

Luminescent gold(I) metallo-acids and their hydrogen bonded supramolecular liquid crystalline derivatives with decyloxystilbazole as hydrogen acceptor†‡

Silverio Coco,* Carlos Cordovilla, Cristina Domínguez and Pablo Espinet*

Received 7th July 2008, Accepted 2nd October 2008

First published as an Advance Article on the web 14th November 2008

DOI: 10.1039/b811482j

Gold complexes of 4-isocyanobenzoic acid, $[\text{AuX}(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]$ ($\text{X} = \text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}$, C_6F_5 , $\text{C}_6\text{F}_4\text{OC}_6\text{H}_{13}$, $\text{C}_6\text{F}_4\text{C}_6\text{F}_4\text{Br}$) and $[(\mu-4,4'-\text{C}_6\text{F}_4\text{C}_6\text{F}_4)\{\text{Au}(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})\}_2]$, have been isolated. These metallo-acids are luminescent. The single crystal X-ray diffraction study of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]_\infty$ confirms a rod-like structure of the molecule, with a linear coordination around the gold atom, which extends into a supramolecular entity supported by hydrogen bond, gold-gold, and fluorophilic ($\text{F}_{\text{ortho}} \cdots \text{F}_{\text{meta}}$) interactions. The carboxylic acid group of the gold isocyanide complexes acts also as a hydrogen donor towards the hydrogen acceptor decyloxystilbazole, affording some hydrogen-bonded supramolecular liquid crystals.

Introduction

Isocyanide complexes of transition metals constitute a large family that includes a variety of geometries.^{1,2} They are of current interest in many areas such as catalysis,^{3,4} materials science,⁵ supramolecular chemistry,⁶ synthesis of carbene complexes,⁷ and radiodiagnosis.⁸ Among the rich diversity of metal isocyanide compounds reported, an interesting type is that of derivatives of CNR isocyanides where R contains a second functional group, making the isocyanide a bifunctional ligand. A number of bifunctional isocyanides and their metal complexes have been reported,^{2,9} including hydroxyalkyl isocyanides,¹⁰ substituted arylisocyanides ($2\text{-OH}-\text{C}_6\text{H}_4\text{NC}$,¹¹ $2,6\text{-(OH)}_2-\text{C}_6\text{H}_4\text{NC}$,² $2\text{-(CH}_2\text{X)}-\text{C}_6\text{H}_4\text{NC}$ ($\text{X} = \text{PPh}_3$,⁹ OSiMe_3 , OH ,¹² N_3 ,¹³ $\text{CpCr}(\text{CO})_3$ or $\text{CpW}(\text{CO})_3$),¹⁴ alkynylaryl isocyanides,¹⁵ pyridylethynylaryl isocyanides,⁶ and 4-isocyanobenzylidene-4-alkoxyarylimines.¹⁶ The interesting 4-isocyanobenzoic acid was reported about fifty years ago.¹⁷ Surprisingly, its chemistry remained unexplored until recently, when we prepared examples of stable gold, palladium and platinum complexes with this unusual isocyanide ligand. These complexes are metallo-acids and can act as hydrogen donors to decyloxystilbazole through the carboxylic acid group, giving rise to supramolecular complexes that display liquid crystalline properties.¹⁸ There are many reports on the effects of intermolecular hydrogen bonding in the field of organic liquid crystals,^{19–21} but only a few cases in the field of metal-containing liquid crystals (metallomesogens),²² namely some hydrogen-bonded ferrocene complexes,^{23,24} a few phenanthroline copper derivatives,²⁵ and the metal complexes of 4-isocyanobenzoic acid just discussed. It might be expected that these metallo-acid complexes should dimerize by H-bridging, as is common for organic carboxylic acids, but this could not be proved by X-ray diffraction. The

only single crystal X-ray diffraction structure of these derivatives is that of the polymeric $[\text{trans-}[\text{PdI}_2(\text{CNC}_6\text{H}_4\text{COOH})_2] \cdot (\mu\text{-O, O-dioxane})]_\infty$, which shows that each oxygen of dioxane is hydrogen bonded to one of the carboxylic groups of the adjacent $\text{trans-}[\text{PdCl}_2(\text{CNC}_6\text{H}_4\text{COOH})_2]$ molecules.

Gold(I) complexes, including gold isocyanide derivatives are frequently luminescent, often displaying auropilic interactions and showing Au-based luminescence.²⁶ The energy of the attractive auropilic interactions ($6\text{--}11 \text{ kcal mol}^{-1}$) is comparable to that of hydrogen bonding in carboxylic acids ($7.4 \text{ kcal mol}^{-1}$),^{27,28} and can control the supramolecular structure and dimensionality.²⁹ On these grounds we decided to extend the study of gold complexes of 4-isocyanobenzoic acid and their hydrogen-bonded derivatives, hoping that the competition or cooperation of auropilicity and hydrogen bonding might modify the properties of the system and generate interesting structural cases. In effect, the crystal structure of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{COOH})]_\infty$ reported here shows the participation, in the formation of a supramolecular structure, of auropilic interactions, fluorophilic interactions, and hydrogen bonding. The latter is structurally similar to the bonding found in dimers of purely organic carboxylic acids.

Results and discussion

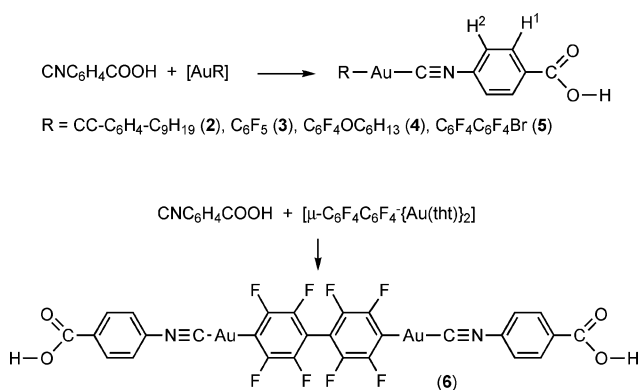
Synthesis and characterization

In order to handle thermally stable gold organometallic complexes, according to the intention to eventually produce thermotropic liquid crystals, alkynyl and fluoroaryl radicals were chosen, which are well known to produce fairly stable Au–C bonds. The reaction of $[\text{CNC}_6\text{H}_4\text{CO}_2\text{H}]$ with $[\text{Au}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19})]_n$ in THF gives the white complex $[\text{Au}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19})(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]$ (**2**). On the other hand, the reactions of 4-isocyanobenzoic acid with $[\text{AuR}(\text{tht})]$ ($\text{R} = \text{C}_6\text{F}_5$, $\text{C}_6\text{F}_4\text{OC}_6\text{H}_{13}$, $\text{C}_6\text{F}_4\text{C}_6\text{F}_4\text{Br}$; tht = tetrahydrothiophene) and $[(\mu-4,4'-\text{C}_6\text{F}_4\text{C}_6\text{F}_4)\{\text{Au}(\text{tht})\}_2]$ in THF afforded the white complexes $[\text{AuR}(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]$ ($\text{R} = \text{C}_6\text{F}_5$ (**3**), $\text{C}_6\text{F}_4\text{OC}_6\text{H}_{13}$ (**4**), $\text{C}_6\text{F}_4\text{C}_6\text{F}_4\text{Br}$ (**5**)) and $[(\mu-4,4'-\text{C}_6\text{F}_4\text{C}_6\text{F}_4)\{\text{Au}(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})\}_2]$ (**6**) respectively, as summarized in Scheme 1.

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071, Valladolid, Castilla y León, Spain. E-mail: espinet@qi.uva.es; Tel: +34 983423231

† This paper is dedicated to the memory of Naomi Hoshino-Miyajima. Her lasting contributions to science will keep her name alive.

‡ CCDC reference number 693068. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b811482j



Scheme 1 Synthesis of isocyanide gold complexes.

C, H, N analyses for the complexes, yields, and relevant IR and NMR data are given in the Experimental section. The IR spectra of 2–6 are all similar and exhibit one $\nu(\text{C}\equiv\text{N})$ absorption for the isocyanide group at higher wavenumbers (*ca.* 90 cm^{-1}) than for the free ligand, as reported for similar gold aryl isocyanide compounds.^{30,31} Note that for the alkynyl derivative (2) the expected $\nu(\text{C}\equiv\text{C})$ absorption is not observed, but this happens very often.³² In addition, all the complexes display $\nu(\text{C}=\text{O})$ (1695 cm^{-1}) and $\nu(\text{O}-\text{H})$ (2925 cm^{-1}) bands in the same region of the free isocyanide ligand.¹⁸

The ^1H and ^{19}F NMR spectra of the complexes were recorded in THF- d_8 , due to their low solubility in CDCl_3 or acetone- d_6 . This low solubility suggests that the solvent needs to split hydrogen bonded dimers in the solid state to get the compound dissolved. Their ^1H NMR spectra show, as expected, two resonances from aryl protons of the isocyanide ligand (AA'XX' spin system). Coordination produces a deshielding for H¹ (*ca.* 0.1 ppm) and H² (*ca.* 0.3 ppm) of the isocyanide. This suggests that coordination reduces the electron density on the aromatic ring, enhancing the acid character of the carboxylic group. Consistent with this, the observation of the acidic H (which is probably interacting with the oxygen atoms of the solvent) required cooling down to 230 K in order to observe a very broad signal at 12.3 ppm for complex 4. Complex 2 shows, in addition, two signals for the aromatic protons of the alkynyl ligand present in the molecule.

The ^{19}F NMR spectra of the complexes show the typical patterns of the corresponding perhalophenyl group. Thus, the C₆F₅ derivatives display the three resonances expected from an AA'MXX' spin system.³⁰ The C₆F₄OC₆H₁₃ complex shows two somewhat distorted “doublets” flanked by two pseudotriplets (strictly an AA'XX' spin system with $J_{\text{AA}'} \approx J_{\text{XX}'}).³¹ The ^{19}F NMR spectra of the 4,4'-octafluorobiphenyl compound show two complex multiplets at *ca.* –117 ppm and –140 ppm, corresponding to F_{ortho} and the F_{meta} , as reported for similar complexes.³⁰ Analogously, the C₆F₄C₆F₄Br derivative shows the four resonances expected from two AA'XX' spin systems.$

The molecular structure of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{COOH})]_n$ was determined by single-crystal X-ray diffraction methods. An ORTEP view of the repeating monomer is given in Fig. 1a. Table 1 collects the data collection and refinement parameters. The compound crystallizes in the monoclinic space group $P2_1/c$, with four formula units in the unit cell. The gold atom has a linear coordination defined by the isocyanide and the pentafluorophenyl groups. The bond angle C(1)–Au(1)–C(9) is 177.1(2)° and the

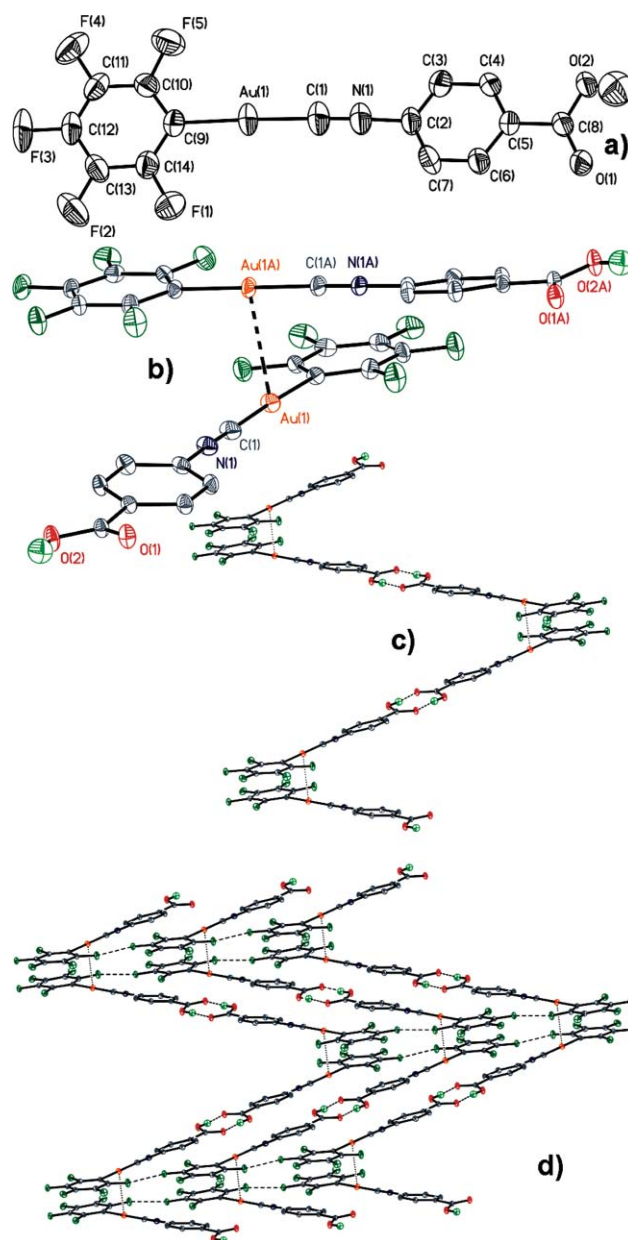


Fig. 1 (a) Crystal structure of 3 with the atom-numbering scheme (displacement ellipsoids at the 50% probability level). (b) Pairs of molecules linked by Au...Au aurophilic interactions. (c) Polymeric chain of molecules supported by hydrogen bonding and Au...Au interactions. (d) Extended network formed by intermolecular hydrogen bonding and Au...Au aurophilic interactions (dotted lines), producing polymeric chains packed to give rise to $F_{\text{ortho}} \cdots F_{\text{meta}}$ fluorophilic contacts (short dashes).

bond distances fall within normal ranges (Fig. 1a). There is a short intermolecular aurophilic interaction ($\text{Au}(1) \cdots \text{Au}(2) = 3.0674(19) \text{ \AA}$) which leads to pairs of molecules with a dihedral angle C(1)–Au(1)–Au(2)–C(2) = 83.76° (Fig. 1b). The isocyanide ligands of neighbouring dimers are linked through hydrogen bonding in one of the typical ways found for carboxylic acids,³³ giving rise to the polymeric chains shown in Fig. 1c. None of the OH hydrogen atoms was located in a difference Fourier map, so their positions were calculated with a riding model. The

Table 1 X-Ray data and data collection and refinement parameters for $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{COOH})]_\infty$ (**3**)

Empirical formula	$\text{C}_{14}\text{H}_5\text{F}_5\text{NO}_2\text{Au}$
FW	511.16
Cryst. system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	13.430(8)
$b/\text{\AA}$	7.756(5)
$c/\text{\AA}$	13.435(9)
$\beta/^\circ$	96.653(11)
$V/\text{\AA}^3$	1390.1(15)
Z	4
$D_{\text{calc}}/\text{g cm}^{-3}$	2.442
μ/mm^{-1}	10.648
$F(000)$	944
Cryst. size/mm	$0.19 \times 0.18 \times 0.05$
T/K	298(2)
θ range for data colln/ $^\circ$	1.53–28.45
$\lambda/\text{\AA}$	0.71073
Index ranges	$-18 \leq h \leq 17$, $-10 \leq k \leq 10$, $-17 \leq l \leq 17$
Reflns collcd	13626
Indpdt reflns	3498 [$R(\text{int}) = 0.0449$]
Completeness to θ	28.45 (99.7%)
Abs corr.	SADABS
Max. and min. transm	1.000000 and 0.408121
Data/restraints/params	3498/0/208
Goodness-of-fit on F^2	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0280$, $wR_2 = 0.0628$
R_{int} indices (all data)	$R_1 = 0.0409$, $wR_2 = 0.0679$
Largest diff. peak and hole/ e \AA^{-3}	0.529 and -1.011

distance $\text{O} \cdots \text{O}$ is 2.620(6) \AA ; after correction for a plausible O-H bond length (0.97 \AA based on neutron diffraction results),³⁴ the estimated $\text{H} \cdots \text{O}$ distance is 1.666(6) \AA and the $\text{O-H} \cdots \text{O}$ angle 168.4(4) $^\circ$. Within each chain the molecules are parallel to each other (Fig. 1d), and are connected by short intermolecular $\text{F}_{\text{ortho}} \cdots \text{F}_{\text{meta}}$ distances (2.651 \AA). Each molecule uses one F_{ortho} and one F_{meta} for these connections. The short intermolecular $\text{F}_{\text{ortho}} \cdots \text{F}_{\text{meta}}$ distances are consistent with intermolecular $\text{F} \cdots \text{F}$ interactions, as calculated for a similar complex,³⁵ and seem to be a factor influencing the packing motif observed.

Hydrogen-bonded decyloxystilbazole complexes

The hydrogen-bonded decyloxystilbazole complexes were prepared by dissolving together equimolar proportions of the corresponding gold complexes **2–6** and decyloxystilbazole in THF at room temperature. Evaporation of the solvent in vacuum afforded **2a–6a** (Scheme 2). All the supramolecular complexes

were isolated as yellow solids, in contrast to the white parent compounds.

The formation of the supramolecular hydrogen-bonded decyloxystilbazole complexes (**2a–6a**) was confirmed by IR spectroscopy. Their infrared spectra in the solid state (KBr) do not show the $\nu(\text{O-H})$ absorption of the precursors at *ca.* 2925 cm^{-1} , instead very broad bands at *ca.* 2500 and 1900 cm^{-1} are observed. The carbonyl stretching absorption bands appear shifted at higher frequencies (*ca.* 10 cm^{-1}) from their positions in the parent complexes. Moreover the pyridyl $\nu(\text{CN})$ band increases from 1590 to 1600 cm^{-1} upon complexation.³⁶ These data support that hydrogen-bond self-association of the metallo-acid precursors through the carboxylic acid group is replaced by hydrogen-bond formation to the decyloxystilbazole, as reported for similar chloro-gold complexes,¹⁸ and for organic compounds of benzoic acid with decyloxystilbazole.^{19a}

Mesogenic behaviour

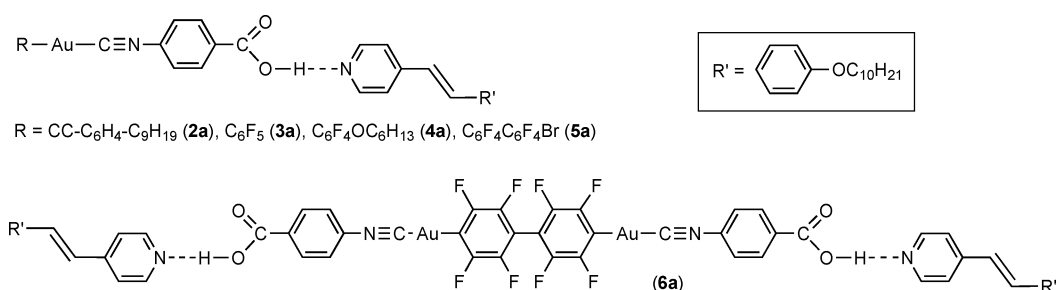
Compounds **2–6** are not mesomorphic and decompose above 200 $^\circ\text{C}$ (120 $^\circ\text{C}$ for **2**) without melting. The decyloxystilbazole used in this work displays a smectic E phase in the range 83–85 $^\circ\text{C}$.^{37,38} The supramolecular compounds **2a–6a** were investigated by DSC and by hot-stage polarized optical microscopy. Their optical, thermal and thermodynamic data are collected in Table 2.

Three out of the five hydrogen-bonded decyloxystilbazole compounds studied display enantiotropic mesophases. Complex **2a** decomposes without melting. The binuclear derivative **6a** decomposes at the melting temperature of the free

Table 2 Optical, thermal and thermodynamic data of decyloxystilbazole complexes

Compound	Transition ^a	Temperature ^b ($^\circ\text{C}$)	ΔH ^b (kJ mol^{-1})
2a	$\text{C} \rightarrow \text{dec}$	150 ^d	
3a	$\text{C} \rightarrow \text{C}'$	79	1.9
	$\text{C}' \rightarrow \text{C}''$	84	1.8
	$\text{C}'' \rightarrow \text{SmC}$	128	12.6
	$\text{SmC} \rightarrow \text{I}$	187 ^d	
4a	$\text{C} \rightarrow \text{C}'$	39	1.9
	$\text{C}' \rightarrow \text{SmC}$	127	21.4
	$\text{SmC} \rightarrow \text{I}$	190 ^d	
5a	$\text{C} \rightarrow \text{SmC}$	160	25.9
	$\text{SmC} \rightarrow \text{I}$	170 ^d	
6a	$\text{C} \rightarrow \text{C}'$	45	−4.8
	$\text{C} \rightarrow \text{I}$	86	186.8 ^c

^a C, crystal; Sm, smectic; I, isotropic liquid. ^b Data referred to the first DSC cycle starting from the crystal. ^c Combined enthalpies. ^d Microscopic data.

**Scheme 2** Supramolecular complexes prepared with decyloxystilbazole.

decyloxystilbazole, and gives immediately an isotropic liquid. The complexes that are mesogens (**3a**, **4a** and **5a**) have a rod-like structure and give rise to SmC mesophases. These have been optically identified by the typical schlieren texture (Fig. 2),³⁹ and by the fact that it is not possible to obtain either homeotropic regions or brownian flashes under mechanical stress.

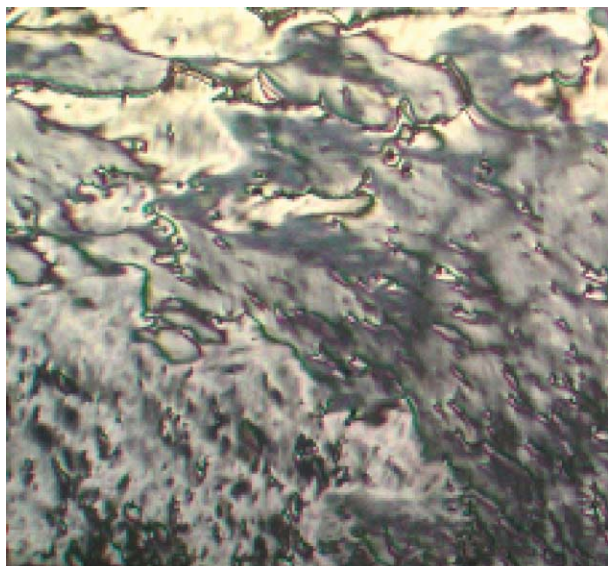


Fig. 2 Polarized optical microscopic texture ($\times 100$) observed for **5a**. The picture shows the schlieren texture of the SmC phase, on heating from the crystal at 165 °C.

DSC heating and cooling cycles of **3a**, **4a**, and **5a**, show the corresponding melting and crystallization transitions (see Fig. 3 for **4a**), while transitions associated to free stilbazole are not observed. The same behaviour is observed in a second heating, which supports the thermal stability of the supramolecular complexes with stilbazole in the mesophase. When the temperature is raised, an apparent clearing point is reached (Table 2) where the formation of some crystals is observed (probably associated with this, these “clearing points” are not detected by DSC). The “clearing” transition is not reversible. This indicates that the “clearing”

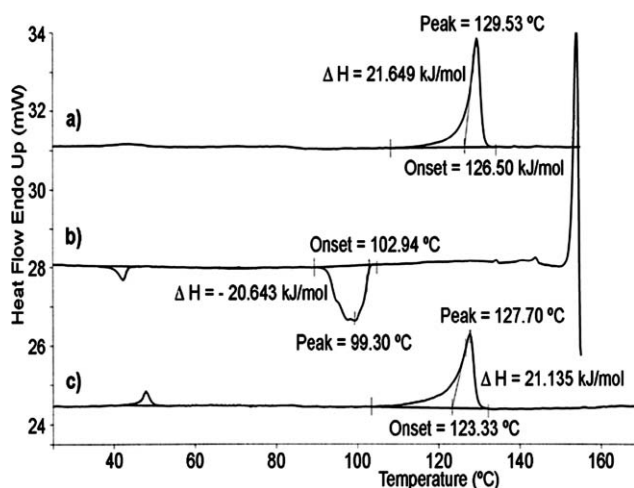


Fig. 3 DSC scans of **4a**: (a) first heating, (b) first cooling and (c) second heating.

Table 3 UV-visible data of the free isocyanide and the gold complexes

Compound	λ^b/nm ($\epsilon^c/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)		
1^a	241 (16525)		
2	260 (35100)	272 (34500)	
3	259 (31988)	269 (sh) (24400)	
4	252 (34617)	276 (sh) (23200)	
5	261 (53614)	268 (sh) (44900)	
6	263 (65662)	282 (65410)	
1a	235 (37593)		325 (24868)
2a	256 (42700)	287 (42552)	325 (46290)
3a	237 (39062)	274 (26800)	326 (29972)
4a	242 (41065)	285 (31909)	326 (34186)
5a	260 (47600)	276 (42200)	326 (30600)
6a	231 (71000)		326 (136642)

^a Free isocyanide ligand. ^b In THF. ^c Apparent molar absorptivity.

transformation is not properly a phase transition without chemical change, but a collapse of the initial supramolecular structure, due to the thermal lability of the hydrogen bond. The kind of change was not investigated in detail but, since free stilbazole was not detected in the samples cooled from the isotropic liquid, it is likely that at the clearing point the supramolecular complex rearranges to the stilbazolinium salt of the metallocarboxylate complex, as reported for similar supramolecular organic liquid crystals.^{19e}

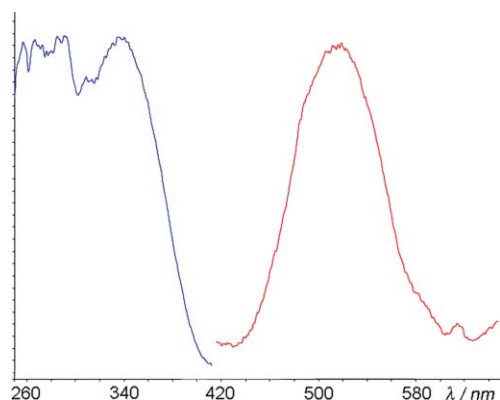
Photophysical studies

The electronic spectra of the free isocyanide and the gold(I) complexes are summarized in Table 3. The electronic spectra are all very similar, and show one absorption maximum at *ca.* 260 nm, in tetrahydrofuran solution. These wavelengths, and the large extinction coefficients of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$, are typical, in all cases studied, of ligand-centred $\pi-\pi^*$ transitions of aromatic groups. Thus the free isocyanide shows a strong UV absorption at 241 nm which is assigned to a $\pi-\pi^*$ transition in the phenyl system, as reported for phenyl isocyanides.⁴⁰ This absorption undergoes a noticeable bathochromic shift upon complexation of the isocyanide ligand to gold complexes, as reported for analogous complexes $[\text{AuX}(\text{CN}(o\text{-xyly}))]$.⁴¹ The UV spectra of the supramolecular stilbazole complexes in solution display the absorption maxima of the parent components, including a strong band at 325 nm corresponding to decyloxystilbazole.⁴²

Luminescence spectroscopic data for the gold complexes and the free isocyanide ligand are listed in Table 4. The free isocyanide is luminescent at room temperature in THF solution and shows a broad emission band at 320 nm. In the solid state (KBr pellets) the luminescence is not lost, but its intensity decreases noticeably as described for other isocyanides.⁴³ The gold compounds **2–6** are luminescent at room temperature. In the solid state they exhibit an “electric-blue” luminescence visually observed under UV irradiation at 365 nm. All the emission spectra are similar and consist of one strong emission band with the maximum in the range 494–523 nm (Fig. 4). The lifetimes measured for the complex **3** in the solid state is 13 μs , supporting a phosphorescent nature of the emission.⁴⁴ In THF solution, although the luminescence is not lost, its intensity decreases noticeably and shifts to higher energy compared to the emission bands in the solid state. This effect is usually observed in the emission spectra of Au(I) complexes and supports that the emission bands in the solid state are

Table 4 Emission (λ_{em}) and excitation (λ_{ex}) maxima (in nm) for free isocyanide ligand and the gold complexes at 298 K

Compound	THF		KBr	
	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}
1^a	276	334	353	469
Stilbazole^b	332	396	292	410
2	274	333	388	494
3	300	332	353	516
4	302	330	344	520
5	302	328	347	523
6	301	331	353	519
1a	285	355	380	452
2a	285	366	391	465
3a	294	363	393	485
4a	332	396	394	469
5a	342	395	394	468
6a	343	393	388	467

^a Free isocyanide ligand. ^b Free stilbazole.**Fig. 4** Luminescence excitation and emission spectra of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]$ in the solid state.

associated with the presence of intermolecular $\text{Au} \cdots \text{Au}$ or π -stacking interactions.⁴⁵ Considering that the X-ray structure of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]_\infty$ shows the existence of $\text{Au} \cdots \text{Au}$ intermolecular interactions in the solid state, and its emission band is structureless, we suggest that in the solid state its luminescence is based on gold-centred phosphorescent emissions, and on ligand-localized transitions in solution, as the free ligand.

The supramolecular metal complexes with stilbazole are luminescent too, and show intense luminescence in the solid state, similar to that of the parent gold complexes. In contrast, **1a**, **2a** and **3a** display in solution what appears to be an emission band at *ca.* 350 nm, that is the average value of the emission bands of the parent components (stilbazole and the gold complex). Compounds **4a**, **5a** and **6a**, the parent gold derivatives of which show a lower emission intensity, display similar emission spectra to that of free stilbazole. This suggests that the emission spectra of the supramolecular complexes with stilbazole are approximately the result of overlapping the spectra of the two constituent complexes, revealing that the hydrogen bond in these systems has been split in THF solution.

In summary, we have prepared uncommon luminescent metallo-acids based on alkynyl or fluoroaryl gold complexes with 4-isocyanobenzoic acid. The single crystal X-ray diffraction structure of $[\text{Au}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]_\infty$ reveals that the crystal

packing is supported by the combination of three types of intermolecular interactions: $\text{Au} \cdots \text{Au}$ aurophilic interactions, hydrogen bonding between the carboxylic acid groups, and intermolecular $\text{F}_{\text{ortho}} \cdots \text{F}_{\text{meta}}$ interactions. Moreover, the reactivity of these metallo-acids with the H-acceptor decyloxystilbazole provides some stable hydrogen-bonded, liquid crystalline, supramolecular gold complexes.

Experimental

Experimental conditions for the analytical, spectroscopic and diffraction studies were as reported elsewhere.¹⁸ Literature methods were used to prepare $[\text{C}\equiv\text{NC}_6\text{H}_4\text{COOH}-p]$,¹⁸ $[\text{C}_6\text{F}_5\text{Au}(\text{tht})]$ (tht = tetrahydrothiophene),⁴⁶ $[\text{HC}_6\text{F}_4\text{OC}_6\text{H}_{13}-p]$,³¹ and $[(\mu-4,4'-\text{C}_6\text{F}_4\text{C}_6\text{F}_4)\{\text{Au}(\text{tht})\}_2]$.⁴⁷

$[\text{Au}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19})]_n$

Gold acetylide was prepared as a yellow solid as described for analogous complexes,³² starting from $[\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19}]$ (0.43 mmol). Yield: 57.25%. IR ($\text{cm}^{-1}/\text{KBr}$): $\nu(\text{C}\equiv\text{H})$: 2920, $\nu(\text{C}\equiv\text{C})$: 2850.

Preparation of $[\text{Au}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19})(\text{CNC}_6\text{H}_4\text{CO}_2\text{H})]$ (**2**)

To a mixture of $[\text{Au}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_9\text{H}_{19})]_n$ (0.50 g, 1.18 mmol) and 50 mL of dry tetrahydrofuran was added $[\text{C}\equiv\text{NC}_6\text{H}_4\text{COOH}]$ (0.17 g, 1.12 mmol). After stirring for 30 min at room temperature, the solution was filtered through Kieselguhr. The solvent was removed under vacuum and the solid obtained was washed with hexane (3×10 mL) and finally recrystallized from tetrahydrofuran/hexane to give a cream solid. Yield: 0.5 g, 74%. Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{AuNO}_2$: C, 52.57; H, 4.94; N, 2.45. Found: C, 52.32; H, 5.10; N, 2.54%. IR ($\text{cm}^{-1}/\text{KBr}$): $\nu(\text{C}\equiv\text{N})$: 2216; $\nu(\text{C}=\text{O})$: 1690. IR ($\text{cm}^{-1}/\text{THF}$): $\nu(\text{C}\equiv\text{N})$: 2211, $\nu(\text{C}=\text{O})$: 1722. ¹H NMR ($\text{THF}-d_8$): 8.2 (d, J = 8.7 Hz, 2H), 7.8 (d, J = 8.7 Hz, 2H), 7.2 (d, J = 8.3 Hz, 2H), 7.0 (d, J = 8.3 Hz, 2H), 2.5 (t, J = 7.5 Hz, 2H), 1.2–1.4 (m, 14H), 0.9 (t, J = 6.8, 3H).

$[\text{AuC}_6\text{F}_5(\text{CNC}_6\text{H}_4\text{COOH})]_\infty$ (**3**)

To a solution of $[\text{C}_6\text{F}_5\text{Au}(\text{tht})]$ (100 mg) in 40 mL of dry diethyl ether was added $[\text{CNC}_6\text{H}_4\text{COOH}]$ (35.46 mg). After stirring for 1 h at room temperature, the solvent was removed under vacuum and the solid obtained was recrystallized from THF/hexane at -15°C to give a white solid. Yield: 70.7 mg, 63%. Anal. Calcd for $\text{C}_{14}\text{H}_5\text{AuF}_5\text{NO}_2$: C, 32.88; H, 0.99; N, 2.74. Found: C, 33.05; H, 1.20; N, 2.72%. IR ($\text{cm}^{-1}/\text{KBr}$): $\nu(\text{C}\equiv\text{N})$: 2216; $\nu(\text{C}=\text{O})$: 1701. IR ($\text{cm}^{-1}/\text{THF}$): $\nu(\text{C}\equiv\text{N})$: 2220, $\nu(\text{C}=\text{O})$: 1725. ¹H NMR ($\text{THF}-d_8$): 8.2 (d, J = 8.6 Hz, 2H), 7.9 (d, J = 8.5 Hz, 2H). ¹⁹F NMR ($\text{THF}-d_8$): -116.2 (m, 1F), -159.3 (m, 2F), -163.8 (m, 2F).

$[\text{Au}(\text{C}_6\text{F}_4\text{OC}_6\text{H}_{13})(\text{C}\equiv\text{NC}_6\text{H}_4\text{COOH})]$ (**4**)

To a solution of $\text{HC}_6\text{F}_4\text{OC}_6\text{H}_{13}$ (0.38 mmol) in 25 mL of dry diethyl ether was added dropwise a solution of LiBu^n in hexane (0.26 mL, 0.38 mmol) at -78°C , under nitrogen. After stirring for one hour at -50°C , solid $[\text{AuCl}(\text{tht})]$ (0.123 g, 0.38 mmol) was added at -78°C and the reaction mixture was slowly brought to room temperature (3 h). Then, a few drops of water were added and the solution was filtered in air through anhydrous MgSO_4 .

[C≡NC₆H₄OOH] (0.056 g, 0.38 mmol) was added to the solution obtained. After stirring for 1 h, the solvent was removed on a rotary evaporator and the white solid obtained was recrystallized from THF/hexane at −15 °C. Yield: 0.059 g, 26%. Anal. Calcd for C₂₀H₁₈AuF₄NO₃: C, 40.47; H, 3.06; N, 2.36. Found: C, 40.31; H, 2.88; N, 2.28%. IR (cm^{−1}/KBr): ν(C≡N): 2210, ν(C=O): 1686. IR (cm^{−1}/(THF)): ν(C≡N): 2217, ν(C=O): 1724, 1706. ¹H NMR (THF-d₈): 8.2 (d, *J* = 8.3 Hz, 2H), 7.9 (d, *J* = 8.3 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 1.50–1.25 (m, 8H), 0.91 (t, *J* = 7.02 Hz). ¹⁹F NMR (THF-d₈): −118.2 (m, 2F), −158.0 (m, 2F).

[Au(C₆F₄C₆F₄Br)(C≡NC₆H₄COOH)] (5)

To a solution of (C₆F₄BrC₆F₄Br) (0.55 mmol) in 35 mL of dry diethyl ether was added drop wise a solution of LiBuⁿ in hexane (0.35 mL, 0.56 mmol) at −78 °C. After stirring for one hour, solid [AuCl(tht)] (0.176 g, 0.38 mmol) was added at −78 °C and the reaction mixture was slowly brought to room temperature (3 h). Then, a few drops of water were added and the solution was filtered in air through anhydrous MgSO₄. The solvent was removed on a rotary evaporator and the white solid obtained was redissolved in 20 mL of THF and [C≡NC₆H₄OOH] (0.081 g, 0.55 mmol) was added to the solution obtained. After stirring for 1 h at room temperature, the solution was reduced to 10 mL under reduced pressure. Addition of 20 mL of hexane gave the product as a white solid. Yield: 0.217 g, 55%. Anal. Calcd. for C₂₀H₅AuBrF₈NO₂: C, 33.34; H, 0.70; N, 1.95. Found: C, 33.64; H, 1.24; N, 2.04%. IR (cm^{−1}/KBr): ν(C≡N): 2208, ν(C=O): 1701. IR (cm^{−1}/(THF)): ν(C≡N): 2221, ν(C=O): 1724. ¹H NMR (THF-d₈): 8.2 (d, *J* = 8.2 Hz 2H), 7.9 (d, *J* = 8.2 Hz, 2H). ¹⁹F NMR (THF-d₈): −116.3 (m, 2F), −134.3 (m, 2F), −138.5 (m, 2F), −140.9 (m, 2F).

[(μ-4,4′-C₆F₄C₆F₄){AuC≡NC₆H₄COOH}]₂ (6)

To a solution of [(μ-4,4′-C₆F₄C₆F₄){Au(tht)}]₂ (0.296 g, 0.34 mmol) in 10 mL of dry THF was added (C≡NC₆H₄COOH) (0.101 g, 0.68 mmol). After the solution was stirred for 15 min at room temperature, the solvent was removed under vacuum. The solid obtained was washed with hexane (3 × 10 mL) and dichloromethane (3 × 10 mL), and finally recrystallized from THF/hexane to give a white solid. Yield: 0.255 g, 76.2%. Anal. Calcd for C₂₈H₁₀Au₂F₈N₂O₄: C, 34.15; H, 1.02; N, 2.85. Found: C, 34.49; H, 1.22; N 3.48%. IR (cm^{−1}/KBr): ν(C≡N): 2206; ν(C=O): 1691. IR (cm^{−1}/(THF)): ν(C≡N): 2221, ν(C=O): 1724. ¹H NMR (THF-d₈): 10.8 (s, 1H), 8.20 (d, *J* = 8.55 Hz, 2H), 7.9 (d, *J* = 8.5 Hz, 2H). ¹⁹F NMR (THF-d₈): −117.3 (m, 4F), −141.1 (m, 4F).

Hydrogen-bonded stilbazole complexes

The supramolecular complexes were all prepared from the pure components. Exact stoichiometric molar amounts of the two compounds were dissolved in dry THF at ambient temperature, and the solvent was eliminated in vacuum.

Experimental procedure for X-ray crystallography

Crystals of [Au(C₆F₅)(CNC₆H₄COOH)] (3) were obtained by slow evaporation of a THF/hexane solution of the complex. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited as supplementary

material, and with the Cambridge Crystallographic Data Centre as supplementary publication with the CCDC reference number 693068. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b811482j

Acknowledgements

This work was sponsored by the D.G.I. (Project CTQ2005-08729/BQU and INTCAT Consolider Ingenio-2010 (CSD2006-0003) and the Junta de Castilla y León (Project VA012A08). C. C. and C. D. thank the Ministerio de Ciencia y Tecnología for a grant.

References

- (a) L. Malatesta, F. Bonati, in *Isocyanide Complexes of Metals*, John Wiley, London, 1969; (b) D. Lentz, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1315–1331.
- M. Tamm and F. E. Hahn, *Coord. Chem. Rev.*, 1999, **182**, 175–209.
- M. Tanabiki, K. Tsuchiya, Y. Kumanomido, K. Matsubara, Y. Motoyama and H. Nagashima, *Organometallics*, 2004, **23**, 3976–3981.
- Y. Ito, M. Sugimone and M. Murakami, *J. Am. Chem. Soc.*, 1991, **113**, 8899–8908.
- Y. Sun, K. Ye, H. Zhang, J. Zhang, L. Zhao, B. Li, G. Yang, B. Yang, Y. Wang, S.-W. Lai and C.-M. Che, *Angew. Chem., Int. Ed.*, 2006, **45**, 5610–5613.
- A. Mayr and J. Guo, *Inorg. Chem.*, 1999, **38**, 921–928.
- C. Bartolomé, M. Carrasco-Rando, S. Coco, C. Cordovilla, P. Espinet and J. Martín-Álvarez, *Organometallics*, 2006, **25**, 2700–2703.
- V. Sharma and D. Piwnica-Worms, *Chem. Rev.*, 1999, **99**, 2545–2560.
- (a) R. A. Michelin, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2001, **218**, 75–112; (b) W. P. Fehlhammer and M. Fritz, *Chem. Rev.*, 1993, **93**, 1243–1280.
- U. Plaia, H. Stolzenberg and W. P. Fehlhammer, *J. Am. Chem. Soc.*, 1985, **107**, 2171–2172.
- K. Bartel and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 599–600.
- G. Facchin, R. A. Michelin, M. Mozzon and A. Tassan, *J. Organomet. Chem.*, 2002, **662**, 70–76.
- M. Basato, F. Benetollo, G. Facchin, R. A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, S. Mazzega Sbovata and A. Tassan, *J. Organomet. Chem.*, 2004, **689**, 454–462.
- G. Facchin, P. Uguagliati and R. A. Michelin, *Organometallics*, 1984, **3**, 1818–1822.
- Z.-L. Lu, A. Mayr and K.-K. Cheung, *Inorg. Chim. Acta*, 1999, **284**, 205–214.
- S. Wang, A. Mayr and K.-K. Cheung, *J. Mater. Chem.*, 1998, **8**, 1561–1565.
- D. Samuel, B. Weinraub and D. Ginsburg, *J. Org. Chem.*, 1956, **21**, 376–377.
- S. Coco, E. Espinet, P. Espinet and I. Palape, *Dalton Trans.*, 2007, 3267–3272.
- (a) T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1989, **111**, 8533–8534; (b) M.-J. Brienne, J. Gabard, J.-M. Lehn and I. Stibor, *J. Chem. Soc., Chem. Commun.*, 1989, 1868–1870; (c) K. Willis, D. J. Price, H. Adams, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1995, **5**, 2195–2199; (d) C. M. Paleos and D. Tsiourvas, *Liq. Cryst.*, 2001, **28**, 1127–1161; (e) D. W. Bruce, in *Advances in Inorganic Chemistry*, 2001, **52**, 151–204; (f) M. Grunet, R. A. Howie, A. Kaeding and C. T. Imrie, *J. Mater. Chem.*, 1997, **7**, 211–214; (g) J.-F. Eckert, U. Maciejczuk, D. Guillon and J.-F. Nierengarten, *Chem. Commun.*, 2001, **14**, 1278–1279; (h) F. Würthner, S. Yao, B. Heise and C. Tschierske, *Chem. Commun.*, 2001, **14**, 2260–2261; (i) N. Mizoshita, H. Monobe, M. Inoue, M. Ukon, T. Watanabe, Y. Shimizu, K. Hanabusa and T. Kato, *Chem. Commun.*, 2002, **15**, 428–429; (j) G. Pickaert, L. Douce, R. Ziessel and D. Guillon, *Chem. Commun.*, 2002, **15**, 1584–1585; (k) S. Jin, Y. Ma, S. C. Zimmerman and S. Z. D. Cheng, *Chem. Mater.*, 2004, **16**, 2975–2977; (l) T. Kajitana, S. Kohmoto, M. Yamamoto and K. Kishikawa, *Chem. Mater.*, 2004, **16**, 2329–2331; (m) J. A. McCubbin, X. Tong, Y. Zhao, V. Snieckus and R. P. Lemieux, *Chem. Mater.*, 2005, **17**, 2574–2581; (n) J. Barberá, L. Puig, P. Romero, J. L. Serrano and T. Sierra, *J. Am. Chem. Soc.*, 2006, **128**, 4487–4492.

- 20 G. W. Gray, in *Molecular Structure and Liquid Crystals*, Academic Press, London, 1967, p. 161, and references therein.
- 21 *Handbook of Liquid Crystals*, eds. D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and D. V. Vill, Wiley-VCH, Weinheim, 1998.
- 22 (a) P. Espinet, M. A. Esteruelas, L. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215–274; (b) *Metallomesogens* (Ed.: J. L. Serrano), VCH, Weinheim, 1996; (c) B. Donnio, D. Guillon, D. W. Bruce and R. Deschenaux, in *Metallomesogens*, Comprehensive Organometallic Chemistry III: From Fundamentals to Applications (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, UK, vol 12, 2006; *Applications III: Functional Materials, Environmental and Biological Applications*, (Ed.: D. O'Hare), ch. 12.05, pp. 195–294.
- 23 R. Deschenaux, F. Monnet, E. Serrano, F. Turpin and A.-M. Levelut, *Helv. Chim. Acta*, 1998, **81**, 2072–2077.
- 24 P. Massiot, M. Imperor-Clerc, M. Veber and R. Deschenaux, *Chem. Mater.*, 2005, **17**, 1946–1951.
- 25 R. Ziessel, G. Pickaert, F. Camerel, B. Donnio, D. Guillon, M. Cesario and T. Prangé, *J. Am. Chem. Soc.*, 2004, **126**, 12403–12413.
- 26 (a) V. W.-W. Yam and K. K.-W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323–334; (b) M. Bardaji, A. Laguna, J. Vicente and P. G. Jones, *Inorg. Chem.*, 2001, **40**, 2675–2681; (c) M. J. Irwin, J. J. Vittal and R. J. Puddephat, *Organometallics*, 1997, **16**, 3541–3547; (d) R. L. White-Morris, M. M. Olmstead, F. Jiang, D. S. Tinti and A. L. Balch, *J. Am. Chem. Soc.*, 2002, **124**, 2327–2336; (e) Y.-A. Lee, J. E. McGarrah, R. J. Lachicotte and R. Eisenberg, *J. Am. Chem. Soc.*, 2002, **124**, 10662–10663; (f) J. P. Fackler, Jr., *Inorg. Chem.*, 2002, **41**, 6959–6972.
- 27 H. Schmidbaur, W. Graf and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 417–419.
- 28 T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76.
- 29 D. B. Leznoff, B.-Y. Xue, R. J. Batchelor, F. W. B. Einstein and B. O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026–6034.
- 30 R. Bayón, S. Coco, P. Espinet, C. Fernández-Mayordomo and J. M. Martín-Álvarez, *Inorg. Chem.*, 1997, **36**, 2329–2334.
- 31 R. Bayón, S. Coco and P. Espinet, *Chem.–Eur. J.*, 2005, **11**, 1079–1085.
- 32 P. Alejos, S. Coco and P. Espinet, *New J. Chem.*, 1995, **19**, 799–805.
- 33 F. H. Allen, W. D. S. Motherwell, P. R. Raithby, G. P. Shields and R. Taylor, *New J. Chem.*, 1999, **23**, 25–34.
- 34 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320–326.
- 35 N. Castillo, C. F. Matta and R. J. Boyd, *Chem. Phys. Lett.*, 2005, **409**, 265–269.
- 36 D. J. Price, K. Willis, T. Richardson, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883–891.
- 37 D. W. Bruce, D. A. Dummur, E. Lalinde, P. M. Maitlis and P. Styring, *Liq. Cryst.*, 1988, **3**, 385–395.
- 38 T. Kato, H. Kihara, T. Uryu, A. Fujishi, a and J. M. J. Fréchet, *Macromolecules*, 1992, **25**, 6836–6841.
- 39 (a) D. Demus, L. Richter, in *Textures of liquid crystals*, VEB, Leipzig, 2nd edn, 1980; (b) G. W. Gray, J. W. Goodby, in *Smectic liquid crystals. Textures and Structures*, Hill, Glasgow, London, 1984; (c) I. Dierking, in *Textures of liquid Crystals*, Wiley-VCH, Weinheim, 2003.
- 40 S. Coco, P. Espinet, S. Falagán and J. M. Martín-Álvarez, *New J. Chem.*, 1995, **19**, 959–964.
- 41 H. Ecken, M. M. Olmstead, B. C. Noll, S. Attar, B. Schlyer and A. L. Balch, *J. Chem. Soc., Dalton Trans.*, 1998, 3715–3720.
- 42 D. J. Price, K. Willis, T. Richardson, G. Ungarb and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883–891.
- 43 S. Coco, C. Cordovilla, P. Espinet, J. Martín-Álvarez and P. Muñoz, *Inorg. Chem.*, 2006, **45**, 10180–10187.
- 44 C. E. Wayne, R. P. Wayne, in *Photochemistry*, Oxford University Press, New York, 1996.
- 45 M.-C. Brandys, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2000, 4601–4606.
- 46 R. Usón, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85–91.
- 47 R. Usón, A. Laguna, I. Cólora and E. de Jesús, *J. Organomet. Chem.*, 1984, **263**, 121–129.