

Addition of alcohols and pyrroles to *trans*-[RuCl₂{(Ph₂P)₂C=CH₂}₂]. A polypyrrole bearing a covalently bound metal–diphosphine complex†

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Alcohols and pyrroles undergo base-catalysed addition to *trans*-[RuCl₂{(Ph₂P)₂C=CH₂}₂] to afford *trans*-[RuCl₂{(Ph₂P)₂CHCH₂Z}]₂ (Z = -OCH₂Ph **2a**, -OCH₂CH₂C₄H₃S-3 **2b**, -NC₄H₄ **3a**, -NC₄H₃C₆H₁₃-3 **3b**); complexes **2b** and **3b** are suitable for electropolymerization to give heterocyclic conducting polymers, and **3b** is copolymerized with *N*-methylpyrrole to afford a polypyrrole incorporating a functionalized metal–diphosphine complex, for the first time.

There is much interest in electrodes modified with polymers containing redox-active metal complexes, since these have potential applications in sensing, in electrocatalysis and in electrochromic displays.^{1,2} The electrochemical polymerization of complexes bearing pendant *N*-pyrroles, by oxidation of the pyrrole moieties, is often employed to prepare such modified electrodes.^{3,4} The complexes used have normally been classical redox-active and potentially electrocatalytic species, for example porphyrins⁴ or complexes of 2,2'-bipyridine (bpy) derivatives;^{1,5} the latter have the advantage that the synthesis of pyrrole-functionalized derivatives is straightforward. In spite of the interest in fixing them to surfaces for catalysis, metal–phosphine complexes (apart from a few examples with bpy derivatives as coligands⁵) have not so far been incorporated into conducting polymers, and have rarely been investigated for electrode modification.⁶

Although the synthesis of chelating phosphine ligands bearing pendant heterocycles, suitable for electropolymerization, might be expected to be problematic, nucleophilic addition to coordinated dppen [dppen = (Ph₂P)₂C=CH₂] offers a route to functionalized diphosphine complexes in one step and in high yield.^{7,8} We have shown that prolonged treatment of *trans*-[RuCl₂(dppen)₂] **1** with a large excess of RNH₂ affords functionalized, redox-active diphosphine complexes *trans*-[RuCl₂{(Ph₂P)₂CHCH₂NHR}]₂, and that one example {R = -(CH₂)₃Si[OEt]₃} could be used to modify oxide surfaces with a ruthenium(II)–diphosphine complex monolayer.⁶ Amine addition is inappropriate for the preparation of derivatives bearing pendant thiophenes or pyrroles for oxidative electropolymerization; the linkage between the heterocycle and metal centre must be non-basic.⁹ Although the reactivity of **1** towards nucleophiles is limited compared with platinum(II) and palladium(II) complexes of dppen,¹⁰ we were gratified to find that treatment of **1** in CH₂Cl₂ with a large (≥ 10-fold) excess of a primary alcohol, in the presence of catalytic amounts of KOBu^t and 18-crown-6, generated the hoped-for adducts [RuCl₂{(Ph₂P)₂CHCH₂Z}]₂ (Z = -OCH₂Ph **2**, -OCH₂CH₂C₄H₃S-3 **2b**) in acceptable yield.‡ These were characterized by ³¹P{¹H} and ¹H NMR spectroscopy, micro-analytical data and FAB mass spectrometry.§ Their spectroscopic properties are similar to those of the primary amine adducts described earlier.^{6,10} The addition of other primary alcohols (EtOH, *n*-C₆H₁₃OH) to **1** also proceeds in solution, as monitored by ³¹P{¹H} NMR spectroscopy, but we did not isolate the products. The adduct **2b** has been the subject of an X-ray crystal structure determination; details will be reported later. Complex **2b** is in principle suitable for incorporation, by electropolymerization, into polythiophenes.

Pyrrole NH groups have pK_as similar to alcohol OH groups.¹¹ Earlier, we found that the very reactive complex [Pd(OAc)₂(dppen)] reacted with pyrrole *via* electrophilic aromatic substitution, to give a mixture of (after metathesis) [PdI₂{(Ph₂P)₂CHCH₂C₄H₃NH-*x*}] (*x* = 2, major isomer; *x* = 3; minor isomer).⁸ Interestingly, on treatment with an excess of pyrrole in chlorobenzene in the presence of catalytic amounts of KOBu^t and 18-crown-6, **1** gave, exclusively and in high yield, *trans*-[RuCl₂{(Ph₂P)₂CHCH₂NC₄H₄}₂] **3a**, also fully characterized; the pyrrole proton resonances (AA'XX' spin system) in the ¹H NMR spectrum were particularly diagnostic.¶ Complex **3a** was insufficiently soluble for electrochemical study, and we therefore added 3-*n*-hexylpyrrole¹² to **1** to give *trans*-[RuCl₂{(Ph₂P)₂CHCH₂NC₄H₃R}]₂ (R = *n*-hexyl, **3b**), which was much more soluble in CH₂Cl₂.||

The cyclic voltammogram** of **3b** in CH₂Cl₂-0.2 M NBu₄BF₄ showed a reversible one-electron oxidation wave at +0.11 V owing to the Ru^{II}-Ru^{III} couple, and a further irreversible oxidation wave commencing at *ca.* +0.87 V owing to the oxidation of the pendant pyrrole units; this high value for a pyrrole is likely a consequence of the fact that it is both *N*- and 3-substituted, and is in a sterically crowded environment. No polymer film formed, even when we used a 10 mM solution of **3b**. Since *N*-functionalized pyrroles have significantly higher oxidation potentials than pyrrole itself, we therefore chose to co-polymerize **3b** (10 mM) with *N*-methylpyrrole (20 mM). Once grown, the copolymer-modified electrodes were washed, and transferred to MeCN-0.2 M NEt₄BF₄ media for redox-cycling experiments.

Fig. 1 compares the cyclic voltammogram (CV) of a poly(*N*-methylpyrrole) film grown using a 30 mM monomer solution, from 0.2 M NBu₄BF₄-CH₂Cl₂ (*i.e.* conditions as similar as possible to those used for copolymer formation), and the CV of the copolymer. The poly(*N*-methylpyrrole) CV closely resembles those of films grown using more conventional media (*e.g.* NEt₄BF₄-MeCN);¹³ use of CH₂Cl₂-NBu₄BF₄ as the electrolyte for film growth does not appear to have a detrimental effect on the voltammetry of the polymer. It can be seen that, at 10 mV s⁻¹ scan rate, a Ru^{II}-Ru^{III} wave is superimposed upon the broad redox wave due to the poly(*N*-methylpyrrole) backbone for the copolymer film. It occurs at a potential *ca.* 0.05 V more positive than that for **3b** in solution in CH₂Cl₂. This

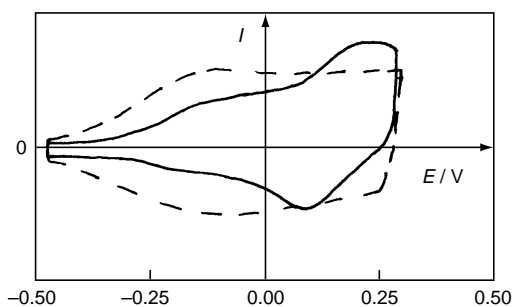


Fig. 1 Cyclic voltammograms of (dashed line) poly(*N*-methylpyrrole) (30 mM s⁻¹) and (full line) a copolymer of *N*-methylpyrrole and **3b** (10 mM s⁻¹). Pt disk electrode, 0.30 cm² area.

is excellent evidence that the copolymerization strategy has worked and we have prepared a polypyrrole bearing a covalently bound metal–diphosphine complex, the first time that this has been demonstrated. Moreover, the electroactivity of the conducting polymer backbone has been preserved. For a surface-localised redox process, there should be no peak separation between anodic and cathodic processes. This is clearly not the case for the Ru^{II}–Ru^{III} wave in the copolymer, but there are likely to be kinetic limitations due to the necessity for ion ingress/egress from the polymer film.

In summary, we have used base catalysis to add alcohols and pyrroles, weak nucleophiles, to **1**, and this affords a convenient route to thiophene- and pyrrole-functionalized ruthenium(II)–diphosphine complexes. We have successfully electrocopolymerized the pyrrole derivative **3b**, immobilising a redox-active ruthenium(II)–diphosphine complex in a polypyrrole matrix for the first time. This chemistry offers the opportunity of coating conducting surfaces with a polymer layer containing defined platinum metal–diphosphine complexes, providing that the latter are stable at the positive potentials needed to electropolymerize the heterocycles.

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Footnotes and References

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† Note added in proof: The synthesis of a derivative of the adduct H₃B–Ph₂PCH₂CH₂PPh₂·BH₃ bearing a pendant *N*-alkylpyrrole function, its electropolymerization to afford a diphosphine-functionalized polypyrrole, and the reaction of this with Pd(OAc)₂, have recently been described (O. Stéphan, N. Riegel and S. Jugé, *J. Electroanal. Chem.*, 1997, **421**, 5). We became aware of this paper after our manuscript had been submitted.

‡ **1** (0.1 g) was dissolved in dry CH₂Cl₂ (50 cm³). To this was added PhCH₂OH **2a** or 2-(3-thienyl)ethanol **2b** (0.5 cm³), KOBu^t (ca. 20 mg) and 18-crown-6 (ca. 20 mg). The mixture was set aside at room temp., and examined periodically using ³¹P NMR spectroscopy (10 mm tube; 5 mm coaxial tube containing CDCl₃ as lock) until the reaction was >95% complete (ca. 5–7 days). The solvent was removed *in vacuo*, the dark brown oil was triturated with MeOH and the resulting yellow solid was filtered off and dried. The crude product was recrystallised from CH₂Cl₂–MeOH. Yields 62–65%.

§ Data: **2a**: Anal. Calc. for C₆₆H₆₀Cl₂P₄O₂Ru·H₂O·CH₂Cl₂: C, 62.67; H, 5.02. Found: C, 62.20; H, 5.19%. FABMS: *m/z* 1182 (100) M⁺; 1147 (82) [M – Cl]⁺; 1109 (20) [M – Cl – HCl]⁺; 1074 (55) [M – ROH]⁺; 1039 (39) [M – ROH – Cl]⁺. ³¹P NMR (101 MHz, CDCl₃), δ 8.06 (s). Selected ¹H NMR data (200 MHz, CDCl₃) δ 7.59 (8 H, m, Ph), 5.71 (2 H, complex m, P₂CHCH₂), 3.72 (4 H, complex m, P₂CHCH₂), 3.27 (4 H, s, PhCH₂O). **2b**: Anal. Calc. for C₆₄H₆₀Cl₂P₄O₂Ru·0.5CH₂Cl₂: C, 61.31; H, 4.87. Found: C, 61.33; H, 4.98%. FABMS: *m/z* 1222 (100) M⁺; 1187 (43) [M – Cl]⁺; 1092 (19) [M – ROH]⁺; 1057 (7) [M – ROH – Cl]⁺. ³¹P NMR (101 MHz; CDCl₃) δ 7.99 (s). Selected ¹H NMR data (200 MHz, CDCl₃) δ 7.55, 7.37 (m, Ph), 6.89, 6.68, 6.66 (6 H, overlapping multiplets, SC₄H₃R-3), 5.55 (2 H, complex m, P₂CHCH₂), 3.58 (4 H, complex m, P₂CHCH₂), 3.28 (4 H, t, J_{HH} 6.3 Hz, OCH₂CH₂C₄H₉S), 2.68 (4 H, t, OCH₂CH₂C₄H₉S).

¶ To **1** (0.15 g, 0.16 mmol) in chlorobenzene (25 cm³) under a nitrogen atmosphere was added pyrrole (0.5 cm³), 18-crown-6 (0.02 g) and KOBu^t (0.02 g). The mixture was stirred for 16 h, whereupon a yellow precipitate of **3a** appeared. This was filtered off, washed with MeOH and dried *in vacuo*. Yield 0.14 g, 81%. Anal. Calcd. for C₆₀H₅₄Cl₂N₂P₄Ru: C, 65.58; H, 4.95; N, 2.55. Found: C, 65.30; H, 4.87; N, 2.54%. FAB MS: *m/z* 1098 (100) M⁺; 1063 (21) [M – Cl]⁺. ³¹P NMR (CH₂Cl₂–CDCl₃) δ 8.89 (s). Selected ¹H NMR data (CD₂Cl₂) δ 6.07, 6.02 (8 H, AA'BB', |J_{AB} + J_{AB'}| 4.1 Hz, *N*-subst. pyrrole), 5.35 (2 H, complex m, P₂CHCH₂), 4.42 (4 H, complex m, P₂CHCH₂).

|| To **1** (0.40 g, 0.415 mmol) in chlorobenzene (50 cm³) under a nitrogen atmosphere was added freshly prepared 3-(*n*-hexyl)pyrrole (0.5 cm³),¹² 18-crown-6 (0.02 g) and KOBu^t (0.02 g). The mixture was stirred for 64 h. Solvent was removed *in vacuo*, and the oily product was triturated with MeOH, whereupon a yellow solid (**3b**) formed. This was filtered off, washed with a little diethyl ether and dried *in vacuo*. Yield 0.46 g, 88%. Anal. Calc. for C₇₂H₇₈Cl₂N₂P₄Ru·0.25CH₂Cl₂: C, 67.35; H, 6.14; N, 2.17. Found: C, 67.47; H, 6.14; N, 2.16%. FABMS: *m/z* 1267 (100) M⁺; 1232 (21) [M – Cl]⁺. ³¹P NMR, δ 8.01 (s). Selected ¹H NMR data, δ 5.88, 5.78, 5.74 (6 H, m, pyrrole CH), 5.61 (2 H, complex m, P₂CHCH₂, app. J_{PH} 6 Hz), 4.06 (4 H, complex m, P₂CHCH₂, app. J_{PH} 5 Hz), 2.24 (4 H, t, J_{HH} 7.4 Hz, NC₄H₃CH₂R), 1.47, 1.30, 1.20 (16 H, m, other hexyl CH₂), 0.80 (6 H, t, J_{HH} 6.5 Hz, hexyl CH₃).

** All potentials quoted in this paper are with respect to the ferrocene–ferrocenium redox couple, which was routinely monitored after electrochemical experiments. Conducting polymer films were grown by repetitive cyclic voltammetric scans from ca. –0.5 V, to a potential ca. 0.1 V beyond the potential at which heterocycle oxidation commenced, using Pt disk or indium-doped tin oxide (ITO)-coated glass working electrodes. The films were removed from the cell with the film in the neutral (reduced) state, washed thoroughly with CH₂Cl₂ to ensure that any Ru complex within the film is covalently anchored, dried and stored. Subsequent voltammetric experiments were conducted in 0.2 M NEt₄BF₄–MeCN. Other details of electrochemical methodology were as previously described.⁶

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