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The preparation of novel ruthenium complexes for use in Langmuir–Blodgett films

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Abstract

A range of cationic cyclopentadienyl bisphosphine ruthenium nitrile complexes $[(\eta^5\text{-}C_5H_5)L_2RuNC\text{-}Aryl]^+$ (L = phosphine or phosphite) have been prepared and characterised for use with the Langmuir–Blodgett deposition technique.

Introduction

The Langmuir–Blodgett (LB) deposition technique has evoked considerable interest in recent years due to the possibility of developing novel electronic and optical devices [1,2]. Substituted benzonitriles are liquid crystal materials which often possess the chemical and electronic properties necessary for the preparation of LB films. Unfortunately the preparation of multilayer LB films from these compounds is often impossible. We have previously reported that complexing molecules of this type to cyclopentadienyl bistriphenylphosphine ruthenium dramatically increases their film forming ability [3,4] and can lead to materials with potentially useful pyroelectric coefficients or non linear optical properties [5]. We now wish to report the synthesis of a variety of complexes containing the cyclopentadienyl bisphosphine ruthenium unit which are currently undergoing studies on their suitability for use with the LB technique.

Results and discussion

Acetonitrile [6,7] and benzonitrile derivatives [8] readily react with $(\eta^5\text{-}C_5H_5)(PR_3)_2RuCl$ in the presence of non-chelating anions to form complexes of the type $[(\eta^5\text{-}C_5H_5)(PR_3)_2RuNCR']^+X^-$ which we considered ideal candidates for LB film work [3]. The ready substitution of the phosphine ligands bound to the ruthenium [9] allows the complexes to be tailored for a wide range of electronic and steric properties.

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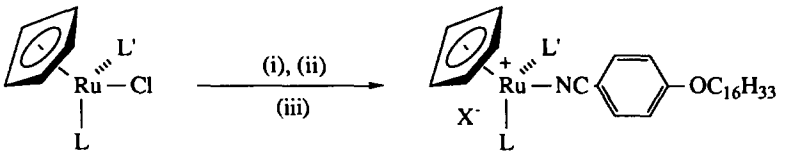
Table 1

Selected analytical data for the cationic ruthenium complexes

No.	Analysis (found (calcd.) (%))			Yield (%)	^{1}H NMR (ppm) (η^5-C_5H_5)
	C	H	N		
1	65.12 (65.18)	6.20 (6.15)	0.92 (1.19)	94	4.54
2	50.90 (50.61)	7.62 (7.49)	1.60 (1.73)	24	4.74
3	59.47 (59.26)	6.82 (6.70)	1.27 (1.41)	75	4.68
4	61.82 (61.88)	6.07 (5.87)	1.19 (1.34)	53	4.81
5	45.35 (45.23)	6.94 (6.70)	1.34 (1.55)	22	5.10
6	68.82 (68.56)	6.70 (6.47)	1.52 (1.25)	23	4.57
7	77.80 (78.09)	7.10 (6.85)	0.92 (1.04)	86	4.36
8	54.65 (54.66)	6.90 (6.88)	1.53 (1.59)	85	4.78
9	64.45 (64.62)	6.91 (6.60)	1.34 (1.25)	74	4.48
10b	65.38 (65.51)	6.13 (5.97)	3.62 (3.27)	79	4.62
11b	65.73 (65.78)	6.31 (6.14)	3.99 (4.32)	54	4.59
12b	61.28 (61.24)	4.35 (4.19)	3.92 (3.97)	86	4.77
13b	48.28 (48.18)	6.23 (6.19)	7.04 (7.02)	81	4.80

A methanol solution of (η^5-C_5H_5)(PPh_3)$_2$RuCl, 4-hexadecyloxybenzonitrile and NH_4PF_6 was heated under reflux for 2 hours to give the cationic complex **1** in near quantitative yield as a yellow crystalline solid. Analogous complexes **2–5** with a variety of phosphine or phosphite ligands were prepared from the appropriate ruthenium chloride complexes [10,11]. The analytical data and the chemical shift of the cyclopentadienyl moiety for all the compounds prepared in this study are given in Table 1. The mechanism of this reaction is believed to involve ionisation of the Ru–Cl bond in methanol followed by trapping of the thus formed [(η^5-C_5H_5)L_2Ru]$^+$ by the nitrile. This ionisation is particularly favoured by electron donating phosphine ligands but not by phosphite ligands. Thus in the preparation of **5** significant amounts of starting material, (η^5-C_5H_5)($P(OMe)_3$)$_2$RuCl, remained even after 24 hours at reflux. The cationic complex **5** was separated from the neutral ruthenium chloride complex with difficulty in low yield as a pale yellow crystalline solid. Furthermore, no product was formed when (η^5-C_5H_5)(PPh_3)(CO)RuCl, containing the electron withdrawing ligand CO, was treated with 4-hexadecyloxybenzonitrile. The bistrimethyl phosphine derivative **2** is relatively unstable towards chromatography, hence its low yield. Complexes with counterions other than PF_6^- (**6,7**) were obtained by carrying out the reaction in the presence of $NaBPh_4$ or $AgBF_4$.

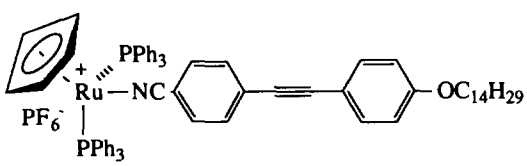


1 - 7

No.	L	L'	X
1	PPh_3	PPh_3	PF_6
2	PMe_3	PMe_3	PF_6
3	PPh_3	PMe_3	PF_6
4	dppe		PF_6
5	$P(OMe)_3$	$P(OMe)_3$	PF_6
6	PPh_3	PPh_3	BF_4
7	PPh_3	PPh_3	BPh_4

Scheme 1. Reagents: (i) $NCC_6H_4OC_{16}H_{33}$, (ii) NH_4PF_6, $NaBPh_4$ or $AgBF_4$ (iii) MeOH.

Complexes **8** and **9** were prepared in high yield from $(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCl$ and the approximate nitrile using the standard complexation conditions. The complexes **1–9** were all obtained as yellow solids.



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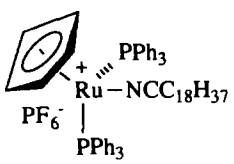

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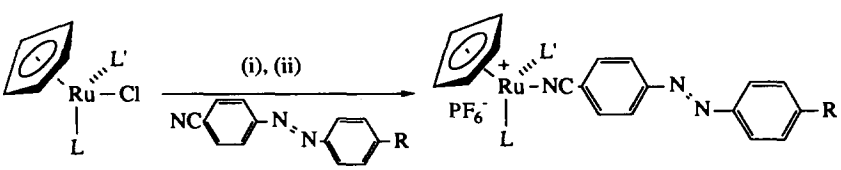
Materials with a strong absorbance near 500 nm were required for nonlinear optics applications. Therefore, several highly conjugated azo compounds were prepared using standard diazotisation procedures [12]. Complexation of these compounds using a similar procedure to that described above gave the novel cationic ruthenium complexes **8–11** as intensely coloured crystalline solids in good yield. Values of λ_{max} and ϵ_0 for both the complexed and uncomplexed azo compounds are given in Table 2.



10a - 13a

10b - 13b

No	L	L	R
10	PPh_3	PPh_3	$OC_{16}H_{33}$
11	PPh_3	PPh_3	$N(Me)C_{16}H_{33}$
12	PPh_3	PPh_3	OH
13	PMe_3	PMe_3	$N(Me)C_7H_{15}$

Scheme 2. Reagents: (i) NH_4PF_6, (ii) MeOH.

Table 2

Values of λ_{max} and ϵ_0 for the complexed and uncomplexed azo compounds

No.	Colour	λ_{max} (nm)	ϵ_0 ($\times 10^3$ mol^{-1} l cm^{-1})
10a	pale strange	362	17.0
10b	bright red	383	17.2
11a	orange	456	25.2
11b	bright red	486	32.4
12a	orange	367	22.1
12b	dark orange	382	23.2
13a	dark red	462	24.7
13b	dark red	490	28.9

Conclusion

Materials suitable for use with the LB deposition technique need to form fluid monolayers; in addition ideally they should possess a large dipole and for nonlinear optics purposes absorb light around 500 nm. Complexing nitriles to (η^5-C_5H_5)(PPh_3)$_2$RuCl enhances the film forming ability of the nitrile, increases its dipole and shifts the absorbance of the material to higher wavelengths as has been demonstrated for the azo compounds.

Experimental

General

N-Heptyl-*N*-methylaniline [13], 4-[(4′-cyanophenyl)azo]phenol (**12a**) [14] and 4-[[4′-(*N*-methyl)phenyl]azo]benzonitrile [15] were prepared using literature procedures. Octadecylnitrile and 4-cyanophenyl-4′-(tridecyloxy)phenylacetylene were kindly provided by Dr. D. Lacey (Hull University, UK). ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini 200 instrument.

4-Hexadecyloxybenzonitrile. An ethanol solution of 4-cyanophenol (1.19 g, 10 mmol), KOH (1 g, 18 mmol) and hexadecylbromide (3.05 g, 10 mmol) was heated at reflux for 8 h. After cooling the product was filtered off and recrystallised from methanol. Yield 2.8 g (82%). M.p. 52–53° C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.26 (m, 26H), 1.60 (m, 2H, CH_2CH_2O), 4.00 (t, J = 6.5 Hz, 2H, CH_2O), 6.96 (d, J = 8.9 Hz, 2H, H2 H6), 7.58 (d, J = 8.9 Hz, 2H, H3 H5).

*4-[{4′-(Hexadecyloxy)phenyl}azo]benzonitrile (**10a**).* An ethanol solution of 4-[(4′-cyanophenyl)azo]phenol (223 mg, 1 mmol), KOH (0.1 g, 1.8 mmol) and hexadecylbromide (400 mg, 1.3 mmol) was heated at reflux for 20 h. After cooling the precipitate was filtered off to give the product as a pale orange solid. Yield 328 mg (73%). M.p. 98–100° C. ^{1}H NMR ($CDCl_3$): 0.89 (t, J = 6.3 Hz, 3H, CH_3), 1.27 (m, 26H), 1.6 (m, 2H, CH_2CH_2O), 4.07 (t, J = 6.4 Hz, 2H, CH_2O), 7.04 (d, J = 9.0 Hz, H2 H6), 7.81 (d, J = 8.4 Hz, 2H, H3′ H5′), 7.96 (d, J = 8.6 Hz, 4H, H2′ H6′ H3 H5).

*4-[{4′-(N-hexadecyl-N-methyl)phenyl}azo]benzonitrile (**11a**).* Sodium hydride (50 mg, 2.1 mmol) was added to a THF solution of 4-[{4′-(*N*-methyl)phenyl}azo]benzonitrile (455 mg, 1.92 mmol). After stirring at room temperature for 1 h, hexade-

cylbromide (588 mg, 1.3 mmol) was added and the resulting solution heated at reflux for 20 h. Water (20 ml) was added and the solution extracted with dichloromethane (3 × 20 ml). Removal of the solvent under reduced pressure gave the product as an orange solid. Yield 854 mg (96%). M.p. 82–84°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.2 Hz, 3H, CH_3), 1.27 (m, 26H), 1.6 (m, 2H, CH_2CH_2N), 3.09 (s, 3H, NMe), 3.44 (t, J = 7.8 Hz, 2H, CH_2N), 6.74 (d, J = 9.2 Hz, H2 H6), 7.75 (d, J = 8.3 Hz, 2H, H3′ H5′), 7.89 (d, J = 8.5 Hz, 4H, H2′ H6′ H3 H5).

4-[{4′-(N-heptyl-N-methyl)phenyl}azo]benzonitrile (13a). Using a procedure similar to that described by Hartman and Dickey [16], 4-cyanoaniline was dissolved in aq. hydrochloric acid (18%, 10 ml) and cooled to 0°C. With stirring a solution of sodium nitrite (0.7 g) in water (10 ml) was added dropwise over 30 min. Addition at 0°C of *N*-heptyl-*N*-methyl aniline (2.0 g) and aq. sodium hydroxide (10%, 10 ml) gave during 30 min stirring the product **13a** as a red precipitate. Filtration, dissolution in chloroform, drying (Na_2SO_4) and chromatography (Al_2O_3, grade V, $CHCl_3$) gave after evaporation **13a** as a bright red solid. Yield 1.1 g (33%). M.p. 78–79°C. ^{1}H NMR ($CDCl_3$) 0.90 (t, J = 6.7 Hz, 3H, CH_3), 1.32 (m, 26H), 1.65 (m, 2H, CH_2CH_2N), 3.09 (s, 3H, NMe), 3.44 (t, J = 7.5 Hz, 2H, CH_2N), 6.61 (d, J = 9.2 Hz, H2 H6), 7.75 (d, J = 8.7 Hz, 2H, H3′ H5′), 7.89 (d, J = 8.6 Hz, 4H, H2′ H6′ H3 H5).

N-[Ruthenium (η^5-cyclopentadienyl)(bistriphenylphosphine)]-4-hexadecyloxybenzonitrile hexafluorophosphate (1). A solution of (η5-cyclopentadienyl)(bistriphenylphosphine)ruthenium chloride [17] (95 mg, 1.3 mmol) 4-hexadecyloxybenzonitrile (46 mg, 1.3 mmol) and ammonium hexafluorophosphate (50 mg, 3 mmol) in methanol was heated under reflux for 2 h. After removal of the methanol under reduced pressure dichloromethane was added and the solution filtered. Column chromatography (Flash silica, eluent: 5% Et_2O : CH_2Cl_2) gave the product. Yield 145 mg (94%). M.p. 68–70°C. ^{1}H NMR ($CDCl_3$) 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.77 (m, 2H, CH_2CH_2O), 3.99 (t, J = 6.4 Hz, 2H, CH_2O), 4.54 (s, 5H, Cp), 6.88 (d, J = 8.9 Hz, H2 H6), 7.1–7.8 (m, 32H, Ar).

A similar procedure was used for the preparation of complexes **2**–**13**.

2: m.p. 95°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.8 Hz, 3H, CH_3), 1.26 (m, 26H, $(CH_2)_{13}$), 1.58 (m, 18H, PMe_3), 1.78 (m, 2H, CH_2CH_2O), 4.00 (t, J = 6.4 Hz, 2H, CH_2O), 4.74 (s, 5H, Cp). 6.98 (d, J = 8.9 Hz, H2 H6), 7.55 (d, J = 8.9 Hz, H3 H5).

3: m.p. 61–62°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.5 Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.35 (d, J = 9.2 Hz, 6H, PMe_3), 1.77 (m, 2H, CH_2CH_2O), 3.99 (t, J = 6.5 Hz, 2H, CH_2O, 4.68 (s, 5H, Cp), 6.90 (d, J = 8.9 Hz, 2H, H2 H6), 7.2–7.5 (m, 17H, Ar).

4: m.p. 71–72°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.72 (m, 2H, CH_2CH_2O), 2.6 (m, 4H, PCH_2CH_2P), 3.90 (t, J = 6.5 Hz, 2H, CH_2O), 4.81 (s, 5H, Cp), 6.45 (d, J = 8.8 Hz, Ar), 6.67 (d, J = 8.9 Hz, Ar) 7.2–7.9 (m, 30H, Ar).

5: m.p. 46–47°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, J = 6.6 Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.74 (m, 2H, CH_2CH_2O), 3.68 (m, 18H, $P(OMe)_3$), 4.00 (t, J = 6.4 Hz, 2H, CH_2O), 5.10 (s, 5H, Cp), 6.99 (d, J = 8.9 Hz, 2H, H2 H6), 7.58 (d, J = 8.9 Hz, H3 H5).

6: m.p. 67°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, J = 6.3 Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.78 (m, 2H, CH_2CH_2O), 4.00 (t, J = 6.5 Hz, 2H, CH_2O), 4.57 (s, 5H, Cp), 6.90 (d, J = 8.9 Hz, 2H, H2 H6), 7.1–7.4 (m, 32H, Ar).

7: m.p. 74°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, $J = 6.4$ Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.77 (m, 2H, CH_2CH_2O), 3.86 (t, $J = 6.4$ Hz, 2H, CH_2O), 4.36 (s, 5H, Cp), 6.7–7.1 (m, 54H, Ar).

8: m.p. 108°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, $J = 6.4$ Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.58 (m, 18H, PMe_3), 1.77 (m, 2H, CH_2CH_2O), 3.98 (t, $J = 6.5$ Hz, 2H, CH_2O), 4.78 (s, 5H, Cp), 6.89 (d, $J = 8.6$ Hz, 2H, H3 H5), 7.47 (d, $J = 8.7$ Hz, 2H, H3′ H5′), 7.59 (s, 4H, H2 H2′ H6 H6′).

9: m.p. 73°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, $J = 6.7$ Hz, 3H, CH_3), 1.27 (m, 32H, $(CH_2)_{16}$), 2.67 (t, $J = 6.8$ Hz, 2H, CH_2CN), 4.48 (s, 5H, Cp), 7.0–7.5 (m, 34H, Ar).

10b: m.p. 90°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, $J = 6.1$ Hz, 3H, CH_3), 1.27 (m, 26H, $(CH_2)_{13}$), 1.35 (m, 2H, CH_2CH_2O), 4.07 (t, $J = 6.7$ Hz, CH_2O), 4.62 (s, 5H, Cp), 7.02 (d, $J = 9.0$ Hz, 2H, H2 H6), 7.1–7.5 (m, 32H, Ph), 7.86 (d, $J = 8.6$ Hz, 2H, H3′ H5′), 7.93 (d, $J = 9.0$ Hz, 4H, H3 H5 H2′ H6′).

11b: m.p. 91°C. ^{1}H NMR ($CDCl_3$): 0.88 (t, $J = 6.1$ Hz, CH_3), 1.26 (m, 26H), 1.62 (m, 2H, CH_2CH_2O), 3.09 (s, 3H, NMe), 3.44 (t, $J = 7.4$ Hz, 2H, CH_2N), 4.59 (s, 5H, Cp), 6.73 (d, $J = 9.3$ Hz, 2H, H2 H6), 7.0–7.5 (m, 32H), 7.79 (d, $J = 8.6$ Hz, 2H, H3′ H5′), 7.87 (d, $J = 9.2$ Hz, 4H, H3 H5 H2′ H6′).

12b: m.p. 147°C. ^{1}H NMR (acetone-d_6): 4.77 (s, 5H, Cp), 7.05 (d, $J = 8.8$ Hz, 2H, H2 H6), 7.2–7.5 (m, 32H, Ar), 7.58 (d, $J = 8.6$ Hz, 2H, H3′ H5′), 7.90 (d, $J = 8.6$ Hz, 2H, Ar), 7.93 (d, $J = 8.3$ Hz, 2H, Ar).

13b: m.p. 113°C. ^{1}H NMR ($CDCl_3$): 0.89 (t, $J = 6.4$ Hz, 3H, CH_3), 1.30 (m, 10H, $(CH_2)_{13}$), 1.61 (m, 18H, PMe_3), 3.10 (s, 3H, NMe), 3.45 (t, $J = 7.1$ Hz, 2H, CH_2N), 4.80 (s, 5H, Cp), 6.73 (d, $J = 9.1$ Hz, 2H, H2 H6), 7.67 (d, $J = 8.1$ Hz, 2H, H3′ H5′), 7.88 (d, $J = 7.1$ Hz, 2H, Ar), 7.92 (d, $J = 8.0$ Hz, 2H, Ar).

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References

1 G.G. Roberts, Adv. Phys., 34 (1985) 475.
2 J. Zyss, Non-Cryst. Solids, 47 (1982) 211.
3 T. Richardson, G.G. Roberts, S.G. Davies, M.E.C. Polywka, Thin Solid Films, 160 (1988) 231.
4 G.G. Roberts, S.G. Davies, T. Richardson, Organo-transition metal complexes for non linear optics applications, Patent application No. 88306310.9-GB 8717566, 24.07.87.
5 See for example (i) T. Richardson, G.G. Roberts, S.G. Davies, M.E.C. Polywka, Thin Solid Films, 179 (1989) 405. (ii) R. Colbrook, B. Holcroft, G.G. Roberts, M.E.C. Polywka and S.G. Davies, Ferroelectrics, 92 (1989) 381.
6 T. Blackmore, M.I. Bruce, F.G.A. Stone, J. Chem. Soc. A, (1971) 2376.
7 S.G. Davies, F. Scott, J. Organomet. Chem., 188 (1980) C41.
8 G.S. Ashby, M.I. Bruce, I.B. Tomkins, R.C. Wallis, Aust. J. Chem., 32 (1979) 1003.
9 S.G. Davies, J.P. McNally, A.J. Smallridge, Adv. Organomet. Chem., (1990) 1 and references therein.
10 P.M. Treichel, D.A. Komar, P.J. Vincenti, Synth. React. Inorg. Met.-Org. Chem., 14 (1984) 383.
11 M.I. Bruce, F.S. Wong, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans., (1981) 1398.
12 E. Vowinkel, J. Bartel, Chem. Ber., 107 (1974) 1221.
13 G.R. Clemo, R. Raper, H.J. Vipond, J. Chem. Soc., (1949) 2095.
14 J. Socha, J. Horska, M. Vecera, Coll. Czech., Chem. Commun., 34 (1969) 2982.
15 T. Yamada, Bull. Chem. Soc. Jpn., 42 (1969) 3565.
16 W.W. Hartman, J.B. Dickey, Organic Syntheses, Coll. Vol. II 1943, p. 163.
17 M.I. Bruce, N.J. Windsor, Aust. J. Chem., 30 (1977) 1601.