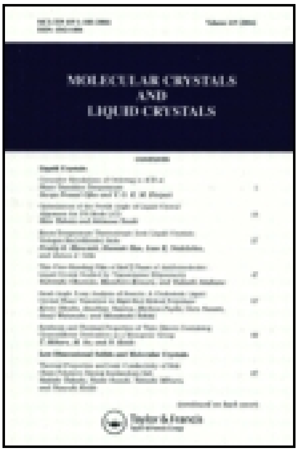

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The Synthesis and Mesomorphism of Some Acetylide Complexes of Platinum(II) and Palladium(II)

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The Synthesis and Mesomorphism of Some Acetylide Complexes of Platinum(II) and Palladium(II)

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Complexes of the general formula *trans*-$[M(acetylene)_2(PR_3)_2]$ (M = Pd, Pt; R = Me, Et, Pr; acetylene = extended, mesomorphic acetylene ligand) were synthesised and their liquid crystal properties evaluated. Platinum complexes with PMe_3 gave rather high temperature nematic phases, but when PEt_3 was used, nematic phases of a wide range were obtained; the use of PPr_3 totally destabilised the nematic phase. Analogous palladium complexes were synthesised but decomposed before melting.

Keywords: Acetylide complexes, platinum (II), palladium (II), nematic phase

1. INTRODUCTION

In 1978, Takahashi[1] reported that polymeric acetylide complexes of platinum(II) (Fig. 1) could be formed by the reaction of $[PtCl_2(PBu_3)_2]$ with either 1,4-butadiyne or 1,4-diethynylbenzene in the presence of copper(I) iodide and base.

This polymerisation gave molecular weight average degrees of polymerisation (M_w) of upto 7×10^4, which corresponded to a number average (n_w) of 108. The lyotropic liquid crystalline properties of the polymers were investigated by dissolving them in trichloroethene at weight percentages of around 36% and nematic phases were observed.

The physical properties of these 1,4-butadiyne metal polymers were studied[2] using both homometallic polymers (Fig. 2; $M = M'$) and heterometallic polymers (Fig. 2; M = Pt, M' = Pd or Ni) and ^{31}P NMR studies showed that all these polymers possessed a negative diamagnetic anisotropy ($\Delta\chi < 0$). This was interpreted largely in terms of the negative diamagnetic anisotropy of the carbon-carbon triple bond.

Subsequent studies of related polymeric materials[3] suggested that the magnetic anisotropy was a complex and delicately balanced function of ligand and metal. Thus, while the butadiyne homopolymer of Pd(II) (Fig. 2, $M = M'$ = Pd) had $\Delta\chi < 0$, the block copolymer (Fig. 3) had $\Delta\chi > 0$ due to the fine balance of the opposite magnetic anisotropies of benzene and carbon-carbon triple bonds in the complexes, which may well have been enhanced by conjugation.

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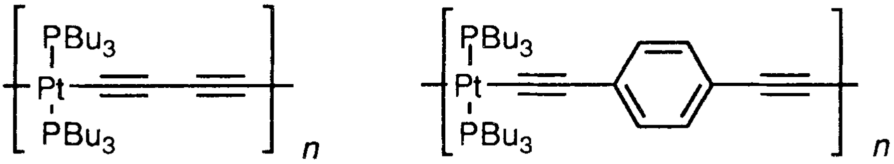


FIGURE 1 Polymeric platinum acetylide complexes.

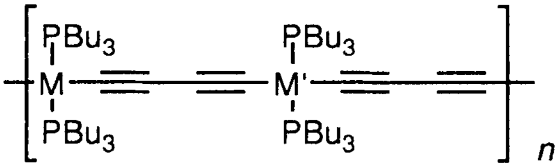


FIGURE 2 Structure of mixed-metal butadiyne polymers.

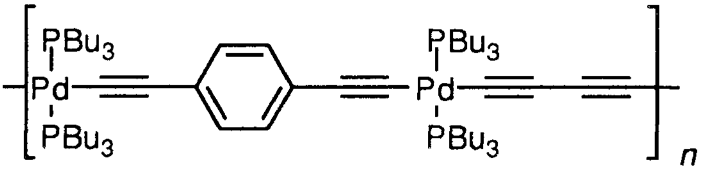


FIGURE 3 Homometallic block co-polymer with $\Delta\chi > 0$.

This work with liquid crystalline polymeric systems was later, and most naturally, extended to the study of related low molar mass systems[4,5] and the platinum(II) complexes shown in Figure 4 were found to exhibit thermotropic mesophases.

These complexes showed smectic A and nematic phases with typical melting points in the region of 170 to 190°C, although shorter chain length homologues melted at higher temperatures. The complexes generally showed a short range nematic phase and cleared at temperatures around 180 to 200°C. Short chain homologues tended to clear at higher temperatures (> 220°C) and some decomposition was seen in these cases.

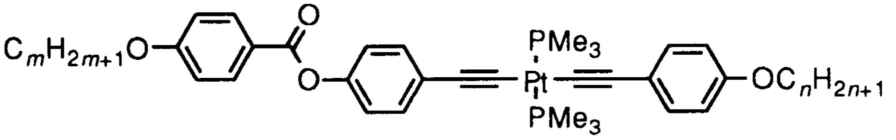


FIGURE 4 Mesomorphic platinum acetylide complexes.

As these complexes were mesomorphic this indicated that the relative bulk of two trimethylphosphine groups in the centre of the molecule did not adversely affect the overall structural anisotropy of the complex, and the high melting and clearing points suggested that the system may tolerate slightly larger groups.

We wished to investigate the effects of changing the acetylide ligand to make it longer and more structurally anisotropic, and then to see how this might affect the size of the central group which may be tolerated. Thus, the acetylenes shown in Figure 5 were synthesised; their mesomorphism has been reported elsewhere.[6]

1.1 Preparation of the Complexes

The acetylene ligands were obtained in the six-stage process outlined in Scheme 1 and described in detail in Ref. 6.

The *trans*-platinum acetylide complexes were formed by stirring two equivalents of the acetylide ligand with one equivalent of *cis*- or *trans*-dichloro*bis*(trialkylphosphine)platinum(II) with a catalytic amount of copper (I) iodide, in a 60:40 mixture of triethylamine/dichloromethane under an atmosphere of argon for 16 h (Fig. 6).

After stirring, the solvents was removed under reduced pressure, water was added to the residue and the product was extracted with dichloromethane. The organic phase was dried over potassium carbonate and the pure complexes were obtained after column chromatography on alumina and crystallisation from dichloromethane/hexane.

These disubstituted complexes were made using three different phosphines, trimethyl-, triethyl- and tripropylphosphine. The *trans* configuration of these complexes was confirmed by the ^{31}P NMR of the complexes which showed the platinum-phosphorous coupling to be of the order of 2360 Hz whichever isomer of starting material was used, indicating that the *trans* product was formed.[7] Several homologues between $n = 6$ and $n = 10$ were synthesised for each phosphine and their mesomorphism is discussed below.

Mono-substituted platinum complexes (Fig. 7) were also synthesised in a similar way using a 1:1 ratio of ligand/metal and a copper (I) chloride catalyst.

1.2 Mesomorphism of the Platinum Complexes

A high temperature enantiotropic nematic phase was observed for the disubstituted trimethylphosphine platinum complexes (Fig. 6; I). Three such complexes were made and their mesomorphism is described in Table 1. Increasing the size of the phosphine

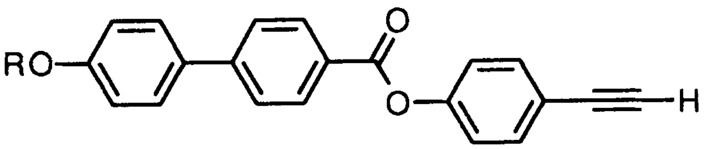
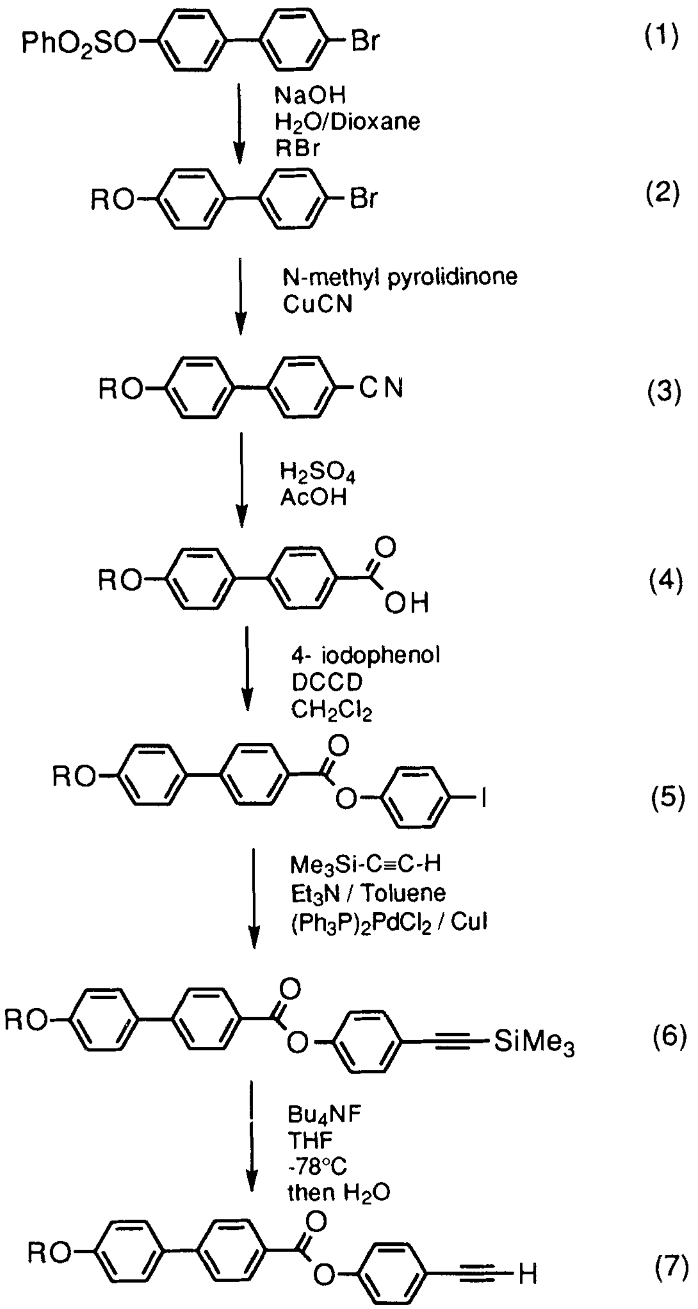


FIGURE 5 The extended acetylide ligand.



SCHEME 1 Reaction scheme for the synthesis of the acetylene ligand precursors.

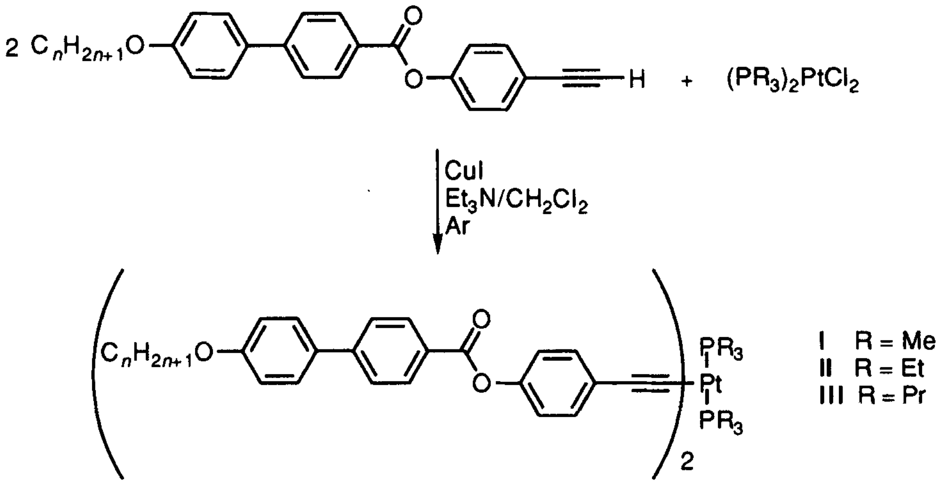


FIGURE 6 Reaction scheme for synthesis of the platinum complexes.

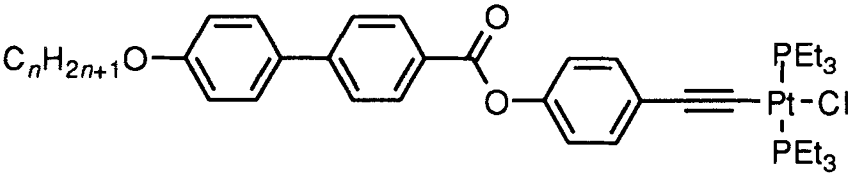


FIGURE 7 Monosubstituted platinum complexes.

TABLE 1

Mesomorphism of the trimethylphosphine complexes (I)

n	Transition	*T*/°C
6	C-N	262
	N-decomp	320
8	C-N	265
	N-decomp	320
10	C-N	258
	N-decomp	320

ligand from trimethylphosphine to triethylphosphine increased the width of the molecule and decreased both the structural anisotropy and the tendency for lateral interactions, thereby disrupting molecular packing and lowering both the melting and clearing points of the complexes. Thus, while the trimethylphosphine complexes melted at around 260°C, the triethylphosphine complexes melted at lower temperatures, typically between 165 and 206°C. A full range of complexes was made with ligand chain lengths between $n = 6$ and $n = 10$ and all were mesomorphic, showing an enantiotropic nematic phase. Again these materials began to decompose slowly at temperatures above 230°C, but they were sufficiently stable to be heated until they cleared at between 266 and 330°C. The thermal data for these complexes are shown in Table 2 below. This does not include thermal data for the clearing transition as the materials had partially decomposed by this point, making these figures somewhat meaningless.

On increasing the size of the phosphine ligand still further to tripropylphosphine (Fig. 6, III), the molecular packing was further disrupted and all complexes made with tripropylphosphine melted at low temperatures. Three such materials were made with ligand chain lengths of 6, 8 and 10 carbon atoms and they were all non-mesomorphic, melting to an isotropic liquid at 120, 111 and 105°C respectively. Further, the complexes could be supercooled to around room temperature without decomposition and without the appearance of any mesophase.

The monosubstituted complexes (Fig. 7) were made for $n = 6$, 8 and 10 and none was mesomorphic; they simply melted to isotropic fluids at 143, 117 and 101°C respectively.

A comparison of these new complexes containing trimethylphosphine with those described by Takahashi was difficult as he described only one symmetric complex based on the $[Pt(PMe_3)_2]$ fragment and containing two-ringed esters; this complex was reported to have a nematic phase above about 200°C.[5] However, a comparison with his triethylphosphine substituted systems[8] was more useful and showed that nematic phases were stabilised in our new materials by around 130°C as might have been expected with the increase in length resulting from the addition of two phenyl rings. However, the crystal phases were only stabilised by the order of 40°C, leading to materials with nematic ranges of around 120°C, not of all which is readily utilised due to decomposition. That our tripropylphosphine complexes were non-mesomorphic

TABLE 2

Thermal data for the disubstituted platinum triethylphosphine complexes

n	Transition	T/°C	ΔH/J g^{-1}
6	$C \rightarrow C'$	161	32.3
	$C' \rightarrow N$	206	23.3
	$N \rightarrow I$	332	–
7	$C \rightarrow C'$	152	29.4
	$C' \rightarrow N$	189	23.7
	$N \rightarrow I$	308	–
8	$C \rightarrow C'$	164	36.8
	$C' \rightarrow N$	179	17.5
	$N \rightarrow I$	292	–
9	$C \rightarrow C'$	143	24.9
	$C' \rightarrow N$	171	26.2
	$N \rightarrow I$	279	–
10	$C \rightarrow C'$	119	34.9
	$C' \rightarrow N$	165	73.8
	$N \rightarrow I$	266	–

was then rather surprising given that the stability of the nematic phase of our triethylphosphine complexes was so high. Indeed it would appear that the drop is greater than 200°C, given that the samples supercooled to around room temperature did not show any evidence of mesomorphism, although curiously, the drop in the melting point was only around 20–30°C.

2. SYNTHESIS AND MESOMORPHISM OF THE PALLADIUM COMPLEXES

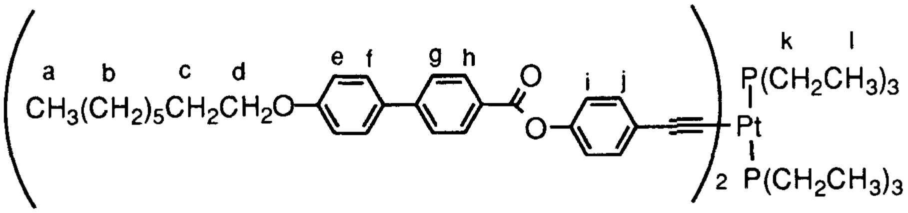
The *trans*-disubstituted palladium acetylide complexes were made in a manner similar to the platinum analogues, although the reduced solubility of the *trans*-dichloro*bis*(trialkylphosphine)palladium(II) meant that the ratio of dichloromethane to triethylamine had to be increased. Also, ^1H and ^{31}P NMR studies showed that initially the reaction did not go to completion and that the product was contaminated with both unreacted acetylene and *trans*-dichloro*bis*(phosphine)palladium(II). To overcome this the reaction time was increased to 48 h and the reaction mixture was heated to between 40–50°C. Disubstituted palladium complexes were made using both trimethyl and triethylphosphine with the hexoxy ligand. Both complexes were non-mesomorphic and remained crystalline before decomposing at temperatures of around 140°C. This instability was attributed to the weakness of the palladium–acetylene bonds. Whilst the chemistry of platinum and palladium is often very similar, the thermal stability of palladium complexes is generally much lower, so these palladium complexes decompose before reaching the temperature at which they would have formed a mesophase.

2.1 Experimental

Elemental analyses were determined by the University of Sheffield Microanalysis Service and NMR spectra were recorded on a Bruker AM250 spectrometer. Analysis by DSC was carried out on a Perkin–Elmer DSC7 instrument using heating rates of $10\,K\,min^{-1}$. Analysis by hot-stage optical microscopy was carried out using a Zeiss Labpol microscope equipped with a Link-Am TH600 hot-stage and PR600 controller. The complexes $[PtCl_2(PMe_3)_2]$,[9] $[PtCl_2(PEt_3)_2]$,[10] $[PdCl_2(PhCN)_2]$,[11] $[PdCl_2(PMe_3)_2]$ and $[PdCl_2(PEt_3)_2]$[12] were synthesised according to literature methods.

***2.1.1 Preparation of* trans*-bis(4-ethynylphenyl-4-octyloxydiphenylate)-bis(triethylphosphine) platinum(II)*[6]** *Trans*-dichlorobis(triethylphosphine)platinum(II) (59 mg, 0.117 mmol), two equivalents of 4-ethynylphenyl-4-octyloxydiphenylate (100 mg, 0.234 mmol) and a catalytic amount of copper (I) iodide were added to a mixture of triethylamine (8 cm^3) and dichloromethane (2 cm^3) under an atmosphere of argon. The reaction was stirred for 72 h, then the solvent was removed under reduced pressure. The solid thus obtained was dissolved in a small amount of dichloromethane and washed with water (10 cm^3) then brine (10 cm^3) and then the organic phase was dried over anhydrous potassium carbonate. The product was purified by column chromatography on silica using dichloromethane as the eluent before being crystallised from dichloromethane/pentane.

Yield: 105 mg (70%).



^{1}H

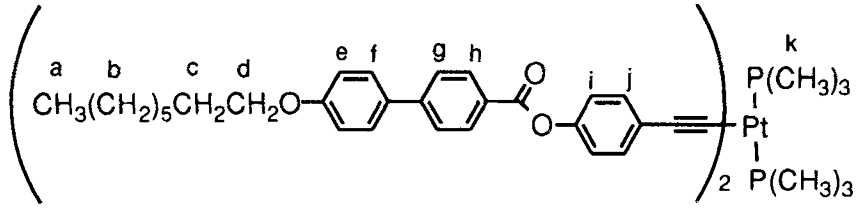
H^a: $\delta 0.87$, (t, 3H);
H^u: $\delta 1.25$, (m, 18H);
H^b: $\delta 1.33$, (m, 10H);
H^c: $\delta 1.85$, (m, 2H);
H^t: $\delta 2.18$, (m, 12H);
H^d: $\delta 4.03$, (t, 2H);
H^f: $\delta 6.99$, (AA'XX', 2H);
H^o: 7.18, (AA'XX', 2H);
H^p: $\delta 7.62$, (AA'XX', 2H);
H^g: $\delta 7.65$, (AA'XX', 2H);
H^j: $\delta 7.73$, (AA'XX', 2H);
H^k: $\delta 8.22$, (AA'XX',M 2H).

^{31}P

δ_P 11.69($^1J_{PtP}$ 2366 Hz).
Infrared data (Nujol mull): $\nu_{C\equiv C}$ 2125 cm^{-1}.

2.1.2 Preparation of trans*-bis(4-ethynylphenyl-4-octyloxydiphenylate)bis trimethylphosphine)platinum(II)*[6] *Trans*-dichlorobis(trimethylphosphine) platium(II) (49 mg, 0.117 mmol), two equivalents of 4-ethynylphenyl-4-octyl-oxy-diphenylate (100 mg, 0.234 mmol) and a catalytic amount of copper (I) iodide were added to a mixture of triethylamine (8 cm^3) and dichloromethane (2 cm^3) under an atmosphere of argon. The reaction was stirred for 72 h, then the solvent was removed under reduced pressure. The solid thus obtained was dissolved in a small amount of dichloromethane and washed with water (10 cm^3) then brine (10 cm^3) and then the organic phase was dried over anhydrous potassium carbonate. The product was purified by column chromatography on silica using dichloromethane as the eluent before being crystallised from dchloromethane/pentane.

Yield: 68 mg (55%).



^1H

H^a: δ0.82, (t, 3H);
H^b: δ1.20, (m, 10H);
H^k: δ1.55, (m, 18H);
H^c: δ1.70, (m, 2H);
H^d: δ3.98, (t, 2H);
H^e: δ6.99, (AA‘XX’, 2H);
H^i: δ7.18, (AA‘XX’, 2H);
H^j: δ7.62, (AA‘XX’, 2H);
H^f: δ7.65, (AA‘XX’, 2H);
H^g: δ7.73, (AA‘XX’, 2H);
H^h: δ8.22, (AA‘XX’, 2H).

^{31}P

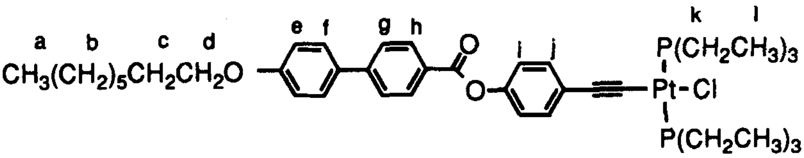
$\delta_P - 20.19(^1J_{PtP}$ 2286 Hz).

Infrared data (Nujol mull): $\nu_{C\equiv C}$ 2125 cm^{-1}.

All other platinum homologues were prepared in this way. Microanalytical data are collected in Table 3 below.

2.1.3 Preparation of trans-*bis(triethylphosphine)-(4-ethynylphenyl-4-octyloxydiphenylate)platinum (II) chloride*

Trans-dichlorobis(triethylphosphine)platinum(II) (300 mg, 0.6 mmol), 4-ethynylphenyl-4-octyloxydiphenylate (255 mg, 0.6 mmol) and a catalytic amount of copper (I) chloride were added to a mixture of triethylamine (4 cm^3) and dichloromethane (10 cm^3) under an atmosphere of argon. The reaction mixture was heated to 40–50°C and stirred for 48 h. The solvents were removed under reduced pressure and the crude product was dissolved in dichloromethane and washed with water (10 cm^3) then brine (10 cm^3). The organic phase was dried over potassium carbonate and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography on silica using dichloro-methane as the eluent before being crystallised from dichloromethane/pentane.



Yield: 430 mg (76%).

^1H

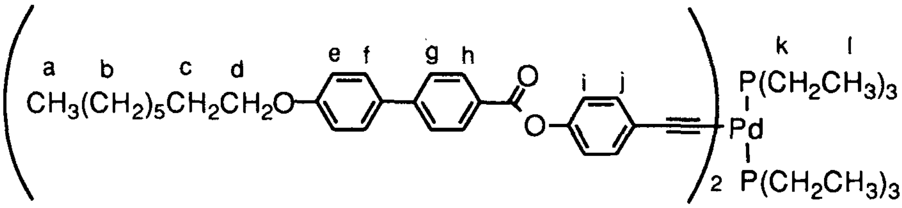
H^a: δ0.87, (t, 3H);
H^u: δ1.25, (m, 18H);
H^b: δ1.33, (m, 10H);
H^c: δ1.85, (m, 2H);
H^l: δ2.18, (m, 12H);
H^d: δ4.03, (t, 2H);
H^f: δ6.99, (AA'XX', 2H);
H^o: δ7.18, (AA'XX', 2H);
H^p: δ7.62, (AA'XX', 2H);
H^g: δ7.65, (AA'XX', 2H);
H^j: δ7.73, (AA'XX',M 2H).
H^k: δ8.22, (AA'XX', 2H).

^{31}P

$\delta_P - 15.3(J_{PtP}\,2390\,Hz)$.
Infrared data (Nujol mull): $\nu_{C\equiv C}\,2125\,cm^{-1}$, $\nu_{PtCl}\,315\,cm^{-1}$.

All other monosubstituted platinum homologues were prepared in this way. Microanalytical data are collected in Table 4.

2.1.4 Preparation of* trans*-bis(4-ethynylphenyl-4-alkoxydiphenylate)-bis(triethylphosphine) palladium (II) complexes *Tras*-dichlorobis(trethylphosphine)palladum(II) (59 mg, 0.117 mmol), two equivalents of 4-ethynylphenyl-4-octyloxydiphenylate (100 mg, 0.234 mmol) and a catalytic amount of copper (I) iodide were added to a mixture of triethylamine (8 cm^3) and dichloromethane (6 cm^3) under an atmosphere of argon. The reaction was stirred for 48 h at between 40 and 50°C, then the solvent was removed under reduced pressure. The solid thus obtained was dissolved in a small amount of dichloromethane and washed with water (10 cm^3) then brine (10 cm^3). Then the organic phase was dried over anhydrous potassium carbonate. The product was purified by column chromatography on silica using dichloromethane as the eluent before being crystallised from dichloromethane/pentane.
Yield: 105 mg (70%).



All other palladium complexes were similarly prepared.

^{1}H

H^{a}:δ0.92, (t, 3H);
H^{l}:δ1.25, (m, 18H);
H^{b}:δ1.33, (m, 10H);
H^{c}:δ1.85, (m, 2H);
H^{k}:δ2.20, (m, 12H);
H^{d}:δ4.03, (t, 2H);
H^{e}:δ6.99, (AA'XX', 2H);
H^{i}:δ7.18, (AA'XX', 2H);
H^{h}:δ7.62, (AA'XX', 2H);
H^{j}:δ7.65, (AA'XX', 2H);
H^{g}:δ7.73, (AA'XX', 2H).
H^{g}:δ8.22, (AA'XX', 2H).

^{31}P

$\delta_P - 13.44$

Infrared data (Nujol mull): $\nu_{C\equiv C}$ 2125 cm^{-1}.

TABLE 3

Microanalytical data for disubstituted platinum complexes

n	Phosphine	Microanalysis Calculated (found)	
		C	H
6	PEt$_3$	64.6 (64.3)	6.7 (6.9)
7	PEt$_3$	65.1 (65.3)	6.8 (7.0)
8	PEt$_3$	65.6 (65.7)	6.9 (7.1)
9	PEt$_3$	66.0 (65.9)	7.1 (7.0)
10	PEt$_3$	66.4 (65.7)	7.2 (7.0)
6	PMe$_3$	63.1 (63.0)	6.0 (5.8)
8	PMe$_3$	64.2 (63.9)	6.4 (6.4)
10	PMe$_3$	65.1 (65.1)	6.8 (6.7)
6	PPr$_3$	66.0 (66.3)	7.1 (7.3)
8	PPr$_3$	66.8 (67.4)	7.4 (7.4)
10	PPr$_3$	67.5 (67.5)	7.7 (7.6)

TABLE 4

Microanalytical data for monosubstituted platinum complexes

n	Phosphine	Microanalysis Calculated (found)		
		C	H	Cl
6	PEt_3	54.2 (54.2)	6.4 (6.4)	4.1 (4.1)
8	PEt_3	55.2 (55.0)	6.7 (6.5)	4.0 (3.8)
10	PEt_3	56.1 (55.7)	6.9 (7.0)	3.9 (3.8)

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