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Articles

Gold(I) N-Heterocyclic Carbene and Carbazolate Complexes

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Gold(I) carbene complexes of the type [Au(NHC)Cl], where NHC represents N-heterocyclic carbenes, have been synthesized. Two crystal structures of this type show that the molecules are stacked to form a linear polymer with Au$\cdots$Au interactions. Luminous [Au(NHC)(cbz)] (cbz = carbazolate) were synthesized from [Au(NHC)Cl]. The crystal structure of one of this series indicates that the carbene and cbz rings are coplanar and two molecules are arranged pairwise in a head-to-tail fashion. While all the compounds prepared exhibit high-energy emission bands at $\sim$400 nm, [Au(NHC)Cl] complexes display additional low-energy emission bands at 580−650 nm, which are attributed to Au-centered transitions involving Au$\cdots$Au interactions. On the other hand, the low-energy emission bands of the [Au(NHC)(cbz)] complexes, which appear at 584−592 nm with fine structures, are likely to arise from the transitions involving mainly carbazolate tuned by Au, as also suggested by the density functional calculations. Crystal structures of Au(I)-dicarbenes are also reported.

Introduction

Since the first stable N-heterocyclic carbene (NHC) was isolated in 1991,[1] tremendous efforts have been made to develop their metallo-NHC derivatives[2] due to their role as an alternative to and extension of the widely used phosphines. The powerful σ-donating ability of NHCs allows them to form strong bonds with metal centers of both high and low oxidation states.[3] Manipulation of their electronic and steric characters can be easily achieved via N-functionalization.[4]

Previously we reported the facile synthesis of benzimidazol-2-ylidene-derived NHC complexes of gold.[5] In our continuing effort regarding the synthesis of gold(I) carbene complexes (Au(I)-NHCs), in this report we describe the synthesis of imidazole- and triazole-derived NHC complexes of Au(I). One of our objectives is to generalize the preparation method of [Au(NHC)(halide)], which are useful starting materials for the synthesis of Au(I)-NHC-containing compounds. Although medicinal applications of Au(I) complexes with phosphine and thiolate cores have long been recognized,[6] a report on the antimitochondrial, antitumor, and antimicrobial activities of Au(I)-NHCs has not appeared until fairly recently.[7] Most importantly, the catalytic activity of Au(I) compounds including Au(I)-NHCs has

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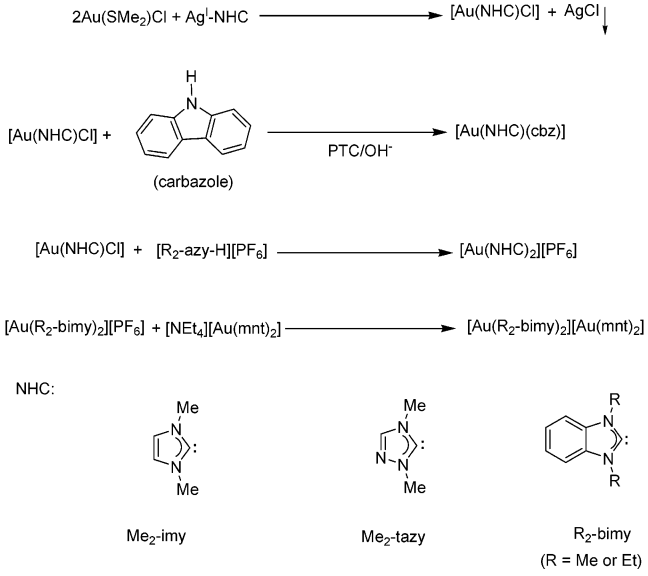
also been realized.[8] The easy access of [Au(NHC)(halide)] is expected to project an interest and potential significance in the study of these subjects. Another objective is to study the photophysical properties of Au(I)-NHCs. Au(I) complexes, especially the Au(I)-phosphine complexes, frequently display strong photoluminescence. In many cases the luminescence is associated with the formation of weak but significant aurophilic interactions between Au(I) centers.[9] In view of the analogy between NHCs and phosphines, Au(I)-NHCs should manifest rich photophysical behaviors. It is our intention to study the photophysical behavior of Au(I)-NHC complexes in the presence of carbazole. Carbazole is recognized as one of the best chromophoric components in organic luminous and optical materials and is known to have good hole-transporting properties.[10] However, only a limited number of metal complexes of carbazolate have been reported[11] thus far. The carbazolate anion (cbz) is therefore incorporated into the Au(I)-NHCs to obtain [Au(NHC)(cbz)] compounds; the combination of NHCs with carbazoles in Au(I) complexes is expected to bring interesting photoelectronic properties.

In the present work, X-ray crystallography, NMR, and electronic spectroscopies are used in scrutinizing the properties of the Au(I) complexes synthesized; ab initio electronic structure density functional theory calculations are performed to elucidate the nature of the optical transitions of [Au(NHC)(cbz)].

Results and Discussion

Synthesis. Representations of the synthetic reactions and the abbreviations of NHCs are outlined in Scheme 1, where the NHCs, imidazol-2-ylidene, triazol-2-ylidene, and benzimidazol-2-ylidene are designated as imy, tazy, and bimy, respectively.

Scheme 1. Synthesis of [Au(NHC)Cl] and the Corresponding Derivatives



Me_2-imy : 1, 3-dimethylimidazol-2-ylidene
Me_2-tazy : 1, 3-dimethyltriazol-2-ylidene
R_2-bimy : 1, 3-dimethyl (or) 1, 3-diethylbenzimidazol-2-ylidene
R_2-azy-H : 1, 3-dimethyl (or) 1, 3-diethyl azolium
mnt : maleonitriledithiolate

While the studies of [Au(Me_2-bimy)Cl] and [Au(Et_2-bimy)Cl] were reported earlier by us,[5] the two new compounds, [Au(Me_2-imy)Cl] and [Au(Me_2-tazy)Cl], were synthesized from the corresponding Ag(I)-NHCs by the carbene-transfer technique.[5,12,13] Addition of an equal molar ratio of Au(SMe_2)Cl to the respective Ag(I)-NHC readily gave the desired [Au(NHC)Cl] product in high yield. The advantages of this method are that no exclusion of air and moisture and no additional bases are required. To synthesize [Au(NHC)(cbz)] complexes, [Au(NHC)Cl] was reacted with carbazole (cbz-H) in 1:1 ratio under basic phase-transfer catalysis conditions. A cationic dicarbene-gold complex, [$Au(NHC)_2$][PF_6], was isolated from [Au(NHC)Cl] in acetone by reacting with an azolium salt of [PF_6]. For the synthesis of mixed Au(I)−Au(III) NHC compounds, [Au(R_2-bimy)$_2$][PF_6] (R = Me, Et) were treated with [(NEt_4)][$Au(mnt)_2$] (mnt = maleonitriledithiolate) to give brown [Au^I(R_2-bimy)$_2$][$Au^{III}(mnt)_2$].

X-ray Crystallography. Six Au(I)-NHC compounds, [Au(Me_2-imy)Cl], [Au(Me_2-tazy)Cl], [Au(Me_2-imy)(cbz)], [Au(Me_2-imy)$_2$][PF_6], [Au(Et_2-bimy)$_2$][PF_6], and [Au(Et_2-bimy)$_2$][$Au(mnt)_2$], have been characterized by X-ray diffraction. Except for [Au(Me2-tazy)Cl], the crystal data and experimental details are given in Tables 1 and 2.

[Au(Me_2-imy)Cl]. Crystals of [Au(Me_2-imy)Cl] were obtained by recrystallization from dichloromethane/hexane. The ORTEP drawing is shown in Figure 1a. The coordination of the Au(I) center is almost linear, with the C(1)−Au−Cl angle being 178.8(3)°. The Au−C bond distance of 1.979(11) Å is comparable with other known Au(I)−NHC linkages.[5,13,14] The Au−Cl bond of 2.288(3) Å is longer than the 2.257(2) Å in $AuCl_2^-$,[15] a conse-

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Table 1. Crystallographic Data for Au(I)-NHC Complexes

	Au(Me_2-imy)Cl	Au(Me_2-imy)(cbz)	Au(Me_2-bimy)$_2$(PF_6)
formula	$C_5H_8Au\ Cl\ N_2$	$C_{17}H_{16}AuN_3PF_6$	$C_{18}H_{20}AuN_4$
fw	328.55	459.29	610.30
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$C1_2/c$	$C1_2/c$
a, Å	14.8881(13)	20.8129(15)	11.636(10)
b, Å	6.9587(6)	11.4130(8)	10.827(20)
c, Å	15.4139(14)	15.5130(11)	17.177(15)
α, deg	90.00	90.00	90.00
β, deg	90.00	120.47(10)	99.42(5)
γ, deg	90.00	90.00	90.00
cell volume, Å^3	1596.91(20)	3175.85(40)	2134.83(470)
Z	8	8	4
$D_{calcd,}$ Mg/m^3	2.773	1.921	1.899
T, K	298(2)	298(2)	298(2)
μ, mm^{-1}	18.676	9.261	7.025
F(000)	1184	1744	1168
cryst size, mm	0.040 × 0.30 × 0.40	024 × 0.40 × 0.50	0.40 × 0.60 × 0.90
θ_{min}, θ_{max}, deg	2.74, 25.06	2.24, 24.99	2.40, 25.02
no. of reflns collected	1254	2401	1860
no. of indep reflns	1145	2304	365
no. of refined params	114	255	152
goodness-of-fit on F^2 [a]	1.216/1.243(o)	1.168/1.168	1.117/1.200
final *R* indices[b] [$I > 2\sigma(I)$]			
R_1	0.0361	0.0356	0.0531
wR_2	0.1018	0.0936	0.1414
R indices (all data)			
R_1	0.0393	0.0368	0.0685
wR_2	0.1046	0.0960	
	0.1557		

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. [b] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2. Crystallographic Data for Au(I)-NHC Complexes

	Au(Et_2-bimy)$_2$(PF_6)	[Au(Et_2-bimy)$_2$]-[Au(mnt)$_2$]
formula	$C_{22}H_{28}AuN_4(PF_6)$	$C_{30}H_{28}Au_2N_8S_4$
fw	692.44	1022.78
cryst syst	orthorhombic	triclinic
space group	$Pna2(1)$	$P\bar{1}$
a, Å	11.493(2)	9.1783(14)
b, Å	21.849(2)	9.8635(14)
c, Å	10.2545(14)	10.5872(15)
α, deg	90.00	95.481(11)
β, deg	90.00	110.129(12)
γ, deg	90.00	110.129(12)
cell volume, Å^3	2574.9(6)	849.4(2)
Z	4	1
$D_{calcd,}$ Mg/m^3	1.786	2
T, K	293(2)	293(2)
μ/mm^{-1}	5.836	8.906
F(000)	1352	486
cryst size,mm	0.40 × 0.65 × 0.65	0.20 × 0.38 × 0.75
θ_{min}, θ_{max}, deg	1.86, 25.00	2.04, 24.99
no. of reflns collected	2391	2959
no. of indep reflns	1866	2187
no. of refined params	290	258
goodness-of-fit on F^2 [a]	1.049/1.081	1.095/1.136
final *R* indices[b] [$I > 2\sigma(I)$]		
R_1	0.0365	0.0388
wR_2	0.0886	0.0966
R indices (all data)		
R_1	0.0549	0.0558
wR_2	0.0992	0.1101

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. [b] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

quence of the trans influence of carbene.[5,8a,13,14d,e] The average C−N bond distances of 1.340 Å for C(1)−N(1) and C(1)−N(2) and 1.375 Å for C(2)−N(1) and C(3)−N(2) are similar to those in our previous reports[5,13] and other Au(I)-NHCs,[14] as illustrated in Table 3, in which the parameters of the corresponding Ag(I)-NHCs[12,13] and azolium salts[5,16] are also provided.

In Figure 1b, the packing diagram shows that the [Au(Me_2-imy)Cl] molecules are stacked to form a linear polymer through Au···Au interactions, in which the two adjacent Au(I) centers are at ~3.54 Å. The neighboring molecular rods cross at 95.52°, and no intermolecular π−π interactions are observed between the imidazole rings. It is worth noting that the reported [Au(Me_2-bimy)Cl] molecules[5] are arranged pairwise with both Au···Au and π−π interactions. Other interactions are also deduced from the crystal structure of [Au(Me_2-imy)-Cl]. The adjacent linear polymers are connected by C−H···Cl (proton on C^2 of the NHC ring) hydrogen bonds as short as 2.79 Å with an angle of ~130°. The C−H···Cl hydrogen bonds are also observed within the linear polymer itself. Similar C−H···Cl hydrogen bonds with comparable distances and angles have been reported.[17] Further, a short distance of 3.0 Å is observed

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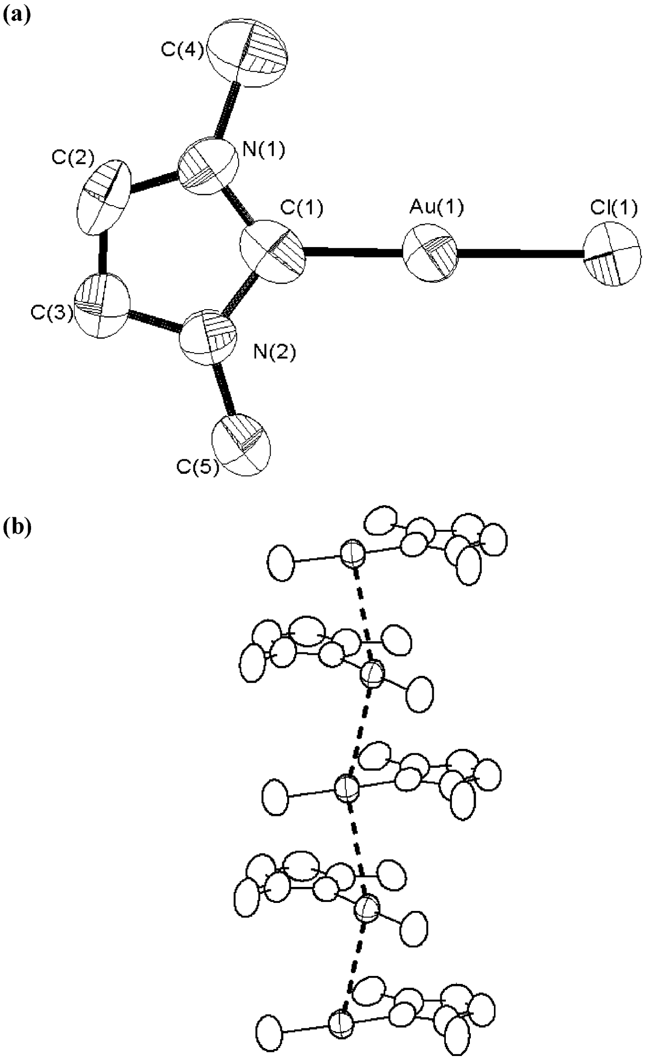

Figure 1. (a) ORTEP diagram (50% probability ellipsoids) of [Au(Me_2-imy)Cl] in the crystal state. Selected bond lengths (Å) and angles (deg): Au−Au, 3.5405(3); Au−C(1), 1.979(11); Au−Cl, 2.288(3); C(1)−N(1), 1.35(2); C(1)−N(2), 1.347(13); C(2)−N(1), 1.36(2); C(3)−N(2), 1.39(2); C(1)−Au−Cl, 178.8(2); N(1)−C(1)−N(2), 105.8(10); C(1)−Au−Au(1), 81.44. (b) Molecular aggregation in [Au(Me_2-imy)Cl] through Au···Au attractions.

between the hydrogen atom of C3 in NHC rings and the Au(I) center of the neighboring polymer with a C−H···Au angle of ~150°. This C−H···Au interaction has been reported by others.[18]

[Au(Me_2-tazy)Cl]. The poor quality of the [Au(Me_2-tazy)Cl] crystals yielded a relatively high *R* value; nevertheless, the skeletal arrangement is presumably correct. This compound has a molecular structure and packing fashion very similar to [Au(Me_2-imy)Cl]. These results are shown in the Supporting Information.

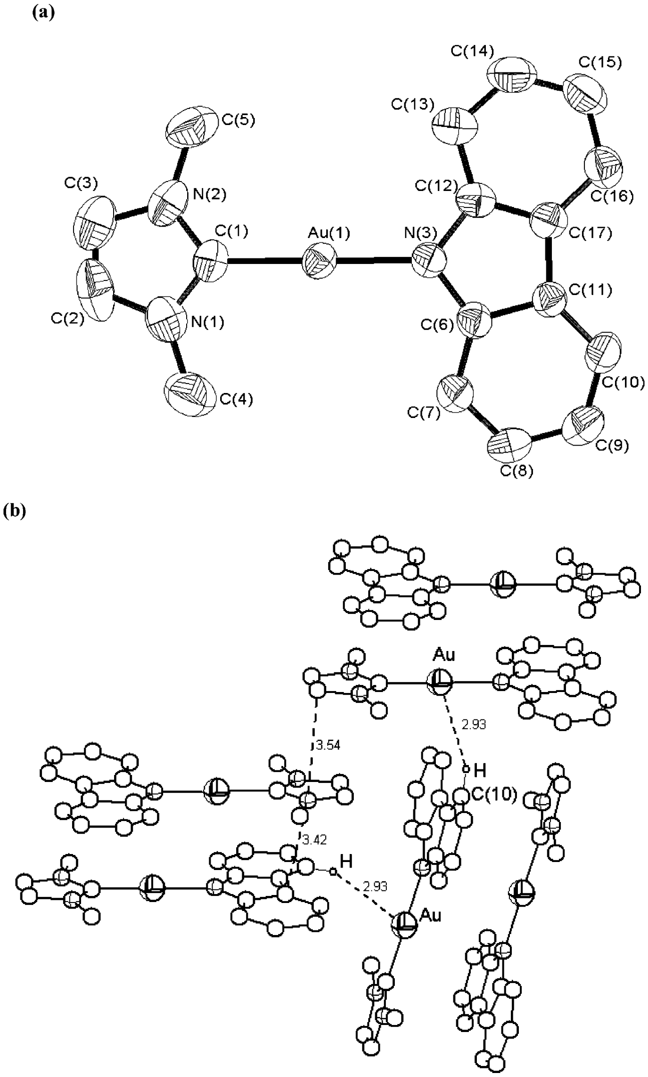

Figure 2. (a) ORTEP diagram (50% probability ellipsoids) of [Au(Me_2-imy)(cbz)] in the crystal state. Selected bond lengths (Å) and angles (deg): Au−Au, 3.9352(5); Au−C(1), 1.986(6); Au−N(3), 2.005(5); C(1)−N(1), 1.341(9); C(1)−N(2), 1.320(10); C(2)−N(1), 1.407(15); C(3)−N(2), 1.377(11); C(6)−N(3), 1.381(8); C(12)−N(3), 1.396(7); C(1)−Au−N(3), 179.2(2); N(1)−C(1)−N(2), 106.1(6). (b) Stacking of [Au(Me_2-imy)(cbz)] through ring−ring interactions and Au···H interactions. Dashed lines are distances in Å.

Table 3. N−$C_{carbene}$ and Averaged C−N Bond Lengths (Å) and Angles (deg) for Au(I)-NHC and Ag(I)-NHC Complexes and the Corresponding Azolium Salts

compound	N−$C_{carbene}$ (Å)	average C−N bond lengths (Å) [C(2)−N(1)+C(3)−N(2)]/2 (or) [C(2)−N(1)+C(7)−N(2)]/2	N−$C_{carbene}$−N (deg)
[Me_2-ImyH]Cl[16]	1.329	1.378	108.33
[Ag(Me_2-imy)$_2$][$AgCl_2$][12]	1.338	1.388	105.34
[Au(Me_2-imy)Cl]	1.346	1.378	105.84
[Au(Me_2-imy)(cbz)]	1.330	1.392	106.09
[Et_2-bimyH]Cl[5]	1.316	1.388	110.88
[Ag(Et_2-bimy)$_2$][$AgBr_2$][13]	1.355	1.363	104.02
[Au(Me_2-bimy)Cl][5]	1.337	1.415	111.61
[Au(Et_2-bimy)Cl][5]	1.323	1.398	108.28
[Au(Me_2-bimy)$_2$][PF_6]	1.346	1.375	106.39
[Au(Et_2-bimy)$_2$][PF_6]	1.346	1.383	107.37
[Au(Et_2-bimy)$_2$][Au(mnt)$_2$]	1.350	1.377	105.14

[Au(Me$_2$-imy)(cbz)]. Crystals of [Au(Me$_2$-imy)(cbz)] were grown by slow diffusion of diethyl ether into a saturated acetonitrile solution at room temperature. The molecular structure is presented in Figure 2a. The Au(I) center is linearly coordinated, as evidenced by the C(1)−Au(1)−N(3) angle being 179.2(2)°. The carbene and carbazolate ligands are coplanar. The Au−C(1) bond of 1.986(6) Å is close to that in [Au(Me$_2$-imy)Cl] and other reported Au(I)-NHC systems.[5,13,14] The average bond lengths of 1.33 and 1.431 Å for C(1)−N(1) and C(1)−N(2), and C(2)−N(1) and C(3)−N(2), respectively, are also similar to other entries[5,13,14] included in Table 1. The Au(1)−N(3) bond distance of 2.005(5) Å in the gold-carbazolate fragment is close to the similar Au−N linkages observed in the Au(I)-(Harmine) complex[19] and Au(I) complexes of pyrazole, imidazole, and benzimidazole.[20]

The packing diagram shows that the two nearest molecules are stacked in a pairwise antiparallel fashion, as illustrated in Figure 2b. The intermolecular Au⋯Au distance of ~3.94 Å is substantially longer than the van der Waals contact of 3.6 Å for the two Au.[9] The closest distance for intermolecular carbene ring−carbazole ring is found to be 3.42 Å, an indication of $\pi-\pi$ interaction. $\pi-\pi$ contacts of 3.54 Å are found between carbenes of different pairs. Au⋯H interactions between two perpendicularly positioned pairs appear to be an additional stabilizing factor. A distance of 2.93 Å with a C−H⋯Au bond angle ~150°, observed between H of C(10) in carbazole and an Au center, is similar to the reported Au⋯H interactions.[18]

[Au(Me$_2$-bimy)$_2$][PF$_6$] and [Au(Et$_2$-bimy)$_2$][PF$_6$]. Crystal structures of two previously reported compounds, [Au(Me$_2$-bimy)$_2$][PF$_6$] and [Au(Et$_2$-bimy)$_2$][PF$_6$], were also investigated. Single crystals of these two complexes have been obtained from a CH$_2$Cl$_2$/hexane solvent system. The molecular structure of the dicarbene complex, [Au(Me$_2$-bimy)$_2$][PF$_6$], is shown in the form of an ORTEP drawing in Figure 3a. As expected, the coordination of the Au(I) center is linear. The Au−C(1) bond length of 2.054(10) Å is within the range of known Au(I)−NHC linkages.[5,13,14] Similarly, the average distance of 1.346 Å has been found for the C(1)−N(1) and C(1)−N(2) bonds and 1.374 Å for C(2)−N(1) and C(7)−N(2) bonds.[5,13,14] The ring−ring distances of 3.566 Å reveal the presence of $\pi-\pi$ interactions, as seen in Figure 3b.

An ORTEP drawing of [Au(Et$_2$-bimy)$_2$][PF$_6$] together with important bond distances and angles is shown in Figure 4. In contrast to the Me$_2$-bimy dicarbene complex, the two Et$_2$-bimy rings are twisted by 52.96°. The two ethyl substituents are oppositely above and below the ring plane, respectively.

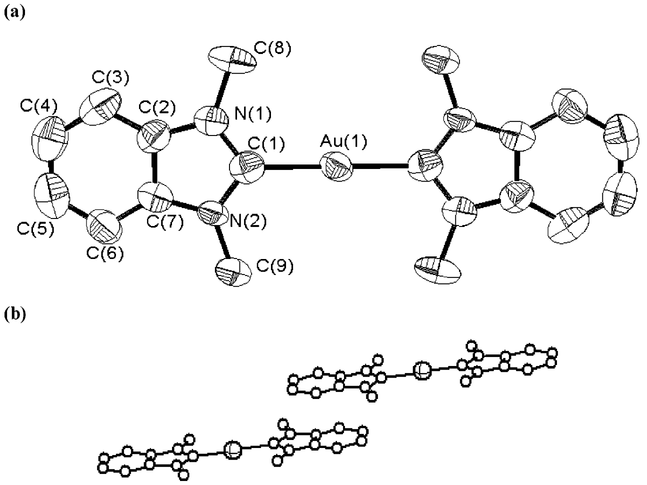

Figure 3. (a) ORTEP diagram (50% probability ellipsoids) of [Au(Me$_2$-bimy)$_2$]$^+$ in the crystal state. The [PF$_6$]$^-$ moiety is omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−C(1), 2.054(10); C(1)−N(1), 1.355(10); C(1)−N(2), 1.339(10); C(3)−N(1), 1.369(12); C(8)−N(2), 1.380(12); C(1)−Au−C(1′), 180.0(2); N(1)−C(1)−N(2), 106.5(8). (b) Staking of [Au(Me$_2$-bimy)$_2$]$^+$ through ring−ring interactions in head-to-tail fashion.

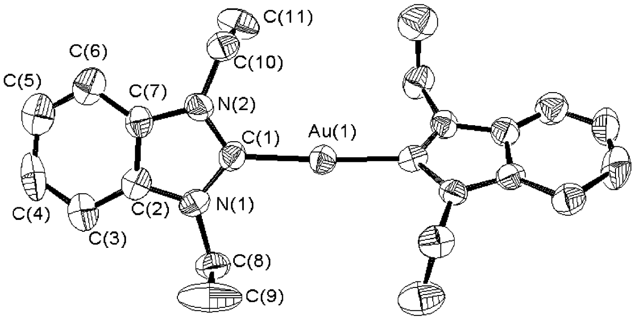

Figure 4. ORTEP diagram (50% probability ellipsoids) of [Au(Et$_2$-bimy)$_2$]$^+$ in the crystal state. The [PF$_6$]$^-$ moiety is omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−C(1), 2.024(12); C(1)−N(1), 1.360(2); C(1)−N(2), 1.330(2); C(2)−N(1), 1.380(2); C(7)−N(2), 1.387(14); C(1)−Au−C(1′), 175.0(14); N(1)−C(1)−N(2), 107.5(10).

[Au(Et$_2$-bimy)$_2$][Au(mnt)$_2$]. The ORTEP diagram of [Au(Et$_2$-bimy)$_2$][Au(mnt)$_2$] in Figure 5 shows that the cation possesses a linear geometry around the Au(I) center. The structure of the complex anion is comparable to the known [Au(mnt)$_2$]$^-$.[21] There is no significant interaction between the cationic Au(I) and anionic Au(III) centers. However, weak $\pi-\pi$ interactions (3.58 Å) between mnt and the benzene ring of the bimy carbene appear as one of the linkers between the cations and anions.[18b,c]

Nature of the M−C$_{\text{carbene}}$ Bonding in Au(I)-NHCs. The NHC ligands have been commonly regarded as pure σ-donors.[2b,4a,22] However, recent molecular-orbital analysis based on calculations of density functional theory for group 11 metal complexes of NHCs[14f,23] suggests non-negligible π-back-bonding from metal to the NHC

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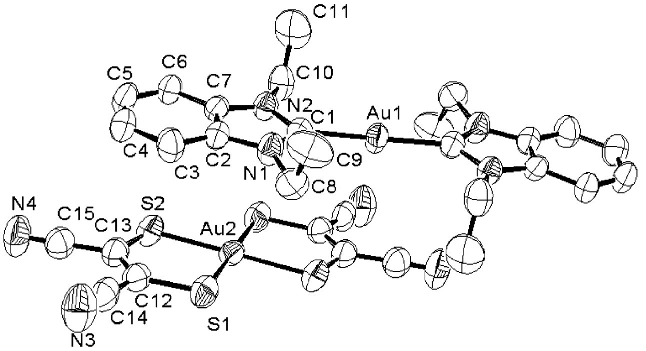

Figure 5. ORTEP diagram (50% probability ellipsoids) of $[Au^{I}(Et_2\text{-bimy})_2]$ $[Au^{III}(mnt)_2]$ in the crystal state. Selected bond lengths (Å) and angles (deg): Au−Au, 4.9317(7); Au(1)−C(1), 2.001(7); Au(2)−S(1), 2.310(2); Au(2)−S(2), 2.304(2); C(1)−N(1), 1.331(10); C(1)−N(2), 1.372(9); C(2)−N(1), 1.398(10); C(7)−N(2), 1.357(9); C(1)−Au−C(1′), 180.0; N(1)−C(1)−N(2), 105.1(6); S(1)−Au(2)−S(1′), 180.0; S(1)−Au(2)−S(2), 90.58; S(1)−Au(2)−S(2′), 89.42(8).

ligands,[24−26] supported by the observed lengthening of the $N-C_{carbene}$ bonds. In this work as listed in Table 3, compared to the free azolium salt the increased $N-C_{carbene}$ bond lengths of the complexes is consistent with the effect of non-negligible π-back-bonding.

Electronic Spectroscopy. Absorption. The electronic absorption spectra of $[Au(Me_2\text{-imy})Cl]$ and $[Au(Me_2\text{-tazy})Cl]$ show notable absorption bands at 220−250 nm in acetonitrile (see the Supporting Information). These bands are comparable to the 200−220 nm bands of the carbene precursors and the metal-centered transitions of $AuCl_2^-$ at 246 nm.[27] The features exhibited by the absorption band of [Au(NHC)(cbz)] complexes in CH_2Cl_2 at 200−370 nm are distinctively different from the [Au(NHC)Cl] series. The free carbazole absorption also spread within this range at 250−370 nm. The density functional, B3LYP[28]/cep-4g,[29] level of calculations on the $[Au(Me_2\text{-imy})(cbz)]$ dimer, of which the geometry is based on the crystal structure of the $[Au(Me_2\text{-imy})(cbz)]$ complex, indicate that the characters of both the HOMO and LUMO of the singlet ground state are predominately of ligands. Namely, the HOMO is composed of the orbitals from carbazolates and golds with the former more than an overwhelming 95%, and the LUMO is contributed entirely from carbenes. The ab initio results seem to hint that the absorptions are related to transition from carbazolate to carbene. The dicarbene complexes showed absorption bands at ca. 220−260 nm in acetonitrile. These bands appear to be mainly from the ligands.

Solid-State Emission. The solid-state emission of the Au(I)-NHCs at room temperature is tabulated in Table 4. For the emission spectra of the neutral [Au(NHC)Cl] series of $[Au(Me_2\text{-imy})Cl]$ and $[Au(Me_2\text{-tazy})Cl]$, in addition to the high-energy (HE) emission bands at 410−420 nm, the low-energy (LE) bands are observed at 650 and 580 nm, respectively. Likewise, for the [Au(NHC)(cbz)] series of $[Au(Me_2\text{-imy})(cbz)]$, $[Au(Me_2\text{-tazy})(cbz)]$, $[Au(Me_2\text{-bimy})(cbz)]$, and $[Au(Et_2\text{-bimy})(cbz)]$, both HE and LE bands are observed upon excitation at 330 nm. Specifically, the HE bands of the former three complexes are around λ_{max} = 404−413 nm and the LE bands appear at 584−592 nm; the last complex exhibits a HE band at λ_{max} = 438 nm and a LE band at λ_{max} = 516 nm. The microsecond time scales of the measured lifetimes indicate that the LE bands of both series are phosphorescent. On the other hand, the cationic dicarbene complexes of $[Au(Me_2\text{-imy})_2][PF_6]$ and $[Au(Me_2\text{-tazy})_2][PF_6]$ show only the HE band at 422 nm.

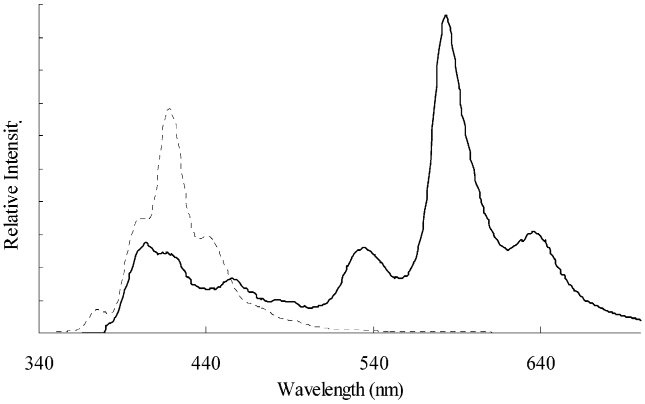

Figure 6. Emission spectra of $[Au(R_2\text{-imy})(cbz)]$ (solid line) and free carbazole (dashed line) measured in the solid state at room temperature (excitation at 330 nm).

Table 4. Emission Spectral Data for Au(I)-NHC Complexes

compound	λ_{em}/nm (lifetime/μs)	λ_{ex}/nm
$[Au(Me_2\text{-imy})Cl]$	420 (24) 650 (30)	330
$[Au(Me_2\text{-tazy})Cl]$	410 (23) 580 (26)	335
$[Au(Me_2\text{-imy})(cbz)]$	404 584 (77)	330
$[Au(Me_2\text{-tazy})(cbz)]$	410 592 (67)	330
$[Au(Me_2\text{-bimy})(cbz)]$	413 589 (45)	330
$[Au(Et_2\text{-bimy})(cbz)]$	438 516 (69)	330
$[Au(Me_2\text{-imy})_2]PF_6$	422 (23)	330
$[Au(Me_2\text{-tazy})_2]PF_6$	422 (25)	307

Since the HE bands in all these compounds exhibit fine structures, they are likely ligands in nature. Similar to $[Au(Me_2\text{-bimy})Cl]$,[5] the featureless LE bands observed for the [Au(NHC)Cl] series appear to be a consequence of spin-forbidden transitions involving metal-centered Au···Au interactions. The X-ray crystallography reveals the presence of aurophilic attractions in the $[Au(Me_2\text{-imy})Cl]$ and $[Au(Me_2\text{-tazy})Cl]$ crystals. Furthermore, upon dissolving these compounds in CH_2Cl_2 followed by rapid precipitation, the intensity of the low-energy bands decreases, likely due to not enough reaction time to allow ordered polymeric Au···Au contacts.

The Au···Au distance of ~3.94 Å in the $[Au(Me_2\text{-imy})(cbz)]$ crystal is beyond the range of aurophilic attraction, which makes the origins of the LE bands intriguing. The fine structures displayed by the LE bands are different from the counterparts of the [Au(NHC)Cl] complexes, but rather resemble those of the carbozole emission bands at around 430 nm. It seems the LE

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emission bands observed for the [Au(azy)(cbz)] complexes mainly involve carbazolate tuned by the gold through spin−orbit interactions. As obtained by the B3LYP/cep-4g calculations, the HOMO of the lowest triplet state of the [Au(Me_2-imy)(cbz)] dimer is basically carbazolate in character, similar to the singlet ground state. Accordingly, provided similar interactions, a phosphorescence band originating from the transition of the lowest triplet state to the ground state of the [Au(Me_2-imy)(cbz)] dimer is expected to bear resemblance to that of carbazole in position and shape. The energy gap between the singlet ground state and the lowest triplet state is predicted to be 404 nm, comparable to the computed 356 nm for carbazole. The observed LE band of 590 nm is decidedly lower than the prediction that the inconsistency is not likely due to inaccuracy in the computations. Since the spin−orbit interactions are not accounted for at the B3LYP/cep-4g level of theory, it would be logical to deduce that the LE band is a probable a result of spin−orbit interactions between carbazole and the gold.

Conclusion

Gold(I) carbene complexes of the type [Au(NHC)Cl] have been synthesized by the transfer of carbene from the corresponding silver(I) carbene complexes. These complexes are found to be useful starting materials to synthesize Au(NHC)-containing compounds. Carbazolate, a chromophoric ligand, has thus been incorporated under basic phase-transfer conditions. Such an approach is expected to allow versatile ligands into the Au(NHC) core with potential applications in novel molecular architectures and fine-tuning of physical and chemical properties of the complexes. The average lengths of $N-C_{carbene}$ are in accord with the presence of non-negligible π-back-bonding between NHC and the metal center. The aurophilic interactions, which have been recognized as being crucial in the supramolecular assemblies and the photophysical properties of gold compounds, are found to depend on the ligands of the Au(I) center. While all the compounds studied in this work show HE emission bands, [Au(NHC)Cl] and [Au(NHC)(cbz)] series possess additional LE emission bands. The HE emission bands appear to arise from transitions mainly involving ligands. The LE bands exhibited by [Au(NHC)Cl] complexes are attributed to aurophilic interactions; on the other hand, those of [Au(NHC)(cbz)] complexes are more likely due to the intraligand transition of carbazolate modified by Au(I).

Experimental Section

The Ag(I)-NHC precursors were prepared according to our previously reported procedures.[5,12,13] Carbazole was purchased from Aldrich. Microanalyses (C, H, and N) were obtained by the Taiwan Instrumentation Center. NMR spectra (^1H, ^{13}C) were recorded on a Bruker AC-F300 spectrometer operated at 300 and 75 MHz, respectively. Absorption spectra were recorded with a Shimadzu UV-2101 PC spectrophotometer. Emission, excitation, and lifetime spectra were recorded on a Aminco Bowman AD2 luminescent spectrofluorometer.

[Au(Me_2-imy)Cl]. A solution of [Ag(Me_2-imy)$_2$][$AgCl_2$] (336 mg, 0.70 mmol) in dichloromethane (30 mL) was treated with Au(SMe_2)Cl (414 mg, 1.40 mmol) under vigorous stirring. Precipitates formed upon mixing. The reaction was kept for a period of 2 h to complete. The solution was then filtered, and the filtrate volume was reduced to ~10 mL, followed by the addition of 10 mL of hexane to get a white precipitate. The solid was recrystallized from CH_2Cl_2/hexane to afford colorless [Au(Me_2-imy)Cl]. Yield: 93%. Mp: 157 °C. ^1H NMR (DMSO-d_6): δ 7.41 (s, 2H, CH), 3.71 (s, 6H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): δ 169 (C−Au), 123 (CH), 38 (CH_3) ppm. Anal. Calcd for $C_5H_8N_2AuCl$: C, 18.28; H, 2.45; N, 8.53. Found: C, 18.06; H, 2.43; N, 8.40.

[Au(Me_2-imy)(cbz)]. A dichloromethane (50 mL) solution of [Au(Me_2-imy)Cl] (195 mg, 0.59 mmol) was treated with carbazole (81 mg, 0.59 mmol) followed by NaOH (0.5 N, 2 mL) and Bu_4NCl (0.06 mmol). The reaction was kept under stirring for 2 days. Later it was treated with 50 mL of deionized water and further stirred for one more hour, and then the organic part was extracted into dichloromethane, which upon concentration gave a yellow residue. Recrystallization from CH_3CN/ether afforded [Au(Me_2-imy)(cbz)]. Yield: 87%. Mp: 225 °C. ^1H NMR (DMSO-d_6): δ 8.02 (d, ^3J = 7 Hz, 2H, CH), 7.68 (d, ^3J = 7 Hz, 2H, CH), 7.50 (s, 2H, CH), 7.25 (t, ^3J = 7 Hz, 2H, CH), 6.94 (t, ^3J = 7 Hz, 2H, CH), 3.93 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{17}H_{16}N_3Au$: C, 44.46; H, 3.51; N, 9.15. Found: C, 44.33; H, 3.48; N, 9.03.

[Au(Me_2-imy)$_2$][PF_6]. [Au(Me_2-imy)Cl] (183 mg, 0.62 mmol) was added to a dichloromethane solution (30 mL) of [Ag(Me_2-imy)$_2$][$AgCl_2$] (297 mg, 0.62 mmol), and the reaction was kept for a period of 1 h under stirring, during which time a white precipitate formed. The resultant solution was filtered, and the filtrate was dried by rotary evaporator under vacuum. The residue was then dissolved in 30 mL of CH_3OH and allowed to react with NH_4PF_6 (101 mg, 0.62 mmol) under stirring for 1 h. The white precipitate that settled in the solution was filtered and was subjected to recrystallization in CH_3CN/ether to obtain [Au(Me_2-imy)$_2$][PF_6]. Yield: 85%. Mp: 248 °C. ^1H NMR (DMSO-d_6): δ 7.47 (s, 4H, CH), 3.84 (s, 12H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): δ 183.7 (C−Au), 123.5 (CH), 37.6 (CH_3) ppm. Anal. Calcd for $C_{10}H_{16}N_4AuPF_6$: C, 22.48; H, 3.02; N, 10.49. Found: C, 22.41; H, 3.12; N, 10.44.

The following three Au-tazy compounds and two Au-bimy compounds were prepared using methods similar to those described for the corresponding Au-imy complexes.

[Au(Me_2-tazy)Cl]. Yield: 88%. Mp: 150 °C. ^1H NMR (DMSO-d_6): δ 8.79 (s, 1H, CH), 3.93 (s, 3H, CH_3), 3.75 (s, 3H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): δ 173 (C−Au), 145 (CH), 35 (CH_3) ppm. Anal. Calcd for $C_4H_7N_3AuCl$: C, 14.58; H, 2.14; N, 12.75. Found: C, 14.47; H, 2.21; N, 12.68.

[Au(Me_2-tazy)(cbz)]. Yield: 85%. Mp: 188 °C. ^1H NMR (DMSO-d_6): δ 8.85 (s, 1H, CH) 8.03 (d, ^3J = 7 Hz, 2H, CH), 7.70 (d, ^3J = 7 Hz, 2H, CH), 7.26 (t, ^3J = 7 Hz, 2H, CH), 6.96 (t, ^3J = 7 Hz, 2H, CH), 4.10 (s, 3H, CH_3), 3.93 (s, 3H, CH_3) ppm. Anal. Calcd for $C_{16}H_{15}N_4Au$: C, 41.75; H, 3.28; N, 12.17. Found: C, 41.55; H, 3.24; N, 12.08.

[Au(Me_2-tazy)$_2$][PF_6]. Yield: 88%. Mp: 235 °C. ^1H NMR (DMSO-d_6): δ 8.88 (s, 2H, CH), 4.07 (s, 6H, CH_3), 3.88 (s, 6H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): δ 185.0 (C−Au), 145.4 (CH), 35.2 (CH_3) ppm. Anal. Calcd for $C_8H_{14}N_6AuPF_6$: C, 17.92; H, 2.63; N, 15.67. Found: C, 17.84; H, 2.70; N, 15.67.

[Au(Me_2-bimy)(cbz)]. Yield: 81%. Mp: 189 °C. ^1H NMR (DMSO-d_6): δ 8.02 (d, ^3J = 7 Hz, 2H, CH), 7.80 (m, 4H, C_6H_4), 7.51 (d, ^3J = 7 Hz, 2H, CH), 7.28 (t, ^3J = 7 Hz, 2H, CH), 6.96 (t, ^3J = 7 Hz, 2H, CH), 4.10 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{21}H_{18}N_3Au$: C, 49.52; H, 3.56; N, 8.25. Found: C, 49.50; H, 3.54; N, 8.17.

[Au(Et_2-bimy)(cbz)]. Yield: 82%. Mp: 197 °C. ^1H NMR (DMSO-d_6): δ 8.05 (d, ^3J = 7 Hz, 2H, CH), 7.91 (m, 2H, CH), 7.70 (d, ^3J = 7 Hz, 2H, CH), 7.51 (m, 2H, CH), 7.29 (t, ^3J = 7 Hz, 2H, CH), 6.97 (t, ^3J = 7 Hz, 2H, CH), 4.72 (q, ^3J = 7 Hz, 4H, CH_2), 1.60 (t, ^3J = 7 Hz, 6H, CH_3) ppm. Anal. Calcd for $C_{23}H_{22}N_3Au$: C, 51.40; H, 4.13; N, 7.82. Found: C, 51.32; H, 4.11; N, 7.77.

[Au(Et$_2$-bimy)$_2$][Au(mnt)$_2$]. [Au(Et$_2$-bimy)$_2$][PF$_6$] (267 mg, 0.39 mmol) was added to a solution of [NEt$_4$][Au(mnt)$_2$] (235 mg, 0.39 mmol) in 50 mL of acetone. After stirring for 1 h, the solvent of the resultant solution was removed by vacuum rotary evaporator. The brown residue was washed with water, then was recrystallized from CH$_2$Cl$_2$/hexane to afford brown crystals of [Au(Et$_2$-bimy)$_2$][Au(mnt)$_2$]. Yield: 75%. Mp: XXXXX °C. ^{1}H NMR (DMSO-d_6): δ 7.60 (m, 8H, C$_6$H$_4$), 4.63 (q, $^3J = 7$ Hz, 8H, CH$_2$) 1.65 (t, $^3J = 7$ Hz, 12H, CH$_3$) ppm. ^{13}C NMR (DMSO-d_6): δ 189.4 (C−Au), 132.9, 125.4, 119.7 (C$_6$H$_4$), 114.8 (CN), 111.6 (CC), 44.0 (CH$_2$), 16.0 (CH$_3$) ppm. Anal. Calcd for $C_{30}H_{28}N_8AuS_4$: C, 35.23; H, 2.76; N, 10.96. Found: C, 35.04; H, 2.62; N, 10.56.

X-ray Structure Determination. Single-crystal X-ray data of [Au(Me$_2$-imy)Cl], [Au(Me$_2$-imy)(cbz)], [Au(Me$_2$-tazy)Cl], [Au(Me$_2$-bimy)$_2$][PF$_6$], [Au(Et$_2$-bimy)$_2$][PF$_6$], and [Au(Me$_2$-bimy)$_2$][Au(mnt)$_2$] were collected on a Siemens P4 diffractometer with the XSCANS software package[30] using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Except for [Au(Me$_2$-tazy)Cl], details of crystal parameters, data collection, and structure refinements for the other five compounds are presented in Tables 1 and 2. The data were corrected for Lorentz−polarization factors. Empirical absorption corrections based on a series of ψ scans were applied to the data. All the structures were solved and refined using SHELXL 97. All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.

Theoretical Method. The calculations of density functional theory were carried out utilizing the Gaussian 98 program.[31]

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Supporting Information Available: Details of X-ray crystal data of six Au(I)-NHCs as CIF files and absorption spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) *XSCANS*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(31) Frisch, M. J.; et al. *GAUSSIAN 98*, *Revision A.5*; Gaussian, Inc.: Pittsburgh, PA, 1998.