

Synthesis, characterization and redox properties of mixed phosphine nitroruthenium(II) complexes. Crystal structure of *trans*-[Ru(NO₂)(terpy)-(PMe₃)(PPh₃)] [ClO₄]·H₂O

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The mixed phosphine complexes *trans*-[Ru(NO₂)(terpy)(PMe₃)(PR₃)] [ClO₄] (terpy = 2,2':6',2''-terpyridine; R = Et, Pr, Bz or Ph) were synthesized in high yields by a stepwise addition of each phosphine. These syntheses demonstrate the utility of ruthenium(II) in the preparation of mixed phosphine complexes. The stereochemistry of *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)] [ClO₄].H₂O was confirmed by a single-crystal X-ray diffraction study. This species crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 11.0199(15), *b* = 18.3888(28), *c* = 19.3089(25) Å, β = 112.845(9)° and *Z* = 4. The two phosphine ligands are mutually *trans*, with P–Ru–P 177.5(1)°. The relative redox stabilities of the mixed phosphine complexes and a related series of *trans*-[Ru(NO₂)(terpy)(PR₃)₂] [ClO₄] (R = Et, Pr, Bz or Ph) complexes were evaluated using cyclic voltammetric peak current ratios (*i*_{pc}/*i*_{pa}) for the ruthenium(III)–ruthenium(II) couples. The rate constants for nitroruthenium(III) decomposition were calculated from the *i*_{pc}/*i*_{pa} data and the contributions of electronic (*E*) and steric (*S*) factors to its rate of decomposition were determined using the relationship $\ln k = aE + bS + c$. The average ratio of steric to electronic ligand effects on $\ln k$ is approximately 30:70.

Tertiary phosphines and related ligands are widely utilized due to the range of steric and electronic effects that they exert on the reactivities of transition-metal complexes.^{1–5} While many phosphine ligand studies involve transition-metal complexes which contain only one type of monodentate phosphine ligand per metal centre, interest in the preparation of mixed phosphine complexes (complexes containing two different monodentate phosphine ligands bonded to the same metal centre) stems from the use of these complexes in the study of the combined and competitive phosphine steric and electronic ligand effects of two types of phosphine ligands.^{6–9} For example, these effects are evident in the synthesis and ligand substitution patterns of mixed phosphine transition-metal complexes. As a result, the preparation of mixed phosphine complexes often requires a carefully designed synthetic strategy involving an inert metal centre, so that the phosphine ligands will not exchange.

In general, ligand effects can be considered in terms of electronic and steric effects.^{2–5,10–12} In order to assess the relative electronic and steric ligand effects on a physical property of a metal complex, the equation $f(x) = aE + bS + c$ [where $f(x)$ = a quantifiable physical property, such as $\ln k$, where k represents a rate constant of metal reactivity, *E* is the electronic ligand effect, *S* is the steric ligand effect and *a*, *b* and *c* are constants for a particular reaction] was developed and used by several research groups.^{2c,3,4a–d,10,11a,12} The types of *E* parameters which have been used for phosphine ligand studies include the *pK_a* values for the dissociation of the acid form of the ligands,^{13,14} the NMR chemical shifts (δ) and coupling constants (*J*) of the ligands,^{14,15} substituent constants for the dissociation of the acid form of the ligand,¹⁶ the *A₁* carbonyl stretching frequencies of Ni(CO)₃PR₃ complexes^{17,18} and the redox potentials of transition-metal complexes which contain the ligands of interest.¹⁹ The types of *S* parameters which have been used for phosphine ligand studies include cone angles, developed by Tolman,¹⁷ and *E_R* values, developed by Brown.²⁰

This paper contains a description of the preparation of mixed phosphine ruthenium complexes of the type *trans*-[Ru(NO₂)-

(terpy)(PMe₃)(PR₃)] [ClO₄] (terpy = 2,2':6',2''-terpyridine; R = Et, Pr, Bz or Ph). The synthetic method presented here uses the substitutionally inert nature of ruthenium(II) to prevent intermolecular phosphine exchange. In this manner, pure and stable mixed phosphine–ruthenium complexes were isolated in high yields. In addition, a single crystal structural analysis of *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)] [ClO₄] was obtained. To the best of our knowledge, this is the first reported crystal structure analysis of a ruthenium complex containing mixed monodentate tertiary phosphine ligands.

The availability of these mixed phosphine complexes provides an opportunity to expand upon our initial studies^{21,22} of ligand effects on the redox stability of the nitroruthenium moiety by testing the additivity of electronic and steric phosphine substituent effects on redox stability. While our initial studies,^{21–23} and those of Meyer and co-workers,²⁴ considered the steric or electronic ligand effects on nitroruthenium redox stability separately, this paper contains the first investigation of the combined steric and electronic ligand effects on nitroruthenium redox stability, where the redox stabilities of the *trans*-[Ru(NO₂)(terpy)(PMe₃)(PR₃)] [ClO₄] complexes (R = Et, Pr, Bz or Ph) and the related *trans*-[Ru(NO₂)(terpy)(PR₃)₂] [ClO₄] complexes (R = Et, Pr, Bz or Ph) are conveniently measured by the cyclic voltammetric peak current ratios (*i*_{pc}/*i*_{pa}) obtained from the Ru^{III}–Ru^{II} couples.

An analysis of the cyclic voltammetric data for our nitroruthenium complexes suggest that a first-order electrochemical–chemical–electrochemical (ECE) mechanism is occurring at the electrode surface,²⁵ where the first-order rate constants (*k*) for the C step of the mechanism were calculated from the *i*_{pc}/*i*_{pa} data using the method of Nicholson and Shain.²⁶ The equation $\ln k = aE + bS + c$ was used to quantify the relative electronic and steric ligand contributions to the natural log of the rate constant of decomposition of the electrochemically generated nitroruthenium(III). An average ratio of steric to electronic ligand effects of approximately 30:70 was observed, which illustrates the relative importance of steric effects on the redox stability of the nitroruthenium moiety.

Experimental

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should only be handled in small quantities, using the appropriate safety procedures.²⁷

Materials

The compound $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was obtained on loan from Johnson Matthey/Aesar/Alfa, 2,2':6',2''-terpyridine was purchased from GFS Chemicals, phosphine ligands were purchased from Aldrich or Strem Chemicals Inc. and all were used as received. Acetonitrile was obtained from Fisher Scientific and was distilled from CaH_2 . All aqueous reactions used house distilled water which was passed through Barnstead HN combination (no. D8922) and HN organic removal (no. D8904) cartridges before use. All other materials were of reagent quality and were used as received.

Preparation of the complexes

The complexes *cis*- $[\text{RuCl}_2(\text{terpy})(\text{PMe}_3)]_2$,^{23b} *trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PEt}_3)_2][\text{ClO}_4]$ **11**,²² *trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PPr}_3)_2][\text{ClO}_4]$ **12**,²² *trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PBz}_3)_2][\text{ClO}_4]$ **13**²² and *trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PPh}_3)_2][\text{ClO}_4]$ **14**²² were prepared as previously described.

***trans*- $[\text{RuCl}(\text{terpy})(\text{PEt}_3)(\text{PMe}_3)][\text{ClO}_4]$ 1.** The compound *cis*- $[\text{RuCl}_2(\text{terpy})(\text{PMe}_3)]$ (0.290 g, 0.603 mmol) was dissolved in acetone–EtOH [300 cm³, 1:1 (v/v)]. To this was added PEt_3 (1.1 equivalents, 0.66 mmol) under an inert atmosphere and the reaction stirred at room temperature for 3 h. The solvent was removed with a rotary evaporator and the residue dissolved in EtOH–water (100 cm³, 3:1). To this was added NaClO_4 (3.0 g) in water (2 cm³) and the volume was reduced with a rotary evaporator, where **1** was produced as a precipitate (0.302 g, 0.455 mmol, 75% yield) (Found: C, 43.30; H, 5.35. $\text{C}_{24}\text{H}_{35}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_2\text{Ru}$ requires C, 43.45; H, 5.30%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 502 (4800), 450 (sh), 355 (sh), 310 (33 000) and 270 (22 000).

***trans*- $[\text{RuCl}(\text{terpy})(\text{PMe}_3)(\text{PPr}_3)][\text{ClO}_4]$ 2.** A sample of *cis*- $[\text{RuCl}_2(\text{terpy})(\text{PMe}_3)]$ (0.350 g, 0.727 mmol) and PPr_3 (1.1 equivalents, 0.80 mmol) were reacted under the same conditions as for complex **1**. The isolated solid was dissolved in warm 95% EtOH (100 cm³) and then cooled to 0 °C, where **2** formed as a precipitate (0.479 g, 0.679 mmol, 93% yield) (Found: C, 45.90; H, 5.85. $\text{C}_{27}\text{H}_{41}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_2\text{Ru}$ requires C, 45.95; H, 5.85%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 502 (4800), 457 (sh), 350 (sh), 310 (34 000) and 273 (21 000).

***trans*- $[\text{RuCl}(\text{terpy})(\text{PBz}_3)(\text{PMe}_3)][\text{ClO}_4]$ 3.** A sample of *cis*- $[\text{RuCl}_2(\text{terpy})(\text{PMe}_3)]$ (0.025 g, 0.053 mmol) and PBz_3 (1.1 equivalents, 0.066 mmol) were reacted under the same conditions as for complex **1**. Complex **3** formed as a precipitate (0.039 g, 0.046 mmol, 87% yield) (Found: C, 54.90; H, 4.90. $\text{C}_{39}\text{H}_{41}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_2\text{Ru}$ requires C, 55.15; H, 4.85%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 491 (4500), 457 (sh), 350 (sh), 311 (30 000) and 274 (18 000).

***trans*- $[\text{RuCl}(\text{terpy})(\text{PMe}_3)(\text{PPh}_3)][\text{ClO}_4]$ 4.** A sample of *cis*- $[\text{RuCl}_2(\text{terpy})(\text{PMe}_3)]$ (0.107 g, 0.223 mmol) and PPh_3 (1.0 equivalent, 0.223 mmol) were reacted under the same conditions as for complex **1**. The resulting residue was dissolved in a minimum amount of 95% EtOH–water (3:1), then solid NaClO_4 was added until precipitation occurred. The volume of the solution was concentrated and the solid was collected by vacuum filtration. The crude solid was purified by column chromatography, using alumina, with toluene–acetonitrile (3:2) as eluent. The purified product **4** was obtained by concentrating the resulting solution with a rotary evaporator

(0.150 g, 0.186 mmol, 84% yield) (Found: C, 53.25; H, 4.40. $\text{C}_{36}\text{H}_{35}\text{Cl}_2\text{N}_3\text{O}_4\text{P}_2\text{Ru}$ requires C, 53.55; H, 4.40%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 485 (4000), 450 (sh), 333 (sh), 310 (28 000) and 275 (16 000).

***trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PEt}_3)(\text{PMe}_3)][\text{ClO}_4]$ 5.** A sample of complex **1** (0.247 g, 0.372 mmol) was added to water–EtOH (150 cm³, 1:1) containing NaNO_2 (24.3 equivalents, 0.625 g). The solution was heated at reflux under N_2 for 3 h, then cooled to room temperature. An excess of NaClO_4 (2.0 g in 20 cm³ of water) was added to the solution and the volume was reduced with a rotary evaporator, where **5** formed as a precipitate (0.206 g, 0.306 mmol, 82% yield) (Found: C, 42.70; H, 5.25. $\text{C}_{24}\text{H}_{35}\text{ClN}_4\text{O}_6\text{P}_2\text{Ru}$ requires C, 42.75; H, 5.20%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 453 (sh), 435 (4900), 309 (28 000) and 273 (18 000). IR spectrum: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1330 [$\nu_{\text{as}}(\text{NO}_2)$] and 1300 [$\nu_{\text{s}}(\text{NO}_2)$]. NMR: δ_{H} (300 MHz, CDCl_3 , standard SiMe_4) phosphine protons 0.4 (m, 18 H), 0.9 (m, 6 H) and terpy protons 7.6 (t, 2 H), 8.0 (t, 3 H), 8.4 (d, 4 H) and 9.7 (d, 2 H); δ_{P} (400 MHz, CDCl_3 , external reference H_3PO_4) –3.18 [d, $^2J(\text{PP})$ 263.7, PMe_3] and 7.79 [d, $^2J(\text{PP})$ 262.8 Hz, PEt_3].

***trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PMe}_3)(\text{PPr}_3)][\text{ClO}_4]$ 6.** A sample of complex **2** (0.300 g, 0.425 mmol) was reacted under the same conditions as for complex **5** to produce **6** (0.280 g, 0.391 mmol, 92% yield) (Found: C, 45.20; H, 5.80. $\text{C}_{27}\text{H}_{41}\text{ClN}_4\text{O}_6\text{P}_2\text{Ru}$ requires C, 45.30; H, 5.75%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 456 (sh), 436 (4900), 309 (28 000) and 273 (18 000). IR spectrum: $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1335 [$\nu_{\text{as}}(\text{NO}_2)$] and 1300 [$\nu_{\text{s}}(\text{NO}_2)$]. NMR: δ_{H} (300 MHz, CDCl_3 , standard CHCl_3) phosphine protons 0.70 (m, 30 H) and terpy protons 7.7 (t, 2 H), 8.2 (t, 3 H), 8.6 (d, 4 H) and 9.9 (d, 2 H); δ_{P} (400 MHz, CDCl_3 , external reference H_3PO_4) –3.16 [d, $^2J(\text{PP})$ 263.7, PMe_3], 3.23 [d, $^2J(\text{PP})$ 263.6 Hz, PPr_3].

***trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PBz}_3)(\text{PMe}_3)][\text{ClO}_4]$ 7.** A sample of complex **3** (0.082 g, 0.097 mmol) was reacted under the same conditions as for complex **5**. The crude product was purified by column chromatography, using alumina with toluene–acetonitrile (1:1) as the eluent. The product **7** was isolated by concentrating the eluent with a rotary evaporator (0.045 g, 0.053 mmol, 92% yield) (Found: C, 54.65; H, 4.80. $\text{C}_{39}\text{H}_{41}\text{ClN}_4\text{O}_6\text{P}_2\text{Ru}$ requires C, 54.45; H, 4.80%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 450 (sh), 430 (3900), 330 (sh), 310 (22 000) and 275 (14 000). NMR: δ_{H} (300 MHz, CDCl_3 , standard SiMe_4) trimethylphosphine protons 0.49 [d, 9 H, $J(\text{PH})$ 7.6], benzylic protons 2.8 [d, 6 H, $J(\text{PH})$ 5.5], terpy and aromatic tribenzylphosphine protons 6.4 (d, 6 H), 7.1 (m, 9 H), 7.6 (t, 2 H), 8.0 (t, 1 H), 8.1 (t, 2 H), 8.3 (d, 2 H), 8.4 (d, 2 H) and 9.6 (d, 2 H); δ_{P} (400 MHz, CDCl_3 , external reference H_3PO_4) –1.54 [d, $^2J(\text{PP})$ 276.4, PMe_3] and 1.66 [d, $^2J(\text{PP})$ 276.4 Hz, PBz_3].

***trans*- $[\text{Ru}(\text{NO}_2)(\text{terpy})(\text{PMe}_3)(\text{PPh}_3)][\text{ClO}_4]$ 8.** A sample of complex **4** (0.135 g, 0.167 mmol) was reacted under the same conditions as for complex **5**. The crude product was purified by column chromatography, using alumina, with acetonitrile–toluene (1:1) as the eluent. The product **8** was isolated by concentrating the eluent with a rotary evaporator (0.067 g, 0.0822 mmol, 72% yield) (Found: C, 51.60; H, 4.55. $\text{C}_{36}\text{H}_{35}\text{ClN}_4\text{O}_6\text{P}_2\text{Ru} \cdot \text{H}_2\text{O}$ requires C, 51.70; H, 4.45%). UV/VIS spectrum (MeCN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 437 (sh), 425 (4400), 333 (sh), 309 (24 000) and 276 (16 000). NMR: δ_{H} (300 MHz, CDCl_3 , standard SiMe_4) 0.61 [d, 9 H, $J(\text{PH})$ 9.4], terpy and triphenylphosphine protons 7.0 (t, 6 H), 7.1 (t, 6 H), 7.2 (d, 3 H), 7.5 (t, 2 H), 7.9 (t, 2 H), 8.1 (t, 3 H), 8.2 (t, 2 H) and 9.8 (d, 2 H); δ_{P} (400 MHz, CDCl_3 , external reference H_3PO_4) 2.55 [d, $^2J(\text{PP})$ 268.6, PMe_3] and 24.35 [d, $^2J(\text{PP})$ 268.5 Hz, PPh_3].

trans-[Ru(NO)(terpy)(PEt₃)(PMe₃)][ClO₄]₃ 9. A sample of complex **5** (0.056 g, 0.0826 mmol) was dissolved in distilled MeCN (3.0 cm³) and was treated dropwise with an excess of HClO₄ (70% w/w, 0.1 cm³). The solution changed from dark brown to light yellow, then an equal volume of Et₂O was added, and **9** was formed as a precipitate (0.060 g, 0.070 mmol, 84% yield) (Found: C, 33.75; H, 4.10. C₂₄H₃₅Cl₃N₄O₁₃P₂Ru requires C, 33.65; H, 4.10%). UV/VIS spectrum (MeCN): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 370 (7600), 306 (sh) and 286 (19 000). IR spectrum: ν_{max}/cm⁻¹ 1900 (ν_{N=O}).

trans-[Ru(NO)(terpy)(PMe₃)(PPr₃)] [ClO₄]₃ 10. A sample of complex **6** (0.114 g, 0.159 mmol) was reacted under the same conditions as for complex **9** to produce **10** (0.118 g, 0.131 mmol, 83% yield) (Found: C, 35.85; H, 4.65. C₂₇H₄₁Cl₃N₄O₁₃P₂Ru requires C, 36.10; H, 4.60%). UV/VIS spectrum (MeCN): λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 370 (7800), 304 (sh) and 286 (19 000). IR spectrum: ν_{max}/cm⁻¹ 1905 (ν_{N=O}).

Instrumentation

Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Infrared spectra were recorded with a Perkin-Elmer 1430 ratio recording, a Mattson Alpha Centauri or a Nicolet Magna IR-55 FT spectrophotometer using Nujol mulls on NaCl plates. Proton NMR spectra were obtained with either a JEOL FX-90Q or a Varian Gemini-300 FT spectrometer, ³¹P NMR spectra using a Varian VXR-400S FT spectrometer. All NMR spectra were obtained in CDCl₃, where the ¹H NMR spectra were referenced to either SiMe₄ or CHCl₃ (δ 7.24 vs. SiMe₄) and the ³¹P NMR spectra externally to H₃PO₄. The UV/VIS spectra were obtained with a Bausch and Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instruments Model 200 recorder, or with a Milton Roy Spectronic 3000 diode array spectrophotometer, equipped with a Hewlett-Packard 7470A plotter.

Electrochemical experiments

Cyclic voltammetric measurements were made with an IBM EC/225 voltammetric analyser, or with a PAR Model 173 potentiostat/galvanostat equipped with a PAR Model 376 logarithmic current converter and a PAR Model 175 universal programmer. In both cases, the current–potential waves were recorded with a Houston Instruments Model 100 recorder. The cyclic voltammetric experiments were performed in three electrode, one compartment cells, equipped with platinum working (Bioanalytical Systems) and auxiliary electrodes and a saturated sodium chloride calomel reference electrode (SSCE). The electrochemical measurements used 0.1 mol dm⁻³ tetraethylammonium perchlorate or 0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate as the supporting electrolyte with acetonitrile as the solvent. The data were collected with the temperature of the cell maintained at 25 ± 1 °C. The method developed by Nicholson²⁸ was used to calculate the peak current ratios (*i*_{pc}/*i*_{pa}) measured from the Ru^{III}–Ru^{II} couple for complexes **5–8** and **11–14** and a minimum of five determinations were made for each complex. The *i*_{pc}/*i*_{pa} values for complexes **8** and **12** were determined at concentrations from 1–7 mmol dm⁻³ and were found to be independent of the concentration, consistent with a first-order electrode process.^{25,29} The first-order rate constants for the C step of our ECE systems were calculated from the peak current ratio (*i*_{pc}/*i*_{pa}) data obtained from cyclic voltammetry, using the method and appropriate working curves of Nicholson and Shain, for first-order EC systems.²⁶ The reported values are the averages of a minimum of five measurements, where the uncertainties are expressed at a 95% confidence interval. The constants *a*, *b* and *c* for the equation ln *k* = *aE* + *bS* + *c* were calculated using SigmaPlot 4.14 for Macintosh. The method devised by Schenkluhn and

co-workers^{10b} was utilized to calculate the relative steric and electronic contributions to the rate constants.^{11a}

Collection of X-ray diffraction data for trans-[Ru(NO₂)(terpy)-(PMe₃)(PPh₃)] [ClO₄]₂·H₂O

Crystals were obtained by crystallization from an acetonitrile–toluene solution and were found to contain adventitious water of crystallization. The crystal selected for the diffraction study was plate-like with approximate dimensions 0.2 × 0.2 × 0.1 mm. It was sealed into a thin-walled capillary, mounted on a eucentric goniometer, and accurately centred on a Siemens R3m/V automated four-circle diffractometer. Unit cell dimensions and the crystal's orientation matrix were determined by a least-square analysis of the automatically centred setting angles (2θ, ω and χ, with φ held constant) of 50 reflections, well dispersed in reciprocal space, with 2θ 25–30° (Mo-Kα radiation, λ = 0.710 730 Å). The crystal belongs to the monoclinic system (C_{2h} diffraction symmetry); the systematic absences *h0l* for *l* = 2*n* + 1 and *0k0* for *k* = 2*n* + 1 uniquely indicate the centrosymmetric monoclinic space group *P*2₁/*c*. Intensity data were collected for the 2θ range 5.0–45.0° for the unique data set defined by the octants *hkl* and *h̄k̄l̄*, details are provided in Table 1. All data were corrected for Lorentz and polarization factors and for the effects of absorption. (Several reflections later found to have |*F*_o| ≪ |*F*_c| and running in sequences, were expunged from the data set; these problems were found to be due to a faulty shutter.) Details of the X-ray diffraction study are contained in Table 1.

Solution and refinement of the structure. The structure was solved by a combination of Patterson, Fourier-difference and least-squares refinement methods by use of the Siemens SHELXTL PLUS³⁰ program package on a VAXstation 3100 computer. All non-hydrogen atoms were located (including the adventitious water of crystallization, the identity of which was confirmed by the successful location and refinement of its two hydrogen atoms). All other hydrogen atoms were included in the appropriate idealized trigonal or staggered tetrahedral positions and were assigned bond lengths of *d*(C–H) 0.96 Å. Refinement of positional and anisotropic thermal parameters converged [(Δ/σ)_{max} = 0.002] with *R* = 0.0509 and *R*' = 0.0683 for those 3376 reflections with *F* > 3σ(*F*) and with *R* = 0.0411 and *R*' = 0.0433 for those (2879) with *F* > 6σ(*F*).

The structure was confirmed by a final Fourier-difference synthesis which showed features only in the background range of –0.42 to +0.40 e Å⁻³. Final atomic coordinates are collected in Table 2. Table 3 contains the interatomic distances and angles for the structure.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

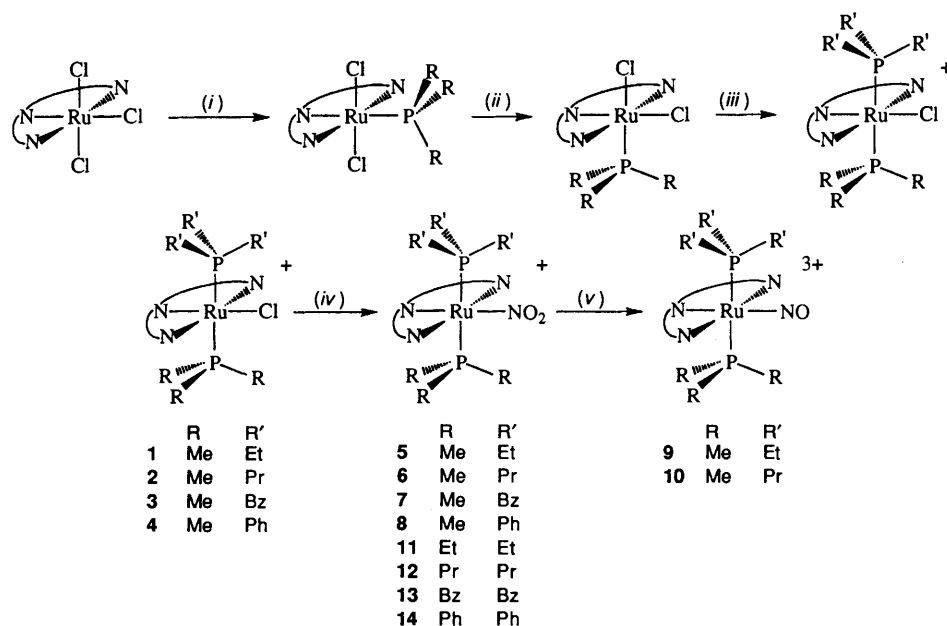
Syntheses and characterization

Scheme 1 outlines the synthetic method used for the preparation of complexes **1–10**. The stepwise ligand substitution chemistry of *cis*-[RuCl₂(terpy)(PMe₃)] allows for the addition of two different phosphine ligands, which results in the formation of complexes **1–4**. This synthetic scheme can be potentially extended to a wide range of phosphines. Complexes **1–10** are stable, where the substitutionally inert nature of ruthenium(II) prevents intermolecular phosphine exchange.

The UV/VIS spectral changes that are observed in the conversion of *cis*-[RuCl₂(terpy)(PMe₃)] to *trans*-[Ru(NO₂)(terpy)(PMe₃)(PR₃)]⁺ are similar to the spectral changes observed in the stepwise synthesis of *trans*-

Table 1 Details of X-ray diffraction study of *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)] [ClO₄]-H₂O

Formula	C ₃₆ H ₃₇ ClN ₄ O ₇ P ₂ Ru
<i>M</i>	836.18
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> /Å	11.0199(15)
<i>b</i> /Å	18.3888(28)
<i>c</i> /Å	19.3089(25)
β/°	112.845(9)
<i>U</i> /Å ³	3605.9(9)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.540
μ(Mo-Kα)/mm ⁻¹	0.640
Transmission (minimum, maximum)	0.8164, 0.8749
2θ Range/°	5.0–45.0
Index ranges (<i>hkl</i>)	–11 to 10, –19 to 0, 0–20
Observed reflections [<i>F</i> > 3σ(<i>F</i>)]	3376
Final <i>R</i> indices (3σ data)	<i>R</i> = 0.0509, <i>R</i> ' = 0.0683 (3376 reflections)
Final <i>R</i> indices (6σ data)	<i>R</i> = 0.0411, <i>R</i> ' = 0.0433 (2879 reflections)
Largest, mean Δ/σ	0.002, 0.000
Largest difference peak, hole/e Å ⁻³	0.40, –0.42

**Scheme 1** (i) PR₃, Zn(Hg), CH₂Cl₂, heat; (ii) CH₂Cl₂, *hν*; (iii) PR₃, acetone–ethanol; (iv) NaNO₂, ethanol–water; (v) H⁺

[Ru(NO₂)(terpy)(PR₃)₂]⁺,^{22,23} and the final spectra of the *trans*-[Ru(NO₂)(terpy)(PMe₃)(PR₃)]⁺ complexes are similar to the previously synthesized *trans*-[Ru(NO₂)(terpy)(PR₃)₂]⁺ complexes^{22,23} indicating that they have similar bonding frameworks and geometries. The spectra of the nitrosylruthenium(II) complexes display absorbances only in the UV region, where the two highest energy transitions are consistent with ligand π → π* bands and the lowest energy transition is consistent with a metal-to-ligand charge-transfer band that shifts to a shorter wavelength in the presence of the strongly π-acidic nitrosyl ligand.

Nuclear magnetic resonance spectroscopy (¹H and ³¹P) was used to establish that complexes **5–8** each contained two different phosphine ligands in the same co-ordination sphere. The chemical shifts and the integration of the resonances in the ¹H NMR spectra of these complexes are consistent with the formulated structures. The ³¹P NMR spectra each contained two resonances (one for each phosphorus atom) and each of these resonances appeared as a doublet due to phosphorus–phosphorus coupling. Resonances occur between δ –3.2 and 24.4, which are typical chemical shift values for phosphorus nuclei co-ordinated to a ruthenium(II) centre.^{31–35} The ²J(PP) coupling constant values ranged from 263 to 276 Hz; these

values are consistent with literature values for phosphine ligands co-ordinated in a *trans* geometry about a ruthenium centre.^{31–35} Notably, this is the first report of ²J(PP) values where there are two different monodentate tertiary phosphine ligands co-ordinated in a *trans* geometry about a ruthenium centre. The ³¹P NMR spectra of complexes **11–14** were also collected. These complexes contained only one singlet resonance at δ 7.72, 3.28, 3.26 and 27.10, respectively.

The values of ν_{as}(NO₂) and ν_s(NO₂) for complexes **5** and **6** are consistent with an N-bound NO₂ co-ordination mode,^{21–23,36a} and ν_{NO} for complexes **9** and **10** occurs at about 1900 cm⁻¹, consistent with a linear co-ordination mode for the nitrosyl ligand.^{21,22,36b,37}

The cyclic voltammograms of complexes **1–4** each display one electrochemically reversible couple, while those of complexes **5–8** each display one quasi-reversible couple. Each couple is assigned as a Ru^{III}–Ru^{II} couple, with the *E*₁ potentials of these couples listed in Table 4. The cyclic voltammograms for complexes **9** and **10** each display one electrochemically reversible wave assigned to the *trans*-[Ru(NO)(terpy)-(PR₃)(PMe₃)]^{3+/2+} couple. We propose that one product from the decomposition of the electrochemically generated nitrosylruthenium(III) complex (**5** or **6**) is the corresponding

Table 2 Atomic coordinates ($\times 10^4$) for *trans*-[Ru(NO₂)(terpy)-(PMe₃)(PPh₃)] [ClO₄] \cdot H₂O

Atom	x	y	z
Ru	4 469(1)	9 921(1)	2 118(1)
P(2)	5 900(2)	9 174(1)	3 176(1)
P(3)	3 183(2)	10 649(1)	1 098(1)
O(1)	4 243(7)	9 015(4)	816(4)
O(2)	3 167(7)	8 578(4)	1 413(4)
N(1)	3 907(7)	9 062(4)	1 370(4)
N(11)	2 895(6)	9 926(4)	2 484(4)
N(21)	4 899(7)	10 787(3)	2 778(3)
N(31)	6 141(6)	10 307(3)	1 985(4)
C(1)	1 526(9)	10 321(8)	599(7)
C(2)	2 949(11)	11 569(6)	1 343(6)
C(3)	3 813(10)	10 753(6)	368(5)
C(12)	2 987(8)	10 486(5)	2 981(5)
C(13)	2 057(11)	10 543(6)	3 287(6)
C(14)	1 006(11)	10 084(8)	3 092(7)
C(15)	910(10)	9 546(6)	2 588(7)
C(16)	1 837(9)	9 483(5)	2 283(5)
C(22)	5 978(8)	11 184(5)	2 848(4)
C(23)	6 255(10)	11 803(5)	3 285(5)
C(24)	5 454(12)	12 010(6)	3 655(6)
C(25)	4 381(11)	11 597(5)	3 572(6)
C(26)	4 108(9)	10 970(5)	3 122(5)
C(32)	6 701(8)	10 052(5)	1 514(5)
C(33)	7 792(9)	10 368(6)	1 458(6)
C(34)	8 334(10)	10 975(6)	1 893(6)
C(35)	7 800(9)	11 241(5)	2 376(6)
C(36)	6 688(8)	10 896(5)	2 398(5)
C(41)	6 840(8)	9 778(4)	3 956(5)
C(42)	6 292(9)	10 010(5)	4 455(5)
C(43)	6 933(13)	10 544(7)	4 989(6)
C(44)	8 112(13)	10 841(6)	5 020(7)
C(45)	8 656(10)	10 584(6)	4 532(7)
C(46)	8 040(8)	10 060(5)	4 008(5)
C(51)	7 168(8)	8 619(4)	3 027(5)
C(52)	8 294(9)	8 374(5)	3 613(5)
C(53)	9 213(9)	7 969(5)	3 493(6)
C(54)	9 022(10)	7 760(5)	2 766(6)
C(55)	7 925(10)	7 991(6)	2 190(6)
C(56)	6 996(9)	8 427(5)	2 300(5)
C(61)	5 163(9)	8 522(5)	3 610(5)
C(62)	5 872(10)	8 246(5)	4 349(5)
C(63)	5 279(13)	7 762(5)	4 642(6)
C(64)	3 986(14)	7 544(7)	4 242(8)
C(65)	3 311(11)	7 782(6)	3 549(8)
C(66)	3 901(9)	8 282(5)	3 220(6)
Cl(1C)	347(3)	12 538(2)	4 125(1)
O(1C)	-191(10)	12 380(6)	4 663(5)
O(2C)	-640(8)	12 673(5)	3 429(4)
O(3C)	1 083(13)	11 971(8)	4 052(7)
O(4C)	1 124(12)	13 145(7)	4 341(7)
O(1S)	1 512(8)	6 571(6)	4 705(4)

nitrosylruthenium complex (**9** or **10**).^{21,22,24} This assertion is consistent with previous studies conducted on nitroruthenium(II) complexes as well as the mechanisms proposed by Meyer and co-workers²⁴ and Mukaida and co-workers³⁸ for the decomposition of the electrochemically generated nitroruthenium(III) complexes.

The peak-current (i_{pc}/i_{pa}) ratios from the cyclic voltammograms of complexes **5–8** and **11–14** were measured by the method of Nicholson²⁸ at 25 ± 1 °C, with the results listed in Table 4. The (i_{pc}/i_{pa}) values for complexes **8** and **12** were determined at concentrations from 1–7 mmol dm⁻³ and were found to be independent of the concentration, consistent with a first-order electrode process.^{25,29}

Phosphine effects on redox stability

Nicholson and Shain²⁶ proposed that the cyclic voltammetric (i_{pc}/i_{pa}) ratio of a redox couple from a first-order EC system is a function of k , the first-order rate constant for the C step of the

mechanism. Since electrochemically generated nitroruthenium(III) complexes are proposed to decompose subsequent to the electron transfer,^{21,24,38} the cyclic voltammetric (i_{pc}/i_{pa}) ratio for complexes **5–8** and **11–14**, can be used to evaluate the first-order rate constants for the decomposition reaction occurring at the electrode surface. Our particular system involves an ECE mechanism, where the second E process involves the reduction of the nitrosylruthenium complex formed in the C step. Because the amount of the nitrosylruthenium decomposition product formed on the time-scale of the experiment is very small and the potential of the nitrosylruthenium couple is separated from the nitroruthenium couple by approximately 0.8 V, we assumed the contribution of this second E process (the nitrosylruthenium couple) to our results was negligible.³⁹

The first-order rate constants were evaluated using the appropriate working curves developed by Nicholson and Shain.²⁶ Our results (Table 4) indicate that the rate constant for the decomposition of the electrochemically generated nitroruthenium(III) complex decreases in the following order: **14** > **13** > **8** > **7** > **12** > **11** \approx **5** \approx **6**. The observed data were fitted to equation (1), where a , b and c are calculated

$$\ln k = aE + bS + c \quad (1)$$

coefficients, k is the observed first-order rate constant, E is a measure of the phosphine electronic effects and S is a measure of the phosphine steric effects. The E values considered for our analyses were: pK_a values,^{13,40} σ^* values^{16a} and Fourier-transform χ values.¹⁸ The actual E values used in our calculations were the mathematical averages of the values for both of the *trans* phosphine ligands. For the S values, the average cone angle, θ_{average} , of the two *trans* phosphine ligands,¹⁷ or the average E_R values²⁰ were used. The results for $E = pK_{a,\text{average}}$ and $S = \theta_{\text{average}}$ are: $a = -0.529 \pm 0.047$, $b = 0.0252 \pm 0.0076$, $c = -2.11 \pm 1.26$ and the plot $\ln k_{\text{obs}}$ versus $\ln k_{\text{calc}}$ was a straight line, with $r^2 = 0.981$. The results for $E = (\sum \sigma^*)_{\text{average}}$ and $S = \theta_{\text{average}}$ are: $a = 1.42 \pm 0.13$, $b = 0.0308 \pm 0.0073$, $c = -7.11 \pm 0.99$ and the plot $\ln k_{\text{obs}}$ versus $\ln k_{\text{calc}}$ was a straight line, with $r^2 = 0.981$. The results for $E = E_R^{\text{FTIR}}$ and $S = E_{R,\text{average}}$ are: $a = 0.382 \pm 0.050$, $b = 0.0420 \pm 0.0121$, $c = -8.35 \pm 0.64$ and the plot $\ln k_{\text{obs}}$ versus $\ln k_{\text{calc}}$ was a straight line, with $r^2 = 0.966$. The percent steric contributions were calculated from the change in $\ln k$ caused by the maximum change in the steric parameters at a constant, minimum electronic parameter while the electronic contributions were calculated from the change in $\ln k$ caused by the maximum change in the electronic parameters at a constant, minimum steric parameter.¹¹ Using the above data to calculate the relative ratio of steric to electronic contributions to $\ln k$ gives an average ratio of 30:70. For these data sets an increase in the size and an increase in the electron withdrawing ability of the ligands resulted in an increase in $\ln k$.

Meyer and co-workers²⁴ investigated the electrochemical oxidation of the *cis*-[Ru(bipy)₂L(NO₂)]ⁿ (bipy = 2,2'-bipyridine, $n = 1$, L = NH₃, pyridine, pyrazine, MeCN or PPh₃; $n = 0$, L = Cl) complexes while Mukaida and co-workers³⁸ investigated the electrochemical and chemical oxidation of the *trans*-[RuL₄(L')(NO₂)]ⁿ (L = pyridine or methylpyridine, $n = 1$, L' = H₂O; $n = 0$, L = Cl) complexes. Meyer proposed a mechanism for the decomposition of nitroruthenium(III) species,²⁴ which was subsequently corroborated and expanded upon by Mukaida.³⁸ In general, the mechanism involved a first-order linkage isomerization of the nitro ligand (k) followed by a second-order irreversible bimolecular reaction (k'). Meyer observed that the ligand (L) *cis* to the nitro ligand had an effect on k and k' . For example, when L = Cl the decomposition was a first-order reaction (k was the rate-determining step), but when L = pyridine the decomposition reaction was second order (k' was the rate-determining step). Meyer proposed that

Table 3 Interatomic distances (Å) and angles (°) for *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)] [ClO₄]-H₂O

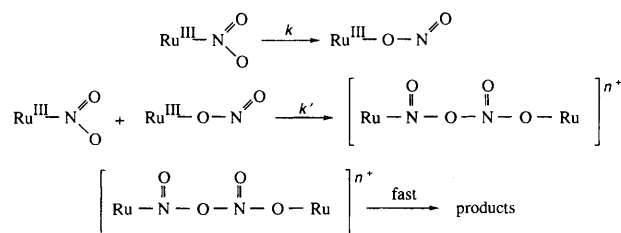
Ru-P(2)	2.458(2)	Ru-P(3)	2.347(2)	C(24)-C(25)	1.361(17)	C(25)-C(26)	1.405(13)
Ru-N(1)	2.067(7)	Ru-N(11)	2.112(8)	C(32)-C(33)	1.376(15)	C(33)-C(34)	1.385(15)
Ru-N(21)	1.979(6)	Ru-N(31)	2.081(8)	C(34)-C(35)	1.372(17)	C(35)-C(36)	1.395(14)
P(2)-C(41)	1.834(8)	P(2)-C(51)	1.841(10)	C(41)-C(42)	1.388(15)	C(41)-C(46)	1.387(13)
P(2)-C(61)	1.825(11)	P(3)-C(1)	1.806(10)	C(42)-C(43)	1.399(14)	C(43)-C(44)	1.390(20)
P(3)-C(2)	1.802(11)	P(3)-C(3)	1.808(12)	C(44)-C(45)	1.381(21)	C(45)-C(46)	1.370(13)
O(1)-N(1)	1.263(12)	O(2)-N(1)	1.230(11)	C(51)-C(52)	1.391(11)	C(51)-C(56)	1.387(14)
N(11)-C(12)	1.384(12)	N(11)-C(16)	1.351(11)	C(52)-C(53)	1.347(15)	C(53)-C(54)	1.389(17)
N(21)-C(22)	1.356(12)	N(21)-C(26)	1.328(13)	C(54)-C(55)	1.354(13)	C(55)-C(56)	1.380(16)
N(31)-C(32)	1.365(13)	N(31)-C(36)	1.342(10)	C(61)-C(62)	1.427(12)	C(61)-C(66)	1.372(12)
C(12)-C(13)	1.371(17)	C(12)-C(26)	1.460(13)	C(62)-C(63)	1.351(17)	C(63)-C(64)	1.390(18)
C(13)-C(14)	1.363(16)	C(14)-C(15)	1.363(19)	C(64)-C(65)	1.328(18)	C(65)-C(66)	1.411(18)
C(15)-C(16)	1.368(18)	C(22)-C(23)	1.379(12)	Cl(1C)-O(1C)	1.411(13)	Cl(1C)-O(2C)	1.385(7)
C(22)-C(36)	1.475(15)	C(23)-C(24)	1.387(18)	Cl(1C)-O(3C)	1.361(15)	Cl(1C)-O(4C)	1.369(13)
P(2)-Ru-P(3)	177.5(1)	P(2)-Ru-N(1)	94.3(2)	N(21)-C(22)-C(23)	118.8(9)	N(21)-C(22)-C(36)	113.2(7)
P(3)-Ru-N(1)	86.0(2)	P(2)-Ru-N(11)	94.0(2)	C(23)-C(22)-C(36)	127.9(9)	C(22)-C(23)-C(24)	120.5(10)
P(3)-Ru-N(11)	88.4(2)	N(1)-Ru-N(11)	100.1(3)	C(23)-C(24)-C(25)	118.9(10)	C(24)-C(25)-C(26)	119.9(12)
P(2)-Ru-N(21)	89.9(2)	P(3)-Ru-N(21)	89.8(2)	N(21)-C(26)-C(12)	115.2(8)	N(21)-C(26)-C(25)	119.5(9)
N(1)-Ru-N(21)	175.7(2)	N(11)-Ru-N(21)	78.7(3)	C(12)-C(26)-C(25)	125.3(10)	N(31)-C(32)-C(33)	122.8(8)
P(2)-Ru-N(31)	88.9(2)	P(3)-Ru-N(31)	88.7(2)	C(32)-C(33)-C(34)	118.5(11)	C(33)-C(32)-C(35)	120.0(11)
N(1)-Ru-N(31)	102.3(3)	N(11)-Ru-N(31)	157.1(3)	C(34)-C(35)-C(36)	118.3(9)	N(31)-C(36)-C(22)	114.9(8)
N(21)-Ru-N(31)	78.6(3)	Ru-P(2)-C(41)	108.6(3)	N(31)-C(36)-C(35)	123.1(9)	C(22)-C(36)-C(35)	121.9(8)
Ru-P(2)-C(51)	117.5(3)	C(41)-P(2)-C(51)	104.1(4)	P(2)-C(41)-C(42)	119.8(7)	P(2)-C(41)-C(46)	120.3(8)
Ru-P(2)-C(61)	119.5(3)	C(41)-P(2)-C(61)	103.3(4)	C(42)-C(41)-C(46)	119.6(8)	C(41)-C(42)-C(43)	119.7(10)
C(51)-P(2)-C(61)	102.0(4)	Ru-P(3)-C(1)	114.5(4)	C(42)-C(43)-C(44)	120.2(13)	C(43)-C(44)-C(45)	118.8(10)
Ru-P(3)-C(2)	114.7(3)	C(1)-P(3)-C(2)	103.6(6)	C(44)-C(45)-C(46)	121.5(11)	C(41)-C(46)-C(45)	120.1(11)
Ru-P(3)-C(3)	115.2(3)	C(1)-P(3)-C(3)	103.5(5)	P(2)-C(51)-C(52)	122.9(8)	P(2)-C(51)-C(56)	119.1(6)
C(2)-P(3)-C(3)	104.0(6)	Ru-N(1)-O(1)	122.5(6)	C(52)-C(51)-C(56)	118.0(9)	C(51)-C(52)-C(53)	122.1(10)
Ru-N(1)-O(2)	122.2(7)	O(1)-N(1)-O(2)	115.3(7)	C(52)-C(53)-C(54)	119.8(8)	C(53)-C(54)-C(55)	118.7(11)
Ru-N(11)-C(12)	112.8(6)	Ru-N(11)-C(16)	129.1(7)	C(54)-C(55)-C(56)	122.3(11)	C(51)-C(56)-C(55)	119.0(8)
C(12)-N(11)-C(16)	118.1(9)	Ru-N(21)-C(22)	118.6(6)	P(2)-C(61)-C(62)	121.7(7)	P(2)-C(61)-C(66)	119.7(7)
Ru-N(21)-C(26)	119.0(6)	C(22)-N(21)-C(26)	122.3(7)	C(62)-C(61)-C(66)	118.6(9)	C(61)-C(62)-C(63)	119.2(9)
Ru-N(31)-C(32)	128.0(5)	Ru-N(31)-C(36)	114.6(7)	C(62)-C(63)-C(64)	121.0(10)	C(63)-C(64)-C(65)	121.1(14)
C(32)-N(31)-C(36)	117.3(8)	N(11)-C(12)-C(13)	119.4(8)	C(64)-C(65)-C(66)	119.5(11)	C(61)-C(66)-C(65)	120.5(9)
N(11)-C(12)-C(26)	114.2(9)	C(13)-C(12)-C(26)	126.4(8)	O(1C)-Cl(1C)-O(2C)	110.8(6)	O(1C)-Cl(1C)-O(3C)	110.8(8)
C(12)-C(13)-C(14)	122.1(11)	C(13)-C(14)-C(15)	118.0(13)	O(2C)-Cl(1C)-O(3C)	108.2(7)	O(1C)-Cl(1C)-O(4C)	109.6(8)
C(14)-C(15)-C(16)	120.4(10)	N(11)-C(16)-C(15)	122.0(9)	O(2C)-Cl(1C)-O(4C)	108.2(6)	O(3C)-Cl(1C)-O(4C)	109.2(9)

Table 4 The i_{pc}/i_{pa} and k values for complexes **5–8** and **11–14**, and E_1 potentials for complexes **1–14** in acetonitrile^a

Complex	E_1/V (vs. SSCE)	$i_{pc}/i_{pa}^{b,c}$	$10^{-2} k/s^{-1c}$
1 [RuCl(terpy)(PEt ₃)(PMe ₃)] [ClO ₄]	+0.70		
2 [RuCl(terpy)(PMe ₃)(PPr ₃)] [ClO ₄]	+0.74		
3 [RuCl(terpy)(PBz ₃)(PMe ₃)] [ClO ₄]	+0.83		
4 [RuCl(terpy)(PMe ₃)(PPh ₃)] [ClO ₄]	+0.85		
5 [Ru(NO ₂)(terpy)(PEt ₃)(PMe ₃)] [ClO ₄]	+1.04	0.952 ± 0.003	2.65 ± 0.16
6 [Ru(NO ₂)(terpy)(PMe ₃)(PPr ₃)] [ClO ₄]	+1.05	0.938 ± 0.004	2.68 ± 0.16
7 [Ru(NO ₂)(terpy)(PBz ₃)(PMe ₃)] [ClO ₄]	+1.13	0.876 ± 0.009	8.89 ± 0.69
8 [Ru(NO ₂)(terpy)(PMe ₃)(PPh ₃)] [ClO ₄]	+1.24 ^d	0.702 ± 0.021	23.8 ± 1.29
9 [Ru(NO)(terpy)(PEt ₃)(PMe ₃)] [ClO ₄] ₃	+0.26		
10 [Ru(NO)(terpy)(PMe ₃)(PPr ₃)] [ClO ₄] ₃	+0.26		
11 [Ru(NO ₂)(terpy)(PEt ₃)] [ClO ₄]	+1.04 ^e	0.936 ± 0.003	2.82 ± 0.17
12 [Ru(NO ₂)(terpy)(PPr ₃) ₂] [ClO ₄]	+1.05 ^e	0.905 ± 0.002	3.84 ± 0.88
13 [Ru(NO ₂)(terpy)(PBz ₃) ₂] [ClO ₄]	+1.17 ^e	0.666 ± 0.006	34.0 ± 1.44
14 [Ru(NO ₂)(terpy)(PPh ₃) ₂] [ClO ₄]	+1.22 ^{d,e}	0.472 ± 0.006	88.1 ± 2.02

^a Conditions: 0.1 mol dm⁻³ NEt₄ClO₄ or 0.1 mol dm⁻³ NBu₄BF₄ in MeCN; Pt working electrode; SSCE reference electrode; scan rate 100 mV s⁻¹; ΔE_p range 0.07–0.08V for each complex. ^b The average value obtained for the peak current ratios with a minimum accuracy of 1% (see ref. 27) is reported. ^c Uncertainties are described as 95% confidence intervals. A minimum of five separate measurements were made for each value. ^d Couple is irreversible, E_{pa} value reported. ^e Data from ref. 22.

the nitro-to-nitrito conversion of the ruthenium(III) complexes might involve a ruthenium(II) five-co-ordinate intermediate, and that ruthenium(II) is better stabilized by pyridine than chloride, while ruthenium(III) is better stabilized by chloride than pyridine.²⁴ Thus, the rate of nitro-to-nitrito conversion is enhanced by pyridine, relative to chloride. Mukaida noted that the spectator ligand (*L'*) *trans* to the nitro ligand had an effect on the rate constants involved in the decomposition reaction as well, although he was not specific regarding the nature of the ligand effect.³⁸ However, in both of these studies, there was no discussion of steric ligand effects and little quantitative discussion of electronic ligand effects on the decomposition of nitroruthenium(III) complexes. For this study, we utilized the

**Scheme 2**

general mechanisms of Meyer and of Mukaida to generate Scheme 2, which we will employ to aid us in the interpretation of our data.

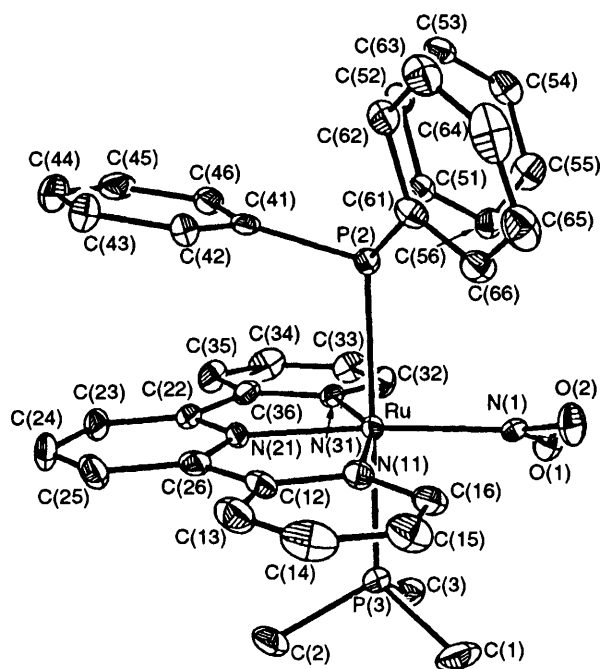


Fig. 1 Geometry of the *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)⁺ cation. ORTEP II⁴³ diagram, 20% probability envelopes for the vibration ellipsoids, all hydrogen atoms omitted for clarity

Three different aspects of our electrochemical data lead us to propose that the rate constants listed in Table 4 correspond to *k* from Scheme 2, the rate constant for the linkage isomerization of the nitro ligand. First, we determined that the C step of our ECE mechanism for complexes **8** and **12** is a first-order reaction, which is consistent with the C step involving the nitro–nitrito interconversion. Secondly, we do not observe the formation of any nitroruthenium complexes in our electrochemical experiments, which suggests that the nitro–nitrito interconversion is rate determining. Thirdly, as the electron-donating abilities of the phosphine ligands increase, the rate constants for the isomerization of the nitro ligand (*k*) decrease. This electronic ligand effect is evident in the negative sign of *a*, the coefficient of the electronic term in equation (1), when $E = pK_a$ (as electron-donating ability increases, pK_a increases) and a positive sign of *a* when $E = \sigma^*$ and ${}^{\text{FT}}\chi$ (as electron-donating ability decreases, σ^* and ${}^{\text{FT}}\chi$ decrease). Since these electronic ligand effects are in agreement with Meyer's assertions regarding the chemistry of *cis*-[Ru(bipy)₂Cl(NO₂)], we suggest that the mechanism of decomposition of complexes **5–8** and **11–14** is reminiscent of the mechanism suggested by Meyer for the decomposition of *cis*-[Ru(bipy)₂Cl(NO₂)] (see above).

The use of tertiary phosphines in this study allows us to examine the combined steric and electronic ligand effects on the rate of nitroruthenium(III) decomposition. The analyses of the data in Table 4 with equation (1) indicate that the ratio of steric to electronic ligand effects on the value of $\ln k$ is *ca.* 30:70. In addition to the electronic ligand effects discussed above, the steric ligand effect on the rate constant of isomerization demonstrates that the size of the *cis*-positioned spectator ligands does influence the redox stability of the nitroruthenium moiety, where an increase in the size of the ligand results in a reduction of redox stability, illustrated by an increase in the value of $\ln k$. This observation is consistent with other linkage isomerization studies, where linkage isomerizations, including the nitro–nitrito isomerization,^{41,42} can be quite sensitive to the steric requirements of the adjacent ligands, where a sterically crowded centre favours the nitrito isomer.

Description of the molecular structure of *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)]⁺[ClO₄]⁻·H₂O

The crystal is composed of an ordered array of *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)⁺ cations, ClO₄⁻ anions and water of crystallization in a 1:1:1 ratio. The *trans*-[Ru(NO₂)(terpy)(PMe₃)(PPh₃)⁺ cation is illustrated in Fig. 1. Interatomic distances and angles are collected in Table 3.

The central Ru^{II} ion is in a distorted octahedral co-ordination geometry. The terpy ligand takes up the expected meridional geometry with the nitro ligand lying in the same plane. The ruthenium–nitrogen distances for the terpy ligand are Ru–N(11) = 2.112(8) and Ru–N(31) 2.081(8) (for the two terminal nitrogen atoms) and Ru–N(21) = 1.979(6) Å (for the central nitrogen atom). The distortions caused by the tridentate terpy ligand are made evident by the angles at the Ru^{II} centre: *viz.* N(11)–Ru–N(21) = 78.7(3), N(21)–Ru–N(31) = 78.6(3) (each reduced by 11.3–11.4° from the idealized *cis* angle of 90°) and N(11)–Ru–N(31) = 157.1(3)° (reduced by 22.9° from the idealized *trans* angle of 180°).

The nitro ligand is associated with the bond length Ru–N(1) = 2.067(7) Å, with N–O distances of 1.263(12) and 1.230(11) Å and with an O(1)–N(1)–O(2) angle of 115.3(7)°. The two phosphine ligands lie *trans* to one another, with P(2)–Ru–P(3) 177.5(1)°. The trimethylphosphine ligand [Ru–P(3) 2.347(2) Å] is associated with a ruthenium–phosphorus distance that is substantially shorter than that for the triphenylphosphine ligand [Ru–P(2) 2.458(2) Å].

The mean deviation of constituent atoms from the Ru–N(11)–N(21)–N(31) plane is 0.023 Å, indicating that the Ru(terpy) moiety is essentially planar. Atom N(1) of the NO₂ group, is displaced from the Ru(terpy) plane by 0.088 Å in a direction towards the PMe₃ ligand. In addition, the NO₂ ligand makes an angle of 24.0° with the Ru(terpy) plane.

In summary, the first ²*J*(PP) values and the first single-crystal X-ray structure for mixed *trans*-positioned, monodentate, tertiary phosphine ruthenium complexes were obtained. Rate constants of decomposition (*k*) of electrochemically generated nitroruthenium(III) complexes were determined from cyclic voltammetric $i_{\text{pc}}/i_{\text{pa}}$ ratios and a ratio (*ca.* 30:70) of steric-to-electronic phosphine ligand effects on $\ln k$ was calculated from a three parameter fit. Notably, this is the first quantification of ligand effects on the redox stability of nitroruthenium(III) complexes. Due to the mixed nature of the *trans*-positioned phosphine ligands, it was possible to measure the ²*J*(PP) values and it was also possible to discover the summative nature of the steric and electronic ligand effects of *trans*-positioned phosphine ligands on the values of $\ln k$.

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