Synthesis, Structure, and Spectroscopic Properties of Gold(I)−Carbene Complexes

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A series of gold(I)−carbene complexes of the type [Au(R_2-bimy)L] (R = Et, Me; bimy = benzimidazol-2-ylidene; L = Cl, Br, I, bimy, thiophenolate, phenylacetylide) have been prepared. These carbene complexes are luminous in acetonitrile solution and in the solid state with long lifetimes at room temperature. Multiple emissions have been observed for different R and L. The crystal structure of [Au(Me_2-bimy)Cl] shows a relatively short intermolecular Au^I−Au^I contact of 3.1664(10) Å and an intermolecular ring π−π interaction with a ring−ring distance of 3.45 Å. The structure of [Au(Et_2-bimy)Cl], however, shows only intermolecular ring−ring interactions with a distance of 3.53 Å. Crystal structure data suggest that bimy is a high-trans-influence ligand.

Introduction

Transition-metal complexes of carbenes derived from imidazolium salts have received much attention recently. One reason is that this type of carbene is ∼120 kcal/mol more stable than the simple methylidene and therefore its isolation and preparation are easier.[1] Second, imidazol-2-ylidene (imy) can stabilize both high- and low-oxidation-state metal ions and is therefore a useful ligand.[2] Finally, this type of carbene forms stable complexes with a wide range of metal ions[3] and has been considered as both an alternative to and extension of more basic phosphines.[4] In this regard, metal−imy complexes have been found to be good catalysts for a variaty of transformations, the Heck reaction being one example.[5]

One of the interesting properties of Au^I compounds is their tendency to form weak Au^I−Au^I interactions.[6] These interactions, which have energies ranging from 29 to 60 kJ/mol, are comparable to those of H-bonds.[7] A large amount of crystallographic data[8−15] as well as some solution data[7] have been reported. Another interesting property of Au^I compounds is their luminescent behavior, especially when Au^I−Au^I interactions are present.[9−15] Au^I−phosphine compounds have been the most extensively studied in this regard. Recently we reported the luminescence of aggregated annular Au^I_2−diphosphine compounds in the solid and solution states.[7b] Herein, this behavior is compared to that of analogous Au^I−imy carbene complexes.

Au^I−carbenes have been known for more than a quarter-century.[16] Their emissive behavior[17] and chemical reactions have been less studied than those of Au^I−phosphine complexes. Most published work dealing with

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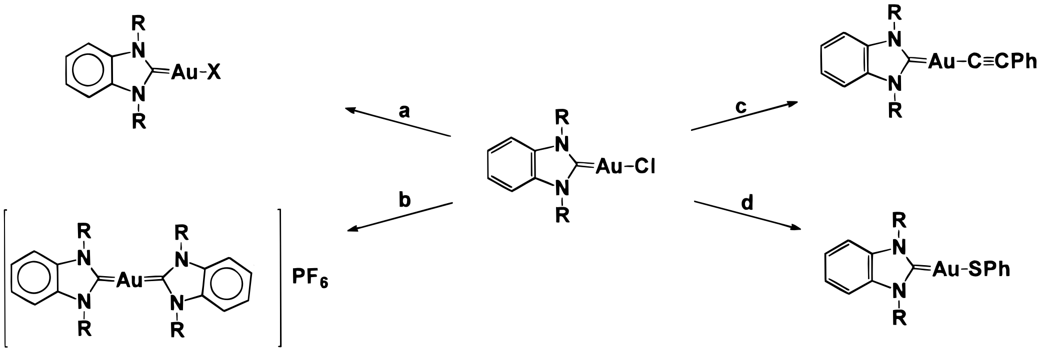
Scheme 1[a]



[a] R = Et, Me. Legend: (a) $AgBF_4$ (i) and KX (ii; X = Br, I); (b) $[R_2\text{-bimyH}]PF_6$, K_2CO_3; (c) HC≡CPh, K_2CO_3; (d) HSPh, KOH.

Au^{I}−carbenes concerns oxidative addition reactions.[18] Our recently reported[19] facile synthesis of Au−bimy (bimy = benzimidazol-2-ylidene) compounds suggested that these may be useful in a general sense. Herein we report structural variations of Au^{I}−bimy complexes and photoluminescent behavior in the solid and solution state. This study may be helpful in designing supramolecules involving Au^{I}−carbene compounds.

Results and Discussion

Synthesis. Reaction of $[R_2\text{-bimyH}]Br$ (R = Et, Me) in 1:1 CH_2Cl_2/EtOH with a 0.5 mol equiv of Ag_2O, followed by the addition of 1 mol equiv of $Au(SMe_2)Cl$ produced $[Au(R_2\text{-bimy})Cl]$ in high yields (R = Et, 91%; R = Me, 71%). The use of an EtOH mixed solvent is crucial for a high yield of $[Au(R_2\text{-bimy})Cl]$. Other Au^{I}−bimy compounds synthesized from $[Au(R_2\text{-bimy})Cl]$ are shown in Scheme 1. $[Au(R_2\text{-bimy})(C{\equiv}CPh)]$ was obtained either by the transfer of C≡CPh from $[Ag(C{\equiv}CPh)]_\infty$ to $[Au(R_2\text{-bimy})Cl]$ or by the direct reaction of $[Au(R_2\text{-bimy})Cl]$ with HC≡CPh in the presence of K_2CO_3 in acetone. $[Au(R_2\text{-bimy})(SPh)]$ was obtained by the reaction of $[Au(R_2\text{-bimy})Cl]$ with HSPh in CH_2Cl_2/EtOH in the presence of NaOH. $[Au(R_2\text{-bimy})_2]PF_6$ was obtained from $[Au(R_2\text{-bimy})Cl]$ by either the transfer of R_2-bimy from $[Ag(R_2\text{-bimy})_2]PF_6$ or reaction with $[R_2\text{-bimyH}]PF_6$ in the presence of K_2CO_3 in acetone. Attempts to prepare the mixed-carbene compound $[Au(R_2\text{-bimy})(R'_2\text{-bimy})]PF_6$ produced a mixture of $[Au(R_2\text{-bimy})(R'_2\text{-bimy})]PF_6$, $[Au(R_2\text{-bimy})_2]PF_6$, and $[Au(R'_2\text{-bimy})_2]PF_6$. Mixing the last two compounds, however, did not give the mixed-carbene compound, suggesting that the homoleptic carbene compounds are not labile. Note that analogous phosphine compounds such as [Au(phosphine)X] (X = Cl, Br, I),[20] $[Au(\text{phosphine})_2]PF_6$,[21] [Au(phosphine)(C≡CPh)],[22] [Au(phosphine)(SR)],[23] and $[Au(\text{phosphine})(py)]^+$ [24] have been reported. We also tried to synthesize $[Au(R_2\text{-bimy})(PPh_3)]^+$ without success. Reaction of $[Au(R_2\text{-bimy})Cl]$ with $AgBF_4$ followed by PPh_3 produced $[Au(PPh_3)_2]^+$ and $[Au(R_2\text{-bimy})_2]^+$ instead of the expected $[Au(R_2\text{-bimy})(PPh_3)]^+$. All the Au^{I}−bimy compounds are light and thermally stable. Conductivity measurements performed in acetonitrile at $\sim 10^{-3}$ M for the ionic compounds $[Me_2\text{-bimyH}]Br$, $[Et_2\text{-bimyH}]Br$, $[Au(Me_2\text{-bimy})_2]PF_6$, and $[Au(Et_2\text{-bimy})_2]PF_6$ gave values of 165, 160, 165, and 162 S cm^2 mol^{-1}, respectively, suggesting that these compounds are 1:1 electrolytes.

Molecular Structure. The molecular structure of $[Au(Me_2\text{-bimy})Cl]$ is depicted in Figure 1a. Crystal data and experimental details are given in Table 1, and selected bond distances and bond angles are given in the figure caption. The molecule is essentially linear around the gold atom (C(1)−Au−Cl = 178.1(3)°). The Au−C(1) distance is 1.985(11) Å and is comparable to that reported[25] for $[Au(\text{carbene})_2]^+$ and [Au(carbene)Cl]. The Au−Cl distance (2.338(2) Å) is substantially longer than the value of 2.257(4) Å found in $[AuCl_2]^-$,[26] suggesting that the bimy ligand has a higher trans influence than that of chloride. The averaged C−N distances of C(1)−N(1) and C(1)−N(2) (1.325 Å) and of C(2)−N(1) and C(7)−N(2) (1.399 Å) are comparable to those found in the other carbene complexes.[25] Two types of intermolecular interactions, Au^{I}−Au^{I} and ring π−π interactions, are observed in the crystal packing of $[Au(Me_2\text{-bimy})Cl]$ (Figure 1b). Two linear molecules are crossed at approximately 90° with a short Au^{I}−Au^{I} contact (3.1664(10) Å) to form a pair. Each molecule in a pair further interacts with neighboring pairs through

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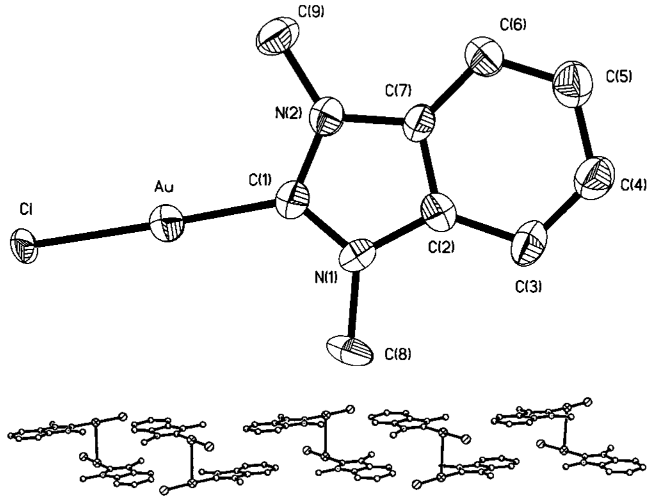

Figure 1. (a, top) ORTEP diagram (50% probability ellipsoids) of [Au(Me_2-bimy)Cl] in the crystal state. Selected bond lengths (Å) and angles (deg): Au–Au, 3.1664(10); Au–C(1), 1.985(11); Au–Cl, 2.338(2); C(1)–N(1), 1.311(14); C(1)–N(2), 1.38(2); C(2)–N(1), 1.394(14); C(7)–N(2), 1.401(14); C(1)–Au–Cl, 178.1(3); N(1)–C(1)–N(2), 107.6(10); C(1)–Au–Au(1), 89.1(4). (b, bottom) Polymeric chain of [Au(Me_2-bimy)Cl], showing the Au^I–Au^I interaction and ring–ring π-stacking.

Table 1. Crystal Data and Experimental Details for [Et_2-bimyH]Br·H_2O, [Au(Me_2-bimy)Cl], and [Au(Et_2-bimy)Cl]

	[Et_2-bimyH]-Br·H_2O	[Au(Me_2-bimy)-Cl]	[Au(Et_2-bimy)Cl]
formula	$C_{11}H_{17}N_2BrO$	$C_9H_{10}AuClN_2$	$C_{11}H_{14}AuClN_2$
fw	273.18	378.61	406.66
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a, Å	8.853(2)	20.510(2)	7.316(2)
b, Å	8.788(2)	8.5624(9)	9.698(3)
c, Å	16.413(2)	13.7848(14)	9.702(3)
V, Å^3	1248.4(4)	2006.3(4)	619.7(3)
α, deg	90	90	115.32(2)
β, deg	102.15(2)	124.028(7)	92.755(8)
γ, deg	90	90	92.821(8)
Z	4	8	2
D(calcd), Mg/m^3	1.453	2.507	2.029
abs coeff, mm^{-1}	3.271	14.884	12.055
F(000)	560	1392	380
no. of data collected	2307	1833	1198
no. of unique data	2163	1766	1190
goodness of fit on F^2 [a]	1.252	1.106	1.073
final R indices[b] ($I > 2\sigma(I)$)			
R1	0.0611	0.0404	0.0650
wR2	0.1194	0.1092	0.1687
R indices (all data)			
R1	0.1221	0.0490	0.0702
wR2	0.1397	0.1154	0.1770

[a] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

ring π–π interactions (ring–ring distance 3.45 Å) in a head-to-tail fashion. The molecular packing of this compound can be viewed as a polymeric chain with alternating Au^I–Au^I and ring–ring interactions.

The molecular structure of [Au(Et_2-bimy)Cl] is depicted in Figure 2a. Important bond distances and bond angles are given in the figure caption. The Au–C(1) and Au–Cl distances are 2.01(3) and 2.297(7) Å, respectively. The averaged C–N distances of 1.315 Å for C(1)–N(1) and C(1)–N(2) and of 1.39 Å for C(2)–N(1) and C(7)–N(2) again are comparable to those of [Au(Me_2-bimy)Cl] and others.[25] One of the notable features in the molecular structure of this compound is that the two ethyl substituents on the bimy moiety point to opposite sides of the bimy plane. The oppositely oriented ethyl groups allow a columnar stacking of the bimy planes. The dihedral angles of C(1)–N(1)–C(9)–C(10) and C(1)–N(2)–C(11)–C(12) are 91.7 and 93.9°, respectively. The plane formed by the two ethyl carbons and the adjacent nitrogen atoms are almost perpendicular to the bimy plane. The crystal packing given in Figure 2b shows that there is only ring π–π interactions (ring–ring distance 3.53 Å) but no Au^I–Au^I interaction. Each molecule interacts through the bimy ring with upper and lower bimy rings of the neighboring molecules in a head-to-tail fashion (Figure 2b).

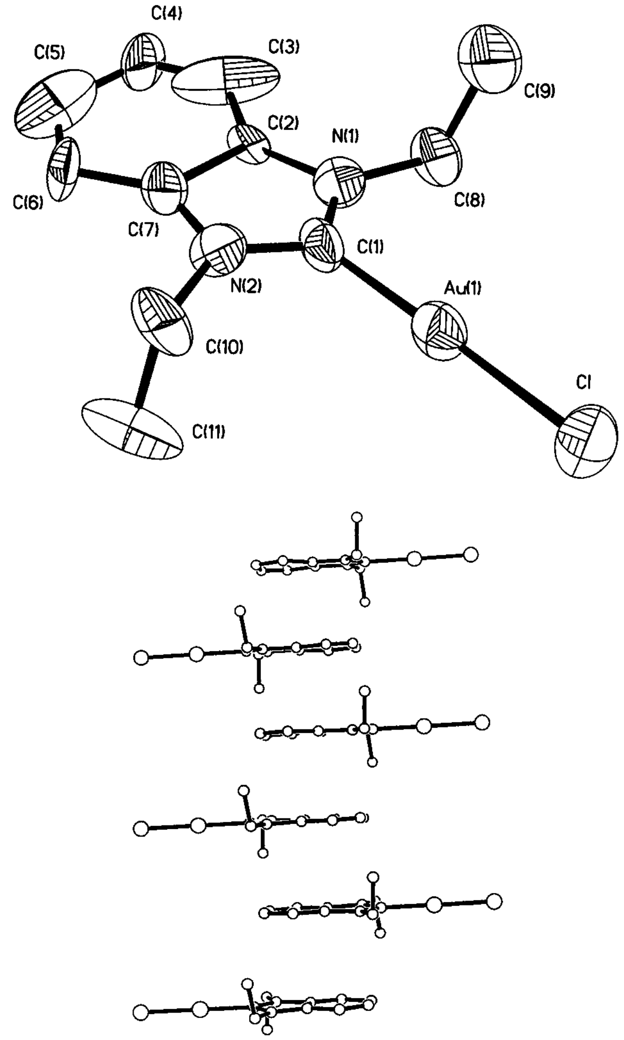

Figure 2. (a, top) ORTEP diagram (50% probability ellipsoids) of [Au(Et_2-bimy)Cl] in the crystal state. Selected bond lengths (Å) and angles (deg): Au–C(1), 2.01(3); Au–Cl, 2.297(7); C(1)–N(1), 1.33(3); C(1)–N(2), 1.30(4); C(2)–N(1), 1.38(4); C(7)–N(2), 1.40(3); C(1)–Au–Cl, 179.5(8); N(1)–C(1)–N(2), 109(2). (b, bottom) Neighboring pairs of [Au(Et_2-bimy)Cl], showing the ring–ring π-stacking.

To compare the trans influence of the carbene ligand with that of other L ligands in L–Au–Cl compounds, we examined the effect of L ligands on the Au–Cl bond distance. If we take 2.318 Å, the averaged Au–Cl bond distance of [Au(Me_2-bimy)Cl] and [Au(Et_2-bimy)Cl], as a reference, shorter Au–Cl bond distances are found in compounds where L is a nitrogen donor atom (2.256(8)

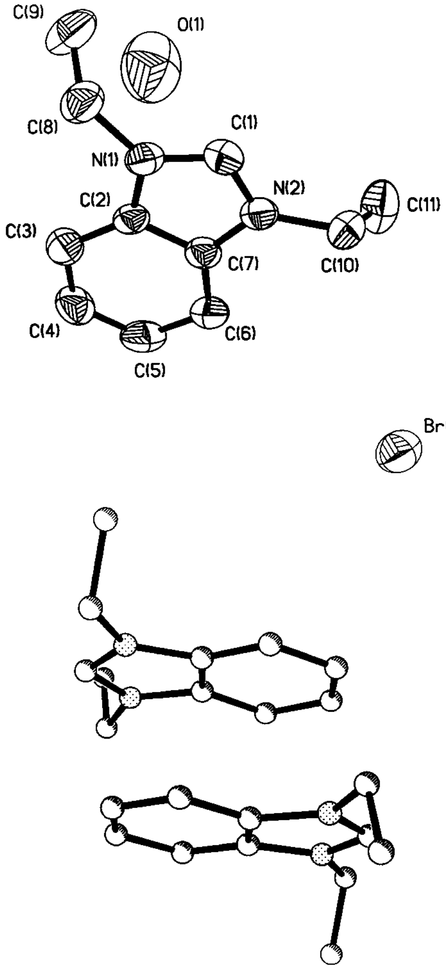

Figure 3. (a, top) ORTEP diagram (50% probability ellipsoids) of [Et$_2$-bimyH]Br·H$_2$O in the crystal state. Selected bond lengths (Å) and angles (deg): C(1)−N(1), 1.315(8); C(1)−N(2), 1.317(8); C(2)−N(1), 1.390(7); C(7)−N(2), 1.386(7); N(1)−C(1)−N(2), 110.8(6). (b, bottom) Neighboring pairs of [Et$_2$-bimyH]Br·H$_2$O, showing the ring−ring π-stacking.

Å, L = piperidine;[27] 2.262(3) Å, L = pyrazole[28]). Slightly shorter Au−Cl bond distances are found for [Au(PPh$_3$)-Cl] (2.279(3) Å)[29a] and [Au(C(OR)NR)Cl] (2.277(2) Å),[29b] but comparable Au−Cl bond distances are found for [Au-(PEt$_3$)Cl] (2.305(8) and 2.306(8) Å).[30] From the lengthening of the Au−Cl bond distances, the trans influence can be arranged in the order: bimy ≥ PEt$_3$ > PPh$_3$ ≈ C(OR)NR > pyrazole ≈ piperidine. Note that the bimy carbene has a larger trans influence than that found in Fischer type carbenes.

To gain a better understanding of the aggregation of Au^{I}−bimy compounds, the bimy precursor [Et$_2$-bimyH]-Br·H$_2$O was structurally characterized. The molecular structure of this compound is depicted in Figure 3a, and important bond distances and bond angles are given in the figure caption. The averaged distances of 1.316 Å for C(1)−N(1) and C(1)−N(2) and of 1.388 Å for C(2)−N(1) and C(7)−N(2) are comparable to those in [Au(Me$_2$-bimy)Cl] and [Au(Et$_2$-bimy)Cl]. The other bond distances and angles of the bimy ring are comparable to those in similar compounds. The two ethyl groups point to the same side of the bimyH ring. The molecular packing (Figure 3b) shows that two imidazolium cations are paired up through bimyH ring−ring interactions (ring−ring distance 3.41 Å). In a pair, two ethyl groups in one molecule are pointing to one direction, and the other two ethyl groups in another molecule are pointing in the opposite direction. The two bimyH rings in a pair also stack in a head-to-tail fashion. Note that the orientation of the ethyl groups influences the packing fashion of the molecules.

NMR Spectroscopy. The ^{13}C NMR resonances of the carbene carbon atoms in [Au(R$_2$-bimy)X] complexes with different R and X occur at δ 179 (Me, Cl), 182 (Me, Br), 187 (Me, I), 177 (Et, Cl), 180 (Et, Br), and 187 (Et, I) ppm, respectively. These signals are shifted downfield from the resonance position of the corresponding benzimidazolium 2-carbon (142 ppm). The ^{13}C NMR resonances of the carbene carbon atoms in the bis(carbene)-gold(I) complexes [Au(Me$_2$-bimy)$_2$]PF$_6$ and [Au(Et$_2$-bimy)$_2$]PF$_6$ are at 190 ppm. The order of the carbene-^{13}C chemical shifts of this Au−bimy series decreases in the order X = bimy > I > Br > Cl. A similar dependence of the ^{31}P chemical shifts on halides has been seen for [Au(phosphine)X] complexes.[18] For comparison, the carbene-^{13}C chemical shifts of [Au(R$_2$-bimy)(SPh)] and [Au-(R$_2$-bimy)(C≡CPh)] are at 186, 188 ppm and 192, 193 ppm, respectively. The ^{1}H chemical shifts of these Au^{I}−bimy complexes are not concentration-dependent in the range 10^{-2}−10^{-4} M, and no dynamic equilibrium between the monomeric and dimeric forms of the complexes can be observed in CDCl$_3$ solution. A concentration dependence of the chemical shift has been observed for [Au(PPh$_2$Me)I], which is a dimer in the solid state.[31]

Absorption Spectroscopy. The electronic absorption spectra of [Au(R$_2$-bimy)X] (X = Cl, Br, I) and [Au-(R$_2$-bimy)$_2$]PF$_6$ in acetonitrile display intense absorption bands at ca. 270−290 nm (Table 2). These bands are very similar to those of the carbene precusors [R$_2$-bimyH]Br in terms of position and band shape (ca. 260−280 nm; Table 2). Therefore, these bands are assigned to an intraligand (IL) transition involving the bimy ligands. For the compounds [Au(R$_2$-bimy)(C≡CPh)], additional peaks due to an intraligand transition of phenylacetylide appear, and the spectra are similar to those reported for phenylacetylide complexes.[32] [Au(R$_2$-bimy)(SPh)] also has an additional absorption band arising from a S → Au charge-transfer transition, which has also been observed in the analogous phosphine compounds.[33] Although we were able to see the aggregation of Au^{I}−carbene compounds in the solid state, we have been unable to observe aggregation in solution.

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Table 2. Photophysical Data for $[R_2\text{-bimyH}]Br\cdot H_2O$ and Au^I−bimy Compounds

compd	λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm^b (lifetime/μs)		λ_{ex}/nm
$[Me_2\text{-bimyH}]Br$	262 (6900)	soln	357 (23)	288
	270 (8360)	solid	470 (23)	288
	277 (7310)			
$[Et_2\text{-bimyH}]Br$	262 (6360)	soln	357 (21)	288
	269 (7180)	solid	470 (23)	288
	277 (6520)			
$Au(Me_2\text{-bimy})Cl$	271 (12 100)	soln	334 (41)	280
	280 (20 500)	solid	420 (30)	350
	288 (24 400)		620 (23)	
$Au(Me_2\text{-bimy})Br$	272 (12 400)	soln	334 (23)	280
	280 (20 900)	solid	438 (27)	350
	288 (23 800)		620 (28)	
$Au(Me_2\text{-bimy})I$	272 (12 400)	soln	335 (23)	280
	280 (21 400)	solid	440 (44)	350
	288 (25 400)		620 (25)	
$Au(Me_2\text{-bimy})(CCPh)$	281 (39 400)	soln	421 (53)	280
	290 (47 500)	solid	421 (32)	350
	299 (37 800)			
$Au(Me_2\text{-bimy})(SPh)$	280 (23 400)	soln	350 (28)	280
	288 (21 100)	solid	425 (22)	315
	322 (11 400)		475 (29)	
$[Au(Me_2\text{-bimy})_2]PF_6$	280 (27 800)	soln	325 (22)	280
	289 (41 300)	solid	441 (24)	350
	296 (33 500)			
$Au(Et_2\text{-bimy})Cl$	271 (9760)	soln	335 (25)	280
	280 (17 100)	solid	435 (61)	350
	288 (20 400)			
$Au(Et_2\text{-bimy})Br$	272 (10 400)	soln	337 (22)	280
	281 (16 800)	solid	397 (56)	350
	289 (20 500)			
$Au(Et_2\text{-bimy})I$	274 (12 400)	soln	348 (22)	280
	283 (23 500)	solid	397 (43)	350
	292 (25 600)			
$Au(Et_2\text{-bimy})(CCPh)$	284 (32 500)	soln	340 (17)	280
	291 (39 000)	solid	421 (41)	350
	299 (32 900)			
$Au(Et_2\text{-bimy})(SPh)$	281 (24 400)	soln	350 (23)	280
	288 (22 200)	solid	425 (31)	315
	328 (11 200)		475 (31)	
$[Au(Et_2\text{-bimy})_2]PF_6$	282 (26 200)	soln	335 (23)	280
	290 (38 400)	solid	397 (93)	350
	298 (30 800)			

[a] In acetonitrile soiution. [b] In 1.0×10^{-5} M acetonitrile solution. Emissions from excimers are not listed.

The ϵ values of the bands are concentration-independent in the range 10^{-3}−10^{-5} M, a result consistent with NMR studies.

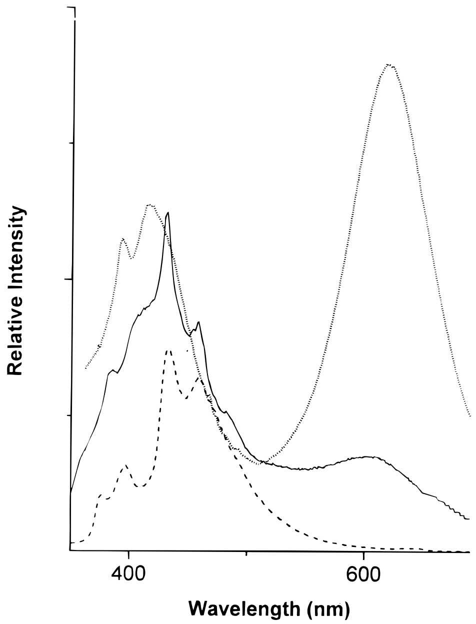

Figure 4. Emission spectra of $[Au(R_2\text{-bimy})Cl]$ measured in the solid state at room temperature: (a, dotted line) R = Me; (b, solid line) R = Me; and (c, dashed line) R = Et. Excitation at 350 nm.

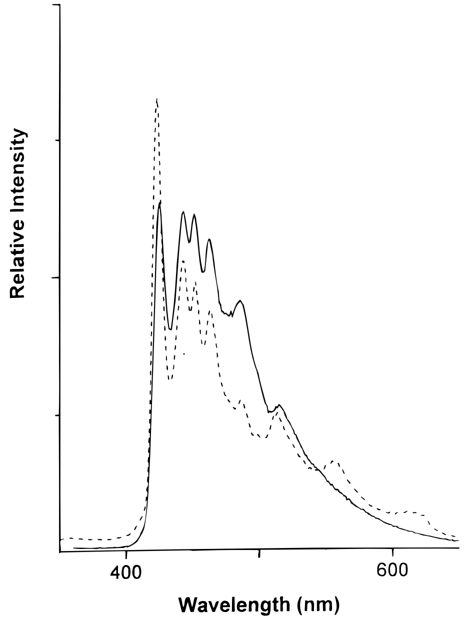

Figure 5. Emission spectra of $[Au(R_2\text{-bimy})(C{\equiv}C)Ph]$ measured in the solid state at room temperature: (a, solid line) R = Me; (b, dashed line) R = Et. Excitation at 350 nm.

Luminescent Properties. At room temperature, all the Au^I−bimy compounds are luminous in the solid state and their photophysical data are given in Table 2. Crystalline $[Au(Me_2\text{-bimy})Cl]$, which has intermolecular Au^I−Au^I and ring π−π interactions, displays a high-energy (HE) emission band at λ_{max} 420 nm (lifetime 44 μs) and an intense low-energy (LE) emission band at λ_{max} 620 nm (lifetime 23 μs), upon excitation at 360 nm (Figure 4a). If the solid sample is obtained by dissolving the crystalline sample in CH_2Cl_2 followed by rapid precipitation through the addition of hexane, the intensity of the 620 nm band decreases (Figure 4b) and varies from batch to batch. The corresponding Br and I compounds have similar emissive behavior. Crystalline $[Au(Et_2\text{-bimy})Cl]$, which does not show an intermolecular Au^I−Au^I interaction, has a band at λ_{max} 397 nm (lifetime 61 μs) and another band at 435 nm (lifetime 110 μs) upon excitation at 350 nm (Figure 4c). The corresponding Br and I compounds have similar emissive behavior. $[Au(Me_2\text{-bimy})(C{\equiv}CPh)]$ and the corresponding Et_2-bimy compound have an intense emission profile with fine structure from 420 to 650 nm with λ_{max} at 421 nm (lifetime 41 μs, Figure 5) upon excitation at 350 nm. $[Au(Me_2\text{-bimy})(SPh)]$ and $[Au(Et_2\text{-bimy})(SPh)]$ have a relatively intense emission band at 425 nm (lifetime 22 μs, excitation at 315 nm) and a shoulder at ~475 nm (lifetime 29 μs). If the spectrum of $[Au(Me_2\text{-bimy})(SPh)]$ is taken at 77 K, the 475 nm band red shifts to 500 nm (excitation at 390 nm) (Figure 6). Crystalline $[Au(Me_2\text{-bimy})_2]PF_6$ has a strong emission at λ_{max} 441 nm (lifetime 24 μs) when excited at 350 nm. If the excitation wavelength is changed to 290 nm, a weak emission profile appears at ~400 nm together with the

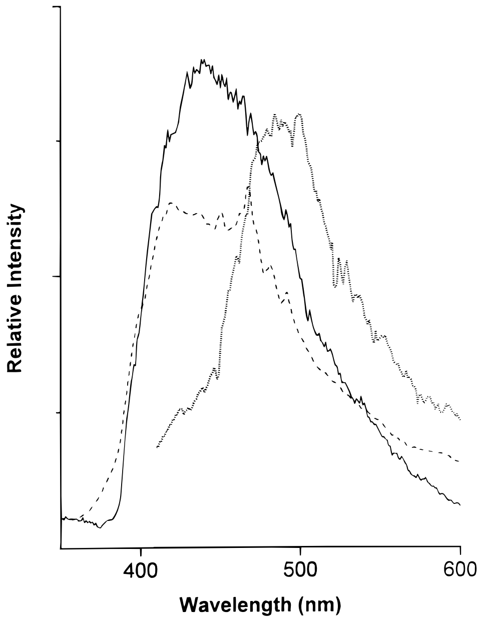

Figure 6. Emission spectra of [Au(Me$_2$-bimy)(SPh)]: (a, solid line) at room temperature upon excitation at 315 nm; (b, dashed line) at 77 K upon excitation at 315 nm; (c, dotted line) at 77 K upon excitation at 390 nm.

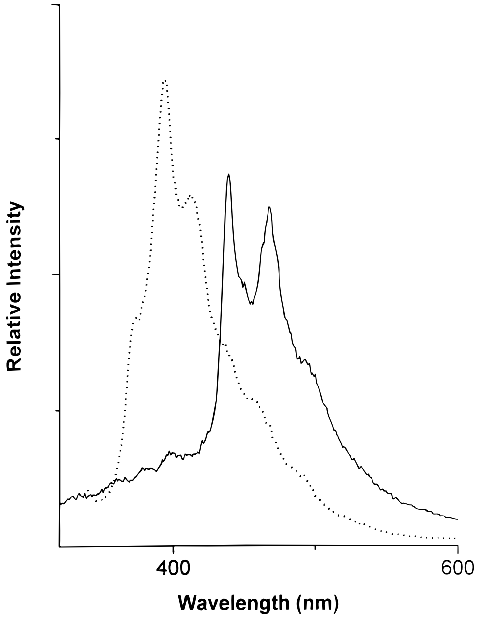

Figure 7. Emission spectra of [Au(R$_2$-bimy)$_2$]PF$_6$ upon excitation at 290 nm: (a, solid line) R = Me; (b, dotted line) R = Et.

strong band at 441 nm. Crystalline [Au(Et$_2$-bimy)$_2$]PF$_6$, on the other hand, has a strong emission at λ_{max} 394 nm (lifetime 93 μs), and the ~440 nm (lifetime 109 μs) band appears as a shoulder (Figure 7). For comparison, the emission spectrum of the crystalline [Et$_2$-bimyH]-Br was taken. Relatively weak emissions appear at 400−500 nm, with a major band at 470 nm and a shoulder at ~400 nm.

Examining the emission spectra of the Au^I−bimy compounds, we noticed that all the compounds except [Au(R$_2$-bimy)(C≡CPh)] exhibit HE emission bands at ~420 ± 20 nm with long lifetimes. Since [Et$_2$-bimyH]-Br is emissive at 400−500 nm, we suggest that the HE emissions observed for the Au^I−bimy compounds arise from spin-forbidden intraligand (^{3}IL) transitions involving bimy rings with different crystal packing. The additional emission at 620 nm observed for [Au(Me$_2$-bimy)X], but not for [Au(Et$_2$-bimy)X], is attributed to a spin-forbidden Au^I−Au^I metal-centered (^{3}MC) transition. This assignment is supported by the following arguments. There is a short intermolecular Au^I−Au^I contact in crystalline [Au(Me$_2$-bimy)Cl] but not in [Au(Et$_2$-bimy)Cl]. The powder sample of [Au(Me$_2$-bimy)Cl] obtained from dissolving the crystalline sample followed by quick precipitation from solution, does not have enough time to form all the possible Au^I−Au^I interactions. To further support the latter argument, XRD spectra of both crystalline and powder samples were taken. The crystalline sample shows two intense peaks corresponding to repeating layer distances of 3.83 and 3.43 Å, while the powder sample shows only a weak peak corresponding to a repeat distance of 3.42 Å, together with many other weak reflections. This suggests that the powder sample is less organized and has a smaller number of Au^I−Au^I contacts. Consequently, the relative intensity of the 620 nm emission band decreases. Note that the halides have no influence on the emission energy of the Au^I−Au^I ^{3}MC transition.

The emission profile for the solid sample of [Au(R$_2$-bimy)(C≡CPh)] is almost identical with those of [(Au(C≡CPh))$_2$(μ-dppe)] (dppe = Ph$_2$P(CH$_2$)$_2$PPh$_2$) and [Au$_2$L(C≡CPh)$_2$] (L = 2,6-bis(diphenylphosphino)pyridine).[34] Therefore, we presume an identical emission assignment: ^{3}IL transitions involving the C≡CPh ligand. A solid sample of [Au(R$_2$-bimy)(SPh)] has an HE emission (425 nm) assignable to an ^{3}IL transition involving the bimy ligand and an LE emission (475 nm) assignable to a spin-forbidden S → Au charge transfer (^{3}CT) transition. These transitions have also been observed for many [Au(phosphine)(SR)] compounds.[35]

In acetonitrile at room temperature, all the gold(I) carbene complexes, except [Au(R$_2$-bimy)(C≡CPh)], exhibit only ^{3}IL emissions at HE. The emission data are given in Table 2. These emissions are concentration and temperature dependent. Take [Au(Me$_2$-bimy)$_2$]PF$_6$, as an example. At the concentration of 5.0×10^{-6} M, two emission bands at 345 and 397 nm with long lifetimes (Figure 8a) are observed. If the concentration is raised to 5.0×10^{-5} M, the relative intensity of the band at 397 nm increases but the relative intensity of the band at 345 nm decreases (Figure 8b). When the temperature decreases from 25 to 10 °C, the relative intensity of the 397 nm band also increases (Figure 8c). Other compounds, including the carbene precusors [R$_2$-bimyH]X, behave similarly. The emission of [Au(R$_2$-bimy)(C≡CPh)] in acetonitrile is dominated by the IL C≡CPh transition, and only very weak HE emission bands appear at λ_{max} 330 nm. Since [R$_2$-bimyH]X species have similar emission behavior at HE, these HE bands are assigned to IL transitions involving the bimy ligands.

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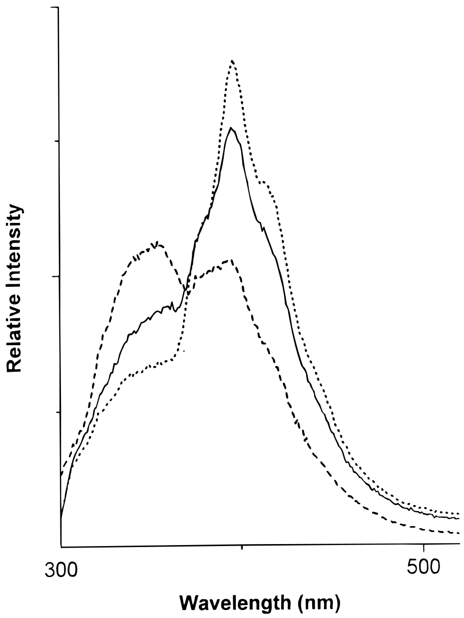

Figure 8. Emission spectra of [Au(Me$_2$-bimy)$_2$]PF$_6$ upon excitation at 270 nm: (a, dashed line) 5.0×10^{-6} M, 300 K;, (b, solid line) 5.0×10^{-5} M, 300 K; (c, dotted line) 5×10^{-5} M, 280 K.

The transition at ~350 nm is an IL transition that arises from monomeric Au−bimy compounds, while the transition at ~400 nm arises from dimeric (Au-bimy)$_2$ compounds. Studies using electronic absorption and NMR spectroscopy suggest that, in the concentration range 10^{-2}−10^{-6} M, no molecular association takes place for the Au−bimy complexes in their ground state. The dimers observed in emission spectroscopy are likely excimer in nature.

Conclusion

This work demonstrates that [Au^{I}(R$_2$-bimy)Cl] complexes are readily accessible and are useful starting materials for the synthesis of Au^{I}−bimy-containing compounds. Thus, compounds with the general formula [Au^{I}(R$_2$-bimy)L] (L = chloride, bromide, iodide, thiophenolate, phenylacetylide, R$_2$-bimy) have been obtained in high yields. The starting material [Au(R$_2$-bimy)Cl] and its bromo and iodo analogues have interesting properties. When the substituent R is methyl, crystalline samples show Au^{I}−Au^{I} and ring π−π intermolecular interactions and exhibit multiple emissions originating from bimy ^{3}IL transitions and Au^{I}−Au^{I} ^{3}MC transitions. When R is ethyl, only emissions originating from the ^{3}IL transitions of bimy are observed. Other Au^{I}−bimy complexes are also highly emissive. Multiple emissions can be observed with the proper choice of L ligand. Because many functionalized imy carbene derivatives can be designed and prepared, the electronic and steric effects of the imy type carbenes can be more finely tuned than those of phosphines. The imy ligands are potentially more useful than phosphine ligands in the design of supramolecules. While both [Au(R$_2$-bimy)X] and [Au^{I}(phosphine)X] are stable complexes, the trans influence of the bimy ligands is slightly larger or comparable to that of phosphine ligands and is greater than that of nitrogen donor ligands and halides.

Experimental Section

The compounds [R$_2$-bimyH]X (R = Et, Me; X = Br) were prepared by known methods.[36] The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-F300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts, δ, are reported relative to the internal standard TMS for both ^{1}H and ^{13}C NMR. Conductivities were measured with a Suntex SC-17A conductivity meter at room temperature with continuous stirring. The cell, fitted with platinum electrodes, was calibrated by use of an aqueous 10^{-2} N KCl solution. The background conductivity for CH$_3$CN was 0.28 $\mu\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Absorption spectra were obtained by a Shimadzu UV-2101 PC spectrophotometer. Emission, excitation, and lifetime spectra were obtained with an Aminco Bowman AD2 luminescent spectrofluorometer. Microanalyses were performed by the Taiwan Instrumentation Center.

[Au(Me$_2$-bimy)Cl]. Ag$_2$O (77 mg, 0.33 mmol) was added to a dichloromethane (30 mL) and ethanol (30 mL) mixed solution of 1,3-dimethylbenzimidazolium bromide (150 mg, 0.66 mmol). The suspension became clear after it was stirred for 2 h at room temperature. Au(SMe$_2$)Cl (195 mg, 0.66 mmol) was then added, and the resultant solution was stirred for an additional 2 h. After the white precipitate was filtered, the solvent was removed to give white residue. Recrystallization from CH$_2$Cl$_2$/hexane gave colorless [Au(Me$_2$-bimy)Cl] in 71% yield (178 mg). Mp: 279 °C. ^{1}H NMR (CDCl$_3$): δ 7.47 (s, 4H, CH), 4.04 (s, 6H, CH$_3$). Anal. Calcd for C$_9$H$_{10}$N$_2$AuCl: C, 28.55; H, 2.66; N, 7.40. Found: C, 27.78; H, 2.62; N, 7.24.

[Au(Me$_2$-bimy)Br]. AgBF$_4$ (76 mg, 0.39 mmol) in 20 mL of EtOH was added to a CH$_2$Cl$_2$ (20 mL) solution of [Au(Me$_2$-bimy)Cl] (147 mg, 0.39 mmol), and the resultant solution was stirred for 5 min. A white precipitate was filtered out, and the filtrate was added to an EtOH (20 mL) solution of KBr (47 mg, 0.39 mmol). The solution was stirred for 30 min, and the solvent was removed under vacuum. The residue was recrystallized from CH$_2$Cl$_2$/hexane to give colorless [Au(Me$_2$-bimy)Br] (yield 115 mg, 70%). Mp: 284 °C. ^{1}H NMR (CDCl$_3$): δ 7.48 (s, 4H, CH), 4.05 (s, 6H, CH$_3$). Anal. Calcd for C$_9$H$_{10}$N$_2$AuBr: C, 25.55; H, 2.38; N, 6.62. Found: C, 25.50; H, 2.27; N, 6.55.

[Au(Me$_2$-bimy)I]. This compound was prepared by the method decribed for [Au(Me$_2$-bimy)Br]. Yield: 55%. Mp: 272 °C. ^{1}H NMR (CDCl$_3$): δ 7.48 (s, 4H, CH), 4.05 (s, 6H, CH$_3$). Anal. Calcd for C$_9$H$_{10}$N$_2$AuI: C, 23.00; H, 2.14; N, 5.96. Found: C, 23.03; H, 2.02; N, 5.93.

[Au(Me$_2$-bimy)(C≡CPh)]. Method a. K$_2$CO$_3$ (58 mg, 0.42 mmol) was added to an acetone solution (50 mL) of phenylacetylene (43 mg, 0.42 mmol) and [Au(Me$_2$-bimy)Cl] (159 mg, 0.42 mmol). The resultant solution was stirred for 1 day and then dried under vacuum. To remove the salts, the white residue was washed with 20 mL of CH$_2$Cl$_2$ and filtered. The clear filtrate was dried to give pale yellow [Au(Me$_2$-bimy)(C≡CPh)] (yield 151 mg, 81%). Recrystallization from CH$_2$Cl$_2$/hexane yielded a pale yellow crystalline product.

Method b. [Ag(C≡CPh)]$_\infty$ (65 mg, 0.31 mmol) was added to a CH$_2$Cl$_2$/EtOH solution (25 mL/25 mL) of [Au(Me$_2$-bimy)Cl] (118 mg, 0.31 mmol). The resultant solution was stirred for 1 h and then filtered and dried. Recrystallization from CH$_2$Cl$_2$/hexane produced a pale yellow crystalline product (yield 107 mg, 78%). Mp: 241 °C dec. ^{1}H NMR (DMSO-d_6): δ 7.74 and 7.47 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 4H, CH), 7.19−7.27 (m, 5H, Ph), 4.01 (s, 6H, CH$_3$). Anal. Calcd for C$_{17}$H$_{15}$N$_2$Au: C, 45.96; H, 3.40; N, 6.31. Found: C, 45.85; H, 3.38; N, 6.25.

[Au(Me$_2$-bimy)(SPh)]. To a mixture of dichloromethane (40 mL) and ethanol (20 mL) were added with stirring 1,3-dimethylbenzimidazolium bromide (94 mg, 0.41 mmol) and

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(36) (a) Abdul-Sada, A. K.; Greenway, A. M.; Hitchcock, P. B.; Mohammed, T. J.; Seddon, K. R.; Zora, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1753. (b) Harlow, K. J.; Hill, A. F.; Welton, T. *Synthesis* **1996**, 697. Molar conductivity (1.0×10^{-3} M acetonitrile): [Me$_2$-bimyH]Br, 165 S cm^2 mol^{-1}; [Et$_2$-bimyH]Br, 160 S cm^2 mol^{-1}.

Ag_2O (48 mg, 0.21 mmol). After 1 h, $Au(SMe_2)Cl$ (120 mg, 0.41 mmol) was added and allowed to react for another 1 h. After the precipitate was removed, the clear solution was mixed with another solution made of thiophenol (46 mg, 0.41 mmol) and NaOH (0.10 N, 0.42 mmol) in a mixture of CH_2Cl_2 (40 mL) and EtOH (20 mL). The resultant solution was allowed to react for additional 3 h and then dried under reduced pressure. Extracting the residue with CH_2Cl_2, followed by the addition of hexane, produced pale yellow crystals. Yield: 65%. Mp: 142 °C dec. ^1H NMR ($CDCl_3$): δ 7.66 (d, 2H, $^3J = 8$ Hz, SPh), 7.47 (s, 4H, CH), 7.11 (d, 2H, $^3J = 7$ Hz, SPh), 6.98 (s, H, SPh), 4.07 (s, 6H, CH_3). Anal. Calcd for $C_{15}H_{15}N_2AuS$: C, 39.83; H, 3.34; N, 6.19. Found: C, 39.25; H, 3.33; N, 6.13.

[Au(Me$_2$-bimy)$_2$]PF$_6$. K_2CO_3 (57 mg, 0.41 mmol) was added to an acetone (50 mL) solution containing the PF_6 salt of 1,3-dimethylbenzimidazolium (120 mg, 0.41 mmol) and [Au(Me$_2$-bimy)Cl] (156 mg, 0.41 mmol) and was stirred for 1 day. The resultant solution was dried, and the white residue was extracted with 30 mL of CH_3OH/H_2O (1:1 by volume). After the filtrate was dried, white [Au(Me$_2$-bimy)$_2$]PF$_6$ (213 mg, 82%) was obtained. Recrystallization from CH_3CN yielded a colorless crystalline product. Mp: 351 °C dec. ^1H NMR (DMSO-d_6): δ 7.85 and 7.54 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 4H, CH), 4.17 (s, 6H, CH_3). Molar conductivity (1.0×10^{-3} M acetonitrile): 165 S cm^2 mol^{-1}. Anal. Calcd for $C_{18}H_{20}N_4AuPF_6$: C, 34.08; H, 3.18; N, 8.83. Found: C, 33.99; H, 3.18; N, 8.84.

Ethyl-substituted compounds were synthesized by the methods described for the corresponding methyl compounds. Characterizations of these compounds are given below.

[Au(Et$_2$-bimy)Cl]. Yield: 91%. Mp: 204 °C. ^1H NMR ($CDCl_3$): δ 7.41−7.50 (m, 4H, CH), 4.54 (q, $^3J = 7$ Hz, 4H, CH_2), 1.54 (t, $^3J = 7$ Hz, 6H, CH_3). Anal. Calcd for $C_{11}H_{14}N_2AuCl$: C, 32.49; H, 3.47; N, 6.89. Found: C, 32.48; H, 3.46; N, 6.90.

[[Au(Et$_2$-bimy)Br]. Yield: 88%. Mp: 223 °C. ^1H NMR ($CDCl_3$): δ 7.42−7.51 (m, 4H, CH), 4.55 (q, $^3J = 7$ Hz, 4H, CH_2), 1.54 (t, $^3J = 7$ Hz, 6H, CH_3). Anal. Calcd for $C_{11}H_{14}N_2AuBr$: C, 29.29; H, 3.13; N, 6.21. Found: C, 29.24; H, 3.12; N, 6.13.

[Au(Et$_2$-bimy)I]. Yield: 82%. Mp: 197 °C. ^1H NMR ($CDCl_3$): δ 7.43−7.52 (m, 4H, CH), 4.55 (q, $^3J = 7$ Hz, 4H, CH_2), 1.55 (t, $^3J = 7$ Hz, 6H, CH_3). Anal. Calcd for $C_{11}H_{14}N_2AuI$: C, 26.52; H, 2.83; N, 5.60. Found: C, 26.59; H, 2.83; N, 5.56.

[Au(Et$_2$-bimy)(C≡CPh)]. Yield: 86%. Mp: 172 °C dec. ^1H NMR (DMSO-d_6): δ 7.83 and 7.46 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 4H, CH), 7.19−7.28 (m, 5H, Ph), 4.53 (q, $^3J = 7$ Hz, 4H, CH_2), 1.45 (t, $^3J = 7$ Hz, 6H, CH_3). Anal. Calcd for $C_{19}H_{19}N_2Au$: C, 48.31; H, 4.05; N, 5.93. Found: C, 48.31; H, 4.05; N, 5.83.

[Au(Et$_2$-bimy)(SPh)]. Yield: 65%. Mp: 95 °C. ^1H NMR ($CDCl_3$): δ 7.66 (d, 2H, $^3J = 7$ Hz, SPh), 7.44−7.51 (m, 4H, C_6H_4), 7.10 (d, 2H, $^3J = 8$ Hz, SPh), 6.97 (s, H, SPh), 4.56 (q, 4H, $^3J = 7$ Hz, CH_2), 1.56 (t, 6H, $^3J = 7$ Hz, CH_3). Anal. Calcd for $C_{17}H_{19}N_2SAu$: C, 42.15; H, 3.99; N, 5.83. Found: C, 42.05; H, 4.01; N, 5.79.

[Au(Et$_2$-bimy)$_2$]PF$_6$. Yield: 89%. Mp: 281 °C. ^1H NMR (DMSO-d_6): δ 7.94 and 7.54 (dd, $^3J = 6$ Hz, $^4J = 3$ Hz, 8H, CH), 4.66 (q, $^3J = 7$ Hz, 8H, CH_2), 1.55 (t, $^3J = 7$ Hz, 12H, CH_3). Molar conductivity (1.0×10^{-3} M acetonitrile): 162 S cm^2 mol^{-1}. Anal. Calcd for $C_{22}H_{28}N_4AuPF_6$: C, 38.26; H, 4.02; N 8.22. Found: C, 38.27; H, 4.09; N, 8.11.

X-ray Structure Determinations. A colorless cuboid crystal of [Et$_2$-bimyH]Br·H$_2$O was grown from a mixture of dichloromethane and hexane at room temperature. A crystal with dimensionsf 0.6 × 0.4 × 0.4 mm was used for X-ray structural analysis. The diffraction experiments were carried out on a Siemens P4 diffractometer with the XSCANS software package[37] using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). A total of 2307 reflections were collected in the θ range of 2.4−25.0° ($0 \leq h \leq 10$, $0 \leq k \leq 10$, $-19 \leq l \leq 19$) in the ω scan mode. The data were corrected for Lorentz−polarization factors. An empirical absorption correction based on a series of ψ scans was applied to the data. The structure was solved by direct methods and was refined by full-matrix least squares on F^2 in SHELXTL-PC version 5.03. All the non-hydrogen atoms were refined anistropically. The experimental details and crystal data are given in Table 1.

A colorless crystal of [Au(Me$_2$-bimy)Cl] was grown from a mixture of dichloromethane and hexane at room temperature. A crystal with dimensions 0.3 × 0.2 × 0.1 mm was used for X-ray structural analysis. A total of 1833 reflections were collected in the θ range 2.4−25.0° ($-16 \leq h \leq 24$, $-10 \leq k \leq 10$, $-16 \leq l \leq 16$) in the ω scan mode. The maximum and minimum transmission factors are 0.8935 and 0.2148. An empirical absorption correction based on a series of ψ scans was applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 in SHELXTL-PC version 5.03. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in ideal positions with $r_{C-H} = 0.95$ Å. The experimental details and crystal data are given in Table 1.

A colorless crystal of [Au(Et$_2$-bimy)Cl] was grown from a mixture of dichloromethane and hexane at room temperature. A crystal with dimensions 0.3 × 0.1 × 0.1 mm was used for X-ray structural analysis. A total of 1198 reflections were collected in the θ range of 2.3−25.0° ($-8 \leq h \leq 8$, $-9 \leq k \leq 10$, $0 \leq l \leq 11$) in the ω scan mode. The structure was solved by direct methods and was refined by full-matrix least squares on F^2 in SHELXTL-PC version 5.03. In the final difference Fourier synthesis, the electron density ranged from 1.823 to −2.224 e Å^{-3}, the largest four peaks of which were associated with Au atoms at distances of 1.011 and 1.422 Å. The experimental details and crystal data are given in Table 1.

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Supporting Information Available: Tables giving positional and isotropic thermal parameters, anisotropic thermal parameters, and bond lengths and angles for the structural analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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[37] XSCANS; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.