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Synthesis and Characterization of Gold(I) Complexes with 9-(4-Isocyanophenyl)carbazole or 9-Ethyl-3-isocyanocarbazole Ligands

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The carbazole derivatives 9-(4-isocyanophenyl)carbazole, 3,6-dibromo-9-(4-isocyanophenyl)carbazole, and 9-ethyl-3-isocyanocarbazole were prepared and used to synthesize [AuX(CN-carbazole)] (X = Cl, C_6F_5, C_6F_4-OEt-*p*) gold complexes. The X-ray structures of [Au(C_6F_4-OEt-*p*){9-(4-isocyanophenyl)carbazole}] and [Au(C_6F_5)(9-ethyl-3-isocyanocarbazole)], and the luminescent properties of the ligands and the complexes in the solid state, in solution at room temperature, and in frozen solution of chloroform at 77 K were determined. All the gold complexes show a redshift in the emissions relative to that of the free ligand. The presence of electron-withdrawing substituents in 3,6-dibromo-9-(4-isocyanophenyl)carbazole quenches the luminescence, but with the introduction of a gold atom some luminescence is recovered.

Introduction

Carbazole (**1**) has a conjugated structure with interesting optical and electronic properties. Since the discovery of photoconductivity in poly(*N*-vinylcarbazole) (PVK) by H. Hoegl,[1] many molecules incorporating the carbazole structure have been investigated as light-emitting materials and as hole-transporting materials in organic light-emitting devices (OLEDs).[2] Carbazole derivatives are also used to produce materials displaying luminescence,[3] mesogenic behavior,[4] nonlinear optical properties (NLO),[5] conductivity,[6] and photorefractivity.[7]

The incorporation of metal centers to carbazole derivatives offers the possibility to develop new materials and, depending on the metal, bring on interesting redox, magnetic, optical, and catalytic properties.[8] Thus, a number of complexes with the carbazole fragment coordinated as an amido ligand through M–N σ-bonds have been reported.[9] There are also metal complexes with carbazole-functionalized ligands: alkynyl,[10] carboxylate,[11] pyridine, isoquinoline, fluorene, phenylpyridine,[12,13] carbazole–diphosphane,[14] β-diketonate,[15] terpyridine,[16] 1,10-phenanthroline,[17] benzoimidazole,[18] and imine.[19] A few, η^6-bonded complexes of carbazole derivatives,[20] and polymers containing metal complexes with a carbazole unit,[21] have been reported. Finally, very recently, complexes derived from insertion into a Pd–Me bond of olefins bearing carbazole substituents have been prepared.[22]

Surprisingly, in spite of the well-known tendency of gold(I) to produce luminescent complexes, this metal center has been only scarcely explored to produce carbazole-containing gold complexes. To the best of our knowledge, only a gold(I) complex with carbazole behaving as an amido ligand,[9] and a few alkynyl complexes containing carbazole spacers, have been reported.[10d,10e] On the basis of our previous experience on luminescent gold complexes containing the isocyanide ligand,[23–25] we decided to functionalize carbazole derivatives with this coordinating function, which is a fairly general and strong coordinating linkage towards many metals. For short, these new ligands will be referred to in the text as carbazole isocyanides. We report here the synthesis of three carbazole isocyanides and their gold(I) complexes.

Results and Discussion

Synthesis and Characterization

The syntheses of 9-(4-isocyanophenyl)carbazole (**5a**) and 3,6-dibromo-9-(4-isocyanophenyl)carbazole (**5b**) are outlined in Scheme 1. Following a literature procedure commercial carbazole (**1**) was fused with potassium hydroxide,[26,27] and the resulting potassium carbazole salt was treated with nitrobenzene to give 9-(4-nitrophenyl)carbazole (**2a**). Treatment of **2a** with bromine in $CHCl_3$ at 0 °C afforded 3,6-dibromo-9-(4-nitrophenyl)carbazole (**2b**). Reduction of **2a**,**b** with stannous chloride in refluxing ethanol

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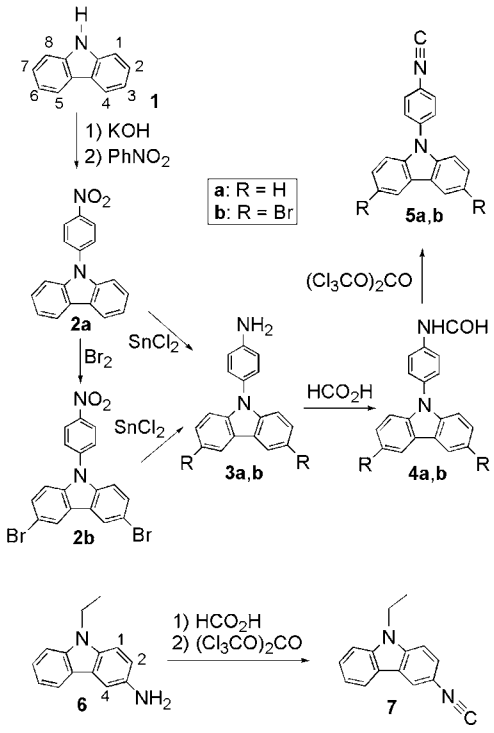
gave 9-(4-aminophenyl)carbazole (**3a)** or 3,6-dibromo-9-(4-aminophenyl)carbazole (**3b**), respectively, which were heated with formic acid in refluxing toluene to prepare the corresponding formanilides (**4a**,**b**). Finally, dehydration of **4a**,**b** with bis(trichloromethyl)carbonate (triphosgene) in CH_2Cl_2[28,29] yielded **5a**,**b**.

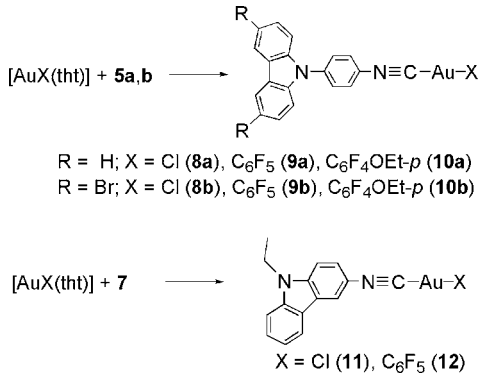


Scheme 1.

The isocyanide 9-ethyl-3-isocyanocarbazole (**7**) was prepared similarly, as shown in Scheme 1, starting from commercial 3-amino-9-ethylcarbazole (**6**). At room temperature, these carbazole isocyanides are white (for **5a**,**b**) or yellow (for **7**) solids, not particularly odoriferous, that can be stored for long periods in the freezer.

For symmetric ligands **5a**,**b** and their corresponding precursors, the ^{1}H NMR spectra (300 MHz) are simple and show the expected one set of signals, with some bands overlapping. The spectra are obviously simpler for the brominated derivatives. Thus, the aromatic hydrogen atoms of **5b** display three resonances as expected: a doublet (J = 8.7 Hz) for H^1 and H^8, a doublet of doublets (J = 8.7, 1.9 Hz) for H^2 and H^7, and a doublet (J = 1.9 Hz) for H^4 and H^5. In addition, an AA′XX′ system is observed in all compounds for the hydrogen atoms of the 1,4-substituted ring. The aromatic resonances for less symmetric **7** are more complex and were assigned with the help of COSY. For the three isocyanides (i.e., **5a**,**b** and **7**) one ν(C≡N) IR absorption is observed at ca. 2125 cm^{-1}.

The gold(I) compounds [AuX(CNR)] (**8a**,**b**–**10a**,**b**; **11**; and **12**) were easily prepared in good yield, as pale yellow solids, by 1:1 reaction in CH_2Cl_2 of [AuX(tht)] (tht = tetrahydrothiophene; X = Cl, C_6F_5, C_6F_4-OEt-*p*) with the corresponding carbazole isocyanide (Scheme 2). The elemental analyses, yields, relevant IR data, and ^{1}H and ^{19}F NMR spectroscopic data for the complexes are given in the Experimental Section. The IR spectra show one ν(C≡N) absorption ca. 2212 cm^{-1}. This is about 90 cm^{-1} higher than for the free isocyanide, as an effect of coordination to gold(I).[25,30]



Scheme 2.

The ^{1}H NMR spectra of gold(I) isocyanide complexes **8a**,**b**–**10a**,**b** are all very similar (compounds **8a**,**b** are insoluble in common organic solvents but their ^{1}H NMR spectra could be recorded in deuterated DMSO). The chemical shifts of the carbazole moiety are essentially unresponsive to coordination, whereas deshielding is observed for the aromatic hydrogen atoms of the aryl group bearing the isocyanide function, as reported for arylisocyanide gold(I) complexes.[25,30,31] For complexes **11** and **12**, a small deshielding is observed for all the aromatic hydrogen atoms, which is larger for H^1, H^2, and H^4. The ^{19}F NMR spectra of the fluorinated compounds **9a**,**b** and **11** show the characteristic AA′MXX′ signals for C_6F_5. The ^{19}F NMR spectra of **10a**,**b** show two complex multiplets corresponding to an AA′XX′ spin system with $J_{AA'} = J_{XX'}$.

X-ray quality crystals could be obtained for the more soluble complexes **10a** and **12**, and their molecular structures were determined by single-crystal X-ray diffraction methods. Their structures and numbering schemes, with selected bond lengths and angles, are shown in Figures 1 and 2, respectively. The data collection and refinement parameters are detailed in the Experimental Section. Compound **10a** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$, with four formula units per unit cell. All the bond lengths are within normal ranges. The gold coordination is almost perfectly linear, with bond angles C(1)–Au–C(21) 179.8° and N(1)–C(1)–Au 179.7°. The steric hindrance between the hydrogen atoms of the carbazole and the aryl ring forces a nonplanar conformation between the plane of the phenyl ring and the carbazole group. For instance, 9-phenylcarbazole shows two angles of 78.11 and 54.18°[32] and 9-(4-cyanophenyl)carbazole displays an angle of 46.25°.[33] The dihedral angle 41.4° found for **10a** is the smallest angle reported for 9-(phenyl)carbazole derivatives. The shortest Au–Au intermolecular distance in the crystal is 5.712 Å,

which clearly excludes the existence of any Au···Au interactions. The shortest F–F distance, larger than 3 Å, also excludes intermolecular fluoro–fluoro interactions.[25]

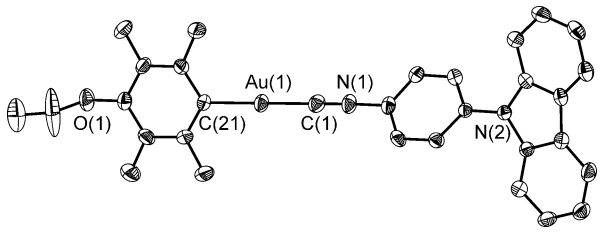


Figure 1. Crystal structure of [Au(C_6F_4OEt-*p*)($C{\equiv}NC_6H_4$-$NC_{12}H_8$)] (**10a**). The ellipsoids are shown at 30% probability (H atoms omitted for clarity). Selected bond lengths [Å]: Au(1)–C(1) 1.965(5), Au(1)–C(21) 1.965(5), C(1)–N(1) 1.153(6), N(1)–C(2) 1.405(6). Selected angles [°]: C(1)–Au(1)–C(21) 179.8(2), N(1)–C(1)–Au(1) 179.7(5), C(1)–N(1)–C(2) 178.1(6).

Compound **12** (Figure 2) crystallizes in the triclinic space group $P\bar{1}$, with two formula units per unit cell. The gold coordination is almost linear [angle C(1)–Au–C(11) 176.6°]. The bond lengths are comparable to those of **10a** and related gold isocyanide complexes.[23,25] The molecules of **12** pack antiparallel, with no significant π–π interaction between the aromatic fragments. The shortest Au–Au intermolecular distance is 6.703 Å.

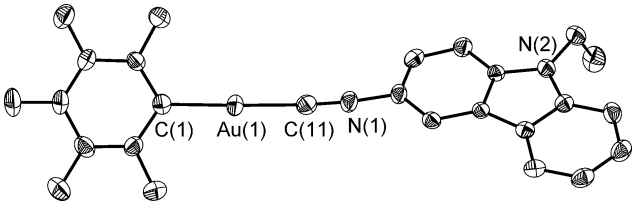


Figure 2. Crystal structure of [Au(C_6F_5)(9-ethyl-3-isocyanocarbazole)] (**12**). The ellipsoids are shown at 30% probability (H atoms omitted for clarity). Selected bond lengths [Å]: Au(1)–C(11) 1.958(6), Au(1)–C(1) 2.018(5), C(11)–N(1) 1.166(7), N(1)–C(15) 1.381(6). Selected angles [°]: C(11)–Au(1)–C(1) 176.61(17), N(1)–C(11)–Au(1) 176.0(4), C(11)–N(1)–C(15)174.6(5).

Photophysical Studies

The UV/Vis absorption and excitation spectra of the free isocyanides and their corresponding gold(I) complexes are summarized in Table 1. The UV/Vis spectra are complex, with multiple overlapping broad bands. Yet some clear differences can be recognized for the three families derived from **5a**,**b** and **7**, respectively.

Ligand **5a** and their complexes **8a**,**b**–**10a**,**b** show very similar UV absorptions (Figure 3a). They are dominated by a strong absorption at ca. 250 nm (with a more or less defined shoulder), and show other broad absorptions in the ranges 275–300 and 300–375 nm. The main differences observed upon complexation are moderate intensity changes and a redshift in the band that appears at 317 nm in free ligand **5a** relative to 340 nm in gold complexes **8a**–**10a**. Because metal–ligand charge transfers are known to appear at shorter wavelengths, generally below 250 nm,[34] all the absorptions are assigned to phenyl-localized π–π* transitions,[35] dominated by a strong absorption band at ca. 243 nm and accompanied by other less-intense absorptions at higher wavelengths. The changes observed for the complexes should be deemed to polarizability changes upon incorporation of the gold center.

Brominated free ligand **5b** and their complexes **8b**–**11b** (Figure 3b) show essentially identical behavior, but in this case energy of the absorption at ca. 350 nm, which is already there in the free ligand, is insensitive to coordination and only its intensity increases.

Finally, the absorption spectra of **7**, **11**, and **12** (Figure 3c) show clearly different behavior. The spectra have in common with the previous ones, the intense band at ca. 245 nm, but the most prominent band (with a shoulder) appears in the 275–300 range. In this case, where the metal is directly coordinated to the carbazole ring, this band (at ca. 275 nm) and its shoulders (at ca. 262 and 290 nm) are very sensitive to coordination and undergo a noticeable change in intensity and energy on going from ligand **7** to their complexes **11** and **12**, and in contrast to the modest effect observed for **8a**,**b**, a redshift is observed. This is not unexpected, as one can reasonably expect larger polarizabil-

Table 1. UV/Vis absorption and emission spectroscopic data for ligands **5a**,**b** and **7**, and their gold complexes in chloroform at 298 K, and excitation and emission data in KBr (at 298 K) and in frozen $CHCl_3$ solution (at 77 K).

	λ_{max} / nm (10^4 ε / $dm^3 mol^{-1} cm^{-1}$)	298 K (KBr)		77 K ($CHCl_3$)	
		λ_{ex} / nm	λ_{em} / nm	λ_{ex} / nm	λ_{em} / nm
5a	244 (4.5), 293 (1.9), 317 (1.4), 337 (0.9)	347	365	330	356
5b	243 (6.8), 303 (2.9), 355 (0.6)			381	439
7	244 (3.2), 277 (4,5), 290 (sh., 1.4), 337 (0.3), 353 (0.3)	325	391	327	356, 375, 394
8a	242 (6.7), 288 (2.6), 339 (1.7)	335	485	380	463 (sh.), 482
9a	241 (9.1), 275 (3.5), 340 (2.2), 347 (2.1)	380	523	394	530
10a	246 (9.7), 284 (4.4), 340 (3.6)	388	525	391	543
8b	243 (8.7), 293 (2.7), 303 (2.9), 342 (1.7), 354 (1.8)			365	445, 469
9b	243 (10.0), 302 (2.1), 354 (2.3)	350	475 (sh.), 527	389	460, 508
10b	244 (3.9), 265 (1.9), 290 (1.0), 303 (1.0), 345 (1.1), 354 (1.1)	399	457, 510 (sh.)	400	489, 516
11	244 (2.6), 275 (sh., 2.8), 290 (5.1), 320 (1.7), 337 (sh., 0.9), 353 (sh., 0.3)	322[a]	456, 474[a]	368	461
12	244 (3.2), 275 (sh., 2.8), 290 (5.3), 319 (1.5), 337 (sh., 0.8) 353 (sh., 0.3)	380	447, 525	391	498

[a] Measured at 77 K.

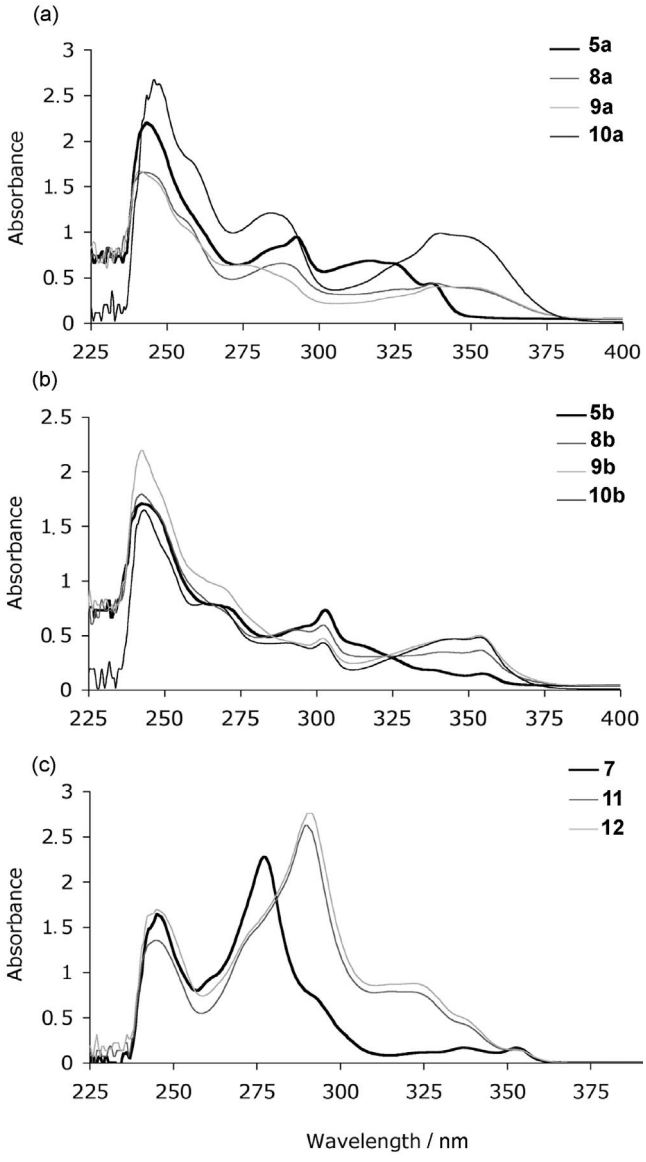


Figure 3. Absorption spectra of ligands **5a** (a), **5b** (b), **7** (c), and their complexes recorded in $CHCl_3$ solution (10^{-4} to 10^{-5} M) at room temperature.

ity changes in the molecule when gold is coordinated to a carbazole aryl ring.

The emission spectra of the ligands and the complexes were measured in the solid state (KBr pellets or dispersion) at room temperature and in frozen chloroform at 77 K. On the basis of the Stoke shifts between absorption and emission for ligands **5a** and **7** and (lower than 3000 cm^{-1}) the luminescence observed is assigned to π–π* fluorescence. For ligand **5b** and all the complexes, the lifetimes seem to be roughly in the lower limit of detection of our instrument (10 μs), suggesting phosphorescence.

Ligand **5a** and its complexes **8a**–**10a** are luminescent at 298 K in the solid state, but not in solution at room temperature (Table 1). For ligand **5a**, the emission spectrum in KBr pellet at room temperature displays a well-resolved vibrational pattern that could be due to the C=C bond, affording a central band at 365 nm flanked by two shoulders (≈1200 cm^{-1}; Supporting Information, Figure S1). The emission bands of **8a**–**10a** are shifted, by at least 120 nm (6700 cm^{-1}), to longer wavelengths from their position in the corresponding free ligand. The deshielding observed in the ^1H NMR spectra for the hydrogen atoms of the aryl ring, when the ligands are coordinated to gold, suggests that the isocyano substituent becomes more electron withdrawing when its carbon lone pair is donated to gold, thus enhancing the charge separation in the carbazole–phenyl system. In the solid state (KBr pellets) the emission spectra of the gold complexes show broad emission bands in the range 400–600 nm. There is a clear shift to lower energy from chloride derivative **8a** (485 nm) to pentafluorophenyl

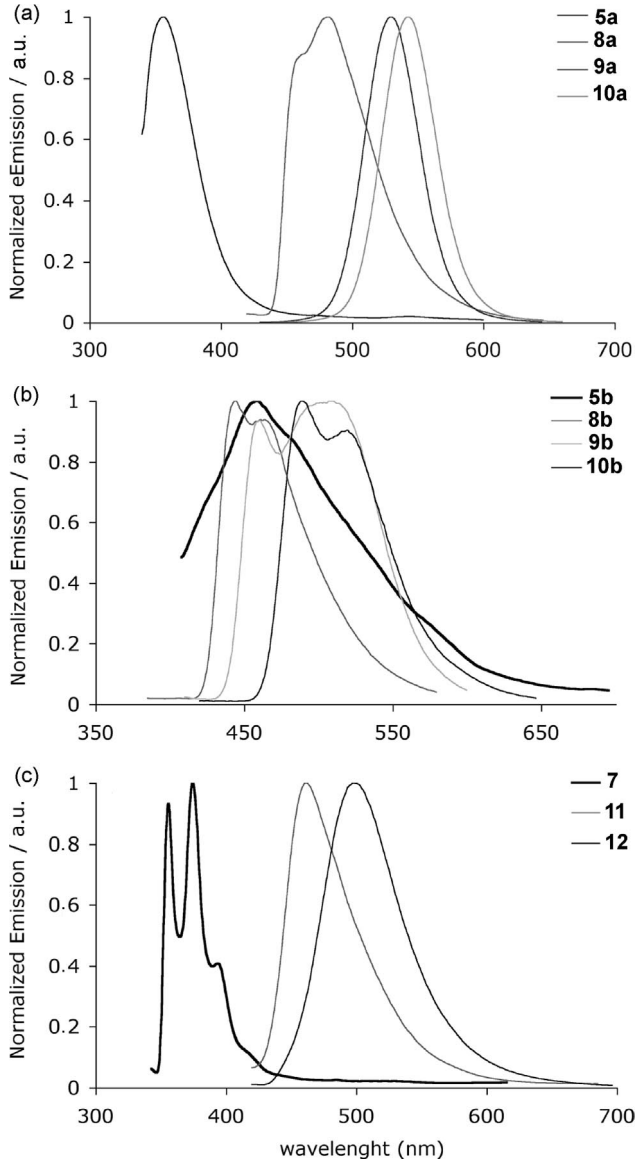


Figure 4. Normalized emission spectra of ligands **5a** (a), **5b** (b), **7** (c), and their complexes in frozen chloroform solution at 77 K.

derivative **9a** (523 nm) or tetrafluorophenyl derivative **10a** (525 nm), which follows the order of decreasing electronegativity of the X substituents on gold.[36] At 77 K in frozen chloroform solution (Figure 4) the luminescence is, qualitatively, more intense and similar shifts are observed.

A different behavior was found for brominated ligand **5b**, which is nonluminescent at room temperature in the solid state. As for the corresponding complexes under the same conditions, complex **8b** is practically nonluminescent; **9b** and **10b** show some luminescence but are clearly less luminescent than their non-brominated analogues. The detrimental effect for luminescence of attaching electron-withdrawing substituents to conjugated molecules has been noticed and discussed before.[37]

In frozen chloroform, free ligand **5b** is luminescent, but it exhibits a broad band (λ_{max} = 439 nm) with an important redshift relative to that of **5a**, and bigger separation between the maxima of excitation (λ_{max} = 381 nm) and emission. These features would fit better with phosphorescence than with fluorescence. Moreover, the quenching of the observed luminescence, in the solid state and in solution (which does not occur in **5a**), is better understood by the heavy atom (Br) effect in **5b**, which facilitates intersystem crossing (ISC) to give phosphorescence, easily quenched by the solvent molecules at room temperature. The corresponding gold(I) complexes, including **8b**, show low luminescence at low temperature (two overlapped bands in the range 400–600 nm, Table 1). In contrast to the emission spectra of **5a** and their complexes, we find that the gold complexes of **5b** show just a modest λ_{max} shift from the free ligand, suggesting a ligand-dominated emissive state.

Ligand **7** is the only ligand that is luminescent in solution in $CHCl_3$ at room temperature, and it displays one emission band at 375 nm; this emission also appears in the solid state at 391 nm and can be assigned to an intraligand π–π* charge transfer similar to the carbazole emission at 360 nm.[38] At low temperature in frozen chloroform solution, **7** displays a well-resolved vibronic structure with a vibrational spacing of ≈1350 cm^{-1} (Figure 4c). Only complex **12** is luminescent in the solid state at room temperature, but both **11** and **12** display two overlapping emission bands at 77 K (Supporting Information, Figures S4 and S5). As for the absorption spectra, the emission bands are shifted to longer wavelengths (more than 5000 cm^{-1}) on going from ligand **7** to its complexes **11** and **12**. The change in the X substituent on gold has a moderate effect on the luminescence: in comparison to the pentafluorophenyl derivative, the chloride derivative is less luminescent (nonluminescent at room temperature) and shows a lower redshift from the ligand (600 cm^{-1} less than C_6F_5) in frozen chloroform solution. Similar redshifts have been observed in other carbazole derivatives with substitutions at the 3-position.[39]

Conclusions

In conclusion, all the gold complexes [AuX(CN-carbazole)] (X = Cl, C_6F_5, C_6F_4-OEt-*p*) derived from 9-(4-isocyanophenyl)carbazole, 3,6-dibromo-9-(4-isocyanophenyl)-carbazole, and 9-ethyl-3-isocyanocarbazole show a redshift in the emissions relative to that of the corresponding free ligand, regardless of the position of attachment of the gold fragment in the carbazole unit. In general, the emission wavelength is sensitive to the X substituents on gold. The presence of electron-withdrawing substituents in the ligand 3,6-dibromo-9-(4-isocyanophenyl)carbazole quenches the luminescence observed for 9-(4-isocyanophenyl)carbazole, which is somewhat recovered upon complexation to gold.

Experimental Section

General Procedures: C, H, and N analyses were carried out with a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded with a Perkin–Elmer FT-1720X spectrometer by using nujol mulls between polyethylene films. UV/Vis data were recorded with a Shimadzu UV-1603 spectrophotometer in chloroform solutions 10^{-4} to 10^{-5} M, and luminescence data were recorded with a Perkin–Elmer LS-55 spectrometer. NMR spectra were run at room temperature with Bruker AC-300 or ARX-300 spectrophotometers (300.13 MHz for ^1H and 282.4 MHz for ^{19}F). Literature methods were used to prepare 9-(4-aminophenyl)carbazole (**4a**) and 3,6-dibromo-9-(4-aminophenyl)carbazole (**4b**) from commercial carbazole.[26–27] Preparation procedures and physical data of the new compounds are given below. When analogous ligands and complexes were prepared in the same way only one preparation is described.

9-(4-Isocyanophenyl)carbazole (5a): The procedure described by Ugi was followed,[28] but by using triphosgene as dehydrating agent. A flask provided with a Dean–Stark apparatus was charged with a solution of 9-(4-aminophenyl)carbazole (2.0 g, 7.74 mmol) in toluene (50 mL). Formic acid (1.5 mL, 98%) was added. The resulting solution was heated at reflux for 2 h and then cooled to room temperature. The solvent was removed under vacuum, and the crude product 9-(4-formanilide)carbazole was obtained (2.18 g, 98%). The crude product was sufficiently pure for use in the next reaction. To a solution of the formanilide (2.0 g, 6.9 mmol) and triethylamine (2.9 mL, 20.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise a solution of triphosgene (0.7 g, 2.3 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 1 h, and the solvent was removed under reduced pressure. The resulting residue was purified by chromatography (silica gel; CH_2Cl_2/hexane, 3:1), and the solvent was evaporated to obtain the product as a yellow solid (1.34 g, 71%). $C_{19}H_{12}N_2$ (268.32): calcd. C 85.05, H 4.51, N 10.44; found C 84.77, H 4.65, N 10.12. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 8.16 (m, 2 H), 7.63 (s, AA′XX′ spin system, 4 H), 7.42 (m, 4 H) 7.33 (m, 2 H) ppm. IR (nujol): $\tilde{\nu}$ = 2124 [ν(C≡N)] cm^{-1}.

3,6-Dibromo-9-(4-isocyanophenyl)carbazole (5b): Yield: 0.854 g (89%). $C_{19}H_{10}Br_2N_2$ (426.11): calcd. C 53.56, H 2.37, N 6.57; found C 53.46, H 2.54, N 6.64. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 8.19 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, H4, H5), 7.64, 7.58 (AA′XX′, $^3J_{H,H}$ = 8.7 Hz, 4 H, C_6H_4), 7.53 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.9 Hz, 2 H, H2, H7), 7.24 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, H1, H8) ppm. IR (nujol): $\tilde{\nu}$ = 2125 [ν(C≡N)] cm^{-1}.

9-Ethyl-3-isocyanocarbazole (7): Yield: 1.645 (89%). $C_{15}H_{12}N_2$ (220.27): calcd. C 81.79, H 5.49, N 12.72; found C 81.50, H 5.24, N 12.27. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 8.11 (d, $^4J_{H,H}$ = 1.5 Hz, 1 H, H4), 8.07, (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H5), 7.54 (m, 1 H, H7), 7.47 (dd, $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, H2), 7.44 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H8), 7.36 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, H1), 7.29

(m, 1 H, H6), 4.38 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 1.45 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3) ppm. IR (nujol): $\tilde{\nu}$ = 2121 [ν(C≡N)] cm^{-1}.

[AuCl{9-(4-isocyanophenyl)carbazole}] (8a): To a solution of [AuCl(tht)] (0.11 g, 0.36 mmol) in dichloromethane (30 mL) was added **5a** (0.10 g, 0.37 mmol). After the mixture had been stirred for 1 h, the solvent was evaporated to ca. 5 mL under reduced pressure. Addition of hexane (20 mL) afforded **8a** as a pale yellow solid, which was filtered off, washed with hexane and vacuum dried (0.114 g, 63%). $C_{19}H_{12}AuClN_2$ (500.74): calcd. C 45.57, H 2.42, N 5.59; found C 45.53, H 2.27, N 5.76. ^{1}H NMR (300.13 MHz, [D_6]-DMSO): δ = 8.26 (m, 2 H), 7.47 (m, 4 H), 7.34 (m, 2 H), 8.14, 7.92 (AA′XX′, $^3J_{H,H}$ = 7.7 Hz, 4 H, C_6H_4) ppm. IR (nujol): $\tilde{\nu}$ = 2213 [ν(C≡N)], 345 [ν(Au–Cl)] cm^{-1}.

[Au(C_6F_5){9-(4-isocyanophenyl)carbazole}] (9a): The method was the same as that above but with the use of [Au(C_6F_5)(tht)]. Yield: 0.186 g (87%). $C_{25}H_{12}AuF_5N_2$ (632.34): calcd. C 47.49, H 1.91, N 4.43; found C 47.82, H 1.86, N 4.80. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.16 (m, 2 H), 7.46 (m, 4 H), 7.36 (m, 2 H), 7.81 (s, 4 H, C_6H_4) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –116.4 (m, 2 F, F^o), –157.6 (t, $^3J_{F,F}$ = 17.9 Hz, 1 F, F^p), –162.7 (m, 2 F, F^m) ppm. IR (nujol): $\tilde{\nu}$ = 2211 [ν(C≡N)] cm^{-1}.

[Au(C_6F_4-OEt-*p*){9-(4-isocyanophenyl)carbazole}] (10a): To a solution of HC_6F_4-OEt-*p* (0.052 mL, 0.373 mmol) in dried diethyl ether (25 mL) was added a solution of BuLi (1.6 M in hexane, 0.233 mL, 0.373 mmol) at –78 °C under an atmosphere of nitrogen. After the solution was stirred for 1 h at –50 °C, solid [AuCl(tht)] (0.1196 g, 0.373 mmol) was added at –78 °C, and the reaction mixture was slowly brought to 10 °C (3 h). Then, a few drops of water were added, and the solution was filtered through anhydrous Na_2SO_4 and **5a** (0.100 g, 0.373 mmol) was added to the solution obtained. After stirring for 1 h, the solution was filtered through Kieselgur and silica gel. The solvent was removed, and the pale yellow solid obtained was recrystallized from dichloromethane/hexane at –20 °C. Yield: 0.111 g (45%). $C_{27}H_{17}AuF_4N_2O$ (658.41): calcd. C 49.25, H 2.60, N 4.25; found C 49.06, H 2.57, N 4.19. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.17 (m, 2 H), 7.81 (m, 4 H), 7.47 (m, 4 H), 7.37 (m, 2 H), 4.24 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 1.41 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –118.1, –157.3 (m, AA′XX′, J_{AX} + $J_{AX'}$ = 17.8 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2207 [ν(C≡N)] cm^{-1}.

[AuCl{3,6-dibromo-9-(4-isocyanophenyl)carbazole}] (8b): Yield: 0.0983 g (63%). $C_{19}H_{10}AuBr_2ClN_2$ (658.53): calcd. C 34.65, H 1.53, N 4.25; found C 34.92, H 1.62, N 4.17. ^{1}H NMR (300.13 MHz, [D_6]acetone): δ = 8.61 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, H4, H5), 8.15, 7.91 (AA′XX′, $^3J_{H,H}$ = 8.8 Hz, 4 H, C_6H_4), 7.62 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.9 Hz, 2 H, H2, H7), 7.41 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H1, H8) ppm. IR (nujol): $\tilde{\nu}$ = 2210 [ν(C≡N)], 356 [ν(Au–Cl)] cm^{-1}.

[Au(C_6F_5){3,6-dibromo-9-(4-isocyanophenyl)carbazole}] (9b): Yield: 0.0576 g (66%). $C_{25}H_{10}AuBr_2F_5N_2$ (790.13): calcd. C 38.00, H 1.28, N 3.55; found C 37.95, H 1.15, N 3.77. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.22 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, H4, H5), 7.84, 7.74 (AA′XX′, $^3J_{H,H}$ = 8.8 Hz, 4 H, C_6H_4), 7.56 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.9 Hz, 2 H, H2, H7), 7.29 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H1, H8) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –116.5 (m, 2 F, F^o), –157.5 (t, $^3J_{F,F}$ = 20.2 Hz, 1 F, F^p), –162.6 (m, 2 F, F^m) ppm. IR (nujol): $\tilde{\nu}$ = 2208 [ν(C≡N)] cm^{-1}.

[Au(C_6F_4-OEt-*p*){3,6-dibromo-9-(4-isocyanophenyl)carbazole}] (10b): Yield: 0.111 g (29%). $C_{27}H_{15}AuBr_2F_4N_2O$ (816.20): calcd. C 39.73, H 1.85, N 3.43; found C 39.38, H 2.19, N 3.13. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.23 (d, $^4J_{H,H}$ = 1.8 Hz, 2 H, H4, H5), 7.85, 7.73 (AA′XX′, $^3J_{H,H}$ = 8.6 Hz, 4 H, C_6H_4), 7.56 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.9 Hz, 2 H, H2, H7), 7.33 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H1, H8), 4.22 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, CH_2), 1.37 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –118.2, –157.3 (m, AA′XX′, J_{AX} + $J_{AX'}$ = 17.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2212 [ν(C≡N)] cm^{-1}.

Table 2. Crystal and structure refinement data for **10a** and **12**.

	10a	**12**
Empirical formula	$C_{27}H_{17}AuF_4N_2O$	$C_{21}H_{12}AuF_5N_2$
Formula weight	658.39	584.29
Temperature / K	298(2)	298(2)
Wavelength / Å	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / Å	11.4625(18)	7.8358(9)
b / Å	10.6421(16)	9.7161(11)
c / Å	18.759(3)	13.1481(15)
α / °	90	98.166(2)
β / °	99.327(3)	99.620(2)
γ / °	90	106.137(2)
V / Å^3	2258.1(6)	929.08(18)
Z	4	2
$D_{calcd.}$ / g cm^{-3}	1.937	2.089
Absorption coefficient / mm^{-1}	6.572	7.975
F(000)	1264	552
Crystal size / mm	0.24 × 0.09 × 0.03	0.12 × 0.10 × 0.04
θ range for data collection / °	1.80 to 23.29	2.23 to 23.28
Reflections collected	10775	5775
Independent reflections	3251	3789
Absorption correction	SADABS	SADABS
Maximum and minimum transmission factor	1.000000 and 0.608741	1.000000 and 0.539600
Data, restraints, parameters	3251, 0, 317	3789, 0, 263
Goodness-of-fit on F^2	1.022	1.021
R_1 [$I > 2\sigma(I)$]	0.0229	0.0265
wR_2 (all data)	0.0581	0.0666

[AuCl(9-ethyl-3-isocyanocarbazole)] (11): Yield: 0.095 g (93%). $C_{15}H_{12}AuClN_2$ (452.69): calcd. C 39.80, H 2.67, N 6.19; found C 39.94, H 2.48, N 6.05. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.26 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, H4), 8.10 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H1), 7.59 (m, 2 H), 7.49 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H), 7.46 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.36 (m, 1 H), 4.42 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 1.47 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. IR (nujol): $\tilde{\nu}$ = 2222 [ν(C≡N)] cm^{-1}.

[Au(C_6F_5)(9-ethyl-3-isocyanocarbazole)] (12): Yield: 0.173 g (65%). $C_{21}H_{12}AuF_5N_2$ (584.30): calcd. C 43.17, H 2.07, N 4.79; found C 42.95, H 2.03, N 4.63. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 8.28 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H), 8.11 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H), 7.60 (m, 2 H), 7.48 (m, 2 H), 7.35 (m, 1 H), 4.42 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2), 1.48 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –116.4 (m, 2 F, F^o), –158.1 (t, $^3J_{F,F}$ = 20.2 Hz, 1 F, F^p), –162.7 (m, 2 F, F^m) ppm. IR (nujol): $\tilde{\nu}$ = 2213 [ν(C≡N)] cm^{-1}.

X-ray Structures: Crystal structure refinement data for **10a** and **12** are given in Table 2. Data were recorded with a Bruker AXS SMART 1000 CCD diffractometer, using ϕ and ω scans, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, and T = 298 K. Raw frame data were integrated with SAINT[40] program. Structures were solved by direct methods with SHELXTL.[41] Semi-empirical absorption correction was made with SADABS.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL.

CCDC-709208 (for **10a**) and -709209 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Emission spectra of **5a**, **8a**, **9a**, **10a**, **9b**, **10b**, **7**, **11**, and **12**.

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