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The use of thermotropic liquid crystals in organometallic chemistry. Synthesis of new mercury, silver and gold complexes with 4,4′-disubstituted azobenzenes

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Abstract

Liquid crystalline 4-$XC_6H_4N{=}NC_6H_4X$-4′ [X = C_4H_9 (**1a**), $C_{10}H_{21}$ (**1b**), OC_4H_9 (**1c**), OC_8H_{17} (**1d**)] can be easily prepared in high yields from the corresponding anilines. In order to study the influence of metals on the thermal properties of these materials, we have obtained adducts [$AuCl_3$(4-$C_4H_9OC_6H_4N{=}NC_6H_4OC_4H_9$-4′)] (**2**) and [$Ag(OClO_3)L_2$] [L = 4-$XC_6H_4N{=}NC_6H_4X$-4′; X = OC_4H_9 (**3a**), OC_8H_{17} (**3b**)]. The silver adducts show thermotropic behaviour. Mercuriation of dialkylazobenzenes **1a–b** takes place with [$Hg(OAc)_2$] and LiCl to give [Hg(R)Cl] [R = C_6H_3(N=NC_6H_4X-4′)-2, X-5; X = C_4H_9 (bpap) (**4a**), $C_{10}H_{21}$ (dpap) (**4b**)] while dialkoxyazobenzenes **1c–d** require [$Hg(OOCCF_3)_2$] to obtain [Hg(R)Cl] [R = C_6H_3(N=NC_6H_4X-4′)-2, X-5; X = OC_4H_9 (bxpap) (**4c**), OC_8H_{17} (**4d**)]. **4a–c** react with NaI to give [HgR_2] [R = bpap (**5a**), dpap (**5b**), bxpap (**5c**), oxpap (**5d**)]. Both chloroaryl-, **4a** and **4c**, and diaryl-mercurials, **5a** and **5c**, act readily as transmetallating agents towards [Me_4N] [$AuCl_4$] in the presence of [Me_4N]Cl to give [Au(η^2-R)Cl_2] [R = bpap (**6a**), bxpap (**6b**)]. After reaction of [$AuCl_3$(tht)] (tht = tetrahydrothiophene) with [Me_4N]Cl and **4b** (1:2:1), [Me_4N][Au(dpap)Cl_3] (**7**) can be isolated. C–H activation of acetone by **6a–b** leads to [Au(η^2-R){CH_2C(O)Me}Cl] [R = bpap (**8a**), bxpap (**8b**)]. None of the complexes **4–8** shows mesomorphic behaviour.

Key words: Gold; Silver; Mercury; Aryl; Transmetallation; Orthometallated complexes

1. Introduction

The preparation of new organometallic materials with mesogenic properties has attracted increasing attention for theoretical and industrial reasons [1].

Our previous experience in the synthesis of 2-phenylazophenylgold(III) complexes and their use as C–H activation and C–C bond formation intermediates [2], has prompted us to extend our studies to long-chain substituted azobenzenes to compare their reactivity with that of azobenzene or azotoluene, and to search for new organometallic materials with mesogenic properties.

4-4′-Disubstituted azobenzenes are a well studied family of thermotropic liquid crystals [3], but their use in organometallic chemistry has been limited as far as we are aware to the synthesis of palladium(II) derivatives with asymmetrically substituted azobenzenes [4]. Examples of mercury- or gold-containing liquid crystals are still very scarce [1]. We therefore searched for new organometallic materials by studying the influence of metals on the thermal properties of liquid crystalline azobenzenes. We now report the synthesis, characterization and thermal behaviour of new *ortho*-metallated and coordination species. Scheme 1 shows the symbols

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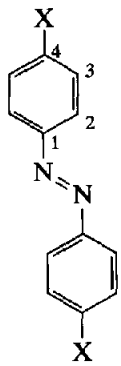
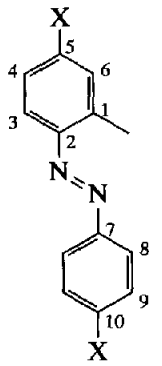




X =		X =	
n-C_4H_9	Hbpap	n-C_4H_9	bpap
n-$C_{10}H_{21}$	Hdpap	n-$C_{10}H_{21}$	dpap
n-C_4H_9O	Hbxpap	n-C_4H_9O	bxpap
n-$C_8H_{17}O$	Hoxpap	n-$C_8H_{17}O$	oxpap

Scheme 1. Carbon atom numbering and symbols used to represent the ligands.

used to represent the ligands. The η notation is used to indicate the number of coordinated atoms. Some of the results reported here have been the object of a preliminary communication [5].

2. Results and discussion

The usual preparation of symmetrically disubstituted azobenzenes requires two steps: the synthesis of the corresponding nitro-derivatives and their reduction with $LiAlH_4$ [6]. We have prepared 4-$XC_6H_4N{=}NC_6H_4X$-4′ [X = n-Bu (Hbpap) (**1a**), n-$C_{10}H_{21}$ (Hdpap) (**1b**), n-BuO (Hbxpap, **1c**), n-$C_8H_{17}O$ (Hoxpap, **1d**)] in a one-step process starting from the corresponding amines, by oxidizing them with air in the presence of copper(I) chloride and pyridine over 24 h (see Schemes 1 and 2). **1a–d** were purified by column chromatography and characterized by their transition temperatures [7] as well as by spectroscopic techniques.

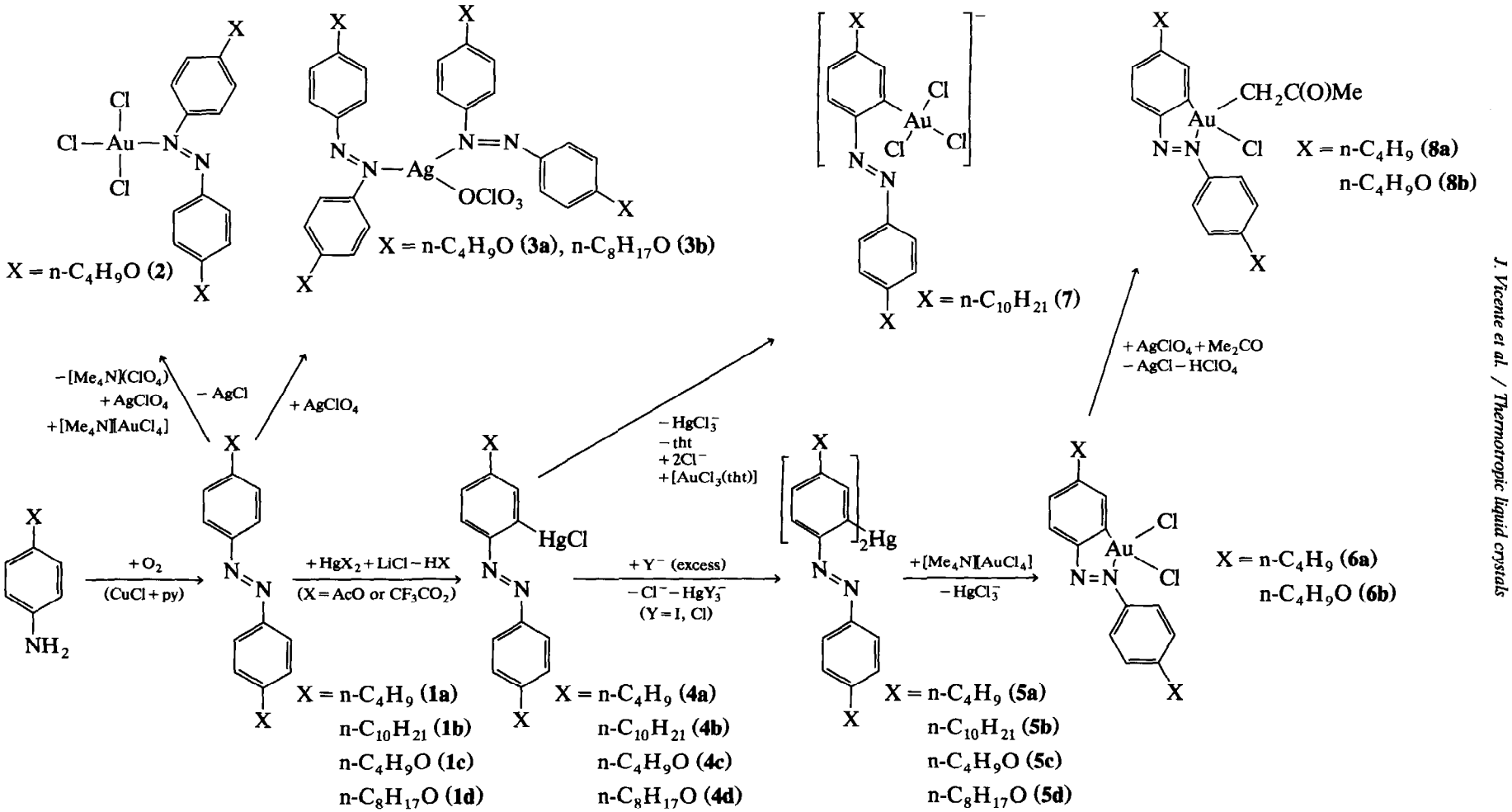
We have tried to obtain gold(III) adducts by reaction of **1c** with $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) in acetone, but after 3 h stirring at room temperature the starting materials were recovered unreacted. We finally obtained $[AuCl_3(Hbxpap)]$ (**2**) (see Schemes 1 and 2) as a purple solid, from **1c** and $[Me_4N][AuCl_4]$ in the presence of $AgClO_4$ (1:1:1). The low yield of this reaction is probably due to the formation of some adduct with $AgClO_4$ (see below). Unfortunately, the new gold(III) adduct **2** shows only a crystal-to-isotropic liquid transition temperature.

When **1c** or **1d** reacts with $AgClO_4$ (2:1) in acetone a deep red solution is immediately formed, but most of the starting ligands are recovered unreacted as judged by their transition temperatures under the microscope and only a low yield of $[Ag(OClO_3)L_2]$ [L = Hbpap (**3a**), Hbxpap (**3b**)] is obtained. The low yield of these reactions is therefore probably due to an equilibrium in solution. Both complexes show unidentified smectic mesophases in a quite large temperature interval, with melting points higher than that of the unbound azo ligands, but heating above the clearing points leads to decomposition.

Dialkylazobenzenes **1a** and **1b** were mercuriated with mercury(II) acetate following a procedure modified from that described for azobenzene [8] giving, after reaction with LiCl, [Hg(bpap)Cl] (**4a**) and [Hg(dpap)Cl] (**4b**) (see Schemes 1 and 2), respectively. In the case of dialkoxyazobenzenes **1c** and **1d** no mercuriation takes place under the above conditions. Even when the more electrophilic mercury(II) trifluoroacetate is used, only a low yield of [Hg(R)Cl] [R = bxpap (**4c**), oxpap (**4d**)] was obtained and most of the 4,4′-dialkoxyazobenzene was recovered. We interpret this unexpected result as a consequence of the low solubility of **1c** and **1d** in MeOH or EtOH. Using other solvents, such as toluene, mixtures containing tolyl mercurials were also obtained. Symmetrization of **4a–4c** to give $[HgR_2]$ [R = bpap (**5a**), dpap (**5b**), bxpap (**5c**)] was achieved using NaI [9] or $[Me_4N]Cl$ [10] (see Scheme 2).

The transmetallation reaction of $[Me_4N]$ $[AuCl_4]$ with $[HgR_2]$ (2:1) gives the cycloaurated complex $[Au(\eta^2\text{-}R)Cl_2]$ [R = bpap (**6a**), bxpap (**6b**)] that can easily be separated from the by-products [see eqn. (3)]. [Hg(R)Cl] can also be used as a transmetallating agent if $[Me_4N]Cl$ is also added as a symmetrizing agent [see Eqn. (2)]. Addition of $[Me_4N]Cl$ when $[HgR_2]$ is used, although pushing equilibrium (3), to the left, reduces the reaction time without decreasing the yield, probably because reaction (2) is the rate-determining step. $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) can also be used as the starting material but the yield is lower due to the formation of mixtures containing **6** and some tetrahydrothiophene complexes. However, a 1:1:2 mixture of $[AuCl_3(tht)]$, [Hg(R)Cl] and $[Me_4N]Cl$ gives the anionic species $[Me_4N][Au(dpap)Cl_3]$ (**7**). This is in contrast to the behaviour observed for $[Au(\eta^2\text{-pap})Cl_2]$ (pap = 2-phenylazophenyl) [11] that reacts with the excess of $[Me_4N]Cl$, probably giving complexes of the type **7**, but all attempts to isolate them yielded the starting complex.

$$2[Me_4N][AuCl_4] + 2[HgR_2] \longrightarrow 2[Au(\eta^2\text{-}R)Cl_2] + 2[Hg(R)Cl] + 2[Me_4N]Cl \quad (1)$$


X = n-C4H9O (2)
X = n-C4H9O (3a), n-C8H17O (3b)
X = n-C10H21 (7)
X = n-C4H9 (8a)
n-C4H9O (8b)
+ O2
(CuCl + py)
+ HgX2 + LiCl − HX
(X = AcO or CF3CO2)
+ Y− (excess)
− Cl− − HgY3−
(Y = I, Cl)
+ [Me4N][AuCl4]
− HgCl3−
+ AgClO4 + Me2CO
− AgCl − HClO4
− [Me4N](ClO4)
+ AgClO4
+ [Me4N][AuCl4]
− AgCl
+ AgClO4
− HgCl3−
− tht
+ 2Cl−
+ [AuCl3(tht)]
X = n-C4H9 (1a)
n-C10H21 (1b)
n-C4H9O (1c)
n-C8H17O (1d)
X = n-C4H9 (4a)
n-C10H21 (4b)
n-C4H9O (4c)
n-C8H17O (4d)
X = n-C4H9 (5a)
n-C10H21 (5b)
n-C4H9O (5c)
n-C8H17O (5d)
X = n-C4H9 (6a)
n-C4H9O (6b)

Scheme 2.

$$2[Hg(R)Cl] + [Me_4N]Cl \longrightarrow [HgR_2] + [Me_4N][HgCl_3]\downarrow \quad (2)$$

$$2\,[Me_4N][AuCl_4] + [HgR_2] \longrightarrow 2[Au(\eta^2\text{-}R)Cl_2] + [Me_4N][HgCl_3]\downarrow + Me_4NCl \quad (3)$$

6a and **6b** react with $AgClO_4$ in acetone to give almost immediately the acetonyl complexes $[Au(\eta^2\text{-}R)\{CH_2C(O)Me\}Cl]$ [R = bpap (**8a**), bxpap (**8b**)]. We have described this type of reaction amply and suggested a possible reaction pathway [12]. These ketonyl complexes decompose when they melt.

We are presently developing the synthesis and reactivity of arylketonyl complexes and diaryl derivatives of the type $[Au(\eta^2\text{-}R)(R')Cl]$ (R = bpap, dpap, bxpap, or oxpap, R' = ketonyl; R or R' = bpap, dpap, bxpap, or oxpap) to use them as precursors for new arylalkylketones and biphenyls [2].

All *ortho*-metallated complexes described in this paper were studied using a microscope equipped with a heated stage between crossed polarizers. Only crystal-to-isotropic liquid transitions were observed, with high melting points (see Experimental section). As expected, mercurials show high thermal stability while some of the gold complexes melt with decomposition.

2.1. Spectroscopic properties of the complexes

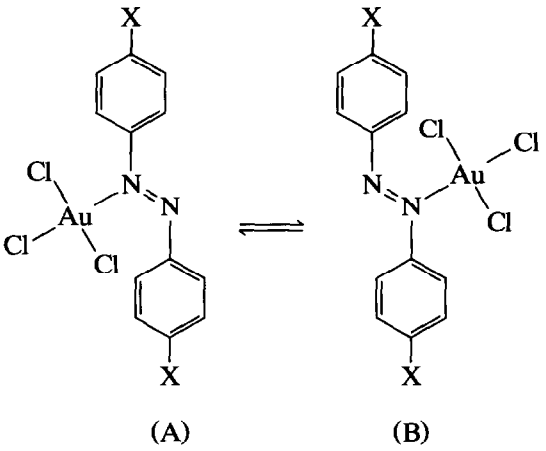
2.1.1. IR spectra

Complex **2** shows only one strong absorption in the region 400–200 cm^{-1}, at 350 cm^{-1}, assignable to gold–chlorine stretching modes.

The IR spectra of the silver complexes **3a–b** show multiple bands in the regions around 1100 and 620 cm^{-1}, typical of a coordinated perchlorate.

Chloroarylmercurials **4a–d** show one absorption in the region 320–330 cm^{-1} not observed for the diarylmercurials **5a–b**, assignable to ν(Hg–Cl). Like comparable gold(III) complexes [9,10], cycloaurated complexes **6a–b** show bands due to ν(Au–Cl) *trans* to nitrogen around 360 cm^{-1} and to ν(Au–Cl) *trans* to phenyl at 305–310 cm^{-1}. As expected this vibration mode appears at lower energy in **7** (288 cm^{-1}) due to its anionic nature [11]. A further band at 350 cm^{-1}, with a slight shoulder on the low energy side, is assigned to the ν(Cl–Au–Cl) symmetric and asymmetric modes.

When one of the chlorides is replaced by the acetonyl group to give complexes **8a–b**, only one absorption is observed in the 400–200 cm^{-1} region, at 305 cm^{-1}. Thus the chloro occupies the position *trans* to the aryl group, as seen in the crystal structure of [Au(mpap)-



Scheme 3.

$\{CH_2C(O)Me\}(py)]ClO_4$ [mpap = C_6H_4-2-(N=NC_6H_4-Me-4')-5-Me] [12]. ν(CO) appears in these complexes at 1680 cm^{-1}, as for other acetonyl species [13].

The azo ligands show strong absorptions at *ca.* 840 cm^{-1} due to the *para*-disubstitution of the aryl groups. In the *ortho*-metallated species, this band is accompanied by several medium bands between 820 and 800 cm^{-1}, assignable to trisubstituted rings.

2.1.2. NMR spectra

Complex **2** shows ^1H NMR resonances at similar yet at a somewhat lower field to that of the free ligand **1c**. The equivalence of both butoxyaryl groups suggests a fast equilibrium in solution between (A) and (B) (see Scheme 3). The low stability in solution of the complexes **3a–b** prevented the recording of their NMR spectra.

In the ^1H NMR spectra of chloroarylmercurials **4a–b**, the resonances corresponding to the alkyl or alkoxy chains bonded to the metallated and to the non-metallated rings are almost equivalent, but the *ortho*-metallation of one of the phenyl rings is clearly established by the aromatic resonances. The low solubility of these species in organic solvents prevented the assignment of their ^{13}C NMR spectra.

The *ortho*-metallation in **5a–c** has been confirmed by ^1H and ^{13}C NMR spectra. By comparing the ^{13}C NMR spectra with that of the azo ligands we have tentatively assigned the resonances. The only difficulty arises when we try to identify the resonances due to the metallated carbon atom and those corresponding to C5 and C10 (see Scheme 1), as they appear in the same region (146–150 ppm for **5a–b**, 160–166 ppm for **5c**).

Whereas in most complexes the proton resonances due to the methyl and methylene groups bonded to

metallated and non-metallated aryl groups appear accidentally at the same frequency, the ^{1}H NMR spectrum of the cycloaurated complex **6b** shows independent signals for the butoxy chains of each ring, at lower field than those of the free 4,4'-butoxyazobenzene. The ^{13}C NMR spectra of **6a–b** show the presence of an *ortho*-metallated arylazoaryl group.

NMR spectra of acetonyl complexes **8a–b** are similar to those of the parent complexes **6a–b** with the presence in the ^{1}H and ^{13}C NMR spectra of two singlets for the methyl and methylene groups of the acetonyl.

3. Experimental section

Recording of the IR and NMR spectra and elemental analyses determinations were performed as described elsewhere [12]. NMR spectra were carried out in $CDCl_3$ solutions with TMS as a reference except where otherwise stated. Numbering schemes are shown in Scheme 1.

Thermal behaviour was monitored by means of a Mettler FP-90 central processor equipped with a FP-82HT heating stage, at a rate of 3°C min^{-1}. The textures were observed by means of an Olympus BH-2 polarizing microscope. 4-Butoxyaniline was obtained as described [14].

3.1. Preparation of the 4,4'-disubstituted azobenzenes 1a–d

4-Alkyl- or 4'-alkoxyanilines (120 mmol) were mixed with solid copper(I) chloride (12 mmol) and pyridine (20 ml). Circulation of air through the mixture for 24 h gave a black residue, which was placed on alumina column (3 × 30 cm) and eluted with hexane. Removal of the solvent afforded orange crystals. Yield (%): 75 (**1a**); 80 (**1b**); 85 (**1c**); 82 (**1d**). ^{1}H NMR (**1a**): δ 0.9 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.3 (sext, 4H, CH_2Me), 1.6 (q, 4H, CH_2Et), 2.6 (t, 4H, $CH_2C_6H_4$), 7.2, 7.7 (AB, 8H, H2, H3, ^3J(HH) = 8 Hz) ppm. (**1b**): δ 0.8 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.2 (m, 28H, $(CH_2)_7$), 1.6 (q, 4H, $CH_2CH_2C_6H_4$), 2.6 (t, 4H, $CH_2C_6H_4$, ^3J(HH) = 7 Hz), 7.3, 7.9 (AB, 8H, H2, H3, ^3J(HH) = 8 Hz) ppm. (**1c**): δ 0.9 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.4 (sext, 4H, CH_2Me), 1.7 (q, 4H, CH_2Et), 3.9 (t, 4H, CH_2O), 6.9, 7.8 (AB, 8H, H2, H3, ^3J(HH) = 8 Hz) ppm. (**1d**): δ 0.9 (m, 6H, Me), 1.3 (m, 20H, $(CH_2)_5$), 1.8 (q, 4H, CH_2CH_2O), 4.0 (t, 4H, CH_2O, ^3J(HH) = 7 Hz), 6.9, 7.8 (AB, 8H, H2, H3, ^3J(HH) = 8 Hz) ppm. ^{13}C NMR (**1a**): δ 14.0 (Me), 22.4, 33.5, 35.7 (CH_2), 122.8, 129.1 (C2, C3), 146.2 (C4), 151.1 (C1) ppm. (**1b**): δ 14.1 (Me), 22.7, 29.3, 29.3, 29.5, 29.6, 31.3, 31.9, 35.9 (CH_2), 122.0, 122.7 (C2,C3), 146.2 (C4), 155.0 (C1) ppm. (**1c**): δ 13.9 (Me), 19.5, 31.4 (CH_2), 64.2 (CH_2O), 114.8 (C3), 124.5 (C2), 149.2 (C1), 161.2 (C4) ppm. (**1d**): δ 14.2 (Me), 22.8, 26.1, 29.3, 29.4, 29.5, 32.0 (CH_2), 64.4 (CH_2O), 114.7 (C3), 124.4 (C2), 147.0 (C1), 161.2 (C4) ppm.

3.2. [$AuCl_3$(Hbxpap)] (2)

To an acetone solution (25 ml) of **1c** (171 mg, 0.52 mmol), solid [Me_4N] [$AuCl_4$] (108 mg, 0.26 mmol) and $AgClO_4$ (54 mg, 0.26 mmol) were added. A red-purple suspension immediately formed. The solvent was removed to dryness, CH_2Cl_2 (15 ml) was added and the suspension filtered through anhydrous $MgSO_4$. The purple filtrate was then concentrated to *ca.* 1 ml and hexane added affording a purple crystalline solid. Yield (%): 20. M.p. (°C): 133. ^{1}H NMR: δ 1.0 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.5 (m, 4H, CH_2Me), 1.9 (q, 4H, CH_2Et), 4.2 (t, 4H, CH_2O, ^3J(HH) = 6 Hz), 7.2, 8.3 (AB, 8H, H2, H3, ^3J(HH) = 8 Hz) ppm. Anal. Calc. for $C_{20}H_{26}AuCl_3N_2O_2$: C, 38.1; H, 4.2; N, 4.4; Au, 31.3. Found: C, 38.2; H, 4.8; N, 4.4; Au, 30.7%.

3.3. [$Ag(OClO_3)L_2$] [L = Hbxpap (3a), Hoxpap (3b)]

To an acetone (20 ml) solution of **1c** or **1d** (1.09 mmol), solid $AgClO_4$ (0.56 mmol) was added and the mixture stirred for 30 min in the dark. The wine-red solution was then concentrated to *ca.* 2 ml and Et_2O added, affording red crystals that were filtered off and dried under vacuum. From the resultant orange solution, the unreacted azobenzenes were recovered. Yield (%): 15 (**3a**), 15 (**3b**). Transition temp. K → S 143 (**3a**), 106 (**3b**). S → I 154 (**3a**), 162 (**3b**). (K = crystal, S = smectic mesophase, I = isotropic liquid). Anal. Calc. for $C_{40}H_{52}AgClN_4O_8$ (**3a**): C 55.9; H, 6.1; N, 6.5. Found: C, 55.6; H, 5.9; N, 6.1%. Anal. Calc. for $C_{56}H_{84}AgClN_4O_8$ (**3b**): C, 61.7; H, 7.8; N, 5.1. Found: C, 62.0; H, 7.6; N, 4.7%.

3.4. [Hg(R)Cl] [R = bpap (4a), dpap (4b)]

To a suspension in MeOH, (50 ml) of the appropriate azobenzene **1a–b** (28 mmol), solid [$Hg(OAc)_2$] (28 mmol) was added and the mixture stirred under reflux for 24 h. The suspension was then allowed to cool to room temperature and LiCl (60 mmol) added, affording an orange precipitate. Addition of water (250 ml) gave a yellow-orange precipitate that was filtered and washed with hexane until the extracts were colourless. The resultant solid was then Soxhlet extracted with Et_2O. Removal of the solvent afforded orange crystals. Yield (%): 63 (**4a**), 60 (**4b**). M.p. (°C): 131 (**4a**), 95 (**4b**). ^{1}H NMR (**4a**): δ 1.0 (t, 3H, Me, ^3J(HH) = 10 Hz), 1.5 (sext, 4H, CH_2Me), 1.6 (q, 4H, CH_2Et), 2.6 (t, 4H, $CH_2C_6H_4$, ^3J(HH) = 9 Hz), 7.3, 8.0 (AB, 4H, H8, H9, ^3J(HH) = 8 Hz), 7.3 (m, 2H, H4, H3), 8.0 (s, 1H, H6) ppm. (**4b**): δ 0.9 (m, 6H, Me), 1.3 (m, 28H, $(CH_2)_7$), 1.6 (m, 4H, $CH_2CH_2C_6H_4$), 2.7 (m, 4H, $CH_2C_6H_4$), 7.3,

8.0 (AB, 4H, H8, H9, ^3J(HH) = 8 Hz), 7.3 (m, 2H, H3, H4), 8.0 (s, 1H, H6) ppm. Anal. Calc. for $C_{20}H_{25}ClH_9N_2$ (**4a**): C, 47.5; H, 2.0; N, 5.5. Found: C, 48.2; H, 2.2; N, 6.1. Anal. Calc. for $C_{32}H_{49}ClHgN_2$ (**4b**): C, 55.1; H, 7.1; N, 4.0. Found: C, 55.0; H, 6.9; N, 4.0%.

3.5. [Hg(R)Cl] [R = bxpap (4c), oxpap (4d)]

To a suspension in MeOH (50 ml) of the appropriate azobenzene (**1c–d**) (28 mmol), solid $[Hg(O_2CCF_3)_2]$ (28 mmol) was added and the mixture stirred under reflux for 24 h. The suspension was allowed to cool to room temperature and LiCl (60 mmol) added affording an orange precipitate. Addition of water (250 ml) gave a yellow-orange precipitate that was filtered and washed with hexane until the extracts were colourless. The resultant solid was then Soxhlet extracted with Et_2O. Removal of the solvent afforded orange crystals. Yield (%) 25 (**4c**), 20 (**4d**). M.p. (°C): 195 (**4c**), 155. ^{1}H NMR (**4c**): δ 1.0 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.5–1.6 (m, 4H, CH_2Me), 1.8 (m, 4H, CH_2Et), 4.0 (t, 4H, CH_2O), 6.9–7.0 (m, 4H, H8, H9), 7.8 (d, 2H, H3, H4), 8.0–8.1 (m, 1H, H6) ppm. (**4d**) (d_6-acetone): δ 0.9 (t, 6H, Me, ^3J(HH) = 8 Hz), 1.3 (m, 16H, CH_2), 1.5 (m, 4H, $CH_2CH_2CH_2O$), 1.8 (q, 4H, CH_2CH_2O), 4.2 (t, 4H, CH_2O), 6.8–7.3 (m, 4H, H8, H9), 8.1 (m, 3H, H3, H4, H6) ppm. Anal. Calc. for $C_{20}H_{25}ClHgN_2O_2$ (**4c**): C, 42.8; H, 4.5; N, 5.0. Found: C, 42.2; H, 4.4; N, 5.2%. Anal. Calc. for $C_{28}H_{41}ClHgN_2O_2$ (**4d**): C, 49.9; H, 6.1; N, 4.2. Found: C, 50.4; H, 6.3; N, 4.5%.

3.6. [Hg(R)$_2$] [R = bpap (5a), dpap (5b), bxpap (5c)]

To an acetone (50 ml) solution of (**4a–c**) (5.0 mmol), solid NaI (50 mmol) was added and the mixture stirred for 4 h. Removal of the solvent to dryness and addition of water (150 ml) gave an orange precipitate that was dried under vacuum and recrystallized from CH_2Cl_2/hexane (1:5). Yield (%): 50 (**5a**), 53 (**5b**), 36 (**5c**). M.p. (°C): 138 (**5a**), 131 (**5b**), 193 (**5c**). ^{1}H NMR (**5a**): δ 0.8–1.1 (m, 12H, Me), 1.2–1.8 (m, 16H, CH_2Me), 2.6 (m, 4H, $CH_2CH_2C_6H_4$), 2.7 (t, 4H, $CH_2C_6H_4$, ^3J(HH) = 10 Hz), 7.1, 7.6 (AB, 8H, H8, H9, ^3J(HH) = 8 Hz), 7.3 (m, 4H, H3, H4), 8.0 (s, 2H, H6) ppm. (**5b**): δ 0.8 (t, 12H, Me, ^3J(HH) = 7 Hz), 1.2 (m, 56H, CH_2), 1.6 (m, 8H, $CH_2CH_2C_6H_4$), 2.6 (m, 8H, $CH_2C_6H_4$), 7.2–7.3 (m, 8H, H8, H9), 7.8 (d, 4H, H3, H4), 7.9–8.0 (m, 2H, H6) ppm. (**5c**): δ 0.9–1.0 (m, 12H, Me), 1.5–1.6 (m, 8H, CH_2Me), 1.8 (m, 4H, CH_2Et), 1.8 (m, 4H, CH_2Et), 3.9 (t, 4H, CH_2O, ^3J(HH) = 7 Hz), 4.1 (t, 4H, CH_2O, ^3J(HH) = 7 Hz), 6.8, 7.6 (AB, 8H, H8, H9, ^3J(HH) = 8 Hz), 7.0 (m, 4H, H3, H4), 7.9 (m, 1H, H6), 8.1 (d, 1H, H6) ppm. ^{13}C NMR (**5a**): δ 14.0, 14.1 (Me), 22.4, 22.4, 33.5, 33.7, 35.6, 36.0 (CH_2), 122.8 (C9), 129.1 (C8), 128.6, 129.4, 139.2 (C3, C4, C6), 145.9, 146.6, 150.3 (C5, C10, C1), 158.0, 159.0 (C2, C7) ppm. (**5b**): δ 14.1 (Me), 22.7, 29.2, 29.3, 29.5, 29.6, 29.7, 31.2, 31.9, 35.9 (CH_2), 123.2 (C9), 128.5, 129.9, 137.4 (C3, C4, C6), 129.4 (C8), 147.5, 148.5, 149.1 (C5, C10, C1), 151.0, 153.0 (C2, C7) ppm. (**5c**): δ 14.0 (Me), 19.3, 19.4, 31.3, 31.5 (CH_2), 67.9, 68.0 (CH_2O), 113.8, 114.0, 131.2 (C3, C4, C6), 114.8, 124.4 (C8, C9), 147.7, 154.0 (C2, C7), 159.6, 160.9, 161.5 (C5, C10, C1) ppm. Anal. Calc. for $C_{40}H_{50}HgN_4$ (**5a**): C, 61.0; H, 6.4; N, 7.1. Found: C, 60.3; H, 6.3; N, 6.9%. Anal. Calc. for $C_{64}H_{96}HgN_4$ (**5b**): C, 68.5; H, 8.6; N, 5.0. Found: C, 67.6; H, 8.0; N, 5.0%. Anal. Calc. for $C_{40}H_{50}HgN_4O_4$ (**5c**): C, 56.4; H, 5.9; N, 6.6. Found: C, 55.6; H, 5.9; N, 6.1%.

3.7. [Au(η^2 – R)Cl$_2$] [R = bpap (6a), bxpap (6b)]

3.7.1. Method a

To an acetone (50 ml) solution of $[Me_4N]$ $[AuCl_4]$ (0.28 mmol) $[HgR_2]$ (**5a–b**) (0.14 mmol) and Me_4NCl (0.28 mmol) were added. The suspension was stirred for 17 h, the solvent removed to dryness and the residue extracted with CH_2Cl_2 (4 × 5 ml) and filtered through anhydrous $MgSO_4$. The deep red solution was then concentrated to *ca.* 2 ml and Et_2O (20 ml) added, affording a crimson solid that was recrystallized for CH_2Cl_2/Et_2O (1:5). Yield (%): 75 (**6a**), 70 (**6b**). M.p. (°C) 137 (**6a**), 146 (**6b**). ^{1}H NMR (**6a**): δ 0.9 (t, 6H, Me, ^3J(HH) = 7 Hz), 1.4 (m, 4H, CH_2Me), 1.6 (m, 4H, CH_2Et), 2.7 (m, 4H, $CH_2C_6H_4$), 7.4 (m, 3H, H4, H9), 7.7 (s, 1H, H3), 7.8 (d, 2H, H8, ^3J(HH) = 8 Hz), 8.0 (d, 1H, H6) ppm. (**6b**): δ 0.9 (t, 3H, Me, ^3J(HH) = 7 Hz), 1.0 (t, 3H, Me, ^3J(HH) = 7 Hz), 1.5, 1.6 (m, 4H, CH_2Me), 1.8 (m, 4H, CH_2Me), 4.0 (t, 3H, CH_2O, ^3J(HH) = 8 Hz), 4.1 (t, 2H, CH_2O, ^3J(HH) = 8 Hz, 7.0, 7.8 (AB, 4H, H8, H9, ^3J(HH) = 8 Hz), 7.4 (m, 2H, H3, H4), 8.0 (d, 1H, H6) ppm. ^{13}C NMR (**6a**): δ 13.8, 13.9 (Me), 22.4, 22.4 (CH_2Me), 32.9, 33.1 (CH_2), 35.6, 37.1 ($CH_2C_6H_4$), 125.2 (C9), 128.4 (C8), 130.1, 132.0, 132.1 (C3, C4, C6), 147.2, 148.9 (C5, C10), 154.5 (C1), 159.8, 160.0 (C2, C7) ppm. (**6b**): δ 13.8, 13.9 (Me), 19.2, 19.2 (CH_2Me), 31.0, 31.2 (CH_2), 68.4, 69.7 (CH_2O), 114.0, 127.1 (C8, C9), 115.9, 118.1, 133.5 (C3, C4, C6), 142.8 (C1), 155.0, 162.5 (C2, C7), 163.2, 164.2 (C5, C10) ppm. Anal. Calc. for $C_{20}H_{25}AuCl_2N_2$ (**6a**): C, 42.5; H, 4.5; N, 5.0; Au, 35.1. Found: C, 42.6; H, 5.0; N, 4.3; Au, 34.9%. Anal. Calc. for $C_{20}H_{25}AuCl_2N_2O_2$ (**6b**): C, 40.5; H, 4.2; N, 4.7; Au, 33.2. Found: C, 40.5; H, 4.2; N, 4.6; Au, 33.0%.

3.7.2. Method b

To an acetone solution of $[Me_4N]$ $[AuCl_4]$ (0.13 mmol), solid [Hg(R)Cl] (**4a–b**) (0.13 mmol), and $[Me_4N]Cl$ (0.14 mmol) were added. Workup as above gave (**6a–b**). Yield (%): 65 (**6a**), 60 (**6b**).

3.8. $Me_4N[Au(dpap)Cl_3]$ (7)

To an acetone (30 ml) solution of $[AuCl_3(tht)]$ (100 mg, 0.25 mmol), solid **4b** (175 mg, 0.25 mmol) and $[Me_4N]Cl$ (55 mg, 0.50 mmol) were added and the mixture stirred for 72 h. The solvent was removed to dryness and the residue extracted with CH_2Cl_2 (5 × 5 ml) and filtered through anhydrous $MgSO_4$. Concentration to *ca.* 1 ml, and addition of Et_2O (20 ml) gave an orange precipitate. Yield (%): 60. M.p. (°C): 118. ^1H NMR: δ 0.9 (t, 6H, Me, $^3J(HH) = 6$ Hz), 1.3 (m, 28H, $(CH_2)_7$, 1.7 (m, 4H, $CH_2CH_2C_6H_4$), 2.8 (m, 4H, $CH_2C_6H_4$), 3.4 (s, 12H, Me_4N), 7.4 (m, 3H, H9, H3), 7.7 (m, 1H, H4), 7.8 (d, 2H, H8, $^3J(HH) = 8$ Hz), 8.0 (d, 1H, H6, $J(HH) = 8$ Hz) ppm. Anal. Calc. for $C_{36}H_{61}AuCl_3N_3$: C, 51.5; H, 7.3; N, 5.0; Au, 23.5. Found: C, 51.4; H, 7.5; N, 4.4; Au, 22.9%.

3.9. [Au (η^2-R) {$CH_2C(O)Me$}Cl] [R = bpap (8a), bxpap (8b)]

To an acetone (25 ml) solution of (**6a–b**) (0.12 mmol), solid $AgClO_4$ (0.12 mmol) was added. After 2 h, the solvent was removed to dryness and the residue extracted with CH_2Cl_2 (3 × 5 ml) and filtered through anhydrous $MgSO_4$. Evaporation to *ca.* 1 ml and addition of hexane (15 ml) gave a brick-red precipitate. Yield: 72 (**8a**), 70 (**8b**). M.p. (°C): 120 (**8a**), 151 (**8b**). ^1H NMR (**8a**): δ 0.9 (two t, 6H, Me, $^3J(HH) = 7$ Hz), 1.3 (m, 4H, CH_2Me), 1.6 (m, 4H, CH_2Et), 2.3 (s, 3H, MeCO), 2.6 (t, 2H, $CH_2C_6H_4$, $^3J(HH) = 8$ Hz), 2.7 (t, 2H, $CH_2C_6H_4$, $^3J(HH) = 8$ Hz), 3.4 (s, 2H, CH_2CO), 7.2 (m, 2H, H3, H4), 7.3, 7.8 (AB, 4H, H8, H9, $^3J(HH) = 8$ Hz), 7.9 (d, 1H, H6, $J(HH) = 7$ Hz) ppm. (**8b**): δ 1.0 (m, 6H, $MeCH_2$), 1.5 (m, 4H, CH_2Me), 1.8 (m, 4H, CH_2Et), 2.4 (s, 3H, MeCO), 3.4 (s, 2H, CH_2CO), 4.0 (t, 2H, CH_2O, $^3J(HH) = 6$ Hz), 4.2 (t, 2H, CH_2O, $^3J(HH) = 6$ Hz), 6.9 (m, 1H, H3), 7.6 (d, 1H, H4, $^3J(HH) = 2$ Hz), 7.0, 7.9 (AB, 4H, H8, H9, $^3J(HH) = 9$ Hz), 8.0 (d, 1H, H6, $J(HH) = 7$ Hz) ppm. ^{13}C NMR (**8a**): δ 14.0 ($MeCH_2$), 22.4 (CH_2Me), 31.2 ($MeCO$), 33.2, 33.3, 35.7, 36.7 (CH_2), 38.7 (CH_2CO), 124.7, 128.9 (C8, C9), 129.0, 132.0, 132.5 (C3, C4, C6), 147.9, 148.0, 148.2 (C5, C10, C1), 152.6, 160.2 (C2, C7), 207.7 (CO) ppm. (**8b**): δ 13.91 ($MeCH_2$), 19.3, 19.3 (CH_2Me), 31.0, 31.1, 31.3 ($CH_2Et + MeCO$), 38.5 (CH_2CO), 68.3, 69.1 (CH_2O), 114.3, 126.3 (C8, C9), 114.7, 118.0, 133.6 (C3, C4, C6), 143.9 (Cl), 150.8, 155.5 (C2, C7), 162.0, 164.1 (C5, C10), 208.3 (CO) ppm. Anal. Calc. for $C_{23}H_{30}AuClN_2O$ (**8a**): C, 47.4; H, 5.2; N, 4.8; Au, 33.8. Found: C, 47.6; H, 5.3; N, 5.0; Au, 33.6%. Anal. Calc. for $C_{23}H_{30}AuClN_2O_3$ (**8b**): C, 44.9; H, 4.9; N, 4.5; Au, 32.0. Found: C, 45.5; H, 5.3; N, 4.4; Au, 32.2%.

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