stronger than their argentophilic analogues, there is a lack of conclusive evidences to support this fact.[13]

In the past we discussed the effect of strong electron donor ligands on closed-shell metal ions, and postulated that M-M interactions may surpass the van der Waals radii.[30-31] In particular, the cationic $[Ag_2(bisNHC)_2]^{2+}$ system behave as host for Ag^+ ions and revealed argentophilic interactions in solution. As a matter of fact, an intriguing cation-cation inclusion complex was isolated: $\{Ag^+ \subset [Ag_2(bisNHC)_2]^{2+}\}$. Within this arrangement, argentophilicity appears as host-guest stabilization force, overcoming their electrostatic repulsion. One interesting feature of the Ag_2 host concerns its dynamic behavior in solution. Such species coexists in two conformers, namely U and Z (Figure S1), or syn/anti,[32] and exhibit different aggregation properties. Switch between both conformers occurs even at moderate temperatures, and the conversion rate depends on external factors as concentration, temperature and the presence of Ag^+ ions in the media.

In order to compare metallophilic interactions, we report on the study of an analogous system: $[Au_2(bisNHC)_2]^{2+}$. Treatment of $[Ag_2(bisMeOEtIm)_2]^{2+}$ (**1**)[30] (bisMeOEtIm = bis(2-methoxyethyl-1-imidazole)methane) under mild conditions with [Au(tht)Cl] (tht = tetrahydrothiophene) results in the transmetallation product $[Au_2(bisMeOEtIm)_2](BF_4)_2 \cdot CH_3CN$ (**2**). Molecular arrangement of **2** (Figure 1) is similar to that of **1**, bearing in mind the expected differences regarding M–C bonds (Supporting Information).[33] In solid state, cation **2** is folded in U-conformation (open-book), with a dihedral angle of 81.4(1)°. The intramolecular Au1−Au2 distance (3.4382(3) Å) is slightly shorter than the corresponding Ag–Ag separation in **1** (3.4512(5) Å), and a minor variance in the spatial positioning of the side arms is likewise observed.

The ^1H NMR spectra of **2** (Figure 2) reveal a noteworthy difference when compared to that of **1**: Methylene bridging protons (denoted as C31 and C61 in Figure 1) split into two signals, drawing an AB system. These protons are non-equivalent owed to the static environment. In other words, cation **2** exists in solution as a single U-conformation, and no dynamic behavior (U⇋Z conversion) is detected at moderate temperatures. In addition, proton signals corresponding to the *N*-CH_2- groups directly attached to the N-imidazole atoms (C16, C26, C46, C56 in Figure 1) suffer hindered rotation, and therefore build a second order multiplet, instead of a triplet. This fact represents an empirical confirmation of the stronger character of aurophilicity in comparison to argentophilicity. Even though the distance between both gold centers in the solid state (Au1–Au2, 3.4382(3) Å) exceeds two times van der Waals radius of gold (3.32 Å), cation **2** exhibits rigidity in solution owed exclusively to intramolecular Au⋯Au contacts.

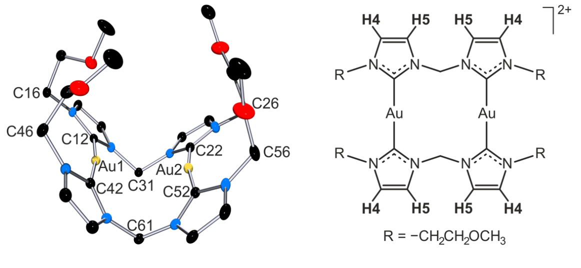

Figure 1. View of cation $[Au_2(bisMeOEtIm)_2]^{2+}$ (**2**) (left), and assignment of ^1H NMR resonances (right).

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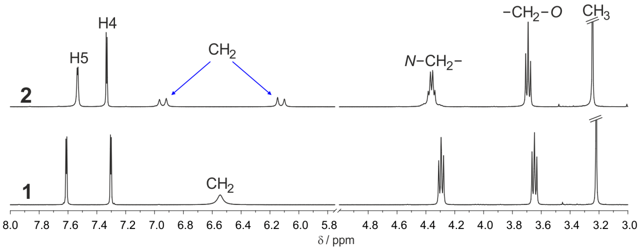

Figure 2. ^{1}H NMR spectra (CD$_3$CN, room temperature, 0.025 M) of [Ag$_2$(bisMeOEtIm)$_2$]$^{2+}$ (**1**)[30] and [Au$_2$(bisMeOEtIm)$_2$]$^{2+}$ (**2**).

We examined by ^{1}H NMR the behavior of cation **2** in solution (CD$_3$CN) at different temperatures (Figure 3). This study revealed that by warming up the sample, methylene bridge signals become wider, and at 340 K they coalesce. The reported cation [Au$_2$(bisNHC)$_2$]$^{2+}$,[34] bearing methyl groups as side arms (R = CH$_3$ in Figure 1), coalesced at 383 K (in DMSO). In contrast, coalescence temperature in **1** was found to occur at 250 K (in CD$_3$CN). The effect of the temperature on the *N*-CH$_2$- signals in **2** is likewise substantial: At low thermal readings, they split forming a dense multiplet, whereas at moderate temperatures (333–348 K), become equivalent appearing as a pseudotriplet, whereas neighboring -CH$_2$-*O* protons show minor variations throughout the temperature range. No significant chemical shift changes are observed. Switch rate constants of **2** were determined by ^{1}H NMR line-shape method, with values ranging from 2.6 s^{-1} (233 K) to 369 s^{-1} (348 K). Enthalpy ($\Delta H^‡$, 5.7±0.5 kcalmol^{-1}) and entropy of activation ($\Delta S^‡$, –31.4±1.7 calK^{-1}mol^{-1}) were estimated using the Eyring analysis.

A further contrast regarding the behavior of **1** and **2** is revealed by concentration-dependent ^{1}H NMR studies (Figure S9). Lowly (0.33×10^{-3} M) and highly (25×10^{-3} M) concentrated samples of cation **2** displayed no significant differences in chemical shifts or shape, including the CH$_2$-bridge resonances, associated to the U⇋Z switch. Thus, in contrast to the flexibility and propensity to form aggregates exhibited by cation **1**, the Au···Au environs of **2** remain virtually unaltered, and we have not found any evidence of intermolecular aurophilicity in solution. It is worth emphasizing here that the lack of U⇋Z interconversion rate is directly associated with the difficulty of separating both gold atoms in the skeleton of **2**, namely, to circumvent their aurophilic attraction.

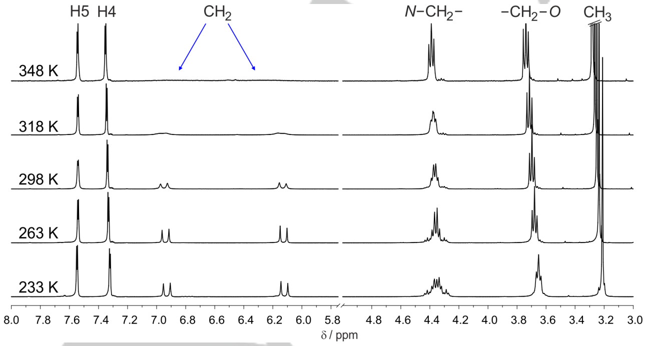

Figure 3. ^{1}H NMR spectra of **2** in CD$_3$CN (0.025 M) recorded at different temperatures (see also the Supporting Information).

The affinity of cation **2** toward Ag$^+$ ions was monitored by ^{1}H NMR spectroscopy. Figure 4 shows the resulting spectra after addition of increasing amounts of AgNO$_3$ to 0.025 M solutions of **2**. There, the chemical shifts of the H5 signals (Δδ = 0.25 ppm) are particularly affected by the presence of silver ions —which is indicative of local heterometallic Ag···Au contacts—, and to a lesser extent, the bridging CH$_2$ protons (Δδ = 0.18 ppm). This experiment was analogous to that performed for **1**,[30] which shows lower affinity toward Ag$^+$ ions, based on the smaller resulting Δδ values (0.11 and 0.05 ppm, respectively). A noteworthy difference is that, in contrast with cation **1**, the conformational U⇋Z switch rate in **2** seems to be not perturbed by the presence of Ag$^+$ ions in solution, even at high concentrations (Supporting Information). At this point, we cannot conclude that heterometallic Ag–Au interactions are stronger than the corresponding Ag–Ag contacts,[35] as the stability of the Au$_2$ platform may significantly influence the host-guest intermetallic connectivity.

By addition of AgBF$_4$ to a solution of **2** in acetonitrile, we isolated [Ag(CH$_3$CN)$_2$ ⊂ Au$_2$(bisMeOEtIm)$_2$](BF$_4$)$_3$·2CH$_3$CN (**3**), which can be considered as a formal modification of cation [Ag(CH$_3$CN)$_2$ ⊂ Ag$_2$(bisMeOEtIm)$_2$]$^{3+}$ (**4**).[30] Cation **3** (Figure 5, left) displays on average longer Au–Ag intermetallic lengths (2.9522(8) and 3.0705(8) Å) than the corresponding Ag–Ag separations in **4** (2.8231(4) and 2.9952(4) Å) (Table 1). Furthermore, separation between both hosting gold ions in **3** (3.8304(7) Å) is considerably lengthier if compared to the precursor **2** (3.4382(3) Å). In essence, cation **3** represents an interesting cation-cation inclusion complex stabilized by ligand-unsupported Au–Ag heterometallophilic interactions.

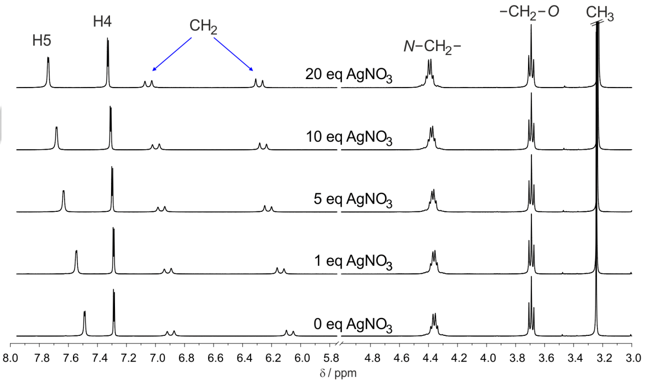

Figure 4. ^{1}H NMR spectra of [Au$_2$(bisMeOEtIm)$_2$]$^{2+}$ (**2**) in CD$_3$CN (0.025 M) with different amounts of AgNO$_3$ added.

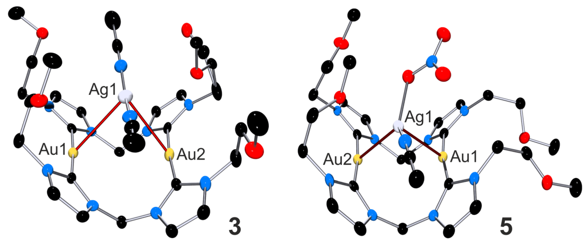

Figure 5. View of the cation-cation host-guest systems **3** and **5**.

Table 1. Intermetallic bond distances [Å] and angles [°] in cations **2**, **3** and **5**.

	2	**3**	**5**
Au1–Ag1	–	3.0705(8)	2.8802(11)
Ag1–Au2	–	2.9522(8)	2.8584(12)
Au1–Au2	3.4382(3)	3.8304(7)	3.5252(14)
Au1–Ag1–Au2	–	78.96(2)	75.80(3)

In a further experiment, we aimed to modify the environment of the guest, and therefore, the nature of the host-guest system. For that, a mixture of tetrabutylammonium nitrate and $AgNO_3$ was added to a solution of **2** in CH_3CN. In principle, this would facilitate the interaction of Ag^+ with nitrate anions. As a result, an intriguing host-guest system was isolated: $[Ag(CH_3CN)(NO_3) \subset Au_2(bisMeOEtIm)_2](NO_3)_2{\cdot}CH_3CN$ (**5**). In this new organization, a nitrate formally replaces one of the acetonitrile ligands (Figure 5, right). The inclusion of nitrate in the coordination sphere of silver provokes a considerable effect in the geometry of the host-guest system: The electrostatic repulsion between host and guest is partially diminished in **5**, and hence the M–M distances are in turn shortened (Table 1). In addition, bond lengths involving the Ag^+ ion are not particularly short, neither with acetonitrile (Ag–N, 2.283(4) Å), nor with nitrate (Ag–O, 2.414(4) Å). Both circumstances may reasonably be interpreted as the result of an important contribution in the stability of the host-guest system of the high affinity of the silver ion toward the Au^I centers, despite of the stabilization offered by the donor ligands. Inclusion of a second NO_3^- in the coordination sphere of silver was not successful, probably due to steric and repulsion reasons.

In order to discard any kind of rigidification imposed by the ligands, we studied our system with the smallest metal of the group (Cu^I), and prepared $[Cu_2(bisMeOEtIm)_2](BF_4)_2$ (**6**). In contrast to the behavior of the Ag_2 and Au_2 complexes, cation **6** proved unstable after contact with water or air, evolving rapidly to the characteristic green patina color. The asymmetric unit of **6** contains two different Cu_2 entities. Intermetallic Cu–Cu distances found in **6** (3.0927(9) and 2.9476(10) Å) are largely shorter than those of **1** and **2**. There are two reported examples of related constructions —same skeleton, different wings— (R = *t*Bu,[36] CH_3[37] in Figure 1), in which the flexibility of the bisNHC ligands allows for Cu–Cu separations of 2.87 and 2.90 Å. These distances are slightly longer than the sum of twice the van der Waals radii for Cu (2.80 Å). This flexibility is also patent in our system: For instance, mutual positioning of the cross-linked imidazole rings attached to Cu3 (83.4(2)°, Figure 6) is nearly perpendicular, whereas the corresponding dihedral angles in **1** and **2** are roughly coplanar. Besides, the ^1H NMR spectrum of **6** (Figure S12) shows the methylene bridge signal at 6.37 ppm as a singlet (rapid U⇋Z conversion). Thus, any constriction imposed by the bisNHC ligands can be definitely ruled out as meaningful stabilization factor. An additional conclusion can be drawn: the rapid U⇋Z conversion observed for the Cu_2 implies that Cu–Cu contacts are weaker than argentophilic interactions.

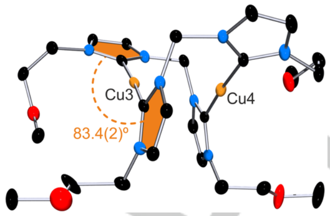

Figure 6. View of a $[Cu_2(bisMeOEtIm)_2]^{2+}$ cation in the asymmetric unit of **6**.

In order to evaluate metallophilic bond strengths, we calculated Wiberg bond indices (WBIs) on compounds **1**–**5**, from experimental X-ray crystal data and from optimized models at the B3LYP-D3 level (see SI for details). The WBI is a measure of the density between atoms A and B and often similar in magnitude to the bond order expected from valence bond theory. Resulting values (Table 2) evidence relatively strong bonding interactions between metals, being the highest WBI values those that correspond to compounds **3** and **4** (0.17), and **5** (0.20).

Table 2. WBIs for metallophilic bonds in cations **1**–**5** at experimental and optimized structures. Bond distances [Å] are shown in square brackets.

	Ag1–Ag2		Ag1–Ag3		Ag2–Ag3	
	exp	opt	exp	opt	exp	opt
1	0.101 [3.451]	0.113 [3.328]	– –	– –	– –	– –
4	0.069 [3.659]	0.080 [3.572]	0.151 [2.995]	0.102 [3.408]	0.174 [2.823]	0.103 [3.404]
	Au1–Au2		**Au1–Ag1**		**Au2–Ag1**	
	exp	opt	exp	opt	exp	opt
2	0.143 [3.438]	0.133 [3.512]	– –	– –	– –	– –
3	0.091 [3.830]	0.106 [3.679]	0.158 [3.071]	0.138 [3.295]	0.171 [2.952]	0.135 [3.261]
5	0.122 [3.525]	0.119 [3.604]	0.204 [2.880]	0.129 [3.312]	0.201 [2.858]	0.128 [3.272]

Existence of metallophilic Au–Au, Ag–Ag and Ag–Au partial bonds in cations **1**–**5** is corroborated by computation, at experimental geometries, of electron delocalization indexes (DI) from atoms in molecules (AIM) theory, and the identification of bond critical points (BCP) between neighboring metals. The delocalization index DI(A,B) measures the average number of electrons delocalized (shared) between atoms A and B. The obtained results suggest the presence in our systems of robust metallophilic interactions with values up to 0.3 (Table 3). It is interesting to point out a particular situation: at this level of theory, both gold atoms in **2** (Au1–Au2, 3.4382(3) Å) exhibit a value of 0.18, while, their separation surpasses the van der Waals limits. A similar situation occurs with cation **1**. This underpins further the existence of interactions beyond the van der Waals sphere.

Table 3. Electron delocalization indexes (DI) and bond critical points (BCP) for metallophilic bonds in cations **1**–**5**.

	Ag1–Ag2		Ag1–Ag3		Ag2–Ag3	
	DI	BCP	DI	BCP	DI	BCP
1	0.12	yes	–	–	–	–
4	0.07	no	0.26	yes	0.18	yes
	Au1–Au2		Au1–Ag1		Au2–Ag1	
	DI	BCP	DI	BCP	DI	BCP
2	0.18	yes	–	–	–	–
3	0.08	no	0.24	yes	0.29	yes
5	0.14	no	0.30	yes	0.28	yes

To get an estimation of the difference between Au–Au and Ag–Au contacts in compounds **1** and **2**, we computed interaction energies of models of **1** and **2** using the spin-component scaling second order Møller–Plesset perturbation method (SCS-MP2) method[38] with extrapolation to complete basis set. This method has proven to produce accurate results for other Au–Au dimers.[29] Models were built deleting C31 and C61 bridges and replacing them by H atoms (see details in the SI). Table 4 shows the computed values for the interaction energies between the two resulting monomers.

Table 4. Computed interaction energies [kcalmol^{-1}] for models of **1** and **2**.

	SCS-MP2 / cc-pVDZ	SCS-MP2 / cc-pVTZ	SCS-MP2 / CBS
1	–3.0	–3.2	–3.9
2	–6.6	–6.6	–7.2

It can be observed that the interaction energy (in absolute value) at the complete basis set limit for **2** is 3.3 kcal mol^{-1} larger than that obtained for **1.** Since the distance between monomers (Au–Au, 3.438 Å; Ag–Ag, 3.451 Å) and dispersion energy (25.2 and 26.0 kcalmol^{-1}, respectively) are very similar in both **1** and **2** complexes the differences between Au and Ag complexes should be attributed to the difference in the metallophilic interaction.

In summary, cation [Au_2(bisMeOEtIm)$_2$]$^{2+}$ (**2**) exhibits considerably stronger metallophilic interactions in solution than its Ag_2 (**1**) analogue. This fact represents an empirical evidence that aurophilicity is stronger than argentophilicity. While cation **1** exhibits two different conformers in solution, with dynamic U⇋Z switch and an aggregation tendency based on intermolecular Ag⋯Ag interactions, cation **2** exists in solution as a single conformer (U) due to the robust Au⋯Au interactions, which prevent to a large degree its conversion to the Z-conformer and intermolecular approaches even at high concentrations. Both **1** and **2** cations act as excellent hosts for Ag$^+$ cations: two unusual cation-cation inclusion complexes were isolated [Ag(CH_3CN)$_2$ $\subset$ M_2(bisMeOEtIm)$_2$]$^{3+}$ (M = Ag, **3**; Au, **4**). Interestingly, when electrostatic repulsions are partially weakened by incorporating a nitrate in the coordination sphere of the guest, metallophilic contacts become stronger and therefore intermetallic Ag⋯Au distances considerably shorter. This is the case of [Ag(CH_3CN)(NO_3) $\subset$ Au_2(bisMeOEtIm)$_2$]$^{2+}$ (**5**). Electron delocalization indexes reveal appreciable metallophilic bond orders. More important, although M–M separations in solid state may lead to the assumption that Au⋯Au and Ag⋯Ag interactions are similar, the solution behavior reveals a stronger character of aurophilicity.

Experimental Section

Experimental details, NMR measurements, and X-ray diffraction data are given in the Supporting Information. CCDC-1954651 (**2**), 1954652 (**3**), 1954653 (**5**), and 1954654 (**6**), contain the crystallographic data.

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Keywords: Aurophilicity • Argentophilicity • Host-Guest Systems • van der Waals radii • Metal-Metal Interactions

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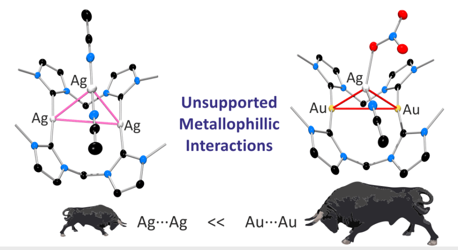
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Au
Ag···Ag << Au···Au

Although they seem to be almost identical in solid state, Au···Au interactions in solution proved to be much stronger than Ag···Ag bonding in our unsupported system. Such interactions take place even beyond the van der Waals limits.

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