Structure of organoruthenium-derived Langmuir monolayers at the air–water interface: a molecular-modelling approach

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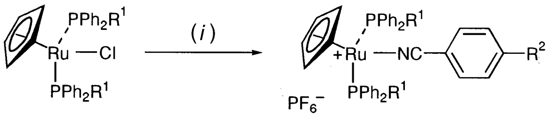
A two-dimensional model for the structure of films fabricated from organoruthenium amphiphiles of the type $[Ru(\eta^5\text{-}C_5H_5)(PPh_2R)_2(p\text{-}NCC_6H_4OR')]PF_6$ (R = Ph, *p*-tolyl or *p*-biphenyl; R′ = Et or $C_{16}H_{33}$) at the air–water interface has been devised.

The large variety of organic materials which are suitable for the Langmuir–Blodgett film-deposition technique offers enormous scope for the fabrication of novel devices capable of operating at the nanometer scale.[1] Recently we have become interested in the fabrication of Langmuir–Blodgett superlattices based upon organoruthenium complexes of the type $[Ru(\eta^5\text{-}C_5H_5)(PR_3)_2(p\text{-}NCC_6H_4OR')]PF_6$.[2–6] Such materials exhibit second-order non-linear physical responses, such as optical second-harmonic generation and pyroelectricity. Consequently, a great deal of interest has been generated in the potential application of such materials as pyroelectric thermal imaging devices. The pyroelectric mechanism almost certainly involves a change in molecular tilt or headgroup conformation.[7,8] As a consequence, an insight into the structure of the two-dimensional superlattice is essential in order to understand and ultimately optimise the pyroelectric response. The relatively versatile synthetic procedure used in the preparation[9] of these metal complexes offers an opportunity to probe those structural features which may be relevant to the optimisation of the pyroelectric response. The ready substitution of the phosphine ligands bound to the ruthenium metal centre allows access to a range of compounds with differing spacial characteristics. In order to gain insight into the conformational space available to the cationic organometallic headgroup of the amphiphile, it was envisaged that crystalline derivatives of such organoruthenium complexes should be prepared and studied.

Results

The synthesis of the organometallic complex $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ **1** (Scheme 1) is achieved[10] by the reaction of $RuCl_3$, cyclopentadiene and triphenylphosphine in refluxing ethanol. It crystallises directly from the crude reaction mixture. The analogous *p*-tolyl **2** and biphenyl **3** complexes were prepared *via* a similar procedure.

Acetonitrile and benzonitrile derivatives readily react with complex **1** in the presence of non-chelating anions to form complexes of the type $[Ru(\eta^5\text{-}C_5H_5)(PR_3)_2(NCR')]^+PF_6^-$. A methanol solution of **1**, 4-ethoxybenzonitrile and NH_4PF_6 was heated under reflux for 2 h to give the cationic complex **4** in near-quantitative yield as a yellow crystalline solid. The analogous complexes **5**–**7** containing the 4-hexadecyloxybenzonitrile ligand and various phosphine ligands were prepared from the appropriate ruthenium chloride complex.



1-3 **4-7**

	R^1	R^2
1	Ph	—
2	*p*-Tolyl	—
3	*p*-Biphenyl	—
4	Ph	OEt
5	Ph	$OC_{16}H_{33}$
6	*p*-Tolyl	$OC_{16}H_{33}$
7	*p*-Biphenyl	$OC_{16}H_{33}$

Scheme 1 (*i*) $p\text{-}NCC_6H_4R^2$, MeOH, NH_4PF_6, heat

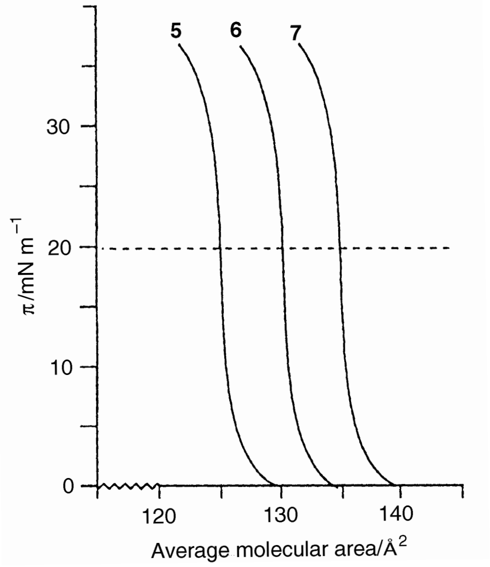


Fig. 1 Pressure *vs.* area (π *vs.* *A*) isotherms for complexes **5**–**7**

Langmuir films were prepared by depositing a chloroform solution of complexes **5**–**7** upon a pure water subphase within a Langmuir trough. After solvent evaporation, the resulting layer was compressed at a rate of 4 $cm^2\ s^{-1}$. Surface pressure (π) *vs.* area isotherms of **5**–**7** are presented in Fig. 1, and are

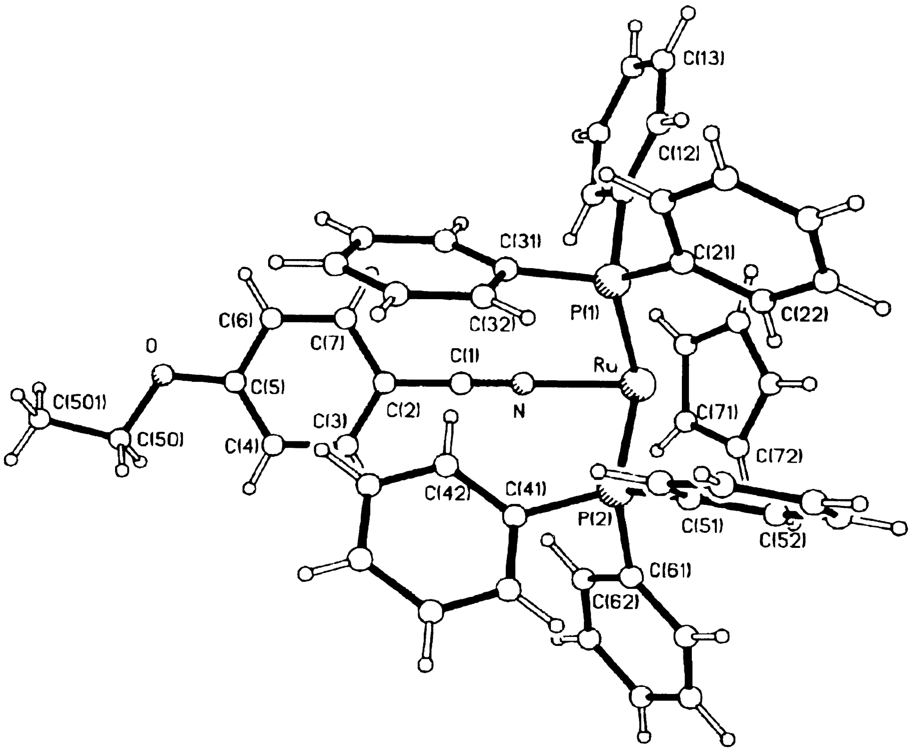


Fig. 2 Crystal structure of complex **4**. The hexafluorophosphate anion has been omitted for clarity

Table 1 Experimentally determined average molecular areas (Å^2) for amphiphiles **5**–**7** at 20 mN m^{-1}, and the associated pyroelectric coefficients (μC m^{-2} K^{-1} at 292 K)

Amphiphile	Average molecular area	Pyroelectric coefficient
5	125	0.53
6	130	0.67
7	135	1.07

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for complex **4**

Ru–C(71)	2.226(5)	Ru–C(72)	2.217(5)
Ru–C(73)	2.213(6)	Ru–C(74)	2.228(6)
Ru–C(75)	2.226(6)	Ru–N	2.041(5)
Ru–P(1)	2.351(2)	Ru–P(2)	2.337(2)
N–Ru–C(71)	95.7(2)	N–Ru–C(72)	127.1(2)
N–Ru–C(73)	155.9(2)	N–Ru–C(74)	126.9(2)
N–Ru–C(75)	95.5(2)	P(1)–Ru–C(71)	147.7(2)
P(1)–Ru–C(72)	141.3(2)	P(1)–Ru–C(73)	104.3(2)
P(1)–Ru–C(74)	89.7(2)	P(1)–Ru–C(75)	110.7(2)
P(1)–Ru–N	90.4(1)	P(2)–Ru–C(71)	110.8(2)
P(2)–Ru–C(72)	88.8(2)	P(2)–Ru–C(73)	103.7(2)
P(2)–Ru–C(74)	139.9(2)	P(2)–Ru–C(75)	147.7(2)
P(2)–Ru–N	92.0(1)	P(2)–Ru–P(1)	100.6(1)
C(72)–C(73)–Ru	71.5(3)	C(74)–C(73)–Ru	72.3(3)

consistent with the formation of stable monolayers at a surface pressure of 20 mN m^{-1}. This corresponds to the pressure at which the Langmuir–Blodgett films are fabricated from these materials. The experimentally determined average surface areas available to each molecule of the amphiphiles **5**–**7** are presented in Table 1. The pyroelectric coefficients which were measured for the Langmuir–Blodgett films fabricated from the amphiphiles **5**–**7**, using a quasi-static technique,[11] are also presented in Table 1.

A single crystal X-ray analysis of complex **4** is shown in Fig. 2, and selected bond angles and lengths are presented in Table 2. As expected, the organoruthenium complex adopts a geometry close to octahedral.[12] The 4-ethoxybenzonitrile and triphenylphosphine ligands occupy three adjacent sites of the pseudo-octahedral structure, with each ligand lying approximately orthogonal (*i.e.* P–Ru–N 91°) to the plane formed by the other two and the metal centre. The remaining three coordination sites available on ruthenium are jointly occupied by the cyclopentadienyl ligand. Within the complex **4**, the rotors associated with the two triphenylphosphine ligands are almost perfectly eclipsed [Cp–Ru–P(1)–C(31) +159°, Cp–Ru–P(2)–C(41) −158°; Cp = centroid of C_5H_5 ring]. Interestingly, the cation has a plane of symmetry in which the triphenylphosphine rotors assume a *meso* arrangement. The rotors possess opposite helical chirality [*i.e.* P(1) anticlockwise (*M*), and P(2) clockwise (*P*)],[13] presumably in order to accommodate the mutually eclipsed nature of these ligands.

Using the CHEM-X molecular-modelling package,[14] complex **4** was constructed using the crystallographically derived data. A computational model was generated by driving the bonds C$_{ipso}$–CN, P(1)–Ru and P(2)–Ru through 0–360° in 10° increments. For each conformation generated the van der Waals energy was minimised by independent rotations about the cyclopentadienyl centroid–ruthenium and C$_{ipso}$–P bonds. The calculation clearly indicated that only one well defined energy minimum was available to **4**, and the calculated lowest-energy conformation was found to be in good agreement with that observed in the crystal. However, in the crystal the plane of the aromatic ring associated with the benzonitrile ligand is approximately perpendicular to the plane defined by Cp–Ru–N [Cp–Ru–C(2)–C(7) −94°]. In the calculated structure the two planes are essentially *gauche* [Cp–Ru–C(2)–C(7) +162°].

Computer models of the headgroups associated with the amphiphiles **6** and **7** were generated by modifying the crystal structure of **4**.

Discussion

Molecular-modelling studies using the CHEM-X package,[14] which employs van der Waals interaction-energy calculations, have proven successful in determining the accessible conformations of organometallic molecules. The crystal structure of complex **4** provided an excellent starting point for conformational modelling studies of the amphiphile headgroup of **5**.

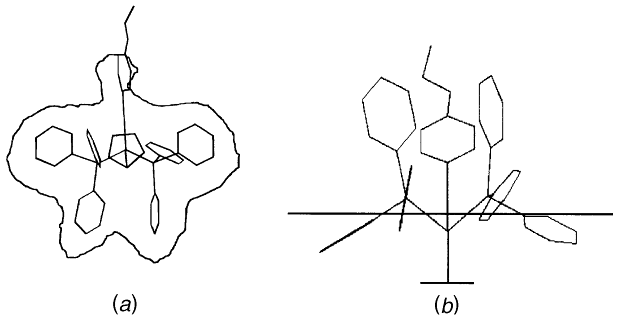


Fig. 3 (*a*) Calculated lowest-energy conformation of complex **4**, as viewed along the cyclopentadienyl centroid–ruthenium bond, and (*b*) the crystal structure of **4** as viewed through the plane of the cyclopentadienyl ligand. Superimposed upon (*a*) is the two-dimensional map representing the extent of the maximum van der Waals surface area

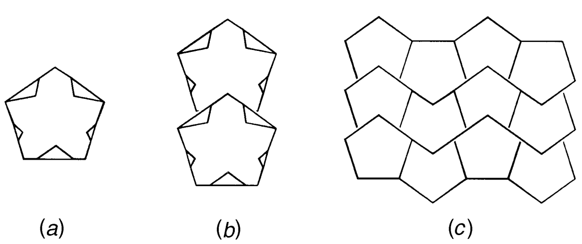


Fig. 4 Diagrammatic representations of (*a*) the van der Waals cross-section of complex **4**, approximating to a regular pentagonal tessera (triangles represent the void space within the tessera), (*b*) interleaving of the base of one tessera, with the apex of another, and (*c*) the construction of a tessellate, minimising the intermolecular void space within the two-dimensional matrix

X-Ray reflectivity studies[15] suggest that within a Langmuir–Blodgett film fabricated from **5** the oligomeric alkyl chain is fully extended. Consequently, we have assumed that within the Langmuir films derived from the amphiphiles **5**–**7** at a pressure of 20 mN m^{-1} the cationic organometallic fragment is oriented towards the air–water interface, with the aliphatic chain being fully extended and oriented away from this interface. For the purposes of modelling the two-dimensional structure of the amphiphile **5** at the air–water interface, we have simplified the task to that of considering models derived from the crystal structure of **4**, which do not contain the C_{16} fragment.

A useful facility within the CHEM-X package is the ability to calculate the cross-sectional area of the van der Waals surface of a molecule (two-dimensional map facility). Thus, *via* an iterative approach, it was possible to identify the orientation of the plane representing the maximum van der Waals cross-sectional area. This approach was applied to the calculated lowest-energy conformation of complex **4**. The plane associated with the maximum cross-sectional area of the van der Waals surface was identified to be approximately parallel to, and displaced 3.5 Å away from, the plane described by the cyclopentadienyl ligand, towards the ruthenium metal centre. A value of 109 Å^2 was calculated for the irregularly shaped figure, which has been superimposed upon the calculated lowest-energy conformation of **4** (Fig. 3).

Approximation of the irregularly shaped figure to a pentagon is an intuitively appealing manner in which to generate a tessera for the construction of a tessellate. This could be achieved by approximating the indentations in the irregularly shaped figure [Fig. 3(*a*)] to triangles within a regular pentagon [Fig. 4(*a*)]. The area of the pentagon now corresponds to the total area displaced by the amphiphilic headgroup, and is calculated to be 123 Å^2. This is in excellent agreement with the experimentally determined molecular area of the headgroup associated with the amphiphile **5** (Table 1). It is instructive that no other cross-sectional area could be identified which would prove consistent with the experimentally determined average molecular area.

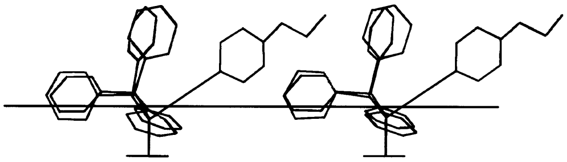


Fig. 5 A side view through the modelled air–water interface

The observed consistency between the calculated maximum molecular area and the experimentally determined area of water available to each molecule encouraged us to persist with our assumptions regarding the manner in which the organoruthenium headgroup is displaced with respect to the air–water interface. That is to say, the average position of the cyclopentadienyl centroid–ruthenium bond is approximately perpendicular, and proximal, to the air–water interface.

Upon identifying a suitable tessera, which approximates to a regular pentagon, a two-dimensional array was constructed. The indentation at the base of the pentagon corresponds to the 'free space' adjacent to the phenyl rings of the phosphine ligands. The apex of the pentagon corresponds to the area occupied by the nitrile ligand, which bears the lipophilic moiety of the amphiphile **5**. The intermolecular void space may be minimised by interleaving the base of one pentagon with the apex of another in a herringbone fashion. Fig. 4(*b*) represents the interleaving of two tesserae. The optimum mosaic for twelve pentagons derived from the tesserae is depicted in Fig. 4(*c*). It should be emphasised that the area of each pentagon (tessera) within the mosaic corresponds to, and is consistent with, the experimentally determined cross-sectional area of the amphiphile at the air–water interface.

An alternative perspective upon the herringbone interleaving of tesserae described above [Fig. 4(*b*)] is provided in Fig. 5. Two interleaved computer-generated models of complex **4** are viewed along the atoms P(1)–P(2). The plane described by the cyclopentadienyl ligand is parallel to, and displaced 3.5 Å below, the horizontal line which represents the air–water interface. Interestingly, the representation demonstrates that the triphenylphosphine ligands within the headgroup may adopt a conformation whereby the hydrophobic phenyl rings are oriented either proximal and parallel or perpendicular and distal to the air–water interface.

Previous experiments[5] in which the pyroelectric response of Langmuir–Blodgett films has been enhanced by increasing the free volume available to the lipophilic chain encouraged us to investigate the properties of amphiphiles possessing larger cationic headgroups. We anticipated that the volume of the cone swept out by free rotation of the triphenylphosphine ligand would essentially govern the volume of the amphiphilic headgroup. To this end, the amphiphiles **6** and **7** were synthesized, and their spacial characteristics at the air–water interface were investigated experimentally (Table 1). Molecular-modelling studies of **6** and **7**, using suitably modified structures derived from the crystal structure of **4**, were carried out in a manner similar to that described previously for the amphiphile **5**. The calculated cross-sectional areas of the amphiphilic headgroups were found to be consistent with the experimentally determined average molecular areas, and the corresponding pentagonal tessera were tessellated in a manner similar to that described previously for complex **4**.

The modelled tessellate proposed here does not accommodate the cross-section associated with the hexafluorophosphate counter ion of the cationic amphiphile. In the crystal this counter ion is displaced 6.6 Å from P(2), approximately within the plane described by the cyclopentadienyl ligand. It would appear reasonable, therefore, to propose that the hexafluorophosphate resides within the phase occupied by the cyclopentadienyl ligand of the headgroup, *i.e.* the aqueous moiety of the air–water interface. Consequently it will not contribute towards the experimentally determined average molecular area.

A direct consequence of the amphiphile headgroup tessellation at the air–water interface is the concomitant ordering of the lipophilic hexadecyl chains. It has been suggested previously[7] that the dominant physical mechanism responsible for the pyroelectric response of complex **5** is molecular tilting, which gives rise to a change in the normal components of molecular dipoles. It can be seen from Table 1 that the pyroelectric response increases with the experimentally determined average molecular area at the air–water interface. This would suggest that the increased free volume associated with the hydrophobic chains facilitates molecular tilting, which in turn correlates qualitatively with the observed increase in pyroelectric response.

The pyroelectric coefficients (p) measured for the Langmuir–Blodgett films derived from complexes **5**–**7** do not increase linearly with the corresponding experimentally determined average molecular areas (*i.e.* $\Delta p_{5/6} = 0.14$; $\Delta p_{6/7} = 0.40\ \mu\mathrm{C\ m^{-2}\ K^{-1}}$). It is reasonable to suggest, therefore, that the hydrophobic environment encountered within the Langmuir–Blodgett multilayers may stabilise alternative conformations of the organoruthenium headgroup associated with complex **7**. Such conformations may induce a lower packing density within the Langmuir–Blodgett monolayer, giving rise to an increase in the free volume available to the hydrophobic chains. The greater than expected pyroelectric response may therefore derive from a greater facility for molecular tilting.

In conclusion, molecular modelling of the headgroups associated with the organoruthenium amphiphiles **5**–**7** suggests a well defined lattice at the air–water interface. Furthermore, the modelled lattice at the air–water interface has been used to discuss the physical mechanism associated with the pyroelectric response of Langmuir–Blodgett films fabricated from these complexes.

Experimental

General

Reactions involving organometallic compounds were carried out under an atmosphere of nitrogen. Melting points are uncorrected. Proton NMR spectra were recorded on a Bruker WM-300 (300 MHz) spectrometer, using $CDCl_3$ as solvent and referenced to residual $CHCl_3$ with chemical shifts being reported at δ (ppm) from tetramethylsilane. The ^{31}P NMR spectra were recorded on a Bruker AM-250 spectrometer operating at 101.26 MHz using $CDCl_3$ as solvent and chemical shifts are reported as δ (ppm) from an external reference of 85% orthophosphoric acid.

Preparations

The complex $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ **1** was prepared *via* the procedure of Bruce and Windsor.[10]

Chloro(η^5-cyclopentadienyl)bis(diphenyl-*p*-tolylphosphine)-ruthenium 2. A filtered solution of hydrated ruthenium trichloride (0.52 g, *ca.* 2 mmol) in dry ethanol (20 cm^3) was added to a stirred solution of diphenyl-*p*-tolylphosphine (2.19 g, 7.9 mmol) in refluxing ethanol (100 cm^3), followed by a solution of freshly distilled cyclopentadiene (1–2 cm^3) in ethanol (10 cm^3). The mixture was refluxed for 1 h, cooled to room temperature, and concentrated to approximately 20 cm^3. A small portion of water (20 cm^3) was added, and the solution was left at 0 °C overnight. The resulting solid was collected and subjected to column chromatography (SiO_2, $CHCl_3$), affording a yellow solid which was characterised as complex **2** (412 mg, 27%), m.p. 205–208 °C (Found: C, 68.4; H, 5.0. $C_{43}H_{39}ClP_2Ru$ requires C, 68.5; H, 5.2%). δ_H(300 MHz, $CDCl_3$) 2.32 (6 H, s, 2 $C_6H_4C\mathit{H}_3$), 4.10 (5 H, s, C_5H_5), 6.95 (4 H, d, *J* 7 Hz, BB′ of AA′BB′ system, 2 $C_6\mathit{H}_4CH_3$) and 7.08–7.80 [28 H, 2 $P(C_6\mathit{H}_5)_2$-$(C_6\mathit{H}_4CH_3)$]. δ_P(101 MHz, $CDCl_3$) 35.3.

Bis(*p*-biphenyldiphenylphosphine)chloro(η^5-cyclopentadienyl)-ruthenium 3. A filtered solution of hydrated ruthenium trichloride (0.52 g, *ca.* 2 mmol) in dry ethanol (20 cm^3) was added to a stirred solution of *p*-biphenyldiphenylphosphine (2.34 g, 6.9 mmol) in refluxing ethanol (100 cm^3) followed by a solution of freshly distilled cyclopentadiene (1–2 cm^3) in ethanol (15 cm^3). The mixture was then refluxed for 1 h, cooled to room temperature, concentrated *in vacuo*, and dissolved in a small amount of dichloromethane. The solution was filtered through a plug of Celite and subjected to column chromatography (SiO_2, $CHCl_3$), furnishing a yellow solid characterised as complex **3** (540 mg, 30%), m.p. 195–198 °C (Found: C, 72.9; H, 5.1. $C_{53}H_{43}ClP_2Ru$ requires C, 72.5; H, 4.9%). δ_H(300 MHz, $CDCl_3$) 4.22 (5 H, s, C_5H_5) and 7.12–7.57 [38 H, m, 2 $P(C_6H_5)_2$-(C_6H_4Ph)]. δ_P(101 MHz, $CDCl_3$) 35.6.

(η^5-Cyclopentadienyl)(4-ethoxybenzonitrile)bis(triphenylphosphine)ruthenium hexafluorophosphate 4. A solution of complex **1** (635 mg, 0.87 mmol) in anhydrous methanol (70 cm^3) was stirred at reflux in the presence of 4-ethoxybenzonitrile (168 mg, 1.14 mmol) and ammonium hexafluorophosphate (220 mg, 1.3 mmol) for 2 h. The clear orange reaction mixture was cooled to room temperature, whereupon an orange solid crystallised. This was collected and recrystallised from dichloromethane–hexane to afford yellow crystals which were characterised as **4** (620 mg, 73%), m.p. 178–180 °C (Found: C, 61.2; H, 4.6. $C_{50}H_{44}F_6NOP_3Ru$ requires C, 61.1; H, 4.5%). δ_H(300 MHz, $CDCl_3$) 1.45 (2 H, t, *J* 6.4, $CH_3C\mathit{H}_2O$), 4.12 (3 H, q, *J* 6.4, $C\mathit{H}_3CH_2O$), 4.58 (5 H, s, C_5H_5), 6.92 (2 H, d, *J* 7 Hz, BB′ of AA′BB′ system, $C_6\mathit{H}_4OEt$) and 7.08–7.44 [32 H, m, AA′ of AA′BB′ system, $C_6\mathit{H}_4OEt$ and 2 $P(C_6H_5)_3$]. Single crystals of **4** suitable for X-ray analysis were grown from a concentrated solution of dichloromethane layered with hexane.

(η^5-Cyclopentadienyl)(4-hexadecyloxybenzonitrile)bis(triphenylphosphine)ruthenium hexafluorophosphate 5.[9] A solution of complex **1** (943 mg, 1.3 mmol) in anhydrous methanol (30 cm^3) was stirred at reflux in the presence of 4-hexadecyloxybenzonitrile (446 mg, 1.3 mmol) and ammonium hexafluorophosphate (400 mg, 3 mmol) for 2 h. The clear orange solution was cooled to room temperature, filtered through a plug of Celite, and concentrated *in vacuo*. Column chromatography on alumina with dichloromethane as eluent afforded **5** (1.44 g, 94%), m.p. 68–70 °C (Found: C, 65.1; H, 6.2. $C_{64}H_{72}F_6NOP_3Ru$ requires C, 65.2; H, 6.15%). δ_H(300 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.5, $C\mathit{H}_3CH_2$), 1.15–1.62 [26 H, m, $CH_3(C\mathit{H}_2)_{13}$], 1.78 (2 H, t, *J* 6.4, $C_6H_4OCH_2C\mathit{H}_2$), 3.99 (2 H, t, *J* 6.4, $C_6H_4OC\mathit{H}_2CH_2$), 4.62 (5 H, s, C_5H_5), 6.85 (2 H, d, *J* 7 Hz, AA′ of AA′BB′ system, $CH_2OC_6\mathit{H}_4CN$) and 7.11–7.62 [32 H, m, BB′ of AA′BB′ $CH_2OC_6\mathit{H}_4CN$ and 2 $P(C_6H_5)_3$].

(η^5-Cyclopentadienyl)bis(diphenyl-*p*-tolylphosphine)(4-hexadecyloxybenzonitrile)ruthenium hexafluorophosphate 6. A solution of complex **2** (300 mg, 0.4 mmol) in anhydrous methanol (50 cm^3) was stirred at reflux in the presence of 4-hexadecyloxybenzonitrile (137 mg, 0.4 mmol) and ammonium hexafluorophosphate (166 mg, 1.25 mmol) for 2 h. The clear orange solution was cooled to room temperature and concentrated *in vacuo*. The resulting solid was dissolved in dichloromethane and the solution was filtered through a plug of Celite and concentrated *in vacuo*. Column chromatography on alumina with dichloromethane as eluent afforded a yellow solid which was characterised as **6** (285 mg, 59%), m.p. 61–63 °C (Found: C, 66.0; H, 6.5. $C_{66}H_{76}F_6NOP_3Ru$ requires C, 65.7; H, 6.3%). δ_H(300 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 6.5, $C\mathit{H}_3CH_2$), 1.17–1.62 [26 H, m, $CH_3(C\mathit{H}_2)_{13}$], 1.80 (2 H, t, *J* 6.4, $C_6H_4OCH_2$-$C\mathit{H}_2$), 2.35 (6 H, s, 2 p-$CH_3C_6H_4$), 4.00 (2 H, t, *J* 6.4, $C_6H_4OC\mathit{H}_2CH_2$), 4.51 (5 H, s, C_5H_5), 6.89 (2 H, d, *J* 7 Hz, AA′ of AA′BB′ system, $CH_2OC_6\mathit{H}_4CN$) and 7.01–7.44 [32 H, m, BB′ of AA′BB′ $CH_2OC_6\mathit{H}_4CN$ and 2 $P(C_6H_5)_3$].

Bis(*p*-biphenyldiphenylphosphine)(η^5-cyclopentadienyl)(4-hexadecyloxybenzonitrile)ruthenium hexafluorophosphate 7. A solution of complex **3** (300 mg, 0.3 mmol) in anhydrous methanol (60 cm^3) was stirred at reflux in the presence of 4-hexadecyloxybenzonitrile (103 mg, 0.3 mmol) and ammonium hexafluorophosphate (166 mg, 1.25 mmol) for 2 h. The clear orange solution was cooled to room temperature and concentrated *in vacuo*. The resulting solid was dissolved in dichloromethane, and the solution was filtered through a plug of Celite and concentrated *in vacuo*. Column chromatography on alumina with dichloromethane as eluent afforded a yellow solid which was characterised as **7** (250 mg, 62%), m.p. 55–57 °C (Found: C, 67.1; H, 7.2. $C_{76}H_{80}F_6NOP_3Ru$ requires C, 68.6; H, 6.0%). δ_H(300 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.5, CH_3CH_2), 1.15–1.62 [26 H, m, $CH_3(CH_2)_{13}$], 1.78 (2 H, t, *J* 6.4, $C_6H_4OCH_2CH_2$), 3.99 (2 H, t, *J* 6.4, $C_6H_4OCH_2CH_2$), 4.62 (5 H, s, C_5H_5), 6.85 (2 H, d, *J* 7 Hz, AA′ of AA′BB′ system, $CH_2OC_6H_4CN$) and 7.11–7.62 [40 H, m, BB′ of AA′BB′ $CH_2OC_6H_4CN$ and 2 $P(C_6H_5)_3$].

Langmuir films derived from amphiphiles 5–7. Monolayers were obtained by spreading chloroform solutions (typically 0.1 mg cm^{-3}) of complexes **5**–**7** onto a purified water (Milli-Q system, Millipore Limited) subphase contained within a Langmuir trough (original area *ca*. 500 cm^2). After the solvent was allowed to evaporate (10 min), the area available to the molecules at the air–water interface was reduced by moving the confinement barrier at a rate of 4 cm^2 s^{-1}. The surface pressure was monitored simultaneously using a Wilhelmy plate arrangement. The amphiphiles formed stable monolayers on pure water. The areas per molecule for **5**–**7** were measured at a surface pressure of 20 mN m^{-1}, which corresponds to the pressure at which the Langmuir–Blodgett films are fabricated from these materials. In all cases at least six isotherms were recorded. The error in the measured area of water available per molecule is estimated to be ± 2%.

Crystallography

Crystal data. $C_{50}H_{44}F_6NOP_3Ru$ **4**, $M = 982.72$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.242(4)$, $b = 1.935(5)$, $c = 18.226(5)$ Å, $\alpha = 84.93(3)$, $\beta = 84.93(3)$, $\gamma = 66.13(2)°$, $U = 2222(1)$ Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflections, $\lambda = 1.541\,84$ Å), $Z = 2$, $F(000) = 1004$. Crystal dimensions 0.30 × 0.45 × 0.48 mm, μ(Cu-Kα) = 43.9 mm^{-1}.

Data collection and processing. Three-dimensional, room-temperature (295 K) X-ray data collected on a Nicolet R3m/V diffractometer with monochromatised Cu-Kα radiation; 2θ–ω mode with scan range (ω) 1.3° plus Kα separation and a variable scan speed (4.0–15.0° min^{-1}). 6591 Reflections measured ($1.0 < 2\theta < 116°$), 5472 with $I > 3.0\sigma(I)$. Empirical absorption correction.

Structure analysis and refinement. Patterson methods followed by successive difference syntheses located all the non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters was used for all the non-hydrogen atoms. Hydrogen atoms were included in calculated positions with common isotropic thermal parameters. Individual weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.0022|F_o|^2]^{-1}$. Refinement converged at R 0.066, R' 0.064, goodness of fit = 1.69. The final electron-density difference synthesis showed no peaks >1.6 or <−2.2 e Å^{-3}. All computations were carried out using the SHELXTL PLUS (μ-VAX II) system of programs.[16]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/290.

Molecular-modelling calculations

All molecular-modelling calculations were conducted using the CHEM-X molecular modelling package[14] on a Vaxstation 3520. Within this package, the van der Waals energy (E_{vdW}) calculation considers contributions from the torsion (V_{tor}), electrostatic (V_{el}), and non-bonded or polarisation (V_{nb}) terms: $E_{vdW} = V_{tor} + V_{el} + V_{nb}$. The electrostatic contribution is computed by default using Coulomb's law. The van der Waals interaction potential (V_{nb}) within the software package is that of Del Re *et al.*[17] and takes the form $V_{nb} = [A\exp(-Br)]r^{-D} - Cr^{-6}$.

The crystal structure of complex **4** provided the starting point for all conformational analyses. The cyclopentadienyl ligand was treated as a rigid body and was rotated about the axis from the centroid of the C_5 ring and the Ru atom. Rotational conformations were generated by driving the designated bonds independently through 0–360°, in 5° increments. The van der Waals energy was minimised for each conformation by independent rotation (maximum of 20 cycles) about all designated bonds, until the default-energy convergence limit had been achieved. The enclosed area of a contour on the van der Waals surface of the structures **5**–**7** (*i.e.* a molecular cross-section) was calculated using the two-dimensional map facility within CHEM-X.

Acknowledgements

We thank the SERC for support of this work.

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Received 30*th July* 1996; *Paper* 6/05348C