# A Novel Method for Oxide Surface Modification using Functionalised Diphosphine Complexes

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A method for preparing bidentate phosphine complexes functionalised for oxide surface modification is developed utilising the chemistry of a coordinated diphosphine; a redox-active ruthenium(II) complex is anchored to indium-doped tin oxide (ITO) surfaces, and the extent of coverage is determined using cyclic voltammetry.

There is much interest in the immobilisation of catalytically active metal–phosphine complexes by covalent attachment to oxide supports, since such systems should combine the advantages of heterogeneous and homogeneous catalysis.[1] Most work to date has employed monodentate phosphine ligands, in particular of the type $Ph_2P(CH_2)_3Si(OR)_3$. Likewise, in electrochemistry, the modification of electrode surfaces by covalent attachment of electrocatalytic centres has also attracted much attention,[2] and recently some attempts to utilise metal complexes of suitable bidentate phosphine ligands have been reported.[3] However, the syntheses of the functionalised diphosphine ligands and their complexes is lengthy, and the free ligands are air-sensitive. We report here a method for synthesising metal–(functionalised bidentate phosphine) complexes and anchoring them to oxide supports. We have demonstrated this using a redox-active ruthenium(II) complex, and have employed indium-doped tin oxide (ITO) as a model oxide surface, enabling electrochemical techniques to be used to characterise the anchored metal centres.

Treatment of a solution of $[RuCl_2(PPh_3)_3]$ with 2 equiv. of dppen $[CH_2{=}C(PPh_2)_2]$ afforded orange–red crystals of *trans*-$[RuCl_2(dppen)_2]{\cdot}CH_2Cl_2$ **1**[†] in good yield;[‡] **1** was reported previously as a serendipitous product of the reaction between $[Ru_2(OAc)_4Cl]$ and dppen.[4] With an excess of $NH_2R$ in toluene at room temperature, **1** reacts to afford adducts *trans*-$[RuCl_2\{(Ph_2P)_2CHCH_2NHR\}_2]$ [**2**; R = *n*-octyl **2a**, $PhCH_2$ **2b**, *R*-PhCHMe **2c**, $H_2N(CH_2)_3$ **2d**, $(EtO)_3Si(CH_2)_3$ **2e**], characterised by microanalyses, $^{31}P\{^1H\}$ and $^1H$ NMR spectroscopy, and (in some cases) fast atom bombardment mass spectrometry.[§] Particularly useful are the $^{31}P\{^1H\}$ NMR spectra, which show a characteristic shift upfield on amine addition, and the proton spectra, which show the disappearance of the vinylidene protons, and distinctive resonances at *ca.* δ 5.4 and 3.0 for the $P_2CHCH_2$– system,[5] in addition to resonances characteristic of the amine R groups. In addition, a crystal structure was obtained for **2d**; details will be reported elsewhere.

ITO electrodes (working area *ca.* 1.5 $cm^2$) were cleaned,[6] dried and soaked in a toluene solution of **2e** for 24 h. They were then washed thoroughly with dichloromethane and acetone, dried and examined using cyclic voltammetry.[¶]

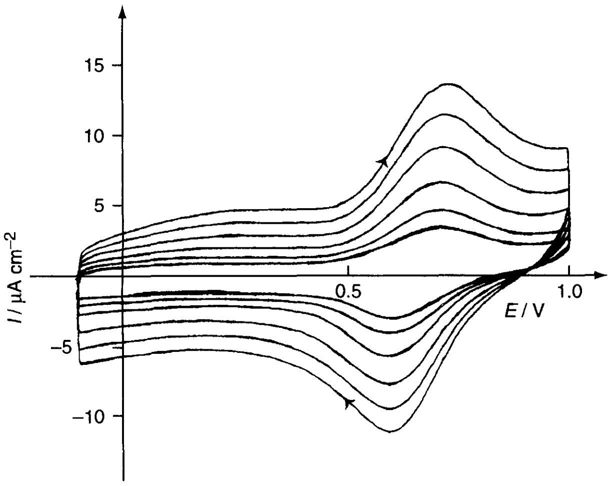

**Fig. 1** Cyclic voltammogram of an ITO electrode modified with **2e**. Conditions as in footnote; potentials shown are *vs.* SCE. Scan rates (in order of increasing peak currents) 50, 70, 100, 150, 200, 250 mV $s^{-1}$.

Fig. 1 shows cyclic voltammograms for an ITO electrode derivatised using this approach. A plot of peak current against scan rate is linear and passes through the origin for scan rates up to 150 mV $s^{-1}$, as expected for a surface-anchored redox couple. For an ideal surface-anchored couple, there should be no difference between anodic and cathodic peak potentials, whereas the peak-to-peak separation observed is 90 mV (constant with scan rate up to 150 mV $s^{-1}$). However, a similar peak-to-peak separation was seen for ferrocene covalently anchored to ITO.[6] The $E_{1/2}$ value (+0.03 V *vs* ferrocene–ferrocenium), corresponds closely to those for **2b–d** in solution.[||] The area under the anodic waves corresponds to a charge of 15 ± 3 μC $cm^{-2}$. Treating the complex as a sphere of radius 5.2 Å (a value calculated using the crystal structure data for **2d** and for **1**[4]), and assuming close packing and a smooth electrode surface, a value of 17.5 μC $cm^{-2}$ corresponds to a monolayer of **2e**. The modified electrodes are quite stable to prolonged cycling under these conditions; after 100 scans between 0.00 and +0.90 V at 150 mV $s^{-1}$, the anodic peak current for the electrode of Fig. 1 had declined by 7%. That the complex is anchored *via* the aminopropylsiloxy bridge is strongly supported by the fact that ITO electrodes, cleaned and then soaked in solutions of either *trans*-$[RuCl_2(Ph_2PCH_2PPh_2)_2]$ or **1**, showed no additional electroactivity compared with blank electrodes.

In conclusion, we have used nucleophilic addition to coordinated dppen to afford a chelate diphosphine complex suitable for surface anchoring, and we have demonstrated that the anchoring reaction works by using the electrochemistry of a surface-localised ruthenium(II) complex. We are now investigating the anchoring of catalytic species to $SiO_2$ using this method.

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## Footnotes

[†] Satisfactory microanalyses were obtained for all compounds described.

[‡] To $[RuCl_2(PPh_3)_3]$ (0.96 g, 1.0 mmol) in $CH_2Cl_2$ (12 $cm^3$) under $N_2$ was added dppen (0.82 g, 2.07 mmol), and the mixture was set aside at room temperature for 3 h. The product was filtered off and dried; a further quantity was obtained by adding EtOH (15 $cm^3$) to the filtrate. Total yield 0.79 g, 85%. NMR (δ, $CDCl_3$): $^{31}P\{^1H\}$ 14.7 (s); $^1H$ 6.12 (complex m; $C{=}CH_2$). FAB-MS (3-nitrobenzyl alcohol, Xe) 965 (100) $M^+$, 930 (27) $[M - Cl]^+$, 895 (16) $[M - Cl - HCl]^+$.

[§] For example, **2d**: to a solution/suspension of **1** (0.20 g, 0.2 mmol) in benzene (10 $cm^3$) was added 1,3-diaminopropane (0.4 $cm^3$), with stirring. After 4 h, solvent was removed under reduced pressure, the residue was triturated with MeOH and the solid then filtered off and dried. Yield 0.13 g, 58%. NMR (δ, $CDCl_3$): $^{31}P\{^1H\}$ 10.7 (s), $^1H$ 5.38 (m, 2 H, '$J_{PH}$' 6.3 Hz, $P_2CHCH_2$), 2.96 (m, 4 H, $PCHCH_2$), 2.55, 2.43 (t, $J_{HH}$ *ca.* 6 Hz, $-NHCH_2CH_2CH_2NH_2$), 1.41 (qnt, $-CH_2CH_2CH_2-$), 1.25 (br s, amine H).

[¶] For modified electrodes, the electrolyte was 0.2 mol $dm^{-3}$ tetraethylammonium tetrafluoroborate in dry acetonitrile. A Pt disc working electrode, Pt gauze counter electrode and saturated calomel reference electrode (RE) (separated from the working compartment by a glass frit and Luggin capillary) were employed. Under identical conditions, $E_{1/2}$ for ferrocene–ferrocenium was +0.58 V *vs.* this RE; potentials in the paper are quoted against ferrocene–ferrocenium.

‖ Insolubility of **1** and **2** in acetonitrile necessitated the use of $CH_2Cl_2$–0.2 mol dm$^{-3}$ tetrabutylammonium tetrafluoroborate. An Ag–0.01 mol dm$^{-3}$ $AgNO_3$–acetonitrile RE was employed. Under identical conditions, $E_{1/2}$ for ferrocene–ferrocenium was +0.19 V. Complexes **1** and **2a–d** all showed reversible $Ru^{II}$–$Ru^{III}$ couples at $E_{1/2}$ $-0.02 \pm 0.03$ V *vs.* ferrocene–ferrocenium.

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