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Symmetrical alkyl-substituted oligothiophenes as ligands: complexation of the $[(\eta\text{-}C_5H_5)Ru]^+$ moiety by hexyl-substituted ter-, quater- and quinque-thiophenes

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The soluble, symmetrical oligothiophenes 3,3″-dihexyl-2,2′:5′,2″-terthiophene **7** and 4′,3‴-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene **9** and the unsymmetrical oligothiophenes 3′-hexyl-2,2′:5′,2″-terthiophene **6** and 3,3″-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene **11** have been prepared by Kumada–type coupling reactions, using 2-bromothiophene, 2,5-dibromothiophene, 2-bromo-3-hexylthiophene and 2,5-dibromo-3-hexylthiophene as building blocks. Their behaviour as ligands towards the cyclopentadienylruthenium(II) moiety has been examined, by carrying out ligand exchange reactions between $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ and an excess of the oligothiophene in CH_2Cl_2, and characterising the product(s) by FAB mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Upon complexation of a thiophene ring (η^5), the thienyl proton resonances of that ring shift upfield, as do the ^{13}C resonances. With terthiophene **7**, in which the outer thiophene rings bear alkyl groups, the product is $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}\mathbf{7})]PF_6$ **13**, a single regioisomer in which exclusively an outer thiophene ring is complexed by the cyclopentadienylruthenium(II) moiety. With terthiophene **6**, however, in which the inner thiophene ring bears an alkyl substituent, a mixture of all three possible regioisomers of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}\mathbf{6})]PF_6$ **12** is obtained. Similarly, with the symmetrical quinquethiophene **9**, two regioisomers of the complex $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}\mathbf{9})]PF_6$ **14** are obtained, one in which an outer thiophene ring is complexed, and one in which an inner alkylthiophene ring is complexed. With the unsymmetrical quaterthiophene **11**, which includes all four types of thiophene ring (inner and outer alkylthiophene, inner and outer unsubstituted thiophene), 93% of the product $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}\mathbf{11})]PF_6$ **15** is the regioisomer in which the outer alkylthiophene ring is complexed. These results show that there are two factors controlling the site of complexation, a tendency for the outermost ring to complex and a tendency for an alkylthiophene ring to complex. Where these conflict, a mixture of regioisomers is obtained. The electrochemistry of both the free oligothiophenes and of their Ru(II) complexes has been compared. On complexation, there is a substantial positive shift in the oxidation potential of the oligothiophene, and a new, irreversible reduction is observed at *ca.* −1 V. Although polythiophene films could be deposited by electrooxidation of the free oligothiophenes in acetonitrile, electroactive polymer films could not be deposited by electrooxidation of the complexes in dichloromethane.

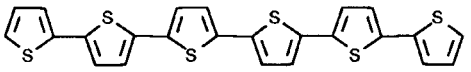
One of the most interesting and promising applications for conjugated polymers and oligomers is as materials in novel organic-based electronic devices. For example, polyphenylenevinylenes (PPVs)[1,2] and polyalkylthiophenes[3] have been successfully employed in light-emitting diodes. Rigorously-purified α-sexithiophene **1**,[4] and more recently α-octithiophene **2**,[5] have been shown to have mobilities comparable with that of porous silicon in field-effect transistors. In these applications, it has become clear that a better picture of the electrode - organic interface is one of the keys to understanding how these devices work, and how they might be improved.[2] To this end, theoreticians are exploring conjugated polymer–metal interactions, which are also of interest from the point of view of modelling the n-doping (reduction to the negatively charged form) of the materials.[6] Surface science groups have been examining the ways in which variously substituted oligothiophenes adsorb on highly-oriented pyrolytic graphite[7,8] or on single crystal metal surfaces,[9,10] using scanning probe microscopy methods and low energy electron diffraction. Interestingly, whereas oligothiophenes adsorb on dielectric substrates (*e.g.* glass, sapphire or oxidised silicon) giving ordered arrangements with their molecular planes perpendicular to the surface, they adsorb on noble metals [*e.g.* Ag(111), Au(110)] or graphite in ordered arrays, but with their molecular planes parallel to the surface.[7–10] The interaction of aromatic π-electrons with the surface is probably important in the latter mode of chemisorption.

Thiophenes, benzo[*b*]thiophenes and dibenzothiophenes are among the most difficult species to remove from crude oil in hydrodesulfurisation using heterogeneous catalysis, a process of great commerical importance. This has stimulated interest in the coordination of these species to organometallic centres, and in their reactivity once coordinated.[11–13] However, until recently, there were no reports of organometallic complexes of oligothiophenes. Soluble complexes of oligothiophenes could help model the interaction of oligo- or poly-thiophenes with precious metal surfaces, a situation relevant to the metal–polymer interface in electrochemically deposited polythiophene films.

Another stimulus for interest in this area is the possibility of 'tuning' the physical and optical properties of polythiophene by complexing the thiophene units to organometallic metal centres. This has not been explored for conjugated polymers, but it is interesting that an organometallic derivative of the similarly intractable aromatic polymer, poly(*p*-phenyleneterephthalamide) (Kevlar™) has been made, in which each $-(O)CNHC_6H_4NHC(O)-$ moiety was complexed to a $[Cr(CO)_3]$ unit.[14] The organometallic polymer was highly soluble in chlorinated hydrocarbons, in sharp contrast to the parent polymer. Films could be cast, and subsequently demet-

allated by treatment with iodine solution. This offers an interesting way of processing otherwise intractable aromatic polymers, and a similar strategy could be applied to conjugated heterocyclic materials if suitably stable complexes could be prepared.

For all of these reasons, the preparation and characterisation of organometallic derivatives of conjugated polymers such as polythiophene seemed of interest. Initially, we chose to begin by studying complexes of oligothiophenes as models. In terms of conjugation length and redox chemistry, quinque- and sexithiophenes are reasonable models of electrogenerated polythiophenes.[15] However, the solubility of α-coupled oligothiophenes falls sharply with increasing chain length. Neither **1** or **2**, for instance, is synthetically useful. Substitution with alkyl groups, particularly β-substitution, greatly increases solubility. We therefore chose to investigate β-alkyl-substituted oligomers. To simplify characterisation of the oligomers and their complexes, we initially examined symmetrically substituted oligomers and chose an air-stable metal centre. We accordingly investigated the syntheses of symmetrically dialkylated oligothiophenes, their redox chemistry and their interaction with $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$, which is a convenient source of complexes $[(\eta\text{-}C_5H_5)Ru(L)]PF_6$ (L = aromatic ring).[16] We were initially interested in whether the reaction of the metal centre with the oligothiophene was regiospecific, in what effect the alkylation of the thiophene rings would have on complexation, and in whether electropolymerisation of the metallated oligothiophene could be used to prepare organometallic polythiophene derivatives.



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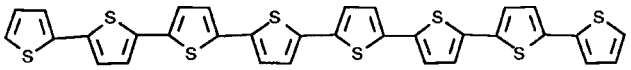

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During the progress of our work, Collard and Henderson reported on the syntheses and electrochemistry of some related symmetrically dialkylated oligothiophenes,[17] and Graf *et al.* reported on reactions between $[(\eta\text{-}C_5R_5)M(CH_3CN)_3]PF_6$ (R = H, Me; M = Ru, Os) and some oligothiophenes and derivatives.[18–20] With 5,5″-diphenylterthiophene, the metal complexed exclusively to the terminal phenyl ring, giving very stable complexes. For the unsubstituted oligothiophenes (and 5,5″-dimethylterthiophene), the metal centre also bound exclusively to the outermost thiophene ring, giving somewhat more labile complexes. The selectivity for the outermost ring was attributed to these being less delocalised (*i.e.* more aromatic). Binding of the metal centre to the outermost ring also causes the least disruption of conjugation to the remaining rings. Mixtures of mono- and di-metallated oligothiophenes were obtained in these reactions, even in reactions with excess oligothiophene.

We found that substitution of the oligothiophenes with alkyl groups enhances the ability of the alkylthiophene units to act as ligands, overcoming to some extent the additional loss of conjugation which occurs when an internal thiophene ring in an oligothiophene is metallated. We have also investigated the effect of complexation on the electrochemistry of the oligothiophenes. We report details of the synthesis, characterisation and redox chemistry of the oligothiophenes and their complexes here.

Experimental

General

Instrumentation and general methods were as previously described.[21] All reactions were carried out using Schlenk techniques under a nitrogen atmosphere. Precautions to exclude air were not necessary in workup procedures. Fast atom bombardment mass spectra were recorded by the EPSRC Mass Spectrometry Service at Swansea. Proton NMR spectra were recorded using a Bruker AMX400 spectrometer, at 400.1344 MHz using internal TMS as reference, and $^{13}C\{^1H\}$ spectra were recorded using a Varian Gemini 300 MHz spectrometer at 75.4602 MHz. Flash chromatography was performed using silica gel (Merck 9385 Kiesel 60, 230–400 mesh). The following were obtained from Aldrich Chemical Co. and used without further purification: 2,5-dibromothiophene, 3-bromothiophene, 1-bromohexane, 1,3-bis(diphenylphosphino)propane (dppp). The following were prepared by literature methods: $[NiCl_2(dppp)]$,[22] 2-bromo-3-hexylthiophene and 2,5-dibromo-3-hexylthiophene.[23] The complex $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ was prepared using a published method[24] from $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}C_6H_6)]Cl$.[25]

Preparation of oligothiophenes

3′-Hexyl-2,2′:5′,2″-terthiophene, *6*. To Mg turnings (3.4 g, 0.138 mol) in dry diethyl ether (30 cm^3) was added 2-bromothiophene (22.5 g, 0.138 mol) in diethyl ether (30 cm^3) at a rate sufficient to maintain reflux. Reflux was then maintained for 20 min. following which $[NiCl_2(dppp)]$ (0.15 g, 0.2 mol%) and, dropwise, 2,5-dibromo-3-hexylthiophene (15 g, 0.046 mol) in diethyl ether (80 cm^3) were added. The mixture was refluxed and stirred for 15 h. After the mixture had been allowed to cool to room temperature, it was poured onto a mixture of crushed ice (100 g) and 2 M HCl (20 cm^3). The mixture was extracted with CH_2Cl_2 (5×30 cm^3). The combined organic extracts were washed to neutrality with saturated sodium hydrogen carbonate, then with water (2×50 cm^3) and dried over $MgSO_4$. Solvent was removed *in vacuo*. The crude product was purified by flash chromatography (40:1 hexane–CH_2Cl_2), and the combined fractions which eluted were further purified by elution with hexane. The solvent was removed to yield the product as an intensely yellow–green oil. Yield 6.81 g, 45%. Elemental analysis, calc. for $C_{18}H_{20}S_3$: C, 65.01; H, 6.06. Found: C, 64.89; H, 6.03%. ^1H NMR ($CDCl_3$): δ 7.32 (1H, dd, H5″, $J_{4''5''}$ 5.1, $J_{3''5''}$ 1.2), 7.23 (1H, dd, H5, J_{45} 5.1, J_{35} 1.2), 7.17 (1H, dd, H3, J_{35} 1.2, J_{34} 3.6), 7.14 (1H, dd, H3″, $J_{3''5''}$ 1.2, $J_{3''4''}$ 3.6), 7.08 (1H, dd, H4″, $J_{4''5''}$ 5.1, $J_{4''3''}$ 3.6), 7.03 (1H, s, H4′), 7.02 (1H, dd, H4, J_{45} 5.1, J_{34} 3.6), 2.74 (2H, t, $ArCH_2$, J_{HH} 7.7), 1.63 (2H, m, $ArCH_2CH_2$), 1.37 (6H, m, $CH_2CH_2CH_2Me$), 0.90 (3H, t, J_{HH} 6.5Hz, $-CH_2CH_3$). $^{13}C\{^1H\}$($CDCl_3$): δ 140.1, 138.5, 137.9, 135.8, 130.2, 128.5, 128.1, 127,2, 126.5, 126.0, 125.0, 124.2, 32.3, 31.2, 30.0, 29.9, 23.3, 14.7. MS (EI): *m*/*z* 331 ([M^+], 100%).

3,3″-Dihexyl-2,2′:5′,2″-terthiophene, *7*. A solution of 2-bromo-3-hexylthiophene (1.00 g, 4.04 mmol) and 1,2-dibromoethane (0.756 g, 4.04 mmol) in diethyl ether (10 cm^3) was added to a suspension of Mg turnings (0.196 g, 8.08 mmol) in ether (10 cm^3) under N_2, and sonicated until the complete disappearence of the Mg. The solution of Grignard reagent was then added dropwise by cannula to a mixture of 2,5-dibromothiophene (0.33 g, 1.35 mmol) and $[NiCl_2(dppp)]$ (0.05 g) at room temperature. The mixture was then refluxed for 18 h, and worked up as for **6**. Flash chromatography was performed using 40–60 °C petroleum ether as eluant. The pure compound was obtained as a yellow oil (0.25 g, 45%). Elemental analysis, calc. for $C_{24}H_{32}S_3$: C, 69.18; H, 7.78. Found: C, 69.28; H, 7.78%. ^1H NMR ($CDCl_3$): δ 7.19 (2H, d, H5, H5″, J_{45} 5.22), 7.08 (2H, s, H3′, H4′), 6.96 (2H, d, H4, H4″, J_{45} 5.22), 2.81 (4H, t, $ArCH_2$, J_{HH} 8.22), 1.60 (4H, m, $ArCH_2CH_2$), 1.36 (12H, m, $CH_2CH_2CH_2Me$), 0.91 (6H, t, J_{HH} 7.0Hz, $-CH_2CH_3$). $^{13}C\{^1H\}$($CDCl_3$) (see Table 1). MS (EI): *m*/*z* 416 ([M^+], 5), 345 ([$M-C_5H_{11}$]$^+$, 100%).

5,5″-Dibromo-3,3″-dihexyl-2,2′:5′,2″-terthiophene, *8*. To a solution of **7** (0.50 g, 1.20 mmol) in dmf (20 cm^3) at 0 °C was added *N*-bromosuccinamide (NBS) (0.384 g, 2.20 mmol) in dmf (20 cm^3), dropwise with stirring, in the dark. The mixture was then stirred for 4 h, allowed to reach room temperature and stirred a further 36 h. It was poured into ice (100 g), extracted with diethyl ether (5×30 cm^3) and the extracts were washed with water (2×50 cm^3), then dried over $MgSO_4$. The crude compound was purified by flash chromatography (40–60 °C petroleum ether) to give a pure yellow oil (0.60 g, 49%). Elemental analysis, calc. for $C_{24}H_{32}Br_2S_3$: C, 50.00; H, 5.25. Found: C, 50.24; H, 5.28%. ^{1}H NMR ($CDCl_3$): δ 6.97 (2H, s, H4, H4″), 6.87 (2H, s, H3′, H4′), 2.70 (4H, t, ArCH_2, J_{HH} 8.0), 1.58 (4H, m, Ar$CH_2C\mathit{H}_2$), 1.30 (12H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$Me), 0.87 (6H, t, J_{HH} 6.6Hz, –$CH_2C\mathit{H}_3$). MS (EI): *m*/*z* 574 ([M^+], 65), 496 ([M-Br]$^+$, 75%).

4′,3‴-Dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, *9*. To a solution of 2-bromomagnesiothiophene (2.79 mmol) prepared in diethyl ether (20 cm^3) was added [$NiCl_2$(dppp)] (0.1 g, 2 mol %), then, dropwise, a solution of **8** (0.53 g, 0.90 mmol) in diethyl ether (20 cm^3). The mixture was then refluxed and stirred for 18 h. Workup was as for **6**. Recrystallisation of the crude product from hexane gave pure **9** as an orange solid (0.423 g, 79%). Elemental analysis, calc. for $C_{32}H_{36}S_5$: C, 66.17; H, 6.25. Found: C, 66.24; H, 6.30%. ^{1}H NMR ($CDCl_3$): δ 7.22 (2H, dd, H5, H5⁗, J_{35} 1.2, J_{45} 5.1), 7.17 (2H, dd, H3, H3⁗, J_{34} 3.6, J_{35} 1.2), 7.08 (2H, s, H3″, H4″), 7.05 (2H, s, H3′, H4‴), 7.04 (2H, dd, H4, H4″, J_{34} 3.6, J_{45} 5.1), 2.78 (4H, t, ArCH_2, J_{HH} 8.0), 1.69 (4H, m, Ar$CH_2C\mathit{H}_2$), 1.36 (12H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$Me), 0.90 (6H, t, J_{HH} 7.0, –$CH_2C\mathit{H}_3$). ^{13}C{^{1}H}($CDCl_3$): δ 140.5, 137.3, 135.9, 135.3, 129.5, 128.0, 126.8, 126.1, 124.5, 123.7, 31.6, 30.5, 29.5, 29.2, 22.5, 14.0. MS (EI): *m*/*z* 580 ([M^+], 100), 509 ([M-C_5H_{11}]$^+$, 14%).

5-Bromo-3,3″-dihexyl-2,2′:5′,2″-terthiophene, *10*. To a solution of **7** (0.20 g, 0.48 mmol) in dmf (20 cm^3) at 0 °C was added NBS (0.076 g, 0.43 mmol) in dmf (20 cm^3), dropwise with stirring, in the dark. The mixture was then stirred for 4 h, allowed to reach room temperature and stirred a further 8 h. Workup and purification was as for **8**. The pure product was a yellow oil. Elemental analysis, calc. for $C_{24}H_{31}BrS_3$: C, 58.16; H, 6.30. Found: C, 58.47; H, 6.36%. ^{1}H NMR ($CDCl_3$): δ 7.06 (2H, AB, H4″, H5″, J_{AB} 5.2), 7.01 (2H, AB, H3′, H4′, J_{AB} 3.6), 6.89 (1H, s, H4), 2.74 (4H, t's, ArCH_2, J_{HH} 8.0), 1.58 (4H, m, Ar$CH_2C\mathit{H}_2$), 1.31 (12H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$Me), 0.90 (6H, t, J_{HH} 6.6, –$CH_2C\mathit{H}_3$). MS (EI): *m*/*z* 496 ([M^+], 100%), 423 ([$M-C_5H_{11}$]$^+$, 31%).

3,3″-Dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene, *11*. To a solution of 2-bromomagnesiothiophene (3.50 mmol) prepared in diethyl ether (20 cm^3) was added [$NiCl_2$(dppp)] (0.1 g, 1.5 mol %), then, dropwise, a solution of **10** (0.585 g, 1.2 mmol) in diethyl ether (20 cm^3). The mixture was then refluxed and stirred for 18 h. Workup was as for **6**. Recrystallisation of the crude product from hexane gave pure **11** as a yellow solid (0.364 g, 62%). Elemental analysis, calc. for $C_{28}H_{34}S_4$: C, 67.42; H, 6.87. Found: C, 67.69; H, 6.92%. ^{1}H NMR ($CDCl_3$): see Table 2 for thienyl and α-CH_2 resonances; δ 1.58 (4H, m, Ar$CH_2C\mathit{H}_2$), 1.35 (12H, m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$Me), 0.90 (6H, m, –$CH_2C\mathit{H}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.3, 139.8, 137.3, 136.1, 135.7, 135.0, 130.2, 130.1, 129.4, 127.9, 126.7, 126.1, 125.9, 124.3, 123.7, 31.8, 30.85, 30.7, 29.5, 29.4, 22.7, 14.2. MS (EI): *m*/*z* 498 ([M^+], 100), 427 ([$M-C_5H_{11}$]$^+$, 17%).

Preparation of complexes

[(η-C_5H_5)Ru(η-6)]PF_6, *12*. To a solution of **6** (0.17 g, 0.51 mmol) in CH_2Cl_2 (10 cm^3) was added [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 (0.10 g, 0.23 mmol). The mixture was refluxed for 72 h. Solvent was then removed *in vacuo*, and hexane (40 cm^3) was added. After the flask contents had been stirred vigorously for 30 min, the suspension which resulted was filtered through a 1 cm thick Celite plug on a coarse glass frit. Hexane was washed through this until the washings were no longer green–yellow. The residue was then recovered by washing through with CH_2Cl_2, and the solvent was removed *in vacuo*. Hexane (30 cm^3) was then added, the compound stirred, re-filtered and treated as before. This washing procedure was repeated a total of three times, twice using CH_2Cl_2 and the final time using $CHCl_3$ to re-dissolve the complex. Finally, the product was reprecipitated from CH_2Cl_2 (1 cm^3) with pentane (10 cm^3). The dark yellow solid which resulted was dried *in vacuo*. Yield 0.08 g, 62%. Elemental analysis, calc. for $C_{23}H_{25}F_6PRuS_3$: C, 42.92; H, 3.91. Found: C, 43.10; H, 4.06%. ^{1}H and ^{13}C NMR: see Results and discussion. MS (FAB, Xe, 3-NOBA): *m*/*z* 499 ([$M-PF_6$]$^+$, 100), 665 (trace [{(η-C_5H_5)Ru}$_2$(η-**6**)]$^+$, 6%).

[(η-C_5H_5)Ru(η-7)]PF_6, *13*. Using **7** (0.398 g, 0.95 mmol) and [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 (0.244 g, 0.56 mmol) in CH_2Cl_2 (15 cm^3), the same procedure was followed as for **12**. The product was a very viscous yellow oil after extensive vacuum drying. Yield 0.156 g, 38%. Elemental analysis, calc. for $C_{29}H_{37}F_6PRuS_3$: C, 47.85; H, 5.12. Found: C, 47.64; H, 5.25%. ^{1}H and ^{13}C{^{1}H} NMR: see Table 1. MS (FAB, Xe, 3-NOBA): *m*/*z* 583 ([$M-PF_6$]$^+$, 49), 416 [$M-C_5H_{11}-PF_6$]$^+$, 100%).

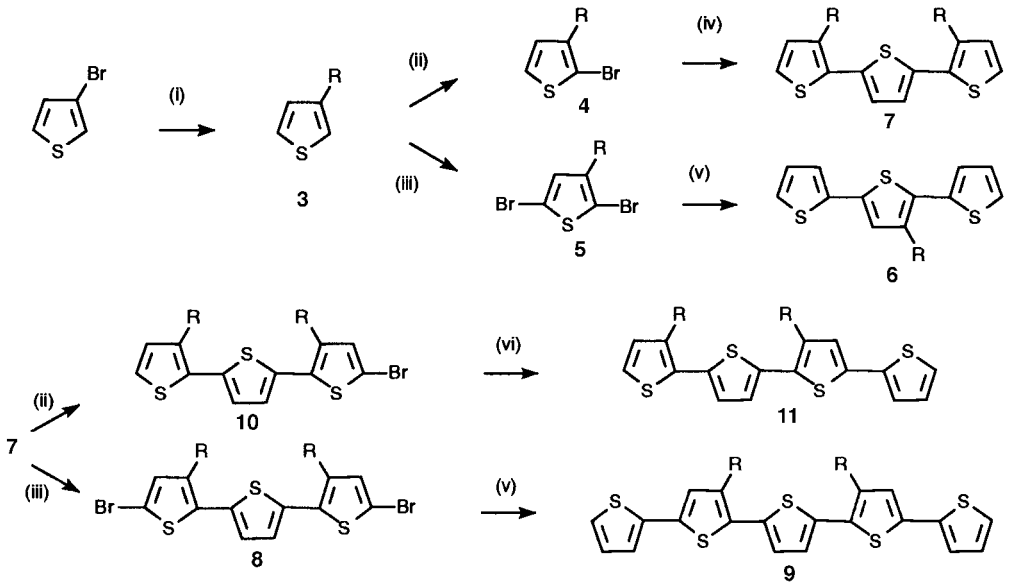
[(η-C_5H_5)Ru(η-)]PF_6, 14. Using **9** (0.45 g, 0.80 mmol) and [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 (0.15 g, 0.359 mmol) in CH_2Cl_2 (15 cm^3), the same procedure was followed as for **12**. Workup was as follows. After evaporation of the CH_2Cl_2, the crude product was suspended/dissolved in CH_3CN (40 cm^3; this solution was handled in the dark), and stirred for a few minutes. Residual **9** was filtered off through a Celite plug, and the solvent was evaporated to dryness. The residue was extracted with $CHCl_3$ (40 cm^3), the extracts were taken to dryness and the residue was dissolved in CH_2Cl_2 (1 cm^3) and carefully reprecipitated with octane (20 cm^3). The product was an orange solid. Yield 0.10 g, 35%. Elemental analysis, calc. for $C_{37}H_{41}F_6PRuS_5$: C, 49.82; H, 4.63. Found: C, 47.66; H, 4.43%. ^{1}H NMR: δ 7.43 (m), 7.23 (m), 7.19, 7.17 (dd's), 7.09, 7.02 (m's) (uncomplexed thienyl ring H's), 6.85 (s, H4′ of complexed alkylthiophene ring), 6.52 (d), 6.47 (t) and 6.22 (d) (H3, H4 and H5, respectively, of complexed outer thiophene ring), 5.405, 5.400 (two overlapping s, C_5H_5 of different regioisomers), 2.745 (complex m, α-CH_2 of complexed alkylthiophene), 2.727 (broad t; α-CH_2 of all non-complexed alkylthiophenes). MS (FAB, Xe, 3-NOBA): *m*/*z* 747 ([$M-PF_6$]$^+$, 100), 913 ([{(η-C_5H_5)Ru}$_2$(η-**9**)]$^+$ impurity, 16%).

[(η-C_5H_5)Ru(η-11)]PF_6, *15*. Using **11** (0.10 g, 0.20 mmol) and [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 (0.05 g, 0.12 mmol) in CH_2Cl_2 (15 cm^3), the same procedure and workup was followed as for **12**. The product was a dark yellow solid. Yield 0.06 g, 64%. ^{1}H and ^{13}C{^{1}H} NMR: see Table 2. MS (FAB, Xe, 3-NOBA): *m*/*z* 665 ([$M-PF_6$]$^+$, 21%).

Results and discussion

Synthesis and characterization of oligothiophenes

We selected hexyl groups as adequate solubilising substituents for our purposes. The synthetic routes to the oligothiophenes are shown in Scheme 1. The necessary 3-hexylthiophene **3** was synthesised by the literature route[26] in high yield and was purified by fractional distillation. Bromination with one equivalent of NBS in dmf afforded 2-bromo-3-hexylthiophene **4**



Scheme 1 Syntheses of oligothiophenes. Throughout this scheme, R = *n*-hexyl. (i) RMgBr, [$NiCl_2$(dppp)] catalyst, Et_2O; (ii) 1 equiv. NBS, dmf; (iii) 2 equiv. NBS, dmf; (iv) 2 equiv. Mg, 1 equiv. $BrCH_2CH_2Br$, Et_2O, sonicate, then 0.5 equiv. 2,5-dibromothiophene, [$NiCl_2$(dppp)] catalyst, Et_2O; (v) 2 equiv. 2-thienylMgBr, [$NiCl_2$(dppp)] catalyst, Et_2O; (vi) 1 equiv. 2-thienylMgBr, [$NiCl_2$(dppp)] catalyst, Et_2O.

cleanly, and with two equivalents of NBS, 2,5-dibromo-3-hexylthiophene **5** was readily obtained as described in the literature.[23] A Kumada coupling reaction between excess 2-thienylmagnesium bromide and **5**, using [$NiCl_2(Ph_2P(CH_2)_3PPh_2$] as catalyst, afforded 3′-hexyl-2,2′:5′,2″-terthiophene **6** as a pure yellow–green oil, but in only moderate yield owing to the need for extensive chromatographic purification. It was recently reported that this reaction, carried out under slightly different conditions, produced significant amounts of 2,2′-bithiophene, 2,2′:3′,2″-terthiophene and 5′-(2-thienyl)-2,2′:3′,2″-terthiophene as byproducts.[27] The identity of **6** was established from the mass spectrum, which showed a parent ion at 332 *m*/z and no higher molecular weight peaks, the ^{1}H NMR spectrum which showed six doublet of doublets and one singlet in the thienyl region, and the $^{13}C\{^1H\}$ NMR spectrum, which showed twelve individual thienyl carbon resonances.

Attempts to prepare 3,3″-dialkylterthiophenes using Kumada-type coupling reactions between 2-bromomagnesio-3-alkylthiophenes and 2,5-dibromothiophene usually give low yields and many byproducts, probably because of difficulty in forming the Grignard reagent, or magnesium–hydrogen exchange reactions.[27] A more satisfactory preparation of the Grignard reagent from **4** required the use of 1,2-dibromoethane as an entraining reagent, and sonication, an approach used earlier for the *n*-octyl analogue.[17] When these conditions were employed, Kumada coupling with commercially available 2,5-dibromothiophene then gave 3,3″-dihexyl-2,2′:5′,2″-terthiophene **7** as a fluorescent yellow oil, in moderate yield after column chromatography. The ^{1}H NMR spectrum of **7** showed one AB pattern for protons H4,4″ and H5,5″ and a singlet for (H3′, H4′), and the ^{13}C NMR spectrum showed 6 thienyl C resonances, consistent with the C_{2v} symmetry. These were assigned (Table 1) by analogy with 3,3″-dimethyl-2,2′:5′,2″-terthiophene, for which ^{1}H–^{13}C 2D NMR experiments were performed.[27] Bromination of **7** with two equivalents of NBS in dmf afforded 5,5″-dibromo-3,3″-dihexyl-2,2′:5′,2″-terthiophene **8**, and Kumada coupling of **8** with two equivalents of 2-thienylmagnesium bromide gave 4′,3‴-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene **9** in good yield. Purification of **9** was straightforward; it was recrystallised from hexane. This synthesis of a symmetrical dialkylquinquethiophene compares favourably with the alternative coupling of 5,5″-dibromo-2,2′:5′,2″-terthiophene with 2-bromomagnesio-3-alkylthiophene, which gave very low overall yields even when the Grignard reagent was prepared using entrainment and sonication, possibly owing to the insolubility of the dibromoterthiophene.[17] The ^{1}H NMR spectrum of **9** showed doublet of doublet resonances for each of the three protons of the terminal thiophene rings, and two singlets for the remaining thiophene protons. The $^{13}C\{^1H\}$ NMR spectrum showed ten aromatic C resonances, again consistent with the C_{2v} symmetry of **9**.

Monobromination of **7** was readily accomplished with NBS in dmf to give **10** in high yield. Chromatography to separate **10** from a small amount of **8** was straightforward. This is preferable to the monobromination of unsymmetrical monoalkylterthiophenes, which inevitably gives a mixture of regioisomers needing tedious chromatographic separation if they are to be synthetically useful.[23] The unsymmetrical 3,3″-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene **11** was then synthesised by Kumada coupling of **10** with 2-thienylmagnesium bromide. The ^{1}H NMR spectrum of **11** showed doublets for H4 and

Table 1 ^{1}H and ^{13}C NMR chemical shifts (δ in ppm from TMS) and coupling constants (Hz) for symmetrical dihexylterthiophene **7**, and its complex **13**

Position	**7** (^{1}H)	**13** (^{1}H)	**7** (^{13}C)	**13** (^{13}C)
H/C5	7.19	6.27	123.6	77.2
H/C4	6.96	6.48	129.9	88.2
C3/H of αCH_2	2.81	2.66	130.4	99.0
C2			136.0	92.5
C2′			139.5	141.4
H/C3′	7.08	7.15	125.9	133.0
H/C4′	7.08	7.04	125.9	125.3
C5′			139.5	129.9
C2″			136.0	139.8
C3″/H of αCH_2	2.81	2.74	130.4	128.8
H/C4″	6.96	6.97	129.9	130.4
H/C5″	7.19	7.265	123.6	123.8
Other alkyl C			31.6, 30.6, 29.25, 29.2, 22.6, 14.0	31.5, 31.3, 30.5, 29.65, 29.3, 29.2, 29.0, 28.65, 23.65, 23.5, 14.0
$J_{4,5}$	5.22	3.04		
$J_{3',4'}$	—	3.84		
$J_{4'',5''}$	5.22	5.16		

Table 2 ^{1}H NMR chemical shifts (δ in ppm from TMS) and coupling constants (Hz) for unsymmetrical dihexylquaterthiophene **11**, and its complex **15**

Position	**11** (^{1}H)	**15** (^{1}H)
H/C5	7.18 (d, $J_{4,5}$ 5.1)	6.28 (d, $J_{4,5}$ 2.9)
H/C4	6.945 (d, $J_{4,5}$ 5.1)	6.47 (d, $J_{4,5}$ 2.9)
C3/H of αCH_2	2.79 (t, J_{HH} 6.9)	2.69 (complex m)
H/C3′	7.08 (AB, $J_{3',4'}$ 3.6)	7.155 (d, $J_{3',4'}$ 3.8)
H/C4′	7.06 (AB, $J_{3',4'}$ 3.6)	7.055 (d, $J_{3',4'}$ 3.8)
C3″/H of αCH_2	2.765 (t, J_{HH} 6.9)	2.73 (t, J_{HH} 7.7)
H/C4″	7.02 (s)	7.04 (s)
H/C3‴	7.17 (dd, $J_{3'',4''}$ 3.6, $J_{3'',5''}$ 1.2)	7.20 (dd, $J_{3'',4''}$ 3.6, $J_{3'',5''}$ 1.2)
H/C4‴	7.015 (dd, $J_{3'',4''}$ 3.6, $J_{4'',5''}$ 5.1)	7.04 (dd, $J_{3'',4''}$ 3.6, $J_{4'',5''}$ 5.1)
H/C5‴	7.21 (dd, $J_{3'',5''}$ 1.2, $J_{4'',5''}$ 5.1)	7.25 (part-obscured by $CHCl_3$)

H5, an AB pattern for H3′ and H4′, a singlet for H4″, and doublet of doublet resonances for H3‴, H4‴ and H5‴ (Table 2). The $^{13}C\{^1H\}$ NMR spectrum showed 16 thienyl carbon resonances as expected (Experimental section). Many of the two sets of alkyl carbon resonances overlapped, so that only seven distinct resonances were resolved.

Syntheses of [(η-C_5H_5)Ru(oligothiophene)]PF_6 complexes

The reaction of [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6[24] with an excess of benzene, thiophene and analogues is a convenient route to complexes [(η-C_5H_5)Ru(L)]PF_6 (L = η-C_6H_6, η-C_4H_4S *etc.*).[16,18] We wished to examine whether there was any regioselectivity for thiophene ring metallation in the reaction of alkyloligothiophenes with [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6. Therefore we treated [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 with an excess of the appropriate oligothiophene in refluxing CH_2Cl_2. Purification from excess oligothiophene was performed by repeated washing with hexane and reprecipitation from CH_2Cl_2. Moderate yields of [(η-C_5H_5)Ru(L)]PF_6 (L = oligothiophene) were obtained; reaction of [(η-C_5H_5)Ru(CH_3CN)$_3$]PF_6 with **6**, **7**, **9** and **11** gave [(η-C_5H_5)Ru(L)]PF_6 (L = **6**; **12**, L = **7**; **13**, L = **9**; **14**, L = **11**; **15**, respectively). In the case of complex **15**, the dialkylquinquethiophene ligand was a solid, and it proved convenient to purify the complex from excess oligothiophene by dissolving it in CH_3CN (in which the oligothiophene is only sparingly soluble) in the dark, rapidly filtering off the free **15**, and removing the solvent.

Graf *et al.* used similar reactions to prepare [(η-C_5R_5)Ru(L)]PF_6 (R = H, Me; L = 2,2′-bithiophene, 2,2′:5′,2″-terthiophene, 5,5″-dimethyl-2,2′:5′,2″-terthiophene, 2,2′:5′,2″:5″,2‴-quaterthiophene), but they found that with the less soluble ter- and quater-thiophenes, it was necessary to add acetone as a co-solvent. Even with an excess of the oligothiophene, mixtures of mono- and bi-metallic oligothiophene complexes were invariably obtained, probably as a result of solvent exchange equilibria, and these required careful separation.[18] The enhanced solubility of the alkyloligothiophenes meant that we were able to use neat CH_2Cl_2, even for the quinquethiophene. For all the complexes **12**–**15** isolated, the microanalyses (C and H) were satisfactory for the pure 1:1 complex except in the case of complex **13** where CH_3CN was used to purify the complex from excess oligomer (see below).

Characterisation of complexes [(η-C_5H_5)Ru(L)]PF_6 (L = oligothiophene)

The complex [(η-C_5H_5)Ru(**7**)]PF_6 **13** was a yellow, very viscous oil. The FAB mass spectrum showed a cluster of peaks at *m/z* 583 with the correct isotopic distribution for [(η-C_5H_5)Ru(**7**)]$^+$, together with a weaker peak for the free oligothiophene, a likely fragmentation product. Significantly, there were no peaks at higher mass, and in particular at *m/z* 749 where [{(η-C_5H_5)Ru}$_2$(**7**)]$^+$ would be expected.

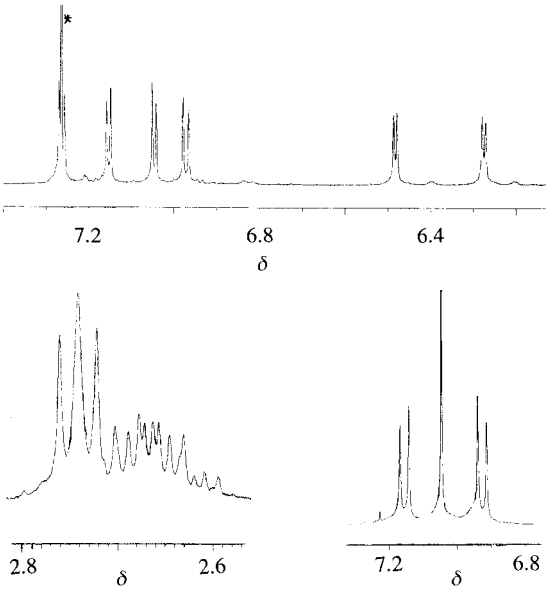
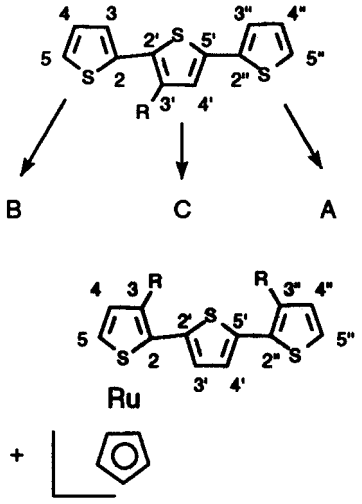


Fig. 1 Clockwise from top, thienyl proton region of 400 MHz ^{1}H NMR spectrum for complex **13** (starred peak $CHCl_3$, δ 6.27, 6.48 H5, H4 respectively, J_{HH} 3.04 Hz; 6.97, 7.19 H4″, H5″ respectively, J_{HH} 5.22 Hz; 7.04, 7.15 H4′, H3′ respectively, J_{HH} 3.84 Hz), thienyl proton region of 200 MHz spectrum for **7**, α-CH_2 region of 400 MHz ^{1}H NMR spectrum for complex **13**.

The ^{1}H NMR spectrum of **13** in $CDCl_3$ showed six doublets for the thiophene protons, indicating that the C_{2v} symmetry of **7** had been lowered to C_1 in **13** (Fig. 1), and that therefore the outermost ring is complexed (as in Scheme 2). Two of these doublets were shifted upfield, to δ 6.48 and 6.27. These are assigned respectively to H4 and H5 (see Scheme 2 for numbering) confirming that complexation had occurred exclusively at the terminal thiophene ring. Deuteration and other studies confirm that whereas H2,5 for free thiophene occur to low field of H3,4, on formation of complexes M(η-C_4H_4S) [M = Cr(0),[28,29] Ru(II)[30]], H2,5 shift significantly further upfield than do H3,4, and for [(η-C_5H_5)Ru(η-C_4H_4S)]$^+$, H2,5 resonate at δ 6.50 and H3,4 at δ 6.57.[30] Moreover, the differences in chemical shift for H4 and H5 for **7** and **13** are



Scheme 2 (Top) Numbering scheme for terthiophene **6**, and the regioisomers of complex **12**; different sites of complexation labelled A, B, C. (Bottom) Numbering scheme for terthiophene **7** and its complex **13**.

similar to those seen for the corresponding protons in terthiophene and $[(\eta\text{-}C_5R_5)Ru(terthiophene)]^+$.[18] The remaining thienyl proton resonances (Table 1) could be assigned straightforwardly by analogy with $[(\eta\text{-}C_5R_5)Ru(L)]^+$ (R = H, Me; L = 2,2′:5′,2″-terthiophene, 5,5″-dimethyl-2,2′:5′,2″-terthiophene).[18]

A singlet at δ 5.41 for **13** is assigned to the cyclopentadienyl protons. The resonances due to the α-CH_2 groups of the hexyl groups are of interest. In free **7** these occur as a triplet at δ 2.78. In **13** there are two α-CH_2 resonances, a triplet at δ 2.74, and a complex multiplet centred at δ 2.67. The latter is assigned to the α-CH_2 of the complexed ring. Since a complex η-$C_4H_2RR'S$ is chiral, the α-CH_2 protons are diastereotopic and therefore inequivalent; similar patterns have been seen for complexes $[Cr(\eta\text{-}C_4H_2RR'S)(CO)_3]$.[31] The resonances due to both α-CH_2 groups are shifted upfield from that for free **7**; the observation of two different α-CH_2 groups confirms the complexation of an outer thiophene ring of **7**. The two β-CH_2 groups are also distinctive, with the metallated ring β-CH_2 a complex multiplet centred at δ 1.64, and the other β-CH_2 a quintet as expected, at δ 1.66.

The $^{13}C\{^1H\}$ NMR spectrum of **13** in $CDCl_3$ showed eight resonances due to the uncomplexed thiophene ring carbons, four resonances due to the thiophene ring complexed to ruthenium at δ 99.0, 92.5, 88.2 and 77.2 (overlapping the solvent resonance), and an intense resonance at δ 82.1. We assign the latter (Table 1) by comparison with published data for $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}terthiophene)]^+$.[18] It is not possible unequivocally to assign the remaining eight thiophene carbons; during data collection (*ca.* 45 min), some decomposition was evident, and the spectrum was complicated by the presence of a little free **7**, and other resonances. The remaining $^{13}C\{^1H\}$ NMR assignments in Table 1 are therefore tentative. Nevertheless, there are some features worthy of comment. As found by Graf *et al.*, whereas the resonances due to the carbons of the complexed thiophene ring are shifted strongly upfield (C2 and C5 to a greater extent than C3 and C4), all of the non–complexed thiophene carbons are shifted downfield slightly, in particular for the ring immediately next to the complexed thiophene.

The product of reaction of oligothiophene **6** with $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ was a viscous yellow oil, **12**. The FAB mass spectrum showed a base peak at *m/z* 499 consistent with $[(\eta\text{-}C_5H_5)Ru(\mathbf{6})]PF_6$, which had the correct isotopic distribution. However, a weak feature (7% of base peak intensity) at *m/z* 665 was also evident, consistent with the presence of a small amount of $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{6})]PF_6$. The ^1H NMR spectrum of **12** ($CDCl_3$) showed a very complex set of resonances in the aromatic region, which we are unable unequivocally to assign. Most useful for characterising the possible regioisomers present (Scheme 2) were the resonances in the region δ 6.2–6.8 (complexed thiophene ring protons), the cyclopentadienyl resonances around δ 5.5, and the α-CH_2 resonances at δ *ca.* 2.7.

The complexed thiophene ring region showed three sets of resonances (Fig. 2). The most intense set consisted of a triplet at δ 6.53, a doublet at δ 6.42 and a doublet at δ 6.32 (coupling constants 3.20 and 3.04 Hz, respectively) A less intense second set consisted of a triplet and a doublet, at δ 6.47 and 6.24 (coupling constants both 2.88 Hz) respectively. The appearence and intensity of the triplet at δ 6.53 suggested that it obscured a second less intense doublet at δ 6.52, and using a more dilute solution, this doublet was partially resolved. Clearly, these resonances are consistent with the presence in solution of both of the two regioisomers of **12** in which the terminal thiophene rings are complexed to ruthenium (A and B; Scheme 2). On steric grounds, it is expected that regioisomer A would be the major product. There is, however, a third species present; a singlet is observed at δ 6.80. This can only be due to the third possible regioisomer C in which the central, alkylthiophene, ring is complexed. In support of this assignment, the change in chemical shift upon coordination for H4′ in C is similar to that seen for H3 and H4 of 5,5″-dimethyl-2,2′:5′,2″-terthiophene.[18] Finally, there are some additional weak resonances in this region (<5% total integrated intensity), presumably due to a small amount of $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{6})]PF_6$, as observed in the FAB mass spectrum. For regioisomer A, the triplet is assigned to H4, the doublet at δ 6.42 to H3 and the doublet at δ 6.32 to H5, by analogy with **13**.

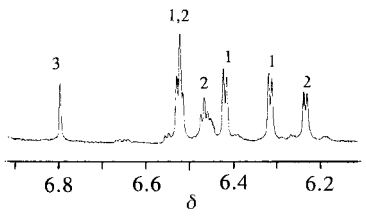


Fig. 2 400 MHz spectrum of complex **12** (complexed thienyl proton region), showing evidence for the presence of all three possible regioisomers.

Consistent with the presence of all three possible regioisomers is the fact that there are three distinct cyclopentadienyl proton resonances, one at δ 5.48 and two, overlapping, at δ 5.41 and 5.40. The latter are assigned to regioisomers A and B in which terminal thiophenes are complexed. Together, these have approximately the same intensity as the resonance at δ 5.48 assigned to regioisomer C. In the α-CH_2 region, there is an overlapping pair of triplets at δ 2.56, and a complex multiplet at δ 2.69 of approximately the same intensity. The triplets are assigned to the α-CH_2 groups of the uncomplexed thiophene rings in regioisomers A and B, and the multiplet to the α-CH_2 group of the complexed ring in regioisomer C, by analogy with the appearence of the α-CH_2 groups in complex **13** discussed earlier. The very complex (and rather noisy) $^{13}C\{^1H\}$ spectra were of little assistance in characterising **12**. However, the two strongest peaks in the spectrum were in the region where cyclopentadienyl resonances are expected, at δ 82.17 and 82.03. We suggest that the resonances due to regioisomers A and B are indistinguishable. Two weaker peaks, at δ 85.9 and 83.4, are tentatively assigned to complexed thiophene ring carbons; the spectra were too noisy to permit identification of any other complexed thiophene ring carbons.

Integration of both the two cyclopentadienyl resonances and the two α-CH_2 resonances in the ^1H NMR spectrum suggests that the ratio of regioisomer C to A and B together is 0.9. However, the ratio calculated from the intensities of the singlet at δ 6.80 due to C, and the two doublets at δ 6.32 and 6.24 due to A and B, is only 0.4. On examining the ^1H NMR spectrum of **6**, it was apparent that the receptivity of proton H4′ is significantly lower than that of the other thienyl protons; the singlet at δ 7.01 due to H4′ was approximately 0.7 times as intense as expected (allowing for the overlap with the doublet of doublets due to H4). Different receptivities for proton resonances in oligothiophenes and their complexes have been observed previously,[18] and we suggest that this accounts for the apparent discrepancy here.

Graf *et al.* found that for their series of oligothiophenes, complexation occurred exclusively at the terminal ring(s).[18] However, our results with **12** suggested that alkylation of the internal thiophene ring in these oligomers could partially overcome the preference for terminal ring complexation. We therefore next examined the metallation of the dialkylquinquethiophene **9**, which possesses non-alkylated terminal thiophenes, and both alkylated and non-alkylated internal thiophenes. Since **9** is also symmetrical (C_{2v}, like **7**), it was anticipated that the characterisation of its complexes might be more straightforward. Reaction of an excess of **9** with $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ in CH_2Cl_2 gave an orange solid, **14**, after removal of excess **9**. The FAB mass spectrum of **14**

showed a base peak at m/z 747, with the correct isotopic distribution for $[(\eta\text{-}C_5H_5)Ru(\mathbf{9})]^+$. However, there was also a weak cluster of peaks at m/z 913 (maximum 10% of base peak intensity) and a very weak feature at m/z 1079 (maximum 5% of base peak intensity), which are assigned to complexes $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{9})]^{2+}$ and $[\{(\eta\text{-}C_5H_5)Ru\}_3(\mathbf{9})]^{3+}$ respectively. The C and H analyses were lower than calculated for the formulation $[(\eta\text{-}C_5H_5)Ru(\mathbf{9})]PF_6$ (Experimental section), consistent with the presence of a significant amount of bimetallic complexes $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{9})]^{2+}$. This may be a consequence of the purification procedure. Dissolution of the complex $[(\eta\text{-}C_5H_5)Ru(\mathbf{9})]^+$ in CH_3CN may have resulted in equilibria of type (1) and (2) being established, although precautions to exclude light were taken. Precipitation of the complex from CH_2Cl_2 with octane would then be expected to enrich the final product in dimetallated oligothiophene complexes $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{9})]^{2+}$.

$$[CpRu(L)]^+ + 3\ CH_3CN \rightleftharpoons [CpRu(CH_3CN)_3]^+ + L \quad (1)$$

$$[CpRu(L)]^+ + [CpRu(CH_3CN)_3]^+ \rightleftharpoons [\{CpRu\}_2(L)]^{2+} + 3\ CH_3CN \quad (2)$$

The ^{1}H NMR spectrum of **14** showed two major sets of resonances in the region δ 6.9–6.2. One of these was a singlet, and the other a triplet and two doublets (Fig. 3). Clearly, the latter can only be due to the regioisomer of **14** in which one of the outermost thiophene rings is complexed to ruthenium. The singlet could, in principle, be due either to the regioisomer in which one of the alkylthiophene rings is complexed, or to that in which the central thiophene ring is complexed. The ratio of the intensity of the singlet to one of the other resonances was 0.75. Once more, further evidence for the presence of the two regioisomers can be gleaned from the cyclopentadienyl resonances. There are two overlapping resonances at δ 5.405 and 5.400. The peaks due to the α-CH_2 groups strongly suggest that the second regioisomer is, in fact, that in which one of the alkylthiophene rings is complexed, since there is a complex multiplet at δ 2.747, of the type seen for the complexed alkylthiophene ring of **13**, and a rather broad triplet centred at δ 2.727 due to the remaining (overlapping) α-CH_2 groups. Overlap of these signals prevented accurate integration, but their relative intensity is not inconsistent with the ratio for the regioisomers observed from the thienyl proton resonances. The same ratio of these regioisomers was consistently obtained in four preparations of **14**. In addition, small resonances, presumably due to bimetallic complexes, were observed, and in one preparation, an additional singlet was seen at δ 6.15. The origin of the latter is uncertain.

Quaterthiophene **11** has one external and one internal alkylthiophene ring, and one external and one internal thiophene ring. Reaction of an excess of **11** with $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ gave a dark yellow solid, **15**, in good yield. The FAB mass spectrum showed a base peak at m/z 498, due to the free oligothiophene, and a peak at m/z 665 (21% of base peak intensity), the correct mass for $[(\eta\text{-}C_5H_5)Ru(\mathbf{11})]^+$. In addition, a weak peak at m/z 831 (3% of base peak intensity) was seen, the correct mass for complexes $[\{(\eta\text{-}C_5H_5)Ru\}_2(\mathbf{11})]^+$.

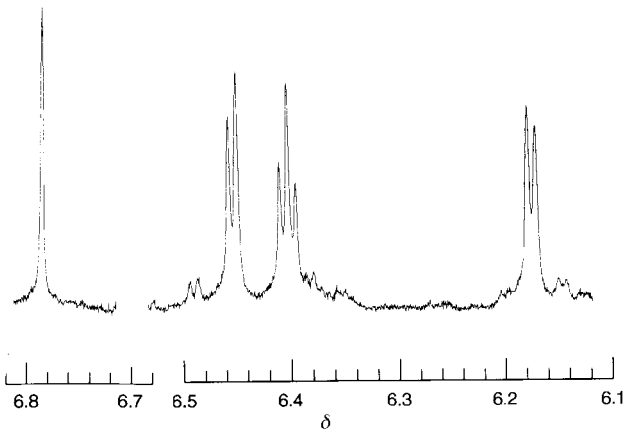


Fig. 3 400 MHz spectrum of complex **14** (complexed thienyl proton region), showing evidence for the presence of two regioisomers.

In the region δ 6.9–6.2, the ^{1}H NMR spectrum of **15** showed two doublets, at δ 6.47 and 6.28 ($^3J_{HH}$ 2.9 Hz), in addition to some broad minor resonances. At least 93% of the integrated intensity was due to the doublets. This AX pattern could be due either to the regioisomer in which the outer, alkylated thiophene ring is complexed to ruthenium, or that in which the internal, non-alkylated ring is complexed. However, the close similarity in chemical shifts and coupling constant to the corresponding resonances for **13** strongly suggest the former. The minor, broad resonances may be due to the bimetallic species evident in the FAB mass spectrum. The cyclopentadienyl region showed one sharp peak, at δ 5.41. The peaks due to the α-CH_2 groups confirm that **15** is exclusively the regioisomer with the outer, alkylated thiophene ring coordinated, since there is a complex multiplet at δ 2.69 and a triplet at δ 2.65, assigned to the complexed ring α-CH_2 and non-complexed ring α-CH_2 groups respectively.

Because only one regioisomer is present, the resonances due to the remaining aromatic protons are also diagnostic. In the free oligothiophene **11**, it is straightforward to assign the individual proton resonances (Table 2). In the complex **15**, the spectrum is similar in appearance to that of **11** (apart from the disappearance upfield of the resonances due to protons H4 and H5), except that the H3′ resonance has moved significantly downfield as a result of the complexation of the adjacent ring, while the H4′ resonance is almost unshifted. The singlet due to H4″ has shifted to δ 7.04 in **15**, from δ 7.02 in **11**, while the resonances due to Hn''' (n = 3,4,5) are almost unshifted from the values for **11**.

From the NMR data for complexes **12**–**15**, some conclusions can be drawn. Firstly, it is clear that alkylation of the thiophene rings in these oligothiophenes enhances complexation to the $[(\eta\text{-}C_5H_5)Ru]^+$ moiety, to an extent which partially overcomes the tendency for outermost ring complexation. This is in agreement with earlier work on complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-}Th)]^+$ (Th = thiophene, mono-, di-, tri-methylthiophenes, or tetramethylthiophene) in which exchange reactions were studied in d^6-acetone solution. The equilibrium constants for the displacement of thiophene by methyl-substituted thiophenes ranged from 6 for 2-methylthiophene up to 1300 for tetramethylthiophene, indicating that the alkylthiophenes are significantly better ligands for $[(\eta\text{-}C_5H_5)Ru]^+$.[32] Secondly, our results with complex **15** support the finding of Graf *et al.* that complexation of the outer thiophene ring of an oligothiophene is otherwise preferred.[18] In this case, of the two alkylthiophene rings in the oligomer, exclusively the outermost ring is complexed. The selectivity for a thiophene ring in **15** which is both external, and which bears an alkyl group, is notable. It is possible that this kind of selectivity could be useful in synthesis, as selective syntheses of extended, unsymmetrical oligothiophenes, for example for NLO applications, is otherwise very difficult.

Finally, in those complexes (**13**, **15**) where single regioisomers were obtained and the spectra could be more definitively assigned, the changes in chemical shifts and coupling constants for the thienyl protons in the complexed rings and adjacent rings follow the trends previously noted.[18] The shift upfield for the protons of the complexed ring was ascribed to a combination of the loss of π-electron density (and hence ring current) on complexation, and the magnetic anisotropy effect from the metal–thiophene ring bond dipole. The proton resonances of the adjoining two rings shift downfield signifi-

Table 3 Electronic absorption bands ($cm^{-1}/10^3$) and extinction coefficients (in parentheses; $dm^3\ mol^{-1}\ cm^{-1}/10^3$) for complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-oligothiophene})]^+$ (10^{-4} M in $CHCl_3$), and corresponding free oligothiophenes

Oligothiophene	$[(\eta\text{-}C_5H_5)Ru(\eta\text{-oligothiophene})]^+$
6 28.74 (16.1)[a]	**12** 25.00 sh (5.0), 27.62 sh (6.1), 29.85 (6.8)
7 29.41 (17.8):[b] 29.59 (45.9)[c]	**13** 25.32 sh (6.2), 31.06 (12.53)
QuiTh 24.04 (55.2)[d]	**15** 25.12 (8.3)

[a]Ref. 27, $CHCl_3$ solution. [b]Ref. 27, 3,3″-dimethyl-2,2′:5′,2″-terthiophene, $CHCl_3$. [c]Ref. 17, 3,3″-dioctyl-2,2′:5′,2″-terthiophene, $CHCl_3$. [d]Ref. 33, QuiTh = 2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene, $CHCl_3$.

cantly as these become less delocalised, hence more aromatic, as the complexed ring is removed from conjugation by complexation to the bulky metal centre. In the case of the quaterthiophene, the resonances due to the ring furthest from the complexed ring are almost unchanged, as was also noted for unsubstituted quaterthiophene.[18]

Electronic spectra

The electronic spectra of oligothiophenes show a strong band due to a π–π* transition involving the entire chromophore, and weaker bands at higher energies due to localised π–π* transitions. For unsubstituted oligothiophenes, the strong band moves to lower energy and becomes more intense with increasing conjugation length.[33] Derivatives of $[(\eta\text{-}C_5H_5)Ru(\eta\text{-benzene})]^+$ show a single band in the near UV, assigned to the $a^1E_1 \leftarrow {}^1A_1$ transition, with molar absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) of *ca.* 10^2.[34] In fused polycyclic aromatic complexes $[(\eta\text{-}C_5H_5)Ru(\eta\text{-arene})]^+$ this band is red–shifted, and the extinction coefficients are greater (*ca.* 10^3); the bands are usually shoulders on more intense charge transfer bands which extend into the UV.[35]

The electronic spectra of the terthiophene complexes **12** and **13** are summarised in Table 3. We suggest that the main band is the π–π* transition of the oligothiophene, broadened and also reduced in intensity by complexation to the metal, and shifted to higher energy than the corresponding free oligothiophenes as the complexed thiophene ring is effectively removed from conjugation by complexation.[18] Although there is a higher energy peak in these complexes in the region where the metal-based $a^1E_1 \leftarrow {}^1A_1$ transition is expected,[34,35] the molar absorption coefficients are too high for this to be purely a d–d transition, and overlap with charge transfer band(s) is a likely explanation. The quinquethiophene complex **15** shows a single, rather broad band in the visible region, the position and intensity of which, when compared with the spectrum of free quinquethiophene, suggests that this band is again due to the oligothiophene π–π* transition, affected by loss of conjugation caused by thiophene ring complexation.

Electrochemistry of the free oligothiophenes

We initially investigated the electrochemistry of oligothiophenes **6**, **7**, **9** and **11** as an aid to interpreting that of their complexes. The electrochemistry of 3,3″-dioctyl-2,2′:5′,2″-terthiophene, and the related symmetrical 3,3‴-dioctyl-2,2′:5′,2″:5″,2‴-quaterthiophene, have been reported recently.[17] Our results with 3,3″-dihexyl-2,2′:5′,2″-terthiophene **7**, and with **6**, were very similar to those reported for the dioctylterthiophene and are not, therefore, discussed here in detail. To summarise, in CH_3CN/0.2 M tetraethylammonium tetrafluoroborate (TEAT) the redox chemistry of **6** and **7** depended upon the concentration and the positive scan limit. When low concentrations (1.0 mM) were employed, and the positive scan limit was restricted to +0.85 V, a sharp redox couple was observed at +0.70 V. On repetitive scanning, both the current and the peak-to-peak separation increased, consistent with the formation of a layer of redox-active and conductive material on the electrode. For the dioctylterthiophene, an exactly similar redox process was seen, and the solid on the electrode was characterised after electrodeposition by ^1H NMR spectroscopy. It was a mixture of the tetraoctylsexithiophene formed by α,α-coupling of the electrogenerated dioctylterthiophene radical cations, and trapped dioctylterthiophene.[17] When we attempted to withdraw our modified electrodes from solution (while they were held at 0.0 V), the material either re-dissolved (**6**) or became dislodged from the electrode surface (**7**), but it is highly likely that the same α,α-coupling reaction had occurred.

When higher monomer concentrations (5 mM **6**, 7 mM **7**) and more positive potential limits (+1.3 V **6**, +1.1 V **7**) were employed, a new irreversible oxidation approaching the positive limit was evident, coupled with the development of new broad redox waves, and robust electrochromic polymer films were deposited on repetitive scanning. These were dark blue in the oxidised form and orange in the reduced form. The films were withdrawn from solution in their neutral state, washed with acetonitrile and studied in fresh background electrolyte. Their voltammetry was typical of electrodeposited polythiophenes, showing a sharp oxidation process with E_p^a *ca.* +0.7 V followed by a broad anodic wave at higher potentials, and a broad reduction wave extending to *ca.* +0.3 V (Fig. 4). Between +0.3 and −1.8 V, no redox waves were seen. Polythiophenes can be reduced to the negatively charged, conducting form ('n-doped') at potentials typically $\leqslant -1.8$ V.[36] At potentials $\leqslant -1.8$ V, both poly-**6** and poly-**7** showed irreversible reductions, presumably due to n-doping. Accessing the n-doped form of the polymer resulted in the loss of electroactivity on repeated potential cycling.

The electrochemistry of unsymmetrical dihexylquaterthiophene **11** was similar to that of the symmetrical dioctylquaterthiophene reported earlier.[17] A sharp, quasi-reversible redox wave at +0.70 V (Pt) is ascribed to the formation of the radical cation, and on repeated cycling, a loosely-adherent film was deposited on Pt or ITO-coated glass electrodes. On extending the positive potential limit, an additional oxidation process resulted in an electrochromic film with redox characteristics typical of a polythiophene being deposited (Fig. 5). Superimposed upon the broad polythiophene redox wave is the sharp redox process at +0.70 V; in the case of **11**, the free quaterthiophene is evidently trapped within the growing film, and this wave is attributed to the reversible formation of $\mathbf{11}^{\cdot+}$ within the film.[17] When 0.2 M TEAT/CH_3CN was employed, the film was dislodged upon removal of the electrode from solution. We have previously shown that the use of tetraethylammonium *p*-toluenesulfonate (TEATos) as electrolyte greatly improved the electrodeposition of polybenzo[c]thiophenes.[37] When 0.2 M TEATos/CH_3CN was employed, the poly-

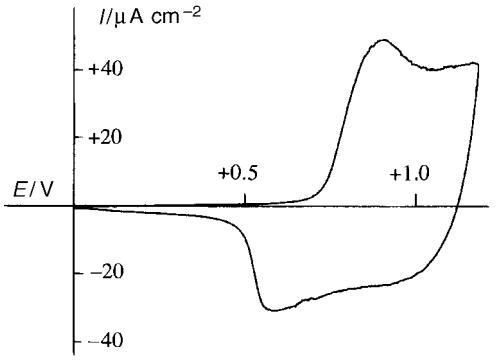


Fig. 4 Cyclic voltammogram of a film of poly-**6** on an ITO working electrode at 15 mV s^{-1} in 0.2 M tetraethylammonium tetrafluoroborate/CH_3CN.

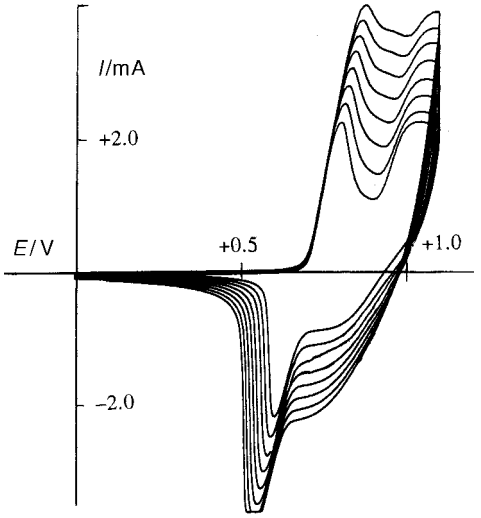


Fig. 5 Formation of a film of poly-**11** on an ITO working electrode (1 cm^2) cycled between 0.0 and +1.1 V at 100 mV s^{-1}.

11 film was much more adherent, and could be removed from the growth solution and cycled in fresh background electrolyte (0.2 M TEAT/CH_3CN). The electrochemistry of the polymer was similar to that of poly-**7**, except for the presence of the sharp, reversible redox process at +0.7 V. After washing the poly-**11** films thoroughly with CH_3CN, this redox wave almost disappeared, suggesting that the trapped **11** had been washed out of the film.

Quinquethiophene **9** was only sparingly soluble in CH_3CN (1.5 mM). Using a Pt working electrode and 0.2 M TEATos/CH_3CN, a single oxidation wave (E_p^a +0.89 V) and two reduction waves (E_p^c +0.70 and +0.57 V) were observed. The voltammogram was similar to those observed earlier for methyl-substituted quinquethiophenes with free α-positions.[38] A film grew on the electrode upon repeated cycling. It is noteworthy that the first oxidation process for the quinquethiophene is at a more positive potential than that seen for ter- or quater-thiophene radical cation formation, but this is not unprecedented. It was observed earlier that 3,3‴″-dioctylquinquethiophene had both a higher energy π–π* transition, and a higher first oxidation potential, than the corresponding quaterthiophene.[17] The reasons for this are unclear. In CH_2Cl_2/0.2 M tetrabutylammonium tetrafluoroborate (TBAT), a reversible oxidation wave at +0.75 V was observed, but polymer films could not be electrodeposited in this medium, even with a high concentration of **9** (8 mM) and high positive potential limit (+1.2 V), as all electrogenerated materials were soluble.

Electrochemistry of complexes [(η-C_5H_5)Ru(η-oligothiophene)]$^+$

It was not possible to examine the electrochemistry of the oligothiophene complexes in CH_3CN as this solvent reacts with [(η-C_5H_5)Ru(η-thiophene)]$^+$ to re-generate [(η-C_5H_5)Ru(CH_3CN)$_3$]$^+$.[13] Therefore, 1 mM solutions of the complexes in CH_2Cl_2/0.2 M TBAT were employed. We summarise the positions of the irreversible redox peaks observed in Table 4. A typical voltammogram is shown in Fig. 6.

On scanning from 0.0 V, all the complexes showed at least one irreversible oxidation, at potentials significantly more positive than for the oxidation of the corresponding free oligothiophene to its radical cation. Corresponding broad reduction peaks are observed. Interestingly, these are observed at more positive potentials than the reduction peaks for the free oligothiophene radical cations. Previously, the electrochemistry of the complexes [(η-C_5R_5)M(L)]$^+$ (R = H, Me; M = Ru, Os; L = bi-, ter- or quater-thiophene) was examined

Table 4 Peak potentials for irreversible oxidations and reductions of [(η-C_5H_5)Ru(η-oligothiophene)]$^+$ complexes. Potentials quoted are *vs.* SCE

	E_p^a (oxidations)	E_p^c (reductions)
12	+1.70 (+1.44, +1.26)	−0.70, −1.25
13	+1.26 (+0.78, +0.60)	−0.82 (minor), −1.36
14	+0.95 (+0.90, +0.50, 0.00)	−0.93
15	+1.12, +1.40 (+0.54 br, *ca.* +0.9 br)	−1.10

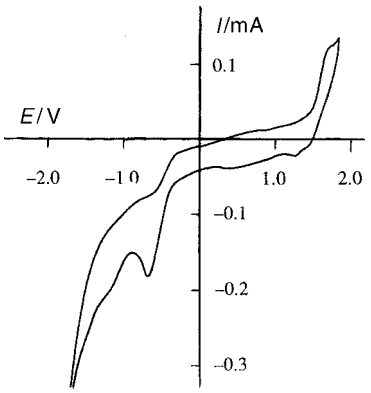
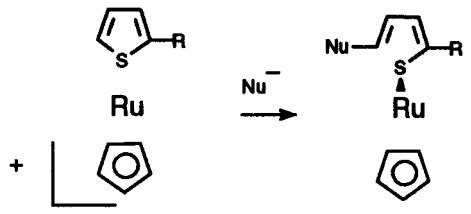


Fig. 6 Cyclic voltammogram of complex **12** (mixture of regioisomers) in CH_2Cl_2/0.2 M tetrabutylammonium tetrafluoroborate, Pt working electrode.

in CH_2Cl_2.[20] It was pointed out that the irreversible oxidative voltammograms seen for these complexes closely resembled those of the corresponding free oligothiophene with one fewer thiophene ring. This was taken as further evidence that complexing the terminal thiophene ring of an oligomer to a [(η-C_5R_5)M]$^+$ moiety effectively removes that ring from conjugation. Our results are similar; there is a clear dependence of oxidation potential on oligothiophene. It is interesting that the quinquethiophene complex **14**, known to be a mixture of regioisomers, shows two distinct oxidation waves at +1.12 and +1.40 V. This is consistent with the oxidation of the quaterthiophene fragment (of the regioisomer with the terminal ring complexed) and the terthiophene fragment (of the regioisomer with the alkylthiophene ring complexed) respectively. The other complex which is a regioisomer mixture, **12**, would not be expected to show two oxidation waves since the two regioisomers with terminal thiophene rings complexed (A and B) should have virtually identical oxidation potentials due to their bithiophene fragments, and the thiophene fragments in regioisomer C should have oxidation potentials more positive than the scan limit employed here.

For the soluble ter- and quater-thiophenes used here, the first oxidation wave is quasi-reversible. However, the oxidations seen for the complexes are all irreversible. Also, whereas the oxidation of the unsubstituted oligothiophene complexes led to coating of the electrode surfaces,[20] we only observed this with the symmetrical terthiophene complex **13**. The oxidation products of the other oligothiophene complexes were all soluble in CH_2Cl_2. For these reasons, assignment of the first oxidation wave for our complexes to the generation of a radical cation localised on the non-complexed thiophene rings (of the terminal regioisomers where a regioisomer mixture is present) must be tentative.

An interesting feature of the electrochemistry of the complexes is the sharp and irreversible reduction wave at < -0.9 V. Neither free oligothiophenes, nor related complexes [(η-C_5H_5)Ru(η-arene)]$^+$, show reductions in this potential region. Other oligothiophene complexes, including both [(η-C_5H_5)Ru(η-thiophene)]$^+$ and [(η-C_5H_5)Ru(η-2,2′-bithiophene)]$^+$, do undergo similar reductions.[20] This irreversible reduction may be related to the known reaction of [(η-



Scheme 3

$C_5H_5)Ru(\eta$-thiophene)]$^+$ with nucleophiles, which results in C–S bond cleavage to give neutral butadienethiolate complexes (Scheme 3).[39] Reduction coupled with proton abstraction from the solvent could result in similar products being formed electrochemically; controlled potential electrolyses are in hand in an effort to isolate the product(s) of these reductions.

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