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Luminescent Gold(I) Carbenes from 2-Pyridylisocyanide Complexes: Structural Consequences of Intramolecular versus Intermolecular Hydrogen-Bonding Interactions

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Isocyanide [AuX(CNPy-2)] (X = Cl, C_6F_5, fluoromesityl, ½ octafluorobiphenyl) and carbene [AuX{C(NR^{1}R^2)(NHPy-2)}] (R^{1}R^{2}NH = primary or secondary amines or ½ primary diamine) gold(I) complexes have been synthesized and characterized. For X = Cl, the carbene complexes show aurophilic interactions. The fragment NHPy-2, formed in the carbenes, can give rise to intra- (for primary amines) or intermolecular (for secondary amines) hydrogen bonds, depending on the amine used. These bonds and contacts have been studied in the solid state and in solution. The intermolecular hydrogen bonds are split in an acetone solution, but the intramolecular ones, which close a six-membered ring, survive in solution. Except for the fluoromesityl derivatives, the carbene complexes display luminescent properties.

Introduction

Carbene metal complexes are an active area of research.[1] Compared to other late-transition-metal carbene complexes, the chemistry of linear gold(I) carbenes is less developed. Recently, there has been a resurgence of interest in gold(I) compounds because of spectacular achievements in catalysis.[2] Many gold(I) complexes also exhibit interesting photophysical and photochemical behavior.[3] Short Au−Au aurophilic contacts have been held responsible for the luminescent properties observed in these kinds of materials,[4] but recent works have shown that short Au···Au contacts are not always needed for luminescence.[5] It has been reported recently, on CO and isocyanide gold complexes, that aurophilicity and ligand π-acceptance ability sensitize the photoreactivity of gold(I) complexes.[6]

Self-organized systems with specific properties and functions are receiving attention as potential advanced materials. Weak forces such as hydrogen bonds and aurophilic interactions can be decisive in self-organization. We have recently reported their participation in gold(I) carbenes [AuX{C(NR^{1}R^2)(NHPy-4)}] (4-Py = 4-pyridyl) for the formation, in the solid state, of supramolecular macrocycles only supported by intermolecular hydrogen bonds, either with N−H groups of other molecules or with water molecules.[7] At variance with the reported 4-Py complexes, the 2-Py group can participate in intra- or intermolecular hydrogen bonding. We report here the synthesis of gold(I) isocyanide and carbene complexes with the 2-Py fragment and the photophysical properties of the latter.

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(1) (a) Zaragoza, F. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Chichester, U.K., 1999. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) Special Issues on Carbene Chemistry: *J. Organomet. Chem.* **2005**, *690*, 5397–6252. (edited by G. Bertrand).

(2) (a) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211, and references cited therein. (b) Nieto-Oberhuber, C.; Muñoz, M. P.; López, S.; Jiménez-Núñez, E.; Nevado, C.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem.—Eur. J.* **2006**, *12*, 1677. (c) Comas-Vives, A.; González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F.; Ujaque, G. *J. Am. Chem. Soc.* **2006**, 4756.

(3) (a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391. (b) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033. (c) Brandys, M.-C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 4839. (d) Yam, V. W. W.; Lo, K. K. W. *Chem. Soc. Rev.* **1999**, *28*, 323.

(4) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033.

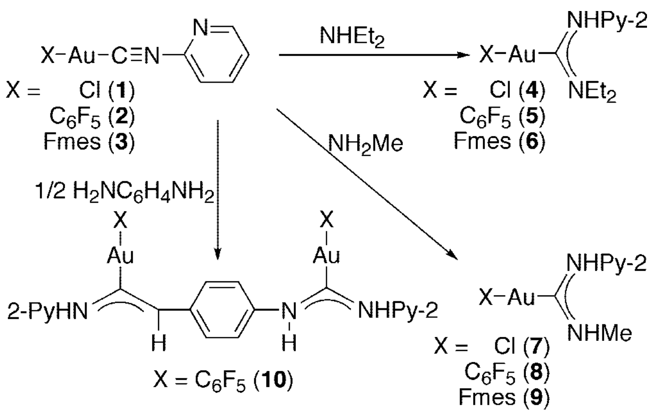
(5) (a) Bayón, R.; Coco, S.; Espinet, P. *Chem.—Eur. J.* **2005**, *11*, 1079. (b) Coco, S.; Cordovilla, C.; Espinet, P.; Martin-Alvarez, J. M.; Muñoz, P. *Inorg. Chem.* **2006**, *45*, 10180.

(6) Elbjeirami, O.; Omary, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 11384–11393.

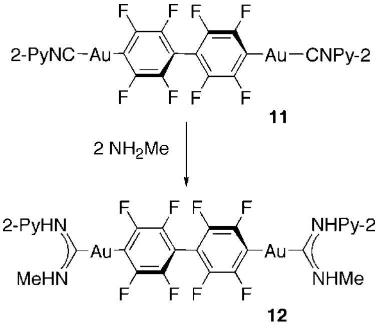
(7) Bartolomé, C.; Carrasco-Rando, M.; Coco, S.; Cordovilla, C.; Espinet, P.; Martin-Alvarez, J. M. *J. Chem. Soc., Dalton Trans.* **2007**, 5339–5345.

10.1021/ic702201e CCC: $40.75

Scheme 1. Synthesis of the Gold Carbene Derivatives **4**−**10**



Scheme 2. Synthesis of **12**



Results and Discussion

All of the complexes reported in this paper were characterized by correct C, H, and N analyses, which, along with yields and relevant IR data, are given in the Experimental Section.

The synthesis of the neutral gold isocyanide complexes **1**−**3** was carried out by displacement of tetrahydrothiophene (tht) for CNPy-2 in their respective precursors [AuX(tht)] (X = Cl,[8] C_6F_5,[8] Fmes[9]), as reported for similar gold compounds.[10]

Their gold carbene derivatives were prepared, as reported for other cases,[11−13] by nucleophilic attack with the appropriate primary or secondary amine to the coordinated isocyanide (Scheme 1).

Similarly, the octafluorobiphenyldigold diisocyanide derivative **11** was obtained from [(μ-$C_6F_4C_6F_4$){Au(tht)}$_2$][14] and transformed into the binuclear gold carbene complex [(μ-$C_6F_4C_6F_4$){Au(C(NHMe)(NHPy-2))}$_2$] (**12**) by the addition of 2 mol of NH_2Me (Scheme 2).

The IR spectra of the isocyanide complexes showed typical ν(C≡N) shifts at higher wave numbers (ca. 100 cm^{-1}) than those for the free ligands. The IR spectra of the gold carbene complexes showed the disappearance of the ν(C≡N) absorption and the appearance of new peaks corresponding to ν(N−H) and ν(C═N) at ca. 3270 cm^{-1} and at 1550–1510 cm^{-1}.[15]

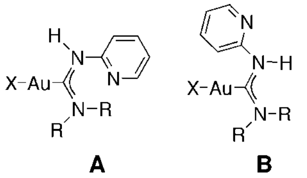


Figure 1. Two possible isomers for carbene complexes derived from R_2NH.

The ^1H NMR spectra of all of the complexes displayed four signals from the four nonequivalent aromatic protons of the 2-pyridyl group. The ^{19}F NMR spectra of the C_6F_5 derivatives displayed three multiplet resonances for the AA′MXX′ spin system at ca. −116 ppm (F_{ortho}), −159 ppm (F_{meta}), and −163 ppm (F_{para}).[16] The ^{19}F NMR spectra of the Fmes derivatives displayed two singlets, one for *o*-CF_3 and one for *p*-CF_3.[9] For the 4,4′-octafluorobiphenyl compounds, two multiplets at ca. −116 and −140 ppm were observed (deceptively simple AA′XX′ spin system), as reported for other 4,4′-octafluorobiphenyl complexes.[10] No NMR data are available for compound **10** because of its insolubility, but luckily crystals suitable for complete X-ray diffraction characterization were obtained.

In the compounds prepared, the kind of amine used controls very clearly the structure of the molecule, which, in turn, determines the supramolecular structure. For secondary amines with identical substituents, such as Et_2NH, assuming easy rotation of the 2-Py ring but severe restriction to rotation about the carbene C−N bond (which has considerable multiple character), only two isomers are possible (Figure 1), labeled anti (**A**) and syn (**B**) depending on the arrangement of the 2-Py group relative to the gold substituent. However, only one isomer was observed in the ^1H and ^{19}F NMR spectra of **4**−**6** at room temperature. The observed isomer shows the N−H signal at ca. 8.2 ppm, in $CDCl_3$. A nuclear Overhauser effect with the methylene of one ethyl group (that at higher field) of the carbene supports the less hindered isomer **B**. An exchange process between the N−H hydrogen and free water was also observed. The same isomer had also been found to be the preferred one for the carbene complexes with 4-Py.[7]

The crystal structures of [AuCl{C(NEt_2)(NHPy-2)}] (**4**) and [AuFmes{C(NEt_2)(NHPy-2)}] (**6**) could be solved and confirmed the proposed assignment. In both cases, the isomer found has the Py group oriented away from the ethyl groups of the amine. This conformation reduces the steric hindrance of the molecule. In solution, the intermolecular hydrogen contacts observed will break down, but the spectroscopic evidence discussed above supports that the conformer found in the solid state is retained in solution.

A perspective view of the structures of **4** and **6** is given in Figures 2 and 3, respectively. Selected bond lengths and angles are listed in Table 1. The two complexes show a

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(8) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

(9) Espinet, P.; Martín-Barrios, S.; Villafañe, F.; Jones, P. G.; Fischer, A. K. *Organometallics* **2000**, *19*, 290.

(10) Bayón, R.; Coco, S.; Espinet, P.; Fernández-Mayordomo, C.; Martin-Alvarez, J. M. *Inorg. Chem.* **1997**, *36*, 2329.

(11) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 1711.

(12) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251.

(13) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069.

(14) Usón, R.; Laguna, A.; Laguna, M.; Cólera, I.; de Jesús, E. *J. Organomet. Chem.* **1984**, *263*, 121.

(15) Busetto, A.; Palazzi, A.; Crociani, B.; Belluco, U.; Bradley, E.; Kilby, B. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1800.

(16) Coco, S.; Espinet, P. *J. Organomet. Chem.* **1994**, *484*, 113.

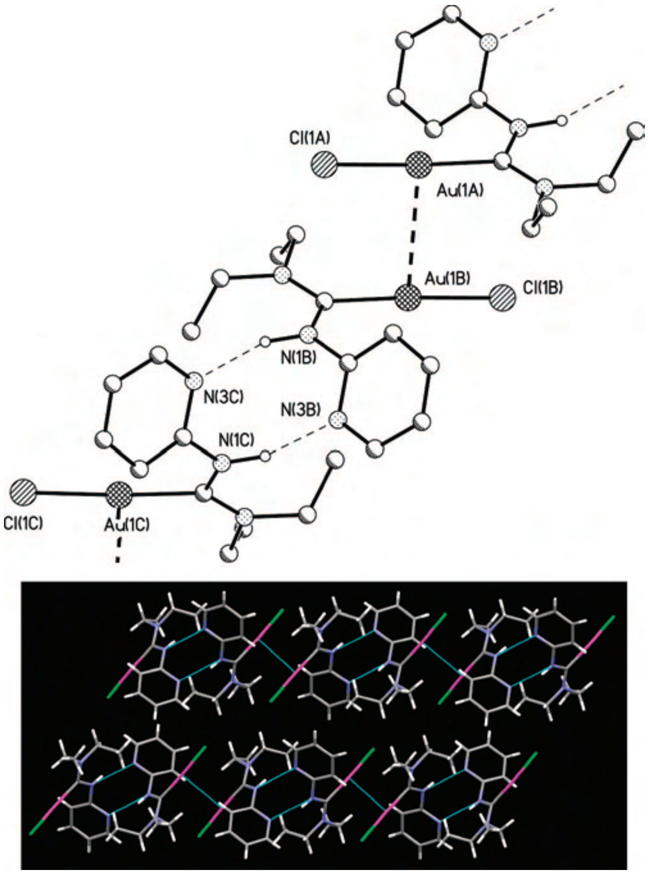

Figure 2. Top: Crystal structure of **4** showing the intermolecular H···N hydrogen bonds and Au···Au interactions observed. Bottom: View of a sequence of molecules in two layers in the crystalline network, showing the alternate connections (in blue) by hydrogen bonding and Au···Au contacts (pink, Au; green, Cl).

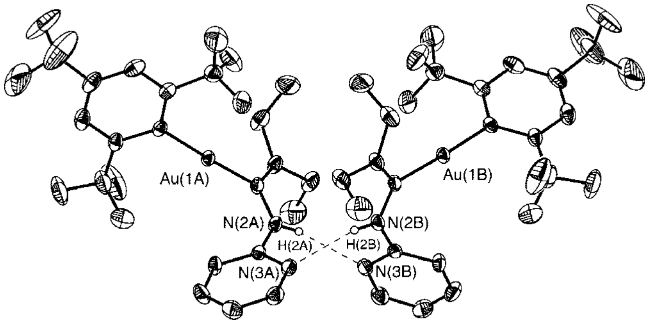

Figure 3. Crystal structure of **6**. Hydrogen bonds are shown as dotted lines.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for **4** and **6**

4		**6**	
Au(1)−C(1)	1.994(5)	Au(1)−C(11)	2.052(4)
Au(1)−Cl(1)	2.2812(17)	Au(1)−C(1)	2.053(4)
C(1)−N(2)	1.329(7)	C(11)−N(1)	1.322(6)
C(1)−N(1)	1.345(7)	C(11)−N(2)	1.341(6)
C(1)−Au(1)−Cl(1)	176.17(16)	C(11)−Au(1)−C(1)	177.63(17)
N(2)−C(1)−N(1)	116.9(5)	N(1)−C(11)−N(2)	116.7(4)
		C(2)−C(1)−C(6)	113.8(4)

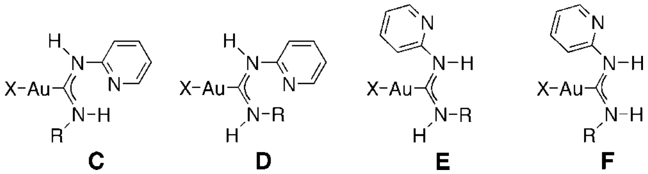

Figure 4. Four possible isomers for carbene complexes derived from RNH_2.

nearly linear C−Au−X geometry, typical for gold(I) complexes. The Au(1)−C(1) distance in **4** [1.994(5) Å] is shorter than the Au(1)−C(11) distance in **6** [2.052(4) Å], showing the higher trans influence of Fmes compared to Cl. The importance of π bonding between carbon and nitrogen in the carbene is confirmed by the short C(1)−N(2) and C(1)−N(1) distances in both complexes.

Figure 2 shows the presence of two kinds of intermolecular interactions in **4**. The molecules self-associate to form extended chains connected by alternate Au···Au and hydrogen-bonding contacts: A short ligand-unassisted intermolecular Au···Au distance of 3.3107(14) Å, in the range of attractive aurophilic interactions proposed in the literature,[17] would define dimers (as represented in the upper part of Figure 2), which further interact by intermolecular hydrogen bonding between the nitrogen of the 2-Py moiety of one unit and the N−H of the carbene group of the neighboring molecule. The H(1)···N(3) distance is 2.627(7) Å, whereas the N(1)−H(1)···N(3) angle is 152.4(5)°.[18] The H(1)···N(3) distance is within the usual range for H−N moderate hydrogen bonds.[19]

In **6**, there are no aurophilic interactions because the shortest distance between gold atoms is 7.154 Å. However, the molecules are associated as dimers through hydrogen bonding between the nitrogen of the 2-Py and the N−H of the carbene group of the neighboring molecule (Figure 3). The H(2)···N(3) distance is 2.152(4) Å (corresponding to a moderate hydrogen bond),[19] whereas the N(2)−H(2)···N(3) angle is 151.8(6)°.[18]

The results were dramatically different for carbenes derived from primary amines, where up to four isomers, two anti and two syn depending on the arrangement of the 2-Py group and the gold (Figure 4; **C/D** and **E/F**), can be formed. Again, only one isomer was observed in the ^1H NMR spectra at room temperature in $CDCl_3$ for complexes **7**−**9** (**10** is insoluble) and **12**, with two distinct signals for two N−H protons, one at ca. 12.5 ppm and another in the range 9.5–8 ppm. The latter undergoes an important low-field shift (to ca. 10.2 ppm) when the spectrum is recorded in acetone-d_6, likely due to hydrogen bonding with the solvent. The chemical shift of the low-field signal reveals the existence in solution of an intramolecular hydrogen bond between the amine proton and the nitrogen of the 2-pyridyl group, which cannot exist in the case of secondary amines, and proves

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(17) (a) Jones, P. G. *Gold Bull.* **1981**, *14*, 102. (b) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391. (c) Karahu, T.; Ishii, R.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1349. (d) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319. (e) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1996**, 561. (f) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417.

(18) To correct the systematic shortening of N−H bonds measured by X-ray diffraction, normalized hydrogen-atom positions were used. An N−H distance of 1.009 Å was imposed. This value has been observed in amines by neutron diffraction. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, S1.

(19) Hydrogen-bonding distance ranges proposed in the literature: strong, 1.2–1.5 Å; moderate, 1.5–2.2 Å; weak, 2.2–3.2 Å: Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997.

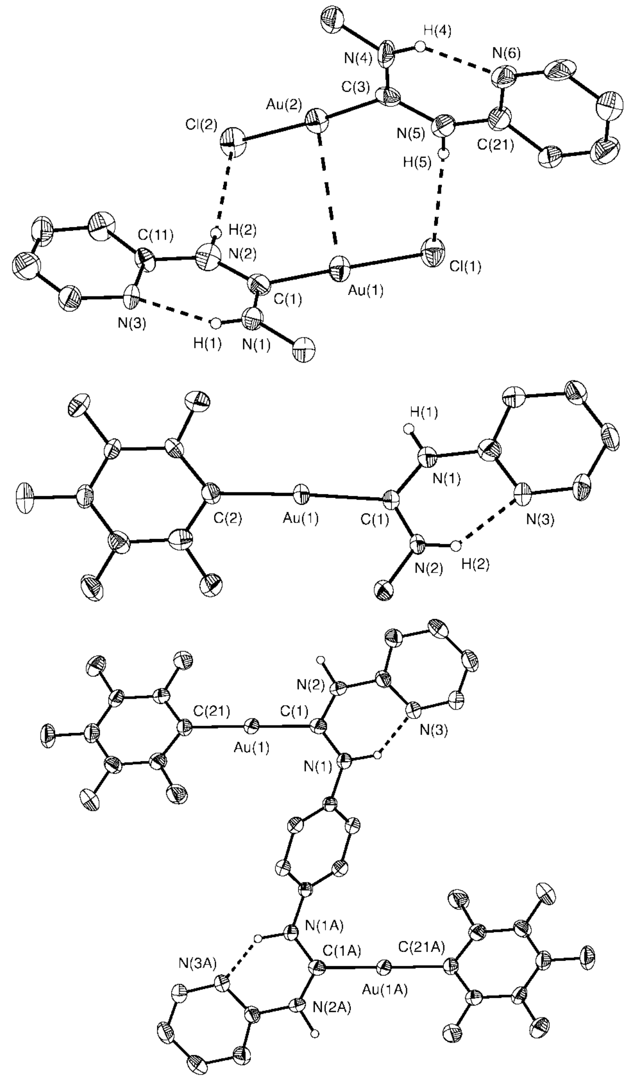

Figure 5. X-ray structures for (top) **7**, (middle) **8**, and (bottom) **10**•$2Me_2CO$. Most hydrogen atoms, and acetone in **10**•$2Me_2CO$, are omitted for clarity.

that the isomer formed is **C**. This hydrogen interaction closes a six-membered ring and seems very stable because it stabilizes exclusively the otherwise less favored anti isomer and is not affected in solution in acetone-d_6. As far as it is stable, this ring is structurally equivalent to a heterocycle and the corresponding carbenes are equivalent to the widely used N-heterocyclic carbenes.

X-ray-quality crystals suitable for single-crystal diffraction could be obtained only for [AuCl{C(NHMe)(NHPy-2)}] (**7**), [Au(C_6F_5){C(NHMe)(NHPy-2)}] (**8**), and (μ-NHC_6H_4HN)-[C(NHPy-2)Au(C_6F_5)]$_2$•$2Me_2CO$ (**10**•$2Me_2CO$) but, unfortunately, not for the interesting **12**, in which the two carbene ligands are flanking the linear gold complexes. The expected intramolecular hydrogen bond was confirmed in the three structures. The molecular structures of **7**, **8**, and **10**•$2Me_2CO$ are shown in Figure 5. Selected bond lengths and angles are given in Table 2.

The three complexes show a nearly linear geometry for gold, with C−Au−X angles in the range 178.6−174.3°. The Au−Cl distance in **7** [2.295(5) Å] is longer than that for $[AuCl_2]^-$ (2.257 Å)[20] as a consequence of the trans influence of the carbene.[21] The Au−C distances are within the range found for similar gold(I) carbenes[22] and arylgold(I) complexes,[23] respectively. The Au(1)−C(1) distance in **7** is shorter than those in **8** and **10**•$2Me_2CO$, which can be attributed mostly to the higher trans influence of C_6F_5, compared to Cl. The C(1)−N(2) and C(1)−N(1) distances are similar to others in related gold(I) carbene complexes and shorter than the theoretical C(sp^2)−N single-bond distance of 1.45 Å,[24] indicating considerable π bonding between carbon and nitrogen atoms. As seen for other crystallographically characterized C_6F_5 complexes, the C−C−C angle at the ipso-carbon in **8** and **10**•$2Me_2CO$ is less than 120° because of the electronic effects of the electropositive metal and electronegative fluorine substituents at the ortho positions.[25]

The conformer found in the three carbenes has the N−H of the formerly amine group oriented toward the pyridyl nitrogen. A comparison of selected hydrogen-bond distances and angles is presented in Table 3. In the three structures, these H⋯N distances and the corresponding N−H⋯N angles are within the range of moderate intramolecular N⋯H hydrogen bonds.[19] The spectroscopic evidence discussed above unambiguously supports that the conformations observed in the solid state are retained in solution.

Several kinds of intermolecular contacts have been observed in the crystal structures of the carbenes. In **7**, the monomeric units are disposed in pairs with an Au⋯Au distance of 3.2547(12) Å, which is much longer than that in metallic gold[26] but close to the highest values found between peripheral atoms in gold clusters.[27] Therefore, attractive aurophilic interactions between the metal centers of different monomers cannot be discarded.[17] An intermolecular N−H⋯Cl hydrogen bond, within the usual range for H⋯Cl hydrogen bonds,[28] reinforces the formation of dimers in the crystalline network. In the crystal packing, these dimers adopt an intermolecular parallel arrangement of their monomers, creating a zigzag chain of dimers (Figure 6).

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(22) (a) Balch, A. L.; Olmstead, M. M.; Vickery, J. C. *Inorg. Chem.* **1999**, *38*, 3494. (b) Beck, W.; Weigand, W.; Nagel, U.; Schaal, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 377. (c) Banditelli, G.; Bonati, F.; Calogero, S.; Valle, G.; Wagner, F. E.; Wordel, R. *Organometallics* **1987**, *6*, 2019. (d) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033.

(23) (a) Usón, R.; Laguna, A. *Coord. Chem. Rev.* **1986**, *70*, 1. (b) Usón, R.; Laguna, A.; Vicente, J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 655.

(24) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; p 282.

(25) (a) Jones, P. G. *J. Organomet. Chem.* **1988**, *345*, 405. (b) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 221. (c) Domenicano, A.; Murray-Rust, P.; Vaciago, A. *Acta Crystallogr., Sect. B* **1983**, *39*, 457 and references cited therein. (d) Norrestam, R.; Schepper, L. *Acta Chem. Scand., Ser. A* **1981**, *35*, 91. (e) Domenicano, A.; Mazzeo, P.; Vaciago, A. *Tetrahedron Lett.* **1976**, 1029.

(26) *Interatomic Distances*; Special Publication of The Chemical Society, Number 18; The Chemical Society: London, 1965.

(27) (a) Albano, V. G.; Bellon, P. L.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1970**, 1210. (b) Albano, V. G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1481. (c) Albano, V. G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2423.

(28) Aullón, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7**, **8**, and **10**·$2Me_2CO$

7		**8**		**10**·$2Me_2CO$	
Au(1)−C(1)	1.96(2)	Au(1)−C(1)	2.018(9)	Au(1)−C(1)	2.029(6)
Au(1)−Cl(1)	2.295(5)	Au(1)−C(2)	2.049(9)	Au(1)−C(21)	2.038(6)
C(1)−N(2)	1.38(2)	C(1)−N(2)	1.322(17)	C(1)−N(1)	1.330(7)
C(1)−N(1)	1.31(2)	C(1)−N(1)	1.346(15)	C(1)−N(2)	1.355(7)
C(1)−Au(1)−Cl(1)	177.8(6)	C(1)−Au(1)−C(2)	174.3(9)	C(1)−Au(1)−C(21)	178.6(2)
N(2)−C(1)−N(1)	116.6(17)	N(2)−C(1)−N(1)	116.4(8)	N(2)−C(1)−N(1)	116.6(5)
		C(3)−C(2)−C(7)	114.7(9)	C(26)−C(21)−C(22)	113.1(5)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Hydrogen Bonds Observed in **7**, **8**, and **10**·$2Me_2CO$

7		**8**		**10**·$2Me_2CO$	
N(3)···H(1)	1.81(2)	N(3)···H(2)	1.869(17)	N(3)···H(1)	1.831(7)
N(6)···H(4)	1.87(2)	N(3)···N(2)	2.666(17)	N(3)···N(1)	2.645(7)
N(3)···N(1)	2.64(2)	N(3)···H(2)−N(2)	133.5(8)	N(3)···H(1)−N(1)	135.3(5)
N(6)···N(4)	2.66(2)			O(1)···H(2)	1.936(7)
N(3)···H(1)−N(1)	136.1(17)			O(1)···N(2)	2.921(7)
N(6)···H(4)−N(4)	133.4(17)			O(1)···H(2)−N(2)	164.5(5)
Cl(1)···H(5)	2.244(5)				
Cl(2)···H(2)	2.258(5)				
Cl(1)···N(5)	3.210(5)				
Cl(2)···N(2)	3.225(5)				
Cl(1)···H(5)−N(5)	159.8(6)				
Cl(2)···H(2)−N(2)	160.0(6)				

Complexes **8** and **10** do not show aurophilic interactions because the shortest distances between two metallic centers are 4.159 Å for **8** and 7.990 Å for **10**·$2Me_2CO$. However, the crystal packing of both complexes shows stacking of molecules in a parallel disposition. In **8**, these stacking interactions connect pyridine and pentafluorophenyl groups of the neighboring molecules and establish tridimensional bridges, as shown schematically in Figure 7. The plane-to-plane distance is 3.3 Å, indicating a significant $\pi-\pi$ stacking interaction.

In **10**·$2Me_2CO$, the binuclear molecules adopt a *Z* conformation about the bridging phenylene fragment, and each half of the molecule is aligned parallel to half of two neighboring molecules, building up a chain as shown in Figure 8. The plane-to-plane distance is 3.567 Å (Figure 8, top), which is noticeably longer than that for **8**. Considering that the sum of the van der Waals radii of fluorine and gold is 3.05 Å,[29] the intermolecular Au···F_{para} distance found (3.641 Å) excludes any covalent Au···F interaction, but electrostatic interactions influencing the orientation cannot be discarded. The compound crystallizes with one molecule of acetone per gold atom. Each H(2)−N(2) group of the carbene molecule is involved in intermolecular hydrogen bonding with the oxygen of one acetone (Figure 8, bottom). The H···O distance and O···H−N(2) angle are listed in Table 3.

Photophysical Properties

The three parent isocyanide gold complexes are not luminescent in the solid state or in solution, but all of the carbenes prepared, except the fluoromesityl derivatives, show intense luminescence in the solid state and in dichloromethane solution at room temperature. The absorption and luminescence spectroscopic data are summarized in Table 4. The electronic spectra are very similar for all of these complexes and show two intense absorption bands at ca. 250 and 280 nm in dichloromethane solution. Their wavelengths and the large extinction coefficients of 10^4 M^{-1} cm^{-1} are typical, in all cases studied, of ligand-centered $\pi-\pi^*$ transitions associated with aromatic groups.[30]

In the solid state, the two chloro derivatives **4** and **7** exhibit a yellow-green luminescence under UV irradiation and produce similar emission spectra consisting of broad emission bands in the range 470–562 nm. In dichloromethane solution, the emission luminescence spectra shift to higher energy (409–457 nm). This effect is often observed for gold(I) complexes and is attributed to the presence of intermolecular aurophilic interactions.[31] The pentafluorophenyl derivatives (**5**, **8**, and **10**) also present an intense luminescence in the solid state, in the same range as that for the chloro complexes, but there is no clear shift upon going from the solid state to the solution for **5** and **8** (**10** is not soluble in common organic solvents), which is consistent with them lacking aurophilic interactions. As for related carbenes derived from 4-PyNC,[7] the fluoromesityl complexes do not show luminescent behavior.

Apparently, the formation of a six-membered planar cycle coplanar with the pyridine by intramolecular hydrogen bonding does not produce significant differences in the photophysical properties of the compounds because the luminescence data obtained for the carbenes derived from primary amines do not differ much from those from the secondary amines.

Conclusions

In the present contribution, we have developed simple synthetic protocols leading to well-defined [AuX{C(NR^1R^2)-

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(29) Emsley, J. *The Elements*, 3rd. ed.; Oxford University Press: New York, 2000.

(30) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991; Chapter 7.

(31) Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *Dalton Trans.* **2000**, 4601.

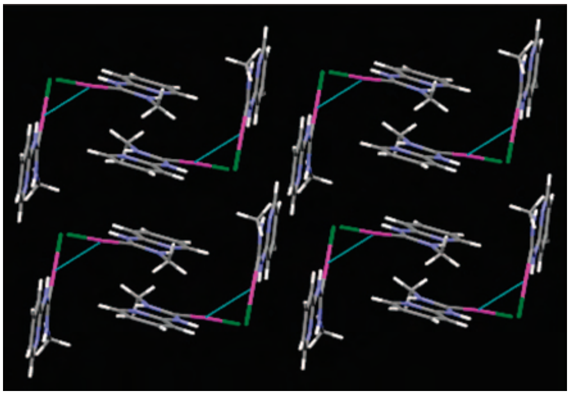

Figure 6. View of the arrangement of the zigzag sequences in the crystal network of **7**. The Au⋯Au interaction connecting each two monomers into dimers is shown in blue (pink, Au; green, Cl).

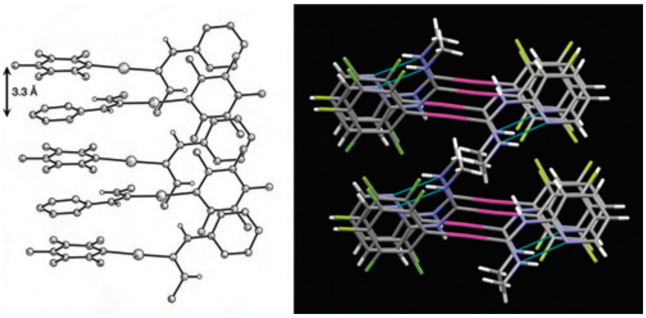

Figure 7. Left: view of a sequence of molecules in **8**, in which one line of $\pi-\pi$ stacking of the pyridine and pentafluorophenyl groups is observed vertically at the left. Right: zigzag chain structure formed through stacking bridges (the intramolecular hydrogen bond is in dashed blue; pink, Au; greenish yellow, F; blue, N).

(NHPy-2)}] carbenes. NMR and single-crystal X-ray diffraction structural analyses of some of the reported complexes prove that the 2-NHPy fragment is capable of generating intra- or intermolecular hydrogen-bonding interactions, depending on the amine used in the synthesis of the carbenes. Interestingly, whenever a primary amine is used, intramolecular hydrogen bonding between the nitrogen atom of the pyridine moiety and the hydrogen formerly of the amine is observed, forcing the pyridyl ring to be in the plane of the carbene. This hydrogen-bond-supported cyclic structure is observed in the solid state and maintained in solution, which makes the carbenes structurally similar to the well-known N-heterocyclic carbenes. Studies of their catalytic activity are underway. The luminescence observed in the complexes herein described is not always due to aurophilic contacts and in some cases has an intramolecular origin.

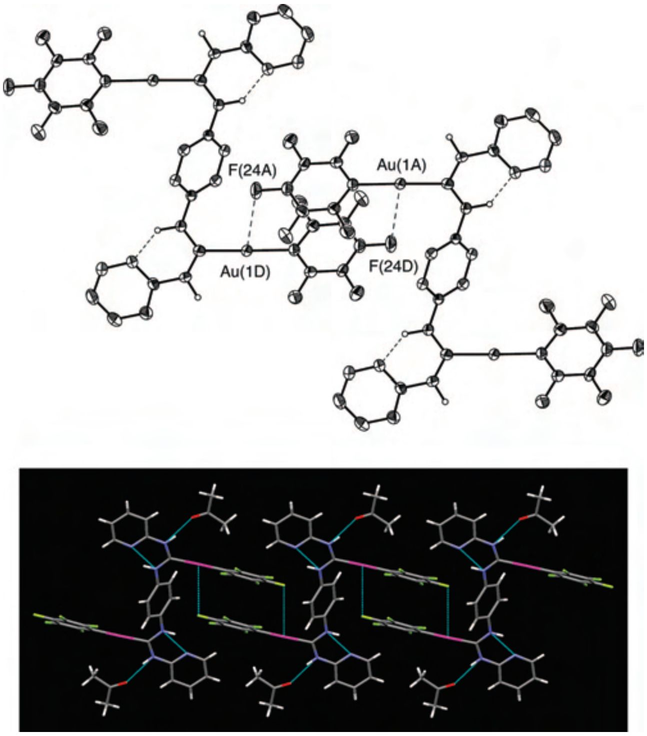

Figure 8. Top: View of two links of one layer in **10**·$2Me_2CO$, *acetone omitted*, showing the Au⋯F_{para} short distances and the intramolecular hydrogen bonds (both in blue). Bottom: Schematic representation of a chain, *including acetone*, showing the Au⋯F_{para} short distances, the intramolecular hydrogen bonds, and the intermolecular hydrogen bonds to acetone (these distances or interactions are all in blue; pink, Au; greenish yellow, F; blue, N; red, O).

Table 4. UV−Vis and Luminescence Data of the Carbenes

	λ_{ex} (KBr)	λ_{em} (KBr)	λ_{ex} (CH_2Cl_2)	λ_{em} (CH_2Cl_2)
4	383	562	364	457
5	360	470	323	438, 477, 508 (sh)
7	334	470	345	409
8	342	484	395	479
10	394	560		
12	343	500	389	447

Experimental Section

General Remarks. All reactions were carried out under dry dinitrogen. The solvents were purified according to standard procedures.[32] [AuCl(tht)],[8] [Au(C_6F_5)(tht)],[8] [Au(Fmes)(tht)],[9] and [(μ-$C_6F_4C_6F_4$){Au(tht)}$_2$][14] were prepared according to literature procedures. 2-PyNC was prepared from the corresponding pyridylamine, as described by Ugi et al.,[33] in 24% yield. The rest of the reactants are commercially available. IR spectra were recorded on Perkin-Elmer 883 or 1720X equipment, as Nujol mulls between polystyrene films, from 4000 to 200 cm^{-1}. UV–vis data were recorded on a Shimadzu UV-1603 spectrophotometer. Luminescent data were recorded on a Perkin-Elmer LS-55 luminescence spectrometer. NMR spectra were recorded with a Bruker AC300 or ARX 300 instrument. ^{1}H and ^{19}F NMR spectra are referenced to tetramethylsilane and $CFCl_3$, respectively. Elemental analyses were performed with a Perkin-Elmer 2400B microanalyzer.

[AuCl(CNPy-2)] (1). 2-CNPy (0.1 mmol, 1 mL, 0.1 M solution in acetone) was added to a solution of [AuCl(tht)] (0.032 g, 0.1 mmol) in acetone (10 mL). After 15 min of stirring at room temperature, the volatiles were pumped off and the pale-gray residue was washed with *n*-hexane (3 × 5 mL) and crystallized from dichloromethane/*n*-hexane. The colorless crystals obtained were decanted, washed with *n*-hexane (3 × 5 mL), and vacuum-dried, yielding 0.029 g (85%). IR: 2227s ν(C≡N). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.61 (dm, $J = 4.9$ Hz, 1.8, H^3, CNC$_5$*H*$_4$N, 1H), 7.95 (td, $J = 7.8$ and 1.8 Hz, H^5, CNC$_5$*H*$_4$N, 1H), 7.57 (m, H^4 and H^6, CNC$_5$*H*$_4$N, 2H). Anal. Calcd for $C_6H_4N_2AuCl$: C, 21.41; H, 1.20; N, 8.32. Found: C, 20.99; H, 1.31; N, 8.11.

[Au(C_6F_5)(CNPy-2)] (2). 2-CNPy (0.22 mmol, 2.2 mL, 0.1 M solution in acetone) was added to a solution of [Au(C_6F_5)(tht)]

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[32] Perrin, D. D.; Armarego, W. F. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

[33] Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(0.090 g, 0.2 mmol) in dichloromethane (10 mL). After 15 min of stirring at room temperature, the volatiles were pumped off and the pale-gray residue was washed with *n*-hexane (3 × 5 mL) and crystallized from dichloromethane/*n*-hexane. The colorless crystals obtained were decanted, washed with *n*-hexane (3 × 5 mL), and vacuum-dried, yielding 0.067 g (71%). IR: 2225s $\nu(C\equiv N)$. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.63 (ddd, J = 4.9, 0.9, and 1.8 Hz, H^3, CNC_5H_4N, 1H), 7.97 (td, J = 7.8 and 1.8 Hz, H^5, CNC_5H_4N, 1H), 7.59 (m, H^4 and H^6, CNC_5H_4N, 2H). ^{19}F NMR (282.5 MHz, $CDCl_3$, 295 K): δ −116.38 (m, $2F^{ortho}$), −157.59 (t, J = 20.1 Hz, $1F^{para}$), −162.73 (m, $2F^{meta}$). Anal. Calcd for $C_{12}H_4N_2F_5Au$: C, 30.79; H, 0.86; N, 5.98. Found: C, 30.86; H, 0.95; N, 5.56.

[Au(Fmes)(CNPy-2)] (3). 2-CNPy (0.29 mmol, 2.9 mL, 0.1 M solution in acetone) was added to a solution of [Au(Fmes)(tht)] (0.150 g, 0.26 mmol) in dichloromethane (15 mL). After 15 min of stirring at room temperature, the volatiles were pumped off and the white residue was washed with *n*-hexane (3 × 5 mL) and crystallized from dichloromethane/*n*-hexane. The colorless crystals obtained were decanted, washed with *n*-hexane (3 × 5 mL), and vacuum-dried, yielding 0.123 g (81%). IR: 2216s $\nu(C\equiv N)$, 684w $\nu(Au-R)$. ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.64 (dm, J = 4.8 Hz, H^3, CNC_5H_4N, 1H), 8,04 (s, 2H, Fmes), 7.97 (td, J = 7.8 and 1.7 Hz, H^5, CNC_5H_4N, 1H), 7.59 (m, H^4 and H^6, CNC_5H_4N, 2H). ^{19}F NMR (282.5 MHz, $CDCl_3$, 295 K): δ −60.55 (s, 6F, *o*-CF_3), −63.26 (s, 3F, *p*-CF_3). Anal. Calcd for $C_{15}H_6N_2F_9Au$: C, 30.95; H, 1.04; N, 4.81. Found: C, 30.85; H, 0.96; N, 4.72.

[AuCl{C(NEt$_2$)(NHPy-2)}] (4). Diethylamine (0.60 mmol, 0.044 g, 61.6 μL) was added to a solution of **1** (0.100 g, 0.30 mmol) in dichloromethane (15 mL). After 15 min of stirring at room temperature, the solution was filtered through a small column of Kieselgur and silica gel and crystallized from dichloromethane/*n*-hexane. The colorless crystals thus obtained were decanted, washed with *n*-hexane (3 × 5 mL), and dried under vacuum, yielding 0.092 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.50 (d, J = 8.4 Hz, NHC_5H_4N, 1H), 8.30 (dm, J = 1.4 Hz, NHC_5H_4N, 1H), 8.13 (br, NHC_5H_4N, 1H), 7.78 (m, NHC_5H_4N, 1H), 7.18 (m, H^4, NHC_5H_4N, 1H), 4.13 (q, J = 7.2 Hz, $N(CH_2CH_3)_2$, 2H), 3.54 (q, J = 7.3 Hz, $N(CH_2CH_3)_2$, 2H), 1.4 (t, J = 7.2 Hz, $N(CH_2CH_3)_2$, 3H), 1.37 (t, J = 7.3 Hz, $N(CH_2CH_3)_2$, 3H). Anal. Calcd for $C_{10}H_{15}N_3AuCl$: C, 29.32; H, 3.69; N, 10.26. Found: C, 29.68; H, 3.22; N, 9.98. UV−vis (CH_2Cl_2): λ 277.0 (ϵ 1.44 × 10^3), 249.5 (ϵ 1.57 × 10^3), 227.0 (ϵ 1.18 × 10^3). λ_{ex} (KBr): 383. λ_{em} (KBr): 562. λ_{ex} (CH_2Cl_2): 364. λ_{em} (CH_2Cl_2): 457.

[Au(C$_6$F$_5$){C(NEt$_2$)(NHPy-2)}] (5). Diethylamine (0.43 mmol, 44.6 μL) was added to a solution of **2** (0.100 g, 0.21 mmol) in dichloromethane (15 mL). After 15 min of stirring at room temperature, the IR of the solution did not show CN absorption. Then the volatiles were pumped off, and the residue was crystallized from dichloromethane/*n*-hexane. The white solid obtained was decanted, washed with *n*-hexane (3 × 5 mL), and dried under vacuum, yielding 0.081 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.78 (dm, J = 8.2 Hz, 1H, NHC_5H_4N), 8.32 (m, 1H, NHC_5H_4N), 8.17 (br, 1H, NHC_5H_4N), 7.80 (m, 1H, NHC_5H_4N), 7.17 (m, 1H, NHC_5H_4N), 4.21 (q, J = 7.2 Hz, 2H, $N(CH_2CH_3)_2$), 3.55 (q, J = 7.4 Hz, 2H, $N(CH_2CH_3)_2$), 1.47 (t, J = 7.2 Hz, 3H, $N(CH_2CH_3)_2$), 1.39 (t, J = 7.4 Hz, 3H, $N(CH_2CH_3)_2$). ^{19}F NMR (282.5 MHz, $CDCl_3$, 295 K): δ −117.00 (m, $2F^{ortho}$), −160.08 (t, J = 20.1 Hz, $1F^{para}$), −163.42 (m, $2F^{meta}$). Anal. Calcd for $C_{16}H_{15}N_3F_5Au$: C, 35.50; H, 2.79; N, 7.76. Found: C, 35.46; H, 2.65; N, 7.49. UV−vis (CH_2Cl_2): λ 276.5 (ϵ 1.29 × 10^4), 248.5 (ϵ 1.82 × 10^4), 228.5 (ϵ 1.18 × 10^4). λ_{ex} (KBr): 360. λ_{em} (KBr): 470. λ_{ex} (CH_2Cl_2): 323. λ_{em} (CH_2Cl_2): 438, 477, 508 (sh).

[Au(Fmes){C(NEt$_2$)(NHPy-2)}] (6). Diethylamine (0.17 mmol, 18 μL) was added to a solution of **3** (0.050 g, 0.86 mmol) in dichloromethane (10 mL). After 5 min of stirring at room temperature, the IR of the solution did not show CN absorption. Then the volatiles were pumped off, and the residue was crystallized from dichloromethane/*n*-hexane. The white solid was decanted, washed with *n*-hexane (3 × 5 mL), and dried under vacuum, yielding 0.042 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 8.56 (d, J = 8.3 Hz, 1H, NHC_5H_4N), 8.35 (br, 1H, NHC_5H_4N), 8.31 (m, 1H, NHC_5H_4N), 7.99 (s, 2H, Fmes), 7.71 (tm, J = 7.9 Hz, 1H, NHC_5H_4N), 7.15 (m, 1H, NHC_5H_4N), 4.21 (q, J = 7.2 Hz, 2H, $N(CH_2CH_3)_2$), 3.57 (q, J = 7.4 Hz, 2H, $N(CH_2CH_3)_2$), 1.42 (t, J = 7.2 Hz, 3H, $N(CH_2CH_3)_2$), 1.40 (t, J = 7.4 Hz, 3H, $N(CH_2CH_3)_2$). ^{19}F NMR (282.5 MHz, $CDCl_3$, 295 K): δ −60.39 (s, 6F, *o*-CF_3), −63.13 (s, 3F, *p*-CF_3). Anal. Calcd for $C_{19}H_{17}N_3F_9Au$: C, 34.82; H, 2.61; N, 6.41. Found: C, 35.14; H, 2.32; N, 6.07.

[AuCl{C(NHMe)(NHPy-2)}] (7). Methylamine (0.3 mmol, 25.5 μL, 40% solution in water) was added to a solution of **1** (0.100 g, 0.3 mmol) in dichloromethane (15 mL). After 5 min of stirring at room temperature, the IR solution did not show CN absorption. The volatiles were pumped off, and the pale-violet residue was crystallized from dichloromethane/*n*-hexane. The colorless crystals obtained were washed with *n*-hexane (3 × 5 mL) and vacuum-dried, yielding 0.079 g (74%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 12.40 (br, 1H, $NHCH_3$), 9.59 (br, 1H, NHC_5H_4N), 8.22 (dm, J = 5.2 Hz, 1H, NHC_5H_4N), 7.73 (m, 1H, NHC_5H_4N), 7.21 (dm, J = 8.3 Hz, 1H, NHC_5H_4N), 7.07 (m, 1H, NHC_5H_4N), 3.41 (d, J = 4.8 Hz, 3H, $NHCH_3$). ^{1}H NMR (300 MHz, Me_2CO-d_6, 295 K): δ 12.50 (br, 1H, $NHCH_3$), 10.15 (br, 1H, NHC_5H_4N), 8.34 (dm, J = 4.8 Hz, 1H, NHC_5H_4N), 7.93 (m, 1H, NHC_5H_4N), 7.25 (m, 2H, NHC_5H_4N), 3.40 (d, J = 4.8 Hz, 3H, $NHCH_3$). Anal. Calcd for $C_7H_9N_3AuCl$: C, 22.87; H, 2.47; N, 11.43. Found: C, 23.25; H, 2.25; N, 11.19. UV−vis (CH_2Cl_2): λ 285 (ϵ 2.66 × 10^4), 247.5 (ϵ 3.65 × 10^4). λ_{ex} (KBr): 334. λ_{em} (KBr): 470. λ_{ex} (CH_2Cl_2): 345. λ_{em} (CH_2Cl_2): 409.

[Au(C$_6$F$_5$){C(NHMe)(NHPy-2)}] (8). Methylamine (0.34 mmol, 29.5 μL, 40% solution in water) was added to a solution of **2** (0.080 g, 0.17 mmol) in dichloromethane (10 mL). After 30 min of stirring at room temperature, the volatiles were pumped off and the white residue was washed with *n*-hexane (3 × 5 mL), yielding 0.066 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ 12.50 (br, $NHCH_3$, 1H), 8.27 (dd, J = 1.4 and 4.8 Hz, H^3, NHC_5H_4N, 1H), 8.01 (br, NHC_5H_4N, 1H), 7.76 (m, H^5, NHC_5H_4N, 1H), 7.11 (m, H^4, NHC_5H_4N, 1H), 6.85 (dm, J = 8.2 Hz, H^6, NHC_5H_4N, 1H), 3.52 (d, J = 4.8 Hz, $NHCH_3$, 3H). ^{19}F NMR (282.5 MHz, $CDCl_3$, 295 K): δ −117.02 (m, $2F^{ortho}$), −158.82 (t, J = 20.3 Hz, $1F^{para}$), −163.22 (m, $2F^{meta}$). ^{1}H NMR (300 MHz, Me_2CO-d_6, 295 K): δ 12.67 (br, 1H, $NHCH_3$), 10.27 (br, 1H, NHC_5H_4N), 8.31 (dm, J = 3.6 Hz, 1H, NHC_5H_4N), 7.90 (m, 1H, NHC_5H_4N), 7.26 (d, J = 8.3 Hz, 1H, NHC_5H_4N), 7.21 (m, 1H, NHC_5H_4N), 3.50 (d, J = 4.7 Hz, 3H, $NHCH_3$). ^{19}F NMR (282.5 MHz, Me_2CO-d_6, 295 K): δ −115.60 (m, $2F^{ortho}$), −160.57 (t, J = 20 Hz, $2F^{para}$), −163.62 (m, $2F^{meta}$). Anal. Calcd for $C_{13}H_9N_3AuF_5$: C, 31.28; H, 1.82; N, 8.42. Found: C, 31.28; H, 1.59; N, 8.11. UV−vis (KBr): 297.5 (0.646), 267 (0.625). UV−vis (CH_2Cl_2): λ 285.0 (ϵ 7.43 × 10^3), 248.0 (ϵ 1.21 × 10^4). λ_{ex} (KBr): 342. λ_{em} (KBr): 484. λ_{ex} (CH_2Cl_2): 395. λ_{em} (CH_2Cl_2): 479.

[Au(Fmes){C(NHMe)(NHPy-2)}] (9). Methylamine (0.20 mmol, 18 μL, 40% solution in water) was added to a solution of **3** (0.060 g, 0.10 mmol) in dichloromethane (10 mL). After 5 min of stirring at room temperature, the IR of the solution did not show the isocyanide absorption. Then the volatiles were pumped off, and

Table 5. Crystal Data and Structure Refinement for **4**, **6**−**8**, and **10**·2Me$_2$CO

	4	**6**	**7**	**8**	**10**·2Me$_2$CO
empirical formula	$C_{10}H_{15}AuClN_3$	$C_{19}H_{17}AuF_9N_3$	$C_7H_9AuClN_3$	$C_{13}H_9AuF_5N_3$	$C_{36}H_{28}Au_2F_{10}N_6O_2$
fw	409.67	655.32	367.59	499.20	1160.58
temperature (K)	298(2)	298(2)	298(2)	298(2)	298(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	*C*2/c	*C*2/c	$P\bar{1}$	P2(1)	$P\bar{1}$
a (Å)	19.322(9)	9.9666(15)	7.5377(11)	5.955(3)	7.5507(17)
b (Å)	7.787(4)	15.700(2)	10.2355(14)	7.525(4)	11.149(3)
c (Å)	18.486(9)	27.822(4)	13.2172(18)	15.220(9)	11.602(3)
α (deg)	90	90	71.407(3)	90	94.708(5)
β (deg)	114.751(7)	94.928(3)	85.147(4)	96.510(10)	103.213(5)
γ (deg)	90	90	84.556(4)	90	97.937(5)
V (Å^3)	2526(2)	4337.3(11)	960.6(2)	677.5(6)	935.2(4)
Z	8	8	4	2	1
D_{calc} (g cm^{-3})	2.155	2.007	2.542	2.447	2.061
abs coeff (mm^{-1})	11.833	6.871	15.542	10.913	7.927
F(000)	1536	2496	672	464	550
cryst size (mm)	0.11 × 0.07 × 0.06	0.27 × 0.26 × 0.19	0.12 × 0.05 × 0.01	0.35 × 0.06 × 0.02	0.14 × 0.09 × 0.04
θ range for data collection	2.32−26.49°	1.47−25.38°	1.63−25.38°	1.35−25.42°	1.82−25.45°
reflns collected	11154	12277	5410	3691	5235
indep reflns	2593	3985	3491	1339	3423
abs corrn	*SADABS*	*SADABS*	*SADABS*	*SADABS*	*SADABS*
max and min transmn factor	0.492 and 0.317	0.271 and 0.170	0.856 and 0.369	0.804 and 0.351	0.728 and 0.322
data/restraints/parameters	2593/0/139	3985/0/292	3491/0/219	1339/1/200	3423/0/255
GOF on F^2	1.036	1.022	1.005	1.005	1.022
R1 [$I > 2\sigma(I)$]	0.0239	0.0253	0.0573	0.0233	0.0322
wR2 (all data)	0.0565	0.0683	0.1390	0.0642	0.0739

the white residue was washed with *n*-hexane (3 × 5 mL), yielding 0.045 g (71%). ^{1}H NMR (300 MHz, CDCl$_3$, 295 K): δ 12.45 (br, N*H*CH$_3$, 1H), 8.28 (d, $J = 4.5$ Hz, NHC$_5$*H*$_4$N, 1H), 8,02 (s, 2H, Fmes), 7.89 (b, N*H*C$_5$H$_4$N, 1H), 7.76 (tm, $J = 8.1$ Hz, H^5, NHC$_5$*H*$_4$N, 1H), 7.11 (m, H^4, NHC$_5$*H*$_4$N, 1H), 6.88 (d, $J = 8.4$ Hz, H^6, NHC$_5$*H*$_4$N, 1H), 3.50 (d, $J = 4.7$ Hz, NHC*H*$_3$, 3H). ^{19}F NMR (282.5 MHz, CDCl$_3$, 295 K): δ −60.09 (s, 6F, *o*-CF$_3$), −63.06 (s, 3F, *p*-CF$_3$). ^{1}H NMR (300 MHz, Me$_2$CO-*d*$_6$, 295 K): δ 12.70 (br, 1H, N*H*CH$_3$), 10.10 (br, 1H, N*H*C$_5$H$_4$N), 8.34 (d, $J = 5.1$ Hz, 1H, NHC$_5$*H*$_4$N), 8.07 (s, 2H, Fmes), 7.88 (tm, $J = 8.6$ Hz, 1H, NHC$_5$*H*$_4$N), 7.28 (d, $J = 8.3$ Hz, 1H, NHC$_5$*H*$_4$N), 7.19 (m, 1H, NHC$_5$*H*$_4$N), 3.49 (d, $J = 4.7$ Hz, 3H, NHC*H*$_3$).^{19}F NMR (282.5 MHz, Me$_2$CO-*d*$_6$, 295 K): δ −59.15 (s, 6F, *o*-CF$_3$), −62.08 (s, 3F, *p*-CF$_3$). Anal. Calcd for $C_{16}H_{11}N_3AuF_9$: C, 31.34; H, 1.81; N, 6.85. Found: C, 31.52; H, 1.57; N, 6.75.

(μ-NHC$_6$H$_4$HN)[C(NHPy-2)Au(C$_6$F$_5$)]$_2$·2Me$_2$CO (10·2Me$_2$CO). 1,4-Phenylenediamine (0.05 mmol, 2 mL, 0.025 M in dichloromethane) was added to a solution of **2** (0.047 g, 0.1 mmol) in a mixture of dichloromethane (25 mL) and acetone (25 mL). After 3 h of stirring at room temperature, the solution was concentrated. Then, *n*-hexane were added, and the solution was cooled to −20 °C. The crystals obtained were decanted, washed *n*-hexane (3 × 5 mL), and dried under vacuum, yielding 0.020 g of **10**·2Me$_2$CO (33%). Anal. Calcd for $C_{36}H_{28}N_6Au_2F_{10}O_2$: C, 37.26; H, 2.43; N, 7.24. Found: C, 37.30; H, 2.27; N, 7.28. λ_{ex} (KBr): 394. λ_{em} (KBr): 560. λ_{ex} (crystals): 381. λ_{em} (crystals): 512. NMR: insolubility prevented NMR characterization.

[(μ-C$_6$F$_4$C$_6$F$_4$){Au(CNPy-2)}$_2$] (11). 2-CNPy (0.28 mmol, 2.24 mL, 0.127 M solution in acetone) was added to a solution of [(μ-C$_6$F$_4$C$_6$F$_4$){Au(tht)}$_2$] (0.123 g, 0.11 mmol) in dichloromethane (40 mL). After 5 min of stirring at room temperature, the volatiles were pumped off and the orange residue was triturated with *n*-hexane (3 × 10 mL) and vacuum-dried, yielding 0.112 g (89%). IR: 2218s ν(C≡N). ^{1}H NMR (300 MHz, Me$_2$CO-*d*$_6$, 295 K): δ 8.69 (d, $J = 4.4$ Hz, H^3, CNC$_5$*H*$_4$N, 2H), 8.22 (td, $J = 1.4$ and 7.9 Hz, H^5, CNC$_5$*H*$_4$N, 2H), 8.06 (d, $J = 4.4$ Hz, H^6, CNC$_5$*H*$_4$N, 2H), 7.80 (ddd, $J = 7.9$, 4.4, and 1.4 Hz, H^4, NHC$_5$*H*$_4$N, 2H). ^{19}F NMR (282.5 MHz, Me$_2$CO-*d*$_6$, 295 K): δ −112.62 (m, (C$_6$F$_4$)$_2$, 4F), −136.68 (m, (C$_6$F$_4$)$_2$, 4F). Anal. Calcd for $C_{24}H_8N_4Au_2F_8$: C, 32.09; H, 0.90; N, 6.24. Found: C, 32.73; H, 1.12; N, 6.49.

[(μ-C$_6$F$_4$C$_6$F$_4$){Au(C(NHMe)(NHPy-2))}$_2$] (12). Methylamine (0.13 mmol, 11.4 μL, 40% solution in water) was added to a solution of **11** (0.059 g, 0.07 mmol) in acetone (50 mL). After 50 min of stirring at room temperature, the solution was concentrated and *n*-hexane was added. The yellow precipitate obtained was washed with *n*-hexane (3 × 5 mL) and vacuum-dried, yielding 0.032 g (50%). ^{1}H NMR (300 MHz, Me$_2$CO-*d*$_6$, 295 K): δ 12.68 (br, N*H*CH$_3$, 2H), 10.29 (br, 2-N*H*C$_5$H$_4$N, 2H), 8.34 (m, H^3, NHC$_5$*H*$_4$N, 2H), 7.90 (m, H^5, NHC$_5$*H*$_4$N, 2H), 7.28 (m, H^6, NHC$_5$*H*$_4$N, 2H), 7.21 (m, H^4, NHC$_5$*H*$_4$N, 2H), 3.52 (d, $J = 4.7$ Hz, NHC*H*$_3$, 6H). ^{19}F NMR (282.5 MHz, Me$_2$CO-*d*$_6$, 295 K): δ −116.67 [m, (C$_6$F$_4$)$_2$, 4F], −141.27 [m, (C$_6$F$_4$)$_2$, 4F]. Anal. Calcd for $C_{26}H_{18}N_6Au_2F_8$: C, 32.52; H, 1.89; N, 8.75. Found: C, 32.63; H, 2.29; N, 8.67. λ_{ex} (KBr): 343. λ_{em} (KBr): 500. λ_{ex} (CH$_2$Cl$_2$): 389. λ_{em} (CH$_2$Cl$_2$): 447.

Experimental Procedure for X-ray Crystallography. Suitable single crystals of **4** and **6**−**8** were obtained by layering hexane in a dichloromethane solution of the corresponding compound, and crystals of **10**·2Me$_2$CO were obtained by lowering the temperature of an acetone/hexane solution. Crystals were mounted in glass fibers, and diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation (λ = 0.710 73 Å).[34] Intensities were integrated from several series of exposures, with each exposure covering 0.3° in ω and the total data set being a hemisphere.[35] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[36] The structures were solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 5).[37] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All of the

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(34) *SMART V5.051 diffractometer control software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(35) *SAINT V6.02 integration software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1999.

(36) Sheldrick, G. M. *SADABS: A program for absorption correction with the Siemens SMART system*; University of Göttingen: Germany, 1996.

(37) *SHELXTL program system*, version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

hydrogen atoms, including those involved in hydrogen bonding, were calculated with a riding model. Complex neutral-atom scattering factors were used.[38] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publications with the following deposition numbers: CCDC-664737, CCDC-664738, CCDC-664739, CCDC-664740, and CCDC-664741 for complexes **4**, **6**−**8**, and **10**·$2Me_2CO$. Copies of the data can be obtained free of charge upon application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (int) + 44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) *International Tables for Crystallography*; Kluwer: Dordrecht, The Netherlands, 1992; Vol. *C*.