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Mesogenic palladium and platinum-diiodide complexes of 4-isocyanobenzylidene-4-alkoxyphenylimines

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A series of 4-isocyanobenzylidene-4-alkoxyphenylimines 4-CN-3,5-$R_2C_6H_2CHNC_6H_4$-4-OC_nH_{2n+1} (R = Me, Pr^i), were prepared from 4-isocyanobenzaldehydes and long-chain 4-alkoxyanilines. The palladium and platinum-diiodide complexes of the methyl-substituted ligands, MI_2(4-CN-3,5-$Me_2C_6H_2CHNC_6H_4$-4-$OC_nH_{2n+1})_2$ exhibit mesomorphic behaviour, forming nematic and smectic C phases (for $n > 10$). The metal centers apparently serve as rigid linear links between the isocyanide ligands, but have little additional influence on the liquid crystal properties, as evidenced by the small differences in transition temperatures between the palladium and platinum compounds. The corresponding complexes with lateral isopropyl substituents (R = Pr^i) do not exhibit mesomorphic properties.

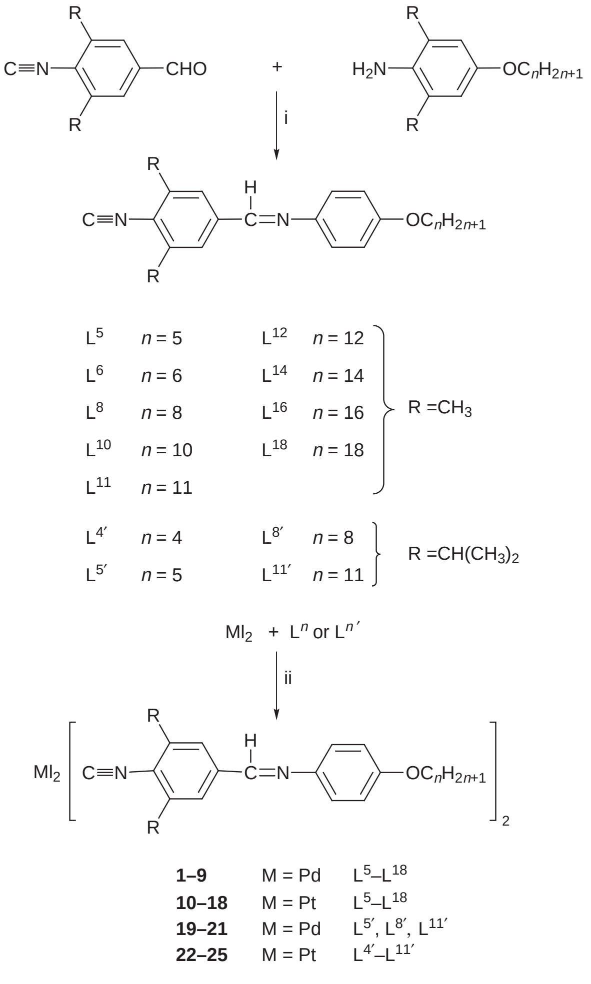
On account of their linear shapes and strong binding properties, isocyanides and acetylides are suitable ligands for the formation of metal complexes with mesomorphic properties.[1] This has been demonstrated for lyotropic polymeric acetylide palladium complexes more than 15 years ago.[2–5] In subsequent studies, a variety of thermotropic liquid crystals based on molecular acetylide complexes of Au^I, Pd^{II}, Pt^{II} and Rh^{III} have been prepared.[6–11] The development of liquid crystals based on corresponding isocyanide metal complexes has been initiated more recently, and since the first reports by Takahashi and co-workers[12–14] and by Espinet and co-workers,[15–17] only a few additional studies have been described.[18,19] The relatively small number of investigations on liquid crystals based on isocyanide metal complexes has been suggested to be a possible consequence of the limited commercial availability of isocyanides as well as their low thermal stability and reputation for being dangerous substances.[15] Considering their good coordinating properties and favorable molecular shapes, the development of new isocyanides for the synthesis of liquid crystalline metal complexes appears to be a promising undertaking.

We have recently employed the formyl-substituted isocyanoarenes 4-CN-3,5-$R_2C_6H_2CHO$ (R = Me, Pr^i) as versatile precursors for the design of isocyanide metal complexes which are capable of undergoing molecular self-assembly.[20] The formyl-substituted isocyanoarenes also lend themselves as precursors for isocyanides bearing long terminal chains. In this contribution, we describe the synthesis of a series of such derivatives by simple Schiff-base formation with long-chain 4-alkoxyanilines. The new isocyanides form linear complexes with PdI_2 and PtI_2 which exhibit mesomorphic properties (with R = Me).

Results and Discussion

Synthesis and characterization of the isocyanides and isocyanide metal complexes

The Schiff-bases 4-CN-3,5-$R_2C_6H_2CHNC_6H_4$-4-OC_nH_{2n+1}, L^n (R = CH_3, n = 5, 6, 8, 10, 11, 12, 14, 16, 18) and $L^{n'}$ (R = Pr^i, n = 4, 5, 8, 11) were obtained by reaction of isocyanobenzaldehydes 4-CN-3,5-$R_2C_6H_2CHO$ with the corresponding anilines in ethanol at room temperature (Scheme 1). The new isocyanides exhibit a characteristic IR absorption at about 2117 cm^{-1} for the isocyanide functionality.[21] The ^{13}C NMR resonance for the isocyanide carbon atom is of low intensity and was found for a few examples near δ 169. The imino groups give rise to ^1H and ^{13}C NMR resonances at around δ 8.4 and 158, respectively. The complexes *trans*-$MI_2(L^n)_2$ and *trans*-$MI_2(L^{n'})_2$ (M = Pt, Pd), **1–25**, form upon combination



Scheme 1 *Reagents and conditions*: i, ethanol, acetic acid, rt, stirring; ii, THF, rt, stirring

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of the isocyanides with PdI_2 and PtI_2 in THF (Scheme 1). The *trans*-geometry of the palladium and platinum complexes is evident from the appearance of only single IR absorptions for the coordinated isocyanide groups at *ca.* 2196 and 2189 cm^{-1}, respectively. The shift of the isocyanide stretching frequencies to higher wavenumbers by 70–80 cm^{-1} upon coordination to the Pd^{II} and Pt^{II} metal centers is of the expected magnitude.[21] The ^{13}C NMR resonances of the metal-coordinated isocyanide carbon atoms have not been observed due to their low intensity, but would be expected to occur in the same region as for the free ligands.[22] The metal centers also exert very little influence on the ^1H NMR resonances of the isocyanides.

Crystal structures of complexes 22 and 24

Attempts to grow crystals suitable for X-ray crystallographic studies of the mesogenic complexes **1–18** have not been successful. Instead, the molecular and crystal structures of compounds **22** and **24** have been determined. Both compounds crystallize in centrosymmetric space groups ($P2_1/c$ and $P2/c$, respectively). The crystal parameters and information on data collection and refinement are summarized in Table 1. The molecular structures of **22** and **24** as well as packing diagrams are shown in Fig. 1 and 2 while bond lengths and angles for **22** and **24** are given in Tables 2 and 3, respectively. The metal atoms are located on centers of inversion. The intramolecular structural parameters of the diiodo–bis-isocyanide metal cores as well as the extended organic groups are within the expected range.[14] The length of the unsaturated core, as measured by the distance between the two oxygen atoms in the 4-positions of the arylimine portions, is *ca.* 30 Å. In the crystal of compound **22**, the molecules are stacked along their flat faces. A lateral shift of *ca.* 4 Å between adjacent molecular units allows the extended π systems to face each other directly despite the sterically demanding iodide ligands and isopropyl groups [Fig. 1(b)]. Nevertheless, the shortest intermolecular atomic contacts between the unsaturated systems are still longer than 3.7 Å. In the crystal of compound **24**, the molecules are also stacked along their flat sides. There is a long lateral shift of *ca.* 16 Å, as estimated by the Pt—Pt separation within the

Table 1 Crystal and data collection parameters data for complexes **22** and **24**

	22	24
formula	$C_{48}H_{60}I_2N_4O_2Pt$	$C_{56}H_{76}I_2N_4O_2Pt$
M_w	1173.93	1286.14
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (no.14)	$P2/c$ (no.13)
a/Å	14.584(2)	15.827(3)
b/Å	6.030(2)	10.085(2)
c/Å	27.184(3)	18.826(3)
β/degrees	91.96(2)	107.54(2)
V/Å^3	2389.2(7)	2865.2(9)
Z	2	2
T/°C	28	28
crystal color	yellow	yellow
D_c/g cm^{-3}	1.632	1.491
μ/cm^{-1}	42.57	35.57
diffractometer	MAR-IPDS	MAR-IPDS
$2\theta_{max}$/degrees	51.2	48.9
unique reflections	4097	3289
reflections used in least-squares refinement	2694	1692
no. of variables	259	295
R^a	0.044	0.041
$R_w{}^a$	0.054	0.045
$(\Delta/\sigma)_{max}$	0.02	0.00
goodness of fit	2.23	1.72
$\Delta\rho$/e Å^{-3}	2.00–1.00	0.87–0.40

$^aR=\sum||F_O|-|F_c||/\sum|F_O|$; $R_w=[\sum w(|F_O|-|F_c|)^2/\sum wF_O{}^2]^{1/2}$; $w=1/\sigma^2(F_O)=4F_O{}^2/\sigma^2(F_O{}^2)$.

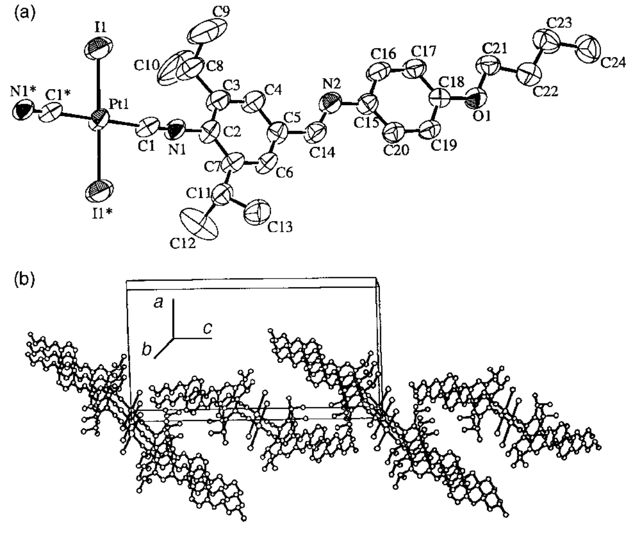

Fig. 1 (*a*) Molecular structure of compound **22**. One of the two symmetry-related isocyanide ligands is truncated to show only the CN-group. (*b*) Packing diagram of compound **22**.

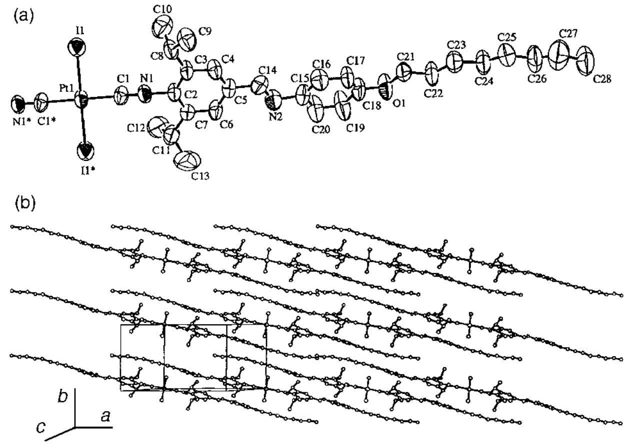

Fig. 2 (*a*) Molecular structure of compound **24**. One of the two symmetry-related isocyanide ligands is truncated to show only the CN-group. (*b*) Packing diagram of compound **24**.

Table 2 Selected bond lengths (Å) and angles (degrees) for complex **22**

Pt(1)—I(1)	2.6013(7)	Pt(1)—C(1)	1.979(8)
N(1)—C(1)	1.112(9)	N(1)—C(2)	1.395(9)
N(2)—C(14)	1.245(10)	N(2)—C(15)	1.418(9)
C(2)—C(3)	1.40(1)	C(5)—C(14)	1.47(1)
I(1)—Pt(1)—I(1)	180.0	I(1)—Pt(1)—C(1)	90.5(2)
I(1)—Pt(1)—C(1)	89.5(2)	C(1)—Pt(1)—C(1)	180.0
C(1)—N(1)—C(2)	178.0(8)	C(14)—N(2)—C(15)	120.4(7)
Pt(1)—C(1)—N(1)	176.9(7)	N(1)—C(2)—C(3)	116.6(8)
N(1)—C(2)—C(7)	119.3(8)	N(2)—C(14)—C(5)	122.7(8)
N(2)—C(15)—C(16)	115.2(7)	N(2)—C(15)—C(20)	126.9(7)

Table 3 Selected bond lengths (Å) and angles (degrees) for complex **24**

Pt(1)—I(1)	2.600(1)	Pt(1)—C(1)	1.94(1)
N(1)—C(1)	1.13(1)	N(1)—C(2)	1.43(2)
N(2)—C(14)	1.23(1)	N(2)—C(15)	1.47(2)
C(2)—C(3)	1.38(2)	C(5)—C(14)	1.50(2)
I(1)—Pt(1)—I(1)	180.0	I(1)—Pt(1)—C(1)	90.4(4)
I(1)—Pt(1)—C(1)	89.6(4)	C(1)—Pt(1)—C(1)	180.0
C(1)—N(1)—C(2)	178(1)	C(14)—N(2)—C(15)	120(1)
Pt(1)—C(1)—N(1)	177(1)	N(1)—C(2)—C(3)	115(1)
N(1)—C(2)—C(7)	117(1)	N(2)—C(14)—C(5)	122(1)
N(2)—C(15)—C(16)	125(1)	N(2)—C(15)—C(20)	115(1)

Table 4 Mesomorphic properties of the complexes **1–25**[a]

compound	transition	$T/°C$	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1 (Pd, L^5)	C–N	257	37.0	69.8
	N–I	284	—[b]	
2 (Pd, L^6)	C–N	228	58.8	117.4
	N–I	275	—[b]	
3 (Pd, L^8)	C–N	223	53.7	108.3
	N–I	294	—[b]	
4 (Pd, L^{10})	C1–C2	138	27.7	67.4
	C2–S_C	198	36.7	77.9
	S_C–N	235	1.5	3.0
	N–I	282	—[c]	
5 (Pd, L^{11})	C1–C2	107	46.9	123.4
	C2–S_C	190	39.2	84.7
	S_C–N	254	1.9	3.6
	N–I	290	3.1	5.5
6 (Pd, L^{12})	C1–C2	94	24.2	65.9
	C2–C3	136	9.9	24.2
	C3–S_C	178	42.4	94.0
	S_C–N	263	2.9	5.4
	N–I	287	4.6	8.2
7 (Pd, L^{14})	C1–C2	117	18.6	47.7
	C2–S_C	174	49.1	109.8
	S_C–N	269	3.7	6.8
	N–I	280	2.9	5.2
8 (Pd, L^{16})	C1–C2	104	37.1	98.4
	C2–S_C	168	56.5	128.1
	S_C–N	271	12.8[d]	23.5
	N–I	281	—[d]	
9 (Pd, L^{18})	C1–C2	76	8.9	
	C2–C3	108	47.0	123.6
	C2–S_C	152	45.2	106.4
	S_C–I	268	14.1	26.1
10 (Pt, L^5)	C–N	244	35.5	68.7
	N–I	318	—[b]	
11 (Pt, L^6)	C–N	206	53.6	111.9
	N–I	301	—[b]	
12 (Pt, L^8)	C–N	219	59.3	120.5
	N–I	295	—[b]	
13 (Pt, L^{10})	C1–C2	136	26.9	65.8
	C2–S_C	195	36.5	78.0
	S_C–N	249	1.4	2.8
	N–I	284	—[c]	
14 (Pt, L^{11})	C1–C2	104	38.2	100.1
	C2–S_C	179	35.5	78.9
	S_C–N	262	2.0	3.8
	N–I	290	—[c]	
15 (Pt, L^{12})	C1–C2	106	25.5	67.3
	C2–C3	147	9.2	21.9
	C3–S_C	167	30.5	69.3
	S_C–N	266	2.7	5.0
	N–I	293	3.3	5.8
16 (Pt, L^{14})	C1–C2	124	19.1	48.11
	C2–S_C	168	55.9	126.8
	S_C–N	277	4.8	8.7
	N–I	289	3.4	6.4
17 (Pt, L^{16})	C1–C2	110	43.3	113.1
	C2–S_C	161	56.3	129.7
	S_C–N	277	12.5[d]	22.7
	N–I	280	—[d]	
18 (Pt, L^{18})	C1–C2	110	66.5	173.6
	C2–S_C	141	43.8	105.8
	S_C–I	271	13.8	25.4
19 (Pd, $L^{5'}$)	C–I	212	73.9	152.4
20 (Pd, $L^{8'}$)	C–I	165	49.9	113.9
21 (Pd, $L^{11'}$)	C–I	172	55.0	123.6
22 (Pt, $L^{4'}$)	C–I	187	27.1	58.9
23 (Pt, $L^{5'}$)	C–I	209	55.3	114.4
24 (Pt, $L^{8'}$)	C–I	168	38.3	86.8
25 (Pt, $L^{11'}$)	C–I	162	44.2	101.6

[a]C = crystal; S_C = smectic C; N = nematic; I = isotropic. [b]Partial decomposition. [c]Not detected by DSC. [d]Peaks not resolved.

rows [Fig. 2(b)]. The shortest intermolecular contacts between the π systems are in the range of 3.53–3.69 Å. Even though the intermolecular distances between adjacent arene rings in the crystal of **22** are longer than those of **24**, the intermolecular contacts of the unsaturated systems in **22** are more extensive. This feature may, at least in part, be responsible for the higher melting point of **22** compared to **24**.

Liquid crystal properties of the palladium and platinum complexes

The palladium and platinum isocyanide complexes **1–25** contain organic fragments, which are well established components of organic liquid crystals,[23] and metal complex cores, which have recently been demonstrated to possess favorable mesogenic properties.[13,14] Azomethine-bridged aromatic compounds with terminal alkoxy groups have been the subject of many studies concerning liquid crystals.[23,24] The conjugated azomethine bridge increases the longitudinal polarizability while maintaining a relatively rigid arrangement of connected aromatic rings. Since Schiff-base linkages are easily established, they provide a convenient means to modify liquid crystal properties systematically, even though their sensitivity towards hydrolysis limits practical applications. The palladium and platinum metal centers extend the length of the linear isocyanides and establish the rigid core. Only the diiodo–palladium and –platinum fragments were employed. Takahashi and coworkers[8] have shown that these possess superior mesomorphic properties over the chloro- and bromo-analogues, primarily due to the higher stability of the *trans* configuration. The mesomorphic behaviour of the free isocyanides has not been studied.

The thermal properties of complexes **1–25** were investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. The N phases show marbled and *schlieren* textures, while the S_C phases exhibit fan-shaped textures (broken fan) on cooling from the N or I phases.[25] The phase transition temperatures and the associated thermal data are listed in Table 4. A plot of the phase transition temperatures of complexes **1–18** *versus* the length of the alkyl chains is shown in Fig. 3. Only the palladium and platinum complexes with the lateral methyl groups form liquid crystalline phases. Both the transition temperatures involving the crystalline (C–N or C–S_C) and the isotropic phases (N–I or S_C–I) decrease with increasing length of the alkyl chains, whereby the melting points decrease faster than the clearing points. Thus the temperature range of the mesophases becomes broader as the

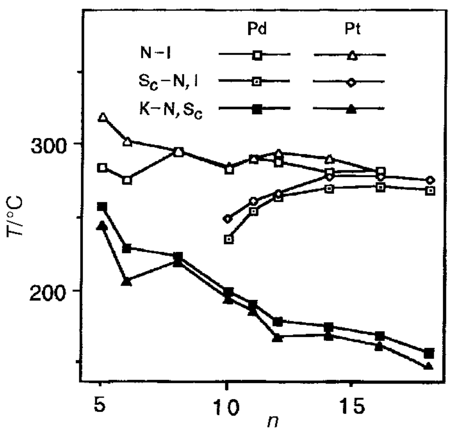

Fig. 3 Mesomorphic transition temperatures (°C) *vs.* the length of the alkoxy chain (OC_nH_{2n+1}) for complexes **1–18**

length of the alkyl chain increases. The compounds with alkyl chain lengths of $n = 5$–8 exhibit only a nematic mesophase. From $n = 10$ on, the appearance of a smectic C phase is observed, which reaches its maximum stability at $n = 16$–18. For $n = 18$, the nematic phase is no longer observed. This dependence of the thermal behaviour on the length of the alkyl chains is fully consistent with models developed for linear organic compounds possessing a rigid lath-shaped, electronically conjugated core and two flexible terminal groups.[24,25] For the complexes with very long alkyl chains, untypically high values for the S_C–N or S_C–I transition enthalpies were found.[24] The physical meaning of these data is unclear. High transition enthalpy values have also been observed for other liquid crystals with long terminal alkyl chains.[26] The platinum complexes exhibit on average slightly lower melting points and higher clearing points than the palladium compounds. Thus the platinum complexes form the more stable mesophases with the broader temperature ranges. This is in contrast to the results by Takahashi and co-workers[14] who found the reverse situation for the compounds $[MI_2(4\text{-}CNC_6H_4\text{-}4\text{-}O_2CC_6H_4OC_nH_{2n+1})_2]$. Nevertheless, since the differences in phase transition temperature between the complexes of the two metals are relatively small, our results confirm the conclusion reached earlier by Kaharu and Takahashi[12] that for a given ligand set a change of metal center exerts only a minor influence. The fact that the mesophases of complexes **1–18** exhibit a broader temperature range than the Takahashi compounds[14] is of interest. Considering that these compounds and the complexes reported here possess the same number of aromatic groups, it appears reasonable to speculate that the lateral methyl groups in compounds **1–18** may have a favourable influence on the mesomorphic properties. The methyl groups extend laterally about as far as the two iodide ligands, thus giving the central portion of the molecules a more even lath-like shape.[23,27] The lack of mesomorphic character of the metal complexes with the lateral isopropyl groups can be attributed to a disruption of the intermolecular interactions by these bulky substituents. The isopropyl-substituted complexes also have distinctly lower melting points than the methyl-substituted compounds, by as much as 51 °C for M = Pt, $n = 8$.

The isocyanide metal complexes, especially the palladium complexes with the shorter side chains, showed signs of decomposition during the investigation of the phase transitions. Slow heating of the samples during the polarized optical microscopy studies caused a marked darkening in colour. For this reason, the DSC scans were performed at a high rate of 20 °C min^{-1}. The data for selected examples were also measured at a scan rate of 10 °C min^{-1}, confirming the results obtained at the higher scan rate. Thermogravimetric analyses were performed on complexes **5**, **9**, **14** and **18**. At a heating rate of 20 °C min^{-1}, the palladium complexes began to decompose at around 335 °C, the platinum compounds near 350 °C. Below those temperatures, no significant signs of decomposition could be discovered at that heating rate.

Experimental

Measurements and reagents

The ^1H and ^{13}C NMR spectra were recorded on Bruker DPX 300 or JEOL 270 spectrometers in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra in CH_2Cl_2 were obtained on a Shimadzu FTIR-8201PC IR spectrophotometer. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. The textures of the mesophases were studied with a Leica polarizing microscope equipped with a Mettler FP82 hot stage. The transition temperatures were obtained by differential scanning calorimetry using a Perkin-Elmer DSC7 with heating rates of 10 or 20 °C min^{-1} under a nitrogen atmosphere. The data were taken from the first heating scan. Elemental microanalyses were conducted by Butterworth Laboratories Ltd.

4-Isocyano-3,5-dimethylbenzaldehyde and 4-isocyano-3,5-diisopropylbenzaldehyde were obtained as previously described.[20] The 4-alkoxynitrobenzenes and corresponding 4-alkoxyanilines were prepared following literature methods.[28,29] All ligands and metal complexes were prepared in the same manner as outlined in Scheme 1. Typical preparative procedures and physical data for the ligands and complexes are given for L^8 and **12**. The spectroscopic data for **6** are given as a typical example for the palladium complexes. Most of the new isocyanides were obtained as oils which are difficult to purify and crystallize. Therefore, no elemental analyses were performed on these compounds. The palladium and platinum complexes were all prepared following the procedure described for **12**. Satisfactory elemental analyses were obtained for all isocyanide metal complexes. A complete set of spectroscopic and microanalytical data is deposited as supplementary material (**SUP 57376**).‡

Selected syntheses and characterisation

L^8. A mixture of 4-isocyano-3,5-dimethylbenzaldehyde (160 mg, 1 mmol), 4-octyloxyaniline (221 mg, 1 mmol) and 2 drops of acetic acid in ethanol (20 ml) was stirred at room temperature. After stirring for 4 h, the solvent was evaporated under vacuum to near dryness to give a light yellow solid which was further purified by recrystallization from ethanol–THF (5 : 1, v/v) (312 mg, 89%). ^1H NMR ($CDCl_3$): δ 8.41 (1 H, s, $-CH{=}N$) 7.63 (2 H, s, Ar-H), 7.24 (2 H, d, $J = 8.8$ Hz, Ar-H), 6.93 (2 H, d, $J = 8.8$ Hz, Ar-H), 3.97 (2 H, t, $J = 6.6$ Hz, $-OCH_2-$), 2.51 (6 H, s, Ar-CH_3), 1.81–1.91 (12 H, m, C_6H_{12}), 0.89 (3 H, t, $J = 6.6$ Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$, 270 MHz): δ 169.4, 158.4, 156.3, 144.0, 136.4, 135.4, 127.7, 122.3, 115.1 ($C{=}N$, C_6H_2, C_6H_4), 68.3 (CH_2O), 31.8, 29.4, 29.3, 26.1, 22.7 (CH_2), 18.9 (Ar-CH_3), 14.1 (CH_3). IR (CH_2Cl_2, cm^{-1}): $\nu(N{\equiv}C)$ 2119 s. MS (EI) *m/z*: 362 (M).

$PtI_2(L^8)_2$ (12). To a solution of L^8 (71 mg, 0.2 mmol) in 15 ml THF was added PtI_2 (45 mg, 0.1 mmol) with stirring under N_2 atmosphere at room temperature. After stirring for 2 h, the resultant yellow solution was filtered, and the solvent was removed under vacuum. The residue was reprecipitated from THF–*n*-hexane to give a yellow microcrystalline solid. Yield: 68 mg (58%); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.44 (1 H, s, $-CH{=}N$), 7.68 (2 H, s, Ar-H), 7.26 (2 H, d, $J = 8.9$ Hz, Ar-H), 6.95 (2 H, d, $J = 8.9$ Hz, Ar-H), 3.98 (2 H, t, $J = 6.6$ Hz,

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‡Available as supplementary material (**SUP 57376**; 18 pp.) deposited with the British Library. Details are available from the editorial office.

$-\mathrm{OCH_2}-$), 2.64 (6 H, s, Ar-$\mathrm{CH_3}$), 1.82–1.29 (12 H, m, $\mathrm{C_6H_{12}}$), 0.89 (3 H, t, $J=6.7$ Hz, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 270 MHz): δ 158.6, 155.7, 143.7, 137.9, 137.3, 128.1, 122.4, 115.1 (CH=N, $\mathrm{C_6H_2}$, $\mathrm{C_6H_4}$), 68.3 ($\mathrm{CH_2O}$), 31.8, 29.4, 29.3, 26.1, 22.7 ($\mathrm{CH_2}$), 19.1 (Ar-$\mathrm{CH_3}$), 14.1 ($\mathrm{CH_3}$). IR ($\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): $\nu(\mathrm{N{\equiv}C})$ 2189 s; Mass (FAB) *m*/*z*: 1174 (M+1). Anal. Calc. for $\mathrm{C_{48}H_{60}I_2N_4O_2Pt}$: C, 49.11; H, 5.12; N, 4.77. Found: C, 49.15; H, 5.16; N, 4.84%.

$\mathrm{PdI_2(L^{12})_2}$ (6). Light orange crystals (76% yield); ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): δ 8.44 (1 H, s, $-$CH=N), 7.68 (2 H, s, Ar-H), 7.26 (2 H, d, $J=8.8$ Hz, Ar-H), 6.95 (2 H, d, $J=8.8$ Hz, Ar-H), 3.98 (2 H, t, $J=6.6$ Hz, $-\mathrm{OCH_2}-$), 2.64 (6 H, s, Ar-$\mathrm{CH_3}$), 1.80–1.27 (20 H, m, $\mathrm{C_{10}H_{20}}$), 0.88 (3 H, t, $J=6.7$ Hz, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 270 MHz): δ 158.6, 155.7, 143.7, 137.9, 137.3, 128.1, 122.4, 115.1, 68.3, 31.9, 29.7, 29.6, 29.4, 29.3, 26.1, 22.7, 19.1, 14.1; IR ($\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): $\nu(\mathrm{N{\equiv}C})$ 2196 s; Mass (FAB) *m*/*z*: 1196 (M). Anal. Calc. for $\mathrm{C_{56}H_{76}I_2N_4O_2Pd}$: C, 56.17; H, 6.35; N, 4.68. Found: C, 56.33; H, 6.53; N, 4.69%.

Crystal structure determinations

The crystal parameters of compounds **22** and **24** and information on data collection and refinement are summarized in Table 1. Diffraction data for compounds **22** and **24** were collected on a MAR Imaging Plate Detector System using graphite-monochromatized Mo-Kα X-ray radiation ($\lambda=0.701\,73$ Å) from an MAR generator (sealed tube 50 kV and 50 mA), and processed by DENZO.[30] No absorption corrections were made. All structure determinations were done using the MSC crystal structure analysis package TeXsan[31] and the full-matrix least-squares refinements were on F using reflections with $I>3\sigma(I)$. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculations, but not refined.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/94.

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