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Liquid-crystalline complexes of palladium(II) and platinum(II) with di- and tri-alkoxystilbazoles: ligand control of mesomorphism

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Liquid-crystalline complexes of palladium and platinum are formed when the metals are complexed to stilbazoles (4-styrylpyridines) bearing either two or three alkoxy chains. The complexes, termed polycatenar, show smectic C mesophases for most 3,4-disubstituted ligands, while the use of trisubstituted ligands leads to complexes showing columnar organisation, demonstrating that the spatial organisation of the metals in the liquid-crystal mesophase can be rather readily controlled. Complexes of these di- and tri-substituted stilbazoles with a *cis*-dicarbonylchloroiridium(I) fragment were not liquid crystalline.

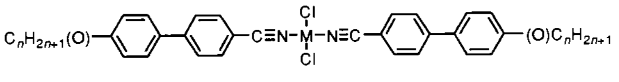
One of the problems which can beset liquid-crystalline metal complexes is that of decomposition on account of the high transition temperatures often found. Various strategies have been adopted to surmount this problem which have met with differing degrees of success. These are well addressed in the review literature to which the reader is directed.[1]

In our first studies of mesomorphic metal complexes[2] we had looked at cyanobiphenyl complexes **1** of Pd^{II} and Pt^{II}. While the palladium complexes showed mesophases roughly in the range 90–130 °C, those of Pt showed mesomorphism at temperatures up to 240 °C where decomposition was a problem. It is interesting that recently Takahashi and co-workers[3] reported the synthesis of the related complexes based on isocyanide derivatives of the biphenyls and found little difference between the mesomorphic behaviour of the complexes of Pd and Pt. As the interaction between organoisocyanides and the Group 10 metals would be expected to be stronger than those of organonitriles, and as third-row transition elements would be expected, in general, to form stronger bonds than second-row transition elements, then we would assign the lower transition temperatures in our palladium complexes to a flexibility about the M−N bond.

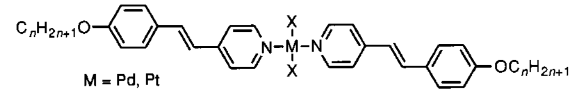
Following these studies of cyanobiphenyl complexes, we had turned our attention to complexes of 4-alkoxy-4′-stilbazoles,[4] which we have studied extensively.[5] The complexes **2** of these stilbazoles (4-styrylpyridines) with Pd^{II} and Pt^{II} give either materials which are non-mesomorphic (Pd) or mesomorphic only at rather high temperatures (Pt), for example above 200 °C. In previous work, Maitlis and co-workers had shown that two successful strategies for reducing the transition temperatures of these complexes were (*i*) to replace the chloro ligands with aliphatic carboxylate groups, **3**, and (*ii*) to replace one of the alkoxystilbazoles with a terminal alkene, **4**. The former strategy gave materials (for Pd) with nematic phases up to around 160 °C,[6] while the latter (for Pt) gave complexes with smectic A (S_A) phases near room temperature.[7] Thus, the former strategy used an increased number of alkyl chains to facilitate a reduction in transition temperature.

A third strategy is represented by lowering the symmetry of the system, and here we would draw attention to stilbazole complexes of Ir^I, **5**, which behave like simple dipolar liquid crystals, melting at temperatures around 80 °C and clearing between 120 and 140 °C.[8]

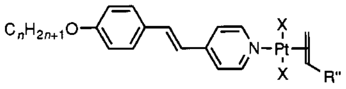
Addition of extra alkyl chains can be a very productive strategy for the reduction of transition temperature, which we have used in liquid-crystalline complexes of silver(I)[9] and in metalloporphyrins.[10] Furthermore, as well as reducing the transition temperatures, addition of further chains can lead to changes in the liquid crystal phase behaviour as more terminal chains can, under the correct conditions, promote columnar mesomorphism, while lateral chains tend to promote nematic phases. With this in mind, we undertook the synthesis of some di- and tri-alkoxystilbazoles and have successfully used them as ligands to silver(I), generating materials with cubic and columnar mesophases.[11] Having these ligands to hand, we therefore undertook the synthesis of some of their complexes with Pd^{II}, Pt^{II} and Ir^I.



1 M = Pd, Pt



2 X = Cl
3 X = O_2C–R′



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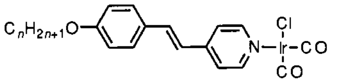

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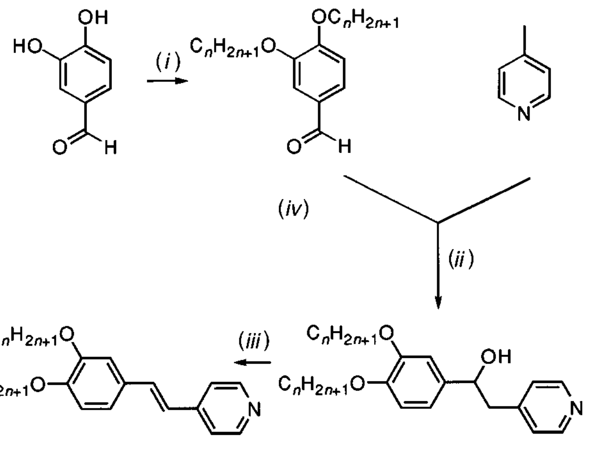
Results and Discussion

Syntheses of the ligands

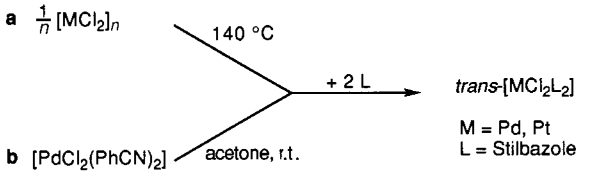
The 3,4-dialkoxystilbazoles were obtained as shown in Scheme 1 and as described in detail in refs. 11(*b*) and 11(*c*). The 2,4-dialkoxy-, 2,3,4- and 2,4,5-trialkoxy-stilbazoles were prepared similarly starting from the corresponding di- or tri-hydroxybenzaldehyde. However, the 3,5-dialkoxy- and 3,4,5-trialkoxy-stilbazoles were prepared in a slightly different manner. Thus, the relevant benzaldehyde was obtained by first alkylating either 3,5-dihydroxy- or 3,4,5-trihydroxy-methylbenzoate. The resulting polyalkoxymethylbenzoate was then reduced to the corresponding benzyl alcohol with $LiBH_4$, and reoxidised to the benzaldehyde with pyridinium chlorochromate. Coupling with 4-methylpyridine was then carried out as for the other benzaldehydes.

Synthesis of the complexes

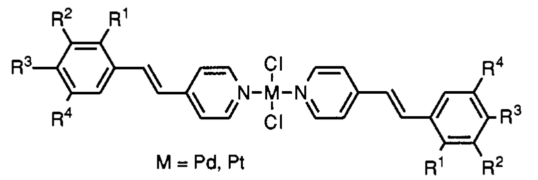
The complexes of Pd and Pt were prepared by two different methods (Scheme 2). The first method was a melt synthesis that



Scheme 1 Synthesis of the alkoxystilbazoles: (*i*) $C_nH_{2n+1}Br$–K_2CO_3–butanone, heat; (*ii*) (*a*) LiNPr$^i_2$–tetrahydrofuran (thf), −78 °C, (*b*) H^+, water, ambient; (*iii*) pyridinium *p*-toluenesulfonate, toluene, heat

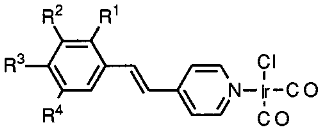


Scheme 2 Preparation of the palladium(II) and platinum(II) complexes; r.t. = room temperature



Tetracatenar: **6** 3,4-dialkoxy: $R^1 = R^4 = H$; $R^2 = R^3 = OC_nH_{2n+1}$
7 3,5-dialkoxy: $R^1 = R^3 = H$; $R^2 = R^4 = OC_nH_{2n+1}$
8 2,4-dialkoxy: $R^1 = R^3 = OC_nH_{2n+1}$; $R^2 = R^4 = H$

Hexacatenar: **9** 3,4,5-trialkoxy: $R^1 = H$; $R^2 = R^3 = R^4 = OC_nH_{2n+1}$
10 2,3,4-trialkoxy: $R^1 = R^2 = R^3 = OC_nH_{2n+1}$; $R^4 = H$
11 2,4,5-trialkoxy: $R^1 = R^3 = R^4 = OC_nH_{2n+1}$; $R^2 = H$



12 $R^1 = R^4 = H$; $R^2 = R^3 = OC_nH_{2n+1}$
Two chains **13** $R^1 = R^3 = H$; $R^2 = R^4 = OC_nH_{2n+1}$
14 $R^1 = R^3 = OC_nH_{2n+1}$; $R^2 = R^4 = H$

Three chains **15** $R^1 = H$; $R^2 = R^3 = R^4 = OC_nH_{2n+1}$

we developed a few years ago[12] in which 1 equivalent of the metal dichloride (MCl_2, M = Pd or Pt) is added to 3 equivalents of the stilbazole in the melt and stirred for half an hour (Scheme 2, reaction **a**). The complexes were then dissolved in chloroform, filtered through a pad of Celite, and then obtained pure by crystallisation from a mixture of chloroform–diethyl ether and then by recrystallisation from acetone. This method was used for a few palladium complexes only and for all the platinum complexes. All other palladium complexes were prepared by direct reaction of the stilbazole with bis(benzonitrile)dichloropalladium(II) in acetone at room temperature (Scheme 2, reaction **b**). The precipitate was filtered off, washed thoroughly with cold acetone, and crystallised from acetone. While both reactions proceeded in good yields, the second method was generally preferred for the palladium complexes.

The complexation of stilbazole with the metal fragments MCl_2 was confirmed by ^1H and ^{13}C NMR spectroscopy. The spectra of the complex and the free stilbazole were very similar, but a significant increase of the chemical shift of some proton–carbon pairs could be observed. For example, the protons *ortho* to the pyridine nitrogen were shifted downfield by 0.2 ppm, while the carbons *ortho* and *para* to the ring nitrogen were shifted by 2–4 ppm. The ^1H NMR spectra also indicated that the ligands retained their *trans* configuration after complexation as evidenced by the coupling constant of the AB system ($J_{AB} = 16.5$ Hz).

In the structures of the complexes, the nomenclature 'tetracatenar' (**6**–**8**) and 'hexacatenar' (**9**–**11**) is used after the normal practice in naming polycatenar (literally 'many-chained') mesogens.[13]

The iridium(I) complexes **12**–**15** were simply prepared in a room-temperature reaction between $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$, (cod = *cis,cis*-cycloocta-1,5-diene) with 2 equivalents of the appropriate stilbazole in dichloromethane under an atmosphere of carbon monoxide, followed by precipitation with hexane. The complexes, forming a yellow solution in dichloromethane, showed the expected two ν(CO) vibrations at 2080 and 1995 cm^{-1} consistent with a mononuclear *cis*-dicarbonyl complex. The *cis* co-ordination was confirmed by ^{13}C NMR spectroscopy which showed two resonances for the carbonyls rather than the one expected for *trans* co-ordination. In the solid state the complexes showed different IR spectra. Two bands were observed for **13** and **14** at 2075, 1990 and 2070, 1990 cm^{-1} respectively, consistent with the solution IR spectra. However, three bands were observed for complex **12** at 2080, 2050 and 1980 cm^{-1} while for **15** four bands were found at 2080, 2060, 1990 and 1980 cm^{-1}. Similar to the iridium complexes which we have previously synthesised,[14] the extra bands were attributed to the solid-state stacking of the complexes. In the far-IR region of all the complexes a broad band was also observed at 320–330 cm^{-1}, attributed to ν(Ir–Cl).

Thermal behaviour of the iridium(I) complexes 12–15

Unlike their counterparts based on monosubstituted 4-alkoxystilbazoles which typically showed enantiotropic nematic (N) and S_A phases in the temperature range 80–140 °C, none of these new complexes displayed mesomorphic properties, simply melting to the isotropic state and showing no evidence of monotropic phase formation. We believe the lack of mesomorphism to be due to the huge reduction of the anistropy of the molecule on the introduction of the extra chain(s), indeed it is normally the case that rod-like molecules containing more than one chain at one end only require several rings in the structure before mesomorphism is observed. However, the melting points, collected in Table 11, are much higher than might otherwise have been expected with the reduced overall anisotropy.

However, we note that Serrette and Swager[15] have observed mesomorphism in dioxomolybdenum(VI) complexes of closely related tricatenar ligands, where the mesomorphism is considered to be promoted by intermolecular Mo···O interactions, stabilising the observed columnar structure. Conversely, we[16] have provided evidence that, in dimeric equivalents of the iridium complexes **5**, intermolecular interactions appear to suppress mesomorphism. This observation, combined with that of Serrette and Swager, shows that in liquid-crystalline metal complexes specific intermolecular interactions can be both friend and foe!

We have previously shown[17] that the related complexes of monoalkoxystilbazoles form well defined Langmuir–Blodgett films, and that in alternate-layer fabrications they exhibit a high pyroelectric response. These complexes are currently under investigation in this domain.

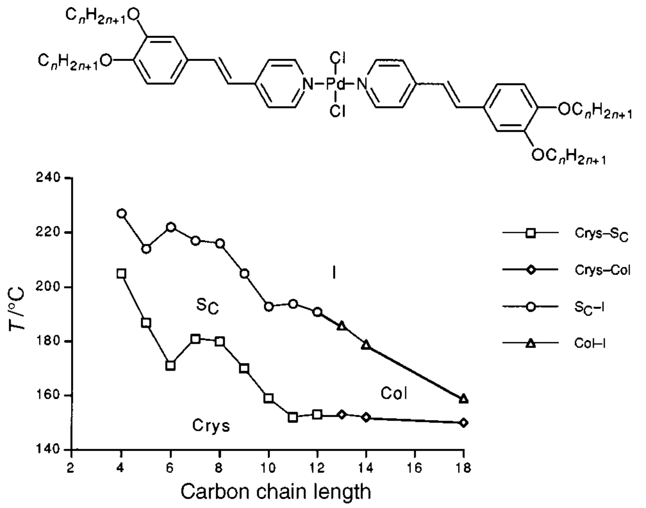


Fig. 1 Phase diagram of the *trans*-bis(3′,4′-dialkoxy-4-stilbazole)-dichloropalladium(II) complexes **6**. Crys = Crystalline modification, Col = columnar, I = isotropic

Thermal behaviour of the palladium(II) and platinum(II) complexes

Four series amongst the seven synthesized displayed mesomorphic properties, namely the tetracatenar complexes of Pd and Pt with 3,4-disubstituted ligands (**6**) and the two hexacatenar complexes with 3,4,5- (**9**) and 2,3,4-trisubstituted (**10**) ligands. This is yet another example of the way in which metal centres can induce mesomorphism in non-mesomorphic systems.

Complexes of 3,4-dialkoxystilbazoles. The two series (Pd and Pt) exhibited a very similar mesomorphism and the phase diagram of the palladium complexes is shown in Fig. 1. The thermal data are collected in Tables 1 and 2 for Pd and Pt respectively. The behaviour will be discussed in terms of the palladium complexes with differences being emphasised later.

The first three members of the palladium series ($n = 1$, 2 and 3) were not liquid crystals and melted at very high temperatures (>260 °C). The decrease in the melting point was very sharp on going from $n = 1$ to $n = 3$, which was expected as the extra alkoxy chain(s) lead to a relatively less efficient packing of the molecules in the crystal state. Compounds with $n = 4$ to $n = 12$ showed a smectic C phase [Fig. 2(*a*)], readily characterised by its optical texture, whose transition temperatures (melting and clearing) decreased rather smoothly as the alkoxy chain length was increased. The phase was identified by its optical texture, namely a schlieren-like texture with four brushes and the development of a broken-focal conic texture on cooling from the isotropic liquid. However, we would draw attention to the clearing point of the complex with $n = 4$ and the melting point of the complex with $n = 6$. Normally, one would expect to see a rather smooth variation in transition temperatures with varying chain length. However, clearly at $n = 4$, a lower-than-expected transition temperature is found, and it does not vary with repeated repurification. The melting point for $n = 6$ is also invariant with repurification. We are therefore confident that the temperatures are accurate and are therefore initiating a more detailed study of this part of the phase diagram.

For $n > 12$ the compounds showed a columnar phase, again identified by the characteristic optical texture, which on the basis of the observation of large homeotropic domains was assigned as a hexagonal phase. The sudden change in mesomorphism was also associated with a slight increase in viscosity. As the chain length increased the stability of the anisotropic domain seemed to decrease, and so to check if liquid-crystalline properties were still present for longer chain lengths we synthesized the compound with $n = 18$. The compound was still mesomorphic and displayed a columnar mesophase, but over a much narrower temperature range ($\Delta T = 10$ °C). Such a sudden change from S_C to columnar (Col) behaviour is not so common in polycatenar systems, and it is often the case that the two phases co-exist in one or two homologues, occasionally accompanied by a liquid-crystal cubic phase. For example, we have found that in tetracatenar derivatives or extended 2,2′-bipyridines the crossover from S_C to columnar phases occurs with the co-existence of S_C and cubic phases in four homologues, the last also co-existing with the columnar phase.[18]

Table 1 Transition temperatures and thermal data for the *trans*-dichlorobis(3′,4′-dialkoxy-4-stilbazole)palladium(II) complexes **6**

n	Transition	*T*/°C	Δ*H*/kJ mol^{-1}	ΔS_m/J K^{-1} mol^{-1}
1[a]	Crys-I	>300	—	—
2	Crys-I	293	—	—
3	Crys-I	266	62.8	117
4	Crys-S_C	205	49.0	102
	S_C-I	227	12.6	25
5	Crys-Crys′	142	5.6	14
	Crys′-S_C	187	32.2	114
	S_C-I	214	7.4	15
6	Crys-Crys′[b]	159	−13.7	−32
	Crys′-Crys″	165	25.5	58
	Crys″-S_C	171	25.1	57
	S_C-I	222	14.1	28
7	Crys-Crys′	155	32.8	77
	Crys′-S_C	181	29.4	65
	S_C-I	217	12.0	24
8	Crys-Crys′	91	9.4	26
	Crys′-Crys″	144	43.9	105
	Crys″-S_C	180	33.2	73
	S_C-I	216	13.5	28
9	Crys-Crys′[b]	62	−8.3	−25
	Crys′-Crys″	86	11.9	33
	Crys″-Crys‴	149	36.8	87
	Crys‴-S_C	170	30.2	68
	S_C-I	205	11.0	23
10	Crys-Crys′	87	13.4	37
	Crys′-Crys″[b]	138	−8.7	−21
	Crys″-Crys‴	149	22.3	53
	Crys‴-S_C	159	25.3	59
	S_C-I	193	10.2	22
11	Crys-Crys′[b]	90	−5.4	−15
	Crys′-Crys″[c]	145	—	—
	Crys″-S_C	152	82.3	194
	S_C-I	194	9.4	20
12	Crys-Crys′	80	17.3	49
	Crys′-Crys″	135	18.2	45
	Crys″-Crys‴	147	21.1	50
	Crys‴-S_C	153	67.9	159
	S_C-I	191	8.6	18
13	Crys-Crys′	96	1.7	05
	Crys′-Crys″	146	18.4	44
	Crys″-Col	153	30.1	71
	Col-I	186	4.0	9
14	Crys-Crys′	67	12.6	37
	Crys′-Crys″	130	16.4	41
	Crys″-Crys‴	143	27.6	66
	Crys‴-Col	152	41.2	97
	Col-I	179	5.2	12
18	Crys-Crys′	125	—	—
	Crys′-Crys″	137	56.7[c]	138[c]
	Crys″-Col	150	30.3	72
	Col-I[d]	159	—	—

[a] Decomposition. [b] Crystallisation peak. [c] Combined Δ*H*/Δ*S*. [d] Not observed by DSC.

The DSC traces showed that the peak corresponding to the columnar-to-isotropic transition was always noticeably broader than the sharp peak associated with the smectic C-to-isotropic transition. The broadness of the columnar-phase-to-isotropic transition could well be the result of lattice melting behaviour,[19] whereby the two-dimensional lattice of the columnar phase (hexagonal or rectangular) is lost, releasing free columns which retained their integrity in the isotropic state before desegre-

Table 2 Transition temperatures and thermal data for the *trans*-dichlorobis(3′,4′-dialkoxy-4-stilbazole)platinum(II) complexes **6**

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J K^{-1} mol^{-1}
4	Crys-S_C	204	49.4	103
	S_C-I	211	7.9	16
5	Crys-Crys′	140	1.4	3
	Crys′-Crys″	157	14.7	34
	Crys″-S_C	182	35.1	77
	S_C-I	213	5.4	11
11	Crys-Crys′	83	11.1	31
	Crys′-Crys″	138	65.6	160
	Crys″-S_C	144	18.0	43
	S_C-I	187	3.2	7
12	Crys-Crys′	77	12.8	37
	Crys′-Crys″	134	77.6	190
	Crys″-S_C	148	18.3	44
	S_C-I	188	8.4	18
13	Crys-Crys′	138	46.5	113
	Crys′-S_C	142	13.6	37
	S_C-I	176	3.8	9
14	Crys-Crys′	136	65.3	160
	Crys′-S_C	139	12.3	30
	S_C-I	168	3.5	8
18	Crys-Crys′	59	6.2	19
	Crys′-Col	136	146.4	358
	Col-I	162	4.9	11

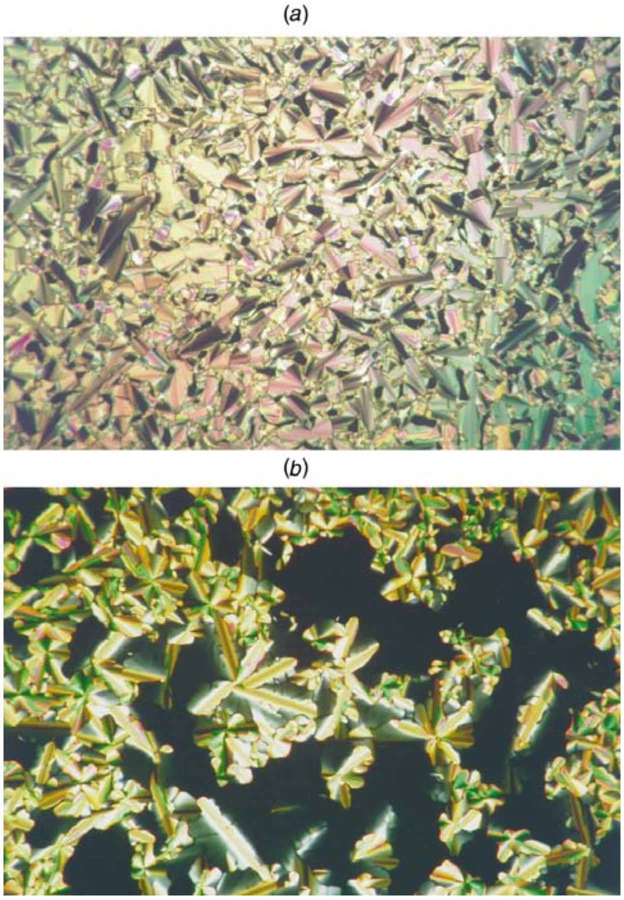


Fig. 2 Optical micrographs of (*a*) the smectic C phase of *trans*-dichlorobis(3′,4′-didodecyloxy-4-stilbazole)palladium(II) at 175 °C on cooling from the isotropic phase, (*b*) the columnar phase of *trans*-dichlorobis(2′,3′,4′-tridodecyloxy-4-stilbazole)palladium(II) at 120 °C on cooling from the isotropic phase

gation. It may also have a contribution from the fact that one might assume that the intermolecular attractive forces may be greater in the columnar phase of a tetracatenar mesogen compared to the smectic C phase in order to retain the columnar integrity. This idea is supported by the observation that the columnar phases of the tetracatenars are less fluid than the smectic C phases. We therefore suspect that this effect may be greater in polycatenar systems than in columnar phases of disc-like molecules, although in both cases there ought to be an observable difference between what are sometimes termed *ordered* and *disordered* columnar phases.

Despite their relatively high transition temperatures, these complexes showed a much more accessible mesomorphism than the related *trans*-bis(4′-alkoxy-4-stilbazole)dichloropalladium(II) complexes **2**. In addition, they were found to be rather stable, showing a reproducible mesomorphic behaviour after several heat–cool cycles.

A few analogous platinum complexes were also synthesized to see if they were liquid crystals and if they were possessed of a similar mesomorphism to their palladium congeners. For $n \leqslant 12$ the platinum complexes behaved in a similar way to palladium complexes, showing a smectic C phase at slightly lower temperatures. However, for $n = 13$ and 14, the platinum complex still displayed the smectic C phase whereas the palladium exhibited a columnar phase; this is discussed in more detail below. The homologue with $n = 18$ displayed a columnar phase, assigned on the basis of its optical textures, over a wider range of temperature ($\Delta T = 30$ °C). Owing to the similarity of the mesomorphism, only a few platinum complexes were made and further studies were carried out with palladium alone.

The general behaviour of these complexes is rather comparable with organic tetracatenar mesogens. Thus, normally one would expect to see a smectic C and perhaps a nematic phase at relatively short chain lengths, passing into a columnar phase as the chain length increases, often *via* a cubic phase at some intermediate chain length. The metal complexes in this case do not show a nematic or cubic phase, but in all other regards are typical tetracatenar mesogens. Thus, by the addition of an alkoxy chain in the 3 position of the ligand, mesophases have been realised and at reduced temperatures.

Palladium complexes of 3,5-dialkoxystilbazoles 7 and of 2,4-dialkoxystilbazoles 8. None of the 3,5-disubstituted materials **7** was mesomorphic with the exception of the derivative with $n = 14$ which showed a viscous, ill defined mesophase (M_1) which supercooled some 45 °C from the isotropic phase and which gave the appearance of being columnar. The general lack of mesomorphism was not entirely surprising as there is only one example of a mesomorphic organic polycatenar material with 3,5-disubstitution.[20] However, the materials did show rather low melting points which decreased rapidly from the butoxy to the nonyloxy homologues, a fact which we connect with the *meta* position of all the alkoxy chains.

None of the palladium complexes with 2,4 disubstitution, **8**, was mesomorphic, either. The total loss of the liquid-crystalline properties was attributed to the lateral chains in the 2 position which, it was assumed, strongly reduced the lateral interactions between the molecules, and also reduced the segregation between the aromatic and aliphatic part of the molecule, these two effects disfavouring a lamellar mesomorphism. The unoccupied volume present between the two chains also disfavoured a columnar rearrangement, the paraffinic matrix being insufficient to sustain the formation of stable columns. However, the complexes **8** may be compared structurally to the palladium complexes of simple 4-alkoxystilbazoles bearing alkylcarboxylate ligands which also possessed a lateral alkyl chain and which showed a nematic phase,[7] and to other organic mesogens[21] which similarly have lateral chains and are mesomorphic. In this context, a lack of mesomorphism in **8** is a little more surprising, although clearly the exact disposition of the lateral chains will be crucial. Thermal data for complexes **7** and **8** are collected in Table 3.

Hexacatenar palladium(II) complexes 9. As expected, these materials showed columnar mesomorphism. The phase diagram is shown in Fig. 3, and the thermal data are collected in

Table 3 Transition temperatures and thermal data for complexes **7** and **8**

n	Complex	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J K^{-1} mol^{-1}
4	**7**	Crys-Crys′	180	16.3	36
		Crys′-I	190	37.4	81
9	**7**	Crys-Crys′	68	83.0	243
		Crys′-I	105	23.1	61
11	**7**	Crys-Crys′	69	81.5	238
		Crys′-I	100	20.7	55
14	**7**	Crys-Crys′	60	6.7	20
		Crys′-M_1	76	98.5	282
		M_1-I	95	9.5	14
7	**8**	Crys-Crys′	79	16.6	47
		Crys′-Crys″	124	32.1	81
		Crys″-I	151	66.6	157
10	**8**	Crys-Crys′	93	36.0	98
		Crys′-I	126	42.2	106
14	**8**	Crys-Crys′	104	44.6	118
		Crys′-I	115	40.5	104

M_1 is an unidentified mesophase.

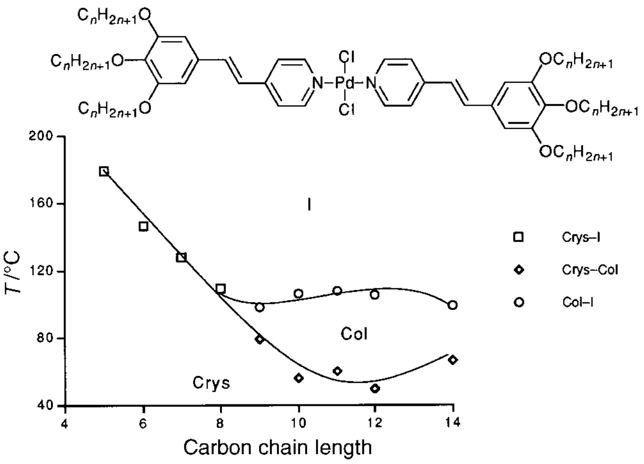


Fig. 3 Phase diagram of the *trans*-dichlorobis(3′,4′,5′-trialkoxy-4-stilbazole)palladium(II) complexes **9**

Table 4. For $n < 9$ the complexes were not liquid crystals and melted directly to the isotropic liquid on heating; however, for larger n, a columnar phase appeared. The texture of the mesophase formed by the complexes was typically characteristic of this type of phase, namely a broken-fan texture on heating and the growth of dendritic monodomains on cooling from the isotropic liquid; the phase seemed to have a hexagonal symmetry as the presence of wide homeotropic monodomains suggested a uniaxial mesophase. The transition temperatures were much lower than in the tetracatenar complexes above, being close to room temperature in some cases, and the mesophases were generally more accessible than those found in organic hexacatenar materials.

Hexacatenar palladium(II) complexes 10. This type of hexacatenar complex was the first to display two mesophases for the same homologue. The thermal behaviour is illustrated graphically in Fig. 4 and the thermal data are collected in Table 5. For $n = 6$ the complex melted directly to the isotropic liquid after undergoing several crystal-to-crystal transitions. The other complexes displayed two mesophases, the microscopic observations suggesting the following behaviour. On heating the crystals melted to a fluid mesophase (M_2) at around 80 °C, confirmed by large enthalpies of transition. On further heating another transition could be observed but owing to the strong paramorphotic texture we were just able to recognise a broken-fan texture, characteristic of a columnar mesophase. This mesophase melted cleanly to the isotropic liquid at around 140 °C. On cooling a typical columnar texture was observed and here again, owing to the development of well defined, growing monodomains as well as wide homeotropic area, the phase was assigned as hexagonal columnar [Fig. 2(*b*)]. On further cooling a clear change in the optical texture could be observed. The homeotropic area disappeared and a spherulitic texture occupied that domain. The behaviour was reproducible on further heat–cool cycles. This transition was not observed by calorimetric studies, indicating a second-order transition and suggesting that the two mesophases must have different symmetry. Such effects had previously been observed with hexacatenar materials (Scheme 3) displaying columnar-to-columnar transitions, such as hexagonal-to-oblique (on cooling) where the transition enthalpy was very small.[22] Owing to the similarities with our systems, we might initially assume that the phase is oblique, a tilted version of the hexagonal columnar phase. Full characterisation must await the results of X-ray diffraction studies which will be reported in due course.

The transitions between these two mesophases were observed at different temperatures for each homologue in the series, the stability of these mesophases being highly dependent on the carbon chain length. For $n = 8$ the M_2 phase occupied most of the anisotropic domain. As n was increased the stability of this mesophase decreased while the temperature range of the other columnar phase increased. A striking feature was the almost constant temperature range of the mesomorphic state, in which the columnar phase grew in at the expense of the M_2 phase (as a function of n and T). The mesomorphic properties were completely reproducible.

Table 4 Transition temperatures and thermal data for the *trans*-dichlorobis(3′,4′,5′-trialkoxy-4-stilbazole)palladium(II) complexes **9**

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J K^{-1} mol^{-1}
5	Crys-Crys′	124	32.5	82
	Crys′-I	179	26.3	58
6	Crys-Crys′	51	10.1	31
	Crys′-I	146	13.2	31
7	Crys-Crys′	73	13.6	39
	Crys′-I	128	17.7	44
8	Crys-Crys′	92	51.0	140
	Crys′-I	109	9.9	26
9	Crys-Col	79	53.7	152
	Col-I	98	1.6	4
10	Crys-Col	56	76.4	232
	Col-I	106	1.8	5
11	Crys-Col	60	82.2	247
	Col-I	108	1.9	5
12	Crys-Col	49	75.1	233
	Col-I	105	1.7	5
14	Crys-Crys′	53	17.6	54
	Crys′-Crys″	63	5.2	15
	Crys″-Col	66	77.4	228
	Col-I	99	1.9	5

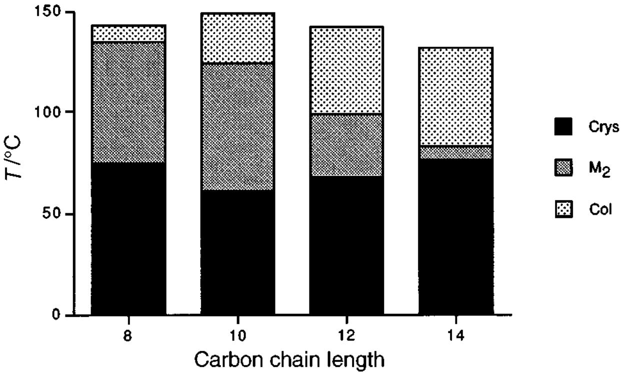
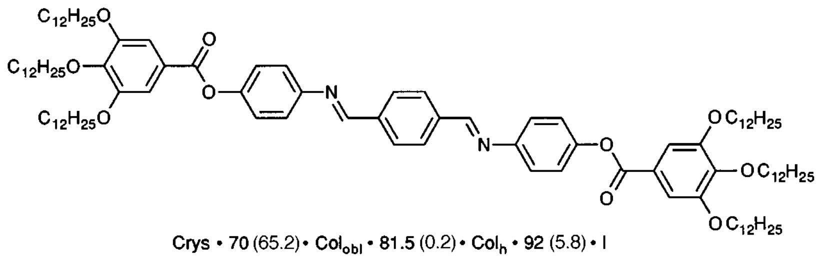


Fig. 4 Phase diagram of the *trans*-dichlorobis(2′,3′,4′-trialkoxystilbazole)palladium(II) complexes **10**



Scheme 3 Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of a hexacatenar compound exhibiting an oblique and hexagonal columnar mesophase

Tetracatenar	3,4-disubstituted, **6**:	M = Pd, S_C ($n \leqslant 12$) and Col ($n \geqslant 13$) M = Pt, S_C ($n \leqslant 14$) and Col ($n = 18$)
	3,5-disubstituted, **7**:	mesophase (probably columnar) for $n \geqslant 14$
Hexacatenar	3,4,5-trisubstituted, **9**:	Col ($n \geqslant 9$)
	2,3,4-trisubstituted, **10**:	two columnar phases ($n \geqslant 8$)

Scheme 4

Hexacatenar palladium(II) complexes 11. This series did not show liquid-crystalline properties. It may be that the same arguments used for complexes **8** can be applied here, that is that, owing to the position of the alkoxy chains, lateral interactions and efficient segregation of the two parts of the molecule (aliphatic/aromatic) have been considerably reduced. A comparison with the complexes **10** indicates clearly that unoccupied volume can lead to the complete loss of the mesomorphic properties. However, these compounds melted (see Experimental section) at low temperatures (<100 °C).

Table 5 Transition temperatures and thermal data for the *trans*-dichlorobis(2′,3′,4′-trialkoxystilbazole)palladium(II) complexes **10**

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS_m/J K^{-1} mol^{-1}
6	Crys-Crys′	110	23.2	60
	Crys′-Crys″	130	18.3	45
	Crys″-I	146	17.8	42
8	Crys-Crys′	55	6.6	20
	Crys′-M_2	75	56.3	162
	M_2-Col*	135	—	—
	Col-I	143	13.2	32
10	Crys-Crys′	39	10.1	32
	Crys′-M_2	61	57.2	171
	M_2-Col*	124	—	—
	Col-I	149	12.6	30
12	Crys-Crys′	60	5.7	17
	Crys′-M_2	68	68.4	200
	M_2-Col*	99	—	—
	Col-I	142	9.5	23
14	Crys-M_2	76	91.7	263
	M_2-Col*	83	—	—
	Col-I	132	8.2	20

* Not observed by DSC.

Discussion

None of the complexes based on 2,4-disubstituted (**8**) and 2,4,5-trisubstituted stilbazoles (**11**) was mesomorphic, which was attributed to the strong reduction in the lateral interactions due to the presence of the chain in the 2 position, although, in common with observations by Praefcke and co-workers,[23] this was not a problem in complexes based on 2,3,4-trisubstituted ligands which showed columnar mesophases. Curiously, however, the nematic phase often associated with 2,3,4-trisubstituted systems in Praefcke's work was absent here. However, mesomorphism was induced for these and three other types of substitution, the phase behaviour being strongly dependent on the position, number and length of the alkoxy chains. The results are summarised in Scheme 4.

Looking at the number and position of the alkoxy substituents, a relationship between the molecular design and mesomorphic properties can be emphasised. The columnar behaviour is clearly connected with the *meta* arrangement, whereas the *para* position seems fairly important to promote mesomorphism. The *ortho* arrangement seemed to disfavour the induction of calamitic mesomorphism, as the lateral interaction and the molecular segregation are reduced, but does not disfavour a columnar mesomorphism when the space is properly filled by aliphatic substituents.

The columnar phase existed over a wider temperature range in the hexacatenar complexes than in the tetracatenar systems, and occurred at much lower temperatures, however the smectic C phase has disappeared completely. This is another similarity with organic polycatenar mesogens, and highlights the strongly amphiphilic character of this type of material, as the mesophases can be described by the curvature at the aromatic–paraffinic interface.[24] The necessity for a minimum of nine (or eight) carbons per chain (for the hexacatenar complexes) or more than thirteen carbons per chain (for the tetracatenar complexes) suggested that a certain ratio between the rigid core and the aliphatic chains was a prerequisite for obtaining the columnar mesomorphism. The curvature at the paraffinic–aromatic interface is dependent on the density (and thus the volume) of the chains (or paraffinic media), and it is therefore possible to predict the type of mesophase, and especially the occurrence of the hexagonal and smectic C phases, by calculating the contribution to the molecular weight of the aliphatic chains (and thus the volume) to the total molecular weight of the metal complexes.[24]

It was found that for the tetracatenar palladium and platinum complexes and for the hexacatenar palladium complexes the contribution of the alkoxy chains to the molecular weight of the complexes must be at least 60% in order to generate a columnar mesophase (Table 6). Below 60%, tetracatenar materials displayed a smectic C phase while the hexacatenar materials were not mesomorphic. This simple correlation can account for the few singularities observed in the three systems. In the case of the platinum complexes the ratio has not been attained for $n = 13$ and 14, owing to the higher atomic weight of platinum, and thus, they still displayed a smectic C phase, while the palladium complexes showed a columnar phase for a same chain length. Similarly, the occurrence of the mesophase for the tetradecyloxy derivative of the 3,5-disubstituted system is in agreement with the correlation as from this type of substitution it was clear that lamellar mesomorphism was not expected due to the reduction of the lateral interactions; however, because of the high density of hydrocarbon chains around the aromatic core of the molecule, a columnar mesomorphism would be expected. This suggests that the mesophase (M_1 above) may be columnar.

It also seems that there is a 'saturation effect'. For example, in the palladium complexes, a decrease in the mesomorphic domain was observed when this ratio reached 70%. This is consistent with the fact that the octadecyloxy platinum complex

Table 6 Comparison of observed mesomorphism with weight percentage of alkoxy chains

Metal	Structural type	*n*	*M*		Contribution of the alkoxy chains (%)	Mesophase
			Complex	Alkoxy chains		
Pd	Hexacatenar	8	1309	776	59	Not LC/Col
		9	1393	860	62	Col
		14	1814	1281	71	Col
Pd	Tetracatenar	12	1277	741	58	S_C
		13	1333	797	60	Col
		14	1389	853	61	Col
		18	1614	1078	67	Col
Pt	Tetracatenar	12	1366	741	54	S_C
		13	1422	797	56	S_C
		14	1478	853	58	S_C
		18	1702	1078	63	Col

still possessed a large columnar phase as the ratio (63%) corresponds to the large anisotropic domain for all the palladium complexes.

The occurrence of the high-temperature mesophase in the 2,3,4-trisubstituted, hexacatenar complexes was almost predicted, as the contribution (59%) of the paraffinic chains is just about 60% of the total molecular weight of the complex ($n = 8$), and the ratio is satisfied for $n \geqslant 10$. The absence of the smectic phase was attributed to the lateral chain in the 2 position, which does not encourage a layer-like structure.

While tetracatenar mesogens showed both smectic and columnar phases, hexacatenar mesogens displayed only columnar phases, consistent with the shapes of the molecules. The hexacatenar complexes have a more disc-like shape and thus, displayed a similar mesomorphism while the tetracatenar complexes were closer to calamitic molecules and thus showed a calamitic mesomorphism. However, when the paraffinic matrix reached a critical density, that is a 60% ratio (see above), the tendency to give a columnar mesomorphism was enhanced.

Several single-crystal X-ray studies[25] have been carried out in order to try to correlate the structure of polycatenar mesogens in the solid state with the thermal behaviour. The study[25] showed that both tetracatenar and hexacatenar molecules are arranged in crystalline planes [Fig. 5(*a*)], the interactions between adjacent planes being weak; this arrangement is typical of a layer structure with segregation of the aliphatic chains and the aromatic core. It is easy to speculate, bearing in mind that the interactions between two molecular planes were found to be weak, that when heated (and *n* increased) these interactions will be even more weakened allowing the planes to undulate [Fig. 5(*b*)]. The void thus created will be filled by the sliding of the adjacent 'layers' [Fig. 5(*c*)]. This hypothesis, proposed by Guillon *et al.*,[26] and supported by previous reports of smectic lamallae breaking into finite ribbons,[27] is supported by the general high enthalpies of transition suggesting a mechanism of transformation containing several steps. However, it must be appreciated that correlation between solid state and mesophase structures can be misleading. This model can also be used to account for the transition from S_C to columnar phase, often seen in polycatenar mesogens.

For these materials we were thus able to predict the occurrence of the hexagonal columnar phase, by a simple correlation between the contribution of the paraffinic media to the total molecular weight of the complexes. X-Ray investigations will be performed on all the mesophases and will be reported in due course.

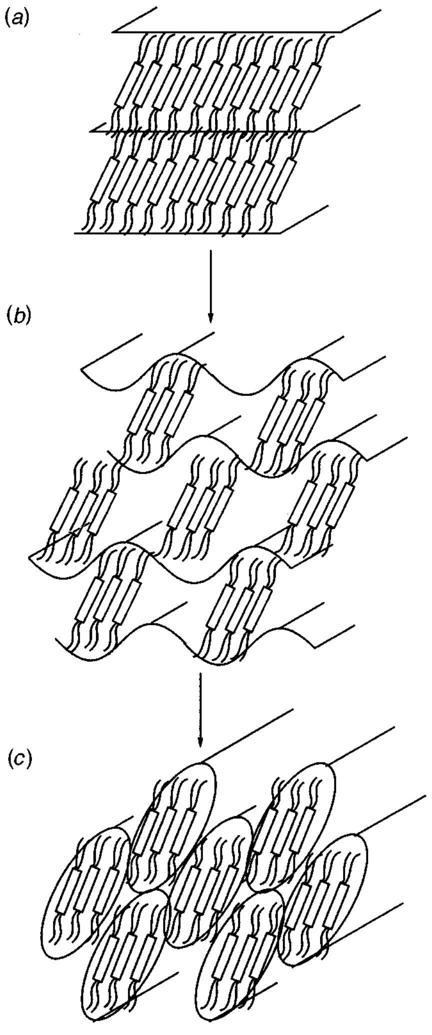


Fig. 5 Proposed model for the formation of the columnar mesophases

The study of these systems has shown quite clearly how the spatial arrangement of the metal may be controlled as a function of the ligand. For example, most 3,4-disubstituted, tetracatenar complexes exhibited a fluid lamellar (S_C) phase in which specific intermolecular interactions are unlikely to be of any significance. Longer-chain derivatives of these systems, plus the more highly substituted (hexacatenar) complexes, show columnar behaviour and here it would be reasonable to consider the possibility of intermolecular interactions. For example, Simon and co-workers[28] have demonstrated that in columnar phases of metallophthalocyanines highly anisotropic (factor of 10^7) conductivity is observed. Although the columnar organisation of these palladium and platinum complexes is not strictly analogous to that found in the columnar phases of the discotic phthalocyanines, the present work does show both that the spatial arrangement of metals may be rather simply controlled, and that this control may be exerted using pre-existing design concepts which are found to apply equally to metal-based and metal-free systems. Further, we have demonstrated another method by which the often high temperatures associated with metal-based liquid crystals can be modulated to provide systems with more accessible mesophases.

Table 7 Analytical data for the tetracatenar palladium and platinum complexes **6**

Metal	*n*	Yield (%)	Analysis (%)* C	H	N	Cl
Pd	1	88	54.2 (54.6)	4.5 (4.6)	4.1 (4.2)	10.3 (10.7)
Pd	2	93	56.6 (57.0)	5.3 (5.3)	3.8 (3.9)	9.8 (9.9)
Pd	3	95	58.9 (59.1)	5.9 (6.0)	3.4 (3.6)	9.2 (9.2)
Pd	4	83	60.9 (60.9)	6.6 (6.6)	3.3 (3.4)	8.5 (8.6)
Pd	5	72	62.8 (62.5)	7.2 (7.1)	3.1 (3.2)	8.1 (8.0)
Pd	6	83	63.6 (63.9)	7.6 (7.5)	2.7 (3.0)	7.3 (7.5)
Pd	7	65	64.7 (65.1)	7.8 (7.9)	2.7 (2.8)	7.2 (7.1)
Pd	8	73	65.8 (66.2)	8.3 (8.2)	2.4 (2.7)	6.7 (6.7)
Pd	9	87	67.1 (67.2)	8.7 (8.5)	2.4 (2.5)	6.5 (6.4)
Pd	10	69	67.8 (68.0)	9.0 (8.8)	2.4 (2.4)	6.1 (6.1)
Pd	11	89	68.8 (68.9)	9.2 (9.1)	2.8 (2.3)	5.9 (5.8)
Pd	12	64	69.3 (69.6)	9.5 (9.3)	2.2 (2.2)	5.4 (5.5)
Pd	13	55	70.0 (70.3)	9.6 (9.5)	2.3 (2.1)	5.6 (5.3)
Pd	14	88	70.9 (70.9)	9.9 (9.7)	2.1 (2.0)	4.9 (5.1)
Pd	18	83	72.7 (72.9)	10.4 (10.4)	1.8 (1.7)	4.6 (4.4)
Pt	4	74	54.7 (55.0)	5.6 (5.9)	3.0 (3.0)	7.7 (7.7)
Pt	5	60	56.4 (56.8)	6.5 (6.4)	3.1 (2.9)	7.5 (7.3)
Pt	11	63	63.8 (64.2)	8.6 (8.5)	2.2 (2.1)	5.3 (5.4)
Pt	12	64	65.4 (65.1)	9.1 (8.7)	2.1 (2.0)	5.0 (5.2)
Pt	13	58	65.7 (65.9)	9.1 (8.9)	2.0 (2.0)	5.0 (5.0)
Pt	14	58	66.6 (66.6)	9.1 (9.1)	1.8 (1.9)	5.0 (4.8)
Pt	18	69	69.1 (69.1)	9.9 (9.8)	1.8 (1.6)	4.1 (4.2)

* Calculated values in parentheses.

Experimental

All solvents and 4-methylpyridine were distilled prior to use according to the standard procedures[29] and the starting stilbazoles[11b,c] and [PdCl$_2$(PhCN)$_2$][30] were prepared as described elsewhere; platinum[12] and iridium[14] complexes were prepared as described previously. Proton and carbon NMR spectra were recorded on a Brüker ACL250 or AM400 spectrometer and referenced to external tetramethylsilane. Elemental analyses were performed by the University of Sheffield microanalytical service. Infrared spectra were recorded (see Tables 7–11) on a Perkin-Elmer 684 spectrophotometer. Analysis by DSC was carried out using a Perkin-Elmer DSC7 instrument using various heating rates. Mesomorphism was studied by hot-stage polarising microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller.

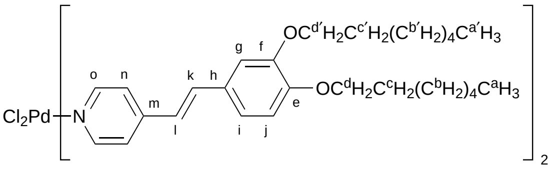
Preparation of the palladium(II) complexes

A sample preparation is given starting from [PdCl$_2$(PhCN)$_2$]. Although some palladium complexes were prepared using a melt method starting from PdCl$_2$ according to ref. 12, we would advise using the following route for palladium complexes.

***trans*-Dichlorobis(3′,4′-dibutoxy-4-stilbazole)palladium(II).** The complex [PdCl$_2$(PhCN)$_2$] (171 mg, 4.4 × 10^{-4} mol) was dissolved in acetone (5 cm^3) and the relevant stilbazole (304 mg, 9.3 × 10^{-4} mol) in acetone (5 cm^3) was added dropwise to the stirring solution. A change of colour could be observed throughout the addition of the ligand (from dark brown to bright yellow). The mixture was left stirring for 1 h until a precipitate formed. The compound was filtered off and washed with acetone (10 cm^3). It was first crystallised from acetone–methanol and then from acetone to give the pure product in 83% (305 mg) yield and of analytical purity.

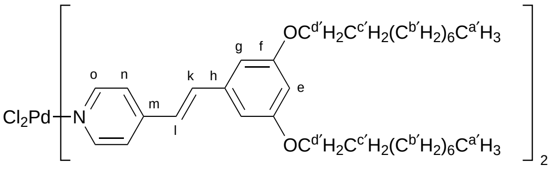
Spectroscopic and analytical data

Dichlorobis(3′,4′-diheptyloxy-4-stilbazole)palladium(II).



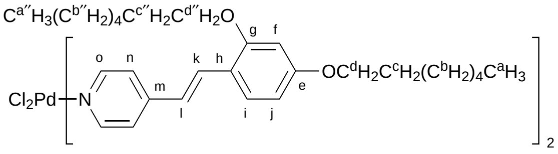
δ_H(250.13 MHz, CDCl$_3$) 0.88, 0.89 (2 t, ^3J = 6.7, 12 H, H^a, H$^{a'}$), 1.44 (m, 32 H, H^b, H$^{b'}$), 1.84 (m, 8 H, H^c, H$^{c'}$), 4.02 (t, ^3J = 6.7, 4 H, H^d), 4.04 (t, ^3J = 6.7, 4 H, H$^{d'}$), 6.80 [AB, ^3J(H^{l}H^k) = 16.5, 2 H, H^l], 6.86 [d, ^3J(H^{j}H^i) = 7.5, 2 H, H^j], 7.07 (dd, ^4J(H^{i}H^g) = 1.8, ^3J(H^{i}H^j) = 7.5, 2 H, H^i], 7.26 [d, ^4J(H^{g}H^i) = 1.8, 2 H, H^g], 7.27 [AB, ^3J(H^{k}H^l) = 16.5, 2 H, H^k], 7.32 (AA′XX′, \|J(H^{n}H^o) + J(H^{n}H$^{o'}$)\| = 6.8, 4 H, H^n] and 8.67 [AA′XX′, \|J(H^{o}H^n) + J(H^{o}H$^{n'}$)\| = 6.8 Hz, 4 H, H^o]. δ_C(62.9 MHz, CDCl$_3$) 14.1 (C^a, C$^{a'}$), 22.6, 25.7, 29.1, 29.2, 31.6 (C^b, C$^{b'}$, C^c, C$^{c'}$), 69.1, 69.4 (C^d, C$^{d'}$), 111.8 (C^g), 113.2 (C^j), 121.5 (C^n), 121.6 (C^i), 121.8 (C^l), 128.3 (C^h), 136.4 (C^k), 147.8 (C^m), 149.3 (C^e), 150.9 (C^f) and 152.8 (C^o). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 367s.

Dichlorobis(3′,5′-dinonyloxy-4-stilbazole)palladium(II).



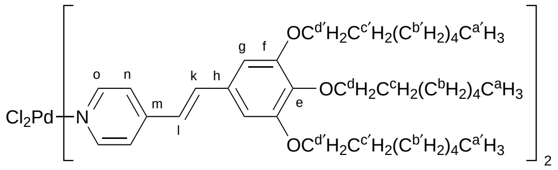
δ_H(250.13 MHz, CDCl$_3$) 0.88 (t, ^3J = 6.7, 12 H, H$^{a'}$), 1.37 (m, 48 H, H$^{b'}$), 1.78 (m, 8 H, H$^{c'}$), 3.96 (t, ^3J = 6.7, 8 H, H$^{d'}$), 6.46 [t, ^4J(H^{e}H^g) = 2.1, 2 H, H^e], 6.65 [d, ^4J(H^{g}H^e) = 2.1, 2 H, H^g], 6.93 [AB, ^3J(H^{l}H^k) = 16.2, 2 H, H^1], 7.25 [AB, ^3J(H^{k}H^l) = 16.2, 2 H, H^k], 7.34 [AA′XX′, \|J(H^{n}H^o) + J(H^{n}H$^{o'}$)\| = 6.7, 4H, H^n] and 8.70 [AA′XX′, \|J(H^{o}H^n) + J(H^{o}H$^{n'}$)\| = 6.7 Hz, 4 H, H^o]. δ_C(62.9 MHz, CDCl$_3$) 14.1 (C$^{a'}$), 22.7, 26.1, 29.3, 29.4, 29.6, 31.9 (C$^{b'}$, C$^{c'}$), 68.2 (C$^{d'}$), 102.7 (C^e), 105.9 (C^g), 121.8 (C^n), 124.2 (C^l), 136.6 (C^k), 1371 (H^h), 147.3 (C^m), 153.0 (C^o) and 160.6 (C^f). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 371s.

Dichlorobis(2′,4′-diheptyloxy-4-stilbazole)palladium(II).



δ_H(250.13 MHz, CDCl$_3$) 0.88, 0.89 (2 t, ^3J = 6.6, 12 H, H^a, H$^{a''}$), 1.38 (m, 32 H, H^b, H$^{b''}$), 1.82 (m, 8 H, H^c, H$^{c''}$), 3.97, 4.00 (2 t, ^3J = 6.6, 8 H, H^d, H$^{d''}$), 6.44 [d, ^4J(H^{f}H^j) = 2.1, 2 H, H^f], 6.49 [dd, ^3J(H^{j}H^i) = 8.5, ^4J(H^{j}H^f) = 2.1, 2 H, H^j], 6.92 [AB, ^3J(H^{l}H^k) = 16.5, 2 H, H^l], 7.29 [AA′XX′, \|J(H^{n}H^o) + J(H^{n}H$^{o'}$)\| = 7.0, 4 H, H^n], 7.46 [d, ^3J(H^{i}H^j) = 8.5, 2 H, H^i], 7.61 (AB, ^3J(H^{k}H^l) = 16.5, 2 H, H^k] and 8.64 [AA′XX′, \|J(H^{o}H^n) + J(H^{o}H$^{n'}$)\| = 7.0 Hz, 4 H, H^o]. δ_C(62.9 MHz, CDCl$_3$) 14.1 (C^a, C$^{a''}$), 22.6, 26.0, 26.2, 29.0, 29.1, 31.8 (C^b, C$^{b''}$, C^c, C$^{c''}$), 68.2, 68.5 (C^d, C$^{d'}$), 99.7 (C^f), 105.9 (C^j), 117.4 (C^h), 121.4 (C^n), 121.6 (C^l), 128.8 (C^i), 131.7 (C^k), 148.7 (C^m), 152.6 (C^o), 158.7 (C^g) and 161.7 (C^e). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 361s.

Dichlorobis(3′,4′,5′-triheptyloxy-4-stilbazole)palladium(II).



δ_H(250.13 MHz, CDCl$_3$) 0.91 (t, ^3J = 6.7, 6 H, H^a), 0.93 (t, ^3J = 6.7, 12 H, H$^{a'}$), 1.38 (m, 48 H, H^b, H$^{b'}$), 1.79 (m, 12 H,

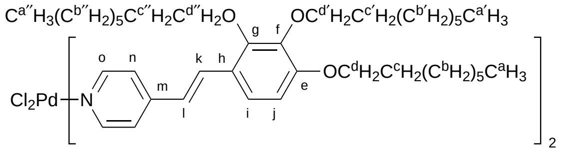
Table 8 Analytical data for the tetracatenar palladium complexes **7** and **8**

Complex	n	Yield (%)	Analysis (%)* C	H	N	Cl
7	1	95	54.1 (54.6)	4.6 (4.6)	4.1 (4.2)	10.9 (10.7)
7	4	65	60.9 (60.9)	6.4 (6.6)	3.1 (3.4)	8.6 (8.6)
7	9	67	67.0 (67.2)	8.6 (8.5)	3.0 (2.5)	6.6 (6.4)
7	11	26	68.7 (68.9)	9.2 (9.1)	2.5 (2.3)	6.1 (5.8)
7	14	76	70.7 (70.9)	9.9 (9.7)	1.9 (2.0)	5.1 (5.1)
8	7	80	64.8 (65.1)	7.9 (7.9)	3.0 (2.8)	7.4 (7.1)
8	10	85	67.8 (68.0)	8.8 (8.8)	2.5 (2.4)	6.3 (6.1)
8	14	54	70.6 (70.9)	9.6 (9.7)	2.3 (2.0)	5.0 (5.1)

* Calculated values in parentheses.

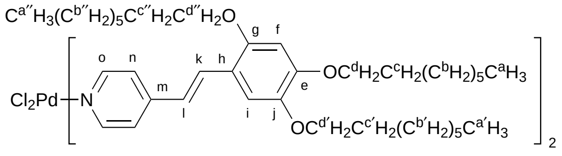
H^{c}, H$^{c'}$), 3.98 (t, ^{3}J = 6.7, 4 H, H^{d}), 4.01 (t, ^{3}J = 6.7, 8 H, H$^{d'}$), 6.73 (s, 4 H, H^{g}), 6.83 [AB, ^{3}J(H^{l}H^{k}) = 16.2, 2 H, H^{l}], 7.24 [AB, ^{3}J(H^{k}H^{l}) = 16.2, 2 H, H^{k}], 7.32 (AA′XX′, |J(H^{n}H^{o}) + J(H^{n}H$^{o'}$)| = 6.7, 4 H, H^{n}] and 8.67 [AA′XX′, |J(H^{o}H^{n}) + J(H^{o}H$^{n'}$)| = 6.7 Hz, 4 H, H^{o}]. δ$_{C}$(62.9 MHz, CDCl$_3$) 14.1 (C^{a}, C$^{a'}$), 22.6, 26.1, 29.1, 29.2, 29.4, 30.3, 31.8, 31.9 (C^{b}, C$^{b'}$, C^{c}, C$^{c'}$), 69.3 (C$^{d'}$), 73.6 (C^{d}), 106.1 (C^{g}), 121.6 (C^{n}), 122.8 (C^{l}), 130.4 (C^{e}), 136.7 (C^{k}), 140.0 (C^{h}), 147.5 (C^{m}), 152.9 (C^{o}) and 153.4 (C^{f}). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 371s.

Dichlorobis(2′,3′,4′-trioctyloxy-4-stilbazole)palladium(II).



δ$_{H}$(250.13 MHz, CDCl$_3$) 0.88, 0.89 (3 t, ^{3}J = 6.7, 18 H, H^{a}, H$^{a'}$, H$^{a''}$), 1.40 (m, 60 H, H^{b}, H$^{b'}$, H$^{b''}$), 1.80 (m, 12 H, H^{c}, H$^{c'}$, H$^{c''}$), 3.97, 3.99, 4.04 (3 t, ^{3}J = 6.7, 12 H, H^{d}, H$^{d'}$, H$^{d''}$), 6.67 [d, ^{3}J(H^{j}H^{i}) = 8.8, 2 H, H^{j}], 6.89 [AB, ^{3}J(H^{l}H^{k}) = 16.5, 2 H, H^{l}], 7.28 [d, ^{3}J(H^{i}H^{j}) = 8.8, 2 H, H^{i}], 7.31 [AA′XX′, |J(H^{n}H^{o}) + J(H^{n}H$^{o'}$)| = 6.7, 4 H, H^{n}], 7.62 [AB, ^{3}J(H^{k}H^{l}) = 16.5, 2 H, H^{k}] and 8.66 [AA′XX′, |J(H^{o}H^{n}) + J(H^{o}H$^{n'}$)| = 6.7 Hz, 4 H, H^{o}]. δ$_{C}$(62.9 MHz, CDCl$_3$) 14.1 (C^{a}, C$^{a'}$, C$^{a''}$), 22.6, 22.7, 26.1, 26.3, 29.3, 29.5, 30.3, 30.4, 31.8, 31.9 (C^{b}, C$^{b'}$, C$^{b''}$, C^{c}, C$^{c'}$, C$^{c''}$), 68.8, 73.7, 74.5 (C^{d}, C$^{d'}$, C$^{d''}$), 108.6 (C^{j}), 121.5 (C^{n}), 121.6 (C^{i}), 122.3 (C^{l}), 122.5 (C^{h}), 131.5 (C^{k}), 141.9 (C^{m}), 148.3 (C^{f}), 152.3 (C^{g}), 152.8 (C^{o}) and 154.9 (C^{e}). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 361s.

Dichlorobis(2′,4′,5′-trioctyloxy-4-stilbazole)palladium(II).



δ$_{H}$(250.13 MHz, CDCl$_3$) 0.88, 0.89 (3 t, ^{3}J = 6.7, 18 H, H^{a}, H$^{a'}$, H$^{a''}$), 1.40 (m, 60 H, H^{b}, H$^{b'}$, H$^{b''}$), 1.82 (m, 12 H, H^{c}, H$^{c'}$, H$^{c''}$), 3.97, 4.00, 4.01 (3 t, ^{3}J = 6.7, 12 H, H^{d}, H$^{d'}$, H$^{d''}$), 6.47 (s, 2 H, H^{f}), 6.84 [AB, ^{3}J(H^{l}H^{k}) = 16.5, 2H, H^{l}], 7.09 (s, 2 H, H^{i}), 7.30 [AA′XX′, |J(H^{n}H^{o}) + J(H^{n}H$^{o'}$)| = 6.7, 4 H, H^{n}], 7.65 [AB, ^{3}J(H^{k}H^{l}) = 16.5, 2 H, H^{k}] and 8.64 [AA′XX′, |J(H^{o}H^{n}) + J(H^{o}H$^{n'}$)| = 6.7 Hz, 4 H, H^{o}]. δ$_{C}$(62.9 MHz, CDCl$_3$) 14.1 (C^{a}, C$^{a'}$, C$^{a''}$), 22.6, 26.0, 26.2, 29.2, 29.3, 29.4, 29.5, 31.8 (C^{b}, C$^{b'}$, C$^{b''}$, C^{c}, C$^{c'}$, C$^{c''}$), 69.2, 69.5, 70.6 (C^{d}, C$^{d'}$, C$^{d''}$), 99.7 (C^{f}), 113.4 (C^{i}), 116.4 (C^{h}), 121.3 (C^{n}), 125.4 (C^{l}), 131.2 (C^{k}), 143.2 (C^{j}), 148.5 (C^{m}), 152.1 (C^{e}), 152.6 (C^{o}) and 153.0 (C^{g}). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 371s. Thermal data [T/ °C (ΔH/kJ mol^{-1})]: $n = 8$, Crys·49 (56.2)·Crys′·96 (42.1)·I; $n = 148$, Crys·53 (4.4)·Crys′·99 (97.8)·I.

Table 9 Analytical data for the hexacatenar palladium complexes **9**

n	Yield (%)	Analysis (%)* C	H	N	Cl
5	58	63.7 (63.6)	7.8 (7.8)	2.8 (2.6)	6.9 (6.7)
6	36	65.4 (65.4)	8.2 (8.3)	2.7 (2.5)	6.3 (6.2)
7	45	66.6 (66.7)	8.8 (8.7)	2.3 (2.3)	5.7 (5.8)
8	64	67.8 (67.9)	9.3 (9.1)	2.0 (2.1)	5.4 (5.4)
9	65	69.0 (69.0)	9.6 (9.4)	2.0 (2.0)	5.0 (5.1)
10	54	69.8 (69.9)	9.8 (9.7)	2.3 (1.9)	4.8 (4.8)
11	77	71.1 (70.8)	10.2 (9.9)	1.4 (1.8)	4.5 (4.5)
12	58	71.5 (71.5)	10.4 (10.2)	1.8 (1.7)	4.3 (4.3)
14	68	72.5 (72.8)	10.4 (10.6)	1.9 (1.5)	4.0 (3.9)

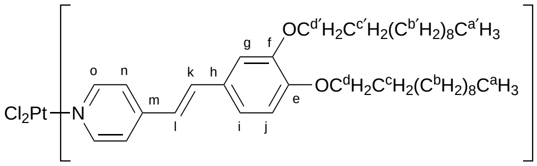
* Calculated values in parentheses.

Table 10 Analytical data for the hexacatenar palladium complexes **10** and **11**

Complex	n	Yield (%)	Analysis (%)* C	H	N	Cl
10	6	72	64.9 (65.3)	8.3 (8.3)	2.6 (2.5)	5.9 (6.2)
10	8	77	67.9 (67.9)	9.2 (9.1)	2.2 (2.1)	5.5 (5.4)
10	10	81	69.9 (69.9)	9.8 (9.7)	2.0 (1.9)	4.8 (4.8)
10	12	72	71.4 (71.5)	10.3 (10.2)	1.9 (1.7)	4.4 (4.3)
10	14	68	72.2 (72.8)	10.6 (10.6)	1.5 (1.5)	4.1 (3.9)
11	8	88	67.7 (67.9)	9.3 (9.1)	2.2 (2.1)	5.3 (5.4)
11	14	44	72.5 (72.8)	10.3 (10.6)	1.2 (1.5)	4.0 (3.9)

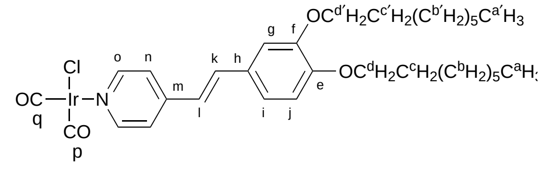
* Calculated values in parentheses.

Dichlorobis(3′,4′-diundecyloxy-4-stilbazole)platinum(II).



δ$_{H}$(250.13 MHz, CDCl$_3$) 0.87 (2 t, ^{3}J = 6.6, 12 H, H^{a}, H$^{a'}$), 1.41 (m, 65 H, H^{b}, H$^{b'}$), 1.84 (m, 8 H, H^{c}, H$^{c'}$), 4.02 (t, ^{3}J = 6.6, 4 H, H^{d}), 4.04 (t, ^{3}J = 6.6, 4 H, H$^{d'}$), 6.81 [AB, ^{3}J(H^{l}H^{k}) = 16.5, 2 H, H^{l}], 6.85 [d, ^{3}J(H^{j}H^{i}) = 7.5, 2 H, H^{j}], 7.08 [dd, ^{4}J(H^{i}H^{g}) = 1.8, ^{3}J(H^{i}H^{j}) = 7.5, 2 H, H^{i}], 7.25 [d, ^{4}J(H^{g}H^{i}) = 1.8, 2 H, H^{g}], 7.29 [AB, ^{3}J(H^{k}H^{l}) = 16.5, 2 H, H^{k}], 7.31 [AA′XX′, |J(H^{n}H^{o}) + J(H^{n}H$^{o'}$)| = 6.4, 4 H, H^{n}] and 8.74 [AA′XX′, |J(H^{o}H^{n}) + J(H^{o}H$^{n'}$)| = 6.4 Hz, 4 H, H^{o}]. δ$_{C}$(62.9 MHz, CDCl$_3$) 14.1 (C^{a}, C$^{a'}$), 22.7, 26.0, 29.1, 29.3, 29.4, 29.6, 31.9 (C^{b}, C$^{b'}$, C^{c}, C$^{c'}$), 69.1, 69.4 (C^{d}, C$^{d'}$), 111.8 (C^{g}), 113.1 (C^{j}), 121.5 (C^{n}), 121.6 (C^{i}), 121.8 (C^{l}), 128.3 (C^{h}), 136.4 (C^{k}), 147.8 (C^{m}), 149.3 (C^{e}), 150.8 (C^{f}) and 153.0 (C^{o}). IR(Polythene–Nujol, cm^{-1}): ν(PdCl) 354s.

Dicarbonylchloro(3′,4′-dioctyloxy-4-stilbazole)iridium(I).



δ$_{H}$(250.13 MHz, CDCl$_3$) 0.88 (2 t, ^{3}J = 6.3, 6 H, H^{a}, H$^{a'}$), 1.40 (m, 20 H, H^{b}, H$^{b'}$), 1.80 (m, 4 H, H^{c}, H$^{c'}$), 4.00 (t, ^{3}J = 6.3, 2 H, H^{d}), 4.10 (t, ^{3}J = 6.3, 2 H, C$^{d'}$), 6.82 [AB, ^{3}J(H^{l}H^{k}) = 16.5, 1 H, H^{l}], 6.86 (d, ^{3}J(H^{j}H^{i}) = 8.0, 1 H, H^{j}], 7.09 [dd, ^{4}J(H^{i}H^{g}) = 2.0, ^{3}J(H^{i}H^{j}) = 8.0, 1 H, H^{i}], 7.10 [d, ^{4}J(H^{g}H^{i}) = 2.0, 1 H, H^{g}], 7.35 [AB, ^{3}J(H^{k}H^{l}) = 16.5, 1 H, H^{k}], 7.45 [AA′XX′, |J(H^{n}H^{o}) + J(H^{n}H$^{o'}$)| = 6.4, 2 H, H^{n}] and 8.60 [AA′XX′, |J(H^{o}H^{n}) + J(H^{o}H$^{n'}$)| = 6.4 Hz, 2 H, H^{o}]. δ$_{C}$(62.9 MHz, CDCl$_3$) 14.1 (C^{a},

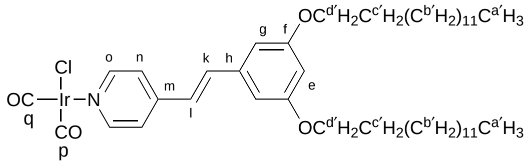
Table 11 Analytical data for the polycatenar iridium complexes

				Analysis (%)*			
Complex	n	Yield (%)	M.p./°C	C	H	N	Cl
12	1	85	183	39.3 (38.9)	2.9 (2.9)	2.5 (2.7)	6.6 (6.7)
12	8	73	120	51.5 (51.6)	5.9 (6.0)	1.9 (1.9)	4.9 (4.9)
12	11	81	114	55.1 (55.2)	6.9 (6.9)	1.7 (1.7)	4.5 (4.4)
12	14	73	104	57.6 (58.0)	7.5 (7.6)	1.4 (1.6)	4.3 (4.0)
12	18	62	107	61.0 (61.1)	8.3 (8.3)	1.9 (1.4)	3.9 (3.5)
13	14	73	60	57.6 (58.0)	7.7 (7.6)	1.9 (1.6)	3.8 (4.0)
14	14	79	62	58.0 (58.0)	7.7 (7.6)	1.9 (1.6)	3.8 (4.0)
15	14	43	100	61.8 (62.1)	8.7 (8.7)	1.6 (1.3)	3.1 (3.2)

* Calculated values in parentheses.

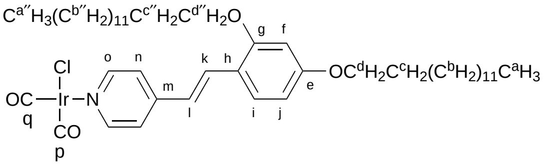
C$^{a'}$), 22.7, 26.0, 29.2, 29.3, 29.4, 31.8 (C^b, C$^{b'}$, C^c, C$^{c'}$), 69.1, 69.5 (C^d, C$^{d'}$), 112.0 (C^g), 113.2 (C^j), 121.1 (C^n), 122.2 (C^i), 122.3 (C^l), 128.0 (C^h), 137.7 (C^k), 149.2 (C^m), 149.4 (C^e), 151.3 (C^f), 152.1 (C^o), 166.1, 169.6 (C^p, C^q). IR (cm^{-1}): (Polythene–Nujol) ν(CO) 2080s, 2050s, 1980s; ν(IrCl) 326 (br); (dichloromethane) ν(CO) 2075s and 1995s. The compounds were yellow for $n = 1$ or 8 and red for $n = 11$, 14 or 18.

Dicarbonylchloro(3′,5′-ditetradecyloxy-4-stilbazole)iridium(I).



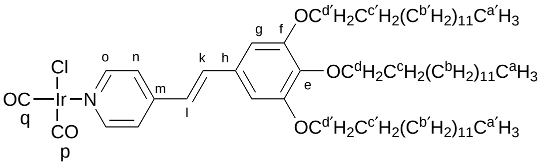
δ_H(250.13 MHz, $CDCl_3$) 0.88 (t, $^3J = 6.4$, 6 H, H$^{a'}$), 1.35 (m, 44 H, H$^{b'}$), 1.78 (m, 4 H, H$^{c'}$), 3.97 (t, $^3J = 6.7$, 4 H, H$^{d'}$), 6.48 [t, ^4J(H^{e}H^g) = 2.1, 1 H, H^e], 6.67 [d, ^4J(H^{g}H^e) = 2.1, 1 H, H^g], 6.97 [AB, ^3J(H^{l}H^k) = 16.4, 1 H, H^l], 7.34 [AB, ^3J(H^{k}H^l) = 16.4, 1 H, H^k], 7.51 [AA′XX′, |J(H^{n}H^o) + J(H^{n}H$^{o'}$)| = 6.4, 2 H, H^n] and 8.65 [AA′XX′, |J(H^{o}H^n) + J(H^{o}H$^{n'}$)| = 6.4 Hz, 2 H, H^o]. δ_C(62.9 MHz, $CDCl_3$) 14.1 (C$^{a'}$), 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9 (C$^{b'}$, C$^{c'}$), 68.2 (C$^{d'}$), 102.9 (C^e), 106.0 (C^g), 122.7 (C^n), 123.8 (C^l), 136.7 (C^k), 137.8 (C^h), 148.7 (C^m), 152.2 (C^o), 160.6 (C^f), 168.1, 169.4 (C^p, C^q). IR (cm^{-1}): (Polythene–Nujol, cm^{-1}) ν(CO) 2075s, 1990s; ν(IrCl) 330 (br); (dichloromethane) ν(CO) 2080s and 1995s.

Dicarbonylchloro(2′,4′-ditetradecyloxy-4-stilbazole)iridium(I).



δ_H(250.13 MHz, $CDCl_3$), 0.87 (2 t, $^3J = 6.7$, 6 H, H^a, H$^{a''}$), 1.38 (m, 44 H, H^b, H$^{b''}$), 1.83 (m, 4 H, H^c, H$^{C''}$), 3.98, 4.02 (2 t, $^3J = 6.7$, 4 H, H^d, H$^{d''}$), 6.45 [d, ^4J(H^{f}H^j) = 2.1, 1 H, H^f], 6.51 [dd, ^3J(H^{j}H^i) = 8.5, ^4J(H^{j}H^f) = 2.1, 1 H, H^j], 6.98 [AB, ^3J(H^{l}H^k) = 16.5, 1H, H^l], 7.45 [AA′XX′, |J(H^{n}H^o) + J(H^{n}H$^{o'}$)| = 6.7, 2 H, H^n], 7.49 [d, ^3J(H^{i}H^j) = 8.5, 1 H, H^i], 7.71 [AB, ^3J(H^{k}H^l) = 16.5, 1 H, H^k] and 8.58 [AA′XX′, |J(H^{o}H^n) + J(H^{o}H$^{n'}$)| = 6.7 Hz, 2 H, H^o]. δ_C(62.9 MHz, $CDCl_3$) 14.1 (C^a, C$^{a''}$), 22.7, 26.0, 26.1, 29.0, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9 (C^b, C$^{b''}$, C^c, C$^{c''}$), 68.2, 68.5 (C^d, C$^{d'}$), 99.6 (C^f), 106.0 (C^j), 117.0 (C^h), 121.1 (C^n), 122.1 (C^l), 129.1 (C^i), 133.0 (C^k), 150.1 (C^m), 151.9 (C^o), 158.9 (C^g), 161.1 (C^e), 168.1, 169.7 (C^p, C^q). IR (cm^{-1}): (Polythene–Nujol) ν(CO) 2070s, 1990s; ν(IrCl) 330 (br); (dichloromethane) ν(CO) 2080s and 1995s.

Dicarbonylchloro(3′,4′,5′-tritetradecyloxy-4-stilbazole)iridium(I).



δ_H(250.13 MHz, $CDCl_3$) 0.87 (2 t, ^3J 6.6, 9 H, H^a, H$^{a'}$), 1.38 (m, 66 H, H^b, H$^{b'}$), 1.78 (m, 6 H, H^c, H$^{c'}$), 3.99 (t, $^3J = 6.6$, 2 H, H^d) 4.01 (t, $^3J = 6.6$, 4 H, H$^{d'}$), 6.75 (s, 2 H, H^g), 6.87 [AB, ^3J(H^{l}H^k) = 16.2, 1 H, H^1], 7.33 [AB, ^3J(H^{k}H^l) = 16.2, 1 H, H^k], 7.49 [AA′XX′, |J(H^{n}H^o) + J(H^{n}H$^{o'}$)| = 6.7, 2 H, H^n] and 8.63 [AA′XX′, |J(H^{o}H^n) + J(H^{o}H$^{n'}$)| = 6.7 Hz, 2 H, H^o]. δ_C(62.9 MHz, $CDCl_3$) 14.1 (C^a, C$^{a'}$), 22.7, 26.1, 29.4, 29.6, 29.7, 30.3, 31.9 (C^b, C$^{b'}$, C^c, C$^{c'}$), 69.3 (C$^{d'}$), 73.6 (C^d), 106.2 (C^g), 122.3 (C^l), 122.4 (C^n), 130.0 (C^e), 137.8 (C^k), 139.5 (C^h), 148.9 (C^m), 152.2 (C^o), 153.5 (C^f), 168.1, 169.6 (C^p, C^q). IR (cm^{-1}): (Polythene–Nujol) ν(CO) 2080s, 2060s, 1990s, 1980s; ν(IrCl) 318 (br); (dichloromethane) ν(CO) 2080s and 1995s.

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