# Functional isocyanide metal complexes as building blocks for supramolecular materials: hydrogen-bonded liquid crystals

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Gold, palladium and platinum complexes with an unusual isocyanide ligand containing a carboxylic acid function, [AuCl(CNC<sub>6</sub>H<sub>4</sub>COOH)], *cis*-[MI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>] and *trans*-[MI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>] (M = Pd, Pt) have been isolated. The carboxylic acid group of the coordinated isocyanide acts as a hydrogen donor for hydrogen-bonding and three series of stable hydrogen-bonded liquid crystalline metal complexes have been prepared with decyloxystilbazole. Although all the metal acid derivatives used are not mesomorphic, and decyloxystilbazole only shows an ordered Smectic E phase, four out of the five hydrogen-bonded decyloxystilbazole complexes studied display enantiotropic smectic A or nematic mesophases. The single crystal X-ray diffraction structure of *trans*-[PdI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>]· C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> has been determined and confirms the formation of a supramolecular array in the solid state supported by hydrogen-bonding.

# Introduction

Isocyanides (C≡NR) are interesting ligands in organometallic chemistry due to their coordination ability to give very stable complexes with many metals.<sup>1,2</sup> Isocyanide metal complexes are catalysts for polymerization,3 and for activation of Si-Si bonds,4 or molecules used for one-dimensional electric conductors,5 and for liquid crystals.<sup>6</sup> Moreover, the reaction of isocyanide complexes with nucleophiles gives carbene complexes,<sup>7</sup> which are also catalytic systems.8,9 The chemical behavior of the organic isocyanides depends on the steric and electronic features of the R group, and this can be used to tune their properties. A second functional group on R makes the molecule a bifunctional ligand. The other possible groups in the molecule are limited by the reactivity of the isocyanide group, but a number of functionalized isocyanides and their corresponding metal complexes have been reported.<sup>2,10</sup> These include: hydroxyalkyl isocyanides;<sup>11</sup> substituted-arylisocyanides such as 2-OH-C<sub>6</sub>H<sub>4</sub>NC,<sup>12</sup> 2,6-(OH)<sub>2</sub>- $C_6H_4NC^2_{,2}$  2-(CH<sub>2</sub>X) $C_6H_4NC(X = PPh_3^+, {}^{10}OSiMe_3, OH, {}^{13}N_3, {}^{14}$ or  $CpM(CO)_3$ <sup>15</sup> with M = Cr, W); alkynylarylisocyanides;<sup>16</sup> pyridylethynylarylisocyanides;17 and 4-isocyanobenzylidene-4alkoxyarylimines.18

Although organic isocyanides are hydrolysed by aqueous acids, the synthesis of stable 4-isocyanobenzoic acid was achieved some fifty years ago.<sup>19</sup> In spite of the very interesting combination of functions which make this molecule a promising building block, further studies with this isocyanide, or its coordination to give metal complexes, have not been reported. One behavior to be expected for the carboxylic acid function, whether in the free ligand or in its isocyanide metal complexes, provided these can be prepared, is its participation in hydrogen-bonds.

Intermolecular hydrogen-bonding is a key attractive interaction stabilizing condensed phases and promoting molecular selfassembly. It is present in many molecular systems ranging from inorganic to biological structures. The lower strength of hydrogenbonds compared to covalent bonds provides some structural flexibility to hydrogen-bonded systems, which results in interesting properties. In the field of liquid crystals it has been known since the early years of the 20th century that 4-alkoxybenzoic acids show liquid crystal behavior as a consequence of their selfassembling by hydrogen-bonds into dimers.<sup>20,21</sup> There are many reports on the effects of intermolecular hydrogen-bonding in the field of organic liquid crystals,<sup>22</sup> but only a few cases in the field of metal-containing liquid crystals (metallomesogens),623 namely some hydrogen-bonded ferrocene complexes,<sup>24,25</sup> and a few phenanthroline copper derivatives.<sup>26</sup> This scarcity is probably due to the usually high melting temperature of metallomesogens, which is hardly compatible with the use of moderately weak hydrogenbonds as the force inducing self organization above the melting point. In fact, the reported hydrogen-bonded organic liquid crystals and metallomesogens usually have fairly low melting temperatures.

Here we report examples of stable gold, palladium and platinum complexes with 4-isocyanobenzoic acid. The single crystal X-ray diffraction structure of {*trans*-[PdI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>].( $\mu$ -O,O-dioxane)}<sub> $\infty$ </sub> was determined. These complexes are hydrogen donors through the carboxylic acid group, giving mesomorphic supramolecular complexes with decyloxystilbazole.

# **Results and discussion**

# Synthesis and characterization

The originally reported synthesis of  $CNC_6H_4CO_2H$  (1) uses the carbylamine reaction on 4-aminobenzoic acid,<sup>19</sup> but gives poor yields and purification of the isocyanide requires successive

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crystallizations. We have improved this synthesis using a slight modification of Ugi's general method for the preparation of isocyanides (Scheme 1):<sup>27</sup> formylation of 4-amine-ethylbenzoate gives 4-*N*-formamido-ethylbenzoate. Dehydration with bis(trichloromethyl)carbonate ("triphosgene") and triethylamine affords 4-isocyanoethylbenzoate. Finally, saponification with sodium hydroxide and subsequent acidification to pH = 5 produces the desired 4-isocyanobenzoic acid.



The IR spectrum of 1 shows a strong  $v(C\equiv N)$  absorption at 2128 cm<sup>-1</sup>. In addition, not reported before, the IR spectrum in KBr shows a strong v(C=O) stretching band at 1694 and a broad v(O-H) band at 2986 cm<sup>-1</sup>, supporting the existence of a hydrogenbonded dimer in the solid state.<sup>28</sup> The <sup>1</sup>H NMR spectrum of 1 has not been reported before. In THF-d<sub>8</sub> at 300 MHz it shows for the aryl hydrogen atoms two distorted "doublets" ( $\delta_1$  8.08,  $\delta_2$  7.54); this is a deceptively simple pattern arising from the strictly speaking AA'XX' spin system. Moreover, at 250 K a broad singlet ( $\delta_{OH}$  11.95) is observed for the acidic H. In CDCl<sub>3</sub> (a less good hydrogen acceptor than THF) the AA'XX' signals appear at  $\delta_1$  8.15,  $\delta_2$  7.49 ( ${}^{3}J_{3,4} + {}^{5}J_{3,4'} = 8.3$  Hz), but the acidic H is not seen at 243 K.

As a ligand,  $[CNC_6H_4CO_2H]$  appears to be less strongly coordinating than other isocyanides; yet it forms easily metal complexes according to eqn 1–3. The reaction of 1 with [AuCl(tht)] (tht = tetrahydrothiophene) in THF gave the white complex [AuCl(CNC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H)] (2). Similarly, reactions of 4isocyanobenzoic acid with  $[MCl_2(tht)_2]$  (M = Pd, Pt) in THF afforded the pale yellow complexes *cis*- $[MCl_2(CNR)_2]$  [M = Pd (3), Pt (4)], very little soluble in the usual organic solvents. Taking advantage of our previous experience that isocyanide iodo-complexes stabilize the *trans* isomer,<sup>29</sup> exchange reactions in acetone with KI afforded the corresponding *trans*- $[MI_2(CNR)_2]$ complexes [M = Pd (5), Pt (6)]. C, H, N analyses for the complexes, yields, and relevant IR and NMR data are given in the experimental section.

$$[\operatorname{AuCl(tht)}] + \operatorname{CNC}_6\operatorname{H}_4\operatorname{CO}_2\operatorname{H}(1) \rightarrow [\operatorname{AuCl(CNC}_6\operatorname{H}_4\operatorname{CO}_2\operatorname{H})](2) + \text{tht}$$
(1)

$$[MCl_{2}(tht)_{2}] + CNC_{6}H_{4}CO_{2}H$$

$$\rightarrow cis - [MCl_{2}(CNC_{6}H_{4}CO_{2}H)_{2}] + 2tht$$

$$M = Pd (3), Pt (4)$$
(2)

$$[MCl_2(CNC_6H_4CO_2H)_2] + 2KI$$
  

$$\rightarrow trans-[MI_2(CNC_6H_4CO_2H)_2] + 2KCl$$
  

$$M = Pd (5), Pt (6)$$
(3)

The IR spectra of **2–6** exhibit  $v(C\equiv N)$  absorptions for the isocyanide group at higher wavenumbers than for the free ligand, by about 100 cm<sup>-1</sup> for Au(I) and 60–80 cm<sup>-1</sup> for Pd(II) and Pt(II) complexes. Linear **2** and *trans*-diiodopalladium and platinum complexes ( $D_{2h}$  symmetry) display one  $v(C\equiv N)$  IR absorption, while *cis*-dichloropalladium and platinum complexes ( $C_{2y}$  symmetry) show two bands, as reported for similar metal aryl isocyanide compounds.<sup>29,30</sup> In addition, their v(C=O) and v(O-H) bands appear in the same region as the free isocyanide ligand.

The <sup>1</sup>H NMR spectra of the complexes were recorded in THFd<sub>8</sub>, due to their low solubility in CDCl<sub>3</sub> or in acetone-d<sub>6</sub>. This low solubility suggests that the solvent needs to split the H-bonds in the solid to get the compound dissolved. They spectra are all similar to that of the free isocyanide ligand, showing two resonances (AA'XX' spin system) for the aryl protons present in the molecule. It is worth noting that coordination of the isocyanide produces a deshielding for H<sup>1</sup> (*ca*. 0.1 ppm) and H<sup>2</sup> (*ca*. 0.3 ppm). This suggests that the coordination of the isocyanide group reduces the electron density on the aromatic ring, enhancing the acid character of the carboxylic group. Consistently, the observation of the acidic H (in complex (2)) required cooling down to 175 K in order to observe a very broad signal at  $\delta_{OH}$  12,54.

The molecular structure of *trans*-[PdI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>] was determined by single crystal X-ray diffraction methods. It crystallizes with one hydrogen-bonded dioxane molecule per Pd atom. An ORTEP view of the compound is given in Fig. 1(a), while Fig. 1(b) shows the crystalline arrangement of molecules in the solid. Table 1 gives the data collection and refinement parameters. The compound crystallizes in the triclinic space group  $P\overline{1}$ , with one formula unit in the unit cell. With the palladium atom being on an inversion centre, the palladium coordination environment must be exactly planar, the *cis* C-Pd-I angles of 89.8(6) and 90.2(6)° are not significantly different from 90° so the palladium has an essentially perfect square-planar environment. Pd-C and Pd-I distances are within the ranges found in similar complexes.<sup>31</sup> The carboxylic acid function is practically coplanar with the aryl ring. Each dioxane oxygen is hydrogen-bonded to one of the



**Fig. 1** (a) Crystal structure of **5** with the atom-numbering scheme. Displacement ellipsoids at the 50% probability level. (b) Extended network formed by intermolecular hydrogen-bonding.

Empirical formula	$C_{20}H_{18}\;I_2\;N_2\;O_6\;Pd$
Formula weight	742.56
Crystal system	Triclinic
Space group	ΡĪ
a/Å	5.085(4)
b/Å	9.923(8)
c/Å	13.415(11)
$\beta$ /deg	79.378(15)
$V/\text{\AA}^3$	618.0(9)
Ζ	1
$D_{ m calc}/ m g~cm^{-3}$	1.995
Abs. coeff./mm <sup>-1</sup>	3.284
F(000)	352
Crystal size/mm	$0.21 \times 0.10 \times 0.07$
Temp./K	298(2)
$\theta$ range for data collection/deg	1.65–23.39
Wavelength/Å	0.71073
Index ranges	$-4 \le h \le 5, -10 \le k \le 10,$
	$-13 \le l \le 14$
Reflections collected	2725
Independent reflections	$1763 [R_{int} = 0.0323]$
Completeness to $\theta$	23.39 (97.8%)
Abs. corr.	SADABS
Max. and min. transmittance	1.000000 and 0.472756
Data/restraints/parameters	1763/0/142
Goodness-of-fit on $F^2$	1.167
Final R indices $[I > 2s(I)]$	$R_1 = 0.0783, wR_2 = 0.2123$
R indices (all data)	$R_1 = 0.0934, wR_2 = 0.2187$
Largest diff. peak and hole/e $A^{-3}$	1.372 and -1.005

Table 1 X-Ray data and data collection and refinement parameters for {\it trans-[PdI\_2(CNC\_6H\_4COOH)\_2]\cdot C\_4H\_8O\_2}

carboxylic groups of the adjacent *trans*-[PdCl<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>] molecules, giving rise to the polymeric chains shown in Fig. 1(b). None of the OH hydrogens was located in a difference Fourier map, so their positions were calculated with a riding model. The distance O  $\cdots$  O is 2.69(2) Å. After correction for a plausible O-H bond length (0.97 Å based on neutron diffraction results),<sup>32</sup> the estimated H  $\cdots$  O distance is 1.74 Å and the O-H  $\cdots$  O angle 164°.

#### Hydrogen-bonded decyloxystilbazole complexes

The hydrogen-bonded decyloxystilbazole complexes were prepared by dissolving together equimolar proportions of the corresponding compound **1–6** and decyloxystilbazole in THF at room temperature, followed by evaporation of the solvent in vacuum to obtain compounds **1a–6a** (Scheme 2). All the metal complexes prepared were orange or yellow solids.

The formation of the supramolecular hydrogen-bonded decyloxystilbazole complexes (1a, 2a, 4a, 5a and 6a) was confirmed by IR spectroscopy. Their infrared spectra in the solid state do not show the v(O-H) absorption of the precursors, and the carbonyl stretching absorption bands appear shifted from their positions in the parent complexes. This change supports that self-association of the precursors through the carboxylic acid group is replaced by hydrogen-bonding to the decyloxystilbazole, as reported for organic compounds of benzoic acid with decyloxystilbazole.<sup>22a</sup>

### Mesogenic behavior

Compounds 1–6 are not mesogenic and decompose above 200  $^\circ$ C without melting. The decyloxystilbazole used in this work displays



Scheme 2

 Table 2
 Optical, thermal and thermodynamic data for decyloxystilbazole complexes

Compound	Transition <sup>a</sup>	Temperature <sup>b</sup> /°C	$\Delta H^{b}/\mathrm{KJ}~\mathrm{mol}^{-1}$
1a	$C \rightarrow SmA$	74.1 <sup>c</sup>	30.4
	$SmA \rightarrow I$	146 <sup><i>d</i></sup>	
2a	$C \rightarrow C'$	118.9	3.6
	$C' \rightarrow SmA$	160.9	24.81
	$SmA \rightarrow I$	$187^{d}$	
4a	$C \rightarrow dec$	$182.0^{d}$	
5a	$C \rightarrow N$	152.0	49.2
	$N \rightarrow I$	$210^{d}$	
6a	$C \rightarrow Sm$	132.7	31.2
	$Sm \rightarrow N$	$182^{d}$	
	$N \rightarrow I$	$210^{d}$	

<sup>*a*</sup> C, crystal, Sm, smectic, N, nematic, I, isotropic liquid. <sup>*b*</sup> Data referred to the first DSC cycle starting from the crystal. <sup>*c*</sup> Combined enthalpies. <sup>*d*</sup> Microscopic data.

a smectic E phase.<sup>33</sup> The supramolecular compounds 1a-6a were investigated by DSC and by hot-stage polarized optical microscopy. Their optical, thermal and thermodynamic data are collected in Table 2.

Four out of the five hydrogen-bonded decyloxystilbazole compounds studied display enantiotropic mesophases. Only 4a, which does not have a rod-like structure, does not show liquid crystal behavior (because of this, the corresponding Pd complex was not made). Complexes 1a and 2a display a SmA mesophase, with typical oil steles and homeotropic textures reorganizing to the fanshaped texture at temperatures close to the clearing point, and the focal-conic texture on cooling from the isotropic liquid (Fig. 2). Compounds 5a and 6a give rise to a N mesophase with typical marbled and schlieren textures (Fig. 3).<sup>34</sup> Compound 5a shows additionally a second viscous mesophase at lower temperatures, displaying lancets and regions with a mosaic texture on cooling from the nematic mesophase. These observations are consistent with a smectic G mesophase.<sup>34</sup> At the clearing transitions to the isotropic liquid formation of some crystals is observed. This suggests that decomposition, most likely due to the thermal lability of the hydrogen-bond, is generating free decyloxystilbazole and



Fig. 2 Polarized optical microscopic texture ( $\times 100$ ) observed for 2a. The picture shows the focal-conic texture of the SmA phase, on cooling from the isotropic liquid at 175 °C.



Fig. 3 Polarized optical microscopic texture ( $\times 100$ ) observed for 6a. The picture shows the marbled texture of the N phase, at 210 °C on heating from the crystal.

the corresponding compound 1–6. Probably for this reason the clearing points, and the smectic to nematic transition of compound **6a** are not observed by DSC.

All complexes that give rise to mesophases have a rod-like structure. Consequently it is not unexpected that they display calamitic mesophases. More interestingly, the symmetric *trans*-palladium (**5a**) and *trans*-platinum (**5b**) supramolecular complexes favor the formation of a nematic phase, as found for other symmetric metallomesogens.<sup>35</sup>

In summary, we have prepared examples of gold, palladium and platinum complexes with an unusual isocyanide ligand containing a carboxylic acid function. They are the first examples of metal complexes of the bifunctional 4-isocyanobenzoic acid, and have a promising structure as metalla-ligands, as metalla-acids, and as amphiphilic metal complexes. In fact these complexes act as hydrogen donors to decyloxystilbazole through the carboxylic acid group, and are building blocks to prepare supramolecular complexes that display liquid crystalline properties. These initial results demonstrate the utility of this bifunctional ligand.

# **Experimental**

Experimental conditions for the analytical, spectroscopic and diffraction studies were as reported elsewhere.<sup>35</sup> Literature methods were used to prepare [AuCl(tht)],<sup>36</sup>  $[PdCl_2(tht)_2]$  and  $[PtCl_2(tht)_2]$ ,<sup>37</sup> (tht = tetrahydrothiophene).

The isocyanide [CN-C<sub>6</sub>H<sub>4</sub>-COOH] that has been described starting directly from the amine [H<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-COOH],<sup>19</sup> was synthesized by an improved method from 4-isocyanoetylbenzoate. Model preparation procedures of the new compounds are given below.

#### Preparation of 4-isocyanoethylbenzoate

The procedure described by Ugi *et al.* for other isocyanides was used,<sup>27</sup> using triphosgene instead of phosgene as a dehydrating agent. To a solution of 4-*N*-formamido-ethylbenzoate (6.70 g, 34.69 mmol), (prepared by reaction of the amine with formic acid) and triethylamine (9.8 mL, 69.38 mmol) in 350 ml of

dichloromethane, was added dropwise a solution of trichloromethylcarbonate (triphosgene) (3.50 g, 11.56 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 30 min and then the solvent was removed on a rotary evaporator. The resulting residue was chromatographed (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/hexane, 2 : 1 as eluent) and the solvent was evaporated to obtain the product as a greenish liquid. (84% yield). IR/(CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C=N): 2128;  $\nu$ (CO): 1718. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_1$  8.09,  $\delta_2$  7.45 (C<sub>6</sub>H<sub>4</sub>, AA'XX' spin system, <sup>3</sup>J<sub>AX</sub> + <sup>5</sup>J<sub>AX'</sub> = 8.5 Hz), 4.40 (q, OCH<sub>2</sub>, J = 7.1 Hz, 1.40 (t, OCH<sub>2</sub>CH<sub>3</sub>, J = 7.1 Hz).

### Improved method for the preparation of 4-isocyanobenzoic acid (1)

To a solution of 4-isocyanoetylbenzoate (3 g, 17.13 mmol) in 500 mL ethanol was added NaOH (2.74 g, 68.50 mmol) dissolved in 15 mL of water. After refluxing for 2 h, the solvent was removed on a rotary evaporator. Water (100 mL) and ether (50 mL) were added to the solid residue obtained and the stirred mixture was treated with 3% hydrochloric acid until pH = 5. The organic phase was collected and the water solution extracted again with ether (3 × 25 mL). The ether extracts were dried over anhydrous magnesium sulfate and filtrated. The solvent was removed on a rotary evaporator to obtain the product as a cream solid, which was dried under vacuum (70% yield). IR (cm<sup>-1</sup>/CH<sub>2</sub>Cl<sub>2</sub>):  $v(C\equiv N)$ : 2128; v(CO): 1702. IR (cm<sup>-1</sup>/KBr): v(O-H): 2986;  $v(C\equiv N)$ : 2128; v(CO): 1694. <sup>1</sup>H NMR (THF-d<sub>8</sub>):  $\delta_1$  8.08,  $\delta_2$  7.54 (AA'XX' spin system,  ${}^{3}J_{1,2} + {}^{5}J_{1,2'} = 8.4$  Hz);  $\delta_{OH}$  11.95 (broad singlet at 250 K).

## Preparation of [AuCl(CNC<sub>6</sub>H<sub>4</sub>COOH)] (2)

To a solution of [AuCl(tht)] (0.500 g, 1.560 mmole) in 70 ml of tetrahydrofurane was added [CNC<sub>6</sub>H<sub>4</sub>COOH] (0.27 g, 1.81 mmole). After stirring for 30 min the solvent was reduced to 15 mL under reduced pressure and hexane (10 mL) was added to obtain the product as a white solid. (61.87% yield). IR (cm<sup>-1</sup>/KBr):  $\nu$ (C=N): 2208;  $\nu$ (C=O): 1696. <sup>1</sup>H NMR (THF-d<sub>8</sub>):  $\delta_1$  8.16,  $\delta_2$  7.84 (AA'XX' spin system, <sup>3</sup>*J*<sub>1,2</sub> + <sup>5</sup>*J*<sub>1,2'</sub> = 8.5 Hz). Anal. calcd for C<sub>8</sub>H<sub>5</sub>AuClNO<sub>2</sub>: C, 25.32; H, 1.33; N, 3.69. Found: C, 25.37; H, 1.36; N, 3.63.

# Preparation of cis-[MCl<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>]

To a solution of  $[MCl_2(tht)_2]$  (M = Pd, Pt) (0.21 mmol) in 20 mL of tetrahydrofurane was added  $[CNC_6H_4COOH]$  (0.47 mmol). The mixture was left stirring for 30 min at room temperature, and then hexane (10 mL) was added to obtain the product as a yellow solid. M = palladium (3): yield 42%. IR (cm<sup>-1</sup>/KBr):  $v(C\equiv N)$ : 2214, v(C=O): 1696; IR(cm<sup>-1</sup>/THF):  $v(C\equiv N)$ : 2214, 2235 (sh). Anal. calcd for  $C_{16}H_{10}PdCl_2N_2O_4$ : C, 40.75; H, 2.14; N, 5.94. Found: C, 40.61; H, 3.01; N, 5.72. M = platinum (4): yield 59%. IR (cm<sup>-1</sup>/KBr):  $v(C\equiv N)$ : 2205, v(C=O): 1696; IR (cm<sup>-1</sup>/(THF):  $v(C\equiv N)$ : 2204, 2235 (sh), v(C=O): 1720. Anal. calcd for  $C_{16}H_{10}PtCl_2N_2O_4$ : C, 34.30; H, 1.80; N, 5.00. Found: C, 34.54; H, 2.05; N, 4.82.

#### Preparation of trans-[MI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>]

KI (0.390 mmol) was added to  $[MCl_2(CNC_6H_4COOH)_2]$  (M = Pd, Pt) (0.15 mmol) in 40 mL of acetone. The mixture was stirred for 3 h and the KCl formed was filtered. The solvent was removed on a rotary evaporator and the solid obtained was recrystallized from tetrahydrofurane–hexane at -15 °C to give an orange solid. M = palladium (5): yield 32%. IR (cm<sup>-1</sup>/KBr): v(C≡N): 2193, v(C=O): 1698. <sup>1</sup>H NMR (THF-d<sub>8</sub>):  $\delta_1$  8.18,  $\delta_2$  7.79 (AA'XX' spin system,  ${}^{3}J_{1,2} + J_{1,2'} = 8.6$  Hz). Anal. calcd for C<sub>16</sub>H<sub>10</sub>PdI<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 29.34; H, 1.52; N, 4.28. Found: C, 29.19; H, 1.54; N, 4.30. M = platinum (6): yield 23%. IR (cm<sup>-1</sup>/KBr): v(C≡N): 2186, v(C=O): 1697. <sup>1</sup>H NMR (THF-d<sub>8</sub>):  $\delta_1$  8.18,  $\delta_2$  7.78 (AA'XX' spin system,  ${}^{3}J_{1,2} + {}^{5}J_{1,2'} = 8.6$  Hz). Anal. calcd for C<sub>16</sub>H<sub>10</sub>PtI<sub>2</sub>N<sub>2</sub>O<sub>4</sub>: C, 25.86; H, 1.36; N, 3.77. Found: C, 25.60; H, 1.55; N, 3.56.

#### Preparation of hydrogen-bonded supramolecular complexes 1a-6a

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

## Experimental procedure for X-ray crystallography

Crystals of *trans*-[PdI<sub>2</sub>(CNC<sub>6</sub>H<sub>4</sub>COOH)<sub>2</sub>]·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> (**5**) were obtained by direct diffusion of hexane into a solution of the complex in 1,4-dioxane. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Centre and as supplementary material: CCDC reference number 643465. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705478e.

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