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Shorter Argentophilic Interaction than Aurophilic Interaction in a Pair of Dimeric {(NHC)MCl}$_2$ (M = Ag, Au) Complexes Supported over a N/O-Functionalized N-Heterocyclic Carbene (NHC) Ligand

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Synthesis, structure, bonding, and photoluminescence studies of a pair of neutral dimeric silver and gold complexes of a N/O-functionalized N-heterocyclic carbene ligand exhibiting closed-shell d$^{10}\cdots$d^{10} argentophilic and aurophilic interactions, are reported. In particular, dimeric complexes of the type {[1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]MCl}$_2$ [M = Ag (**2**); Au (**3**)] displayed attractive metallophilic interaction in the form of a close ligand-unsupported metal$\cdots$metal contact [3.1970(12) Å in **2**; 3.2042(2) Å in **3**] as observed from X-ray diffraction study and also was further verified by low temperature photoluminescence study at 77 K that showed the characteristic emission [527 nm for **2**; 529 nm for **3**] owing to the metal$\cdots$metal interaction. The nature of the metallophilic interaction in these complexes was further probed using computational studies that estimated the metal$\cdots$metal interaction energy to be 12.8 (**2**) and 8.6 kcal/mol (**3**). Notably, the argentophilic interaction was found to be stronger than the aurophilic interaction in this series of neutral dimeric complexes. The complexes **2** and **3** were synthesized sequentially, with the silver **2** complex prepared by the reaction of the 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride with Ag$_2$O in 66% yield, while the gold **3** complex was obtained by the transmetallation reaction of the silver **2** complex with (SMe$_2$)AuCl in 86% yield.

Introduction

While open-shell species interact to form covalent bonds and the closed-shell ones of opposing electric charges form ionic bonds, the attractive interaction between the closed-shell species of neutral or like (both cationic or anionic) charges,[1] which are expected to repel each other, thus runs counterintuitive to the conventional bonding principles and hence has been of interest lately.[2−4] Such weak attractive closed-shell interaction in transition metals was first witnessed by Schmidbaur in the gold(I) complexes exhibiting close Au$\cdots$Au contacts.[5] Though originally seen in gold(I) and commonly referred to as aurophilicity, similar closed-shell interactions are also shown by other transition metals, such as Cu(I),[6] Ag(I),[7] Tl(I),[8] Pd(II),[9] and Pt(II),[10] and, thus, are more aptly called metallophilic interactions.[2,3] These

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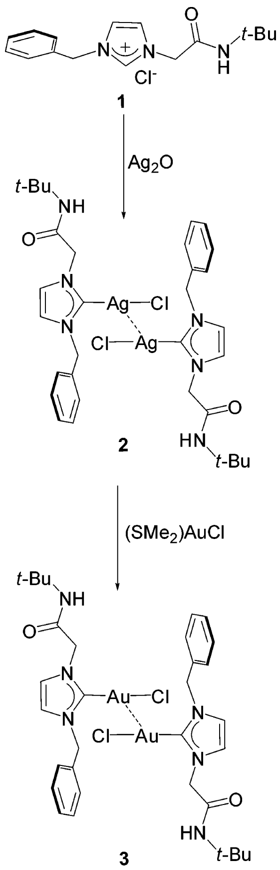
Scheme 1



closed-shell interactions arise primarily due to the dispersive forces[3] and appear weakly attractive in lighter elements, e.g., He_2 ($D_e = 2 \times 10^{-2}$ kcal/mol),[11] but are significantly strengthened by relativistic effects in the heavier elements, such as in gold, for which the Au···Au interaction energy is reported to vary from 6 to 12 kcal/mol and which displays a Au···Au contact of 2.8−3.3 Å.[2−4] For example, in a series of the neutral dimeric $[(PH_3)MCl]_2$ (M = Cu, Ag, Au) complexes, the strength of metallophilic interaction increases by ~50% on going from the lighter to the heavier congener (Cu to Au) along the series due to greater dominance of relativistic effects.[12] The experimental evidence for these closed-shell interactions, particularly for the most commonly observed and also significantly stronger Au···Au interactions, come from a variety of studies that involve X-ray single-crystal diffraction,[13] NMR,[14] and optical spectroscopic measurements.[15] It is noteworthy that the Au···Au interactions are quite strong and are comparable to hydrogen bonding interactions.[2−4] In contrast to aurophilicity, which is more acute due to the predominating relativistic effects, cuprophilicity and argentophilicity have remained relatively obscured primarily due to fewer known examples of such interactions, and that in a sense has contributed to the hindrance in studying these interactions.[2−4]

Significantly, the closed-shell metallophilic interactions are becoming extremely popular in a variety of exciting high-end materials related applications that include rewritable phosphorescent paper for use as color-switchable luminescent materials,[16] phosphorescent organogels for reversible RGB-color switching,[17] luminescence chemosensors,[18] optoelectronic "on−off" devices,[19] etc. In addition, the weak attractive nature of closed-shell metallophilic interaction is often gainfully exploited in building a wide array of extended supramolecular networks in designing engineering materials.[20] Thus, the closed-shell metallophilic interaction by virtue

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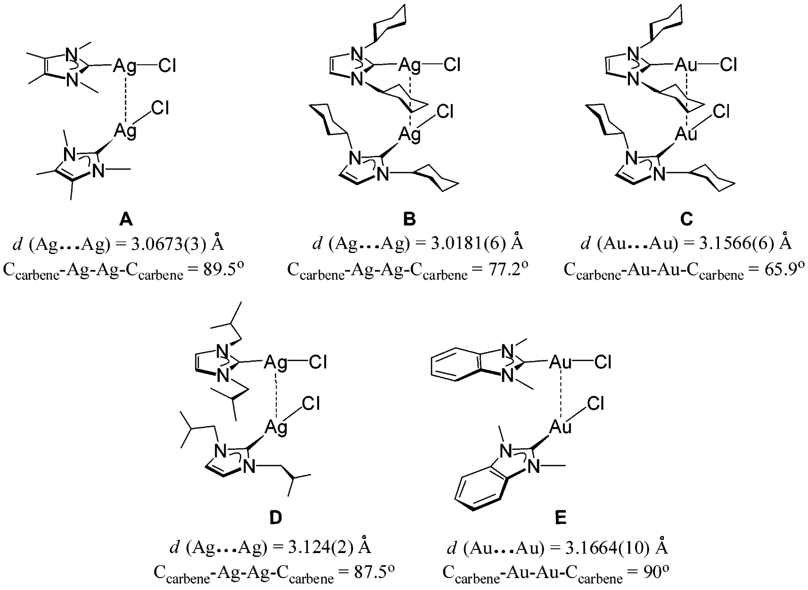


A d (Ag$\cdots$Ag) = 3.0673(3) Å, $C_{carbene}$-Ag-Ag-$C_{carbene}$ = 89.5°

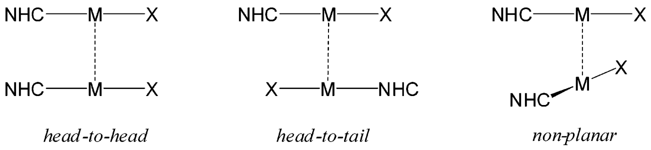
B d (Ag$\cdots$Ag) = 3.0181(6) Å, $C_{carbene}$-Ag-Ag-$C_{carbene}$ = 77.2°

C d (Au$\cdots$Au) = 3.1566(6) Å, $C_{carbene}$-Au-Au-$C_{carbene}$ = 65.9°

D d (Ag$\cdots$Ag) = 3.124(2) Å, $C_{carbene}$-Ag-Ag-$C_{carbene}$ = 87.5°

E d (Au$\cdots$Au) = 3.1664(10) Å, $C_{carbene}$-Au-Au-$C_{carbene}$ = 90°

Figure 1. Representative examples of structurally characterized $\{(NHC)MCl\}_2$ (M = Ag, Au) type dimeric complexes exhibiting metallophilic interactions.



(M = Ag, Au; X = Cl, Br, I)

Figure 2. Possible structural arrangements for $\{(NHC)MX\}_2$ (M = Ag, Au) dimeric type complexes.

of its subtle but significant influence has aroused interest in recent years and has made an impact in frontline application oriented research.

Our interest lies in design and synthesis of transition metal complexes of nonfunctionalized and N/O-functionalized N-heterocyclic carbenes[21] for their potential use in chemical catalysis and biomedical applications.[22] In this regard we have recently reported a series of Pd-based N-heterocyclic carbene (NHC) complexes as efficient catalysts for C−C bond forming reactions[23] and also have employed a variety of Ag−NHC and Au−NHC complexes for producing biodegradable polylactide polymer through ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions.[24,25] During the course of developing the silver and gold chemistry of N-heterocyclic carbenes, we became interested in looking for the existence of these weak closed-shell $d^{10}\cdots d^{10}$ argentophilic[26] and aurophilic[27] interactions in these complexes.

Here in this contribution we report the synthesis, structure, bonding, and photophysical studies of a pair of neutral dimeric silver and gold complexes namely, {[1-(benzyl)-3-(*N-tert*-butylacetamido)imidazol-2-ylidene]MCl}$_2$ [M = Ag (**2**); Au (**3**)] (Scheme 1), which exhibit significant closed-shell metallophilic interactions in the form of a close M$\cdots$M contact observed in the X-ray diffraction studies and as emission peaks arising out of the M$\cdots$M interaction (M = Ag, Au) in the photoluminescence studies. More importantly, contrary to the common notion of metallophilic interaction being maximum for gold among the coinage metals, this pair of dimeric silver **2** and gold **3** complexes display shorter argentophilic interaction than aurophilic interaction.

Results and Discussion

Of the extended and intriguing network of assemblies displayed by metallophilic interactions, the dimeric ones are by far the simplest of all and thus provide an ideal platform for studying such interactions. For example, pioneering studies by Pyykkö,[28] Magnko,[12] Werner,[29] and Kaltsoyannis[30] on simple dimeric $\{(PH_3)MX\}_2$ (M = Cu, Ag, Au, X = halide, pseudohalide) complexes spreading over the entire

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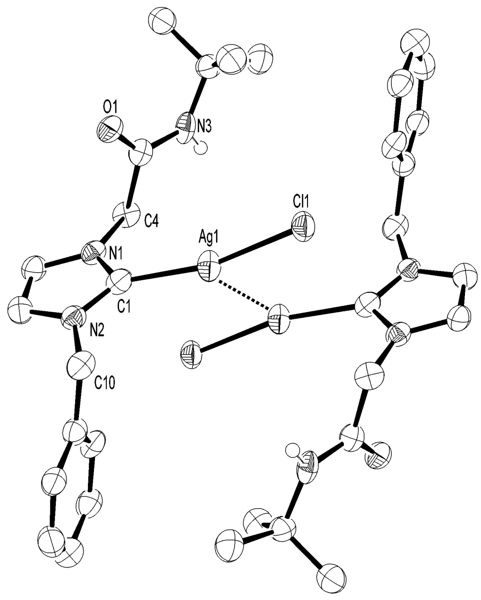

Figure 3. ORTEP of **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Ag−C(1) 2.116(8), Ag−Cl(1) 2.362(2), N(1)−C(1) 1.324(10), N(2)−C(1) 1.368(10), Ag(1)⋯Ag(1) 3.1970(12), C(1)−Ag−Cl(1) 167.3(2), N(2)−C(1)−N(1) 104.9(7).

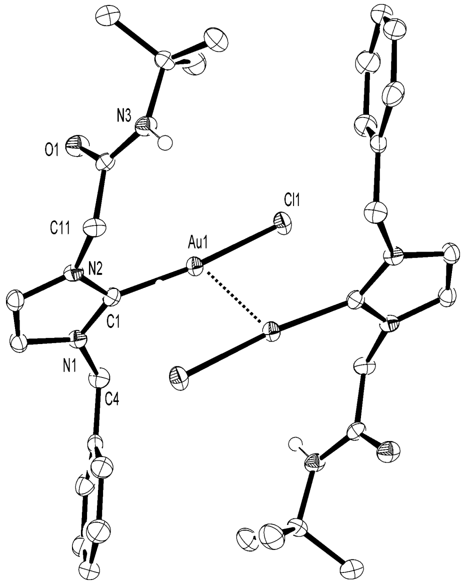

Figure 4. ORTEP of **3** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Au−C(1) 1.983(3), Au−Cl(1) 2.3009(7), N(1)−C(1) 1.346(3), N(2)−C(1) 1.355(3), Au(1)⋯Au(1) 3.2042(2), C(1)−Au−Cl(1) 172.38(8), N(2)−C(1)−N(1) 104.9(2).

Table 1. X-ray Crystallographic Data for **2** and **3**

compound	2	3
lattice	monoclinic	monoclinic
formula	$C_{16}H_{21}AgClN_3O$	$C_{16}H_{21}AuClN_3O$
formula weight	414.68	503.77
space group	$P2_1/c$	$P2_1/c$
a/Å	14.3695(10)	14.3314(2)
b/Å	6.0275(3)	6.16040(10)
c/Å	20.8243(13)	20.1740(3)
α/deg	90.00	90.00
β/deg	103.407(7)	102.760(2)
γ/deg	90.00	90.00
V/Å^3	1754.48(19)	1737.12(5)
Z	4	4
temperature (K)	150(2)	150(2)
radiation (λ, Å)	0.710 73	0.710 73
ρ(calcd), g cm^{-3}	1.570	1.926
μ(Mo Kα), mm^{-1}	1.306	8.627
θ, deg	3.53−25.00	3.18−24.99
no. of data	2939	3053
no. of parameters	202	206
R_1	0.0785	0.0145
wR_2	0.2210	0.0326
GOF	1.055	1.072

past decade provided the much-needed theoretical foundation for the metallophilic interaction. In this regard it is worth mentioning that, of the plethora of extended structures of silver and gold complexes of N-heterocylic carbenes (NHC) that display such metallophilic interactions,[31] the structurally characterized examples of simple dimeric ones of the type {(NHC)MX}$_2$ (M = Ag, Au; X = halide) exhibiting such interactions are conspicuously fewer. Indeed, we are aware of only a handful of {(NHC)MCl}$_2$ (M = Ag, Au) type complexes of silver and gold, namely, {(1,3,4,5-tetramethylimidazol-2-ylidene)AgCl}$_2$ (**A**),[32] {[1,3-bis(cyclohexyl)imidazol-2-ylidene]AgCl}$_2$ (**B**),[32] {[1,3-bis(cyclohexyl)imidazol-2-ylidene]AuCl}$_2$ (**C**),[33,34] {[1,3-bis(*iso*-butyl)imidazol-2-ylidene]AgCl}$_2$ (**D**),[32] and {[1,3-dimethylbenzimidazol-2-ylidene]AuCl}$_2$ (**E**),[35] all of which are supported over nonfunctionalized N-heterocyclic carbene ligands (Figure 1). As our program revolves around designing new N/O-functionalized carbenes and their complexes, we became interested in looking for the existence of such metallophilic interactions in our N/O-functionalized carbene metal complexes, particularly in the silver and gold compounds.

A pair of silver and gold complexes supported over an amido-functionalized N-heterocylic carbene ligand was synthesized with the objective of investigating the influence of metallophilic interactions in these complexes. Specifically, the reaction of the imidazolium chloride salt, 1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazolium chloride[23] **1**, with Ag_2O gave the silver complex {[1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]AgCl}$_2$ **2**, in 66% yield (Scheme 1). The formation of the silver complex **2** proceeded with the deprotonation of the (NC*H*N) proton of imidazolium chloride salt **1** by Ag_2O and was verified by ^{1}H NMR spectroscopy that showed the absence of the characteristic acidic imidazolium (NC*H*N) resonance in the downfield

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(31) For representative examples see: (a) Chiu, P. L.; Chen, C. Y.; Zeng, J. Y.; Lu, C. Y.; Lee, H. M. *J. Organomet. Chem.* **2005**, *690*, 1682−1687. (b) Liu, Q.-X.; Xu, F.-B.; Li, Q.-S.; Zeng, X.-S.; Leng, X.-B.; Chou, Y. L.; Zhang, Z. Z. *Organometallics* **2003**, *22*, 309−314. (c) Chen, W.; Liu, F. *J. Organomet. Chem.* **2003**, *673*, 5−12. (d) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204−5208.

(32) Frémont, P. De; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301−6309.

(33) Baker, M. V.; Barnard, P. J.; Berners-Price, S. J.; Brayshaw, S. K.; Hickey, J. L.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2005**, *690*, 5625−5635.

(34) Another similar dimeric structure of the same compound showing longer Au⋯Au separation of 3.787 Å has also been reported. See: Frémont, P. De; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411−2418.

(35) Wang, H. M. J.; Chen, C. Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216−1223.

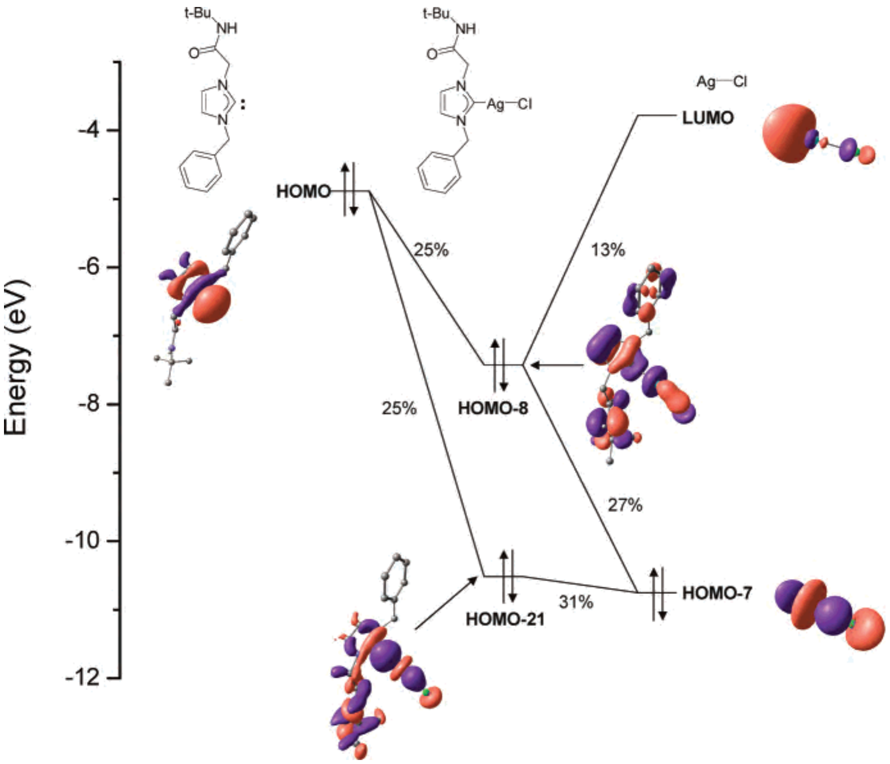
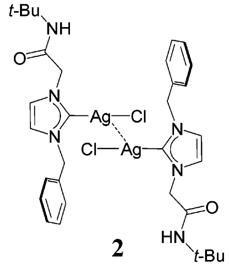
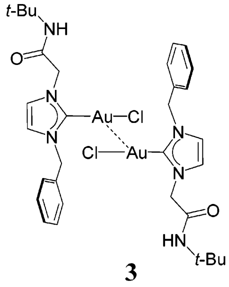


Figure 5. Simplified orbital interaction diagram showing the major contributions of the NHC−silver bond in **2**.

Table 2. Wiberg Indices (Bond Order), M···M Interaction Energies, and M···M Distances for **2** and **3**

Complexes	M•••M distance (Å)	Wiberg Indices (Bond Order) M•••M interaction	M•••M interaction energy (kcal/mol)
 **2**	3.1970(12)	0.216	12.8
 **3**	3.2042(2)	0.259	8.6

region of the spectrum, while the $^{13}C\{^1H\}$ NMR spectrum showed the appearance of the resulting metal bound carbene (N*C*N) peak at a much downfield shifted region at 181.7 ppm. The amido −CONH− moiety appeared at 1681 cm^{-1} in the infrared spectrum.

The gold complex **3** was subsequently synthesized from the silver complex **2** by treatment with $(SMe_2)AuCl$ in 86% yield employing a frequently followed transmetalation route for preparing the transition metal complexes of N-heterocyclic carbene ligands (Scheme 1). In the $^{13}C\{^1H\}$ NMR spectrum, the gold−carbene (N*C*N) resonance appeared at 184.4 ppm, slightly shifted from that observed in the case of the silver complex **2** (181.7 ppm). Overall, the close resemblances of the ^1H and $^{13}C\{^1H\}$ NMR spectral features

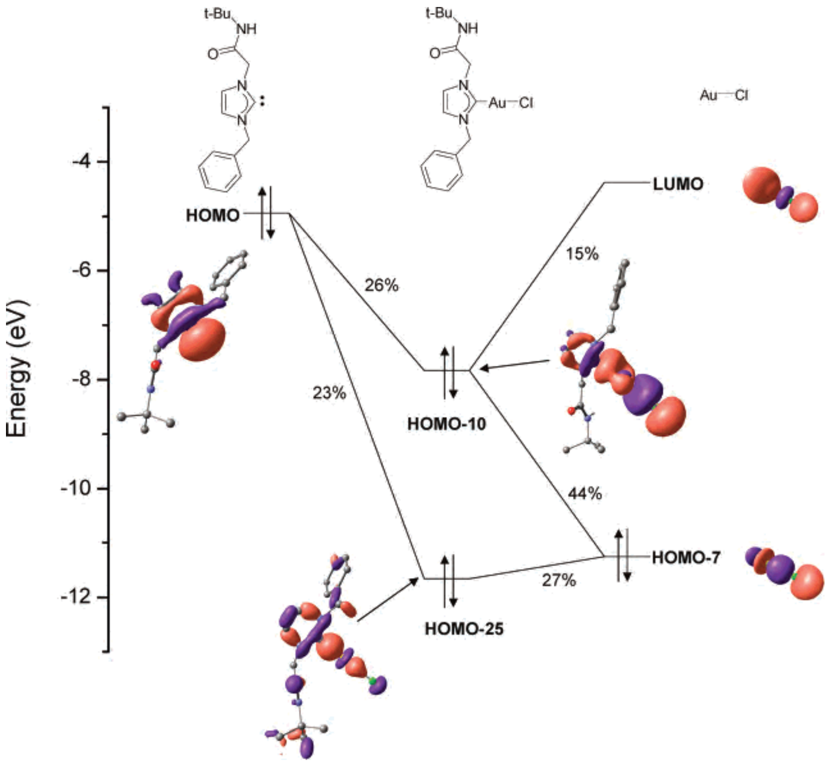


Figure 6. Simplified orbital interaction diagram showing the major contributions of the NHC−gold bond in **3**.

of the gold **3** with the silver **2** complex point toward their structural homology.

The molecular structures of the silver **2** and the gold **3** complexes as determined by X-ray-diffraction studies (Figures 3 and 4) show that they are indeed isostructural. The most remarkable aspect of these complexes is their dimeric nature, {[1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]MCl}$_2$ [M = Ag (**2**); Au (**3**)], that exhibits close M···M contact [M = Ag (**2**) 3.1970(12) Å; Au (**3**) 3.2042(2) Å], thereby indicating the presence of significant closed-shell $d^{10}\cdots d^{10}$ argentophilic and aurophilic interactions. Though numerous N-heterocylic carbene complexes of silver and gold are known, examples of structurally characterized discrete dimeric {(NHC)MX}$_2$ (M = Ag, Au; X = halide) type complexes exhibiting similar metallophilic interactions are surprisingly fewer. Specifically, in the silver **2** and gold **3** complexes, the two monomeric units, [1-(benzyl)-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene]MCl [M = Ag (**2**); Au (**3**)], approach in *head-to-tail* fashion through the central metal atom displaying close M···M contact [M = Ag (**2**) 3.1970(12) Å; Au (**3**) 3.2042(2) Å], which is shorter than twice the van der Waals radii of the corresponding Ag (3.44 Å) and Au (3.32 Å) atoms[36] in the respective complexes. In this regard it is worth mentioning that in the dimeric {(ligand)MX}$_2$ (M = Ag, Au, X = halide) type complexes three possible arrangements, *head-to-tail*, *head-to-head*, and *nonplanar* orientations are often seen (Figure 2). It is worth noting that, of the handful of numbers of structurally characterized dimeric {(NHC)MCl}$_2$ (M = Ag, Au) type complexes that exist,[32,33,35] all of them exhibit nonplanar orientations (Figures 1 and 2), and in that respect the silver **2** and the gold **3** complexes to our knowledge are the only examples of *head-to-tail* orientation. For example, the M···M contact and the $C_{carbene}-M-M-C_{carbene}$ dihedral angle displayed in various structurally characterized dimeric {(NHC)MCl}$_2$ (M = Ag, Au) type complexes are {(1,3,4,5-tetramethylimidazol-2-ylidene)AgCl}$_2$ (**A**) [3.0673(3) Å, 89.5°],[32] {[1,3-bis(cyclohexyl)imidazol-2-ylidene]AgCl}$_2$ (**B**) [3.0181(6) Å, 77.2°],[32] {[1,3-bis(cyclohexyl)imidazol-2-ylidene]AuCl}$_2$ (**C**) [3.1566(6) Å, 65.9°],[33] {[1,3-bis(*iso*-butyl)imidazol-2-ylidene]AgCl}$_2$ (**D**) [3.124(2) Å, 87.5°],[32] and {[1,3-dimethylbenzimidazol-2-ylidene]AuCl}$_2$ (**E**) [3.1664(10) Å, ~90°][35] (Figure 1). Interestingly enough, these complexes supported over nonfunctionalized N-heterocyclic carbene ligands, as in the compounds **A**, **B**, **C**, **D**, and **E** (Figure 1), displayed nonplanar arrangements, while the silver **2** and gold **3** complexes, supported over a N/O-functionalized N-heterocyclic carbene ligand, exhibited *head-to-tail* orientations (Figure 2).

Important is the comparison of the metal···metal contact in the silver **2** [3.1970(12) Å] and gold **3** [3.2042(2) Å] complexes with the other structurally characterized pairs of dimeric {(NHC)MCl}$_2$ (M = Ag, Au) type complexes. Quite interestingly, the only available pair, {[1,3-bis(cyclohexyl)-imidazol-2-ylidene]MCl}$_2$ (M = Ag,[32] Au[33,34]), of the handful of examples of dimeric NHC complexes that exist,[32−35] showed similar a trend displaying shorter Ag···Ag contact [3.0181(6) Å][32] than the Au···Au contact [3.1566(6) Å],[33,34] thereby implying stronger argentophilic than aurophilic

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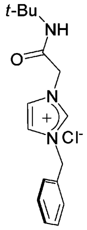
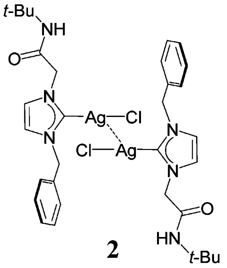
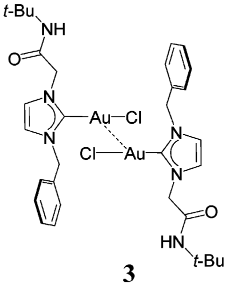
[36] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

Table 3. Absorption and Emission Data for the **1**, **2**, and **3** Complexes

Compounds	λ_{abs}/nm (ε_{max} mm^{3}mol^{-1}cm^{-1})	λ_{em}/nm^a
 **1**	242 (41600)	470, 575
 **2**	244 (54000)	483, 527, 580
 **3**	263 (52700)	427, 529, 575

^{a} Excited at 244 nm and the spectrum recorded in glassy solution of EtOH:MeOH (4:1, v/v) mixture at 77 K.

interaction in this pair of complexes, analogous to what is observed in the pair of silver **2** and gold **3** complexes. However, more examples of structurally characterized pairs of dimeric silver and gold NHC complexes are needed before any generalization of the relative strengths of metallophilic interaction present in these complexes can be made.

The geometry around the metal centers in both these **2** and **3** complexes is off-linear [$\angle$C1$-$Ag1$-$Cl1 = 167.3(2)° (**2**); $\angle$C1$-$Au1$-$Cl1 = 172.38(8)° (**3**)] and is consistent with the linear geometries often observed for two-coordinated d^{10} metals.[37] Quite interestingly, a direct consequence of the strength of a M···M (M = Ag, Au) interaction occurring through the central metal atom (Ag1 in **2** and Au1 in **3**) in these dimeric complexes (Figures 3 and 4) is evidenced by the slightly bent $\angle$C1$-$Ag1$-$Cl1 angle [167.3(2)°] at silver in **2** compared to the more linear $\angle$C1$-$Au1$-$Cl1 angle [172.38(8)°] at gold in **3**, thereby suggesting stronger argentophilic interaction than the aurophilic interaction in this pair of complexes (**2** and **3**). Consistent with larger covalent radii of Ag(I) compared to Au(I),[38] the Ag$-$C$_{carbene}$ distance in **2** [2.116(8) Å] is longer than the corresponding Au$-$C$_{carbene}$ distance in **3** [1.983(3) Å] and compares well with that observed in other N-heterocyclic carbene complexes of silver and gold.[39,40] The two N-substituents, the benzyl and *tert*-butylacetamido, of the NHC ligand on one monomer unit (NHC)MCl (M = Ag, Au) are deposed trans to that of the other in the dimeric {(NHC)MCl}$_2$ [M = Ag (**2**), Au (**3**)] complexes due to obvious steric reasons.

In order to gain a better understanding of the metallophilic interactions present in the silver **2** and gold **3** complexes and also to obtain a deeper insight into the nature of NHC$-$metal interactions in these complexes, detailed density functional theory (DFT) studies were carried out. In particular, the M···M interaction energies and the M···M bond order (Wiberg indices) were computed using the B3LYP/SDD, 6-31G(d) level of theory with the objective of estimating the strength of the closed-shell metallophilic interaction present in these complexes (Table 2). The computed bond order (Wiberg indices) for the M···M interaction in these silver **2** (0.22) and the gold **3** (0.26)

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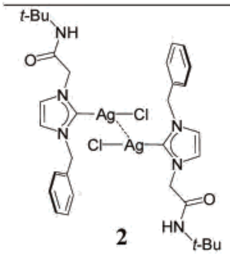
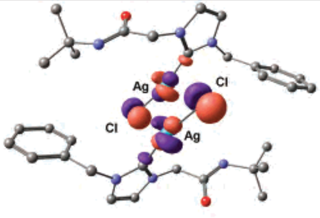
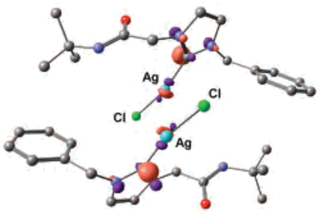
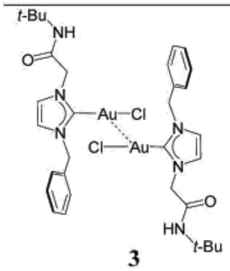
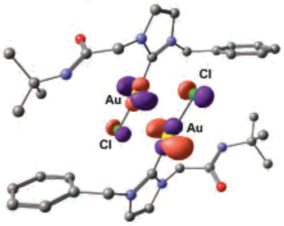
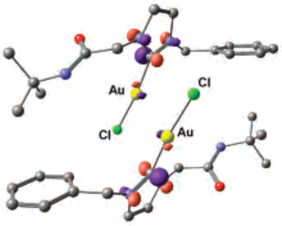
(37) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc.: New York, 1999; pp 1084−1107.

(38) Tripathi, U. M.; Bauer, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 2865−2868.

(39) (a) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978−4008. (b) Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2005**, *83*, 812−825. (c) Díaz-Requejo, M. M.; Pěrez, P. J. *J. Organomet. Chem.* **2005**, *690*, 5441−5450. (d) Arnold, P. L. *Heteroat. Chem.* **2002**, *13*, 534−539. (e) Lee, K. M.; Wang, H. M. J.; Lin, I. J. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2852−2856. (f) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(40) Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2005**, *83*, 812−825.

Table 4. Singlet Excitation Energies Having Maximum Oscillatory Strengths for **2** and **3**[a]

Complexes	HOMO	LUMO	HOMO-LUMO Excitation wavelength (nm)	Oscillatory strength (f)	Type of Transition
 **2**	 Orbital # 182	 Orbital # 183	258	0.1737	4 % MLCT (π→π*)
 **3**	 Orbital # 182	 Orbital # 183	258	0.1737	37 % MLCT (π→π*)

[a] Computed using B3LYP/SDD, 6-31G(d) level of theory.

complexes were approximately on the order of about one-fourth of a single covalent bond. Consistent with the observation of a slightly shorter Ag···Ag contact in **2** [3.1970(12) Å] compared to the corresponding Au···Au contact in **3** [3.2042(2) Å], the M···M interaction energy in the silver **2** complex (12.8 kcal/mol) is estimated to be higher than that in the gold **3** complex (8.6 kcal/mol). Despite being bigger than gold in size,[36,38] the shorter Ag···Ag distance in **2** is indicative of a stronger argentophilic interaction, which becomes all the more interesting given the fact that metallophilic interaction is often perceived to be maximum for gold (aurophilicity) among the coinage metals (Cu, Ag, and Au) due to its greater relativistic effect. However, in this regard, it is worth mentioning that for a series of dimeric {(PH$_3$)MCl}$_2$ (M = Cu, Ag, Au) complexes, O'Grady and Kaltsoyannis[30] have recently shown using several different computational methods that the argentophilic interaction is indeed the strongest among the three coinage metals and the metallophilic interaction need not increase upon going down group 11 (Cu, Ag, Au), as has been the popular belief.[3] The significance of stronger metallophilic interaction in **2** assumes importance when viewed in the backdrop of the fact that genuine examples of argentophilicity are much fewer than those of aurophilicity. Furthermore, the argentophilic interaction in the ligand-unsupported complex **2** becomes very interesting given the fact that majority of the silver complexes that are known to show such metallophilic interactions are primarily ligand assisted while the examples of ligand-unsupported ones are much rarer.

The nature of the NHC−M (M = Ag, Au) interaction in the silver **2** and gold **3** complexes was assessed by post-wave function natural bond orbital (NBO)[41] analysis. Specifically, both the natural charge (Tables S5 and S6) and Mulliken charge (Tables S7 and S8) analyses show that, upon electron donation from the free carbene (NHC) fragment to the metal center in the respective MCl (M = Ag, Au) fragment in **2** and **3**, the positive charge at the metal is significantly reduced. Along the same line, the carbene carbon of the (NHC) fragment in **2** and **3** exhibits an opposite trend with significantly increased positive charge relative to the carbene carbon of the free (NHC) fragment. A similar relationship is also encountered in the case of the monomeric unit (NHC)MCl (M = Ag, Au) of the dimeric silver **2** and gold **3** complexes (Tables S5−S8). The electron donation from the carbene (NHC) fragment to the metal center in the respective MCl (M = Ag, Au) fragment in the **2** and **3** complexes occurs at the unfilled 5s (silver) and 6s (gold) orbitals. Specifically, the occupancy of the respective 5s (silver) and 6s (gold) orbitals in the **2** [5s$^{0.64}$, 4d$^{9.82}$, 5p$^{0.01}$, 7p$^{0.01}$] and **3** [6s$^{0.96}$, 5d$^{9.65}$, 7p$^{0.01}$] complexes are substantially increased in comparison to that in the MCl [M = Ag (5s$^{0.36}$, 4d$^{9.95}$, 5p$^{0.03}$), Au (6s$^{0.65}$, 5d$^{9.86}$, 6p$^{0.02}$)] fragment upon coordination to the latter free carbene (NHC) ligand fragment.

The NHC−metal interaction in the silver **2** and gold **3** complexes was further probed using charge decomposition analysis (CDA), which estimated the [NHC $\xrightarrow{\sigma}$ MCl] (M = Ag in **2**, Au in **3**) donation, designated by *d*, and the [NHC $\xleftarrow{\pi}$ MCl] back donation, designated by *b*, occurring in these

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(41) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

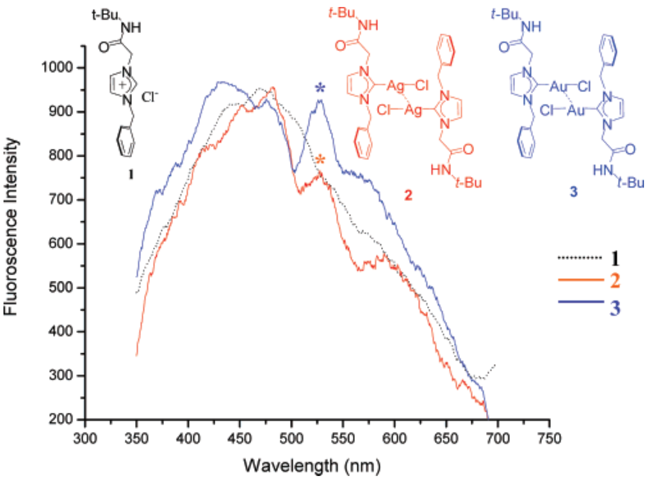

Figure 7. Overlay plot of the emission spectra of the ligand precursor **1**, the silver complex **2**, and the gold complex **3** measured in a glassy solution of EtOH:MeOH (4:1, v/v) mixture at low temperature (77 K) (excitation at 244 nm). The peak due to M···M (M = Ag and Au) interaction is marked by asterisks (∗) in the plot.

complexes. Hence the *d*/*b* ratio, which provides an insight into the extent of forward (σ) and back (π) donations occurring in the NHC−metal bond, suggests a higher [NHC $\xleftarrow{\pi}$ MCl] back donation in the gold **3** complex relative to that in the silver **2** complex, implying a stronger NHC−Au bond in the former. Indeed, the NHC−metal bond dissociation energies D_e(NHC−M) (M = Ag, Au) in the silver **2** and gold **3** complexes as computed using the B3LYP/SDD, 6-31G(d) level of theory for the monomer unit (NHC)MCl (M = Ag, Au) of **2** and **3** show that the NHC−Au bond energy (82.7 kcal/mol) is higher than the NHC−Ag bond energy (62.2 kcal/mol). It is worth noting that the greater back (π) donation usually observed in Au−NHC complexes relative to its Ag counterparts is often ascribed to the dominant relativistic effects of gold that result from the contraction of s and p orbitals while the d and f orbitals remain diffuse.[2a,3b,4a]

Correlation diagrams depicting the contributions of the free carbene (NHC) and the MCl (M = Ag, Au) fragments toward the molecular orbitals (MOs) of the monomer unit (NHC)-MCl (M = Ag, Au) of the silver **2** and the gold **3** complexes provide further understanding of the NHC−metal bonding present in these complexes. The correlation diagram, constructed using AOMix software,[42] revealed that the NHC−metal interaction in the silver **2** and the gold **3** complexes is primarily a three-centered−four-electron interaction with a part of the electron donation from the NHC fragment occurring at the σ^* M−Cl (M = Ag, Au) antibonding orbital (Figures 5 and 6) of the MCl (M = Ag, Au) fragment. In this regard it is worth mentioning that Frenking and coworkers had earlier proposed a similar three-centered−four-electron interaction for the (NHC)MCl (M = Cu, Ag, Au) complexes.[43]

The electronic spectrum of these compounds showed single absorbance peaks for the silver **2** (244 nm) and the gold **3** (263 nm) complexes, like its N-heterocyclic carbene ligand precursor **1** (242 nm) (Table 3). The vertical transitions of the singlet excitation energies obtained using time-dependent DFT calculations at the B3LYP/SDD, 6-31G(d) level of theory suggest that the absorbance bands in the silver and the gold complexes arise due to $\pi \rightarrow \pi^*$ metal−ligand charge transfer (MLCT) processes (Tables 4 and S12−S14 in the Supporting Information). Specifically, the experimentally observed 244 nm band in **2** (computed wavelength 258 nm) and the 263 nm band in **3** (computed wavelength 258 nm) have been assigned to the HOMO → LUMO $\pi \rightarrow \pi^*$ MLCT transitions (Tables 3 and 4) based on comparison of the observed and the computed transitions of comparable intensities and was arrived at by examining the respective absorptivity and oscillator strength values.

The presence of metallophilic interactions in the silver **2** and the gold **3** complexes received further substantiation from the photoluminescence studies carried out in a glassy solution at 77 K that showed emission peaks [527 nm (**2**); 529 nm (**3**)] arising out of the M···M interaction. Specifically, the excitation wavelengths (244 nm) of these complexes were obtained from the respective electronic spectrum. The emission spectrum showed three peaks for the silver **2** (483 nm, 527 nm, 580 nm) and the gold **3** (427 nm, 529 nm 575 nm) complexes (Figure 7). The two high and low energy emissions of the silver **2** (483 nm, 580 nm) and the gold **3** (427 nm, 575 nm) complexes have been assigned to ligand-based transitions based on the emissions of the ligand precursor **1** (Table 3 and Figure 7). In this regard, it is worth mentioning that similar emissions have been reported for several dimeric Ag−NHC and Au−NHC complexes.[35,44,45] It is noteworthy that attempts to seek a direct correlation between the luminescence energy and the crystallographic M···M distance (M = Ag, Au) in silver and gold complexes, at present, is difficult to obtain given the fact that these interactions are not fully understood and also because there exists a variety of examples showing such correlation or inverse correlation or even no correlations between the luminescence energy and the crystallographic M···M distance. In contrast, for metals such as Pt(II), which has long been extensively studied, a clear correlation has been established between the luminescence energy and the Pt(II)···Pt(II) distance.[46,47]

Conclusion

In summary, a pair of neutral dimeric silver and gold complexes, namely, {[1-(benzyl)-3-(*N*-*tert*-butylacetamido)-imidazol-2-ylidene]MCl}$_2$ [M = Ag (**2**); Au (**3**)], displaying

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(42) Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*; York University: Toronto, Canada, 1997; http://www.sg-chem.net/.

(43) (a) Nemcsok, D.; Wichmann, K.; Frenking, G. *Organometallics* **2004**, *23*, 3640−3646. (b) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428−1438.

(44) Wang, H. M. J.; Vasam, C. S.; Tsai, T. Y. R.; Chen, S.-H.; Chang, A. H. H.; Lin, I. J. B. *Organometallics* **2005**, *24*, 486−493.

(45) Catalano, V. J.; Moore, A. L. *Inorg. Chem.* **2005**, *44*, 6558−6566.

(46) (a) Ma, B.; Li, J.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 28−29. (b) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-M.; Li, C.; Hui, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7639−7651.

(47) (a) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87−153. (b) Yersin, H.; Gliemann, G. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 539−559.

strong metallophilic interactions have been synthesized. The shorter M···M contact in the silver **2** complex [3.1970(12) Å] relative to that in the gold **3** complex [3.2042(2) Å], despite the size, as indicated by the covalent as well as van der Waals radii of Ag being bigger than those of Au, indicate a stronger metallophilic interaction in the former. The metal···metal interaction energy in these complexes is estimated to be 12.8 (**2**) and 8.6 kcal/mol (**3**). Both structural and computational studies indicate that in this series of neutral dimeric silver and gold complexes the argentophilic interaction is stronger than the aurophilic interaction. The emission bands at 527 (**2**) and 529 nm (**3**) have been tentatively assigned to originate from the metal···metal interaction based on photoluminescence studies. The nature of the NHC−metal interaction has been examined by DFT studies that revealed that the NHCs are effective σ-donating ligands with relatively weaker π-accepting properties and that the electron donation from the carbene NHC fragment occurs primarily at the σ^* M−Cl (M = Ag, Au) antibonding orbital of the MCl (M = Ag, Au) fragment in these complexes.

Experimental Section

General Procedures. All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. Ag_2O was purchased from SD-fine Chemicals (India) and used without any further purification. $(SMe_2)AuCl$[48] and 1-(benzyl)-3-(*N-tert*-butylacetamido)imidazolium chloride[23a] **1** were synthesized according to reported literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Varian 400 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), and multiplet (m). Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Absorption and fluorescence spectra were recorded on a JASCO V570 spectrophotometer and Perkin-Elmer LS55 spectrofluorimeter, respectively. X-ray diffraction data for **2** and **3** were collected on Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F_2 with SHELXTL (version 6.10).

Synthesis of {[1-(Benzyl)-3-(*N-tert*-butylacetamido)imidazol-2-ylidene]AgCl}$_2$ (2). A mixture of 1-(benzyl)-3-(*N-tert*-butylacetamido)imidazolium chloride (**1**) (1.89 g, 6.15 mmol) and Ag_2O (0.713 g, 3.07 mmol) in dichloromethane (ca. 30 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered and the solvent was removed under vacuum to give the product **2** as a white solid (1.67 g, 66%). Single crystals for X-ray diffraction studies were grown from acetonitrile employing slow-evaporation technique. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.55 (s, 1H, N*H*), 7.38 (br, 1H, NC*H*CHN), 7.23−7.22 (m, 3H, *o*- and *p*-C_6H_5), 7.03−7.02 (br, 2H, *m*-C_6H_5), 6.81 (br, 1H, NCHC*H*N), 5.14 (s, 2H, CH_2), 5.11 (s, 2H, CH_2), 1.37 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 181.7 (N*C*N−Ag), 165.9 (*C*O), 135.4 (*ipso*-C_6H_5), 128.6 (*m*-C_6H_5), 128.0 (*p*-C_6H_5), 127.0 (*o*-C_6H_5), 123.2 (N*C*HCHN), 120.3 (NCH*C*HN), 55.0 (*C*H_2), 54.2 (*C*(CH$_3$)$_3$), 51.2 (*C*H_2), 28.3 (C(*C*H$_3$)$_3$). IR data cm^{-1} KBr pellet: 1681 (s) (ν_{CO}). Anal. Calcd for $C_{16}H_{21}AgClN_3O{\cdot}0.5CH_2Cl_2$: C, 43.35; H, 4.85; N, 9.19. Found: C, 42.77; H, 4.99; N, 9.97.

Synthesis of {[1-(Benzyl)-3-(*N-tert*-butylacetamido)imidazol-2-ylidene]AuCl}$_2$ (3). A mixture of {[1-(benzyl)-3-(*N-tert*-butylacetamido)imidazol-2-ylidene]AgCl}$_2$ (**2**) (0.196 g, 0.475 mmol) and $(SMe_2)AuCl$ (0.139 g, 0.475 mmol) in dichloromethane (ca. 30 mL) was stirred at room temperature for 6 h, when the formation of an off-white AgCl precitpitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to give the product **3** as a white solid (0.205 g, 86%). Single crystals for X-ray diffraction studies were grown from acetonitrile employing slow-evaporation technique. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.96 (s, 1H, N*H*), 7.33 (br, 1H, NC*H*CHN), 7.26−7.24 (m, 3H, *o*- and *p*-C_6H_5), 7.09 (br, 2H, *m*-C_6H_5), 6.86 (br, 1H, NCHC*H*N), 5.30 (s, 2H, CH_2), 5.16 (s, 2H, CH_2), 1.39 (s, 9H, C(CH_3)$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 184.4 (N*C*N−Au), 165.5 (*C*O), 134.9 (*ipso*-C_6H_5), 128.7 (*m*-C_6H_5), 128.2 (*p*-C_6H_5), 127.0 (*o*-C_6H_5), 123.9 (N*C*HCHN), 120.3 (NCH*C*HN), 54.3 (*C*H_2), 53.6 (*C*(CH$_3$)$_3$), 51.3 (*C*H_2), 28.4 (C(*C*H$_3$)$_3$). IR data cm^{-1} KBr pellet: 1679 (s) (ν_{CO}). Anal. Calcd for $C_{16}H_{21}AuClN_3O$: C, 38.15; H, 4.20; N, 8.34. Found: C, 37.89; H, 4.35; N, 8.11.

Computational Methods. Density functional theory calculations were performed on the silver **2** and gold **3** complexes using the Gaussian 03[49] suite of quantum chemical programs. The Becke three-parameter exchange functional in conjunction with Lee−Yang−Parr correlation functional (B3LYP) has been employed in this study.[50,51] The Stuttgart−Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD), is used for silver[52] and gold.[53] All other atoms are treated with the 6-31G(d) basis set.[54]

Inspection of the metal−ligand donor−acceptor interactions was carried out using charge decomposition analysis (CDA).[55] CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.[56] The orbital contributions in the (NHC)MCl (M = Ag, Au) type complexes (**2** and **3**) complexes can be divided into three parts: (i) σ-donation from the [NHC $\xrightarrow{\sigma}$ MCl] fragment, (ii) π-back-donation from the [NHC $\xleftarrow{\pi}$ MCl] fragment, and (iii) a repulsive interaction arising between the occupied MOs of these two fragments.

The CDA calculations were performed using the program AOMix,[42] using the B3LYP/SDD, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix program.[42,57] The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) were

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performed using AOMix-CDA.[58] Natural bond orbital (NBO) analysis was performed using the NBO 3.1 program implemented in the Gaussian 03 package.[41]

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Supporting Information Available: CIF files giving crystallographic data for **2** and **3** and B3LYP coordinates of single-point geometries of **2** and **3** and of their respective monomer units. This material is available free of charge via the Internet at http://pubs.acs.org.

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