Liquid-crystalline Gold(I)–Carbene Complexes

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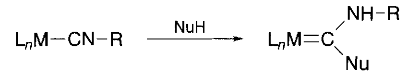
Gold(I)–(alkoxy)(amino)carbenes, the first liquid-crystalline transition metal–carbene complexes, are prepared and shown to form enantiotropic smectic A phases.

Since the first discovery[1] of chromium–carbene complexes by Fischer and Maasböl in 1964, a large number of transition metal–carbene complexes have been synthesized from various precursors and by diverse methods.[2] Today the chemistry of transition metal–carbene complexes has been developed for applications in the field of synthetic organic chemistry as useful reagents and effective catalysts.[3] However, little attention has been paid to the carbene complexes from the viewpoint of materials chemistry, although novel physical properties based on the direct metal–carbon multiple bond may be expected for the carbene complexes.

On the other hand, liquid crystals incorporating transition metals, the so-called metallomesogens, have attracted much recent interest and a large number of papers on metallomesogens have appeared in the literature, while there are limited examples of organometallic liquid crystals.[4] Recently we reported new families of organometallic liquid crystals which include isonitrile complexes of platinum[5] and gold.[6] Here we report the synthesis and mesomorphic properties of gold–carbene complexes which are derived from gold–isonitrile complexes.

Representatives of thermally stable transition metal–carbene complexes include platinum- and gold–carbene complexes, some of which are prepared starting from their acetylide and isonitrile complexes by the attack of the appropriate nucleophiles on the positively charged carbon atom in M–C≡CR and M–C≡NR.[7] As we had a variety of samples of liquid-crystalline isonitrile–platinum and -gold complexes, we tried to convert them to liquid-crystalline carbene complexes by the reaction with nucleophiles (eqn. 1). On treatment with an amine nucleophile, bis(isonitrile)platinum(II) complexes gave bis(carbene)platinum(II) complexes for which, however, we have not yet found any mesomorphic properties.[8]

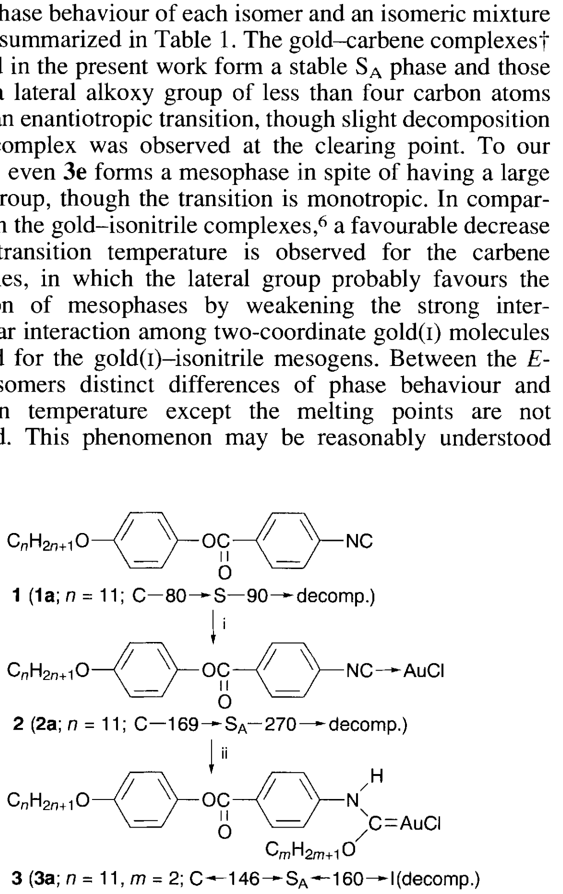
Our previous works[6] showed that the rod-like structure of gold(I)–isonitrile complexes with a two-coordinate geometry is quite suitable for forming liquid crystals and even a rather large lateral group does not disturb the formation of mesophases but leads to a favourable lowering of transition temperatures. On the basis of this finding, we attempted to transform gold–isonitrile complexes **2** to carbene complexes **3** by a nucleophilic addition of alcohols.[9] Thus, liquid-crystalline gold–isonitrile complex **2a** was suspended in ethanol and stirred at 65 °C under nitrogen for 12 h, giving carbene complex **3a** as white crystals in 70–80% yield after recrystallization from CH$_2$Cl$_2$–hexane (Scheme 1). The infrared spectrum of **3a** showed the disappearance of the band at 2240 cm^{-1} due to ν(C≡N) observed for **2a** 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 exhibited the existence of a carbene carbon at δ 208, indicating **3a** to be a gold–(alkoxy)(amino)carbene complex. The carbene complexes thus obtained have been demonstrated to exhibit mesomorphic properties. For example, the crystals of **3a** melt at 146 °C to form a smectic A (S$_A$) phase, which is transformed to an isotropic phase at 160 °C, accompanied by a slight decomposition. The identification of mesophases has been made on the basis of optical textures, and **3a** shows a focal conic texture after the appearance of bâtonnets on cooling from an isotropic phase.



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

The detailed spectral analyses for **3** suggest the existence of two geometric isomers (*ca.* 3 : 1) due to the partial double-bond character of the C–N bond which was observed in their infrared spectra.[10] For example, **3a** shows two bands at 1730 and 1710 cm^{-1} assigned to ν(C=O). In addition, the ^{1}H NMR spectrum showed two sets of signals due to the amide proton as well as due to the protons on the aromatic ring bonded to an N atom, and the isomer ratio may be estimated by an analysis of the ^{1}H NMR spectrum. The geometric isomers exist in thermodynamical equilibrium in a solution and the slightly more stable isomer has been found to be an *E*-form. The isomers of **3** can be separated by fractional crystallization from CHCl$_3$–Et$_2$O[11] because the *Z*-isomer is less soluble. The complete separation has been made for complexes **3a** and **3b**; however, it may be difficult for complexes possessing a rather long alkoxy group. The pure *E*- or *Z*-isomer is stable in the solid state, but isomerizes in chloroform solution even at room temperature into an equilibrium mixture of the *E*- and *Z*-forms. The preliminary single-crystal X-ray structural analysis[12] has revealed that complex ClAu{C(OEt)(NHC$_6$H$_4$CO$_2$C$_6$H$_4$OEt)} **3f**, which is a model complex of **3** exhibiting a higher ν(C=O) in the IR spectrum, takes an *E*-form around the C–N bond and an extended linear form with an alkoxy lateral group, and that there are no Au—Au interactions in the crystals.[6]

The phase behaviour of each isomer and an isomeric mixture of **3** are summarized in Table 1. The gold–carbene complexes† prepared in the present work form a stable S$_A$ phase and those having a lateral alkoxy group of less than four carbon atoms exhibit an enantiotropic transition, though slight decomposition of the complex was observed at the clearing point. To our surprise, even **3e** forms a mesophase in spite of having a large lateral group, though the transition is monotropic. In comparison with the gold–isonitrile complexes,[6] a favourable decrease in the transition temperature is observed for the carbene complexes, in which the lateral group probably favours the formation of mesophases by weakening the strong intermolecular interaction among two-coordinate gold(I) molecules as found for the gold(I)–isonitrile mesogens. Between the *E*- and *Z*-isomers distinct differences of phase behaviour and transition temperature except the melting points are not observed. This phenomenon may be reasonably understood



1 (**1a**; n = 11; C—80→S—90→decomp.)

2 (**2a**; n = 11; C—169→S$_A$—270→decomp.)

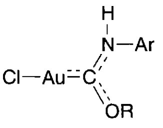
3 (**3a**; n = 11, m = 2; C⇀146⇀S$_A$⇀160→I(decomp.)

Scheme 1 *Reagents and conditions*: i, AuCl(Me$_2$S), CH$_2$Cl$_2$; ii, C$_m$H$_{2m+1}$OH, 65 °C

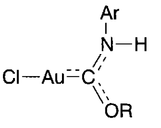
Table 1 Phase transition temperatures (°C) for complex **3**

	n	m	E-form	Z-form	Isomeric mixture[a]
3a	11	2	$C \xleftrightarrow{142} S_A \xleftrightarrow{160} I^b$	$C \xleftrightarrow{149} S_A \xleftrightarrow{160} I^b$	$C \xleftrightarrow{146} S_A \xleftrightarrow{160} I^b$
3b	10	2	$C \xleftrightarrow{143} S_A \xleftrightarrow{158} I^b$	$C \xleftrightarrow{152} S_A \xleftrightarrow{158} I^b$	$C \xleftrightarrow{150} S_A \xleftrightarrow{158} I^b$
3c	11	3	$C \xleftrightarrow{116} S_A \xleftrightarrow{128} I$		$C \xleftrightarrow{114} S_A \xleftrightarrow{129} I^b$
3d	11	4			$\begin{tikzcd} C \arrow[r, "113"] & I \arrow[dl, "96"] \\ S^c & \end{tikzcd}$
3e	11	5			$\begin{tikzcd} C \arrow[r, "113"] & I \arrow[dl, "77"] \\ S^c & \end{tikzcd}$

[a] A mixture of E:Z = *ca.* 3:1. [b] With some decomposition. [c] Unidentified phases.



E-isomer



Z-isomer

because the transition from a crystalline phase of either pure E- or Z-isomer to an S_A phase may result in an isomerization leading to a thermodynamic mixture of the two isomers. In fact the crystals obtained after cooling an isotropic liquid of **3b** was confirmed to consist of two isomers with an E:Z molar ratio of *ca.* 3:1. The different melting points and the same clearing temperatures of the two pure isomers may be consistent with the above observation.

In conclusion, the gold–carbene complexes exhibit mesomorphic properties and provide the first examples of liquid-crystalline metal–carbene complexes. Efforts are now in progress to extend the range of carbene complexes to other transition metals.

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Footnote

† All new gold complexes were identified by elemental analyses and IR and ^1H NMR spectra.