Direct nitration of aryl groups σ-bound to ruthenium(II)

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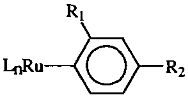
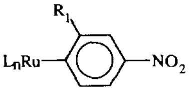
Abstract

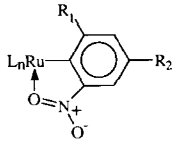
A new method has been developed for the preparation of nitroaryl transition metal complexes using copper(II) nitrate in the presence of acetic anhydride (Menke conditions) to directly nitrate an aryl group which is already σ-bound to a transition metal centre. Under these conditions ruthenium(II) aryl complexes of the type:



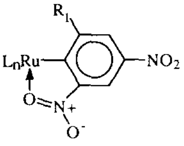
(where $R_1=R_2=H$; $R_1=H$, $R_2=CH_3$; $R_1=CH_3$, $R_2=H$) react to yield three distinct types of nitroaryl-containing products (**I–III**).



I
(R_1 = H, CH3)



II
(R_1 = H; R_2 = H, CH3)
(R_1 = CH3; R_2 = H)



III
(R_1 = H, CH3)

The preparation and characterisation of these compounds are described. X-ray crystallographic data for one example of each of the three types of compound, are also reported. The compounds that have been studied crystallographically are $Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ (**1a**), $C_{45}H_{37}NO_5P_2Ru\cdot(CH_2Cl_2)_{0.5}$, $a=20.254(5)$, $b=19.437(8)$, $c=22.629(3)$ Å, $\beta=115.390(10)°$, monoclinic, space group $C2/c$, $Z=8$; $\overline{Ru(C_6H_4N[O]O}\text{-}2)Cl(CO)(PPh_3)_2$ (**4a**), $C_{43}H_{34}ClNO_3P_2Ru$, $a=9.331(3)$, $b=12.443(2)$, $c=16.346(3)$ Å, $\alpha=82.81(2)$, $\beta=85.03(2)$, $\gamma=74.76(2)°$, triclinic, space group $P\bar{1}$, $Z=2$; $\overline{Ru(C_6H_2CH_3\text{-}2,NO_2\text{-}4,N[O]O}\text{-}6)Cl(CO)(PPh_3)_2$ (**5b**), $C_{44}H_{35}ClN_2O_5P_2Ru\cdot(CH_2Cl_2)_2$, $a=19.497(3)$, $b=14.502(3)$, $c=19.340(5)$ Å, $\beta=122.79(1)°$, monoclinic, space group Cc, $Z=4$.

Key words: Crystal structures; Ruthenium complexes; Aryl complexes; Nitro complexes; Nitration reaction

Introduction

There is at present, in organometallic chemistry, a general interest in the use of aryl groups functionalised with reactive substituents, as ligands for transition metals [1]. One reason for this is the possibility of modifying the reactive substituent into another functionality which is amenable to the construction of more complex ligand systems. In this regard, nitroaryls are particularly appealing because of the already well established organic chemistry for the conversion of an aryl nitro group into an aryl amino group [2].

To date, only a limited number of transition metal complexes containing nitroaryl ligands has been reported in the literature. Most have been synthesised using transmetalation reagents (e.g. organotin [3], organolithium [3, 4] and organomercury compounds [5, and refs. therein]) to transfer one or more nitroaryl groups to a suitable transition metal containing substrate. Other examples have been synthesised by methods which

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include the direct reaction of a nitroaryl with a metal halide [6], the oxidative addition of nitroaryl halides [7] and 2,2-diphenyl-1-picrylhydrazyl [8] to low-valent transition metal centres, and the reaction of 4-nitrophenylhydrazine with a metal halide [9].

To our knowledge, no report has appeared considering the use of direct nitration of an aryl group which is already σ-bound to a transition metal centre, as a method for preparing a nitroaryl-containing complex. In organic chemistry the use of copper(II) nitrate in the presence of acetic anhydride (Menke conditions [10]) as a nitrating medium for aromatics which are reactive and acid-sensitive is well known [11]. In this paper, we present preliminary details of our use of this method to prepare nitroaryl complexes through the direct and regioselective nitration of the σ-bound aryl group in several ruthenium(II) complexes.

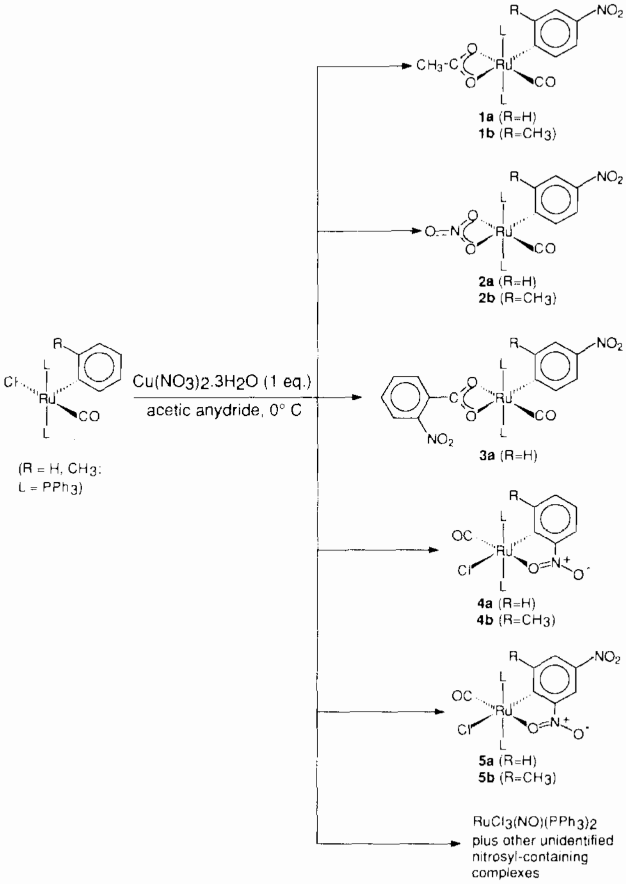
Experimental

Analytical data were obtained from the Microanalytical Laboratory, University of Otago. IR spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS-7 spectrometer as KBr discs. ^1H NMR spectra (in $CDCl_3$) were recorded on a Bruker AC 200 spectrometer. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Ruthenium trichloride was obtained commercially from Johnson Matthey Chemicals Ltd. and $Ru(C_6H_5)Cl(CO)(PPh_3)_2$, $Ru(C_6H_4CH_3\text{-}2)Cl(CO)(PPh_3)_2$ and $Ru(C_6H_4CH_3\text{-}4)Cl(CO)(PPh_3)_2$ were prepared as in ref. 12. Except where specifically mentioned, the following preparations were carried out in undried solvents without special precautions to exclude oxygen.

$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ *(1a)*

Acetic anhydride (12 ml) and finely ground copper(II) nitrate 3-hydrate (0.310 g, 1.28 mmol) were added to a flask which was cooled in an ice bath and had been purged with N_2 (gas) for 10 min. The mixture was stirred for 15 min. $Ru(C_6H_5)Cl(CO)(PPh_3)_2$ (1.00 g, 1.31 mmol) was then added and the resulting slurry stirred at 0 °C for 2 h. After this time, the ice bath was removed and the dark green suspension which had formed was stirred for a further 1 h as it warmed up to room temperature. A mixture of sodium acetate (1 g) dissolved in water (30 ml) and ice (30 g) was then added. A yellow oil separated out and this solidified during the 2 h in which the two phase system was then stirred. Filtration and washing with water gave a dark yellow solid which was dried under vacuum at room temperature (0.905 g). This solid was a mixture of several nitroaryl-containing complexes as well as $RuCl_3(NO)(PPh_3)_2$ and some other unidentified nitrosyl complexes (see Scheme 1). Chromatography on a silica gel column (3.5 × 6 cm) using dichloromethane as eluant effected partial separation of these compounds as follows below. $RuCl_3(NO)(PPh_3)_2$ (identified by comparison with an authentic sample [13]) was present as an impurity in all fractions of the column, but its removal from samples could be effected by repeated fractional crystallisation or by further column chromatography of the crude samples on a second much longer silica gel column (e.g. 2.5 × 20 cm) using dichloromethane as eluant.

(i) The first coloured band to elute (a dark yellow band) yielded a yellow solid. After crystallisation with ethanol/heptane, this was found to be a mixture (~50:50) of $Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2$ (**2a**) and $Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CC_6H_4NO_2\text{-}2)(CO)(PPh_3)_2$ (**3a**), 0.325 g, ~28%. The two components of this mixture proved to be inseparable by further column



Scheme 1. Products obtained from the reaction of the σ-aryl complexes $RuArCl(CO)(PPh_3)_2$ ($Ar = C_6H_5$, $C_6H_4CH_3\text{-}2$) with 1 mole equivalent of $Cu(NO_3)_2 \cdot 3H_2O$ in acetic anhydride at 0 °C. Reaction conditions which maximise specific products are given in 'Experimental'. (Note that the particular depiction of the chelating nitrophenyl ligand given for **4a,b** and **5a,b** is only one of several possible valence bond structures and was chosen for convenience rather than to indicate relative bond distances.)

chromatography or fractional crystallisation. Crystals of each compound were morphologically different (**2a**, plates and **3a**, needles) and so small, pure samples of each were obtained by mechanical sorting. Using these small samples the characterisations of **2a** and **3a** were confirmed by comparison of their IR and ^{1}H NMR spectra with those from larger authentic samples of each produced by converting the mixture initially obtained into either **2a** or **3a** (see below).

(ii) The second coloured band to elute was also a dark yellow in colour and this gave the bright yellow product $Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ (**1a**, 0.140 g, 13%) after crystallisation with ethanol/heptane. Crystallisation of an analytically pure sample from dichloromethane/ethanol afforded fluorescent yellow plates containing 0.5 mol dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 208–211 (dec.) °C. *Anal.* Found: C, 61.97; H, 4.29; N, 1.67. Calc. for $C_{45}H_{37}NO_5P_2Ru \cdot (CH_2Cl_2)_{0.5}$: C, 62.29; H, 4.37; N, 1.60%. Crystals suitable for X-ray diffraction were grown from dichloromethane/ethanol.

(iii) The third coloured band was dark purple and was much slower to elute. A purple solid (~0.01 g) was isolated after addition of heptane. Fractional recrystallisation of the sample from dichloromethane/ethanol yielded dark brown needles of $\overline{Ru(C_6H_4N[O]O}\text{-}2)Cl(CO)(PPh_3)_2$ (**4a**, 0.004 g, <1%).

(iv) In some preparations small quantities of $\overline{Ru(C_6H_4N[O]O}\text{-}2, NO_2\text{-}4)Cl(CO)(PPh_3)_2$ (**5a**) also formed in the reaction mixture. When this occurred it was very difficult to separate **5a** totally from **1a** using column chromatography on silica gel as the bands for these two complexes always overlapped to some extent, even on quite a long column (~25 cm). Because **1a** eluted partially ahead of **5a**, a clean sample of **1a** could usually be obtained (although in reduced yield), but samples of **5a** were generally contaminated with **1a**. Such 'contaminated' fractions were usually saved and combined with similar fractions from other preparations for further purification later when sufficient of such material had been accumulated.

$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2$ (2a)

A sample of the mixture containing **2a** and **3a** (0.175 g), obtained after the initial chromatography in the preparation of **1a** above, was dissolved in a solution of dichloromethane (20 ml) and ethanol (5 ml). Addition of a drop of concentrated nitric acid was immediately followed by the removal of the dichloromethane under reduced pressure. The yellow–orange product which crystallised was filtered off and washed with ethanol and hexane. The small amount of $RuCl_3(NO)(PPh_3)_2$ present was removed by chromatography on a silica gel column (2.5 × 20 cm) with dichloromethane as eluant. The dark yellow band was collected and on the addition of ethanol a yellow–orange solid was obtained (0.150 g). Recrystallisation from dichloromethane/ethanol afforded an analytically pure sample of **2a** as thin yellow–orange plates containing 0.33 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 190–193 (dec.) °C. *Anal.* Found: C, 60.03; H, 3.78; N, 3.24. Calc. for $C_{43}H_{34}N_2O_6P_2Ru \cdot (CH_2Cl_2)_{0.33}$: C, 60.09; H, 4.03; N, 3.24%.

$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CC_6H_4NO_2\text{-}2)(CO)(PPh_3)_2$ (3a)

A sample of the mixture containing **2a** and **3a** (0.100 g), obtained after the initial chromatography in the preparation of **1a** above, was dissolved in a solution of dichloromethane (10 ml) and ethanol (5 ml). A solution of sodium 2-nitrobenzoate (0.100 g) dissolved in water (2 ml) and ethanol (5 ml) was added. Reduction of the solvent volume gave **3a** (along with a trace of $RuCl_3(NO)(PPh_3)_2$) as a lemon coloured solid which was filtered off and washed with water before drying under vacuum at room temperature (0.100 g). Fractional recrystallisation of a sample for analysis from dichloromethane/ethanol afforded fluorescent yellow needles of **3a** containing 0.125 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 180–182 (dec.) °C. *Anal.* Found: C, 63.22; H, 3.86; N, 2.82. Calc. for $C_{50}H_{38}N_2O_7P_2Ru \cdot (CH_2Cl_2)_{0.125}$: C, 63.21; H, 4.05; N, 2.94%.

$\overline{Ru(C_6H_4N[O]O}\text{-}2)Cl(CO)(PPh_3)_2$ (4a)

The preparation of this complex was described in the preparation of **1a** above. Fractional recrystallisation of the sample from dichloromethane/ethanol yielded dark brown needles of **4a** (0.004 g, <1%), m.p. >350 °C. As yet insufficient material has been isolated for an elemental analysis or for an adequate ^{1}H NMR spectrum to be obtained. Crystals obtained by recrystallisation of the sample from dichloromethane/ ethanol were suitable for X-ray diffraction (see later).

$\overline{Ru(C_6H_3N[O]O}\text{-}2, NO_2\text{-}4)Cl(CO)(PPh_3)_2$ (5a)

$Ru(C_6H_5)Cl(CO)(PPh_3)_2$ (0.200 g, 0.261 mmol) was treated with a solution of acetic anhydride (8 ml) and copper(II) nitrate 3-hydrate (0.252 g, 1.04 mmol) as described for the preparation of **1a** above. After the reaction mixture warmed up to room temperature, the dark red suspension which had formed was treated with a mixture of sodium acetate (0.6 g) dissolved in water (24 ml) and ice (24 g). A dark red oil separated out and this solidified during the 2 h in which the two phase system was then stirred. Filtration and washing with water gave a dark red–brown solid which was dried under vacuum at room temperature. The crude product was purified by chromatography on a silica gel column (3.5×6 cm) using dichloromethane as eluant. The dark red band was collected and on addition of hexane gave **5a** as a dark red–brown crystalline solid

(0.070 g, 31%). Recrystallisation of a sample for analysis from dichloromethane/ethanol gave dark red–brown needles containing 0.125 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 231–233 °C. *Anal.* Found: C, 59.35; H, 4.13; N, 3.18. Calc. for $\mathrm{C_{43}H_{33}ClN_2O_5P_2Ru \cdot (CH_2Cl_2)_{0.125}}$: C, 59.75; H, 3.87; N, 3.23%.

$\mathrm{Ru(C_6H_3CH_3\text{-}2,\ NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2}$ (**1b**)

$\mathrm{Ru(C_6H_4CH_3\text{-}2)Cl(CO)(PPh_3)_2}$ (1.00 g, 1.28 mmol) was treated in a similar manner to $\mathrm{Ru(C_6H_5)Cl(CO)(PPh_3)_2}$ as described in the preparation of **1a** above. After treatment with a mixture of sodium acetate (5.0 g) dissolved in water (30 ml) and ice (30 g), a crude product containing a mixture of compounds analogous to those formed in the preparation of **1a** was isolated (0.930 g). Chromatography on a silica gel column (3.5×6 cm) using dichloromethane as eluant effected some separation of these compounds.

(i) The first coloured band to elute (an orange band) yielded a yellow solid (0.080 g) after crystallisation with ethanol/heptane. This product was a mixture and its components proved to be inseparable by further column chromatography or fractional crystallisation. One of the components present was identified as the η^2-$\mathrm{NO_3}$ containing complex $\mathrm{Ru(C_6H_3CH_3\text{-}2,\ NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2}$ (**2b**) from the distinctive IR band for such complexes at ~1240 cm^{-1}. Recrystallisation of the mixed product in the presence of nitric acid effected total conversion of the mixture to this product (see below). The identity of the other components in the initial mixture remains unresolved. From ^{1}H NMR and IR spectra the compounds appear to be various methyl nitrobenzoate analogues of **3a**.

(ii) The second coloured band to elute (a dark yellow colour) gave, after crystallisation with ethanol/heptane, **1b** (0.450 g, 41%) as bright yellow crystals. Recrystallisation from dichloromethane/ethanol gave an analytically pure sample as large bright yellow needles of **1b** containing 1 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 130–132 °C. *Anal.* Found: C, 60.51; H, 4.29; N, 1.45. Calc. for $\mathrm{C_{46}H_{39}NO_5P_2Ru \cdot CH_2Cl_2}$: C, 60.45; H, 4.43; N, 1.50%.

(iii) The third coloured band was dark purple and was much slower to elute. A purple solid (~0.003 g) was isolated with heptane. Fractional recrystallisation of the sample from dichloromethane/ethanol yielded dark brown needles of $\mathrm{\overline{Ru(C_6H_3CH_3\text{-}2,N[O]O}\text{-}6)Cl(CO)(PPh_3)_2}$ (**4b**, 0.001 g, <1%).

(iv) In some preparations small quantities of $\mathrm{\overline{Ru(C_6H_3CH_3\text{-}2,NO_2\text{-}4,N[O]O}\text{-}6)Cl(CO)(PPh_3)_2}$ (**5b**) also formed in the reaction mixture. When this occurred it was as difficult to separate as **5a** was in the preparation of **1a** above, and it was accordingly dealt with in a similar manner.

$\mathrm{Ru(C_6H_3CH_3\text{-}2,\ NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2}$ (**2b**)

A sample of the mixture containing **2b** (0.150 g), obtained after the initial chromatography in the preparation of **1b** above, was dissolved in a solution of dichloromethane (20 ml) and ethanol (5 ml). Addition of a drop of concentrated nitric acid was immediately followed by the removal of the dichloromethane. The yellow product which crystallised was filtered off and washed with ethanol and hexane. The small amount of $\mathrm{RuCl_3(NO)(PPh_3)_2}$ present was removed by fractional crystallisation of the product. Recrystallisation from dichloromethane/ethanol afforded an analytically pure sample as fluorescent yellow plates of **2b** containing 0.5 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 163–167 (dec.) °C. *Anal.* Found: C, 60.04; H, 4.05; N, 3.12. Calc. for $\mathrm{C_{44}H_{36}N_2O_6P_2Ru \cdot (CH_2Cl_2)_{0.5}}$: C, 59.79; H, 4.17; N, 3.13%.

$\mathrm{\overline{Ru(C_6H_3CH_3\text{-}2,\ N[O]O}\text{-}6)Cl(CO)(PPh_3)_2}$ (**4b**)

The preparation of this complex was described in the preparation of **1b** above. Fractional recrystallisation of the sample from dichloromethane/ethanol yielded dark brown needles of **4b** (0.001 g, <1%), m.p. >350 °C. As yet insufficient material has been isolated for an elemental analysis or for an ^{1}H NMR spectrum to be obtained.

$\mathrm{\overline{Ru(C_6H_2CH_3\text{-}2,\ NO_2\text{-}4,\ N[O]O}\text{-}6)Cl(CO)(PPh_3)_2}$ (**5b**)

$\mathrm{Ru(C_6H_4CH_3\text{-}2)Cl(CO)(PPh_3)_2}$ (0.200 g, 2.56 mmol) was treated in a similar manner to $\mathrm{Ru(C_6H_5)Cl(CO)(PPh_3)_2}$ above in the preparation of **5a** to give **5b** as a dark red–brown crystalline solid (0.092 g, 40%) after chromatography. Recrystallisation of a sample for analysis from dichloromethane/ethanol gave dark red–brown needles containing 0.5 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 174–177 (dec.) °C. *Anal.* Found: C, 58.88; H, 4.38; N, 3.04. Calc. for $\mathrm{C_{44}H_{35}ClN_2O_5P_2Ru \cdot (CH_2Cl_2)_{0.5}}$: C, 58.56; H, 3.98; N, 3.07%. Crystals suitable for X-ray diffraction were grown from dichloromethane/deuterated chloroform/ethanol.

$\mathrm{\overline{Ru(C_6H_3CH_3\text{-}4,\ N[O]O}\text{-}2,)Cl(CO)(PPh_3)_2}$ (**4c**)

$\mathrm{Ru(C_6H_4CH_3\text{-}4)Cl(CO)(PPh_3)_2}$ (0.200 g, 0.261 mmol) was treated with a solution of acetic anhydride (8 ml) and copper(II) nitrate 3-hydrate (0.062 g, 0.257 mmol) as described for the preparation of **1a** above. After the reaction mixture warmed up to room temperature, the purple suspension which had formed was treated with a mixture of sodium acetate (0.6 g) dissolved in water (24 ml) and ice (24 g). A dark purple oil separated out and this solidified during the 2 h in which the two phase system was then stirred. Collecting by filtration and washing with water gave a purple solid which was dried under vacuum at room temperature. The crude product was purified by chromatography on a silica gel column (3.5×6 cm) using dichloromethane as eluant. The purple band was collected and on addition of hexane gave **4c** as a dark purple crystalline solid (0.130 g, 31%). Recrystallisation of a sample for analysis from dichloromethane/ethanol gave dark red–brown needles of **4c** containing 0.25 mol of dichloromethane of solvation (confirmed by ^{1}H NMR), m.p. 259–261 °C. *Anal.* Found: C, 62.88; H, 4.18; N, 1.55. Calc. for $C_{43}H_{33}ClN_2O_5P_2Ru\cdot(CH_2Cl_2)_{0.25}$: C, 62.79; H, 4.35; N, 1.66 %.

Structure determinations

Crystal structures were determined for compounds **1a**, **4a** and **5b**. Intensity data were collected with $\omega/2\theta$ scans on a Nonius CAD-4 diffractometer using graphite-monochromated X-rays. Empirical absorption corrections [14] were applied for **1a** and **4a**, but no corrections were deemed necessary for **5b**. A summary of the crystal data is given in Table 1. The structures of **1a** and **4a** were solved by conventional Patterson and electron density maps. The structure of **5b** was much more difficult to solve because of false symmetry in the early maps.

Phenyl hydrogen atoms were included in calculated positions (C–H 0.95 Å) assuming the riding model, with isotropic temperature factors set to 1.2 times those of the attached atoms. The preferred orientation of the methyl group in **5b** was derived from a difference electron density map.

Intensity statistics, structure solution and subsequent satisfactory refinement confirmed the choice of the three space groups. Final positions for non-hydrogen atoms are listed in Tables 2, 3 and 4. See also 'Supplementary material'.

Results and discussion

Reaction of the σ-aryl complexes $RuArCl(CO)(PPh_3)_2$ ($Ar=C_6H_5$, $C_6H_4CH_3$-2) with one mole equivalent of copper(II) nitrate in acetic anhydride at 0 °C leads to the formation of a number of nitroaryl-containing products (see Scheme 1). Separation of most of these from the crude reaction mixture is effected by column chromatography on silica gel with dichloromethane as eluant (see 'Experimental' for details).

Complexes **1–3** for each of the aryl ligands are analogues of each other—varying only by the nature of the bidentate ligand present and as such are interconvertible (within each aryl ligand set) under metathesis reaction conditions. The IR spectra of these complexes all show a strong band in the 1325–1345 cm^{-1} region which has been assigned to the $\nu_{sym}(NO_2)$ mode of a σ-bound aryl nitro group in which the oxygen atoms of the nitro group are free of any direct bonding interaction with the metal centre [5i]. The $\nu_{asym}(NO_2)$

TABLE 1. Crystal data, intensity data collection and structure refinement parameters

Compound	**1a**	**4a**	**5b**
Empirical formula	$C_{45}H_{37}NO_5P_2Ru\cdot0.5CH_2Cl_2$	$C_{43}H_{34}ClNO_3P_2Ru$	$C_{44}H_{35}ClN_2O_5P_2Ru\cdot2CH_2Cl_2$
Formula weight	877.23	811.17	1040.05
Temperature (K)	193(2)	193(2)	298(2)
Wavelength (Å)	0.71070	0.71070	0.71070
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*Cc*
a (Å)	20.254(5)	9.331(3)	19.497(3)
b (Å)	19.437(8)	12.443(2)	14.502(3)
c (Å)	22.629(3)	16.346(3)	19.340(5)
α (°)	90.0	82.81(2)	90.0
β (°)	115.390(10)	85.03(2)	122.79(1)
γ (°)	90.0	74.76(2)	90.0
Volume (Å^3)	8048(4)	1813.9(7)	4597(2)
Z	8	2	4
μ (mm^{-1})	0.583	0.636	0.749
Absorption corrections: max., min.	0.997, 0.969	0.993, 0.963	not applied (negligible)
Crystal size (mm)	0.34×0.31×0.17	0.31×0.16×0.16	0.37×0.20×0.11
Colour	lemon	red–purple	deep red–brown (almost black)
Habit	thick plates	needles	needles
θ_{max} (°)	25.5	25.0	25.0
Data collected	$h, k, \pm l$	$\pm h, k, \pm l$	$h, k, \pm l$
Reflections	7362	6848	7973
Unique reflections	7156	6367	4155
Final *R* indices R^1, R^2_w ($I>2\sigma(I)$)	0.0399, 0.0933	0.0431, 0.1154	0.0395, 0.0843

TABLE 2. Atomic coordinates (×10^5 for Ru, P, ×10^4 for other atoms) and equivalent isotropic displacement parameters Å^2×10^3 for **1a**

	x	y	z	U_{eq}^{a}
Ru(1)	73330(2)	25691(1)	24494(1)	20(1)
P(1)	74812(5)	25824(5)	35475(5)	22(1)
P(2)	72687(5)	25120(5)	13703(5)	22(1)
N(1)	5440(2)	−110(2)	1801(2)	41(1)
O(1)	8783(2)	1878(2)	2934(2)	40(1)
O(2)	5713(2)	−671(2)	1972(2)	41(1)
O(3)	4786(2)	−40(2)	1437(3)	95(2)
O(4)	6389(1)	3239(1)	2141(1)	25(1)
O(5)	7451(1)	3735(1)	2456(1)	29(1)
C(1)	8213(2)	2140(2)	2740(2)	28(1)
C(2)	6008(2)	1719(2)	2000(2)	26(1)
C(3)	5573(2)	1141(2)	1848(2)	30(1)
C(4)	5889(2)	501(2)	1996(2)	30(1)
C(5)	6644(2)	418(2)	2307(2)	28(1)
C(6)	7066(2)	1003(2)	2450(2)	27(1)
C(7)	6778(2)	1669(2)	2298(2)	21(1)
C(8)	6764(2)	3785(2)	2247(2)	29(1)
C(9)	6395(3)	4463(2)	2129(3)	47(1)
C(11)	8340(2)	2931(2)	4149(2)	25(1)
C(12)	8707(2)	3429(2)	3960(2)	35(1)
C(13)	9339(2)	3729(3)	4420(2)	45(1)
C(14)	9616(2)	3536(3)	5068(2)	41(1)
C(15)	9259(2)	3042(2)	5261(2)	35(1)
C(16)	8626(2)	2743(2)	4804(2)	30(1)
C(21)	6794(2)	3080(2)	3692(2)	24(1)
C(22)	6986(2)	3609(2)	4146(2)	30(1)
C(23)	6453(3)	3996(2)	4219(2)	37(1)
C(24)	5725(2)	3860(2)	3843(2)	37(1)
C(25)	5523(2)	3337(2)	3388(2)	34(1)
C(26)	6047(2)	2954(2)	3303(2)	28(1)
C(31)	7467(2)	1715(2)	3853(2)	25(1)
C(32)	8069(2)	1293(2)	3991(2)	32(1)
C(33)	8039(3)	600(2)	4120(2)	41(1)
C(34)	7402(3)	323(2)	4111(2)	46(1)
C(35)	6816(3)	743(2)	3987(2)	43(1)
C(36)	6841(2)	1432(2)	3865(2)	34(1)
C(41)	8152(2)	2728(2)	1387(2)	26(1)
C(42)	8514(2)	3314(2)	1733(2)	34(1)
C(43)	9195(3)	3480(3)	1778(2)	44(1)
C(44)	9542(3)	3057(3)	1514(2)	45(1)
C(45)	9195(2)	2480(3)	1178(2)	42(1)
C(46)	8500(2)	2311(2)	1107(2)	36(1)
C(51)	7063(2)	1671(2)	959(2)	26(1)
C(52)	6516(2)	1578(2)	334(2)	38(1)
C(53)	6395(3)	930(3)	46(2)	47(1)
C(54)	6810(3)	376(2)	384(3)	45(1)
C(55)	7365(3)	470(2)	1005(2)	43(1)
C(56)	7491(2)	1114(2)	1288(2)	34(1)
C(61)	6624(2)	3101(2)	769(2)	25(1)
C(62)	6834(2)	3555(2)	407(2)	32(1)
C(63)	6327(3)	3993(2)	−47(2)	40(1)
C(64)	5609(3)	3974(3)	−144(2)	47(1)
C(65)	5390(3)	3523(3)	213(2)	44(1)
C(66)	5895(2)	3092(2)	670(2)	35(1)
Cl(S)	4480(1)	5592(1)	1831(1)	91(1)
C(S)	5000	6109(4)	2500	53(2)

^{a}U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Atomic coordinates (×10^5 for Ru, P, Cl, ×10^4 for other atoms) and equivalent isotropic displacement parameters Å^2×10^3 for **4a**

	x	y	z	U_{eq}^{a}
Ru(1)	12432(4)	15246(3)	26260(2)	26(1)
P(1)	4453(13)	35209(9)	25193(6)	28(1)
P(2)	20270(12)	−4740(9)	28549(7)	29(1)
Cl(1)	37071(13)	16478(10)	29583(7)	41(1)
N	1246(5)	1462(3)	852(2)	38(1)
O(1)	−457(4)	1535(3)	4223(2)	52(1)
O(2)	2123(3)	1545(2)	1370(2)	34(1)
O(3)	1639(4)	1469(3)	113(2)	55(1)
C(1)	206(5)	1518(4)	3623(3)	35(1)
C(2)	−184(5)	1381(4)	1151(3)	34(1)
C(3)	−1202(6)	1293(4)	588(3)	47(1)
C(4)	−2602(7)	1240(5)	902(4)	58(2)
C(5)	−2939(6)	1244(5)	1750(4)	54(1)
C(6)	−1915(5)	1328(4)	2294(3)	43(1)
C(7)	−469(5)	1399(3)	2016(3)	32(1)
C(11)	3281(5)	−1175(4)	2053(3)	36(1)
C(12)	4330(5)	−653(4)	1656(3)	40(1)
C(13)	5352(5)	−1163(4)	1062(3)	47(1)
C(14)	5359(6)	−2209(5)	870(4)	57(1)
C(15)	4330(7)	−2740(5)	1261(4)	65(2)
C(16)	3290(7)	−2235(4)	1850(4)	56(2)
C(21)	2991(5)	−1075(4)	3807(3)	35(1)
C(22)	3611(7)	−2219(4)	3932(4)	63(2)
C(23)	4276(8)	−2691(4)	4660(4)	76(2)
C(24)	4386(6)	−2041(4)	5253(4)	55(2)
C(25)	3802(6)	−913(4)	5129(3)	44(1)
C(26)	3115(5)	−425(4)	4408(3)	41(1)
C(31)	435(5)	−1077(3)	2956(3)	33(1)
C(32)	−331(5)	−1167(4)	3727(3)	40(1)
C(33)	−1641(6)	−1516(4)	3794(4)	57(2)
C(34)	−2194(6)	−1780(5)	3112(5)	63(2)
C(35)	−1444(6)	−1683(4)	2355(4)	58(2)
C(36)	−158(6)	−1330(4)	2272(3)	46(1)
C(41)	1034(6)	4273(4)	1578(3)	37(1)
C(42)	2493(6)	3913(4)	1265(3)	41(1)
C(43)	3042(7)	4551(6)	609(3)	61(2)
C(44)	2123(10)	5553(6)	287(4)	78(2)
C(45)	688(9)	5911(5)	580(4)	71(2)
C(46)	139(7)	5278(4)	1214(3)	52(1)
C(51)	−1566(5)	4056(3)	2606(3)	34(1)
C(52)	−2433(6)	3921(5)	1999(4)	64(2)
C(53)	−3958(7)	4212(6)	2093(5)	82(2)
C(54)	−4670(7)	4621(6)	2788(5)	72(2)
C(55)	−3862(7)	4732(7)	3386(4)	86(2)
C(56)	−2300(7)	4455(6)	3306(3)	65(2)
C(61)	1054(5)	4204(3)	3307(3)	29(1)
C(62)	928(6)	5339(4)	3183(3)	43(1)
C(63)	1337(7)	5881(4)	3772(4)	55(1)
C(64)	1882(6)	5297(4)	4493(3)	45(1)
C(65)	1994(5)	4168(4)	4627(3)	42(1)
C(66)	1586(5)	3625(4)	4039(3)	39(1)

^{a}U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

mode for the nitro group is observed as a medium-strong band in the 1485–1495 cm^{-1} region. The site of nitration on the aryl ligands in complexes **1–3** is

TABLE 4. Atomic coordinates ($\times 10^5$ for Ru, $\times 10^4$ for other atoms) and equivalent isotropic displacement parameters $Å^2 \times 10^3$ for **5b**

	x	y	z	U_{eq}[a]
Ru	1(6)	−62(5)	50000(6)	26(1)
Cl(1)	266(2)	473(2)	6337(1)	43(1)
P(1)	1276(2)	679(2)	5375(1)	31(1)
P(2)	−1240(1)	−665(2)	4753(1)	31(1)
O(1)	−867(5)	1684(6)	4036(5)	71(2)
O(2)	624(4)	−1212(5)	5661(4)	38(2)
O(3)	1050(6)	−2552(5)	5549(5)	70(2)
O(4)	643(8)	−3456(7)	2943(7)	102(4)
O(5)	−131(6)	−2628(7)	1876(6)	77(3)
N(1)	703(5)	−1826(5)	5230(5)	41(2)
N(2)	227(7)	−2759(7)	2612(8)	65(3)
C(1)	−519(7)	1036(8)	4411(6)	41(3)
C(2)	376(5)	−1628(6)	4387(5)	37(2)
C(3)	494(6)	−2291(6)	3948(6)	39(2)
C(4)	149(7)	−2094(8)	3130(7)	44(2)
C(5)	−250(6)	−1280(7)	2793(6)	44(2)
C(6)	−357(5)	−624(6)	3244(5)	33(2)
C(7)	−33(5)	−771(6)	4095(5)	28(2)
C(8)	−792(6)	249(7)	2814(6)	51(3)
C(11)	2123(5)	−93(6)	6041(5)	34(2)
C(12)	2201(5)	−337(7)	6781(6)	45(2)
C(13)	2826(7)	−931(9)	7331(7)	62(3)
C(14)	3362(8)	−1293(10)	7150(8)	78(4)
C(15)	3301(8)	−1032(10)	6437(8)	76(4)
C(16)	2676(6)	−438(8)	5866(7)	56(3)
C(21)	1372(5)	991(7)	4513(6)	35(2)
C(22)	1366(6)	1911(8)	4329(6)	48(3)
C(23)	1380(8)	2188(10)	3631(8)	70(4)
C(24)	1382(7)	1504(12)	3130(7)	74(4)
C(25)	1388(7)	604(10)	3324(7)	63(3)
C(26)	1388(5)	331(8)	4018(6)	44(2)
C(31)	1598(5)	1723(6)	5999(6)	37(2)
C(32)	2422(6)	1981(8)	6432(7)	54(3)
C(33)	2682(8)	2789(8)	6895(8)	68(3)
C(34)	2134(8)	3346(8)	6904(8)	65(3)
C(35)	1315(8)	3118(8)	6477(8)	62(3)
C(36)	1068(7)	2314(8)	6025(7)	56(3)
C(41)	−1089(5)	−1816(6)	5208(6)	36(2)
C(42)	−1473(7)	−2621(8)	4767(7)	57(3)
C(43)	−1336(8)	−3465(8)	5149(8)	72(4)
C(44)	−815(7)	−3501(8)	5994(8)	69(4)
C(45)	−439(7)	−2730(8)	6428(8)	64(3)
C(46)	−566(7)	−1884(8)	6068(7)	51(3)
C(51)	−2093(5)	−787(7)	3688(5)	37(2)
C(52)	−2029(6)	−1385(7)	3155(6)	45(2)
C(53)	−2687(6)	−1532(8)	2363(6)	50(3)
C(54)	−3410(7)	−1074(8)	2074(6)	55(3)
C(55)	−3467(6)	−445(7)	2568(6)	48(2)
C(56)	−2812(6)	−318(6)	3386(6)	43(2)
C(61)	−1748(5)	−31(8)	5183(5)	44(2)
C(62)	−2260(7)	−539(9)	5345(7)	61(3)
C(63)	−2743(8)	−77(14)	5553(8)	93(5)
C(64)	−2728(9)	881(13)	5582(8)	88(5)
C(65)	−2219(9)	1345(10)	5435(8)	77(4)
C(66)	−1701(7)	894(9)	5255(8)	62(3)
Cl(2)	4921(4)	394(5)	4389(4)	159(2)
Cl(3)	4721(7)	−1144(7)	3380(8)	271(6)
Cl(4)	3737(7)	8660(8)	4819(7)	247(5)
Cl(5)	2191(6)	8087(7)	3600(7)	265(6)
C(71)	5185(17)	−136(17)	3742(18)	250(18)
C(72)	3027(12)	8725(22)	3776(11)	237(19)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

expected to be *para* to the ruthenium metal centre if one assumes a strongly activating, *para*-directing effect from the metal centre. In the case of the *o*-tolyl complexes this effect would presumably dominate any *ortho*, *para*-directing effect from the *ortho*-methyl group. The aromatic C–H out-of-plane deformation modes of substituted aromatics often give information about the substitution pattern on the aromatic ring [15]. The IR spectra of **1a**–**3a** all show bands of medium intensity at ~850 and ~840 cm^{-1} which are most likely assignable to the $\delta(NO_2)$ mode for the NO_2 group and the C–H out-of-plane deformation mode of the aryl ring, respectively. The latter assignment would support a 1,4-disubstitution pattern for the aromatic ring [15]. However, it must be noted that it has been found that a nitro substituent shifts bands due to the aromatic ring to higher frequencies and so it is not always possible to rely on IR measurements alone to establish the position of the nitro group in the ring [16]. An X-ray structural characterisation of **1a** shows *para*-substitution of the aryl ligand by the nitro group and so supports our assignment based on IR data.

The IR spectra of the acetate-containing derivatives **1a** and **1b** show bands consistent with the acetate ligands being bidentate (see Table 5). In the ^1H NMR spectra the methyl protons of the acetate ligands of the respective complexes appear as singlets at δ 0.67 and 0.74. For **1a** the ^1H NMR resonances due to the nitroaryl group are obscured by the resonances of the PPh_3 ligands. For **1b** two of the aromatic protons of the nitroaryl group are shifted significantly from the resonances for the PPh_3 ligands and appear as doublets at δ 7.14 and 8.07; the third, however, is obscured by the complex multiplets of the PPh_3 ligands. A singlet is observed at δ 1.68 for the methyl group on the nitroaryl ligand.

The η^2-nitrate complexes, **2a** and **2b**, both exhibit IR bands appropriate for bidentate nitrate ligands (see Table 5). In the ^1H NMR spectrum of **2a**, as for that of **1a**, the resonances due to the nitroaryl ligand protons are obscured by resonances for the PPh_3 ligands. For **2b**, again only two of the three aromatic protons of the nitroaryl group are shifted significantly from the resonances for the PPh_3 ligands (see Table 6). A singlet is observed at δ 1.49 for the methyl group on the nitroaryl ligand.

The IR spectrum of complex **3a** shows bands at 1539m and 1427sh assignable to $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$, respectively, for the 2-nitrobenzoate ligand. In the ^1H NMR spectrum of **3a** the doublet at δ 7.87 is tentatively assigned to one of the aromatic protons of the 2-nitrobenzoate ligand. Other resonances for this ligand and the 4-nitrophenyl group are obscured by the signals for the PPh_3 ligands. The origin of the 2-nitrobenzoate ligand in **3a** is uncertain. Its formation

TABLE 5. IR data for new compounds[a]

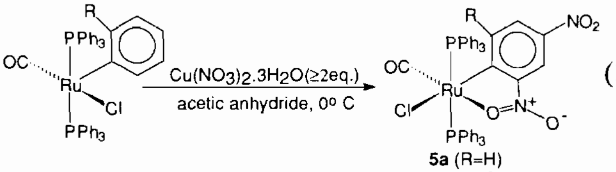
Compound	ν(C–O)[b]	Other bands
Ru(C$_6$H$_4$NO$_2$-4)(η^2-O$_2$CCH$_3$)(CO)(PPh$_3$)$_2$ (**1a**)	1921	3057w ν(C–H); 1582m, 1559m ν(C=C) nitroaryl; 1532wm ν(COO asym); 1493ms ν(NO$_2$ asym); 1456ms ν(COO sym); 1335s ν(NO$_2$ sym); 1312ms; 1115w; 1040m; 851m δ(NO$_2$); 839 m δ(C–H)
Ru(C$_6$H$_3$CH$_3$-2,NO$_2$-4)(η^2-O$_2$CCH$_3$)(CO)(PPh$_3$)$_2$ (**1b**)	1919	3081w, 3057w ν(C–H); 1587wm, 1555m ν(C=C) nitroaryl; 1525w ν(COO asym); 1489ms ν(NO$_2$ asym); 1462ms ν(COO sym); 1329s ν(NO$_2$ sym); 1015wm; 598wm
Ru(C$_6$H$_4$NO$_2$-4)(η^2-O$_2$NO)(CO)(PPh$_3$)$_2$ (**2a**)	1942	3083w, 3058w ν(C–H); 1584m, 1570m ν(C=C) nitroaryl; 1532wm ν(N=O) η^2-NO$_3$; 1495ms ν(NO$_2$ asym) nitroaryl; 1337s ν(NO$_2$ sym) nitroaryl; 1314m; 1242m ν(NO$_2$ asym) η^2-NO$_3$; 1110w; 1042m ν(NO$_2$ sym) η^2-NO$_3$; 851m δ(NO$_2$); 837m δ(C–H)
Ru(C$_6$H$_3$CH$_3$-2,NO$_2$-4)(η^2-O$_2$NO)(CO)(PPh$_3$)$_2$ (**2b**)	1937	3059w, 2925w ν(C–H); 1587w, 1559wm ν(C=C) nitroaryl; 1524m ν(N=O) η^2-NO$_3$; 1502ms ν(NO$_2$ asym) nitroaryl; 1331s ν(NO$_2$ sym) nitroaryl; 1292m; 1263wm; 1242m ν(NO$_2$ asym) η^2-NO$_3$; 1015wm ν(NO$_2$ sym) η^2-NO$_3$; 924w; 801w; 596w
Ru(C$_6$H$_4$NO$_2$-4)(η^2-O$_2$CC$_6$H$_4$NO$_2$-2)(CO)(PPh$_3$)$_2$ (**3a**)	1923	3057w ν(C–H); 1582wm, 1559m ν(C=C) nitroaryl; 1539m ν(COO asym); 1497ms ν(NO$_2$ asym) nitroaryl; 1427sh ν(COO sym); 1333s ν(NO$_2$ sym) nitroaryl; 1308m; 1109w; 1038m; 872w; 849m δ(NO$_2$); 841m δ(C–H)
$\overline{\mathrm{Ru(C_6H_4N[O]O}}$-2)Cl(CO)(PPh$_3$)$_2$ (**4a**)	1944	3057w ν(C–H); 1576m, 1543m ν(C=C) nitroaryl; 1489ms ν(NO$_2$ asym); 1323 wm; 1260m ν(NO$_2$ sym); 1217m; 1078wm
$\overline{\mathrm{Ru(C_6H_3CH_3\text{-}2,N[O]O}}$-6)Cl(CO)(PPh$_3$)$_2$ (**4b**)	1939	3056w, 2957w, 2926w ν(C–H); 1578w, 1549w ν(C=C) nitroaryl; 1497ms ν(NO$_2$ asym); 1308wm; 1254wm ν(NO$_2$ sym); 1229wm
$\overline{\mathrm{Ru(C_6H_3CH_3\text{-}4,N[O]O}}$-2)Cl(CO)(PPh$_3$)$_2$ (**4c**)	1944	3055w, 3007w, 2957w, 2924w ν(C–H); 1508w ν(C=C) nitroaryl; 1491ms ν(NO$_2$ asym); 1263wm ν(NO$_2$ sym); 1219wm; 1201wm; 1082wm; 833w
$\overline{\mathrm{Ru(C_6H_3N[O]O}}$-2,NO$_2$-4)Cl(CO)(PPh$_3$)$_2$ (**5a**)	1954 1942cs	3053w, 2957w, 2953w, 2858w ν(C–H); 1587m, 1570m ν(C=C) nitroaryl; 1506ms ν(NO$_2$ asym); 1341s ν(NO$_2$ sym); 1254ms ν(NO$_2$ sym); 1219m; 1144wm; 833wm
$\overline{\mathrm{Ru(C_6H_2CH_3\text{-}2,NO_2\text{-}4,N[O]O}}$-6)Cl(CO)(PPh$_3$)$_2$ (**5b**)	1950	3059w, 2957w, 2928w, 2857w ν(C–H); 1578m, 1559sh ν(C=C) nitroaryl; 1512s ν(NO$_2$ asym); 1327s ν(NO$_2$ sym); 1254m ν(NO$_2$ sym); 592 wm

[a] In cm^{-1}. Spectra recorded as KBr discs. Bands due to triphenylphosphine ligands not included. [b] All carbonyl bands are strong unless indicated otherwise; s, strong; m, medium; w, weak; sh, shoulder; cs, crystal splitting.

is possibly via a radical reaction during the nitration process.

It is possible to increase the yield of the acetate containing derivatives **1a** and **1b** from the nitration reactions relative to the nitrate- and nitrobenzoate-containing species, **2** and **3**, by the addition of more sodium acetate during the work-up phase of the reaction. Samples of **2** and **3** obtained from the reaction may also be converted to **1** by recrystallisation in the presence of an excess of sodium acetate. The actual yield of **1a** and **1b** from the nitration reaction then approaches 50%. Work is currently being undertaken to further optimise the yields from this reaction.

Sometimes the nitration reaction with one mole equivalent of copper(II) nitrate gave small quantities of the di-nitrated products **5a** and **5b**. These appear to be the first reported examples of σ-bound dinitroaryl transition metal complexes. These complexes can also be obtained in higher yield and purity by treating the starting σ-aryl complexes RuArCl(CO)(PPh$_3$)$_2$ (Ar = C$_6$H$_5$, C$_6$H$_4$CH$_3$-2) with an excess (2 or more mole equivalents) of copper(II) nitrate in acetic anhydride (eqn. (1)).



5a (R=H)
5b (R=CH$_3$)

(1)

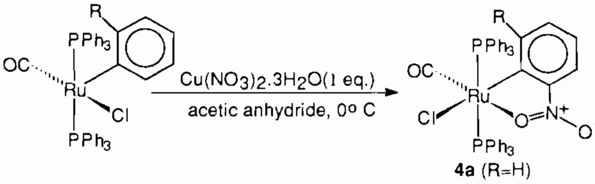
TABLE 6. ${}^1H$ NMR data for new compounds[a]

Compound	Chemical shifts (ppm) and coupling constants (Hz)
$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ (**1a**)	0.67 (s, 3, CH_3CO_2) 7.17–7.42 (m, 34, $C_6H_4NO_2$, C_6H_5)
$Ru(C_6H_3CH_3\text{-}2,NO_2\text{-}4)(\eta^2\text{-}O_2CCH_3)(CO)(PPh_3)_2$ (**1b**)	0.74 (s, 3, CH_3CO_2) 1.68 (s, 3, $C_6H_3CH_3NO_2$) 7.14 (d, J(HH) 2.7, 1, $C_6H_3CH_3NO_2$) 7.25–7.42 (m, 31, $C_6H_3CH_3NO_2$, C_6H_5) 8.07 (d, J(HH) 8.9, 1, $C_6H_3CH_3NO_2$)
$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2$ (**2a**)	7.12–7.47 (m, 34, $C_6H_4NO_2$, C_6H_5)
$Ru(C_6H_3CH_3\text{-}2,NO_2\text{-}4)(\eta^2\text{-}O_2NO)(CO)(PPh_3)_2$ (**2b**)	1.49 (s, 3, $C_6H_3CH_3NO_2$) 6.78–6.94 (m, 1, $C_6H_3CH_3NO_2$) 7.19–7.46 (m, 31, $C_6H_3CH_3NO_2$, C_6H_5) 7.56 (d, J(HH) 8.8, 1, $C_6H_3CH_3NO_2$)
$Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}O_2CC_6H_4NO_2\text{-}2)(CO)(PPh_3)_2$ (**3a**)	7.01–7.48 (m, 33, $O_2CC_6H_4NO_2$, $C_6H_4NO_2$, C_6H_5) 7.87 (d, J(HH) 8.8, 1, $O_2CC_6H_4NO_2$)
$\overline{Ru(C_6H_3CH_3\text{-}4,N[O]O}\text{-}2)Cl(CO)(PPh_3)_2$ (**4c**)	2.13 (s, 3, $C_6H_3CH_3N[O]O$) 6.28 (dd, J(HH) 8.0, 1.9, 1, $C_6H_3CH_3N[O]O$) 6.49 (d, J(HH) 8.0, 1, $C_6H_3CH_3N[O]O$) 7.19–7.59 (m, 31, $C_6H_3CH_3N[O]O$, C_6H_5)
$\overline{Ru(C_6H_3N[O]O}\text{-}2,NO_2\text{-}4)Cl(CO)(PPh_3)_2$ (**5a**)	6.81 (d, J(HH) 8.7, 1, $C_6H_3N[O]ONO_2$) 7.14 (dd, J(HH) 8.7, 2.4, 1, $C_6H_3N[O]ONO_2$) 7.22–7.60 (m, 30, C_6H_5) 8.07 (d, J(HH) 2.4, 1, $C_6H_3N[O]ONO_2$)
$\overline{Ru(C_6H_2CH_3\text{-}2,NO_2\text{-}4,N[O]O}\text{-}6)Cl(CO)(PPh_3)_2$ (**5b**)	1.35 (s, 3, $C_6H_2CH_3NO_2N[O]O$) 7.20–7.45 (m, 31, $C_6H_2CH_3NO_2N[O]O$, C_6H_5) 8.04 (d, J(HH) 2.4, 1, $C_6H_2CH_3NO_2N[O]O$)

[a] As $CDCl_3$ solutions at 20 °C.

Despite the normal deactivating influence of a nitro group on an aromatic ring toward further substitution, the addition of a second nitro group to the ruthenium bound aryl ligands appears to be extremely facile under the very mild reaction conditions used. This suggests that the influence of the ruthenium centre on the reactivity of the aryl group is considerable. The second site of nitration is the position *ortho* to the metal as shown in eqn. (1). This nitro group is bonded to the ruthenium centre through an oxygen atom, giving a five-membered chelate ring. This type of coordination is known for other 2-nitroaryl-containing complexes [1a, 5d, 5e, 5i] and generally leads to very stable products because of the formation of the five-membered metallacycle. The IR spectra of **5a** and **5b** show, as well as the usual strong band in the 1325–1345 cm^{-1} region for $\nu_{sym}(NO_2)$ of the uncoordinated 4-nitro group, a band of medium intensity at 1254 cm^{-1} for the $\nu_{sym}(NO_2)$ of the chelated *ortho*-nitro group. The position of $\nu_{asym}(NO_2)$ for the two nitro groups in each complex (at 1505–1515 cm^{-1}) is relatively unchanged from the positions observed for the same band in the complexes **1**–**3**. This band appears to be less sensitive to the coordination of the nitro group to the metal centre than $\nu_{sym}(NO_2)$ [5i]. In the ${}^1H$ NMR spectrum of **5a** the protons of the nitroaryl group are shifted relative to the signals for aromatic protons of the PPh_3 ligands (see Table 6). The proton in the 3-position on the ring (between the two nitro groups) is seen as a doublet which is shifted considerably downfield to δ 8.07, J(HH) = 2.4 Hz, while the protons in positions 5 and 6 are shifted upfield to δ 7.14(dd) and δ 6.81(d), respectively. In the ${}^1H$ NMR spectrum of **5b** the proton in the 5-position on the ring (between the two nitro groups) is seen as a doublet shifted downfield to δ 8.04, J(HH) = 2.4 Hz, while the other aromatic proton on the nitroaryl ring (in the 3-position) is obscured by the signals for the PPh_3 ligands. A singlet is seen at δ 1.35 for the methyl group of the nitroaryl ligand. The structure of **5b** has been confirmed by a crystal structure determination.

Very minor products of the nitration of the aryl complexes $RuArCl(CO)(PPh_3)_2$ ($Ar = C_6H_5$, $C_6H_4CH_3\text{-}2$) are the compounds $\overline{Ru(C_6H_4N[O]O}\text{-}2)Cl(CO)(PPh_3)_2$ (**4a**) and $\overline{Ru(C_6H_3CH_3\text{-}2,N[O]O}\text{-}6)Cl(CO)(PPh_3)_2$ (**4b**), respectively. Both are isolated in yields of < 1% which has limited the amount of data that is available for each. These are the products expected if the initial site of nitration of the aryl group is in the position *ortho* to the ruthenium centre (eqn. (2)).



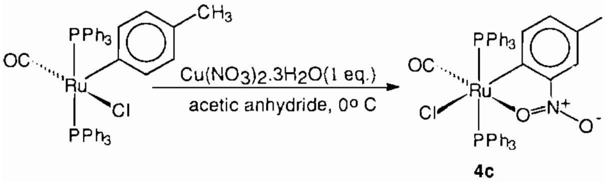
4a (R=H)
4b (R=CH3)

(2)

The presence of the chelating nitro group in each complex is supported by the presence of the expected $\nu_{sym}(NO_2)$ band at ~1260 cm^{-1} and **4a** has been further characterised by an X-ray crystal structure analysis. The very low yields of **4a** and **4b** relative to the isolated products showing mono-nitration in the *para*-position suggest that, under the reaction conditions used, it is possible to regioselectively nitrate the phenyl and *o*-tolyl ligands in the complexes $RuArCl(CO)(PPh_3)_2$ ($Ar = C_6H_5$, $C_6H_4CH_3$-2) with a *para* preference of greater than 95% in useful yields (~50%).

Major contaminants of the crude reaction mixture from the nitration reactions are various nitrosyl-containing complexes. The mechanism of formation of these compounds is unknown, but the presence of such species is hardly surprising given the composition of the reaction mixture and the propensity of ruthenium to form nitrosyl-containing complexes in acidic nitrate-containing media [17]. Column chromatography on silica gel can easily remove all of the nitrosyl-containing complexes except $RuCl_3(NO)(PPh_3)_2$. Removal of this compound from samples of complexes **1–5** requires further chromatography or repeated fractional crystallisations.

The complex $Ru(C_6H_4CH_3\text{-}4)Cl(CO)(PPh_3)_2$ already has a methyl group occupying the preferred site of nitration. Therefore, on treatment of this complex under the nitrating conditions shown in Scheme 1, the site of nitration was expected to be the position *ortho* to the metal. Indeed, $Ru(C_6H_3CH_3\text{-}4,N[O]O\text{-}2)Cl(CO)(PPh_3)_2$ (**4c**) is the major product isolated from this reaction (eqn. (3)). The IR spectrum shows a band at 1263 cm^{-1} indicative of the $\nu_{sym}(NO_2)$ of the chelated 2-nitro group. A band of medium intensity is seen at 1491 cm^{-1} for $\nu_{asym}(NO_2)$ of the nitroaryl ligand. In the ^1H NMR spectrum of **4c** signals for two of the aromatic protons of the nitroaryl group are clearly observed (see Table 6). These are assigned to the protons in positions 5 and 6. The proton in the 3-position is seen as a poorly resolved doublet positioned between the complex multiplets of the PPh_3 ligands. A singlet is seen at δ 2.13 for the methyl group of the nitroaryl ligand.



4c

(3)

Structural considerations

The molecular geometries and atomic numbering schemes for compounds **1a**, **4a**, and **5b** are shown in Figs. 1, 2, and 3, respectively. In each case the coordination geometry about Ru is octahedral. Selected bond distances and angles are presented in Table 7. The coordination octahedron is distorted by the presence of chelating ligands and by the bulky phosphine groups. The P–Ru–P angles are 175.74(4), 175.23(4) and 174.68(11)° for **1a**, **4a** and **5b**, respectively. The Ru–C7(arene) bonds are all at the short end of the commonly observed range of 2.0 to 2.2 Å. There is no indication of short/long bonds in the aromatic rings of the ligands. The C(4)–N distances for non-coordinated nitro groups are 1.445(5) Å for **1a** and 1.457(13) Å for **5b**, whereas the C(2)–N distances for coordinated nitro groups are 1.405(6) Å for **4a** and 1.422(12) Å for **5b**. For the coordinated nitro groups the N–O(coordinated) distances, 1.258(5) Å in **4a**, 1.284(10) Å in **5b**, are slightly longer than the N–O(non-coordinated) distances 1.232(5) Å in **4a**, 1.223(10) Å in **5b**. In **1a** the nitro group is significantly twisted relative to the aromatic ring (10.8°), whilst the nitro groups in **4a** and **5b** are essentially coplanar with their aromatic rings (dihedral angles; **4a**, 1.5°; **5b**, 0.6°(coordinated), 1.2°(non-coordinated). One feature of interest is the

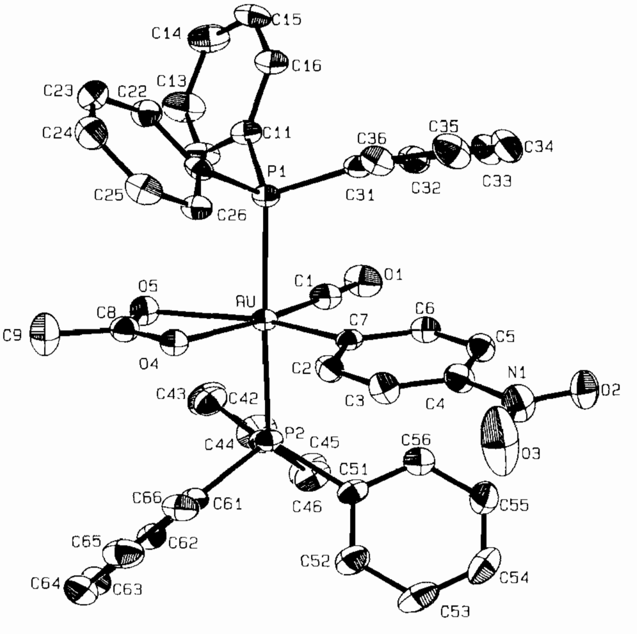


Fig. 1. Molecular geometry for **1a**.

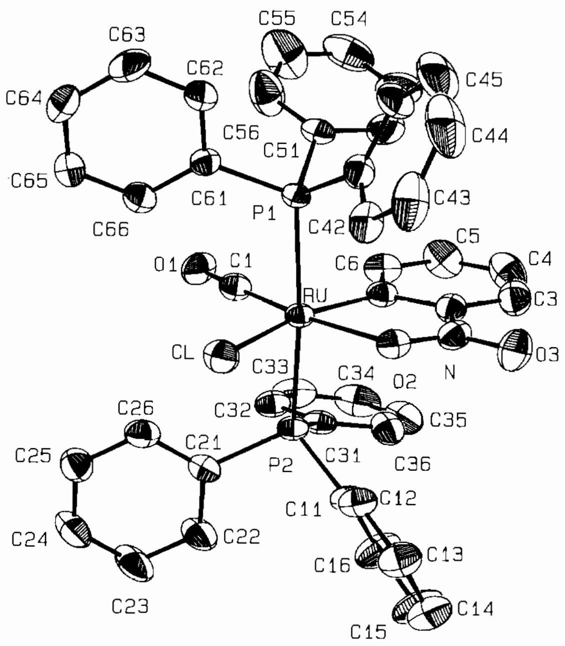


Fig. 2. Molecular geometry for **4a**.

unsymmetrical acetate coordination in **1a** where the Ru–O(5) distance *trans* to the σ-aryl group (2.279(3) Å) is significantly longer than the Ru–O(4) distance *trans* to CO (2.166(3) Å) indicating a stronger structural *trans* influence of aryl over CO.

Conclusions

A convenient synthetic route to a number of nitroaryl derivatives of ruthenium has been developed. In the five-coordinate compounds the chloride ligand is labile. This feature allows formation of various derivatives, both cationic and neutral. These derived compounds are being studied further and these results, together with experiments designed to modify the aromatic nitro groups will be reported subsequently.

Supplementary material

Full details of crystal data, intensity data collection and refinement parameters, hydrogen atom positions, anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors are available from author G.R.C.

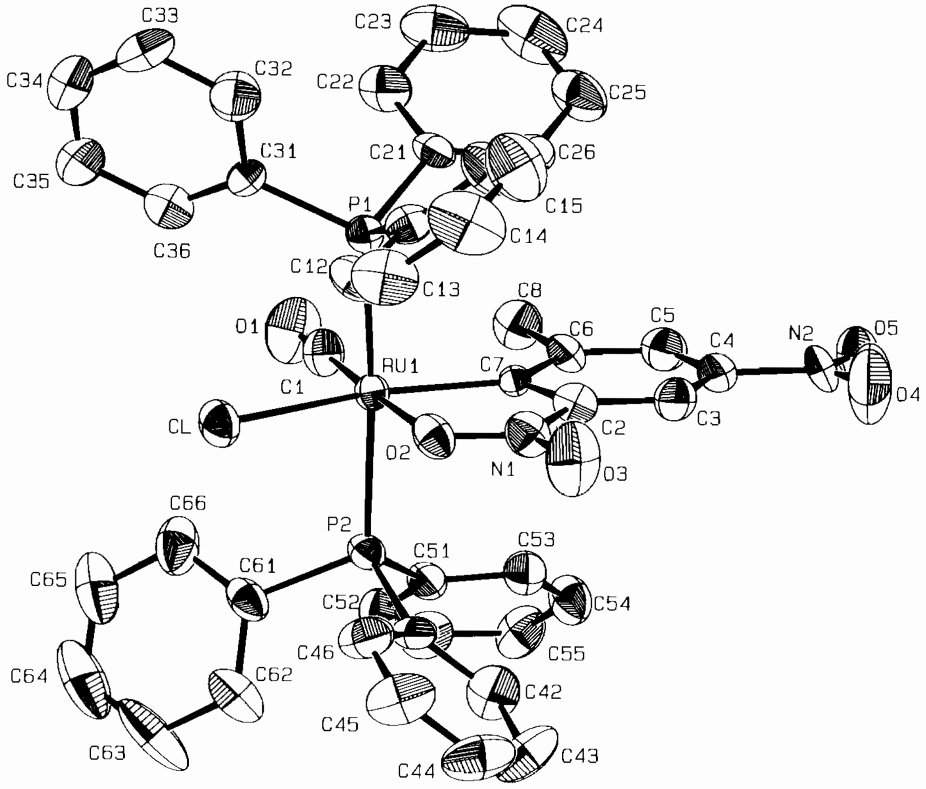


Fig. 3. Molecular geometry for **5b**.

TABLE 7. Selected bond lengths and angles for compounds **1a**, **4a** and **5b**

	1a	**4a**	**5b**
Ru–Cl(1)		2.4549(11)	2.446(3)
Ru–P(1)	2.372(1)	2.3868(12)	2.397(3)
Ru–P(2)	2.392(1)	2.3911(12)	2.396(3)
Ru–O(2)		2.144(3)	2.117(7)
Ru–C(1)	1.818(4)	1.822(5)	1.833(11)
Ru–C(7)	2.029(4)	2.005(5)	2.042(8)
Ru–O(4)	2.166(3)		
Ru–O(5)	2.279(3)		
Cl(1)–Ru–P(1)		88.62(4)	88.33(9)
Cl(1)–Ru–P(2)		90.22(4)	86.40(9)
P(1)–Ru–P(2)	175.74(4)	175.23(4)	174.68(11)
C(1)–Ru–C(7)	93.0(2)	93.3(2)	99.4(4)
O(2)–Ru–C(7)		77.4(2)	79.0(3)

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