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Preparation of mono- and bis-(hydrazine) complexes of ruthenium(II)†

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Hydrazine complexes $[RuH(R^1NHNH_2)L_4]BPh_4$ **1**–**3**, $[Ru(R^1NHNH_2)_2L_4][BPh_4]_2$ **4**–**6** [R^1 = H, Me, Ph, 4-MeC_6H_4 or 4-$O_2NC_6H_4$; L = $P(OEt)_3$, $PPh(OEt)_2$ or $P(OMe)_3$] were prepared by allowing the hydride species $[RuH_2L_4]$ to react, first with triflic acid (CF_3SO_3H) and then with an excess of the appropriate hydrazine. The derivatives $[RuH(Me_2NNH_2)\{P(OEt)_3\}_4]BPh_4$ **1f**, $[Ru(\eta^1\text{-}OSO_2CF_3)(Me_2NNH_2)\{P(OEt)_3\}_4]BPh_4$ **9** and $[Ru(\eta^2\text{-}PhCONHNH_2)L_4][BPh_4]_2$ **7**,**8** [L = $P(OEt)_3$ or $PPh(OEt)_2$] were also obtained. The formulation and geometry in solution of the compounds were established by infrared and ^1H and ^{31}P NMR spectroscopy. The reaction of the bis(nitrile) complexes $[Ru(R^2CN)_2L_4][BPh_4]_2$ [R^2 = Me or MeC_6H_4; L = $P(OEt)_3$ or $PPh(OEt)_2$] with hydrazines depends not only on the experimental conditions, but also on the nature of the phosphite and the hydrazine used. Thus, nitrilehydrazine $[Ru(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ **10**–**13** [L = $P(OEt)_3$ or $PPh(OEt)_2$] or amidrazone derivatives $[Ru\{\eta^2\text{-}NH{=}C(R^2)N(R^1)NH_2\}\{P(OEt)_3\}_4][BPh_4]_2$ **14**,**15** (R^1 = H or Me) were obtained together with the bis(hydrazine) compounds $[Ru(R^1NHNH_2)_2L_4][BPh_4]_2$. Reaction of the arylhydrazine complexes **1**–**6** and **10**–**13** with $Pb(O_2CMe)_4$ at −30 °C in CH_2Cl_2 resulted in selective oxidation of the arylhydrazine ligand giving the aryldiazene derivatives $[RuH(R^1N{=}NH)L_4]BPh_4$, $[Ru(R^1N{=}NH)_2L_4][BPh_4]_2$ and $[Ru(R^1N{=}NH)(R^2CN)L_4][BPh_4]_2$ (R^1 = Ph, 4-MeC_6H_4 or 4-$O_2NC_6H_4$). Treatment of hydrazine NH_2NH_2 and methylhydrazine $MeNHNH_2$ complexes **1**–**6** with $Pb(O_2CMe)_4$, instead, afforded the acetate $[Ru(\eta^2\text{-}O_2CMe)L_4]BPh_4$ derivatives which were characterised by a crystal structure determination of $[Ru(\eta^2\text{-}O_2CMe)\{P(OEt)_3\}_4]BPh_4$. The co-ordination of ruthenium is distorted octahedral with approximate C_{2v} symmetry and the acetate is bidentate.

Transition-metal complexes containing aryldiazenido, aryldiazene or hydrazine ligands are currently of interest as possible intermediates in the chemistry of co-ordinated dinitrogen and its reduction to NH_3 catalysed by nitrogenases.[1] Although a number of studies on the chemistry of 'diazo' derivatives have been reported over the past 25 years, relatively few are concerned with hydrazine complexes[1] and therefore several aspects of the co-ordination chemistry of NH_2NH_2 and substituted hydrazines still remain unclear. Among them we can cite the influence that the central metal and the ancillary ligand may have in determining the co-ordination mode, *i.e.* η^1, η^2, μ, *etc.*, of the hydrazine ligand and in which way the co-ordination to a metal fragment may change the properties of the NH_2NH_2 or $RNHNH_2$ molecule towards reduction, oxidation and deprotonation reactions.

We are interested in the chemistry of partially reduced dinitrogen ligands and have previously reported[2] the synthesis and the reactivity of some aryldiazenido and aryldiazene complexes of transition metals stabilised by phosphite ligands. Now we have extended these studies to include hydrazine and substituted hydrazines as ligands and in this report we describe the synthesis, characterisation and some reactivity studies on hydrazine derivatives of ruthenium(II).

Mono- and di-nuclear hydrazine complexes of ruthenium(II) are known and often contain a 'diene'[3] or a polydentate NS_4-, OS_4- or OS_5-type group[4] as an ancillary ligand. With phosphine or phosphite the reported compounds are very few and, apart from the $[RuX_2(RNHNH_2)L_3]$, $[\{RuX_2(N_2H_4)L_2\}_2]$ (X = Cl or Br; R = H or Ph; L = tertiary phosphine) and $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$ derivatives,[3b,5] only recently the phosphine complexes $[\{RuCl[P(OMe)_3]_2\}_2(\mu\text{-}Cl)(\mu\text{-}NH_2NH_2)(\mu\text{-}S)]$[6] and $[RuX(CO)_2(NH_2NH_2)(PPh_3)_2]$[7] (X = Cl or Br) have been prepared and fully characterised. It is therefore of interest to report the synthesis of new hydrazine complexes of ruthenium(II) together with some new properties shown by this class of compounds.

Experimental

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmospheres dry-box. Once isolated, the complexes were relatively stable in air, but were stored under an inert atmosphere −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphites $P(OMe)_3$ and $P(OEt)_3$ (Aldrich) were purified by distillation under nitrogen, while $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[8] The hydrazines $MeNHNH_2$, $PhNHNH_2$, 4-$O_2NC_6H_4NHNH_2$, $PhCONHNH_2$ and Me_2NNH_2 were Aldrich products used as received. The *p*-tolylhydrazine 4-$MeC_6H_4NHNH_2$ was prepared by treating under nitrogen the corresponding salt 4-$MeC_6H_4NHNH_3{}^+Cl^-$ with a slight excess of NaOH in aqueous solution. A solid separated which, after 15 min of stirring, was filtered off, washed with water and dried over P_2O_5 under vacuum for 24 h. It was stored under nitrogen at −25 °C. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate ($NH_2NH_2\cdot C_3H_3N_3O_3$) (Fluka) following the reported method.[9] Other reagents from commercial sources were of the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 Fourier-transform spectrophotometer, NMR spectra (^1H, ^{13}C, ^{31}P) on a Bruker AC200 spectrometer at temperatures between −90 and +30 °C, unless otherwise noted.

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† *Supplementary data available* (No. SUP 57295, 3 pp.): physical and spectroscopic characterisation data. See *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

The SWANMR software package has been used in treating the NMR data.[10] Proton and ^{13}C spectra are referred to internal tetramethylsilane, ^{31}P-{^{1}H} chemical shifts with respect to 85% H$_3$PO$_4$, downfield shifts being considered positive. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in MeNO$_2$ at 25 °C were measured with a Radiometer CDM 83 instrument. Physical constants and elemental analyses for all the complexes and spectroscopic data for the triflate, dinitrile and aryldiazene complexes are available as SUP 57295.

Synthesis of the complexes

The hydride species [RuH$_2$L$_4$] [L = P(OMe)$_3$, P(OEt)$_3$ or PPh(OEt)$_2$] were prepared following previous methods.[11]

[Ru(η^2-O$_2$SOCF$_3$){P(OEt)$_3$}$_4$]BPh$_4$. To a solution of [RuH$_2${P(OEt)$_3$}$_4$] (0.26 mmol, 2 g) in toluene (10 cm^3) cooled to −78 °C was added an equivalent amount of CF$_3$SO$_3$H (0.26 mmol, 23 µl) and the mixture brought to 0 °C and stirred for 1 h. The solution was cooled again to −78 °C and another equivalent of CF$_3$SO$_3$H (0.26 mmol, 23 µl) added. After room temperature was reached the reaction mixture was stirred for 2 h and then evaporated to dryness. The oil obtained was treated with ethanol (5 cm^3) giving a pale yellow solution to which an excess of NaBPh$_4$ (1 mmol, 0.34 g) in ethanol (2 cm^3) was added. A white solid slowly separated which was filtered off and crystallised from CH$_2$Cl$_2$ (2 cm^3) and ethanol (5 cm^3); yield ⩾90%.

[RuH(η^1-OSO$_2$CF$_3$){P(OEt)$_3$}$_4$]. An equimolar amount of triflic acid (CF$_3$SO$_3$H) (0.26 mmol, 23 µl) was added to a solution of [RuH$_2${P(OEt)$_3$}$_4$] (0.26 mmol, 0.20 g) in ethanol (6 cm^3) cooled to −78 °C. The reaction mixture was brought to 0 °C, stirred for 2 h and then the solvent removed under reduced pressure. The oil obtained was treated with light petroleum (b.p. 40–60 °C) (3 × 3 cm^3), filtered and the resulting solution evaporated to dryness leaving an oily product. We were not able to crystallise this oil, but the IR and NMR spectra indicate the presence of only one, pure compound and confirm the proposed formulation.

[Ru(4-MeC$_6$H$_4$CN)$_2$L$_4$][BPh$_4$]$_2$ and [Ru(MeCN)$_2$L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ or PPh(OEt)$_2$]. To a solution of the appropriate hydride [RuH$_2$L$_4$] (0.5 mmol) in toluene (10 cm^3) cooled to −78 °C were sequentially added first one and then a second equivalent of CF$_3$SO$_3$H in order to generate in solution the [Ru(η^2-O$_2$SOCF$_3$)L$_4$]$^+$ cation, as previously described. An excess of the appropriate nitrile (2 mmol) was added to the resulting solution, which was stirred for 4 h and then evaporated to dryness. The oil obtained was treated with ethanol containing an excess of NaBPh$_4$ (2 mmol, 0.68 g) and the resulting solution stirred until a white solid separated, which was filtered off and crystallised from CH$_2$Cl$_2$ (3 cm^3) and ethanol (8 cm^3); yield ⩾80%.

[RuH(RNHNH$_2$)L$_4$]BPh$_4$ [L = P(OEt)$_3$ 1, PPh(OEt)$_2$ 2 or P(OMe)$_3$ 3; R = H a, Me b, Ph c, 4-MeC$_6$H$_4$ d or 4-O$_2$NC$_6$H$_4$ e]. An equimolar amount of CF$_3$SO$_3$H (0.26 mmol, 23 µl) was added to a solution of the appropriate hydride [RuH$_2$L$_4$] in ethanol (or methanol) (6 cm^3) cooled to −78 °C and the reaction mixture brought to 0 °C and stirred for 1 h. An excess of the appropriate hydrazine (0.5 mmol) was added to the resulting solution, which was stirred at room temperature for a period varying between 3 h, in the case of NH$_2$NH$_2$, and 5 h, in the case of the arylhydrazines. The addition of an excess of NaBPh$_4$ (1.1 mmol, 0.376 g) caused the precipitation of a white solid which was filtered off and crystallised from CH$_2$Cl$_2$ (3 cm^3) and ethanol (7 cm^3); yield from 50 to 80%.

[RuH(Me$_2$NNH$_2$){P(OEt)$_3$}$_4$]BPh$_4$ 1f. This complex was prepared like **1**–**3** using a reaction time of 9 h; yield ⩾70%.

[Ru(RNHNH$_2$)$_2$L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 4, PPh(OEt)$_2$ 5 or P(OMe)$_3$ 6; R = H a, Me b or Ph c]. A solution of the appropriate hydride [RuH$_2$L$_4$] (0.65 mmol) in toluene (10 cm^3) was treated sequentially with 2 equivalents of CF$_3$SO$_3$H (0.65 mmol, 58 µl) in order to prepare a suspension of the triflate cation [Ru(η^2-O$_2$SOCF$_3$)L$_4$]$^+$. An excess of the appropriate hydrazine (3 mmol) was added and the mixture was stirred for 3 h and then evaporated to dryness. The oil obtained was treated with ethanol (or methanol) (2 cm^3) and an excess of NaBPh$_4$ (2.6 mmol, 0.89 g) in alcohol (3 cm^3) was added to the resulting solution, giving a white solid which was filtered off and crystallised from CH$_2$Cl$_2$ (2 cm^3) and ethanol (or methanol) (5 cm^3); yield ⩾80%.

[Ru(η^2-PhCONHNH$_2$)L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 7 or PPh(OEt)$_2$ 8]. These complexes were prepared following the method reported above for the bis(hydrazine) derivatives **4**–**6**. In this case, an excess of solid benzoylhydrazine (1 mmol, 0.136 g) was added to a freshly prepared suspension of [Ru(η^2-O$_2$SOCF$_3$)L$_4$]$^+$ (0.26 mmol) in toluene (10 cm^3) and the reaction mixture, after the addition of CH$_2$Cl$_2$ (10 cm^3), stirred for 24 h. After filtration, the solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 cm^3). The addition of an excess of NaBPh$_4$ (1 mmol, 0.342 g) in ethanol (5 cm^3) to the resulting solution gave a white solid which was filtered off and crystallised from CH$_2$Cl$_2$ (3 cm^3) and ethanol (5 cm^3); yield ⩾60%.

[Ru(η^1-OSO$_2$CF$_3$)(Me$_2$NNH$_2$){P(OEt)$_3$}$_4$]BPh$_4$ 9. An excess of *N*,*N*-dimethylhydrazine (1.2 mmol, 91 µl) was added to a freshly prepared suspension of [Ru(η^2-O$_2$SOCF$_3$)L$_4$]$^+$ (0.3 mmol) in toluene (10 cm^3) and the reaction mixture stirred for 24 h. The solvent was removed under reduced pressure to give an oily product which was treated with ethanol (4 cm^3) containing an excess of NaBPh$_4$ (2 mmol, 0.68 g). A white solid slowly separated under vigorous stirring, which was filtered off and crystallised from CH$_2$Cl$_2$ (2 cm^3) and ethanol (5 cm^3); yield ⩾70%.

[Ru(RNHNH$_2$)(MeCN)L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 10 or PPh(OEt)$_2$ 11; R = H a, Ph c or 4-O$_2$NC$_6$H$_4$ e]. To a solution of [Ru(MeCN)$_2$L$_4$][BPh$_4$]$_2$ (0.25 mmol) in CH$_2$Cl$_2$ (6 cm^3) was added an equimolar amount of the appropriate hydrazine (0.25 mmol) and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol (2 cm^3) and vigorously stirred at 0 °C until a white solid separated from the resulting solution. The solid was filtered off and crystallised by slow cooling to −25 °C of its solution prepared by dissolving the compound in ethanol (5 cm^3) and enough CH$_2$Cl$_2$ to obtain a saturated solution at room temperature; yield ⩾45%.

[Ru(RNHNH$_2$)(4-MeC$_6$H$_4$CN)L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 12 or PPh(OEt)$_2$ 13; R = Ph c or 4-MeC$_6$H$_4$ d]. These complexes were prepared exactly like the related **10** and **11** by treating the dinitrile complex [Ru(4-MeC$_6$H$_4$CN)$_2$L$_4$][BPh$_4$]$_2$ with an equimolar amount of the appropriate hydrazine in CH$_2$Cl$_2$ for 24 h; yield ⩾50%.

[Ru(4-O$_2$NC$_6$H$_4$NHNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 12e and [Ru(Me$_2$NNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 12f. To a solution of [Ru(4-MeC$_6$H$_4$CN)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ (0.12 mmol, 0.20 g) in CH$_2$Cl$_2$ (20 cm^3) was added an excess of the appropriate hydrazine (0.30 mmol) and the reaction mixture stirred for 24 h. The solvent was removed under reduced pressure giving an oil which was triturated with ethanol (3 cm^3). The resulting solution was vigorously stirred until a solid separated which was filtered off and crystallised from a mixture of CH$_2$Cl$_2$ and ethanol. A typical crystallisation involved the preparation of a solution of the compound by treating the solid sample with ethanol (7 cm^3) and enough CH$_2$Cl$_2$ to obtain a saturated solution at room temperature which was slowly cooled to −25 °C giving microcrystals of the product; yield ≥55%.

[Ru{η^2-NH=C(4-MeC$_6$H$_4$)NHNH$_2$}{P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 14 and [Ru{η^2-NH=C(Me)N(Me)NH$_2$}{P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 15. An equimolar amount of the hydrazine NH_2NH_2 or $MeNHNH_2$ (0.2 mmol) was added to a solution of the appropriate nitrile complex [Ru(RCN)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ (R = 4-MeC$_6$H$_4$ or Me) (0.2 mmol) in CH_2Cl_2 (10 cm^3) and the reaction mixture stirred for 24 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol (3 cm^3) containing an excess of $NaBPh_4$ (0.3 mmol, 0.1 g). A white solid separated from the resulting solution which was filtered off and fractionally crystallised in order to separate the amidrazone complex in pure form. A typical separation involved the addition of ethanol (7 cm^3) to the raw solid sample and enough CH_2Cl_2 to obtain a saturated solution at room temperature. By slow cooling to 0 °C a first fraction of the complex **14** or **15** was obtained. Further cooling of the solution to −30 °C gave an impure fraction which must be recrystallised. The total yield obtained of the pure compound was about 35%.

Oxidation reactions

The oxidation of the hydrazine complexes was carried out at low temperature (−30 to −40 °C) using Pb(O$_2$CMe)$_4$ as an oxidant. In a typical reaction a sample of the appropriate complex (0.2 mmol) was placed in a three-necked flask (25 cm^3) fitted with a solid-addition sidearm containing an equimolar amount or an excess of Pb(O$_2$CMe)$_4$. Dichloromethane was added, the solution cooled to −30 or −40 °C and the Pb(O$_2$CMe)$_4$ added portionwise in about 20–30 min to the cold stirred solution. Then the solution was filtered and the solvent removed under reduced pressure giving an oil which was treated with ethanol (5 cm^3) containing an excess of $NaBPh_4$ (0.4 mmol, 0.14 g). A yellow or white solid slowly separated which was filtered off and crystallised.

[Ru(η^2-O$_2$CMe){P(OEt)$_3$}$_4$]BPh$_4$ 16. This complex was obtained in high yield (≥80%) as a white solid from the oxidation of the [Ru(NH$_2$NH$_2$)$_2$L$_4$]$^{2+}$ or the [Ru(MeNHNH$_2$)$_2$L$_4$]$^{2+}$ cation (0.2 mmol) with Pb(O$_2$CMe)$_4$ (0.4 mmol, 0.177 g). The complex was crystallised from ethanol.

[RuH(PhN=NH){P(OEt)$_3$}$_4$]BPh$_4$ 18. The compound was prepared by oxidation of [RuH(PhNHNH$_2$){P(OEt)$_3$}$_4$]BPh$_4$ (0.2 mmol, 0.24 g) with an equimolar amount of Pb(O$_2$CMe)$_4$ (0.2 mmol, 0.089 g). The reaction product also contains the [Ru(η^2-O$_2$CMe){P(OEt)$_3$}$_4$]BPh$_4$ complex which was removed by fractional crystallisation from ethanol giving a pure sample of [RuH(PhN=NH){P(OEt)$_3$}$_4$]BPh$_4$; yield ≥20%.

[Ru(PhN=NH)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 19. The compound was prepared by oxidation of [Ru(PhNHNH$_2$)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ (0.2 mmol, 0.32 g) with Pb(O$_2$CMe)$_4$ (0.4 mmol, 0.177 g) in a 1 : 2 ratio. A mixture of [Ru(PhN=NH)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ and [Ru(η^2-O$_2$CMe){P(OEt)$_3$}$_4$]BPh$_4$ was obtained from which the bis(diazene) derivative was separated by fractional crystallisation from ethanol; yield ≥25%.

Crystallography

Suitable crystals of complex **16** for X-ray analysis were obtained by recrystallisation from ethanol. Automatic peak search and indexing procedures carried out on a Siemens AED diffractomer yielded a monoclinic primitive cell. Inspection of systematic absences and *E* statistics indicated unambiguously the space group as *P*2$_1$/*n*. Pertinent crystal data and basic information about data collection and structure refinement are given in Table 2. During data collection the intensity of one standard reflection was monitored to check crystal decomposition or loss of alignment. A decay (15%) was detected and a correction applied during data reduction. Lorentz-polarisation effects were also considered.

$$[RuH_2L_4] \xrightarrow{(i)} [RuH(\eta^1\text{-}OSO_2CF_3)L_4] \xrightarrow{(iii)} \underset{\mathbf{1,2,3}}{[RuH(RNHNH_2)L_4]^+}$$

$$[RuH_2L_4] \xrightarrow{(ii)} [Ru(\eta^2\text{-}O_2SOCF_3)L_4]^+ \xrightarrow{(iii)} \underset{\mathbf{4,5,6}}{[Ru(RNHNH_2)_2L_4]^{2+}}$$

Scheme 1 L = P(OEt)$_3$ **1** or **4**, PPh(OEt)$_2$ **2** or **5** or P(OMe)$_3$ **3** or **6**; R = H **a**, Me **b**, Ph **c**, 4-MeC$_6$H$_4$ **d** or 4-O$_2$NC$_6$H$_4$ **e** or Me$_2$-NNH$_2$ **f**. (*i*) One equivalent of CF_3SO_3H at −78 °C; (*ii*) 2 equivalents of CF_3SO_3H at −78 °C; (*iii*) an excess of $RNHNH_2$

The structure consists of discrete [Ru(η^2-O$_2$CMe){P(OEt)$_3$}$_4$]$^+$ cations and BPh$_4^-$ anions. The phase problem was solved by direct methods[12] and the structure refined by full-matrix least squares based on F^2 with non-hydrogen atoms belonging to the cation allowed anisotropic vibration. All hydrogen atoms were introduced in idealised positions and refined riding on their attached atoms. To prevent overfitting, the C–C and C–O bond distances were restrained to be similar for all ethoxy groups, and the thermal motion of carbon atoms was restrained to be approximately isotropic and to fulfil rigid-bond requirements, as implemented in SHELXL 93.[13] Neutral scattering factors were employed and anomalous dispersion terms were included for non-hydrogen atoms. Calculations were performed on an ENCORE91 computer using the programs SIR 92,[12] SHELXL 93,[13] PARST 95[14] and ZORTEP.[15] Use was made of the Cambridge Structural Database[16] facilities at the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. in Parma.

CCDC reference number 186/719.

Results and Discussion

Preparation of hydrazine complexes

Hydridehydrazine [RuH(RNHNH$_2$)L$_4$]BPh$_4$ **1**–**3** and bis(hydrazine) complexes [Ru(RNHNH$_2$)$_2$L$_4$][BPh$_4$]$_2$ **4**–**6** were prepared by treating hydride species [RuH$_2$L$_4$] first with triflic acid and then with the appropriate hydrazine, as shown in Scheme 1. The reaction of [RuH$_2$L$_4$] with 1 equivalent of CF_3SO_3H at low temperature proceeds with the formation of the dihydrogen cations[17] [RuH(η^2-H$_2$)L$_4$]$^+$CF$_3$SO$_3^-$ (detected by the ^{1}H NMR spectra of the solution) which slowly afford the final triflate complexes [RuH(η^1-OSO$_2$CF$_3$)L$_4$] by substitution of the H$_2$ ligand with the CF$_3$SO$_3^-$ ion. In the case of the P(OEt)$_3$ coligand the [RuH(η^1-OSO$_2$CF$_3$){P(OEt)$_3$}$_4$] complex was also separated as an oily product and characterised by IR and NMR spectroscopy. Treatment of the η^1-triflate complexes with further CF_3SO_3H probably results in the formation of new, unstable dihydrogen derivatives [Ru(η^2-H$_2$)(η^1-OSO$_2$CF$_3$)L$_4$]$^+$ which lose H$_2$ and give the η^2-triflate [Ru(η^2-O$_2$SOCF$_3$)L$_4$]$^+$ cations which can be isolated as BPh$_4^-$ salts and characterised. The η^2 coordination of the CF$_3$SO$_3$ ligand in these monocationic[18] complexes is further supported by the symmetric A$_2$B$_2$ multiplet observed in the ^{31}P-{^{1}H} NMR spectra. By treating both the η^1- and η^2-triflate complexes with the appropriate hydrazine the new ruthenium derivatives **1**–**6** can easily be prepared and characterised.

Good analytical data were obtained for all the hydrazine complexes **1**–**6** which are pale yellow or white solids, stable in the air and soluble in polar organic solvents where they behave as 1 : 1 (**1**–**3**) or 2 : 1 (**4**–**6**) electrolytes.[18] Their infrared and NMR data are reported in Table 1. The presence of the hydra-

Table 1 Infrared and NMR data for the ruthenium complexes

	IR[b]		^{1}H NMR[c,d]			^{31}P-{^{1}H} NMR[c,e]
Compound[a]	$\tilde{\nu}$/cm^{-1}	Assignment	δ	Assignment	Spin system	δ (*J*/Hz)
1a $[\mathrm{RuH(NH_2NH_2)}$-	3376m	ν(NH)	4.20–3.78 (m)[f]	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{AB_2C}$[f]	δ_A 148.9, δ_B 142.5, δ_C 137.4
$\{\mathrm{P(OEt)_3}\}_4]^+$	3338m		3.14 (br)	$\mathrm{RuNH_2}$		$J_{AB} = 62.7$, $J_{AC} = 39.2$,
	3273m		1.29 (t), 1.25 (t)	$\mathrm{POCH_2C}H_3$		$J_{BC} = 45.2$
	1879m	ν(RuH)	1.21 (t)			
	1592w	δ($\mathrm{NH_2}$)	−7.68 to −8.68 (m)	RuH		
1b $[\mathrm{RuH(MeNHNH_2)}$-	3348m	ν(NH)	4.28–3.90 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{AB_2C}$	δ_A 150.9, δ_B 143.9, δ_C 139.3
$\{\mathrm{P(OEt)_3}\}_4]^+$	3322m		3.10 (m)	$\mathrm{CH_3N}H$		$J_{AB} = 62.7$, $J_{AC} = 39.8$,
	1839m	ν(RuH)	2.49 (d)	$CH_3\mathrm{NH}$		$J_{BC} = 44.6$
			1.31 (t), 1.29 (t),	$\mathrm{POCH_2C}H_3$		
			1.24 (t)			
			−7.60 to −8.60 (m)	RuH		
1c $[\mathrm{RuH(PhNHNH_2)}$-	3367m	ν(NH)	4.89 (m)[g]	$\mathrm{C_6H_5N}H$	$\mathrm{AB_2C}$[g]	δ_A 148.4, δ_B 141.4. δ_C 136.8
$\{\mathrm{P(OEt)_3}\}_4]^+$	3323m		4.79 (m)	$\mathrm{RuNH_2}$		$J_{AB} = 62.8$, $J_{AC} = 39.3$,
	3312m		4.12–3.78 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{BC} = 45.6$
	1839m	ν(RuH)	1.27 (t), 1.21 (t),	$\mathrm{POCH_2C}H_3$		
	1605m	δ($\mathrm{NH_2}$)	1.18 (t)			
			−7.67 to −8.67 (m)	RuH		
1d $[\mathrm{RuH(4\text{-}MeC_6H_4NHNH_2)}$-	3356w	ν(NH)	5.21 (m, br)	$\mathrm{4\text{-}MeC_6H_4N}H$	$\mathrm{AB_2C}$	δ_A 150.0, δ_B 142.8, δ_C 138.3
$\{\mathrm{P(OEt)_3}\}_4]^+$	3331w		4.94 (m, br)	$\mathrm{RuNH_2}$		$J_{AB} = 62.8$, $J_{AC} = 39.5$,
	3322w		4.30–3.95 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{BC} = 45.4$
	1875m	ν(RuH)	2.23 (s)	$\mathrm{CH_3}$ *p*-tolyl		
	1605m	δ($\mathrm{NH_2}$)	1.34 (t), 1.28 (t).	$\mathrm{POCH_2C}H_3$		
			1.23 (t)			
			−7.43 to −8.43 (m)	RuH		
1e $[\mathrm{RuH(4\text{-}O_2NC_6H_4NHNH_2)}$-	3392m	ν(NH)	6.39 (m)	$\mathrm{4\text{-}O_2NC_6H_4N}H$	$\mathrm{AB_2C}$	δ_A 149.2, δ_B 142.1, δ_C 137.7
$\{\mathrm{P(OEt)_3}\}_4]^+$	3369m		5.24 (m)	$\mathrm{RuNH_2}$		$J_{AB} = 63.4$. $J_{AC} = 40.4$,
	3312m		4.34–3.94 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{BC} = 45.5$
	1844m	ν(RuH)	1.35 (t), 1.28 (t),	$\mathrm{POCH_2C}H_3$		
	1602m	δ($\mathrm{NH_2}$)	1.23 (t)			
			−7.35 to −8.35 (m)	RuH		
1f $[\mathrm{RuH(Me_2NNH_2)}$-	3316m	ν(NH)	4.30 (m, br)	$\mathrm{RuNH_2}$	$\mathrm{AB_2C}$	δ_A 151.6, δ_B 142.9, δ_C 137.4
$\{\mathrm{P(OEt)_3}\}_4]^+$	1879m	ν(RuH)	4.26–3.95 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{AB} = 62.7$, $J_{AC} = 36.2$,
			2.50 (s)	$\mathrm{N(CH_3)_2}$		$J_{BC} = 47.1$
			1.31 (t), 1.26 (t)	$\mathrm{POCH_2C}H_3$		
			−7.33 to −8.36 (m)	RuH		
2a $[\mathrm{RuH(NH_2NH_2)}$-	3370w	ν(NH)	4.00–3.16 (m)[f]	$\mathrm{POC}H_2\mathrm{CH_3}$	$\mathrm{AB_2C}$[f]	δ_A 170.3, δ_B 165.0, δ_C 159.9
$\{\mathrm{PPh(OEt)_2}\}_4]^+$	3333w		3.44 (m, br)	$\mathrm{RuNH_2}$		$J_{AB} = 46.6$, $J_{AC} = 28.7$,
	3265w		1.25 (t), 1.22 (t),	$\mathrm{POCH_2C}H_3$		$J_{BC} = 31.8$
	1922m (br)	ν(RuH)	1.18 (t), 0.88 (t)			
			−7.43 to −8.33 (m)	RuH		
2b $[\mathrm{RuH(MeNHNH_2)}$-	3341w	ν(NH)	4.26 (br)	$\mathrm{RuNH_2}$	$\mathrm{AB_2C}$	δ_A 171.9, δ_B 166.0, δ_C 161.0
$\{\mathrm{PPh(OEt)_2}\}_4]^+$	3305 m		4.10–3.25 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{AB} = 46.8$, $J_{AC} = 29.3$,
	1942m	ν(RuH)	3.60 (m)	$\mathrm{CH_3N}H$		$J_{BC} = 30.6$
			2.36 (d)	$CH_3\mathrm{NH}$		
			1.28 (t), 1.27 (t),	$\mathrm{POCH_2C}H_3$		
			1.23 (t), 0.91 (t)			
			−7.32 to −8.22 (m)	RuH		
2c $[\mathrm{RuH(PhNHNH_2)}$-	3380w	ν(NH)	5.44 (br)	$\mathrm{C_6H_5N}H$	$\mathrm{AB_2C}$	δ_A 171.4, δ_B165.7, δ_C 161.6
$\{\mathrm{PPh(OEt)_2}\}_4]^+$	3305w		4.49 (br)	$\mathrm{RuNH_2}$		$J_{AB} = 46.8$, $J_{AC} = 30.1$,
	3228w		4.50–3.30 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{BC} = 31.8$
	1908m	ν(RuH)	1.28 (t), 1.16 (t),	$\mathrm{POCH_2C}H_3$		
	1601m	δ($\mathrm{NH_2}$)	1.04 (t), 0.97 (t)			
			−7.15 to −8.05 (m)	RuH		
3a $[\mathrm{RuH(NH_2NH_2)}$-	3365w	ν(NH)	4.50 (br)	$\mathrm{RuNH_2}$	$\mathrm{AB_2C}$[f]	δ_A 154.0, δ_B 148.3, δ_C 142.2
$\{\mathrm{P(OMe)_3}\}_4]^+$	3340m		4.35 (br)	$\mathrm{NH_2}$		$J_{AB} = 63.6$, $J_{AC} = 40.0$,
	3279w					$J_{BC} = 44.4$
	1875m	ν(RuH)	4.01 (br)[f]	$\mathrm{RuNH_2}$		
			3.68 (t), 3.61 (d),	$\mathrm{POCH_3}$		
			3.48 (d)			
			−7.59 to −8.59 (m)	RuH		
4a $[\mathrm{Ru(NH_2NH_2)_2}$-	3375m	ν(NH)	4.38 (br)[f]	$\mathrm{RuNH_2}$	$\mathrm{A_2B_2}$[f]	δ_A 130.2, δ_B 120.5
$\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3325w		4.20–3.90 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{AB} = 61.8$
	3315 (sh)		2.90 (br)	$\mathrm{NH_2}$		
	3266w		1.33 (t), 1.29 (t)	$\mathrm{POCH_2C}H_3$		
	1617m	δ($\mathrm{NH_2}$)				
4b $[\mathrm{Ru(MeNHNH_2)_2}$-	3350w	ν(NH)	4.98 (br)	$\mathrm{RuNH_2}$	$\mathrm{A_2B_2}$	δ_A 131.3, δ_B 121.3
$\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3313w		4.45–4.20 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		$J_{AB} = 62.1$
	3299w		2.90 (br)	$\mathrm{CH_3N}H$		
	1597w	δ($\mathrm{NH_2}$)	2.68 (d)	$CH_3\mathrm{NH}$		
			1.42 (t), 1.37 (t)	$\mathrm{POCH_2C}H_3$		
4c $[\mathrm{Ru(PhNHNH_2)_2}$-	3317m	ν(NH)	6.65 (t, br)	$\mathrm{C_6H_5N}H$	$\mathrm{A_2B_2}$	δ_A 130.0, δ_B 120.6
$\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3298w		5.85 (br)	$\mathrm{RuNH_2}$		$J_{AB} = 62.0$
	3240w		4.54–4.30 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$		
	1601w	δ($\mathrm{NH_2}$)	1.42 (t), 1.39 (t)	$\mathrm{POCH_2C}H_3$		

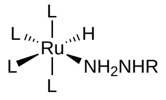
Table 1 (*Continued*)

	IR[b]		^{1}H NMR[c,d]			^{31}P-{^{1}H} NMR[c,e]
Compound[a]	ṽ/cm^{-1}	Assignment	δ	Assignment	Spin system	δ (J/Hz)
5a $[\mathrm{Ru(NH_2NH_2)_2\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3370w	ν(NH)	4.00–3.30 (m)[f]	POCH_2CH$_3$	A$_2$B$_2$[f]	δ_A 159.6, δ_B 151.4
	3342w		3.95 (br)	RuNH$_2$		$J_{AB} = 48.0$
	3317w		2.86 (br)	NH$_2$		
	3263w		1.27 (t), 1.24 (t)	POCH$_2$CH_3		
	1603m	δ(NH$_2$)				
5b $[\mathrm{Ru(MeNHNH_2)_2\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3334w	ν(NH)	4.23 (br)	RuNH$_2$	A$_2$B$_2$	δ_A 159.8, δ_B 152.0
	3302w		4.00–3.60 (m)	POCH_2CH$_3$		$J_{AB} = 47.9$
	3259w		3.95 (br)	CH$_3$NH		
			2.27 (d)	CH_3NH		
			1.39 (t), 1.36 (t)	POCH$_2$CH_3		
5c $[\mathrm{Ru(PhNHNH_2)_2\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3330w	ν(NH)	5.33 (br)	RuNH$_2$	A$_2$B$_2$	δ_A 159.3, δ_B 152.1
	3305w		4.30–3.70 (m)	POCH_2CH$_3$		$J_{AB} = 47.4$
	3294w		1.36 (t), 1.26 (t)	POCH$_2$CH_3		
	1601m	δ(NH$_2$)				
6a $[\mathrm{Ru(NH_2NH_2)_2\text{-}\{P(OMe)_3\}_4}]^{2+}$	3374w	ν(NH)	5.06 (br)[h]	RuNH$_2$	A$_2$B$_2$[h]	δ_A 137.4, δ_B 126.6
	3344w		3.82 (t), 3.68 (m, br)	POCH$_3$		$J_{AB} = 61.4$
	3312m		2.48 (br)	NH$_2$		
	3270m					
	1609m	δ(NH$_2$)				
7 $[\mathrm{Ru(\eta^2\text{-}PhCONHNH_2)\text{-}\{P(OEt)_3\}_4}]^{2+}$	3296m	ν(NH)	7.60 (t, br)[f]	NH	ABC$_2$	δ_A 134.9, δ_B 132.0, δ_C 119.7
	3236w		5.55 (m, br)	RuNH$_2$		$J_{AB} = 84.7$, $J_{AC} = 60.0$,
	3207w		4.20–3.90 (m)	POCH_2CH$_3$		$J_{BC} = 59.9$
	1632m	ν(CO)	1.32 (t), 1.30 (t)	POCH$_2$CH_3		
	1603m	δ(NH$_2$)	1.18 (t)			
8 $[\mathrm{Ru(\eta^2\text{-}PhCONHNH_2)\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3509w	ν(NH)	5.20 (m, br)[f]	RuNH$_2$	ABC$_2$[f]	δ_A 160.0, δ_B 158.7, δ_C 148.0
	3295w		4.10–3.50 (m)	POCH_2CH$_3$		$J_{AB} = 63.8$, $J_{AC} = 45.2$,
	1627m	ν(CO)	1.38 (t), 1.32 (t),	POCH$_2$CH_3		$J_{BC} = 45.2$
	1603m	δ(NH$_2$)	1.23 (t), 1.20 (t)			
9 $[\mathrm{Ru(\eta^1\text{-}OSO_2CF_3)(Me_2\text{-}NNH_2)\{P(OEt)_3\}_4}]^{+}$	3302m	ν(NH)	5.12 (m, br)	RuNH$_2$	ABC$_2$	δ_A 134.1, δ_B 129.8, δ_C 120.8
	3232w		4.44–4.10 (m)	POCH_2CH$_3$		$J_{AB} = 75.5$, $J_{AC} = 59.6$,
	1616m	δ(NH$_2$)	2.72 (s)	N(CH$_3$)$_2$		$J_{BC} = 65.3$
			1.41 (t), 1.38 (t),	POCH$_2$CH_3		
			1.37 (t), 1.35 (t)			
10c $[\mathrm{Ru(PhNHNH_2)(MeCN)\text{-}\{P(OEt)_3\}_4}]^{2+}$	3365w	ν(NH)	5.78 (br)	C$_6$H$_5$NH	ABC$_2$	δ_A 130.0, δ_B 125.5, δ_C 120.1
	3357w		5.56 (br)	RuNH$_2$		$J_{AB} = 71.6$, $J_{AC} = 57.6$,
	3311w		4.40–4.20 (m)	POCH_2CH$_3$		$J_{BC} = 63.1$
	1601m	δ(NH$_2$)	2.67 (s)	CH$_3$CN		
			1.41 (t), 1.37 (t).	POCH$_2$CH_3		
			1.34 (t)			
10e $[\mathrm{Ru(4\text{-}O_2NC_6H_4NHNH_2)\text{-}(MeCN)\{P(OEt)_3\}_4}]^{2+}$	3390w	ν(NH)	7.14 (m, br)	RuNH$_2$	ABC$_2$	δ_A 134.8, δ_B 132.6, δ_C 120.1
	3289w		4.40–4.10 (m)	POCH_2CH$_3$		$J_{AB} = 74.5$, $J_{AC} = 62.3$,
	3235w		2.22 (s)	CH$_3$CN		$J_{BC} = 57.2$
	1635m	δ(NH$_2$)	1.40 (t), 1.38 (t),	POCH$_2$CH_3		
			1.34 (t), 1.31 (t)			
11a $[\mathrm{Ru(NH_2NH_2)(MeCN)\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3371w	ν(NH)	4.10–3.60 (m)[f]	POCH_2CH$_3$	ABC$_2$[f]	δ_A 158.5, δ_B 155.5, δ_C 149.7
	3316w		2.24 (br)	RuNH$_2$		$J_{AB} = 55.5$, $J_{AC} = 41.9$,
	3265w		1.34 (t), 1.31 (t),	POCH$_2$CH_3		$J_{BC} = 47.9$
			1.28 (t)			
			0.87 (s)	CH$_3$CN		
11c $[\mathrm{Ru(PhNHNH_2)(MeCN)\text{-}\{PPh(OEt)_2\}_4}]^{2+}$	3373w	ν(NH)	5.08 (m, br)	C$_6$H$_5$NH	ABC$_2$	δ_A 158.6, δ_B 155.9, δ_C 149.8
	3292w		4.89 (m, br)	RuNH$_2$		$J_{AB} = 56.7$, $J_{AC} = 42.4$,
	3225w		4.20–3.80 (m)	POCH_2CH$_3$		$J_{BC} = 47.4$
	1601m	δ(NH$_2$)	1.49 (s)	CH$_3$CN		
			1.43 (t), 1.41 (t),	POCH$_2$CH_3		
			1.37 (t), 1.09 (t)			
12c $[\mathrm{Ru(PhNHNH_2)(4\text{-}Me\text{-}C_6H_4CN)\{P(OEt)_3\}_4}]^{2+}$	3360w	ν(NH)	5.93 (m)	C$_6$H$_5$NH	ABC$_2$	δ_A 129.9, δ_B 125.2, δ_C 119.6
	3311w		5.69 (m)	RuNH$_2$		$J_{AB} = 71.6$, $J_{AC} = 57.6$,
	3245w		4.50–4.25 (m)	POCH_2CH$_3$		$J_{BC} = 63.0$
	2260m	ν(CN)	2.47 (s)	CH$_3$ *p*-tolyl		
	1602m	δ(NH$_2$)	1.41 (t), 1.37 (t),	POCH$_2$CH_3		
			1.33 (t)			
12d $[\mathrm{Ru(4\text{-}MeC_6H_4NHNH_2)\text{-}(4\text{-}MeC_6H_4CN)\{P(OEt)_3\}_4}]^{2+}$	3358w	ν(NH)	5.78 (br)	4-CH$_3$C$_6$H$_4$NH	ABC$_2$	δ_A 130.0, δ_B 125.2, δ_C 119.7
	3313w		5.62 (br)	RuNH$_2$		$J_{AB} = 71.6$, $J_{AC} = 57.5$,
	3247w		4.45–4.25 (m)	POCH_2CH$_3$		$J_{BC} = 62.8$
	2260m	ν(CN)	2.46 (s)	4-CH$_3$ (CN)		
	1604m	δ(NH$_2$)	2.26 (s)	4-CH$_3$ (NHNH$_2$)		
			1.40 (t), 1.32 (t)	POCH$_2$CH_3		
12e $[\mathrm{Ru(4\text{-}O_2NC_6H_4NHNH_2)\text{-}(4\text{-}MeC_6H_4CN)\{P(OEt)_3\}_4}]^{2+}$	3380w	ν(NH)	4.42–4.20 (m)	POCH_2CH$_3$	ABC$_2$	δ_A 133.9, δ_B 132.2, δ_C 119.7
	3290w		2.29 (s)	CH$_3$ *p*-tolyl		$J_{AB} = 74.0$, $J_{AC} = 62.3$,
	3237w		1.41 (t), 1.36 (t),	POCH$_2$CH_3		$J_{BC} = 57.8$
	2263m	ν(CN)	1.33 (t)			
	1609m	δ(NH$_2$)				

Table 1 (*Continued*)

	IR[b]		^{1}H NMR[c,d]			^{31}P-{^{1}H} NMR[c,e]
Compound[a]	$\tilde{\nu}$/cm^{-1}	Assignment	δ	Assignment	Spin system	δ (*J*/Hz)
12f $[Ru(Me_2NHNH_2)(4\text{-}MeC_6H_4CN)\{P(OEt)_3\}_4]^{2+}$	3308w	ν(NH)	4.68 (m, br)	$RuNH_2$	ABC_2	δ_A 130.2, δ_B 124.0, δ_C 119.8
	2264m	ν(CN)	4.50–4.20 (m)	$POCH_2CH_3$		$J_{AB} = 67.2$, $J_{AC} = 57.5$,
	1603m	$\delta(NH_2)$	2.69 (s)	$N(CH_3)_2$		$J_{BC} = 64.8$
			2.46 (s)	CH_3 *p*-tolyl		
			1.41 (t), 1.40 (t), 1.38 (t)	$POCH_2CH_3$		
13c $[Ru(PhNHNH_2)(4\text{-}MeC_6H_4CN)\{PPh(OEt)_2\}_4]^{2+}$	3377w	ν(NH)	5.26 (br)	C_6H_5NH	ABC_2	δ_A 158.9, δ_B 155.1, δ_C 149.9
	3293w		5.09 (br)	$RuNH_2$		$J_{AB} = 56.1$, $J_{AC} = 41.9$,
	2250m	ν(CN)	4.30–3.50 (m)	$POCH_2CH_3$		$J_{BC} = 48.0$
	1602m	$\delta(NH_2)$	2.38 (s)	CH_3 *p*-tolyl		
			1.47 (t), 1.40 (t)	$POCH_2CH_3$		
14 $[Ru\{\eta^2\text{-}NH{=}C(4\text{-}MeC_6H_4)NHNH_2\}\{P(OEt)_3\}_4]^{2+}$	3397w	ν(NH)	9.57 (br)	NH=	ABC_2[f]	δ_A 135.2, δ_B 133.1, δ_C 120.4
	3333w		7.50 (m, br)	NH		$J_{AB} = 73.1$, $J_{AC} = 62.1$,
	3310w					$J_{BC} = 57.3$
	1635m	$\delta(NH_2)$	7.20 (br)[f]	NH=		
			5.83 (m, br)	$RuNH_2$		
			5.52 (m, br)	NH		
			4.20–3.90 (m)	$POCH_2CH_3$		
			2.39 (s)	CH_3 *p*-tolyl		
			1.32 (s), 1.28 (t), 1.22 (t)	$POCH_2CH_3$		
15 $[Ru\{\eta^2\text{-}NH{=}C(Me)N(Me)NH_2\}\{P(OEt)_3\}_4]^{2+}$	3399w	ν(NH)	7.80 (br)	NH=		132–118 (m)
	3307w		6.55 (br)	$RuNH_2$		
	1641m	$\delta(NH_2)$	4.45–4.15 (m)	$POCH_2CH_3$		
			2.55 (s), 2.45 (s)	$NCH_3 + CCH_3$		
			1.40 (t), 1.38 (t), 1.34 (t)	$POCH_2CH_3$		
16 $[Ru(\eta^2\text{-}O_2CMe)\{P(OEt)_3\}_4]^{+}$[i]	1524m	ν(CO)	4.25–4.05 (m)	$POCH_2CH_3$	A_2B_2[f]	δ_A 139.5, δ_B 126.4
			1.86 (s)	CH_3CO_2		$J_{AB} = 57.2$
			1.32 (t), 1.29 (t)	$POCH_2CH_3$		

[a] All compounds are BPh_4^- salts. [b] In KBr pellets. [c] In $(CD_3)_2CO$. [d] Phenyl-proton resonances are omitted. [e] Positive shift downfield from 85% H_3PO_4. [f] In CD_2Cl_2. [g] In $CDCl_3$. [h] In $(CD_3)_2SO$. [i] ^{13}C NMR: δ 187.8 (m, CO), 165–122 (m, Ph), 62.5 (t), 62.3 (t) (CH_2), 24.3 (s, $MeCO_2$), 16.5 (t), 16.3 (t) (CH_3 of phosphite).



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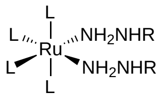


II

zine ligand in all the compounds is confirmed by the IR spectra which show the characteristic ν(NH) and $\delta(NH_2)$ bands, observed at 3392–3228 (weak) and at 1617–1592 (medium) cm^{-1}, respectively. Furthermore, in the ^{1}H NMR spectra the NH_2 and NH proton signals of the hydrazine ligand have been identified and properly attributed by accurate integration and decoupling experiments, so confirming the co-ordination of the $RNHNH_2$ ligand. Finally, in the complexes **1a**–**6a** containing the NH_2NH_2 ligand both the signals of the co-ordinated and free NH_2 protons appear in the ^{1}H spectra, so excluding the presence of a dimeric complex with NH_2NH_2 bridging.

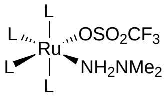
The infrared spectra of the hydridehydrazine derivatives $[RuH(RNHNH_2)L_4]^+$ **1**–**3** also show a medium-intensity ν(RuH) band at 1922–1839 cm^{-1}. Furthermore, in the ^{1}H NMR spectra the hydride ligand appears as a multiplet between δ −8.68 and −7.15. Finally, in the temperature range from +30 to −90 °C the ^{31}P-{^{1}H} NMR spectra appear as a AB_2C multiplet simulable with the parameters reported in Table 1 and suggesting the existence in solution of a type **I** geometry with the hydride and the hydrazine ligands in a mutually *cis* position.

The ^{31}P-{^{1}H} NMR spectra of the bis(hydrazine) $[Ru(RNHNH_2)_2L_4]^{2+}$ **4**–**6** cations appear as a symmetric A_2B_2 multiplet in agreement, in this case, with a *cis* arrangement (geometry **II**) of the two hydrazine ligands.

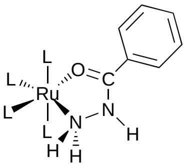
$$[Ru(\eta^2\text{-}O_2SOCF_3)L_4]^+ \xrightarrow{\text{excess } Me_2NNH_2} [Ru(\eta^1\text{-}OSO_2CF_3)(Me_2NNH_2)L_4]^+$$

9

Scheme 2 L = $P(OEt)_3$



III



IV

Treatment of the η^2-triflate complexes $[Ru(\eta^2\text{-}OSO_2CF_3)L_4]^+CF_3SO_3^-$ with an excess of the disubstituted *N*,*N*-dimethylhydrazine Me_2NNH_2 did not afford the bis(hydrazine) derivative but, surprisingly, a compound separated as a white solid in the case of L = $P(OEt)_3$ and characterised as the new hydrazinetriflate complex $[Ru(\eta^1\text{-}OSO_2CF_3)(Me_2NNH_2)L_4]BPh_4$ **9** (Scheme 2). The infrared spectrum shows two ν(NH) bands at 3302 and 3232 cm^{-1} and $\delta(NH_2)$ at 1616 cm^{-1} indicating the presence of the hydrazine ligand. One band at 1325 cm^{-1} seems to confirm the η^1-O co-ordination of the triflate ion.[19] The complex is a diamagnetic, 1 : 1 electrolyte[18] and the ^{1}H NMR spectrum confirms the presence of both the hydrazine (NH_2 protons at δ 5.12) and the phosphite ligands. Furthermore, the ^{31}P-{^{1}H} NMR spectrum appears as an ABC_2 multiplet which excludes the presence of a bis(hydrazine) complex and suggests a type **III** geometry with the triflate and the Me_2NNH_2 ligands in a mutually *cis* arrangement. The exclusive formation of monohydrazine complexes with the disubstituted Me_2NNH_2 ligand may be reasonably attributed to the greater steric hindrance of the latter as compared to monosubstituted hydrazines which prevents the co-ordination of two ligands in a *cis* position to the RuL_4 fragment.

Benzoylhydrazine also reacts with the η^2-triflate cations

$$[Ru(\eta^2\text{-}O_2SOCF_3)L_4]^+ \xrightarrow{PhCONHNH_2} [Ru(\eta^2\text{-}PhCONHNH_2)L_4]^{2+}$$
7,**8**

Scheme 3

$$[Ru(R^2CN)_2\{PPh(OEt)_2\}_4]^{2+} \xrightarrow{R^1NHNH_2} [Ru(R^1NHNH_2)(R^2CN)\{PPh(OEt)_2\}_4]^{2+}$$
11,**13**

$$\xrightarrow{R^1NHNH_2} [Ru(R^1NHNH_2)_2\{PPh(OEt)_2\}_4]^{2+}$$
5

R^1 = H, Me, Ph, 4-MeC_6H_4, 4-$O_2NC_6H_4$
R^2 = Me **11**, 4-MeC_6H_4 **13**

$$[Ru(R^2CN)_2\{P(OEt)_3\}_4]^{2+} \xrightarrow{R^1NHNH_2} [Ru(R^1NHNH_2)(R^2CN)\{P(OEt)_3\}_4]^{2+}$$
10,**12**

$$\xrightarrow{R^1NHNH_2} [Ru(R^1NHNH_2)_2\{P(OEt)_3\}_4]^{2+}$$
4

R^1 = Ph, 4-MeC_6H_4, 4-$O_2NC_6H_4$
R^2 = Me **10**, 4-MeC_6H_4 **12**

$$[Ru(R^2CN)_2\{P(OEt)_3\}_4]^{2+} \xrightarrow{R^1NHNH_2} [Ru\{\eta^2\text{-}NH{=}C(R^2)N(R^1)NH_2\}\{P(OEt)_3\}_4]^{2+}$$
14,**15**

$$+ [Ru(R^1NHNH_2)_2\{P(OEt)_3\}_4]^{2+}$$
4

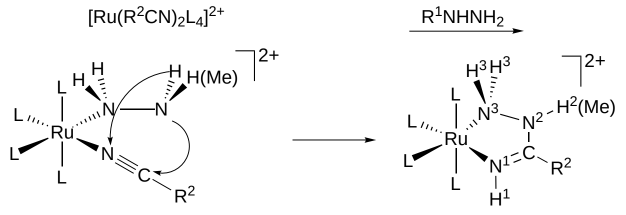
R^1 = H, Me
R^2 = Me, 4-MeC_6H_4

Scheme 4

$[Ru(\eta^2\text{-}OSO_2CF_3)L_4]^+$ to give the corresponding complexes $[Ru(\eta^2\text{-}PhCONHNH_2)L_4][BPh_4]_2$ **7** and **8** which were isolated and characterised (Scheme 3). The spectroscopic data (Table 1) support the formulation of the compounds and suggest an η^2 co-ordination of the benzoylhydrazine ligand, as shown in the type **IV** geometry.

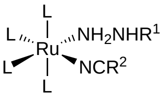
New hydrazine complexes of ruthenium of the type $[Ru(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ **10**–**13** were prepared by treating the bis(nitrile) complexes $[Ru(R^2CN)_2L_4][BPh_4]_2$ with the appropriate hydrazine. The reaction proceeds easily, but depends on several factors, including the nature of the phosphite ligand and of the hydrazine and the reaction conditions, as shown in Scheme 4. The reaction of the bis(nitrile) cations containing $PPh(OEt)_2$, $[Ru(R^2CN)_2\{PPh(OEt)_2\}_4]^{2+}$, with hydrazines proceeds with the substitution of both the R^2CN ligands giving a mixture of mono $[Ru(R^1NHNH_2)(R^2CN)L_4]^{2+}$ **11**,**13** and bis(hydrazine) derivatives $[Ru(R^1NHNH_2)_2L_4]^{2+}$ **5**. However, also operating at a low $[Ru(R^2CN)_2L_4]^{2+}$: R^1NHNH_2 ratio, a mixture containing both the two hydrazine complexes (**11** or **13** and **5**) was always obtained, the separation of which was rather difficult and laborious. In only three cases, **11a**, **11c** and **13c**, we were able to separate by fractional crystallisation the nitrilehydrazine complexes in pure form.

Also the related bis(nitrile) complexes $[Ru(R^2CN)_2\{P(OEt)_3\}_4][BPh_4]_2$ containing the $P(OEt)_3$ phosphite ligands react quickly with hydrazines R^1NHNH_2, but the reaction depends on the nature of the substituent on the same hydrazine molecule. With arylhydrazine it proceeds to give a mixture of mono- and bis-(hydrazine) derivatives $[Ru(R^1NHNH_2)(R^2CN)L_4]^{2+}$ **10** and **12** and $[Ru(R^1NHNH_2)_2L_4]^{2+}$ **4** (R^1 = Ph, 4-MeC_6H_4 or 4-$O_2NC_6H_4$), respectively, from which the nitrilehydrazine complexes **10** and **12** can be separated by fractional crystallisation and characterised. With *N*,*N*-dimethylhydrazine, instead, the reaction is slow and affords only the monosubstituted nitrilehydrazine $[Ru(Me_2NNH_2)(4\text{-}MeC_6H_4CN)\{P(OEt)_3\}_4][BPh_4]_2$ **12f** derivative which was isolated and characterised. Treatment of the $[Ru(R^2CN)_2\{P(OEt)_3\}_4]^{2+}$ derivatives with the hydrazine NH_2NH_2 and the methylhydrazine $MeNHNH_2$ does not give the nitrilehydrazine complexes but a mixture containing the known bis(hydrazine) compounds **4** and new complexes which were separated and characterised (see below) as the amidrazone[20] derivatives $[Ru\{\eta^2\text{-}NH{=}C(R^2)N(R^1)NH_2\}L_4][BPh_4]_2$ (R^1 = H or Me; R^2 = 4-MeC_6H_4 or Me) **14** and **15**.



VI

Scheme 5 L = $P(OEt)_3$; R^1 = H or Me; R^2 = 4-MeC_6H_4 or Me



V

The nitrilehydrazine complexes $[Ru(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ **10**–**13** are white or pale yellow solids stable in air and are 1 : 2 electrolytes.[18] The spectroscopic properties, Table 1, confirm their formulation and suggest that the hydrazine and the nitrile ligands are in a mutually *cis* position as in a type **V** geometry.

The IR spectra of the amidrazone complexes $[Ru\{\eta^2\text{-}NH{=}C(R^2)N(R^1)NH_2\}L_4][BPh_4]_2$ **14** and **15** (Table 1) display $\nu(NH)$ and $\delta(NH_2)$ bands at 3399–3307 and 1641–1635 cm^{-1}, respectively, but do not show any $\nu(CN)$ band of the RCN group. In the ^1H NMR spectrum of the complex $[Ru\{\eta^2\text{-}NH{=}C(4\text{-}MeC_6H_4)NHNH_2\}\{P(OEt)_3\}_4][BPh_4]_2$ **14** three slightly broad signals of intensity ratio 1 : 2 : 1 are present at δ 7.20, 5.83 and 5.52 (CD_2Cl_2) which were assigned by homodecoupling experiments to the H^1, H^3 and H^2 protons, respectively, of the amidrazone ligand schematised in geometry **VI**. Good elemental analyses were obtained for the two complexes **14** and **15**, the ^{31}P NMR spectra of which are consistent with a type **VI** geometry.

The formation of an amidrazone complex from the reaction of a bis(nitrile) derivative with hydrazine NH_2NH_2 or methylhydrazine is not completely unexpected, taking into account that a co-ordinated nitrile can undergo nucleophilic attack by several reagents such as alcohols, amines and carbanions to give iminoethers, amidines and imines,[21–24] respectively. Therefore, taking into account that the first step of the reaction of the bis(nitrile) with hydrazine is probably the substitution of one R^2CN ligand to give the $[Ru(R^1NHNH_2)(R^2CN)L_4]^{2+}$ cations (see Scheme 4), the formation of the amidrazone complexes can be explained according to a reaction course that involves a nucleophilic attack of one end of R^1NHNH_2 on the cyanide carbon atom of the co-ordinated nitrile followed by a hydrogen shift, giving a five-membered metallacycle (Scheme 5). A similar reaction, giving an amidrazone complex, has been observed by us in iron derivatives[25] and therefore it seems certain that also a hydrazine molecule can behave as a reagent for nucleophilic attack upon co-ordinated nitrile[24] giving the amidrazone complexes. However, this cyclisation reaction is influenced both by the substituent on the hydrazine and by the nature of the ancillary phosphine ligand. In fact, the cyclisation reaction does not take place with any arylhydrazine R^1NHNH_2 (R^1 = Ph,

$$\underset{\mathbf{12,13}}{[\mathrm{Ru(R^1NHNH_2)(R^2CN)L_4}]^{2+}} \xrightarrow{(i)} [\mathrm{Ru(R^1N{=}NH)(R^2CN)L_4}]^{2+} + \underset{\mathbf{16,17}}{[\mathrm{Ru(\eta^2\text{-}O_2CMe)L_4}]^{+}}$$

$$\underset{\mathbf{1,2}}{[\mathrm{RuH(R^1NHNH_2)L_4}]^{+}} \xrightarrow{(i)} \underset{\mathbf{18}}{[\mathrm{RuH(R^1N{=}NH)L_4}]^{+}} + \underset{\mathbf{16,17}}{[\mathrm{Ru(\eta^2\text{-}O_2CMe)L_4}]^{+}}$$

$$\underset{\mathbf{4,5}}{[\mathrm{Ru(R^1NHNH_2)_2L_4}]^{2+}} \xrightarrow{(i)} \underset{\mathbf{19}}{[\mathrm{Ru(R^1N{=}NH)_2L_4}]^{2+}} + \underset{\mathbf{16,17}}{[\mathrm{Ru(\eta^2\text{-}O_2CMe)L_4}]^{+}}$$

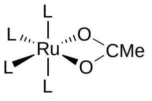
$$\left.\begin{array}{r} {[\mathrm{RuH(NH_2NH_2)L_4}]^{+}} \\ {[\mathrm{Ru(NH_2NH_2)_2L_4}]^{2+}} \\ {[\mathrm{Ru(MeNHNH_2)_2L_4}]^{2+}} \end{array}\right\} \xrightarrow{(i)} \underset{\mathbf{16,17}}{[\mathrm{Ru(\eta^2\text{-}O_2CMe)L_4}]^{+}}$$

Scheme 6 L = $P(OEt)_3$ **1**,**4**,**12**,**16**,**18**,**19**, $PPh(OEt)_2$ **2**,**5**,**13**,**17**; R^1 = Ph, 4-MeC_6H_4; R^2 = 4-MeC_6H_4. (*i*) $Pb(O_2CMe)_4$, CH_2Cl_2, −30 °C

4-MeC_6H_4 or 4-$O_2NC_6H_4$) and this absence of reactivity may be reasonably attributed to the steric hindrance of the aryl substituent of the co-ordinated hydrazine. Furthermore, the amidrazone complexes are formed only with the $P(OEt)_3$ ligand, while no evidence of such a reaction has been observed with the nitrilehydrazine derivatives $[Ru(NH_2NH_2)(R^2CN)L_4]^{2+}$ and $[Ru(MeNHNH_2)(R^2CN)L_4]^{2+}$ containing $PPh(OEt)_2$ as ancillary ligands. Therefore, it seems that a nitrile bonded to a $Ru(RNHNH_2)L_4$ fragment can undergo nucleophilic attack on the cyanide carbon atom only when the phosphines are good π-acceptor ligands such as $P(OEt)_3$ and when a hydrazine such as NH_2NH_2 or $MeNHNH_2$ is used. With the less π-acidic $PPh(OEt)_2$,[26] instead, the cyclisation reaction does not take place, so emphasising the important influence that the ancillary ligands have in the formation of the amidrazone complexes.

Oxidation reactions

Hydrazine complexes of ruthenium(II) react with $Pb(O_2CMe)_4$ in CH_2Cl_2 at −30 °C to give the corresponding diazene derivatives and/or the acetate $[Ru(\eta^2\text{-}O_2CMe)L_4]BPh_4$ complexes as shown in Scheme 6. Treatment of both mono- (**1**,**2**,**12**,**13**) and bis-(arylhydrazine) (**4**,**5**) complexes with $Pb(O_2CMe)_4$ at −30 °C results in the formation of the corresponding aryldiazenes which, however, can be isolated as a mixture of products containing also the acetate complex $[Ru(\eta^2\text{-}O_2CMe)L_4]BPh_4$ **16** and **17** and the starting hydrazine compound. The amount of the three products in the mixture depends on the ratio between the hydrazine complexes and the $Pb(O_2CMe)_4$ and on the reaction time. In each case a mixture of products was obtained from which the separation of pure samples of aryldiazene was rather difficult. However, although the presence of the diazene complex can easily be detected by the ^1H NMR spectra, in the case of the oxidation of $[Ru(PhNHNH_2)_2\{P(OEt)_3\}_4][BPh_4]_2$ **4c** and $[RuH(PhNHNH_2)\{P(OEt)_3\}_4]BPh_4$ **1c** we were able to separate by fractional crystallisation the compounds $[Ru(PhN{=}NH)_2\{P(OEt)_3\}_4][BPh_4]_2$ **19** and $[RuH(PhN{=}NH)\{P(OEt)_3\}_4]BPh_4$ **18** in pure form. Their characterisation is supported by the characteristic high-frequency NH signal at δ 15–14 observed in the ^1H NMR spectra and by the A_2B_2 and ABC_2 multiplets, respectively, in the ^{31}P spectra. Furthermore, a comparison of their spectroscopic data with those of the phenyldiazene complexes $[Ru(PhN{=}NH)_2\{P(OEt)_3\}_4][BPh_4]_2$ or $[RuH(PhN{=}NH)\{P(OEt)_3\}_4]BPh_4$, previously prepared by us[2b] from the reaction of the hydride $[RuH_2\{P(OEt)_3\}_4]$ with the benzenediazonium salt $PhN_2^+BF_4^-$, further confirms the proposed formulation and emphasises that aryldiazene complexes of ruthenium(II) can be obtained both by the insertion reaction of RN_2^+ into a Ru–H bond and by the oxidation of an arylhydrazine derivative.



VII

Oxidation of hydrazine complexes giving stable diazene derivatives has been reported in a few cases[4c,7,27] and often involves dinuclear complexes with a diazene bridging unit. It can be finally noted that the presence of the acetate complex **16** and **17** in the final oxidation product is not surprising as it may be formed by substitution of the diazene ligand with the acetate ion present in solution owing to the use of $Pb(O_2CMe)_4$ as oxidising agent.

The results obtained on the oxidation of arylhydrazine complexes prompted us to extend these studies to the hydrazine NH_2NH_2 and methylhydrazine $MeNHNH_2$ derivatives in an attempt to prepare the corresponding 1,2-diazene NH=NH and methyldiazene MeN=NH complexes of Ru^{II}. Unfortunately, although the oxidation reaction proceeds easily with $Pb(O_2CMe)_4$, the only isolated products were the acetate $[Ru(\eta^2\text{-}O_2CMe)L]BPh_4$ complexes in high yield. Probably, also in this case, the oxidation reaction proceeds to give the diazene ligand which is labile in the complexes and can be substituted by the acetate ion giving $[Ru(\eta^2\text{-}O_2CMe)L_4]^+$ as the final product. We also attempted to oxidise the hydrazine ligand using other reagents such as O_2, H_2O_2, Bu^tO_2H, but the formation of the diazene complexes was not observed. Equimolar amounts of the hydrazine complex and the oxidizing agent gave no reaction, while the use of an excess of reagent or reflux conditions caused decomposition of the complex. Therefore, it seems that only $Pb(O_2CMe)_4$ can give selective oxidation of the co-ordinated hydrazine affording the corresponding diazene which is rather labile and can be substituted by the $MeCO_2^-$ ion giving $[Ru(\eta^2\text{-}O_2CMe)L]BPh_4$ as final product. The acetate complex has also been obtained in pure form and fully characterised in the case of $[Ru(\eta^2\text{-}O_2CMe)\{P(OEt)_3\}_4]BPh_4$ **16** containing $P(OEt)_3$ as supporting ligand and its spectroscopic data are reported in Table 1. Compound **16** is a white solid stable in the air and in solutions of polar organic solvents where it behaves as a 1 : 1 electrolyte.[18] In the IR spectrum the ν(CO) band of the acetate ligand is observed at 1524 cm^{-1}, while in the ^1H NMR spectrum the methyl protons of the $MeCO_2$ group appear as a singlet at δ 1.86. Furthermore, in the ^{13}C spectrum the carbonyl carbon atom of the acetate ligand appears as a multiplet at δ 187.8 while the methyl carbon atom appears at δ 24.3. Finally, in the temperature range between +20 and −80 °C the ^{31}P spectra appear as a symmetric A_2B_2 multiplet consistent with the formulation proposed containing a η^2-acetate ligand[28] and schematised in geometry **VII**.

Such a geometry is confirmed by a crystal structure determination of compound **16** the asymmetric unit of which contains a $[Ru(\eta^2\text{-}O_2CMe)\{P(OEt)_3\}_4]^+$ cation and a BPh_4^- anion. A perspective view of the cation is shown in Fig. 1, along with the labelling scheme. Relevant geometric parameters are reported in Table 3. The ruthenium is co-ordinated to four phosphorus and two oxygen atoms in a distorted octahedral fashion. The acetate acts as a symmetric bidentate ligand [Ru–O(13) 2.195(6), Ru–O(14) 2.221(6) Å] and lies in the plane containing Ru, P(1) and P(4). The line defined by Ru, C(49) and C(50) bisects the angle P(1)–Ru–P(4) [P(1)–Ru–C(49) 132, P(4)–Ru–C(49) 136°]. If the ethoxy groups are neglected, the geometry of the complex closely approximates the $C2_v$ point-group symmetry, with the two-fold axis placed along the

Table 2 Crystal data and structure refinement for [Ru(η^2-O_2CMe){P(OEt)$_3$}$_4$]BPh_4 **16**

Empirical formula	$C_{50}H_{83}BO_{14}P_4Ru$
M	1143.99
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	13.472(3)
b/Å	24.268(5)
c/Å	18.965(4)
β/°	94.68(5)
U/Å^3	6180(2)
Z	4
D_c/Mg m^{-3}	1.224
μ/mm^{-1}	0.412
F(000)	2396
λ/Å	0.710 69
θ Range for data collection/°	3 to 27
Index ranges	$-17 < h < 17, 0 \leq k \leq 31, 0 \leq l \leq 24$
Reflections collected	13 871
Independent reflections	13 478
Data, restraints, parameters	13 478, 337, 537
Goodness of fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0756$, $wR2 = 0.1993$
Largest ΔF peak and hole/e Å^{-3}	0.672, −0.521

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Ru–P(1)	2.216(3)	Ru–O(14)	2.221(6)
Ru–P(2)	2.342(3)	O(13)–C(49)	1.277(13)
Ru–P(3)	2.339(3)	O(14)–C(49)	1.254(12)
Ru–P(4)	2.222(3)	C(49)–C(50)	1.493(14)
Ru–O(13)	2.195(6)		
P(1)–Ru–P(2)	96.98(9)	P(3)–Ru–O(13)	86.35(17)
P(1)–Ru–P(3)	95.05(10)	P(3)–Ru–O(14)	83.82(17)
P(1)–Ru–P(4)	91.95(10)	P(4)–Ru–O(13)	165.51(16)
P(1)–Ru–O(13)	102.54(17)	P(4)–Ru–O(14)	106.75(18)
P(1)–Ru–O(14)	161.30(17)	O(13)–Ru–O(14)	58.8(2)
P(2)–Ru–P(3)	167.52(9)	Ru–O(13)–C(49)	92.0(5)
P(2)–Ru–P(4)	90.04(9)	Ru–O(14)–C(49)	91.5(6)
P(2)–Ru–O(13)	87.78(17)	O(13)–C(49)–O(14)	117.8(10)
P(2)–Ru–O(14)	83.71(17)	O(13)–C(49)–C(50)	120.2(9)
P(3)–Ru–P(4)	92.90(9)	O(14)–C(49)–C(50)	121.9(8)

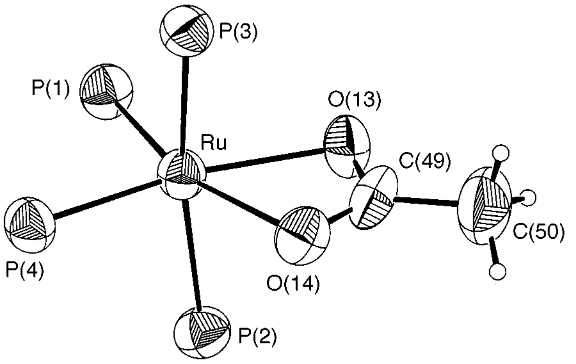


Fig. 1 An ORTEP view of [Ru(η^2-O_2CMe){P(OEt)$_3$}$_4$]$^+$ with thermal ellipsoids shown at 30% probability level. Ethoxy groups are omitted for clarity

Ru–C(49)–C(50) vector, one mirror plane defined by the acetate, Ru, P(1) and P(4) atoms and the second mirror plane defined by Ru, P(3), P(2), C(49) and C(50). The Ru–P bonds which are *trans* to the acetate are noticeably shorter than those which are *trans* to each other, with average values of 2.219 and 2.341 Å respectively. The angle P(2)–Ru–P(3) deviates by more than 10° from 180° due to the steric hindrance among the phosphite ethoxy groups which results in displacement of P(2) and P(3) towards the acetate. This deformation is also reflected in the compression of the angles P(3)–Ru–O and P(2)–Ru–O (average = 85.4°) with respect to P(3)–Ru–P and P(2)–Ru–P (average = 93.7°). The steric origin of this deformation is confirmed by comparison of the above average values with those (84.2 and 94.4° respectively) found in the structure of [Ru{P(OPh)(OMe)$_2$}$_4$(O_2CMe)]PF_6,[29] where, in addition, the larger repulsion due to the bulkier phosphite substituents increases the angle P(1)–Ru–P(4) involving the groups *trans* to the acetate (98.5 compared with 91.9° found in this work). The geometry of the co-ordinated anion agrees well with the average structure found for bidentate acetates bound to Ru (average values for 20 molecules in the Cambridge Structural Database: C–C 1.50, C–O 1.27, Ru–O 2.19 Å; O–C–O 118.0, O–Ru–O 59.6°).

Acknowledgements

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