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Luminescence and Mesogenic Properties in Crown-Ether-Isocyanide or Carbene Gold(I) Complexes: Luminescence in Solution, in the Solid, in the Mesophase, and in the Isotropic Liquid State

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A crown ether isocyanide CNR (R = benzo-15-crown-5) has been synthesized by dehydration of the corresponding formamide. Substitution reactions with the appropriate gold(I) precursors afford the luminescent mononuclear derivatives [AuX(CNR)] (X = Cl, C_6F_5, Br, I), [Au($C_6F_4OCH_2C_6H_4OC_nH_{2n+1}$-*p*)(CNR)] ($n$ = 4, 8, 10, 12), and [Au($C_6F_4OCH_2C_6H_2$-3,4,5-$(OC_nH_{2n+1})_3$(CNR)] (n = 4, 8, 12). X-ray diffraction studies of [AuCl(CNR)] show the molecules associated in a tetranuclear manner with an antiparallel orientation and gold−gold distances of 3.420 and 3.427 Å (Au···Au···Au angles are 121.2°). These tetranuclear units generate infinite zigzag chains through longer Au···Au distances of 3.746 Å and weak C−H···O nonclassic interactions. Nucleophilic attack to the coordinated isocyanide in [AuCl(CNR)] by methanol or a primary amine produces the carbene derivatives [AuCl{C((NHR)(OMe)}] and [AuCl{C(NHR′)(NHR)}] (R′ = Me, *n*-Bu). The ether crown in these complexes is able to coordinate sodium from $NaClO_4$, affording the corresponding bimetallic complexes (Na/Au = 1:1). The derivatives containing one alkoxy chain are liquid crystals, displaying a smectic C mesophase (for $n > 4$), whereas the trialkoxy derivatives display unidentified or smectic C mesophases, depending on the alkyl chain length. After complexation of sodium salts, the mesogenic behavior is lost. All of the derivatives are luminescent at room temperature in the solid state with emission maxima in the range 405–550 nm; they emit at 77 K from 410 to 572 nm. Only the ligand and the fluoroaryl complexes emit in solution at room temperature, but all of the compounds are luminescent at 77 K. Very interestingly, some fluoroaryl derivatives with alkoxy chains are luminescent not only in the solid, and in solution, but also in the mesophase, and in the isotropic liquid at moderate temperatures. These are the first metal complexes ever reported to show luminescence in the isotropic liquid state.

Introduction

The synthesis of closed-shell gold(I) derivatives has attracted attention in recent years because of the frequent presence of short gold−gold distances, which have been attributed to correlation effects reinforced by relativistic effects and electrostatic contributions.[1] Many gold(I) compounds, with or without gold−gold contacts, are luminescent in the visible region,[1a,2] and some of them have been proposed for applications as sensors or as light-emitting diodes.[3]

On the other hand, gold(I) displays typically a linear geometry, which has been very useful to prepare, after coordination of promesogenic ligands, calamitic molecules behaving as liquid crystals. In this context, isonitrile ligands are most suited because of the high thermal stability of their complexes and the prolongation of the linearity along the CN bond.[4] Many reported isocyanide gold metallomesogens, which were not checked for luminescence at the time of preparation, should probably be luminescent in the solid state and in solution, but in fact the metallomesogens reportedly photoluminescent in the solid state or in solution are just a few lanthanide, palladium, or gold complexes.[5] A very different matter is luminescence in the mesophase, and only very recently, metallomesogens have been reported to display this property in the liquid crystal state. These are some

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(1) (a) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412. (b) Runeberg, N.; Schütz, M.; Werner, H. J. *J. Chem. Phys.* **1999**, *110*, 7210.

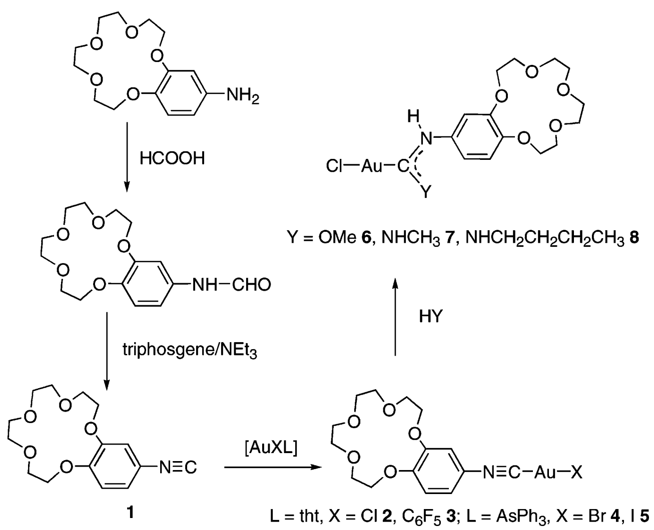
(2) (a) Roundhill, D. M.; Fackler, J. P., Jr. *Optoelectronic Properties of Inorganic Compounds*; Plenum Press: New York, 1998. (b) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3.

10.1021/ic701831v CCC: \$40.75

lanthanide-, zinc-, or silver-based columnar metallomesogens[6] and some noncolumnar gold(I) derivatives from our group.[7] No metallomesogen has been reported to luminesce above the clearing point, in the isotropic liquid state.

A most relevant property of crown ethers is to coordinate cations, which has been exploited to detect or extract cations, for ionic transport, or to prepare stationary phases in chromatography.[8] Although metallomesogens combining transition metals and crown ethers have been recently reported, very often the crown cavity is occupied by the metal providing metallomesogenic character, and it is this occupancy that induces the mesogenic behavior. In these complexes, the crown is already coordinated, and it is not possible to further complex an alkali salt. Moreover, the coordination is typically facilitated by using crowns with nitrogen or sulfur atoms replacing some oxygen atoms.[6,9]

Scheme 1



Continuing previous studies on new polyfunctional complexes combining suitable fragments,[7,10] in this paper, we report Au(I) complexes containing a crown isocyanide or its derived carbene ligands. Within the group of complexes reported we find the following properties: luminescence, mesogenic behavior, and coordination to alkaline cations. Most interesting, some complexes behave as liquid crystals at very moderate temperatures and display luminescence in solution, in the solid state, in the mesophase, and even in the isotropic liquid state.

Results and Discussion

Synthesis and Characterization. A crown ether functionalized isocyanide was prepared and used to synthesize mononuclear gold(I) complexes by substitution of weaker tetrahydrothiophene (tht) or arsine ligands (Scheme 1). Nucleophilic attack of the coordinated isocyanide by methanol or by a primary amine afforded gold(I) carbene complexes.[11]

Compounds **1**–**8** are air-stable solids at room temperature that were characterized by elemental analysis, IR, and NMR spectroscopy. The IR spectra of **2**–**5** show the characteristic shift upon coordination of $\nu(C\equiv N)$, from 2122 cm^{-1} in the free ligand **1** to 2218–2229 cm^{-1}. This band disappears in the carbene complexes **6**–**8**. In the ^1H NMR spectra, the crown ether ligand in the complexes shows a slightly shifted AMX spin system for the aromatic protons and the methylene resonances (quite coordination-insensitive). Additionally, the carbene derivative (**6**) shows two N−H resonances corresponding to the two possible isomers arising from rotational restriction around the $C{=}N$ carbene bond. For **7**–**8**, up to four isomers are possible. For **7**, at least two isomers are observed, while for **8**, the broad signals suggest the presence of several isomers, but no well-separated resonances are observed.

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(3) (a) Yam, V. W. W.; Chan, C. L.; Li, C. K.; Wong, K. M. C. *Coord. Chem. Rev.* **2001**, *216–217*, 173. (b) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329. (c) Ma, Y.; Che, C. M.; Chao, H. Y.; Zhou, X.; Chan, W. H.; Shen, J. *Adv. Mater.* **1999**, *11*, 852. (d) Fave, C.; Cho, T. Y.; Hissler, M.; Chen, C. W.; Luh, T. Y.; Wu, C. C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254.

(4) (a) Espinet, P. *Gold Bull.* **1999**, *32*, 127. (b) Benouazzane, M.; Coco, S.; Espinet, P.; Martín-Alvarez, J. M. *J. Mater. Chem.* **1995**, *5*, 441. (c) Alejos, P.; Coco, S.; Espinet, P. *New J. Chem.* **1995**, *19*, 799. (d) Bayón, R.; Coco, S.; Espinet, P.; Fernández-Mayordomo, C.; Martín-Alvarez, J. M. *Inorg. Chem.* **1997**, *36*, 2329. (e) Benouazzane, M.; Coco, S.; Espinet, P.; Martín-Alvarez, J. M. *J. Mater. Chem.* **1999**, *9*, 2327. (f) Bayón, R.; Coco, S.; Espinet, P. *Chem. Mater.* **2002**, *14*, 3515. (g) Benouazzane, M.; Coco, S.; Espinet, P.; Martín-Alvarez, J. M.; Barberá, J. *J. Mater. Chem.* **2002**, *12*, 691. (h) Coco, S.; Fernández-Mayordomo, C.; Falagán, S.; Espinet, P. *Inorg. Chim. Acta* **2003**, *350*, 366. (i) Ballesteros, B.; Coco, S.; Espinet, P. *Chem. Mater.* **2004**, *16*, 2062. (j) Bartolomé, C.; Carrasco-Rando, M.; Coco, S.; Cordovilla, C.; Espinet, P.; Martín-Alvarez, J. M. *Organometallics* **2006**, *25*, 2700.

(5) (a) Piechocki, C.; Simon, J.; André, J. J.; Guillon, D.; Petit, P.; Skoulios, A.; Weber, P. *Chem. Phys. Lett.* **1985**, *122*, 124. Binnemans, K.; Malykhina, L.; Mironov, V. S.; Haase, W.; Driesen, K.; Van Deun, R.; Fluyt, L.; Gorller-Walrand, C.; Galyametdinov, Y. G. *ChemPhysChem* **2001**, *2*, 680. (c) Nozary, H.; Piguet, C.; Rivera, J. P.; Tissot, P.; Morgantini, P. Y.; Weber, J.; Bernardinelli, G.; Bünzli, J. C. G.; Deschenaux, R.; Donnio, R.; Guillon, D. *Chem. Mater.* **2002**, *14*, 1075. (d) Ghedini, M.; Pucci, D.; Crispini, A.; Aiello, I.; Barigelletti, F.; Gessi, A.; Francescangeli, O. *Appl. Organomet. Chem.* **1999**, *13*, 565. (e) Coco, S.; Cordovilla, C.; Espinet, P.; Martín-Alvarez, J. M.; Muñoz, P. *Inorg. Chem.* **2006**, *45*, 10180.

(6) (a) Suárez, S.; Mamula, O.; Imbert, D.; Piguet, C.; Bünzli, J. C. G. *Chem. Commun.* **2003**, 1226. (b) Suárez, S.; Imbert, D.; Gumy, F.; Piguet, C.; Bünzli, J. C. G. *Chem. Mater.* **2004**, *16*, 3257. (c) Cavero, E.; Uriel, S.; Romero, P.; Serrano, J. L.; Giménez, R. *J. Am. Chem. Soc.* **2007**, *129*, 11608. (d) Barberio, G.; Bellusci, A.; Crispini, A.; Donnio, B.; Giorgini, L.; Ghedini, M.; La Deda, M.; Pucci, D.; Szerb, E. I. *Chem.—Eur. J.* **2006**, *12*, 6738.

(7) Bayón, R.; Coco, S.; Espinet, P. *Chem.—Eur. J.* **2005**, *11*, 1079.

(8) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495. (b) Pedersen, C. J. *Science* **1988**, *241*, 536. (c) Gokel, G. W. *Crown Ethers and Cryptands*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, U.K., 1991; Monographs in Supramolecular Chemistry Series. (d) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723.

(9) (a) Liebmann, A.; Mertesdorf, C.; Plesnivy, T.; Ringsdorf, H.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1375. (b) Lattermann, G.; Schmidt, S.; Kleppinger, R.; Wendorff, J. H. *Adv. Mater.* **1992**, *4*, 30. (c) Neve, F.; Ghedini, M.; Levelut, A. M.; Francescangeli, O. *Chem. Mater.* **1994**, *6*, 70. (d) Schmidt, S.; Lattermann, G.; Kleppinger, R.; Wendorff, J. H. *Liq. Cryst.* **1994**, *16*, 693. (e) Neve, F.; Ghedini, M.; Levelut, A. M.; Francescangeli, O. *Liq. Cryst.* **1996**, *21*, 625. (f) Richtzenhain, H.; Blake, A. J.; Bruce, D. W.; Fallis, I. A.; Li, W. S.; Shröder, M. *Chem. Commun.* **2001**, 2580.

(10) Arias, J.; Bardají, M.; Espinet, P. *J. Organomet. Chem.* **2006**, *691*, 4990.

(11) (a) Usón, R.; Laguna, A.; Vicente, J.; García, J.; Bergareche, B. *J. Organomet. Chem.* **1979**, *173*, 349. (b) Usón, R.; Laguna, A.; Brun, P.; Laguna, M.; Abad, M. *J. Organomet. Chem.* **1981**, *218*, 265. (c) Parks, J. E.; Balch, A. L. *J. Organomet. Chem.* **1974**, *71*, 453. (d) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1973**, *59*, 403.

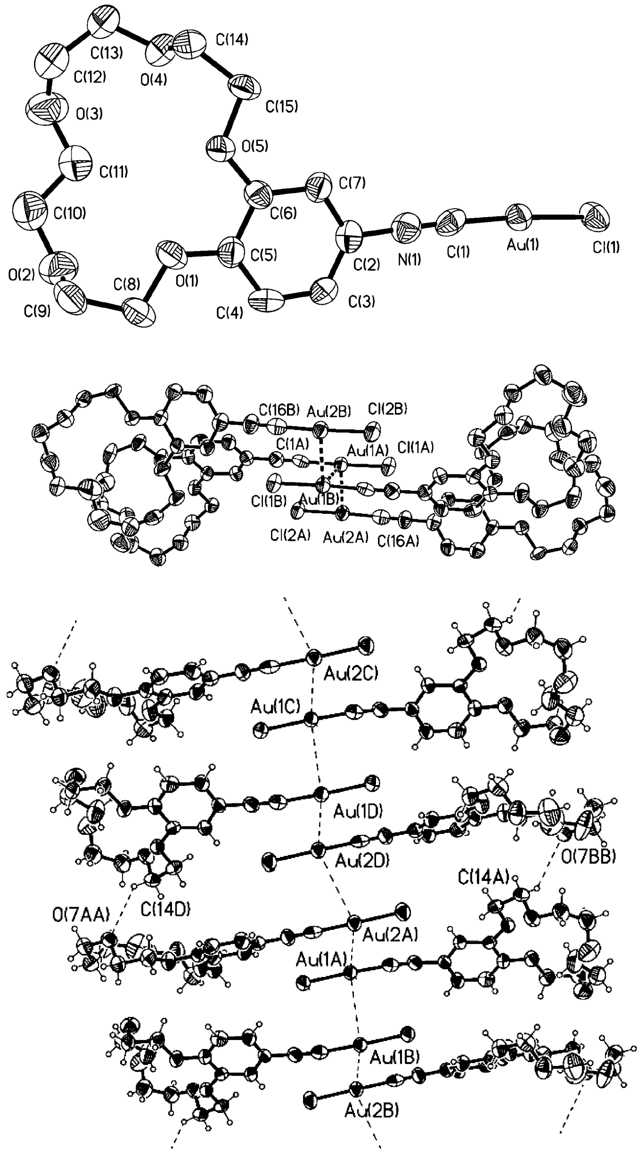

Figure 1. (Top) Structure of one independent molecule of **2**, showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. H atoms have been omitted for clarity. (Center) Extended structure of **2**, showing the tetranuclear zigzag cluster (H atoms omitted for clarity; displacement ellipsoids at the 50% probability level). (Bottom) View showing the longer distance connections of two tetranuclear zigzag clusters.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Au(1)−C(1)	1.920(11)	Au(2)−C(16)	1.925(12)
Au(1)−Cl(1)	2.261(2)	Au(2)−Cl(2)	2.261(3)
C(1)−N(1)	1.153(12)	C(16)−N(2)	1.160(13)
N(1)−C(2)	1.400(12)	N(2)−C(17)	1.379(13)
C(5)−O(1)	1.330(10)	C(20)−O(6)	1.355(10)
C(5)−C(6)	1.403(12)	C(20)−C(21)	1.396(12)
C(1)−Au(1)−Cl(1)	176.5(3)	C(16)−Au(2)−Cl(2)	177.3(3)
N(1)−C(1)−Au(1)	174.8(8)	N(2)−C(16)−Au(2)	178.9(9)
C(1)−N(1)−C(2)	175.9(9)	C(16)−N(2)−C(17)	178.1(11)
C(3)−C(2)−N(1)	120.0(8)	C(22)−C(17)−N(2)	120.3(9)

The structure of complex **2** shown in Figure 1 was established by X-ray diffraction. Selected bond lengths and angles are given in Table 1. Complex **2** crystallizes as two very similar independent molecules in the asymmetric unit, labeled Au(1) and Au(2) in Table 1. The C−Au−Cl angles (176.5(3) and 177.3(3)°) confirm a typical linear geometry around the gold atom. The Au−Cl and Au−C bond lengths are within normal ranges for chloro isocyanide gold complexes.[12] There are four molecules per unit cell which are connected by gold−gold bonds: two antiparallel molecules with a gold−gold interaction at 3.420 Å (Au(1A)−Au(2A) or Au(1B)−Au(2B)) are connected to a second identical pair with a Au(1A)−Au(1B) distance of 3.427 Å, giving rise to a tetranuclear zigzag cluster. Both angles, Au(2A)−Au(1A)−Au(1B) and Au(1A)−Au(1B)−Au(2B), are 121.2°. The tetranuclear units are further connected to others, describing infinite zigzag gold chains, by weak nonclassical C−H···O bonds (d(H···O) = 2.702 Å; d(C···O) = 3.330 Å; C−H···O angle = 122.88°) and longer possible gold−gold contacts at 3.746 Å, with an Au−Au−Au angle of 139°. Although the zigzag chains in the crystal are packed in such a way that the crown ether rings would appear to form a channel, this view is deceptive, as they are about 8.4 Å apart from each other.

Neutral [AuCl(CNR)] compounds reported in the literature display diverse arrays of supramolecular structures including (a) dimers with short gold−gold distances (e.g., 3.063 Å for R = (p-toluenesulfonyl)methyl)[13] or 3.336 Å for R = mesityl);[14] (b) monodimensional zigzag chains, typically with one single gold−gold distance longer than the short one for complex **2** (e.g., 3.637 Å for R = Me, 3.564 Å for R = Et, and 3.547 Å for R = Pr),[12,14] although in other cases, the chain is formed with a short and a long gold distance as found for R = Cy (3.388 and 3.587 Å);[15] (c) bidimensional polymeric sheets, as reported for 1,1′-diisocyanoferrocene gold complexes, with gold−gold distances of 3.354 and 3.484 Å.[16] The arrangement observed here is somewhat different from all of these.

In view of the successful synthesis of the C_6F_5 derivative **3**, a promesogenic fluorinated aryl ligand containing one or three alkoxy chains was used, searching for complexes with liquid crystal behavior (Scheme 2).[4f,4i,5e,7]

Complexes **9–10** are air-stable white solids at room temperature. They were readily characterized by (a) consistent elemental analysis; (b) their characteristic coordinated isocyanide stretching absorption at *ca.* 2215 cm^{-1}; (c) an AA′XX′ spin system in the ^{19}F NMR spectra (with the deceptive appearance of two doublets centered at *ca.* −118 and −156 ppm) typical of the Au−C_6F_4 moiety; and (d) ^{1}H NMR spectra displaying signals corresponding to one or three alkoxy chains, the crown ether fragment, a benzyl resonance at *ca.* 5.10 ppm, and signals for the remaining aromatic protons, as assigned in the experimental section.

Complexation of **9–10** (for chain length $n = 8$) with $NaClO_4$ was achieved by the addition of sodium perchlorate in a ratio of 1:1 15-crown-ether/Na (Scheme 3). Sodium was

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[12] Bachman, R. E.; Fioritto, M. S.; Fetics, S. K.; Cocker, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 5376.

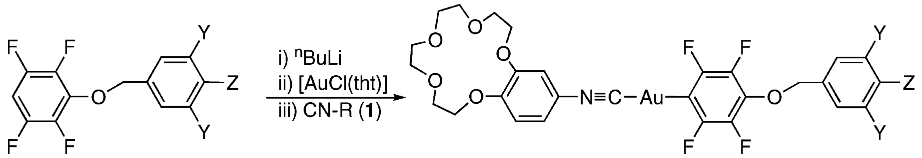
[13] Elbjeirami, O.; Omary, M. A.; Stender, M.; Balch, A. L. *Dalton Trans.* **2004**, 3173.

[14] Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch., B: Chem. Sci* **1996**, *51*, 790.

[15] White-Morris, R. L.; Olmstead, M. M.; Balch, A. L.; Elbjeirami, O.; Omary, M. A. *Inorg. Chem.* **2003**, *42*, 6741.

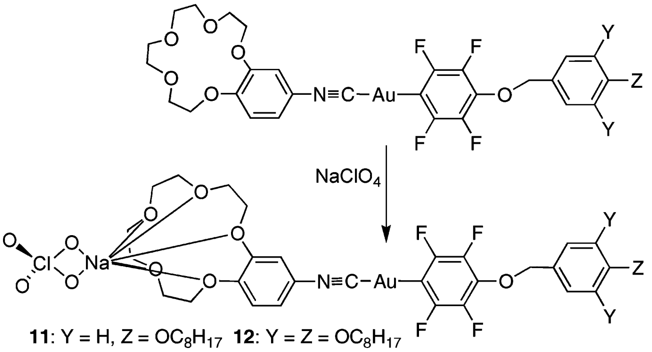
[16] Siemeling, U.; Rother, D.; Bruhn, C.; Fink, H.; Weidner, T.; Trager, F.; Rothenberger, A.; Fenske, D.; Priebe, A.; Maurer, J.; Winter, J. *J. Am. Chem. Soc.* **2005**, *127*, 1102.

Scheme 2



Y = H, Z = OC_4H_9 **9a**, OC_8H_{17} **9b**, $OC_{10}H_{21}$ **9c**, $OC_{12}H_{25}$ **9d**;
Y = Z = OC_4H_9 **10a**, OC_8H_{17} **10b**, $OC_{12}H_{25}$ **10c**;

Scheme 3



11: Y = H, Z = OC_8H_{17} **12**: Y = Z = OC_8H_{17}

chosen because its radius fits best the 15-crown ether moiety.[8] The complexes are brownish solids at room temperature and were characterized by elemental analysis and IR and NMR spectroscopy. They are soluble in $CDCl_3$ (where $NaClO_4$ is insoluble), and their ^{1}H NMR spectra show small shifts of some aromatic protons and splitting of the methylene crown ether resonances, due to the descent of symmetry upon sodium coordination. Their IR spectra show several absorptions around 1100 cm^{-1} (corresponding to the typical splitting associated with covalently bonded perchlorate, C_{2v} symmetry), as well as combination bands originating from the crown ether moiety, while no changes are observed in the CN absorption compared to their precursors. The spectral data, in conjunction with the solubility of the complexes in $CDCl_3$, suggest tight association of the perchlorate anions to the cationic complex, including covalent interactions of two oxygen atoms of the perchlorate group to Na.

Mesogenic Behavior. Complexes **9–10** displayed monotropic or enantiotropic mesophases upon heating from the solid state or upon cooling from the isotropic liquid. Optical, thermal, and thermodynamic data, obtained by optical microscopy under polarized light (POM) and by differential scanning calorimetry (DSC), are collected in Table 2. The smectic C (SmC) mesophases were assigned by optical microscopy.

The derivatives with one alkoxy chain, **9**, are monotropic liquid crystals. Increasing the alkoxy chain length reduces the melting temperature. As the isotropic liquid is cooled down, the material becomes very viscous, and the mesophase appears very slowly at temperatures close to room temperature, while crystallization is only detected for **9a** and **9c**, because of supercooling of the mesophase. Only the transitions between the mesophase and isotropic liquid (and glass-mesophase for **9b**) are observed in the subsequent heating and cooling cycles of derivatives **9b–9d**, and for **9a**, only the glass−isotropic liquid transition is seen. The SmC mesophases show a sanded Schlieren texture with the point singularities being very small and blurred (Figure 2). Overall, the use of the fairly bulky and flexible crown ether fragment in the ligand apparently results in a reduction of intermolecular attractions, producing lower melting points, less-ordered mesophases, and shorter mesophase ranges than found for the related derivatives [AuCl(CNR)] (R = $C_6H_4OC_nH_{2n+1}$-*p*: enantiotropic SmA mesophases).[17]

Table 2. Optical, Thermal, and Thermodynamic Data for Derivatives **9** and **10**

derivative	*n*	transition[a]	*T*/°C[b]	Δ*H*/kJ mol^{-1} [c]
9a	4	C−C′[d]	92.9	12.62
		C′−I	102.8	27.07
		(I−SmC)[e]	(35)	
		SmC−g[d]	16.4	0.169[c]
9b	8	C−C′[d]	43.4	0.44
		C′−I	93.6	37.77
		(I−SmC)	(21.7)	(−0.499)
9c	10	C−C′[d]	42.9	0.68
		C′−I	77.5	42.24
		(I−SmC)	(36.9)	(−1.35)
		SmC−g[d]	2.23	0.12[c]
9d	12	C−C′[d]	38.1	1.08
		C′−I	54.9	4.27
		(I-SmC)	(41.6)	(−1.21)
10a	4	C−C′[d]	1.4	−0.2
		C′−C″[d]	24.5	0.0895
		C″−I	75.7	39.3
		(I−M)	(88.1)	(−0.06)
		M−g[d]	10.6	0.161[c]
10b	8	C−SmC[e]−I[f]	47.3	36.44[g]
		I−SmC[e]	55	
		SmC−g[d]	3.4	0.119[c]
10c[h]	12	C−M[e]−I[f]	31.4	38.17 [g]
		I−M	17.2	−0.84
		M−C[d]	15.2	−20.34

[a] C, C′, C″ = crystal, *I* = isotropic liquid, g, g′ = glass, M = unidentified mesophase. [b] Data for the first heating scan. [c] For glass transitions, the value given is the specific heat capacity change, J/g °C. [d] Only observed by DSC. [e] Only observed by POM. [f] There are two close consecutive transitions, and the melting point is not sharp. [g] Combined enthalpies. [h] Measured at 1 K min^{-1}.

The derivatives **10** with three alkoxy chains behave as monotropic (**10a**) or enantiotropic (**10b–10c**) liquid crystals. The latter display very viscous mesophases upon heating that are rapidly mixed with isotropic liquid. As observed for derivatives **9**, the increase of the alkoxy chain length reduces the melting temperature. Upon cooling, the mesophase appears very slowly to give an unidentified mesophase (M) for **10a** and **10c** and a SmC phase for **10b**. As observed for derivatives **9**, the subsequent heating and cooling cycles only show the glass−mesophase (for **10a** and **10b**) and the mesophase−isotropic liquid transitions (for **10a**). Only for **10c** are the first heating and cooling cycles kept. The SmC mesophase shows a sanded Schlieren texture similar to that

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(17) Coco, S.; Espinet, P.; Falagán, S.; Martín-Alvarez, J. M. *New. J. Chem.* **1995**, *19*, 959.

Figure 2. Polarized optical microscopic image of the SmC sanded Schlieren texture (100×) observed for **9c** at room temperature.

observed for **9**. Compound **10c** shows a texture different from that of **10b**. In related complexes, the change in molecular aspect (from distorted rodlike to semidiscotic) associated with the introduction of two additional alkoxy chains leads to compounds exhibiting columnar mesophases.[18,4e] In the case of **10c**, the texture observed is ill-defined, and small angle X-ray diffraction studies were unsuccessful because of the short mesophase range and crystallization during exposure to X-rays, so unambiguous mesophase assignment is not possible. These results show that again the presence of the crown ether fragment in the complexes reported here worsens the liquid crystal behavior.

Often, the complexation of alkaline cations with organic liquid crystals leads to more complicated mesophases (frequently, calamitic becomes columnar) depending on the cation and the counteranion, although decreases of mesophase stability or a loss of the mesogenic behavior have been reported as well.[19] It was also reported that the addition of sodium salts to ether crown imine orthopalladated mesogens leads to the loss of liquid crystal properties.[10] In the cases discussed here, **11** shows a lower melting point (46.2 °C, 3.60 kJ/mol) than **9b**, and the mesogenic behavior on cooling is lost. The trialkoxy derivative **12** gives, upon melting, a very viscous nonmesomorphic material. Upon cooling from the isotropic liquid, crystallization of these materials takes several hours or even days, which precludes the observation of any transition phase by DSC or POM. Thus, the isotropic liquid is metastable at room temperature for very long periods.

Luminescence Studies. The emission and excitation spectra of the free ligand and the gold complexes were determined in the solid state and in CH_2Cl_2 solution, at 298 and 77 K. The results are summarized in Table 3. For the complexes displaying low melting points and liquid crystal behavior, additional variable-temperature luminescence studies were undertaken, which are discussed later.

All of the derivatives, including the starting crown ether isocyanide ligand, emit at 77 and 298 K in the solid state and in solution at 77 K, but only some of the complexes emit in CH_2Cl_2 solution at 298 K. In the solid state, the emission of the complexes containing fluoroaryls (**3**, **9d**, **10c**, **11**, and **12**) is visible by the naked eye under an UV–vis chromatography lamp at 298 K. The emission range goes from 405 to 550 nm (449–550 nm for gold derivatives) at 298 K, and from 410 to 572 nm (450–572 nm for gold derivatives) at 77 K. The low-temperature emission spectra are more intense and slightly blue- (for **3**, **9d**, and **11**) or red-shifted (for **1**, **2**, and **5**), while the excitation spectra are similar with some small blue (for **4** and **9d**) or red (for **1**) shifts. In CH_2Cl_2 solution at 298 K, only the complexes containing fluoroaryl (**3**, **9d**, **10c**, **11**, and **12**) emit (at 426 and 450 nm), while all of the gold complexes are luminescent at 77 K in the range 424–515 nm.

When the excitation and emission spectra at 298 K for each compound (**1**, **3**, **9d**, **10c**, **11**, and **12**) are compared with those observed at any temperature in the solid state, the energies are very different. The excitation and emission spectra of the halo derivatives **2**, **4**, and **5** in solution at 77 K are also quite different from their corresponding solid-state spectra at any temperature, but curiously almost identical to those shown at 298 K by the complexes containing fluoroaryl. Finally, the excitation and emission spectra of the fluoroaryl derivatives **3**, **9d**, **10c**, **11**, and **12** undergo a red shift upon cooling to 77 K and become quite similar to the corresponding solid-state spectra at that temperature.

There are many reports on photoluminescent isocyanide gold(I) derivatives where the emission has been assigned to an intraligand-localized $\pi-\pi^*$ orbital with little Au contribution, as calculated for [AuClCNPh].[20] Other cases are assigned to a metal-to-ligand charge-transfer (MLCT) transition; for example, the complexes [AuX(CNCy)] (X = Cl, Br, I) show excitation maxima around 270 nm and emission maxima around 620 nm for any X, due to the formation of exciplexes, as occurs also for $[Au(CN)_2]^-$.[15] These are also plausible explanations for the solution spectra at 77 K of the halo derivatives **2**, **4**, and **5** and at 298 K for the fluoroaryl derivatives **3**, **9d**, **10c**, **11**, and **12**, which display high-energy excitation spectra and almost the same emission spectra. However, the solid-state emission spectra of the complexes containing fluoroaryls, which are also coincident with their

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(18) Coco, S.; Espinet, P.; Martín-Alvarez, J. M.; Levelut, A. M. *J. Mater. Chem.* **1997**, *7*, 19.

(19) (a) He, G. X.; Wada, F.; Kikukawa, K.; Shinkai, S.; Matsuda, T. *J. Org. Chem.* **1990**, *55*, 541. (b) Johansson, G.; Percec, V.; Ungar, G.; Abramic, D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 447. (c) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 9855. (d) Goodby, J. W.; Mehl, G. H.; Saez, I. M.; Tuffin, R. P.; Mackenzie, G.; Auzély-Velty, R.; Benvegnu, T.; Plusquellec, D. *Chem. Commun.* **1998**, 2057. (e) Schröter, J. A.; Tschierske, C.; Wittenberg, M.; Wendorff, J. H. *Angew. Chem., Int. Ed.* **1997**, *36*, 1119. (f) Leblanc, K.; Berdagué, P.; Rault, J.; Bayle, P. P.; Judeinstein, P. *Chem. Commun.* **2000**, 1291. (g) Schultz, A.; Laschat, S.; Saipa, A.; Gießelmann, F.; Nimtz, M.; Schulte, J. L.; Baro, A.; Miehlich, B. *Adv. Funct. Mater.* **2004**, *14*, 163. (h) Steinke, N.; Frey, W.; Baro, A.; Laschat, S.; Drees, C.; Nimtz, M.; Hägele, C.; Giesselmann, F. *Chem.—Eur. J.* **2005**, *12*, 1026.

(20) Gagnon, J.; Drouin, M.; Harvey, P. D. *Inorg. Chem.* **2001**, *40*, 6052.

Table 3. Excitation and Emission Data (in nm) in the Solid State and in CH_2Cl_2 Solution for the Isocyanide Ligand **1**, the Isocyanide Derivatives **2–5** and **9–12**, and the Carbene Derivatives **6–8**

	solid	298 K	solid	77 K	CH_2Cl_2	298 K	CH_2Cl_2	77 K
compd.	λ_{exc}	λ_{emis}	λ_{exc}	λ_{emis}	λ_{exc}	λ_{emis}	λ_{exc}	λ_{emis}
1	322	405	327sh, 342	410, 438sh	247,[a] 281	317	216, 235,[a] 249	311
2	324	436, 462,[a] 485	321	446, 474[a]			250–315	424, 445
3	354	520	357 (331)[b]	450sh, 516 (450sh, 497)[b]	250–320	427sh, 450	312sh, 356 (329)[b]	506 (429, 454sh, 483)[b]
4	352	449, 486	325	440sh, 460, 515sh			250–310	425, 447
5	360, 396, 412,[a] 435	550	356, 401, 411[a]	572			250–330	425, 447
6	362	518	357	511			357	515
7	334	454	320	445			296	434
8	336	460	322	445			296	434
9d	364, 380sh	511	353 (329)[b]	492 (431sh, 455, 485sh)[b]	260–305	426sh, 445	355 (329)[b]	497 (424, 449, 482)[b]
10c	342	457	345	450, 470	250–310	426, 445	344	425, 450sh, 481
11	293, 344[a]	495	294, 346[a] (294, 328)[b]	435sh, 486 (435sh, 467)[b]	250–310	411sh, 433	293, 388[a] (293, 363[a])[b]	511 (425sh, 498)[b]
12	289, 346[a]	491	293, 352[a] (295, 329)[b]	435sh, 488 (435sh, 464)[b]	250–305	410sh, 433	359 (380)[b]	423sh, 488 (513)[b]

[a] Most intense peak. [b] In parentheses: the second excitation or emission spectrum with less intensity.

low-temperature emission spectra, are different and suggest that the fragment C_6F_5 might be involved in some molecular transitions; besides that, a second less-intense spectral pattern can be observed for these complexes, showing that the MLCT transitions are still occurring in the solid state and at 77 K, although with much less intensity than the fluoroaryl related transitions. The coordination of $NaClO_4$ does not change significantly the spectra of the parent compounds, except for the trialkoxy derivative in the solid state. In summary, it seems that the spectra of the fluoroaryl derivatives contain several emissions (centered around 425, 450, 485, and 515 nm) related to different but close excitations, which can be tentatively assigned to MLCT (high-energy, less intensity) and LLCT (low-energy, more intensity) transitions. This explains why the emission maxima observed depend on the excitation frequency used in these spectra.

On the other hand, the photoluminescence observed for the halo derivatives **2**, **4**, and **5** in the solid state could be explained by association modes in the ground state due to the presence of Au···Au interactions (for instance, zigzag chains for **2**),[21] although the existence of different associations in the excited state (exciplexes) has also been proposed in related complexes.[13]

Finally, the N,N-carbene derivatives **7–8** emit in the solid state around 455 nm, while the N,O-carbene derivative **6** emits at 518 nm; lowering the temperature only produces a small blue shift. In solution, the carbene derivatives (which only emit at 77 K) display spectra close to those obtained in the solid state at 77 K. The luminescence of related N-heterocyclic carbene gold(I) complexes has been assigned to ligand-centered transitions.[22] In our case, the fact that the excitation and emission spectra are similar in solution and in the solid state, and there is a clear difference between the N,N- and the N,O-carbenes, strongly suggests that the luminescence should be mainly related to a ligand-centered transition, modified by the gold fragment.

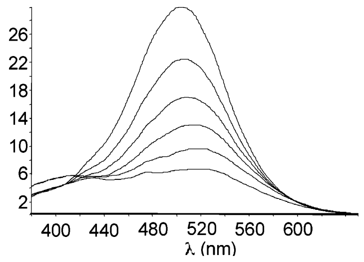

Figure 3. Emission spectrum of **9d** on heating at 25 (highest intensity), 35, 45, 55, 65, and 75 °C with $\lambda_{exc} = 360$ nm. Emission intensity in arbitrary units.

Complexes **9d** and **10c**, which display different thermal mesomorphic behavior, were chosen for variable-temperature monitoring of luminescence. The emission spectra of **9d** were recorded from 25 to 75 °C (heating at 10 °C/min; see Experimental Section), and a plot of the spectral variation with temperature is shown in Figure 3. The intensity decreases when the temperature increases, but the overall profile of the spectrum is maintained even beyond the clearing transition to the isotropic liquid state (at 54.9 °C). Around 75 °C, the emission has fully disappeared. Upon cooling, including the transition to the liquid crystalline state at 41.6 °C, the emission is recovered. Therefore the solid-state emission persists in the liquid crystalline and isotropic liquid states, although with less intensity.

The emission spectra of **10c** versus temperature (heating at 1 °C/min) similarly show a decrease of intensity upon heating, but in this case, the shape of the spectrum changes (Figure 4): a shoulder at *ca.* 510 nm becomes visible from the starting broad emission at high temperatures, as if it had been always there overlapped by the other more intense bands. Above 39 °C, the emission maximum appears red-shifted because the intensity of the shoulder has a higher contribution. At 43 °C, the emission is already centered at 510 nm (remember that the melting point is 31.4 °C, but it is quite ill-defined and solid, liquid crystal, and liquid

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(21) (a) Humphrey, S. M.; Mack, H. G.; Redshaw, C.; Elsegood, M. R. J.; Young, K. J. H.; Mayerb, H. A.; Kaska, W. C. *Dalton Trans.* **2005**, 439. (b) White-Morris, R. L.; Stender, M.; Tinti, D. S.; Balch, A. L.; Rios, D.; Attar, S. *Inorg. Chem.* **2003**, *42*, 3237.

(22) (a) Zhou, Y.; Chen, W. *Organometallics* **2007**, *26*, 2742. (b) Catalano, V. J.; Malwitz, M. A.; Etogo, A. O. *Inorg. Chem.* **2004**, *43*, 5714.

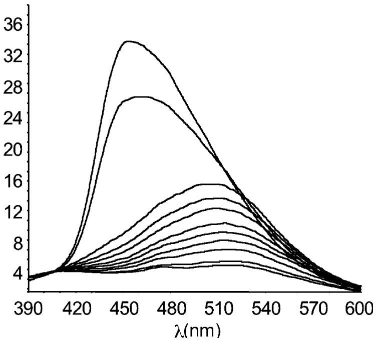

Figure 4. Emission spectrum of **10c** upon cooling from 70 to 30 °C (5 °C steps) with $\lambda_{exc} = 340$ nm (emission intensity in au). The last two more-intense spectra are at 25 °C (30 min and 1 h later).

apparently coexist up to 42 °C; Table 2), and around 70 °C, the emission disappears. Upon cooling from 70 to 30 °C (5 °C/min), the emission intensity is recovered and keeps centered at 510 nm due to hysteresis. About 30 min later, having reached the temperature of 25 °C, partial crystallization occurs (seen by POM) and the most intense emission at 450 nm is recovered. It seems reasonable to assign the intense emission at 450 nm to the solid state, while a second less-intense emission at 510 nm (displayed by the solid, liquid, and liquid crystal states) is the only one surviving in the isotropic liquid state.

Extraction Experiments. Measurements on the extraction ability of a sodium salt (picrate) from aqueous solutions were carried out for selected compounds. The extraction efficiency is low (ranging from 2 to 12%) and decreases in the order [AuCl(CNR)] > CNR > [Au(CNR)($C_6F_4OCH_2C_6H_4OC_8H_{17}$-*p*] > [Au($C_6F_5$)(CNR)]. The crown ether isocyanide ligand is not a good extractor, but its ability is similar to that found for crown ether imines under the same conditions (7% in 40 min). Coordination to the Au−Cl fragment increases slightly the extraction power, but the coordination to Au-fluoroaryl diminishes it. This effect is opposite that of the coordination of a crown ether imine to palladium, which improved dramatically the extraction efficiency (up to 86% in 12 min!).[10] Due to the poor extracting properties observed, no further extraction experiments were undertaken.

Conclusions

A crown ether functionalized isocyanide, CNR, proves to be an excellent ligand toward gold(I) and allows for the preparation of a variety of neutral [AuX(CNR)] derivatives. The X-ray diffraction structure of [AuCl(CNR)] shows the molecules associated by aurophilic interactions in tetranuclear units, which further organize in a zigzag chain through possible longer-distance interactions between the end gold atoms of these units, combined with weak nonclassical C−H···O bonds. Nucleophilic attack to the coordinated isocyanide by methanol or primary amines affords carbene derivatives. The complexes show photoluminescence in the solid state with emission maxima in the range 449–550 nm (450–572 nm at 77 K) and in CH_2Cl_2 solutions from 426 to 450 nm (424–515 nm at 77 K). These derivatives can further coordinate alkaline cations, as observed by changes in the NMR spectra, extraction experiments, and isolation of the sodium adducts. The fluoroaryl derivatives with alkoxy chains behave as liquid crystals with fairly low melting and clearing points and are luminescent in solution, in the solid, in the mesophase, and in the isotropic liquid at moderate temperatures.

Experimental Section

Emission and excitation spectra were measured at 298 and 77 K in the solid state as finely pulverized KBr mixtures, in deoxygenated CH_2Cl_2 solutions in quartz tubes, or in the mesophase by means of a remote fiber optic accessory (and the Mettler FP-82HT hot stage) with a Perkin-Elmer LS-55 spectrofluorometer. Other technical details were as previously reported.[10] 4-Aminobenzo-15-crown-5 (Aldrich) was used as received, and literature methods were used to prepare [AuX(tht)] (X = Cl,[23] C_6F_5),[24] [AuX($AsPh_3$)] (X = Br, I),[25] and $HC_6F_4OCH_2C_6H_4OC_nH_{2n+1}$-*p* and $HC_6F_4OCH_2C_6H_2$-3,4,5-$(OC_nH_{2n+1})_3$.[26] Only example procedures and IR and NMR data for $n = 8$ are described here, as the syntheses and the IR and NMR data were similar for the rest of the compounds. Yields and analytical data are given for all of the compounds. In the ^{19}F NMR spectra, F_o refers to ortho with respect to the Au substituent.

Synthesis of the Formamide R-NHCHO and the Isocyanide R-NC (1) (R = Benzo-15-crown-5). R-NHCHO and R-NC (**1**) were prepared by adapting the general method of Ugi et al.[27] Yield of R-NHCHO: 1.075 g (98%). Anal. Calcd (%): C, 57.87; H, 6.80; N, 4.50. Found: C, 57.89; H, 6.41; N, 4.55. ^1H NMR: 3.74 (s, 8H, O-CH_2-CH_2-O), 3.89 (m, 4H, Ph-O-CH_2-CH_2-O), 4.10 (m, 4H, Ph-O-CH_2-CH_2-O). Cis isomer (59%): 6.76 (d, *J*(HH) = 8.6 Hz, 1H, Ph), 6.87 (dd, *J*(HH) = 8.6 and 2.2 Hz, 1H, Ph), 7.29 (d, *J*(HH) = 2.2 Hz, 1H, Ph), 7.73 (brs, 1H, NH), 8.30 (d, *J*(HH) = 1.3 Hz, 1H, CHO). Trans isomer (41%): 6.59 (d, *J*(HH) = 2.2 Hz, 1H, Ph), 6.63 (dd, *J*(HH) = 8.5 and 2.2 Hz, 1H, Ph), 6.82 (d, *J*(HH) = 8.5 Hz, 1H, Ph), 7.90 (d, *J*(HH) = 11.2 Hz, 1H, NH), 8.51 (d, 1H, CHO). Yield of **1**: 1.236 g (87%). Anal. Calcd (%): C, 61.42; H, 6.53; N, 4.78. Found: C, 61.32; H, 6.31; N, 5.39. ^1H NMR: 3.75 (s, 8H, O-CH_2-CH_2-O), 3.90 (m, 4H, Ph-O-CH_2-CH_2-O), 4.11 (t, 4H, *J*(HH) = 4.4 Hz, Ph-O-CH_2-CH_2−O), 6.77 (d, *J*(HH) = 8.3 Hz, 1H, Ph), 6.84 (d, *J*(HH) = 2.2 Hz, 1H, Ph), 6.95 (dd, *J*(HH) = 8.3 and 2.2 Hz, 1H, Ph). IR (CH_2Cl_2): 2122 ν(C≡N) cm^{-1}.

[AuX(CNR)] (R = Benzo-15-crown-5; X = Cl (2), C_6F_5 (3), Br (4), I (5)). To a dichloromethane solution (20 mL) of [AuXL] (0.1 mmol; L = tht; X = Cl, 32 mg; C_6F_5, 45 mg; L = $AsPh_3$; X = Br, 58 mg; I, 70 mg)[28] was added the stoichiometric amount of the isocyanide **1** (29 mg, 0.1 mmol). The solution was stirred for about 1 h and concentrated to *ca.* 2 mL. The addition of diethyl ether (20 mL) afforded complexes **2**–**5** as white or yellow (**5**) solids, which were washed with diethyl ether (2 × 5 mL). Yield of **2**: 47 mg, 89%. Anal. Calcd (%): C, 38.37; H, 2.91; N, 2.13. Found: C, 38.18; H, 2.58; N, 1.75. ^1H NMR: 3.76 (s, 8H, O-CH_2-CH_2-O), 3.93 (m, 4H, Ph-O-CH_2-CH_2-O), 4.16 (m, 4H, Ph-O-CH_2-CH_2-O), 6.87 (d, *J*(HH) = 8.6 Hz, 1H, Ph), 6.97 (d, *J*(HH) = 2.2 Hz, 1H, Ph), 7.14 (dd, *J*(HH) = 8.6 and 2.4 Hz, 1H, Ph). IR (CH_2Cl_2): 2221 ν(C≡N) cm^{-1}. Yield of **3**: 41 mg, 63%. Anal. Calcd (%): C, 34,27; H, 3.64; N, 2.66. Found: C, 33.96; H, 3.26; N, 2.65.

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(23) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.
(24) Usón, R.; Laguna, A.; Vicente, J. *Chem. Commun.* **1976**, 353.
(25) McAuliff, C. A.; Parish, R. V.; Randal, P. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1730.
(26) Mitsunobu, O. *Synthesis* **1981**, *1*, 1.
(27) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.
(28) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748.

^{1}H NMR: 3.75 (s, 8H, O-CH_2-CH_2-O), 3.91 (m, 4H, Ph-O-CH$_2$-CH_2-O), 4.15 (m, 4H, Ph-O-CH_2-CH$_2$-O), 6.86 (d, J(HH) = 8.6 Hz, 1H, Ph), 7.0 (d, J(HH) = 2.4 Hz, 1H, Ph), 7.14 (dd, J(HH) = 8.4 and 2.4 Hz, 1H, Ph). ^{19}F NMR: −116.42 (m, 2F, F$_o$), −157.97 (m, 1F, F$_p$), −162.84 (m, 2F, F$_m$). IR (CH$_2$Cl$_2$): 2216 ν(C≡N) cm^{-1}. Yield of **4**: 42 mg, 74%. Anal. Calcd (%): C, 31.59; H, 3.35; N, 2.46. Found: C, 31.57; H, 3.11; N, 2.76. ^{1}H NMR: 3.76 (s, 8H, O-CH_2-CH_2-O), 3.93 (m, 4H, Ph-O-CH$_2$-CH_2-O), 4.16 (m, 4H, Ph-O-CH_2-CH$_2$-O), 6.86 (d, J(HH) = 8.8 Hz, 1H, Ph), 6.96 (d, J(HH) = 2.2 Hz, 1H, Ph), 7.14 (dd, J(HH) = 8.8 and 2.2 Hz, 1H, Ph). IR (CH$_2$Cl$_2$): 2229 ν(C≡N) cm^{-1}. Yield of **5**: 46 mg, 45%. Anal. Calcd (%): C, 29.19; H, 3.1; N, 2.27. Found: C, 29.32; H, 2.83; N, 2.12. ^{1}H NMR: 3.76 (s, 8H, O-CH_2-CH_2-O), 3.93 (m, 4H, Ph-O-CH$_2$-CH_2-O), 4.16 (m, 4H, Ph-O-CH_2-CH$_2$−O), 6.86 (d, J(HH) = 10.5 Hz, 1H, Ph), 6.96 (d, J(HH) = 2.6 Hz, 1H, Ph), 7.13 (dd, J(HH) = 10.5 and 2.6 Hz, 1H, Ph). IR (CH$_2$Cl$_2$): 2218 ν(C≡N) cm^{-1}.

[AuCl{C(NHR)(OMe)}] (6) (R = Benzo-15-crown-5). A methanol suspension (20 mL) of [AuCl(CNR)] (0.2 g, 0.38 mmol) in a Schlenk flask protected from light was refluxed for 24 h. The mixture was cooled, and the unreacted derivative was filtered. The clear solution was concentrated, diethyl ether added, and the mixture evaporated to dryness to afford derivative **6** as a brownish solid. Yield: 112 mg, 53%. Anal. Calcd (%): C, 34.45; H, 4.16; N, 2.51. Found: C, 34.68; H, 4.15; N, 2.42. ^{1}H NMR: 3.76 (s, 16H, O-CH_2-CH_2-O), 3.90 (s, 8H, Ph-O-CH$_2$-CH_2-O), 4.10 (s, 8H, Ph-O-CH_2-CH$_2$-O). There are two isomers at *ca.* 2.5:1 molar ratio. Isomer a: 4.24 (s, MeO), 6.74 (d, J(HH) = 8.5 Hz, Ph), 7.01 (dd, J(HH) = 8.5 and 2.4 Hz, Ph), 7.17 (d, J(HH) = 2.4 Hz, Ph), 10.58 (brs, NH-Ph). Isomer b: 4.26 (s, MeO), 6.78 (d, J(HH) = 8.6 Hz, Ph), 6.93 (d, J(HH) = 2.4 Hz, Ph), 7.17 (dd, J(HH) = 8.6 and 2.4 Hz, Ph), 10.53 (brs, NH-Ph).

[AuCl{C(NHMe)(NHR)}] (7) (R = Benzo-15-crown-5). To a dichloromethane solution (20 mL) of [AuCl(CNR)] (**2**; 0.256 g, 0.48 mmol) in a Schlenk flask was added NH$_2$Me (84 μL, 0.97 mmol). The solution was stirred protected from light until the infrared absorption of the isocyanide disappeared (around 30 min). Then, it was filtered through kiesselgur (some gold decomposition), concentrated, and precipitated by the addition of diethyl ether to give a derivative, **7**, as a white solid. Yield: 163 mg, 60%. Anal. Calcd (%): C, 34.51; H, 4.34; N, 5.03. Found: C, 34.52; H, 4.19; N, 5.04. ^{1}H NMR: 3.74–4.12 (m, 16H, CH_2-O), 6.65 (d, J(HH) = 8.5 Hz, 1H, Ph), 6.74 (dd, J(HH) = 8.5 and 1.9 Hz, 1H, Ph), 6.81 (d, J(HH) = 1.9 Hz, 1H, Ph), 9.02 (brs, 1H, NH-Ph). There are two isomers: 3.20 (s, MeN) and 7.99 (brs, NH-Me), 3.21 (s, MeN) and 8.00 (brs, NH-Me).

[AuCl{C(NH$_n$Bu)(NHR)}] (8) (R = Benzo-15-crown-5). The preparation of **8** was the same as for **7**, but with NH$_2$Bu in place of NH$_2$Me. Yield: 38 mg, 16%. Anal. Calcd (%): C, 38.11; H, 5.05; N, 4.68. Found: C, 37.76; H, 4.77; N, 4.79. ^{1}H NMR: 0.92 (t, J(HH) = 7.0 Hz, 3H, CH$_3$), 1.26–1.78 (m, 4H, CH$_2$-C), 3.75–4.11 (m, 18H, CH_2-O + CH_2-N), 6.55–6.91 (m, 3H, Ph), 8.59 (brs, 1H, NH-CH$_2$), 10.11 (brs, 1H, NH-Ph).

Table 4. Details of Crystal Data and Structure Refinement for Complex **2**

compound	**2**
empirical formula	$C_{15}H_{19}AuClNO_5$
fw	525.73
temp (K)	296(2)
wavelength (Å)	0.71073
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dim.: a (Å)	8.4334(15)
b (Å)	9.4916(16)
c (Å)	21.699(4)
α (deg)	84.300(3)
β (deg)	79.043(3)
γ (deg)	88.603(3)
vol. (Å^3)	1696.8(5)
Z	4
density (calcd) (Mg/m^3)	2.058
abs coeff (mm^{-1})	8.850
F(000)	1008
cryst habit	plate
cryst size (mm)	0.39 × 0.17 × 0.04
Θ range for data colln	0.96 to 23.30°
index ranges	$-9 \le h \le 7$, $-10 \le k \le 9$, $-24 \le l \le 23$
reflns collected	7956
ind. reflns	4878 [R(int) = 0.0393]
max. and min. trans.	1.0000 and 0.3439
data/restraints/params	4878/0/415
GOF on F^2	1.005
final R indices [$I > 2\sigma(I)$]	R1 = 0.0434, wR2 = 0.1185
R indices (all data)	R1 = 0.0531, wR2 = 0.1312
larg. diff. peak hole (e.Å^{-3})	1.307 and −2.297

[Au(C$_6$F$_4$OCH$_2$C$_6$H$_4$OC$_n$H$_{2n+1}$-p)(CNR)] (n = 4 (9a), 8 (9b), 10 (9c), 12 (9d)) and [Au(C$_6$F$_4$OCH$_2$C$_6$H$_2$-3,4,5-(OC$_n$H$_{2n+1}$)$_3$(CNR)] (n = 4 (10a), 8 (10b), 12 (10c); R = benzo-15-crown-5). A solution of nBuLi in hexane (0.214 mL, 0.342 mmol) was added to a solution of the corresponding tetrafluoro derivative (0.342 mmol; HC$_6$F$_4$OCH$_2$C$_6$H$_4$OC$_n$H$_{2n+1}$-p or HC$_6$F$_4$OCH$_2$C$_6$H$_2$-3,4,5-(OC$_n$H$_{2n+1}$)$_3$) in dried diethyl ether at −78 °C under nitrogen. After the reaction was stirred for 1 h at −50 °C, [AuCl(tht)] (0.1096 g; 0.342 mmol) was added at −78 °C, and the reaction mixture was slowly brought to room temperature. A drop of water was added, and the solution was filtered in the air through anhydrous MgSO$_4$ and kiesselgur. The isocyanide **1** (0.1003 g; 0.342 mmol) was added and the reaction stirred for 30 min. Then, the solution was evaporated to dryness and the residue recrystallized from ethanol at −18 °C to obtain derivatives **9**–**10** as white solids. Yield of **9a**: 81 mg, 29%. Anal. Calcd (%): C, 47.01; H, 4.19; N, 1.71. Found: C, 47.21; H, 3.83; N, 1.64. Yield of **9b**: 155 mg, 52%. Anal. Calcd (%): C, 49.49; H, 4.85; N, 1.60. Found: C, 49.41; H, 4.82; N, 1.53. Yield of **9c**: 116 mg, 18%. Anal. Calcd (%): C, 50.62; H, 5.14; N, 1.55. Found: C, 50.98; H, 5.14; N, 1.48. Yield of **9d**: 121 mg, 38%. Anal. Calcd (%): C, 51.67; H, 5.42; N, 1.51. Found: C, 51.54; H, 5.36; N, 1.42. Yield of **10a**: 154 mg, 47%. Anal. Calcd (%): C, 49.95; H, 5.24; N, 1.46. Found: C, 49.68; H, 5.20; N, 1.24. Yield of **10b**: 162 mg, 42%. Anal. Calcd (%): C, 55.27; H, 6.60; N, 1.24. Found: C, 55.39; H, 6.36; N, 1.30. Yield of **10c**: 53 mg, 12%. Anal. Calcd (%): C, 59.20; H, 7.61; N, 1.08. Found: C, 59.37; H, 7.62; N, 1.04. ^{1}H NMR of **9b**: 0.95–1.81 (m, 15H, CH_3-CH_2-C), 3.76 (m, 8H, O-CH_2-CH_2-O), 3.91–3.98 (m, 6H, Ph-O-CH$_2$-CH_2-O + C-CH$_2$-CH_2-O), 4.16 (m, 4H, Ph-O-CH_2-CH$_2$-O), 5.10 (s, 2H, Ph-CH_2-O-Ph), 6.86 (d, J(HH) = 8.5 Hz, 1H, Ph-crown), 6.87 (d, 2H, J(HH) = 8.6 Hz, Ph), 6.96 (d, J(HH) = 2.2 Hz, 1H, Ph-crown), 7.13 (dd, J(HH) = 8.5 and 2.2 Hz, 1H, Ph-crown), 7.34 (d, 2H, J(HH) = 8.6 Hz, Ph). ^{19}F NMR: −118.1 (m, N = 18.1 Hz, F$_o$), −156.4 (m, N = 18.1 Hz, F$_m$). IR (CH$_2$Cl$_2$): 2215 ν(C≡N) cm^{-1}. ^{1}H NMR of **10b**: 0.86–1.81 (m, 45H, CH_3-CH_2-C), 3.76 (s, 8H, O-CH_2-CH_2-O), 3.92–3.99 (m, 10H, Ph-O-CH$_2$-CH_2-O + C-CH$_2$-CH_2-O), 4.15 (m, 4H, Ph-O-CH_2-CH$_2$-O), 5.08 (s, 2H, Ph-CH_2-O-Ph), 6.64 (s, 2H, Ph), 6.87 (d, J(HH) = 8.8 Hz, 1H, Ph-crown), 6.97 (d, J(HH) = 2.2 Hz, 2H, Ph-crown), 7.14 (dd, 2H, J(HH) = 8.8 and 2.2 Hz, Ph-crown). ^{19}F NMR: −118.0 (m, N = 18.1 Hz, F$_o$), −156.4 (m, N = 18.1 Hz, F$_m$). IR (CH$_2$Cl$_2$): 2215 ν(C≡N) cm^{-1}.

General Procedure for Complexation with NaClO$_4$. Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive; however, in this case, the perchlorate anion is not bonded to Au and is not expected to be problematic.* To an acetonitrile (for derivative **9b**) or acetonitrile−dichloromethane solution (for complex **10b**) was added the stoichiometric amount of NaClO$_4$. The resulting clear solution was stirred for 10 min and then concentrated to dryness to give a brownish solid. Yield of **11**: 43 mg, 70%. Anal. Calcd (%): C, 43.41; H, 4.25; N, 1.41. Found: C, 43.55; H, 4.13; N, 1.51. ^{1}H NMR: 0.95–1.81 (m, 15H, CH_3-CH_2-C), 3.75–3.80 (m, 8H, O-CH_2-CH_2-O), 3.91–3.98 (m, 6H, Ph-O-CH_2-CH_2-O + C-CH_2-CH_2-O), 4.27 (m, 4H, Ph-O-CH_2-CH_2-O), 5.10 (s, 2H, Ph-CH_2-O-Ph), 6.86 (d, J(HH) = 8.5 Hz, 1H, Ph-crown), 6.97 (d, 2H, J(HH) = 8.6 Hz, Ph), 7.08 (d, J(HH) = 2.2 Hz, 1H, Ph-crown), 7.18 (dd, J(HH) = 8.5 and 2.2 Hz, 1H, Ph-crown), 7.34 (d, 2H, J(HH) = 8.6 Hz, Ph). ^{19}F NMR: −117.8 (m, N = 18.1 Hz, F_o), −156.4 (m, N = 18.1 Hz, F_m). IR (CH_2Cl_2): 2215 $\nu(C\equiv N)$ cm^{-1}. IR (Nujol): 2213 $\nu(C\equiv N)$, 1080, 623 $\nu(ClO_4^-)$ cm^{-1}. Yield of **12**: 68 mg, 67%. Anal. Calcd (%): C, 49.86; H, 5.95; N, 1.12. Found: C, 50.40; H, 5.52; N, 0.77. ^{1}H NMR: 0.86–1.81 (m, 45H, CH_3-CH_2-C), 3.74–3.79 (m, 8H, O-CH_2-CH_2-O), 3.94–3.99 (m, 10H, Ph-O-CH_2-CH_2-O + C-CH_2-CH_2−O), 4.27 (m, 4H, Ph-O-CH_2-CH_2-O), 5.07 (s, 2H, Ph-CH_2-O-Ph), 6.64 (s, 2H, Ph), 6.98 (d, J(HH) = 8.8 Hz, 1H, Ph-crown), 7.10 (d, J(HH) = 2.2 Hz, 2H, Ph-crown), 7.20 (dd, 2H, J(HH) = 8.8 and 2.2 Hz, Ph-crown). ^{19}F NMR: −117.7 (m, N = 18.1 Hz, F_o), −156.4 (m, N = 18.1 Hz, F_m). IR (CH_2Cl_2): 2215 $\nu(C\equiv N)$ cm^{-1}. IR (Nujol): 2213 $\nu(C\equiv N)$, 1080, 623 $\nu(ClO_4^-)$ cm^{-1}.

Crystal Structure Determination of 2. The crystal was mounted on a glass fiber and transferred to the Bruker SMART CCD diffractometer. Crystal data and details of data collection and structure refinement are given in Table 4. Cell parameters were retrieved using SMART[29] software and refined with SAINT[30] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were based on multiple scans (program SADABS).[31] The structure was refined anisotropically on F^2.[32] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions.

Extraction Experiments. To a dichloromethane solution (10 mL) of the extracting gold compound (5×10^{-4} M) was added an aqueous solution of sodium picrate (10 mL, 5×10^{-5} M) prepared in situ by mixing solutions of picric acid and sodium hydroxide. The mixture was vigorously stirred, and samples were taken every 5 min to monitor the diminution of sodium picrate concentration in the aqueous phase by UV–vis spectroscopy (λ = 356 nm), until successive determinations showed no variation. This was taken as indication that equilibrium had been reached.

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Supporting Information Available: A Crystallographic Information File, containing structural data for **2**, is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) *SMART V5.051, software for the CCD Detector System*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

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

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

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