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Syntheses and Mesomorphic Properties of Gold(I)−Carbene Complexes

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The liquid-crystalline gold(I)−carbene complexes $ClAu{=}C(YC_mH_{2m+1})(NHC_6H_4CO_2C_6H_4\text{-}OC_nH_{2n+1})$, Y = O and NH, have been prepared by reactions of gold(I)−isonitrile complexes $[ClAu\{CNC_6H_4CO_2C_6H_4OC_nH_{2n+1}\}]$ with alcohols and amines, respectively. The gold(I)−(alkoxy)(amino)carbene complexes show stable enantiotropic smectic A phases over the range of around 15 °C. The partial double-bond character of the C−N bond in the carbene complex gives rise to two geometrical isomers (*E*:*Z* = *ca.* 3:1). Their molecular structures were spectroscopically characterized, and the *E*-isomer was confirmed by an X-ray structural analysis. The phase behaviors of *E*- and *Z*-isomers which were isolated by repeated recrystallization from $CHCl_3/Et_2O$ or CH_2Cl_2/C_6H_{14} were examined. In the gold(I)−diaminocarbene complexes, a novel dinuclear gold−carbene complex, $[ClAu\{C(NHC_6H_4\text{-}CO_2C_6H_4OC_nH_{2n+1})\}](NCH_3C_mH_{2m}NCH_3)[ClAu\{C(NHC_6H_4CO_2C_6H_4OC_nH_{2n+1})\}]$, was synthesized by the reaction with a secondary diamine. This dinuclear complex generated a smectic mesophase although it decomposed at temperatures below its clearing temperature.

Introduction

Transition metal−carbene complexes have attracted much attention as useful reagents, as effective catalysts, and as molecules displaying unique bonding. Their chemistry has been widely developed for application in the fields of both catalytic reactions and stoichiometric organic synthesis over the last three decades.[1] However, little attention has been paid to the carbene complexes from the viewpoint of material science, though the complexes have expectantly novel physical properties based on the direct metal−carbon double bond.

In contrast, liquid crystals incorporating transition metals, so-called metallomesogens, have attracted much more interest due to the perceived advantages of combining the properties of liquid-crystal systems with those of transition metals. A large number of studies on metallomesogens have been performed in the last 20 years, and the area has been well reviewed recently.[2] Organometallic liquid crystals which contain a direct metal−carbon bond have received much less attention, and their study has been limited due to their thermal and chemical instability. In an attempt to remedy this, we had previously developed liquid-crystalline platinum−alkynyls stabilized by trialkylphosphine ligands[3] and new families of organometallic liquid crystals including isonitrile complexes of platinum[4] and gold.[5] In contrast to platinum−isonitrile complexes which display stable mesomorphic properties over a high and wide temperature range without any decomposition, most gold−isonitrile complexes have suffered from considerable decomposition due to high phase-transition temperatures caused by strong intermolecular interactions.[6]

In our preliminary report,[7] an effort was made to decrease the transition temperatures of the gold−isonitrile complexes by synthesizing liquid-crystalline transition metal−carbene complexes by the nucleophilic addition of alcohols to gold−isonitrile complexes (see Scheme 1). The gold−carbenes exhibited exclusively smectic phases with lower clearing temperatures than the corresponding gold−isonitrile complexes due to the introduction of lateral alkyl chains which weaken intermolecular interaction. We now report the detailed synthesis, complete characterization, and mesomorphic properties of gold(I)−(alkoxy)(amino)carbene complexes. This paper also reports the preparation of gold(I)−diaminocarbene complexes by the nucleophilic reaction of gold(I)−isonitrile complexes with amines. Addition-

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(6) (a) Adams, H.; Albeniz, A. C.; Bailey, N. A.; Bruce, D. W.; Cherodian, A. S.; Dhillon, R.; Dummur, D. A.; Espinet, P.; Feijoo, J. L.; Lalimde, E.; Maitlis, P. M.; Richardson, P. M.; Urgan, G. *J. Mater. Chem.* **1991**, *1*, 843. (b) Bruce, D. W.; Lalimde, E.; Styring, P.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 581. (c) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319. (d) Irwin, M. J.; Jia, G.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 51.

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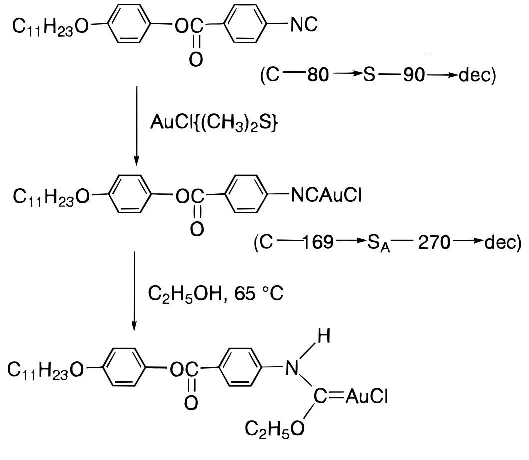
Scheme 1

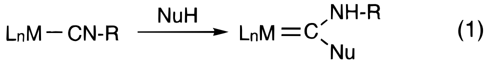


1e (C←146→S$_A$←160→I)

ally, we attempted to synthesize a variety of liquid-crystalline gold−carbene complexes by the following approaches: (1) using branched alcohols instead of linear alcohols as a nucleophile; (2) synthesizing a carbene complex containing an amino ligand with three aromatic rings; (3) replacing the chlorine attached to gold with sterically large iodine by a halogen exchange reaction; (4) preparing a dinuclear gold−carbene complex by reaction with a diamine.

Results and Discussion

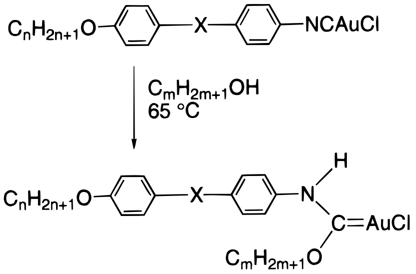
Synthesis and Characterization. Examples of thermally stable transition metal−carbene complexes are platinum− and gold−carbene complexes, which can be prepared from acetylide and isonitrile complexes by the attack of appropriate nucleophiles at the positively charged α-carbon atom of MC≡CR and MC≡NR.[8] As we have a variety of samples of liquid-crystalline platinum− and gold−isonitrile complexes in our laboratory, we tried to convert them to liquid-crystalline carbene complexes by the reaction with nucleophiles (eq 1). Treatment of bis(isonitrile)platinum(II) complexes with amine nucleophiles gave bis(diaminocarbene)platinum(II) complexes, which have not yet been found to exhibit mesomorphic properties.[9]



$$L_nM-CN\text{-}R \xrightarrow{NuH} L_nM=C\begin{matrix}NH\text{-}R\\ Nu\end{matrix} \qquad (1)$$

Our previous work showed that the rodlike structure of gold(I)−isonitrile complexes with a two-coordination geometry is quite suitable for the formation of liquid crystals and even a rather large lateral group does not disturb the mesophase stability but leads to a favorable lowering of the transition temperatures.[5] On the basis of this finding, we transformed gold−isonitrile complexes to carbene complexes by the nucleophilic addition reactions with alcohols and amines.[10] For example, a gold−isonitrile complex (Scheme 1, n = 11, m = 2) was suspended in ethanol and stirred at 65 °C under nitrogen for 12 h, to give carbene complex **1e** (n = 11, m = 2) as white crystals in 70−80% yield after recrystallization from CH_2Cl_2/hexane. Several gold(I)−diaminocarbene complexes were similarly prepared by adding secondary and primary amines to CH_2Cl_2 or benzene suspensions of the gold−isonitrile complexes at room temperature. The products thus obtained are numbered as shown in Schemes 2 and 3. Gold(I)−(alkoxy)(amino)carbene complexes containing three aromatic rings and branched alkoxy groups were prepared similarly. The yields of the products and the results of elemental analyses are summarized in Table 5 (see Experimental Section).

Scheme 2



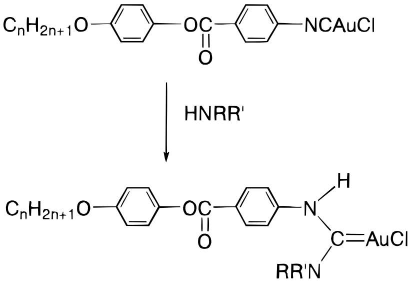
1: X = −OC(=O)− ; n = 9~12; m = 2~5.

2: X = −C(=O)O− ; n = 10~12; m = 2, 3.

3: X = −C≡C− ; n = 8~10; m = 2, 3.

4: X = −CH$_2$CH$_2$− ; n = 8; m = 2.

Scheme 3



8: R = Me, Et; R' = n-Bu, Et.

9: R = H; R' = n-Bu, n-Pr, Et.

All the gold−carbene complexes were identified by elemental and spectral analyses including IR and NMR spectra. For example, the infrared spectrum of **1e** showed the disappearance of the C≡N band at 2240 cm^{-1} for the corresponding isonitrile complex and the appearance of two new bands at 3230 and 1550 cm^{-1} attributable to ν(NH) and ν(C=N), respectively. The ^{13}C NMR spectrum displays a carbene carbon at δ 208 ppm, indicating that **1e** is a gold−(alkoxy)(amino)carbene complex.

The detailed spectral analyses for **1** suggests the existence of two geometrical isomers (*ca.* 3:1 ratio) due

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[8] (a) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 1711. (b) Badley, E. M.; Chatt, J.; Richards, R. L.; Sim, G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 1322. (c) Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1970**, *24*, 251; *25*, 255. (d) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069. (e) Parks, J. E.; Balch, A. L. *J. Organomet. Chem.* **1974**, *71*, 453. (f) Banditelli, G.; Bonati, F.; Calogero, S.; Valle, G. *J. Organomet. Chem.* **1984**, *275*, 153.

[9] Zhang, S.-W.; Kaharu, T.; Pirio, N.; Ishii, R.; Uno, M.; Takahashi, S. *J. Organomet. Chem.* **1995**, *489*, C62.

[10] Bonati, F.; Minghetti, G. *Syn. Inorg. Met.-Org. Chem.* **1971**, *1*, 299.

[11] Bonati, F.; Minghetti, G. *J. Organomet. Chem.* **1973**, *59*, 403.

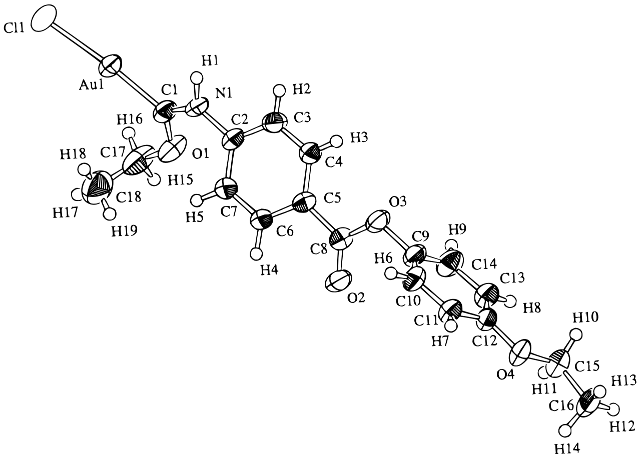
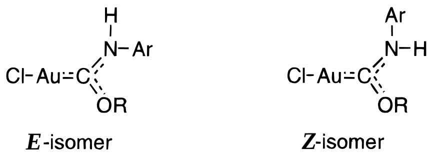


Figure 1. Crystal structure of (*E*)-ClAu{C(OC_2H_5)(NHC_6H_4-$CO_2C_6H_4OC_2H_5$)}. Selected bond distances (Å) and angles (deg) are as follows: Au(1)−C(1) = 1.985(7), Au(1)−Cl(1) = 2.277(2), C(1)−N(1) = 1.325(9), C(1)−O(1) = 1.317(8); C(1)−Au(1)−Cl(1) = 176.2(2), H(1)−N(1)−C(1) = 117.9, O(1)−C(1)−N(1) = 113.0(6).

to the partial double-bond character of the C−N bond which was observed in the infrared spectra.[12] For example, **1e** shows two bands at 1730 and 1710 cm^{-1} assigned to the ester C═O. In addition, ^1H NMR spectrum shows two sets of signals due to the amide proton and the protons on the neighboring aromatic ring which allows the isomer ratio to be estimated by analysis of the ^1H NMR spectrum. The geometrical isomers exist as a thermodynamic mixture in a solution, and one of the isomers is a little more stable. The isomers of **1** can be separated from each other by fractional crystallization from $CHCl_3/Et_2O$[12] or CH_2Cl_2/C_6H_{14} because one of them is less soluble than the other. Complete separation of the isomers was successful with the complexes which have short alkoxy groups. However, for the complexes having rather long alkoxy groups could not be separated as they have almost the same solubility. The pure *E*- and *Z*-isomers are stable in the solid state, but they both isomerize even at room temperature in a chloroform solution to give an equilibrium mixture of *E*- and *Z*-forms.



To distinguish the *E*-isomer from the *Z*-isomer by spectral methods, we have synthesized a gold(I)−(alkoxy)(amino)carbene complex, ClAu{C(OC_2H_5)($NHC_6H_4CO_2C_6H_4OC_2H_5$)}, as a model complex for **1**. The single-crystal X-ray structural determination of the less soluble isomer revealed that the complex exhibits an *E*-form around the C−N bond and thus an extended linear structure with an alkoxy lateral group. The molecular structure and the atom-labeling scheme of (*E*)-ClAu{C(OC_2H_5)($NHC_6H_4CO_2C_6H_4OC_2H_5$)} are presented in Figure 1. The Au---$C_{carbene}$ distance of 1.985(7) Å is similar to those reported for ClAu{C(OC_2H_5)($NHC_6H_4CH_3$-p)} (1.983(3) Å)[12a] and cationic Au{C(OC_2H_5)($NHC_6H_4CH_3$-*p*)}$_2^+$ (2.02(2) Å).[12b] The C(1)−Au(1)−Cl(1) angle is 176.2(2)°, showing a linear dicoordinate structure of gold(I), and the two planes of the aromatic rings are almost perpendicular to each other. It has been reported that only weak intermolecular interaction can be expected when the Au---Au distance of is over the range 2.75−3.40 Å.[5,6c] Since the shortest intermolecular Au---Au distance present is >4 Å, it is inferred that there are no Au---Au interactions. This may account for the large reduction in the clearing temperature. By utilization of the IR and ^1H NMR spectral data, the *E*- and *Z*-isomers of all the gold(I)−carbene complexes can be clearly distinguished, and the mesomorphic properties are attributed to the isolated isomers.

Thermal Behavior of Gold(I)−Carbene Complexes. The carbene complexes obtained above exhibit mesomorphic properties. For example, crystals of **1e** melt at 146 °C to form a smectic A (S_A) phase, which transforms to an isotropic phase at 160 °C with slight decomposition. The mesophases were identified on the basis of optical textures, and cooling **1e** from an isotropic phase shows a focal conic texture after the initial appearance of bâtonnets.

The phase behaviors of each isomer of **1b**,**e**,**f** and an isomeric mixture of **1** are summarized in Table 1. The gold(I)−(alkoxy)(amino)carbene complexes prepared in the present work exhibit a stable S_A phase, and those having a lateral alkoxy group with less than four carbon atoms exhibit an enantiotropic transition with slight decomposition at the clearing point. To our surprise, in spite of having a large lateral group, **1h** was found to be mesomorphic although the transition is monotropic. In contrast to gold−isonitrile complexes, a favorable decrease of transition temperatures is attained for the carbene complexes, in which the lateral group probably improves the mesophase stability by interrupting the strong intermolecular interactions between two-coordinate gold(I) molecules. Comparison between the *E*-isomer and *Z*-isomer showed no obvious differences of phase behavior and transition temperatures except for the initial melting points. This is reasonable because the transition from a crystalline phase of either pure *E*- or *Z*-isomer to an S_A phase could result in isomerization to a thermodynamic mixture of the two isomers. In fact, the isomerization between the *E*- and *Z*-isomers has been confirmed to proceed not only in solutions but also in the melt. The crystals obtained by rapidly cooling the melted *E*- and *Z*-isomers of **1b** after heating to 150 and 155 °C, respectively, consist of a mixture of *E*- and *Z*-isomers with different ratios. The solids obtained from the isotropic liquids were confirmed to comprise two isomers with an *E*/*Z* molar ratio of *ca.* 3:1 (Table 2), which is the same as the equilibrium ratio observed in a chloroform solution. The fact that the two pure isomers have different melting points and the same clearing temperatures is consistent with the above observation.

In order to extend the range of liquid-crystallinity of the gold−carbene complexes, we replaced the −COO− joint combining the two aromatic rings of the isonitrile ligands by −OCO−, −C≡C−, and $-CH_2CH_2-$ groups. The results are summarized in Table 3. All of the gold−carbene complexes **2** having a −OCO− joint showed

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[12] (a) Banditelli, G.; Bonati, F.; Calogero, S.; Valle, G.; Wagner, F. E.; Wordel, R. *Organometallics* **1986**, *5*, 1346. (b) Minghetti, G.; Baratto, L.; Bonati, F. *J. Organomet. Chem.* **1975**, *102*, 397.

Table 1. Phase Transition Temperatures (°C) for Complex 1

Complex	n	m	isomeric mixture[a]	*E*-form	*Z*-form
1a	9	2	$C \xrightarrow{113} I$		
1b	10	2	$C \xleftrightarrow{150} S_A \xleftrightarrow{158} I^b$	$C \xleftrightarrow{143} S_A \xleftrightarrow{158} I^b$	$C \xleftrightarrow{152} S_A \xleftrightarrow{158} I^b$
1c	10	3	$C \xrightarrow{134} I$ $S^c \xleftarrow{118}$		
1d	10	4	$C \xrightarrow{120} I$ $S^c \xleftarrow{91}$		
1e	11	2	$C \xleftrightarrow{146} S_A \xleftrightarrow{160} I^b$	$C \xleftrightarrow{142} S_A \xleftrightarrow{160} I^b$	$C \xleftrightarrow{149} S_A \xleftrightarrow{160} I^b$
1f	11	3	$C \xleftrightarrow{114} S_A \xleftrightarrow{129} I^b$	$C \xleftrightarrow{116} S_A \xleftrightarrow{128} I$	$C \xleftrightarrow{126} S_A \xleftrightarrow{128} I^b$
1g	11	4	$C \xrightarrow{113} I$ $S^c \xleftarrow{96}$		
1h	11	5	$C \xrightarrow{113} I$ $S^c \xleftarrow{77}$		
1j	12	2	$C \xleftrightarrow{151} S_A \xleftrightarrow{166} I$		
1k	12	3	$C \xleftrightarrow{121} S_A \xleftrightarrow{137} I^b$		
1m	12	4	$C \xrightarrow{125} I$ $S^c \xleftarrow{104}$		

Table 2. *E*/*Z* Ratios of 1b (*n* = 10, *m* = 2) Isomeration at Melted States[a]

	solid	150 °C	155 °C	165 °C
E-isomer	1/0	2.4/1	3.6/1	3.4/1
Z-isomer	0/1	1/1	2.9/1	2.3/1

[a] Determined by means of ^{1}H NMR data after rapidly cooling the samples at the temperature.

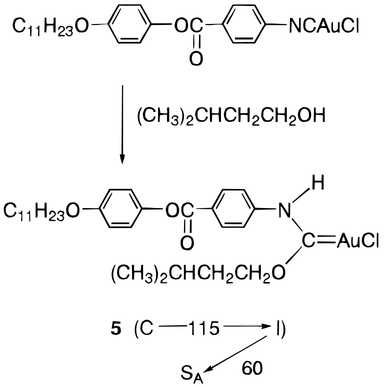
Table 3. Phase Transition Temperatures (°C) for Complexes 2−4

Complex	n	m	Transition Temperature (°C)
2b	10	2	$C \xrightarrow{128} I$ $S_A \xleftarrow{102}$
2c	10	3	$C \xrightarrow{125} I$ $S^b \xleftarrow{109}$
2m	12	4	$C \xrightarrow{93} I$ $S^b \xleftarrow{67}$
3b	10	2	$C \xrightarrow{158} I^a$
3c	10	3	$C \xrightarrow{141} I$
3p	8	2	$C \xrightarrow{178} I$ $S_A \xleftarrow{125}$
3q	8	3	$C \xrightarrow{162} I$ $S^b \xleftarrow{132}$
4	8	2	$C \xrightarrow{125} I$

[a] With some decomposition. [b] Unidentified phases.

mesogenic properties but with only generated monotropic character. Comparison between **1b** and **2b** (*n* = 10, *m* = 2), both of which are regioisomers, reveals that **1b** formed a stable S_A phase while **2b** gave a monotropic S_A phase with a lower melting temperature. The carbene complexes **3p** (*n* = 8, *m* = 2) and **3q** (*n* = 8, *m* = 3) having a −C≡C− joint group showed mesomorphic properties, while the remaining two complexes, **3b**,**c**, did not. Replacement by a $-CH_2CH_2-$ joint group resulted in loss of mesomorphic properties as seen in complex **4**.

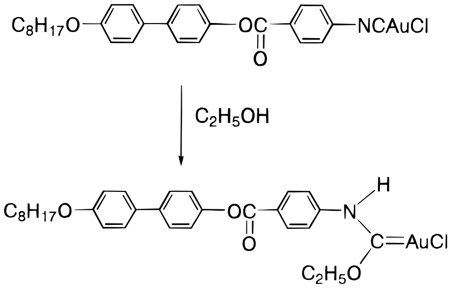
Scheme 4



Second, instead of a linear alcohol, we employed a branched alcohol in the preparation of the carbene complexes. Complex **5** prepared with 3-methylbutanol showed a monotropic S phase (Scheme 4). However, in the cases of 2-propanol and 1-methylpropanol, no mesophases were observed. Carbene complex **6** contains three aromatic rings and showed an smectic phase, but it decomposed before the transition to the isotropic phase. This result is probably due to the high transition temperature (Scheme 5). The carbene complexes with three aromatic rings obtained from other alcohols or amines did not show improved mesomorphic characteristics.

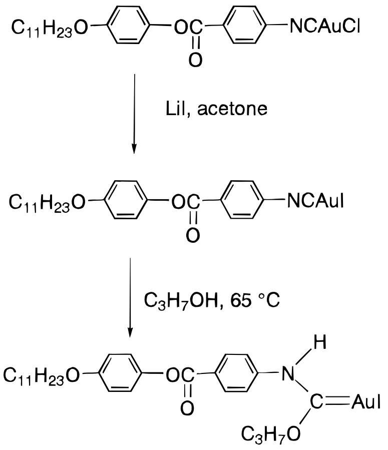
We prepared an iodogold−carbene complex by a halogen exchange reaction. Because direct exchange reaction with the chlorogold−carbene complexes failed to produce pure iodide derivatives, an alternative synthetic route was taken as shown in Scheme 6. An iodogold−isonitrile complex was first prepared by treatment of a chloro analog with LiI in acetone[13] and then transformed to an iodogold−carbene complex by reac-

Scheme 5



6 a: *Z*-isomer C—186→S (decomp.)
b: *E*-isomer C—194→S (decomp.)

Scheme 6



7 (C—131→S_A (decomp.))

Table 4. Phase Transition Temperatures (°C) for Complexes 8 and 9

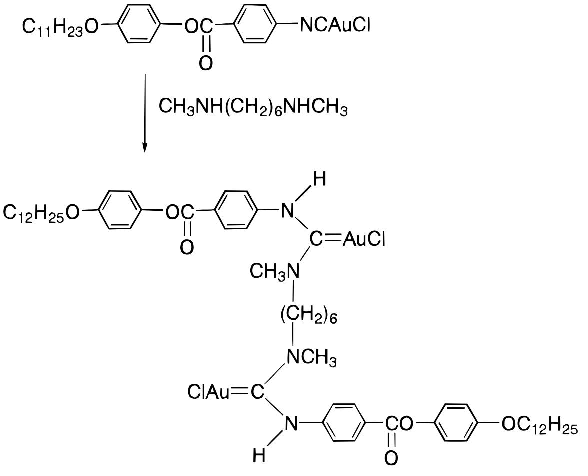
Complex	n	R	R'	Transition Temperature (°C)
8a	9	Me	n-Bu	C $\xrightarrow{175}$ I[a]
8b	10	Et	Et	C $\xrightarrow{133}$ decomposition
8c	12	Me	n-Bu	C $\xrightarrow{176}$ I[a]
9a	10	H	n-Pr	C $\xrightarrow{113}$ S_A → decomposition
9b	12	H	n-Pr	C $\xrightarrow{137}$ S_A → decomposition
9c	12	H	n-Bu	C $\xrightarrow{133}$ S_A → decomposition

[a] With some decomposition.

tion with an alcohol nucleophile. The resulting complex **7** shows a higher melting point than the corresponding chloro derivative **1f** and decomposes before reaching the isotropic temperature.

Finally, we prepared gold(I)−diaminocarbene complexes **8** and **9** (Scheme 3), some of which exhibit mesomorphic behavior. Their phase transition temperatures are summarized in Table 4. Complexes **8** were prepared from secondary amines and did not show any mesomorphic properties. In contrast complexes **9**, prepared from primary amines, formed S_A phases although they gradually decompose in the S_A phases.

Scheme 7



10 (C—211→S (decomp.))

The absence of mesomorphic properties for complexes **8** may be attributed to bulky dialkyl lateral groups which are unsuitable for the formation of mesophases. An illustration is the fact that **9c** having a lateral butylamino group showed a monotropic S_A phase while **8c** which bears both methyl and butyl substitutes on the amino group did not exhibit mesomorphic properties. It is noteworthy that a dinuclear gold−carbene complex **10**, prepared from *N*,*N'*-dimethyl-1,6-diaminohexane, formed a smectic mesophase although it decomposed before transition to an isotropic phase (Scheme 7). Efforts to extend the liquid-crystalline behavior of carbene complexes to other transition metals is in progress.

Conclusions

This report provides the first detailed report of liquid-crystalline metal−carbene complexes. Both gold(I)−(alkoxy)(amino)carbene complexes and gold(I)−diaminocarbene complexes show mesogenic behaviors, and in particular, the former display enantiotropic S_A phases with lower clearing temperatures than the corresponding gold−isonitrile complexes. The structure of a model complex has been determined by X-ray crystallography, which suggests that the introduction of lateral alkyl groups weakens intermolecular interactions. Two kinds of geometric isomers, *E* and *Z*, exist for the gold(I)−carbene complexes, which can be separated by fractional recrystallization. The *E*-isomers show the almost same thermal behavior as the *Z*-isomers with the exception of their melting points. This effect is due to isomerization which occurs during heating to afford an equilibrium mixture of *E*- and *Z*-isomers with a 3:1 molar ratio. A dinuclear gold−carbene complex can be prepared by using a diamine nucleophile. However, these new carbene complexes decompose in the mesophases before reaching their clearing point due to their high transition temperatures.

Experimental Section

Gold−isonitrile complexes were prepared by the known methods.[5] Elemental microanalyses were performed by the Material Analysis Center, ISIR, Osaka University (Table 5). IR spectra were obtained with a Perkin-Elmer 2000 FT-IR system. ^1H NMR spectra were recorded on a Brucker WM-

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(13) Benouazzane, M.; CoCo, S.; Espinet, P.; Martin-Alvarez, J. *J. Mater. Chem.* **1995**, *5*, 441.

Table 5. Yields and Elemental Analyses of Gold(I)−Carbene Complexes 1−10

com-plex	yield (%)	anal. (%): found (calcd)			
		C	H	N	Cl(I)
1a	75	46.81 (46.63)	5.22 (5.17)	2.20 (2.18)	5.33 (5.51)
1b	76	47.15 (47.46)	5.26 (5.36)	2.05 (2.13)	5.34 (5.39)
1c	78	48.41 (48.26)	5.62 (5.55)	2.01 (2.08)	5.10 (5.28)
1d	74	49.20 (49.02)	5.67 (5.73)	2.01 (2.04)	5.28 (5.17)
1e	87	48.18 (48.26)	5.30 (5.52)	2.28 (2.08)	5.01 (5.28)
1f	76	49.03 (49.02)	5.70 (5.73)	1.97 (2.04)	5.12 (5.17)
1g	83	49.57 (49.76)	5.75 (5.90)	1.97 (2.00)	5.05 (5.06)
1h	75	50.40 (50.46)	6.00 (6.07)	1.84 (1.96)	5.01 (4.96)
1j	87	48.73 (49.02)	5.69 (5.73)	1.95 (2.04)	5.30 (5.17)
1k	59	49.93 (49.76)	5.79 (5.90)	1.93 (2.00)	5.15 (5.06)
1m	47	50.64 (50.46)	5.97 (6.07)	1.81 (1.96)	4.75 (4.96)
2b	93	47.26 (47.46)	5.21 (5.36)	2.03 (2.13)	5.30 (5.39)
2c	85	48.43 (48.26)	5.48 (5.52)	2.03 (2.08)	5.18 (5.28)
2m	40	50.25 (50.46)	6.05 (6.07)	1.89 (1.96)	4.74 (4.96)
3b	90	50.64 (50.83)	5.30 (5.53)	2.11 (2.20)	5.78 (5.56)
3c	85	51.30 (51.58)	5.51 (5.72)	2.14 (2.15)	5.32 (5.44)
3p	68	48.96 (49.23)	4.90 (5.12)	2.43 (2.30)	5.65 (5.81)
3q	69	49.95 (50.05)	5.11 (5.33)	2.18 (2.24)	5.65 (5.68)
4	81	48.62 (48.91)	5.50 (5.75)	2.09 (2.28)	5.88 (5.77)
5	90	50.68 (50.46)	6.01 (6.07)	1.85 (1.96)	4.69 (4.96)
6a	26	50.97 (51.04)	4.85 (5.00)	1.91 (1.98)	5.28 (5.02)
6b	42	51.21 (51.04)	4.91 (5.00)	1.87 (1.98)	5.26 (5.02)
7	82	43.28 (43.26)	4.94 (5.06)	1.59 (1.80)	16.55 (16.32)
8a	90	48.91 (49.09)	5.71 (5.89)	4.30 (4.09)	5.27 (5.18)
8b	93	49.15 (49.09)	5.76 (5.89)	3.93 (4.09)	5.00 (5.18)
8c	73	51.00 (51.21)	6.31 (6.38)	3.62 (3.85)	4.66 (4.88)
9a	47	48.54(48.33)	5.56 (5.71)	3.98 (4.17)	5.35 (5.28)
9b	41	50.04 (49.83)	5.99 (6.06)	3.93 (4.01)	5.03 (5.07)
9c	59	50.30 (50.53)	6.12 (6.22)	3.85 (3.93)	5.13 (4.97)
10	82	50.71 (50.60)	6.08 (6.09)	3.80 (3.93)	4.99 (4.98)

360 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. The textures of liquid crystals were observed using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP 52 hot-stage and FP 5 control unit, and phase transition temperatures were also determined using a Shimazu DSC-50 differential scanning calorimeter. Representative preparation procedures and physical data for gold−carbene complexes are given below.

Chloro[(ethoxy){4-((4′-(*n*-decyloxy)phenyl)carbonyl)phenyl)amino}carbene]gold (1b). A solution of chloro[4-((4′-(*n*-decyloxy)phenyl)carbonyl)phenyl isonitrile]gold (207 mg, 0.34 mmol) in ethanol (15 mL) was stirred at 65 °C under nitrogen atmosphere for 12 h. The solvent was removed on a rotary evaporator, and the residue was recrystalized from $CHCl_3/Et_2O$ to give a white powder of product as a mixture of *E*- and *Z*-isomers (169 mg, 76% yield). By fractional recrystallization from $CHCl_3$, pure *Z*-isomer was obtained as a white powder (30 mg, 13%) at the first cycle. After removal of the solvent of the mother liquor, the residue was recrystalized from $CHCl_3/Et_2O$ again. The same operation was repeatedly carried out, and finally the *E*-isomer was also separated as a white powder. (*Z*)-Chloro[(ethoxy){4-((4′-(*n*-decyloxy)phenyl)carbonyl)phenylamino}carbene]gold: IR (KBr) 3230 (ν_{N-H}), 1714 ($\nu_{C=O}$), 1546 ($\nu_{C=N}$), 1249, 1193, 1088 (ν_{C-O}) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 8.99 (s, 1H, NH), 8.28 (m, 2H, Ar), 7.77 (m, 2H, Ar), 7.11 (m, 2H, Ar), 6.93 (m, 2H, Ar), 4.94 (q, 2H, J = 7.0 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$), 3.96 (t, 2H, J = 6.6 Hz, $\mathrm{OC}H_2\mathrm{C}_9\mathrm{H}_{19}$), 1.84−1.74 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_8H_{17}}$), 1.59−1.49, 1.46−1.18 (m, 17H, $\mathrm{OCH_2C}H_3$, $\mathrm{O\ (CH_2)_2(C}H_2)_7\mathrm{CH_3}$), 0.89 (t, 3H, J = 6.9 Hz, $\mathrm{O(CH_2)_9C}H_3$); ^{13}C-NMR ($CDCl_3$) δ 208.0 ($\mathrm{Au{=}}C$), 164.0 ($C{=}\mathrm{O}$), 157.1, 131.4, 128.8, and 115.2 ($\mathrm{HN}C_6\mathrm{H_4CO_2}$), 144.1, 139.9, 122.7, and 122.2 ($\mathrm{CO_2}C_6\mathrm{H_4OC_{10}H_{21}}$), 76.2 ($\mathrm{O}C\mathrm{H_2CH_3}$), 68.5 ($\mathrm{O}C\mathrm{H_2C_9H_{19}}$), 32.1, 31.9, 30.0, 29.6, 29.4, 26.3, 26.1, and 22.7 ($\mathrm{OCH_2}C_8\mathrm{H_{16}CH_3}$), 15.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 14.1 ($\mathrm{OC_9H_{18}}C\mathrm{H_3}$). (*E*)-Chloro[(ethoxy){4-((4′-(*n*-decyloxy)phenyl)carbonyl)phenylamino}carbene]gold: IR (KBr) 3305 (ν_{N-H}), 1733 ($\nu_{C=O}$), 1548 ($\nu_{C=N}$), 1245, 1192, 1074 (ν_{C-O}) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 10.38 (s, 1H, NH), 8.23 (m, 2H, Ar), 7.62 (m, 2H, Ar), 7.11 (m, 2H, Ar), 6.96 (m, 2H, Ar), 4.98 (q, 2H, J = 7.0 Hz, $\mathrm{OC}H_2\mathrm{CH}_3$), 3.96 (t, 2H, J = 6.6 Hz, $\mathrm{OC}H_2\mathrm{C}_9\mathrm{H}_{19}$), 1.84−1.74 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_8H_{17}}$), 1.59−1.49, 1.46−1.18 (m, 17H, $\mathrm{OCH_2C}H_3$, $\mathrm{O(CH_2)_2(C}H_2)_7\mathrm{CH_3}$), 0.89 (t, 3H, J = 6.9 Hz, $\mathrm{O(CH_2)_9C}H_3$); ^{13}C-NMR ($CDCl_3$) δ 208.4 ($\mathrm{Au{=}}C$), 164.5 ($C{=}\mathrm{O}$), 157.1, 131.4, 128.6, and 115.2 ($\mathrm{HN}C_6\mathrm{H_4CO_2}$), 144.1, 140.1, 123.7, and 122.7 ($\mathrm{CO_2}C_6\mathrm{H_4OC_{10}H_{21}}$), 76.6 ($\mathrm{O}C\mathrm{H_2CH_3}$), 68.5 ($\mathrm{O}C\mathrm{H_2C_9H_{19}}$), 31.9, 30.1, 29.6, 29.4, 29.3, 26.1, 25.9, and 22.7 ($\mathrm{OCH_2}C_8\mathrm{H_{16}CH_3}$), 15.1 ($\mathrm{OCH_2}C\mathrm{H_3}$), 14.1 ($\mathrm{OC_9H_{18}}C\mathrm{H_3}$).

Chloro[(propoxy){4-((4′-(*n*-decyloxy)benzoyl)oxy)phenyl)amino}carbene]gold (2c). A solution of chloro[4-((4′-(*n*-decyloxy)benzoyl)oxy)phenyl isonitrile]gold (91.6 mg, 0.150 mmol) in propanol (15 mL) was stirred at 65 °C under nitrogen atmosphere for 12 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from $CHCl_3/Et_2O$ to give a white powder of product as an isomeric mixture (85.4 mg, 85%): IR (KBr) 3296, 3236 (ν_{N-H}), 1713, 1724 ($\nu_{C=O}$), 1545, 1549 ($\nu_{C=N}$) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 10.09, 9.08 (s, 1H, NH), 8.13 (m, 2H, Ar), 7.61, 7.49 (m, 2H, Ar), 7.30−7.21 (m, 2H, Ar), 6.98 (m, 2H, Ar), 4.82−4.76 (m, 2H, $\mathrm{OC}H_2\mathrm{CH_2CH_3}$), 4.04 (t, 2H, J = 6.4 Hz, $\mathrm{OC}H_2\mathrm{C_9H_{19}}$), 1.93−1.80 (m, 4H, $\mathrm{OCH_2C}H_2\mathrm{CH_3}$ $\mathrm{OCH_2C}H_2\mathrm{C_8H_{17}}$), 1.59−1.28 (m, 17H, $\mathrm{OCH_2CH_2C}H_3$, $\mathrm{O(CH_2)_2(C}H_2)_7\mathrm{CH_3}$), 0.89 (t, 3H, J = 6.6 Hz, $\mathrm{O(CH_2)_9C}H_3$).

Chloro[(ethoxy){4-((4′-(*n*-octyloxy)phenyl)ethynyl)phenyl)amino}carbene]gold (3p). A solution of chloro[4-((4′-(*n*-octyloxy)phenyl)ethynyl)phenyl isonitrile]gold (90 mg, 0.16 mmol) in ethanol (15 mL) was stirred at 65 °C under nitrogen atmosphere for 12 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from CH_2Cl_2/hexane to give a white powder of product as an isomeric mixture (67 mg, 68%): IR (KBr) 3223 (ν_{N-H}), 2216 ($\nu_{C\equiv C}$), 1541 ($\nu_{C=N}$) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 9.88, 8.88 (s, 1H, NH), 7.56−7.40 (m, 6H, Ar), 6.89−6.83 (m, 2H, Ar), 4.90 (dq, 2H, J = 7.0, 2.0 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.97 (t, 2H, J = 6.6 Hz, $\mathrm{OC}H_2\mathrm{C_7H_{15}}$), 1.82−1.74 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_6H_{13}}$), 1.56−1.29 (m, 13H, $\mathrm{OCH_2C}H_3$, $\mathrm{O(CH_2)_2(C}H_2)_5\mathrm{CH_3}$), 0.89 (t, 3H, J = 6.7 Hz, $\mathrm{O(CH_2)_7C}H_3$).

Chloro[(ethoxy){4-((4′-(*n*-octyloxy)phenyl)ethyl)phenyl)amino}carbene]gold (4). A solution of chloro[4-((4′-(*n*-octyloxy)phenyl)ethyl)phenyl isonitrile]gold (74 mg, 0.13 mmol) in ethanol (15 mL) was stirred at 65 °C under nitrogen atmosphere for 12 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from CH_2Cl_2/hexane to give a white powder of product as an isomeric mixture (65 mg, 81%): IR (KBr) 3233 (ν_{N-H}), 1537 ($\nu_{C=N}$) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 9.47, 8.81 (s, 1H, NH), 7.46−7.15 (m, 4H, Ar), 7.04 (m, 2H, Ar), 6.84−6.79 (m, 2H, Ar), 4.86 (q, 2H, J = 6.9 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.92 (dt, 2H, J = 6.6, 1.7 Hz, $\mathrm{OC}H_2\mathrm{C_7H_{15}}$), 2.87−2.07 (m 4H, $\mathrm{Ph(C}H_2)_2\mathrm{Ph}$), 1.82−1.72 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_6H_{13}}$), 1.56−1.25 (m, 13H, $\mathrm{OCH_2C}H_3$, $\mathrm{O(CH_2)_2}$-$\mathrm{(C}H_2)_5\mathrm{CH_3}$), 0.89 (t, 3H, J = 6.9 Hz, $\mathrm{O(CH_2)_7C}H_3$).

Chloro[(3-methylbutoxy){4-((4′-(undecyloxy)phenyl)carbonyl)phenyl)amino}carbene]gold (5). A solution of chloro[4-((4′-(undecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (161 mg, 0.26 mmol) in 3-methylbutanol (12 mL) was stirred at 65 °C under nitrogen atmosphere for 12 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from CH_2Cl_2/hexane to give a white powder of product as an isomeric mixture (165 mg, 90%): IR (KBr) 3235, 3200 (ν_{N-H}), 1720, 1712 ($\nu_{C=O}$), 1542, 1530 ($\nu_{C=N}$) cm^{-1}; ^{1}H-NMR (270 MHz, $CDCl_3$) δ 10.02, 9.00 (s, 1H, NH), 8.27, 8.22 (d, d, 2H, Ar), 7.78, 7.56 (d, d, 2H, Ar), 7.14−7.08 (m, 2H, Ar), 6.96−6.91 (m, 2H, Ar), 4.93−4.86, 4.81−4.46 (m, 2H, $\mathrm{OC}H_2\mathrm{CH_2CH_2}$-$\mathrm{(CH_3)_2}$), 3.96 (t, 2H, J = 6.4 Hz, $\mathrm{OC}H_2\mathrm{C_{10}H_{21}}$), 1.93−1.80 (m, 4H, $\mathrm{OCH_2C}H_2\mathrm{CH_2(CH_3)_2}$, $\mathrm{OCH_2C}H_2\mathrm{C_9H_{19}}$), 1.59−1.28 (m, 18H, $\mathrm{OCH_2CH_2C}H_2\mathrm{(CH_3)_2}$, $\mathrm{O(CH_2)_2(C}H_2)_8\mathrm{CH_3}$), 1.10−0.89 (m, 9H, $\mathrm{OCH_2CH_2CH_2(C}H_3)_2$, $\mathrm{O(CH_2)_9C}H_3$).

Chloro[(ethoxy){4-((4″-(*n*-octyloxy)diphenyl)carbonyl)phenyl)amino}carbene]gold (6). To the solution of chloro[(ethoxy){4-((4″-(*n*-octyloxy)diphenyl)carbonyl)phenyl isocyanide]gold (69 mg, 0.105 mmol) in $CHCl_3$ (10 mL) was added ethanol (20 mL). After the solution was stirred for 18 h at 65 °C under nitrogen in dark, the solvent was evaporated and the resultant residue was purified by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. The crystals in the first cycle was collected as the *Z*-isomeric product (19.4 mg, 26%). At the second cycle, a white powder was found to be the *E*-isomeric product (30.9 mg, 42%). The third recrystallization from $\mathrm{CH_2Cl_2}$/hexane gave a white powder product as an isomeric mixture. (*Z*)-Chloro[(ethoxy)-{(4-((4″-(*n*-octyloxy)diphenyl)carbonyl)phenyl)amino}carbene]-gold: IR (KBr) 3226 ($\nu_{\mathrm{N-H}}$), 1713 ($\nu_{\mathrm{C=O}}$), 1547 ($\nu_{\mathrm{C=N}}$); ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 9.01 (s, 1H, NH), 8.31 (d, 2H, $J = 8.6$ Hz, Ar), 7.79 (d, 2H, $J = 8.6$ Hz, Ar), 7.60 (d, 2H, $J = 8.6$ Hz, Ar), 7.51 (d, 2H, $J = 8.9$ Hz, Ar), 7.26 (d, 2H, $J = 8.6$ Hz, Ar), 6.98 (d, 2H, $J = 8.6$ Hz, Ar), 4.95 (q, 2H, $J = 7.1$ Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.00 (t, 2H, $J = 6.4$ Hz, $\mathrm{OC}H_2\mathrm{C_7H_{15}}$), 1.84−1.76 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_6H_{13}}$), 1.57−1.52, 1.30−1.25 (m, 13H, $\mathrm{OCH_2C}H_3$, $\mathrm{O(CH_2)_2(C}H_2\mathrm{)_5CH_3}$), 0.90−0.87 (m, 3H, $\mathrm{O(CH_2)_7C}H_3$). (*E*)-Chloro[(ethoxy){(4-((4″-(*n*-octyloxy)diphenyl)carbonyl)phenyl)-amino}carbene]gold: IR (KBr) 3228 ($\nu_{\mathrm{N-H}}$), 1727 ($\nu_{\mathrm{C=O}}$), 1553 ($\nu_{\mathrm{C=N}}$); ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 10.22 (s, 1H, NH), 8.27 (d, 2H, $J = 8.9$ Hz, Ar), 7.67−7.58 (m, 4H, Ar), 7.51 (d, 2H, $J = 8.6$ Hz, Ar), 7.26 (d, 2H, $J = 8.6$ Hz, Ar), 6.98 (d, 2H, $J = 8.9$ Hz, Ar), 4.96 (q, 2H, $J = 7.1$ Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.00 (t, 2H, $J = 6.4$ Hz, $\mathrm{OC}H_2\mathrm{C_7H_{15}}$), 1.84−1.76 (m, 2H, $\mathrm{OCH_2C}H_2\mathrm{C_6H_{13}}$), 1.59−1.53, 1.30−1.25 (m, 13H, $\mathrm{OCH_2C}H_3$, $\mathrm{O(CH_2)_2(C}H_2\mathrm{)_5CH_3}$), 0.90−0.87 (m, 3H, $\mathrm{O(CH_2)_7C}H_3$).

Iodo[(propoxy){(4-((4′-(*n*-undecyloxy)phenyl)carbonyl)-phenyl)amino}carbene]gold (7). To a solution of chloro-[(4-((4′-(*n*-undecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (281 mg, 0.50 mmol) in acetone (50 mL) was added LiI (301 mg, 2.5 mmol). After the solution was stirred for 12 h at room temperature, the solvent was evaporated and benzene as washing solvent was added to the resultant residue. Then the precipitate was collected by filtration to give a yellow powder as product, iodo[4-((4′-(*n*-undecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (281 mg, 87%). A solution of iodo[4-((4′(*n*-undecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (93 mg, 0.13 mmol) in propanol (15 mL) was stirred at 65 °C under nitrogen atmosphere for 2 h. The solvent was removed on a rotary evaporator, and the residue was recrystallized from $\mathrm{CH_2Cl_2}$/hexane to give a pale yellow powder product as an isomeric mixture (83 mg, 82%): IR (KBr) 3224 ($\nu_{\mathrm{N-H}}$), 1727, 1713 ($\nu_{\mathrm{C=O}}$), 1549 ($\nu_{\mathrm{C=N}}$) cm^{-1}; ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 9.07, 9.00 (s, 1H, NH), 8.26, 8.06 (m, 2H, Ar), 7.79, 7.50 (m, 2H, Ar), 7.13−7.07 (m, 2H, Ar), 6.95−6.87 (m, 2H, Ar), 4.89 (dt, 2H, $J = 6.6$, 2.1 Hz, $\mathrm{OC}H_2\mathrm{CH_2CH_3}$), 3.96 (t, 2H, $J = 6.4$ Hz, $\mathrm{OC}H_2\mathrm{C_{10}H_{21}}$), 1.97−1.11 (m, 20H, $\mathrm{OCH_2C}H_2\mathrm{CH_3}$, $\mathrm{OCH_2(C}H_2\mathrm{)_9CH_3}$), 1.05 (dt, 3H, $\mathrm{OCH_2CH_2C}H_3$), 0.89 (t, 3H, $J = 6.6$ Hz, $\mathrm{O(CH_2)_{10}C}H_3$).

Chloro[(*N*-methyl-*n*-butylamino){(4-((4′-(*n*-dodecyloxy)-phenyl)carbonyl)phenyl)amino}carbene]gold (8c). To the solution of chloro[4-((4′-(*n*-dodecyloxy)phenyl)carbonyl)-phenyl isonitrile]gold (83.6 mg, 0.131 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) was added *N*-methyl-*n*-butylamine (0.1 mL, 0.84 mmol). After the solution was stirred for 3 h at room temperature under nitrogen, the solvent was evaporated and the resultant residue was purified by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. A white powder (69.6 mg, 73%) was obtained as an isomeric mixture: IR (KBr) 3338 ($\nu_{\mathrm{N-H}}$), 1741, 1708 ($\nu_{\mathrm{C=O}}$), 1552 ($\nu_{\mathrm{C=N}}$) cm^{-1}; ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 8.19 (m, 2H, Ar), 7.70 (m, 2H, Ar), 7.51 (s, 1H, NH), 7.10 (m, 2H, Ar), 6.93 (m, 2H, Ar), 4.08, 3.47 (t, 2H, $J = 7.3$ Hz, $\mathrm{NC}H_2\mathrm{(CH_2)CH_3}$), 3.96 (t, 2H, $J = 6.4$ Hz, $\mathrm{OC}H_2\mathrm{C_{11}H_{23}}$), 3.69, 3.16 (s, 3H, $\mathrm{NC}H_3$), 1.84−1.67 (m, 4H, $\mathrm{NCH_2C}H_2\mathrm{C_2H_5}$, $\mathrm{OCH_2C}H_2\mathrm{(CH_2)_8CH_3}$), 1.46−1.27 (m, 20H, $\mathrm{N(CH_2)_2C}H_2\mathrm{CH_3}$, $\mathrm{O(CH_2)_2(C}H_2\mathrm{)_9CH_3}$), 1.06−0.96 (m, 3H, $\mathrm{N(CH_2)_3C}H_3$), 0.88 (t, 3H, $J = 6.8$ Hz, $\mathrm{O(CH_2)_{11}C}H_3$).

Chloro[(propylamino){(4-((4′-(*n*-dodecyloxy)phenyl)-carbonyl)phenyl)amino}carbene]gold (9a). To the solution of chloro[4-((4′-(*n*-dodecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (84.1 mg, 0.131 mmol) in benzene (20 mL) was added propylamine (0.022 mL, 0.26 mmol). After the solution was stirred for 5 h at room temperature under nitrogen, the solvent was evaporated and the resultant residue was purified by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. A white powder (42.7 mg, 47%) was obtained as an isomeric mixture: IR (KBr) 3299 ($\nu_{\mathrm{N-H}}$), 1732 ($\nu_{\mathrm{C=O}}$), 1560 ($\nu_{\mathrm{C=N}}$) cm^{-1}; ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 8.20 (bd, 2.5−3H, NH, Ar), 7.84 (bs, −0.5H, NH), 7.75 (m, 2H, Ar), 7.36 (bs, 1H, NH), 7.12−7.07 (m, 2H, Ar), 6.94−6.87 (m, 2H, Ar), 3.95 (t, 2H, $J = 6.4$ Hz, $\mathrm{OC}H_2\mathrm{C_{11}H_{23}}$), 3.72, 3.27 (bm, 2H, $\mathrm{NC}H_2\mathrm{C_2H_5}$), 1.81−1.73 (m, 2H, $\mathrm{NCH_2C}H_2\mathrm{CH_3}$,), 1.71−1.67, 1.57−1.26 (m, 20H, $\mathrm{NCH_2C}H_2\mathrm{CH_3}$, $\mathrm{O(CH_2)_2(C}H_2\mathrm{)_9CH_3}$), 1.10, 0.97 (t, 3H, $J = 7.4$, 6.6 Hz, $\mathrm{N(CH_2)_2C}H_3$), 0.88 (t, 3H, $J = 6.6$ Hz, $\mathrm{O(CH_2)_{11}C}H_3$).

Dinuclear Gold−Carbene Complex, $[\mathbf{ClAu\{C(NHC_6H_4CO_2C_6H_4OC_\mathit{n}H_{2\mathit{n}+1})\}](NCH_3C_\mathit{m}H_{2\mathit{m}}NCH_3)[ClAu\{C(NHC_6H_4CO_2C_6H_4OC_\mathit{n}H_{2\mathit{n}+1})\}]}$ (10). To the solution of chloro[4-((4′-(*n*-dodecyloxy)phenyl)carbonyl)phenyl isonitrile]gold (82.6 mg, 0.13 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL) was added *N*,*N*′-dimethyl-1,6-hexamethylenediamine (0.01 mL, 0.065 mmol). The mixture was stirred at room temperature under nitrogen for 1 h. The solvent was evaporated and the resultant residue was purified by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. A white powder (75.3 mg, 82%) was obtained as a product: IR (KBr) 3322 ($\nu_{\mathrm{N-H}}$), 1713 ($\nu_{\mathrm{C=O}}$), 1554 ($\nu_{\mathrm{C=N}}$) cm^{-1}; ^{1}H-NMR (270 MHz, $\mathrm{CDCl_3}$) δ 8.03 (d, 4H, $J = 7.9$ Hz, Ar), 7.91 (s, 2H, NH), 7.64 (d, 4H, $J = 7.6$ Hz, Ar), 7.09 (d, 4H, $J = 9.2$ Hz, Ar), 6.85 (d, 4H, $J = 9.2$ Hz, Ar), 4.23 (m, 4H, $\mathrm{(NC}H_2\mathrm{C_2H_4)_2}$), 3.94 (t, 4H, $J = 6.6$ Hz, $\mathrm{(OC}H_2\mathrm{C_{11}H_{23})_2}$), 3.21 (m, 4H, $\mathrm{(NCH_2C}H_2\mathrm{CH_2)_2}$), 1.89−1.27 (m, 24H, $\mathrm{(NC_2H_4C}H_2\mathrm{)_2}$, $\mathrm{OCH_2CH_2)_8CH_3}$), 1.46−1.27 (m, 20H, $\mathrm{N(CH_2)_2C}H_2\mathrm{CH_3}$, $\mathrm{(O(CH_2)_2(C}H_2\mathrm{)_{10}CH_3)_2}$), 0.90 (t, 6H, $J = 6.9$ Hz, $\mathrm{(O(CH_2)_{11}C}H_3\mathrm{)_2}$).

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Supporting Information Available: Text describing X-ray procedures, tables of crystal data and details of the structure solution, positional and displacement parameters, and bond distances and angles, and ORTEP diagrams (20 pages). Ordering information is given on any current masthead page.

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