ORGANOMETALLICS

N-Heterocyclic Carbene Coinage Metal Complexes as Intense Blue-Green Emitters

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Supporting Information

ABSTRACT: The reaction of N-methyl (Me) or N-benzyl (Bn) imidazole with 9chloroacridine (9-ClAcr) gives the corresponding imidazolium salts, [(RimAcr)H]Cl (R = Me, Bn), which can further react with AgBF₄ or [Au(C₆F₅)(tht)], affording the new salts [(RimAcr)H]BF₄ or [(RimAcr)H][Au(C₆F₅)Cl]. Silver(I) carbene complexes of the form [AgCl(RimAcr)] or [Ag(RimAcr)₂]BF₄ are synthesized by reaction of the corresponding imidazolium salts with Ag₂O or Ag₂O and NaOH. Transmetalation reactions allow the synthesis of the gold and copper derivatives [MCl(RimAcr)] (M = Au, Cu) and [Au(RimAcr)₂]BF₄. Treatment of [(RimAcr)H][Au(C₆F₅)Cl] with NaH affords the synthesis of the carbene complexes [Au(C₆F₅)(RimAcr)]. The crystal structures of these complexes show interesting $\pi \cdots \pi$ stacking interactions between the acridine and/or the pentafluorophenyl groups. The imidazolium salts and the gold and silver complexes are intense blue-green emitters.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) have become a wellestablished type of compound in coordination metal chemistry since Arduengo and co-workers first isolated a free imizadole-2ylidene.¹ NHCs have powerful σ -donating properties, better than the ubiquitous phosphine ligands, and this can lead to stable M-NHCs with strong metal–carbon bonds. The electron richness of NHCs can be of significance in many reactions, and indeed metal NHC complexes are more effective in many catalytic reactions than the corresponding phosphine derivatives.² Several methods for the synthesis of these NHC metal complexes have been described, the most used being the direct reaction of the metal complex with the free carbene, usually obtained by deprotonation of the imidazolium salt, or the transmetalation reaction with silver(I) NHC complexes, which is the favorite for the coinage metal NHC complexes.

Coinage metal N-heterocyclic carbene complexes are of interest for their intriguing structural properties and numerous applications in catalysis, medicine, and materials chemistry.³ Silver(I) NHC complexes are the most widely studied because of their facile preparation via the Ag₂O route and their usefulness as transmetalating agents.⁴ The importance of the use of NHC complexes of the three metals in catalysis is reflected in the large number of reports and reviews dealing with this topic. The gold derivatives are used primarily in cycloisomerization, addition of water to alkynes and nitriles, and C-H activation,⁵ silver derivatives in alkene diboration and ring-opening polymerization,⁶ and copper species in reduction and cycloaddition reactions.⁷ Several reports have been published on functional materials containing gold(I) NHC moieties. In many cases, the presence of the adapted substituent⁸ or the metal-metal interactions⁹ result in very

interesting optical properties, allowing the possibility of application as luminescent chemosensors or optoelectronic on/off switches.¹⁰ Liquid crystalline silver(I) or gold(I) NCH complexes have been described by the use of imidazolium salts with long alkyl side chains.¹¹ Some gold(I) and silver(I) compounds show in vitro antimicrobial activity against a variety of Gram-positive and Gram-negative bacteria and fungal species.¹² Furthermore, several gold(I) NHC complexes have shown good antitumor properties, especially lipophilic cationic compounds that selectively target the mitochondria of carcinoma cells.¹³

In our group we are focused on the synthesis of new imidazolium salts with different substituents that can provide metal complexes with interesting properties. We believe that acridine is an excellent candidate for this purpose. Bierbach et al. have demonstrated that some gold(I) complexes with this ligand show a selective antimicrobial activity against *Mycobacterium tuberculosis*, although show less anticancer activity than the analogous platinum compound in non-small-cell lung cancer cells.¹⁴ In addition, the optical properties of a few derivatives with this ligand have been studied.¹⁵ The investigations confirm that these properties arise from the acridine, due to $n-\pi^*$ and $\pi-\pi^*$ transfers, metal-to-ligand charge transfer (MLCT), and face-to-face $\pi\cdots\pi$ stacking interactions.

Here we report on the synthesis of new imidazolium salts containing the acridine group and the corresponding group 11 metal complexes. Coinage metal complexes with stoichiometry [MCl(NHC)], $[M(NHC)_2]^+$, or $[Au(C_6F_5)(NHC)]$, obtained through a novel method starting from the imizadolium gold

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salts, have been described. The optical properties presented by the imidazolium salts and some of the metal complexes have been studied.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Imidazolium Salts. The reaction of N-methyl (Me) or N-benzyl (Bn) imidazole with 9-chloroacridine in toluene under reflux rapidly gives the corresponding salt 1 or 2 in good yield (Scheme 1). In

Scheme 1. Synthesis of the Imidazolium Salts



the ¹H NMR spectrum of 1 resonances for the imidazole, the acridine, and the methyl protons are observed. The presence of a singlet at 9.95 ppm corresponding to the NCHN imidazolium proton confirms the formation of 1. Analogous signals are observed for 2 corresponding to the acridine and imidazole rings. Additionally, a multiplet centered at 7.64 ppm and a singlet at 5.73 ppm corresponding to the phenyl and methyl groups, respectively, appear. The results obtained from the elemental analysis and mass spectra are consistent with the proposed salts. Metathesis reactions of these salts with AgBF₄ in dichloromethane afford 3 or 4 in good yield. In the ¹H NMR spectra no significant changes were observed in relation to 1 or 2_{i} but a singlet at -153.03 ppm in the ¹⁹F NMR spectrum confirms the presence of the BF_4^- counteranion. Finally, we have prepared the first imidazolium salt that contains the fragment $[AuCl(C_6F_5)]^-$ as a counteranion. Addition of $[Au(C_6F_5)(tht)]$ to a solution of 1 or 2 in a mixture of dichloromethane/methanol gives the new derivative 5 or 6. Again no significant changes were observed for the ¹H and $^{13}C{^{1}H}$ NMR spectra, but the appearance of two multiplets at -117.30 and -166.87 and a triplet of triplets at -166.19 ppm in the ¹⁹F NMR spectrum with ${}^{3}J_{F-F} = 19.76$ and ${}^{4}J_{F-F} = 2.34$ and a peak in the mass spectrum with an m/z ratio of 398.7 confirm the presence of the $[AuCl(C_6F_5)]^-$ counteranion.

The gold-imidazolium salt 5 has been characterized by X-ray diffraction and crystallized as a dichloromethane adduct, $5 \cdot CH_2Cl_2$. The solid-state molecular structure is depicted in Figure 1 together with a selection of bond lengths and angles. The coordination around the gold center is linear, with a C1–Au1–C18 angle of $178.1(2)^{\circ}$ and bond distances Au–C1 of 2.321(3) Å and Au–C18 of 1.997(10) Å. Although aurophilic interactions are likely in gold(I) complexes, there are none



Figure 1. ORTEP diagram of 5 with 50% probability ellipsoids. Most hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au(1)–C(18) 1.997(10), Au(1)–Cl(1) 2.321(3), N(1)–C(1) 1.313(11), N(1)–C(2) 1.386(11), N(1)–C(4) 1.462(10), N(2)–C(1) 1.353(11), N(2)–C(3) 1.394(11), N(2)–C(5) 1.433(10), C(2)–C(3) 1.331(12), C(18)–Au(1)–Cl(1) 178.1(2), C(1)–N(1)–C(2) 109.6(7).

present in this complex, probably because of the presence of a bulky countercation. In none of the crystal structures reported with the $[Au(C_6F_5)Cl]^-$ fragment are these aurophilic interactions present.¹⁶

In addition, in the packing of 5 we found the association of molecules through $\pi-\pi$ interactions (Figure 2). The shortest is between the two acridines related by symmetry, with a centroid-centroid separation between the two parallel acridine rings of 3.585 Å with an average interplanar separation of 3.417 Å. The displacement angle of 16.61° suggests the existence of significant intramolecular offset $\pi\cdots\pi$ stacking interactions. Furthermore there are $\pi-\pi$ interactions between the acridine and the pentafluorophenyl ring and also between two pentafluorophenyl moieties. Consequently a bidimensional chain is constructed by means of these $\pi-\pi$ interactions, with a distribution of the molecules by charge ++--++--, which is an example of $\pi-\pi$ interactions versus Coulombic repulsions.

Synthesis and Characterization of the Complexes. The reaction of 1 or 2 with Ag_2O in dichloromethane gives the new silver(I) complexes [AgCl(RimAcr)] (R = Me (7), Bn (8)) (see Scheme 2). Upon silver complex formation, the ¹H NMR signals for C2-H imidazolium protons disappear, confirming the presence of the new carbene species. In the mass spectra, peaks at m/z 366.0 and 442.0 corresponding to $[M - Cl]^+$ provide further evidence for the formation of these new derivatives. The corresponding gold complexes [AuCl-(RimAcr) (R = Me (9), Bn (10)) are obtained, as pale yellow solids, through carbene transfer reactions from 7 or 8 with [AuCl(tht)] in dichloromethane. In the mass spectra the molecular peaks, $[M]^+$, appear at m/z = 492.1 and 568, respectively. The same transmetalation route is employed to obtain the corresponding copper complexes, using CuCl as a copper source. The addition of CuCl to a solution of 7 or 8 in a dichloromethane/methanol (5:1) mixture leads to the precipitation of AgCl and the subsequent formation of the corresponding copper(I) complexes [CuCl(RimAcr)] (R = Me (11), Bn (12)) as orange-red solids, confirmed by the presence of peaks at 357.9 and 434.0 m/z ratio, corresponding to $[M]^+$ in the mass spectra.



Figure 2. Offset $\pi \cdots \pi$ stacking interactions of **5**. Acr–Acr contact: centroid–centroid distance (3.585 Å), interplanar distance (3.417 Å), torsion angle (0.00°), and angle displacement (16.61°); Acr–C₆F₅ contact: centroid–centroid distance (3.728 Å), interplanar distance (3.643 Å), torsion angle (13.62°), and angle displacement (12.26°); C₆F₅–C₆F₅ contact: centroid–centroid distance (3.649 Å), interplanar distance (3.478 Å), torsion angle (0.00°), and angle displacement (17.61°).





Silver(I) bis(carbenes) $[Ag(RimAcr)_2]BF_4$ (R = Me (13), Bn (14)) (Scheme 2) were synthesized from imidazolium salts with noncoordinating counteranions (3, 4). The reaction with Ag₂O does not produce the desired bis(carbene) derivatives, and consequently an additional base, NaOH, was added in a similar manner to that reported by Catalano et al.^{9a} In this case, in the mass spectra, peaks at 625.1 and 777.2 m/z ratio corresponding to $[M - BF_4]^+$ appear. Again, the treatment of these silver(I) complexes with [AuCl(tht)] leads to the corresponding bis(carbene)gold(I) complexes [Au(RimAcr)_2]-BF₄ (R = Me (15), Bn (16)). All of the gold(I) and silver(I) derivatives mentioned until now are yellow and show a high

polar solubility in solvents such as methanol and DMSO. We did not obtain the expected results on attempting to prepare the copper(I) bis(carbene) due to decomposition to unknown copper(II) derivatives, which are easily detectable by the appearance of a blue color in the reaction mixture.

Finally, we have designed an easy method for the preparation of gold(I) complexes with two different organometallic ligands of the scarcely represented type NHC–Au–C₆F₅. The treatment of gold-imidazolium salt **5** or **6** with NaH in dried THF rapidly gives the corresponding free carbene, which is able to displace the chlorine atom and coordinate to the gold center, giving the complexes $[Au(C_6F_5)(RimAcr)]$ (R = Me (17), Bn (18)). The formation of the carbene species is confirmed by the disappearance of the resonance for the C2–H imidazolium proton and by the presence of the molecular peaks in the mass spectra at m/z = 624.1 and 700.1, respectively.

 $^{13}C{^{1}H}$ NMR spectroscopy is a useful tool for the study of NHCs. All the chemical shifts of the C2–H corresponding to the imidazolium salts were found around 135 ppm. The formation of the Ag(I) complexes [AgCl(NHC)] and [Ag-(NHC)₂Ag]BF₄ causes a downfield shift in the carbene carbon signals between 38 and 48 ppm (Table 1). The chemical shifts

Table 1. Chemical Shifts (ppm) of the Carbenic Carbon of the Imidazolium Salts (δ_{Salt}) and Complexes (δ_{C})

compound	$\delta_{C(Salt)} \text{ (ppm) of } 1-$ 5, $\delta_{C} \text{ (ppm) of } 7-$ 17, R = Me	$\delta_{C(Salt)}$ (ppm) of 2– 6, δ_{C} (ppm) of 8– 18, R = Bn		
[(RimAcr)H]Cl ^a	(1) 135.5	(2) 135.7		
[(RimAcr)H]BF ₄	$(3) 135.1^{b}$	(4) 134.0 ^{<i>a</i>}		
$[(RimAcr)H][AuCl(C_6F_5)]^b$	(5) 135.1	(6) 135.1		
[AgCl(RimAcr)] ^a	(7) 174.0	(8) 179.1		
[AuCl(RimAcr)] ^a	(9) 171.4	(10) 171.7		
[CuCl(RimAcr)] ^c	(11) 182.0	(12) 180.8		
$[Ag(RimAcr)_2]BF_4^a$	(13) 182.2	(14) 181.7		
$[Au(RimAcr)_2]BF_4^a$	(15) 184.2	(16) 184.1		
$[Au(C_6F_5)(RimAcr)]^b$	(17) 191.7	(18) 191.7		
^{<i>a</i>} NMR in DMSO- <i>d</i> ₆ . ^{<i>b</i>} NMR in Acetone- <i>d</i> ₆ . ^{<i>c</i>} NMR in CD ₂ Cl ₂ .				

observed for the [MCl(NHC)] complexes range from 171 to 182 ppm, and an upfield displacement is observed in the order [CuCl(NHC)] > [AgCl(NHC)] > [AuCl(NHC)]. For the bis(carbene) complexes no comparison with the copper derivative can be made, but the chemical shifts of the silver and gold species are similar at 182.2 and 184.2 ppm, respectively, and downfield related to the [MCl(NHC)] complexes. These chemical shifts are comparable to other group 11 NHC complexes reported.^{7d,9,17,18} It is noteworthy commenting that in the bis(carbene) silver species [Ag-(PhCH₂imAcr)₂]BF₄ the resonance for the carbene carbon appears as two doublets as a consequence of the coupling with the two silver nuclei, with coupling constants of ${}^{1}J_{C-107Ag} =$ 184.4 and ${}^{1}J_{C-109Ag} = 212.6$ Hz. The chemical shift of [Au(C₆F₅)(NHC)] is the highest, 191.7 ppm. This is in accordance with previous work reported by Hashmi in which the deshielding of the carbene carbons is due to the poor π donor ability of the pentafluorophenyl ring.¹⁸ Some studies of the relation of the carbene chemical shift and the basicity of the ligands coordinated *trans* to it have been carried out. For the gold complexes we have chemical shifts of 171.4, 184.2, and 191.7 for the chlorine, carbene, and pentafluorophenyl ligands, which is in agreement with the increasing basicity of the ligands.¹⁹

X-ray Structure Analysis. The molecular structures of complexes [MCl(MeimAcr)] (M = Ag (7), Au (9), Cu (11)) have been established by X-ray diffraction. In the structures of the silver and copper species, 7 and 11, two molecules are associated around an inversion center, giving dimeric structures with lateral metal–chlorido interactions (Figure 3). While the length of direct silver–chlorido bond is 2.3818(11) Å, the length of the additional interaction is substantially longer at 2.9113(10) Å. For the copper derivative the direct Cu–Cl bond is 2.2060(9) Å, with an interaction of 2.58322(7) Å. This is reflected in the C_{carbene}–M–Cl angles, where a proportional decrease from linearity around 15° for Ag(I) and 25° for Cu(I) is observed (Table 2). The interplanar angle between the acridine and the carbene rings for 7 is almost perpendicular, 82.66°, while for 11 the angle is 77.59°.

The structure of the gold compound is mononuclear with a linear geometry, C–Au–Cl angle of $177.7(2)^{\circ}$, and shows a very weak aurophilic interaction of 3.622 Å, which, despite being at the limit of the sum of the van der Waals radii for gold, 3.6 Å, could influence the packing of the molecule in the solid state. The M–C bond lengths are 2.091(3) for silver, 1.969(8) for gold, and 1.901(2) Å for copper, which are similar to those found in the same type of carbene complexes.^{7d,20} The largest corresponds to the silver complex, in accordance with the fact that the covalent radius for gold is smaller than that of silver. The interplanar angle between the acridine and the carbene rings for **9** is 72.14°.

All of the complexes NHC–M–Cl (7, 9, and 11) in the solid state show $\pi \cdots \pi$ stacking interactions between the acridine rings of different molecules. For the complexes of NHC–M--X type (7, 9, and 11) the interplanar and centroid–centroid distances found were from 3.319 to 3.616 and 3.607–3.887 Å, respectively, causing a parallel displacement from 14.22° to



Figure 3. ORTEP diagram of 7 (a) and 11 (b) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.

compound	M-C _{carbene}	M–X	$C_{carbene}$ -M-X	torsion $angle^d$	torsion angle
7	2.091(3)	$2.3818(11)^a$	$162.63(9)^a$	82.66	
9	1.969(8)	$2.286(2)^a$	$177.7(2)^{a}$	72.14	
11	1.901(2)	$2.2060(9)^a$	$153.77(7)^a$	77.59	
13	2.096(4)	$2.095(5)^{c}$	$173.62(16)^{c}$	67.80	83.53 ^e
15	2.019(4)	$2.019(4)^{c}$	$180.000(1)^{c}$	69.96	0.00^{e}
17	2.014(8)	$2.041(9)^{b}$	$177.1(3)^{b}$	67.36	15.96 ^f
a Y - Cl b Y - C	$^{c}V - C$	d _{Torsion} angle between th	a acriding and the corbone	rings eTorsion angle bot	waan tha carbana ring

 ${}^{a}X = Cl. {}^{b}X = C_{pentafluorophenyl}$, ${}^{c}X = C_{carbene}$. "Torsion angle between the acridine and the carbene rings." Torsion angle between the carbene rings.

 31.36° . Curiously, only for the silver(I) complex is there a pyridine-pyridine ring contact, while for the gold(I) and copper(I) complexes there are pyridine-arene ring contacts (Table 3).

Table 3. Interplanar Distance (Å), Centroid–Centroid Distance (Å), Displacement Angle (deg), and Aromatic Contact for Complexes 7, 9, 11, 13, 15, and 17

compound	interplanar distance	centroid—centroid distance	displacement angle	aromatic contact
5	3.417	3.585	16.61	ру-ру
7	3.616	3.796	17.71	ру-ру
9	3.319	3.887	31.36	py-ph
11	3.542	3.739	21.11	py-ph
13	3.342	3.607	22.10	ру-ру
15	3.323	3.632	23.80	py-ph
17	3.509	3.620	14.22	py-ph

Figure 4b shows the crystal packing for compound **9** with the aurophillic and the $\pi \cdots \pi$ stacking interactions.

The solid-state structures of the complexes 13 and 15 (as perchlorate salts) have been established by X-ray diffraction analysis and are depicted in Figure 5. Several attempts to crystallize complex 15, $[Au(RimAcr)_2]BF_4$, led to crystals with a pronounced pseudosymmetry; for this reason the complex with a different counteranion, perchlorate, was prepared and the X-ray structure determined. There is an increase of the

C_{carbene}-M bond distance compared with the [MCl(NHC)] complexes, as has been observed previously in other bis(carbene) derivatives.⁹ In the solid state, complex 13 shows a C_{carbene}-Ag(I)-C_{carbene} bond angle of 173.62(16)°, corresponding to an almost linear environment around the silver(I) center, but with the carbene rings almost in a perpendicular disposition, with a torsion angle of 83.53°. For complex 15 the $C_{carbene}$ -Au(I)- $C_{carbene}$ bond angle is the ideal 180° because the gold atom lies in a symmetry center. In both cases, there is a decrease of the interplanar angle between the acridine and the carbene rings, but more accentuated in the silver(I) complex than in the gold(I) derivative, with values of 14.86° and 2.18° for 13 and 15, respectively, compared to the values found in the NHC-M-Cl complexes (Table 2). Both complexes show $\pi \cdots \pi$ stacking interactions in the solid state. The interplanar distance and the centroid-centroid distance are 3.342 and 3.607 Å for 13 and 3.323 and 3.632 Å for 15, causing displacement angles of 22.10° and 23.80°, respectively. Once again, the aromatic contact is pyridine-pyridine for the Ag(I) complex, while for the Au(I) complex the aromatic contact is pyridine-phenyl (Table 3).

The solid-state molecular structure of 17 (Figure 6a) reveals a displacement of 15.96° in the torsion angle between the acridine and carbene rings. The $C_{carbene}-M$ and $M-C_{pentafluorophenyl}$ distances of 2.014(8) and 2.041(9) Å, respectively, are consistent with the other example with a pentafluorophenyl ligand.¹⁸ The Au-C_{carbene} distance is higher



Figure 4. (a) ORTEP diagram of 9 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively. (b) Crystal packing of 9. View along the crystallographic *b* axis.



Figure 5. ORTEP diagram of 13 (a) and 15 (b) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively.



Figure 6. (a) ORTEP diagram of 17 with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are depicted in Tables 2 and 3, respectively. (b) Offset $\pi \cdots \pi$ stacking interactions of 17.

than in the corresponding chlorido derivatives, showing the higher *trans* influence of the pentafluorophenyl ring. Figure 6b shows a bidimensional chain of complex 17 where the molecules are disposed in such a way that the acridine and the pentafluorophenyl rings are found almost in a parallel disposition between themselves. The interplanar distance between the acridine rings is 3.509 Å, and the centroid–centroid distance between the aromatic rings is 3.620 Å with a parallel displacement of 14.22° (Table 3); for the $C_6F_5-C_6F_5$ contact the centroid–centroid distance is 3.567 Å, the interplanar distance 3.334 Å, and the angle of displacement 20.82°. All these data confirm the presence of $\pi \cdots \pi$ stacking interactions.

Optical Properties. The diffuse reflectance spectrum of the 9-chloroacridine in the solid state has been measured for comparison purposes and shows absorptions at 240, 270, and 360 nm. The imidazolium salts show strong absorption bands between 250 and 400 nm. The metal carbene complexes display a similar broad band that goes from 250 to 400 nm. These bands can be attributed to the acridine chromophore $\pi \rightarrow \pi^*$ or

 $n{\rightarrow}\pi^*$ transitions, which are in agreement with the reported data for acridine-based derivatives. 21

The emission spectrum of the 9-chloroacridine shows two moderate bands at 280 and 390 nm, which is different from the emission spectra of the imidazolium salts 1-6, which are emissive at room temperature and at low temperature, showing a strong green fluorescence around 530–540 nm (see Table 4), with a not very intense shoulder around 390 nm. The substitution of the chloro by an imidazol moiety changes the emission properties of the compound, and this is similar to other 9-substituted acridine systems such as 9-aminoacridine.²² These moderately intense emissions can be assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The presence of a gold atom as a counteranion in the gold-imidazolium salts 5 and 6 does not change the emission behavior of the initial salt. There is no difference between the energy of the emissions for the Me and the Bn derivatives at room temperature for chloride as counteranion, although a small blue shift is observed for the Bn derivatives with BF_4^- or $[Au(C_6F_5)Cl]^-$ as counteranions. At low temperature this difference is present for all the imidazolium salts.

Table 4. Emission Maxima	(nm) for the Compounds in the
Solid State upon Excitation	(values given in parentheses)

compound	$\lambda_{\rm max}$ (298 K)	$\lambda_{\rm max}~(77~{ m K})$
9-chloroacridine	390(250)	380(250)
$[(CH_3imAcr)H]Cl(1)$	390(245), 530(370)	390(245), 545(370)
$[(PhCH_2imAcr)H]Cl (2)$	390(245), 530(370)	390(245), 560(370)
$[(CH_3 imAcr)H]BF_4$ (3)	540(370)	540(370)
[(PhCH ₂ imAcr)H] BF ₄ (4)	530(370)	555(370)
$[(CH_3imAcr)H][AuCl(C_6F_5)] (5)$	360(245), 530(370)	550(370)
[(PhCH2imAcr)H][AuCl(C6F5)] (6)	360(245), 540(360)	560(360)
$[AgCl(CH_3imAcr)] (7)$	390(245), 507(370)	390(245), 515(370)
[AgCl(PhCH ₂ imAcr)] (8)	390(245), 480(370)	390(245), 475(370)
$[AuCl(CH_3imAcr)] (9)$	390(245), 530(370)	390(245), 520(370)
[AuCl(PhCH ₂ imAcr)] (10)	390(245), 470(370)	390(245), 480(370)
[CuCl(CH ₃ imAcr)] (11)	390(245)	390(245)
$[CuCl(PhCH_2imAcr)]$ (12)	390(245)	390(245)
$[Ag(CH_3imAcr)_2]BF_4$ (13)	470(370)	475(370)
$[Ag(PhCH_2imAcr)_2]BF_4$ (14)	520(370)	525(370)
$[Au(CH_3imAcr)_2]BF_4 (15)$	390(245), 530(370)	390(245), 525(370)
$[Au(PhCH_2imAcr)_2]BF_4 (16)$	390(245), 470(370)	390(245), 475(370)
$[Au(C_6F_5)(CH_3imAcr)] (17)$	500(370)	510(370)
$[Au(C_6F_5)(PhCH_2imAcr)] (18)$	515(360)	535(360)

The behavior of these imidazolium salts with the acridine moiety resembles those of other imidazolium salts derived from the 4,5-bis-bromomethylacridine, which acts as a fluorescent chemosensor for pyrophosphate and dihydrogen phosphate,²³ or the anthracene-substituted imidazolium salts, in which the assignments of the emitting states are based on the $\pi \rightarrow \pi^*$ excited states of the anthracene ligand.^{8a}

The metal complexes are luminescent in the solid state at room temperature, showing similar emissions around 500 nm with a small blue shift. A much less intense shoulder at 390 nm is observed for some of the complexes. The copper derivatives show only the band at 390 nm. These emissions are clearly intraligand transitions, and the increase in the energy of the emissions can be attributed to the destabilization of the π^* orbital of the acridine moiety. As the carbenes are good σ -electron donors, a withdrawing of electron density from the acridine would take place when the free carbene coordinates to a metal center, producing a larger energy gap between the orbitals involved in the transitions. The emission spectra of the imidazolium salts 1 and 2 and their metal complexes are shown in Figure 7. The presence of the methyl or benzyl subtituent in the imidazolium moiety produces a more pronounced blue shift in the emissions, exemplified by the gold compounds 9 and 10, [AuCl(RimAcr)], which changes from 530 to 470 nm on going from Me to Bn (see Figure 8). Again this change can be



Figure 8. Emission spectra for complexes 9 and 10 in the solid state at room temperature.

attributed to a stabilization of the π^* orbital of the acridine because the presence of a substituent with better electronic properties, the methyl group, could require less electron density from the acridine moiety. At 77 K all the complexes show the same emissions, with the exception of **5** and **6**, where only the lower energy emission is observed with a slightly red shift. For the rest of the complexes the first emission remains at the same energy and the second emission is red-shifted.



Figure 7. (a) Normalized room-temperature emission spectra for compound 1 and complexes 7, 9, 13, 15, and 17 in the solid state upon excitation at 370 nm. (b) Normalized room-temperature emission spectra for compound 2 and complexes 8, 10, 14, 16, and 18 in the solid state upon excitation at 370 nm.

Although the emission energies point to a fluorescent nature of the emissions, the lifetimes of two representative compounds have been measured. The imidazolium salt 1 and the gold complex 17 show values of 34.8 and 35 ns, respectively, which indicates, as expected, a fluorescent nature of the emissions.

Comparison with other N-heterocyclic gold complexes such as [AuCl(NHC)], where NHC is the anthracene-substituted carbene, shows this complex is not luminescent in the solid state, but the corresponding complexes with acetylide ligands are. The origin of the emissions has been proposed to be localized at the ${}^{1}\pi-\pi^{*}$ excited states of the NHC ligand and not the ${}^{3}\pi-\pi^{*}$ of the acetylide.^{8a} Other NHC gold complexes such as [AuCl(MeimMe)] present two different emissions in the solid state, one attributed to an intraligand transition and the other to a Au-centered transition, because aurophilic interactions are present. The corresponding carbazole derivative [Au(cbz)(MeimMe)] presents low-energy emission bands at 584–592 nm, which are likely to arise from the transitions involving mainly carbazole tuned by Au.²⁴

The electronic absorption spectra in methanol solutions have been measured for the imidazolium salt [(CH₃imAcr)H]Cl (1), the silver complex [AgCl(CH₃imAcr)] (7), and the gold derivative [AuCl(CH₃imAcr)] (9). All the compounds present similar absorption spectra to that of 9-chloroacridine or acridine itself; the latter shows one absorption at 250 nm and another at 355 nm. The imidazolium salt 1 shows also the same two absorptions at 250 (ε 78 000) and 365 (ε 9900) nm, for the silver complex 7 at 245 (ε 83 000) and 360 (ε 9700) nm, and for the gold derivative 9 at 260 (ε 100 000) and 365 (ε 9700), which are also assigned at an intraligand absorption involving the acridine group. The methanol solutions of 1, 7, and 9 are luminous when irradiated with a UV lamp. The emission spectra show an intense structured band with maxima around 410, 435, and 455 nm, independently when excited at 270 or 375 nm (see Figure 9). The imidazolium salt and the metal



Figure 9. Excitation and emission spectra for complex 7 in methanol at room temperature ($c = 1.22 \times 10^{-3}$ M).

complexes display a similar behavior, and both correspond to the emissions observed for acridine in solution; consequently an intraligand origin for the emissions is proposed. There is a big difference in the emissions of the compounds in solution compared with the solid state; a great blue shift is observed and the emissions are very similar among acridine, imidazolium salts, and the metal complexes. This different behavior in the luminescent properties can be due to the extended $\pi - \pi$ interactions present in these molecules in the solid state that are not present in solution.

In Figure 10 it is possible to appreciate the different luminescence in the solid state and in solution for the



Figure 10. (a) Samples of 1 (solid state and solution) and 17 (solid state and solution) under normal light. (b) The same samples under UV light.

imidazolium salt $[(CH_3imAcr)H]Cl$ (1) and for the gold complex $[Au(C_6F_5)(CH_3imAcr)]$ (17).

CONCLUSIONS

New imidazolium salts containing the acridine chromophore with different counteranions have been synthesized. The salt $[(CH_3imAcr)H][AuCl(C_6F_5)]$ shows an interesting structural framework with formation of a bidimensional chain through $\pi \cdots \pi$ stacking interactions between cations and anions of the form ++--++, an example of such interactions versus Coulombic respulsions. Silver(I) N-heterocyclic carbene complexes have been obtained by reaction of the imidazolium salts with Ag₂O. [AgCl(NHC)] complexes have been prepared from the imidazolium salts with a chloride counteranion, and the bis(carbene) species, $[M(NHC)_2]^+$, from the imidazolium salts with a noncoordinating counteranion. The corresponding group 11 metal complexes have been synthesized by the transfer of the carbene from the corresponding silver(I) carbene complexes. The gold-imidazolium salts can lead directly to the gold-carbene derivatives by reaction with a base. The crystal structures of these complexes show $\pi \cdots \pi$ stacking interactions between the acridine and pentafluorophenyl rings of different molecules. The [AuCl(NHC)] species show a supramolecular structure based on the aurophilic and $\pi \cdots \pi$ stacking interactions.

The imidazolium salts and most of the complexes are intense blue-green emitters in the solid state and blue emitters in solution. The coordination of the metals produces a blue shift of the emissions. The origin of the emissions can be assigned to intraligand $\pi - \pi^*$ transitions. Further studies of the potential of these complexes as catalysts, anticancer agents, or optical materials are being undertaken.

EXPERIMENTAL SECTION

Instrumentation. C, H, and N analysis were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a Bruker Esquire 3000 PLUS, with the electrospray (ESI) technique, and on a Bruker Microflex (MALDI-TOF). ¹H, ¹³C{H}, and ¹⁹F NMR, including 2D experiments, were recorded at room temperature on a Bruker Avance 400 spectrometer (¹H, 400 MHz; ¹³C, 100.6 MHz; ¹⁹F, 376.5 MHz) or on a Bruker Avance II 300 spectrometer (¹H, 300 MHz; ¹³C, 75.5 MHz; ¹⁹F, 282.3 MHz), with chemical shifts (δ , ppm) reported relative to the solvent peaks of the deuterated solvent.²⁵ The solution absorption spectra were recorded with a Unicam UV-4 in methanol. The diffuse-reflectance UV spectra of solid samples were recorded with a Unicam UV-4 Labsphere integrating sphere. The solid

samples were mixed with silica to form a homogeneous powder. The mixtures were placed in a homemade cell equipped with a quartz window. Steady-state photoluminescence spectra were recorded with a Jobin-Yvon-Horiba fluorolog FL-3-11 spectrometer using band pathways of 3 nm for both excitation and emission.

Starting Materials. The starting materials $[AuCl(tht)]^{26}$ and $[Au(C_6F_5)(tht)]^{27}$ were prepared according to published procedures. All other reagents were commercially available. Solvents were used as received without purification or drying, except for tetrahydrofuran (THF), which was dried with a SPS solvent purification system.

General Procedure for the Synthesis of 1 and 2. 1-Methylimidazole or 1-benzylimidazole (1.80 mmol) was added to a suspension of 9-chloroacridine (0.3367 g, 1.58 mmol) in toluene (ca. 10 mL), and the solution was heated at 140 °C for 12 h with stirring. A yellow precipitate started to form during the course of reaction. After cooling, the solid was collected by filtration, washed with hexane (ca. 20 mL), and dried under vacuum to give the product 1 or 2 as a yellow solid.

[(CH₃imAcr)H]Cl (1). Yield: 0.4540 g (97.6%). ¹H NMR (DMSOd₆, 400 MHz, 294 K): δ 9.95 (s, 1H, im), 8.37 (d, ³J = 8.74 Hz, 2H, acr), 8.32 (m, 2H, im), 8.03 (ddd, ³J = 8.71 Hz, ³J = 6.43 Hz, ⁴J = 1.47 Hz, 2H, acr), 7.82–7.74 (m, 4H, acr), 4.13 (s, 3H, CH₃). ¹³C{¹H} NMR (DMSO-d₆, 100.6 MHz, 294 K): δ 148.5 (acr), 139.3 (acr), 135.5 (im), 131.4 (acr), 129.3 (acr), 128.8 (acr), 124.9 (im), 124.9 (im), 122.2 (acr), 121.6 (acr), 36.6 (CH₃). MALDI⁺-MS, *m/z*: 260.1 [M]⁺. Anal. Calcd (%) for C₁₇H₁₄N₃Cl: C, 69.03; H, 4.77; N, 14.21. Found: C, 69.42; H, 4.38; N, 13.93.

[(PhCH₂imAcr)H]Cl (2). Yield: 0.4906 g (83.5%). ¹H NMR (DMSO- d_{6} 400 MHz, 294 K): δ 10.15 (s, 1H, im), 8.40 (d, ³J = 1.54 Hz, 2H, acr), 8.39 (s, 1H, im), 8.37 (s, 1H, im), 8.03 (dddd, ³J = 8.70 Hz, ³J = 6.62 Hz, ⁴J = 1.29 Hz, 2H, acr), 7.81 (ddd, ³J = 8.74 Hz, ³J = 6.62 Hz, ⁴J = 1.08 Hz, 2H, acr), 7.68–7.64 (m, 2H, acr, 2H, Ph), 7.54–7.44 (m, 3H, Ph), 5.73 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO- d_{6} , 100.6 MHz, 294 K): δ 148.4 (acr), 139.0 (acr), 135.7 (im), 134.2 (Ph), 131.4 (acr), 129.4 (acr), 129.1 (Ph), 129.0 (acr), 128.9 (Ph), 128.7 (Ph), 125.6 (im), 123.9 (im), 121.9 (acr), 121.4 (acr), 52.8 (CH₂). MALDI⁺-MS, *m/z*: 336.2 [M]⁺. Anal. Calcd (%) for C₂₃H₁₈N₃Cl: C, 74.29; H, 4.88; N, 11.30. Found: C, 74.03; H, 4.63; N, 11.12.

General Procedure for the Synthesis of 3 and 4. $AgBF_4$ (0.127 g, 0.65 mmol) was added to a solution of 1 or 2 (0.65 mmol) in a mixture (ca. 18 mL) of CH₂Cl₂/MeOH (5:1), and the solution was heated at room temperature for 2 h with stirring. A white precipitate started to form during the course of reaction. Then, the mixture was filtered through Celite, the bright yellow filtrate was reduced to minimum volume under vacuum, and the product was precipitated with Et₂O to give the product 3 or 4 as a yellow solid.

[(CH₃imAcr)H]BF₄ (3). Yield: 0.185 g (82%). ¹H NMR (acetoned₆, 400 MHz, 294 K): δ 9.66 (s, 1H, im), 8.37 (dm, ³J = 8.83 Hz, 2H, acr), 8.31 ("t", ³J = 1.73 Hz, 1H, im), 8.27 ("t", ³J = 1.81 Hz, 1H, im), 8.01 (ddd, ³J = 8.81 Hz, ³J = 6.02 Hz, ⁴J = 1.92 Hz, 2H, acr), 7.83– 7.76 (m, 4H, acr), 4.38 (s, 3H, CH₃). ¹³C{¹H} NMR (acetone-d₆, 75.5 MHz, 294 K): δ 151.0 (acr), 137.2 (acr), 135.1 (im), 133.1 (acr), 131.8 (acr), 130.9 (acr), 128.2 (im), 127.3 (im), 123.9 (acr), 123.7 (acr), 38.7 (CH₃). ¹⁹F NMR (acetone-d₆, 376.5 MHz, 294 K): δ –153.03. MALDI⁺-MS, *m/z*: 260.1 [M]⁺. Anal. Calcd (%) for C₁₇H₁₄N₃BF₄: C, 58.82; H, 4.07; N, 12.11. Found: C, 59.12; H, 3.84; N, 11.78.

[(PhCH₂imAcr)H]BF₄ (4). Yield: 0.2063 g (75.0%). ¹H NMR (DMSO- d_{6} , 400 MHz, 294 K): δ 9.94 (s, 1H, im), 8.38 (d, ³J = 8.93 Hz, 2H, acr), 8.39 (s, 1H, im), 8.32 (s, 1H, im), 8.04 (ddd, ³J = 8.60 Hz, ³J = 6.62 Hz, ⁴J = 1.04 Hz, 2H, acr), 7.82 (ddd, ³J = 8.56 Hz, ³J = 6.65 Hz, ⁴J = 0.75 Hz, 2H, acr), 7.67 (d, ³J = 8.64 Hz, 2H, acr), 7.62–7.61 (m, 2H, Ph), 7.54–7.47 (m, 2H, Ph), 5.68 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO- d_{6} , 100.6 MHz, 294 K): δ 148.5 (acr), 139.0 (acr), 135.4 (Ph), 134.0 (im), 131.4 (acr), 129.4 (acr), 129.1 (Ph), 129.0 (acr, Ph), 128.7 (Ph), 125.7 (im), 123.9 (im), 121.9 (acr), 121.5 (acr), 52.9 (CH₂). ¹⁹F NMR (DMSO- d_{6} , 376.5 MHz, 294 K): δ –148.24. ESI⁺-MS, *m*/*z*: 336.1 [M]⁺. Anal. Calcd (%) for C₂₃H₁₈N₃BF₄: C, 65.27; H, 4.29; N, 9.93. Found: C, 65.52; H, 4.38; N, 10.13.

General Procedure for the Synthesis of 5 and 6. A mixture of 1 or 2 (0.2 mmol) and $[Au(C_6F_5)(tht)]$ (0.0904 g, 0.2 mmol) in dichloromethane (ca. 15 mL) was stirred at room temperature for 3 h, at which point the formation of an off-white precipitate was observed. Then the solution was filtered through Celite, the yellow filtrate was reduced to minimum volume under vacuum, and the product was precipitated with hexane to give 5 or 6 as a yellow solid.

[(CH₃imAcr)H][AuCl(C₆F₅)] (5). Yield: 0.1 g (66.85%). ¹H NMR (acetone- d_{6} , 400 MHz, 294 K): δ 9.77 (s, 1H, im), 8.38–8.37 (m, 1H, acr), 8.36–8.35 (m, 2H, acr, im), 8.31 (m, 1H, im), 8.02 (ddd, ³J = 8.76 Hz, ³J = 5.44 Hz, ⁴J = 2.50 Hz 2H, acr), 7.82–7.76 (m, 4H, acr), 4.43 (s, 3H, CH₃). ¹³C{¹H} NMR (acetone- d_{6} , 100.6 MHz, 294 K): δ 151.0 (acr), 141.1 (acr), 135.1 (im),133.0 (acr), 131.8 (acr), 130.9 (acr), 127.3 (im), 127.3 (im), 123.8 (acr), 123.6 (acr), 38.8 (CH₃). ¹⁹F NMR (acetone- d_{6} , 376.5.3 MHz, 294 K): δ –117.30 (m, o-F), –166.19 (tt, ³J = 19.76 Hz, ⁴J = 2.34 Hz, p-F), –166.87 (m, m-F). ESI⁺-MS, *m*/*z*: 260.1 [M]⁺. ESI⁻-MS: 398.7 [M]⁻. Anal. Calcd (%) for C₂₃H₁₄N₃ClF₅Au: C, 41.87; H, 2.14; N, 6.37. Found: C, 41.68; H, 2.43; N, 6.07.

[(PhCH₂imAcr)H][AuCl(C₆F₅)] (6). Yield: 0.1080 g (73.4%). ¹H NMR (acetone- $d_{6^{j}}$ 400 MHz, 294 K): δ 9.88 (s, 1H, im), 8.40–8.39 (m, 1H, im) 8.39–8.38 (m, 1H, im), 8.35 (d, ³J = 8.83 Hz, 2H, acr), 8.01 (ddd, ³J = 8.80 Hz, ³J = 6.18 Hz, ⁴J = 1.76 Hz, 2H, acr), 7.80– 7.73 (m, 4H, acr, 2H, Ph), 7.56–7.50 (m, 3H, Ph), 5.97 (s, 2H, CH₂). ¹³C{¹H} NMR (acetone- $d_{6^{j}}$ 100.6 MHz, 294 K): δ 151.0 (acr), 140.6 (acr), 135.4 (Ph), 135.1 (im) 133.0 (acr), 131.9 (acr), 131.3 (Ph), 131.3 (Ph), 131.0 (Ph), 131.0 (Acr), 127.9 (im), 126.2 (im), 123.7 (acr), 123.5 (acr), 55.9 (CH₂). ¹⁹F NMR (acetone- $d_{6^{j}}$ 376.5.3 MHz, 294 K): δ –117.27 (m, o-F), –166.13 (tt, ³J = 19.80 Hz, ⁴J = 2.35 Hz, p-F), –166.82 (m, m-F). ESI⁺-MS, *m/z*: 336.1 [M]⁺. ESI⁻-MS: 398.7 [M]⁻. Anal. Calcd (%) for C₂₉H₁₈N₃ClF₅Au: C, 47.33; H, 2.47; N, 5.71. Found: C, 46.98; H, 2.65; N, 5.35.

General Procedure for the Synthesis of 7 and 8. $Ag_2O(0.038$ g, 0.165 mmol) was added to a solution of 1 or 2 (0.33 mmol) in a mixture (ca. 18 mL) of CH₂Cl₂/MeOH (5:1). The mixture was protected from light and stirred for 4 h at room temperature. Then the solution was filtered through Celite, the bright yellow filtrate was reduced to minimum volume under vacuum, and the product was precipitated with Et₂O to give 3 or 8 as a yellow solid.

[AgCl(CH₃imAcr)] (7). Yield: 0.1002 g (75.4%). ¹H NMR (DMSO- d_{6} , 400 MHz, 294 K): δ 8.26 (d, ³*J* = 8.70 Hz, 2H, acr), 7.90–7.82 (m, 4H, acr, im), 7.53 (br, 2H, acr), 7.33 (br, 2H, acr), 3.60 (br, 3H, CH₃). ¹³C{¹H} NMR (DMSO- d_{6} , 100.6 MHz, 294 K): δ 174.0 (im_{carb}), 148.4 (acr), 139.7 (acr), 130.8 (acr), 129.3 (acr), 127.8 (acr), 125.0 (im), 123.8 (im), 122.1 (acr), 121.8 (acr), 37.9 (CH₃). ESI⁺-MS, *m*/*z*: 366.0 [M - Cl]⁺, 260.1 [M - Ag - Cl]⁺. Anal. Calcd (%) for C₁₇H₁₃N₃ClAg: C, 50.71; H, 3.25; N, 10.44. Found: C, 50.94; H, 2.91; N, 10.13.

[AgCl(PhCH₂imAcr)] (8). Yield: 0.1106 g (70.0%). ¹H NMR (DMSO- $d_{6'}$ 400 MHz, 294 K): δ 8.22 (br, 2H, acr), 7.86 (br, 2H, acr, 2H, im), 7.45 (br, 2H, acr), 7.31–7.21 (m, 2H, acr, 3H, Ph), 6.93 (br, 2H, Ph), 4.93 (br, 2H, CH₂). ¹³C{¹H} NMR (DMSO- $d_{6'}$ 100.6 MHz, 294 K): δ 179.1 (im_{carb}), 148.4 (acr), 139.5 (acr), 136.2 (Ph), 130.8 (acr), 129.3 (Ph), 128.7 (acr), 128.0 (Ph), 127.9 (Ph), 127.3 (acr), 125.6 (im), 122.9 (im), 121.8 (acr), 121.7 (acr), 54.1 (CH₂). ESI⁺-MS, m/z: 442.0 [M – Cl]⁺. Anal. Calcd (%) for C₂₃H₁₇N₃ClAg: C, 57.70; H, 3.58; N, 8.78. Found: C, 57.58; H, 3.35; N, 8.56.

General Procedure for the Synthesis of 9 and 10. A mixture of 7 or 8 (0.15 mmol) and [AuCl(tht)] (0.048 g, 0.15 mmol) in dichloromethane (ca. 20 mL) was protected from light and stirred at room temperature for 1.5 h, at which point the formation of an off-white AgCl precipitate was observed. Then the solution was filtered through Celite, the bright yellow filtrate was reduced to minimum volume under vacuum, and the product was precipitated with hexane to give 9 or 10 as a yellow solid.

[AuCl(CH₃imAcr)] (9). Yield: 0.065 g (88.3%). ¹H NMR (DMSOd₆, 400 MHz, 294 K): δ 8.35 (d, ³J = 8.72 Hz, 2H, acr), 8.00–7.97 (m, 2H, acr, 2H, im), 7.75 (m, 2H, acr), 7.56 (d, ³J = 8.63 Hz, 2H, acr), 4.02 (s, 3H, CH₃). ¹³C{¹H} NMR (DMSO-d₆, 100.6 MHz, 294 K): δ 171.4 (im_{carb}), 148.7 (acr), 139.6 (acr), 131.2 (acr), 129.3 (acr), 128.2 (acr), 124.5 (im), 123.9 (im), 122.6 (acr), 122.4 (acr), 38.0 (CH₃). ESI⁺-MS, m/z: 492.1 [M]⁺. Anal. Calcd (%) for C₁₇H₁₃N₃ClAu: C, 41.52; H, 2.66; N, 8.55. Found: C, 41.75; H, 2.49; N, 8.29.

[AuCl(PhCH₂imAcr)] (10). Yield: 0.0728 g (85.5%). ¹H NMR (DMSO- d_{6} 400 MHz, 294 K): δ 8.36 (d, ³J = 8.75 Hz, 2H, acr), 8.11 (d, ³J = 1.90 Hz, 1H, im), 8.06 (d, ³J = 1.88 Hz, 1H, im), 7.99 (ddd, ³J = 8.51 Hz, ³J = 6.67 Hz, ⁴J = 0.97 Hz, 2H, acr), 7.79–7.76 (m, 2H, acr), 7.55–7.49 (m, 2H, acr, 4H, Ph), 7.12–7.17 (m, 1H, Ph), 5.63 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO- d_{6} , 100.6 MHz, 294 K): δ 171.7 (im_{carb}), 148.7 (acr), 139.5 (acr), 136.3 (Ph), 131.3 (acr), 129.4 (Ph), 128.9 (acr), 122.7 (acr), 54.0 (CH₂). ESI⁺-MS, *m/z*: 568.0 [M]⁺. Anal. Calcd (%) for C₂₃H₁₇N₃ClAu: C, 48.65; H, 3.02; N, 7.40. Found: C, 48.43; H, 3.17; N, 7.63.

General Procedure for the Synthesis of 11 and 12. A mixture of 7 or 8 (0.082 mmol) and CuCl (8.2 mg, 0.082 mmol) in dichloromethane (ca. 15 mL) was protected from light and stirred at room temperature for 3 h, at which point the formation of an off-white AgCl precipitate was observed. Then the solution was filtered through Celite, the orange filtrate was reduced to minimum volume under vacuum, and the product was precipitated with Et_2O to give 11 or 12 as an orange solid.

[CuCl(CH₃imAcr)] (11). Yield: 0.0245 g (83.2%). ¹H NMR (CD₂Cl₂- d_2 , 400 MHz, 294 K): δ 8.31 (d, ³J = 8.83 Hz, 2H, acr), 7.84 (ddd, ³J = 8.72 Hz, ³J = 6.22 Hz, ⁴J = 1.65 Hz, 2H, acr), 7.62–7.56 (m, 4H, acr), 7.37 (d, ³J = 1.693 Hz, 1H, im), 7.28 (d, ³J = 1.68 Hz, 1H, im), 4.13 (s, 3H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂- d_6 , 100.6 MHz, 294 K): δ 182.0 (im_{carb}), 149.7 (acr), 140.0 (acr), 131.1 (acr), 130.3 (acr), 128.3 (acr), 127.3 (im), 123.9 (im), 123.1 (acr), 122.7 (acr), 39.1 (CH₃). ESI⁺-MS, *m*/*z*: 357.9 [M]⁺. Anal. Calcd (%) for C₁₇H₁₃N₃ClCu: C, 56.99; H, 3.66; N, 11.73. Found: C, 56.78; H, 3.83; N, 11.51.

[CuCl(PhCH₂imAcr)] (12). Yield: 0.0314 g (88.1%). ¹H NMR (CD₂Cl₂- d_2 , 300 MHz, 294 K): δ 8.35 (d, ³J = 8.80 Hz, 2H, acr), 7.88 (ddd, ³J = 8.66 Hz, ³J = 6.38 Hz, ⁴J = 1.458 Hz, 2H, acr), 7.81 (ddd, ³J = 8.74 Hz, ³J = 6.62 Hz, ⁴J = 1.084 Hz, 2H, acr), 7.67–7.56 (m, 4H, acr), 7.52–7.45 (m, 5H, Ph), 7.33 (d, ³J = 1.80 Hz, 1H, im), 7.29 (d, ³J = 1.80 Hz, 1H, im), 5.62 (s, 2H, CH₂). ¹³C{¹H} NMR (CD₂Cl₂- d_2 , 75.5 MHz, 294 K): δ 180.8 (im_{carb}), 149.9 (acr), 141.8 (acr), 136.0 (Ph), 131.2 (acr), 130.6 (Acr), 129.7 (Ph), 129.3 (Ph), 128.5 (acr), 125.1 (im), 123.2 (Acr), 122.6 (acr), 121.8 (acr), 56.3 (CH₂). ESI⁺-MS, *m/z*: 434.04 [M]⁺. Anal. Calcd (%) for C₂₃H₁₈N₃ClCu: C, 63.59; H, 3.94; N, 9.67. Found: C, 63.42; H, 4.23; N, 9.43.

General Procedure for the Synthesis of 13 and 14. A mixture of 3 or 4 (0.26 mmol), Ag₂O (0.0151 g, 0.065 mmol), and Bu₄NBF₄ (10 mg) in dichloromethane (ca. 20 mL) was stirred at room temperature for 1.5 h. The entire time the mixture was protected from light, then NaOH (1 N, 3 mL) was added, and stirring was continued for a further 15 min. Then the solution was filtered through Celite, the yellow-orange filtrate was reduced to minimum volume under vacuum, and the product was precipitated with Et₂O to give 13 or 14 as a yellow solid.

[Ag(CH₃imAcr)₂]BF₄ (13). Yield: 0.07 g (75.7%). ¹H NMR (DMSO- d_{6j} 400 MHz, 294 K): δ 8.25 (d, ³*J* = 8.63 Hz, 2H, acr), 7.87–7.83 (m, 1H, im, 2H, acr), 7.76 (s, 1H, im), 7.47 (br, 2H, acr), 7.26 (br, 2H, acr), 3.49 (br, 3H, CH₃). ¹³C{¹H} NMR (DMSO- d_{6j} 100.6 MHz, 294 K): δ 182.2 (im_{carb}), 148.4 (acr), 139.6 (acr), 130.7 (acr), 129.4 (acr), 127.7 (acr), 125.0 (im), 123.8 (im), 122.0 (acr), 121.7 (acr), 37.9 (CH₃). ¹⁹F NMR (DMSO- d_{6j} 376.5 MHz, 294 K): δ –148.23. ESI⁺-MS, m/z: 625.1 [M]⁺. Anal. Calcd (%) for C₃₄H₂₆N₆BF₄Ag: C, 57.25; H, 3.67; N, 11.78. Found: C, 57.53; H, 3.41; N, 11.46.

[Ag(PhCH₂imAcr)₂]BF₄ (14). Yield: 0.0828 g (73.6%). ¹H NMR (DMSO-*d*₆, 400 MHz, 294 K): δ 8.20 (d, ³J = 8.73 Hz, 2H, acr), 7.85–7.81 (m, 2H, acr, 2H, im), 7.43 (ddd, ³J = 8.64 Hz, ³J = 6.62 Hz, ⁴J = 0.99 Hz, 2H, acr), 7.31–7.27 (m, 1H, Ph), 7.20 (d, ³J = 7.67 Hz, 2H, Ph), 7.16 (d, ³J = 8.50 Hz, 2H, acr), 6.99 (d, ³J = 7.19 Hz, 2H, Ph), 4.88 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO-*d*₆, 100.6 MHz, 294 K): δ 181.7 (2d, ¹J_{C-107Ag} = 184.4 Hz, ¹J_{C-109Ag} = 212.6 Hz, im_{car}b), 148.3 (acr), 139.3 (acr), 136.0 (Ph), 130.8 (acr), 129.4 (Ph), 128.7 (acr),

128.1 (Ph), 127.9 (Ph), 127.2 (acr), 125.7 (im), 122.9 (im), 121.7 (acr), 121.6 (acr), 54.0 (CH₂). ¹⁹F NMR (DMSO- d_6 , 376.5 MHz, 294 K): δ –148.24. ESI⁺-MS, m/z: 777.2 [M]⁺. Anal. Calcd (%) for C₄₆H₃₄N₆BF₄Ag: C, 63.84; H, 3.96; N, 9.71. Found: C, 63.56; H, 4.12; N, 9.92.

General Procedure for the Synthesis of 15 and 16. A mixture of 13 or 14 (0.075 mmol) and [AuCl(tht)] (0.0241 g, 0.075 mmol) in dichloromethane (ca. 15 mL) was stirred at room temperature for 30 min, at which point the formation of an off-white AgCl precipitate was observed. Then the solution was filtered through Celite, the bright yellow filtrate was reduced to minimum volume under vacuum, and the product was precipitated with Et_2O to give 15 or 16 as a yellow solid.

[Au(CH₃imAcr)₂]BF₄ (15). Yield: 0.0338 g (55.4%). ¹H NMR (DMSO- d_{64} 400 MHz, 294 K): δ 8.25 (d, ³J = 8.70 Hz, 2H, acr), 7.85 (d"t", J = 7.60 Hz, 2H, acr), 7.81–7.79 (m, 2H, im), 7.48 (d"t", J = 7.52 Hz, 2H, acr), 7.23 (d, ³J = 8.62 Hz, 2H, acr), 3.39 (s, 3H, CH₃). ¹³C{¹H} NMR (DMSO- d_{66} 100.6 MHz, 294 K): δ 184.2 (im_{carb}), 148.2 (acr), 138.5 (acr), 130.7 (acr), 129.3 (acr), 127.8 (acr), 124.9 (im), 124.2 (im), 122.0 (acr), 121.7 (acr), 36.8 (CH₃). ¹⁹F NMR (DMSO- d_{66} 282.3 MHz, 294 K): δ –148.23. ESI⁺-MS, *m/z*: 715.1 [M]⁺. Anal. Calcd (%) for C₃₄H₂₆N₆BF₄Au: C, 57.25; H, 3.67; N, 11.78. Found: C, 57.03; H, 3.42; N, 11.92.

[Au(PhCH₂imAcr)₂]BF₄ (16). Yield: 0.0619 g (86.5%). ¹H NMR (DMSO- $d_{6^{4}}$ 400 MHz, 294 K): δ 8.35 (d, ³J = 8.79 Hz, 2H, acr), 8.10 (d, ³J = 1.52 Hz, 1H, im), 8.05 (d, ³J = 1.73 Hz, 1H, im), 8.00 (ddd, ³J = 8.45 Hz, ³J = 6.57 Hz, ⁴J = 0.90 Hz, 2H, acr), 7.79–7.76 (m, 2H, Acr), 7.55–7.48 (m, 2H, Acr, 4H, Ph), 7.31 (t, ³J = 7.43 Hz, 1H, Ph), 5.63 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO- $d_{6^{4}}$ 100.6 MHz, 294 K): δ 184.1 (im_{carb}), 148.7 (acr), 140.8 (acr), 136.0 (Ph), 130.9 (acr), 129.4 (Ph), 129.0 (acr), 128.7 (Ph), 127.5 (Ph), 127.1 (acr), 122.3 (im), 121.7 (im), 117.8 (acr), 117.3 (acr), 62.9 (CH₂). ¹⁹F NMR (DMSO- $d_{6^{4}}$ 376.5 MHz, 294 K): δ –148.24. ESI⁺-MS, *m*/*z*: 867.25 [M]⁺. Anal. Calcd (%) for C₄₆H₃₄N₆BF₄Au: C, 57.88; H, 3.59; N, 8.80. Found: C, 57.65; H, 3.87; N, 8.51.

General Procedure for the Synthesis of 17 and 18. A mixture of 5 or 6 (0.2 mmol) and an excess of HNa in dried THF (ca. 15 mL) was stirred at room temperature for 1.5 h, at which point the color of the solution changed from yellow to yellow-green. Then, the solution was filtered through Celite, and the filtrate was evaporated under vacuum. The product was redissolved with dichloromethane (ca. 3 mL) and finally precipitated with hexane to give 17 or 18 as a yellow solid.

[Au(C₆F₅)(CH₃imAcr)] (17). Yield: 0.1054 g (84.5%). ¹H NMR (acetone- $d_{6^{\prime}}$ 400 MHz, 294 K): δ 8.31 (dm, ³J = 8.82 Hz, 2H, Acr), 7.96 (d, ³J = 1.81 Hz, 1H, im), 7.93 (ddd, ³J = 8.93 Hz, ³J = 4.79 Hz, ⁴J = 1.54 Hz 2H, acr), 7.87 (d, ³J = 1.91 Hz, 1H, im), 7.71–7.70 (m, 4H, acr), 4.23 (s, 3H, CH₃). ¹³C{¹H} NMR (acetone- $d_{6^{\prime}}$ 100.6 MHz, 294 K): δ 191.7 (im_{carb}), 151.3 (acr), 141.8 (acr), 132.6 (acr), 131.7 (acr), 129.7 (acr), 126.4 (im), 125.5 (im), 124.9 (acr), 124.7 (acr), 39.5 (CH₃). ¹⁹F NMR (acetone- $d_{6^{\prime}}$ 376.5.3 MHz, 294 K): δ –118.11 (m, o-F), -163.88 (tt, ³J = 19.55 Hz, ⁴J = 1.295 Hz, p-F), -166.34 (m, m-C₆F₅). ESI⁺-MS, *m/z*: 624.1 [M]⁺. Anal. Calcd (%) for C₂₃H₁₃N₃F₃Au: C, 44.32; H, 2.10; N, 6.74. Found: C, 44.11; H, 2.28; N, 6.51.

[Au(C₆F₅)(PhCH₂imAcr)] (18). Yield: 0.1108 g (79.2%). ¹H NMR (acetone- d_6 , 400 MHz, 294 K): δ 8.32 (d, ³J = 8.80 Hz, 2H, acr), 8.04 (d, ³J = 1.95 Hz, 1H, im), 7.94 (ddd, ³J = 8.77 Hz, ³J = 6.32 Hz, ⁴J = 1.63 Hz, 2H, acr), 7.92 (d, ³J = 1.85 Hz, 1H, im), 7.75–7.65 (m, 4H, acr, 2H, Ph), 7.52–7.44 (m, 3H, Ph), 5.82 (s, 2H, CH₂). ¹³C{¹H} NMR (DMSO- d_6 , 100.6 MHz, 294 K): δ 191.7 (im_{carb}), 151.3 (acr), 144.0 (Ph), 138.4 (acr), 132.6 (acr), 131.7 (acr), 130.9 (Ph), 130.4 (Ph), 130.1 (Ph), 129.8 (acr), 127.0 (im), 125.8 (im), 124.8 (acr), 124.5 (acr), 56.5 (CH₂). ¹⁹F NMR (acetone- d_6 , 376.5.3 MHz, 294 K): δ –118.07 (m, o-F), –163.78 (tt, ³J = 19.55 Hz, ⁴J = 1.21 Hz, p-F), –166.30 (m, m-F). ESI⁺-MS, *m*/*z*: 700.1 [M]⁺. Anal. Calcd (%) for C₂₉H₁₇N₃F₅Au: C, 49.80; H, 2.45; N, 6.01. Found: C, 49.69; H, 2.35; N, 6.18.

Crystallography. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of an Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attach-

ment. Data were collected using monochromated Mo K α radiation (λ = 0.71073 Å). Scan type: ω . Absorption corrections based on multiple scans were applied with the program SADABS²⁸ or using spherical harmonics implemented in SCALE3 ABSPACK²⁹ scaling algorithm (15). The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.³⁰ All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were included in calculated positions and refined using a riding model. Refinements were carried out by full-matrix least-squares on F^2 for all data. Further details of the data collection and refinement are given in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

Seven X-ray crystallographic files, in CIF format, for compounds 5, 7, 9, 11, 13, 15, and 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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