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Preparation of new diazene complexes of ruthenium and osmium†

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The hydrazine complexes [Ru(NH_2NH_2)L_5](BPh_4)$_2$ **1**, **8** or [Ru(NH_2NH_2)L′L_4](BPh_4)$_2$ **2** [L = P(OEt)$_3$, L′ = PPh(OEt)$_2$] were prepared by allowing the corresponding hydride species [RuHL_5]BPh_4 or [RuHL′L_4]BPh_4 to react first with HBF_4 and then with hydrazine. Oxidation of these hydrazine complexes or [Os(NH_2NH_2)L_5](BPh_4)$_2$ with Pb(OAc)$_4$ at −30 °C led to the corresponding stable and isolable 1,2-diazene complexes [M(NH=NH)L_5](BPh_4)$_2$ **3**, **5** (M = Ru, Os) or [Ru(NH=NH)L′L_4](BPh_4)$_2$ **4**. The phenyldiazene derivatives [M(PhN=NH)L_5](BPh_4)$_2$ **6**, **7** (M = Ru, Os) were also prepared by treating the hydride [MHL_5]BPh_4 species with phenyldiazonium tetrafluoroborate. The aquo-complex, [Ru(H_2O){P(OEt)$_3$}$_5$](BPh_4)$_2$ **8**, was obtained by substitution of the NH=NH ligand in [Ru(NH=NH)L_5](BPh_4)$_2$ and was characterised by X-ray crystal structure determination. Oxidation reactions of the bis(hydrazine) complexes [Ru(NH_2NH_2)$_2L_4$](BPh_4)$_2$ or [Ru(CH_3NHNH_2)$_2L_4$](BPh_4)$_2$ [L = P(OEt)$_3$] with Pb(OAc)$_4$ were reinvestigated and were found to give the diazene complexes [Ru(NH=NH)$_2L_4$](BPh_4)$_2$ **9**, [Ru(CH_3N=NH)$_2L_4$](BPh_4)$_2$ **11** or [Ru(CH_3N=NH)(CH_3NHNH_2)L_4](BPh_4)$_2$ **10**.

Introduction

Diazene NH=NH is a very reactive molecule in the free state, and disproportionates[1] at −150 °C into N_2 and NH_2NH_2. Nevertheless, it is an important molecule of possible relevance as a metal-bound intermediate in inorganic and bioinorganic N_2 fixation processes,[2] and useful as a reagent in stereoselective *cis*-hydrogenation of unsaturated organic compounds.[3] Stabilisation of NH=NH in standard conditions has only been achieved in a few cases by coordination to transition metals, mainly in bimetallic complexes containing a μ-NH=NH ligand.[4] Stable derivatives containing monodentate diazene have also been reported.[5]

We are interested in the chemistry of partially reduced dinitrogen ligands, and have previously reported[6] the synthesis of both methyldiazene and aryldiazene complexes of ruthenium and osmium, obtained by oxidation of the related hydrazine derivatives. However, no evidence of formation of stable complexes containing coordinated 1,2-diazene was obtained. We have therefore extended those studies, searching for an appropriate metal fragment stabilising the diazene NH=NH molecule by coordination, and results are reported here. Reinvestigation of our previous reports[6a,c] on oxidation of bis(hydrazine) [M(NH_2NH_2)$_2L_4$]$^{2+}$ (M = Ru, Os) derivatives, which allows bis(1,2-diazene) complexes to be prepared, is also described here.

Experimental

All synthetic work was carried out in an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphite P(OEt)$_3$ (Aldrich) was purified by distillation under nitrogen; PPh(OEt)$_2$ was prepared by the method of Rabinowitz and Pellon.[7] Diazonium salts were obtained in the usual way.[8] Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[9] $RuCl_3 \cdot 3H_2O$ salt was a ChemPur product and $(NH_4)_2OsCl_6$ was purchased from Johnson Matthey; both salts were used as received. High-grade (99.99%) lead(IV) acetate was purchased from Aldrich. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^{1}H, ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^{1}H spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83 instrument.

Preparation of complexes

Hydrides RuH_2L_4 [L = P(OEt)$_3$, PPh(OEt)$_2$] and [OsH{P(OEt)$_3$}$_5$]BPh_4 were prepared following previous methods.[6c,10]

[RuHL_5]BPh_4 [L = P(OEt)$_3$ and PPh(OEt)$_2$]. Hydrides [RuHL_5]BPh_4 were prepared by a modification of the method previously reported.[11] An equimolar amount of the appropriate phosphite (0.56 mmol) was added to a solution of RuH_2L_4 (0.56 mmol) in 5 cm^3 of ethanol and the mixture cooled to −196 °C. A slight excess of $HBF_4 \cdot Et_2O$ (0.57 mmol, 82 μL) was then added and the reaction mixture, brought to room temperature, stirred for about 2 h. The addition of an excess of $NaBPh_4$ (1.2 mmol, 0.41 g) caused the separation of a white solid, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥ 80%. (For [RuH{P(OEt)$_3$}$_5$]BPh_4 Found: C, 51.64; H, 7.85. $C_{54}H_{96}BO_{15}P_5Ru$ requires C, 51.80; H, 7.73%. Λ_M = 56.2 S cm^2

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† Electronic supplementary information (ESI) available: observed and calculated $^{31}P\{^1H\}$ NMR spectra of compounds [Ru(NH_2NH_2){PPh(OEt)$_2$}{P(OEt)$_3$}$_4$](BPh_4)$_2$ **2** (Fig. S1) and [Ru(NH=NH){PPh(OEt)$_2$}{P(OEt)$_3$}$_4$](BPh_4)$_2$ **4** (Fig. S2). See http://www.rsc.org/suppdata/dt/b2/b202888n/

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mol^{-1}. IR (KBr) ν/cm^{-1}: 1915 (m) ν(Ru–H). δ_H [(CD$_3$)$_2$CO, 25 °C]: 7.40–6.78 (m, 20 H, Ph), 4.11 (m, 30 H, CH$_2$), 1.31, 1.30 (t, 45 H, CH$_3$), −9.25 to −10.03 (m, 1 H, H$^-$). δ_P [(CD$_3$)$_2$CO, 25 °C]: A$_4$B spin system, δ_A 142.0, δ_B 140.4, J_{AB} = 46.6 Hz).

[RuH{PPh(OEt)$_2$}{P(OEt)$_3$}$_4$]BPh$_4$. A slight excess of HBF$_4$·Et$_2$O (0.42 mmol, 60 μL) was added to a solution of RuH$_2${P(OEt)$_3$}$_4$ (0.4 mmol, 0.31 g) in 10 cm^3 of C$_2$H$_5$OH and the reaction mixture was brought to about −30 °C and stirred for 30 min. A slight excess of PPh(OEt)$_2$ (0.42 mmol, 83 μL) was added and the resulting solution brought to room temperature. After 1 h of stirring, an excess of NaBPh$_4$ (0.8 mmol, 0.27 g) was added and the white solid obtained filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥ 80%. (Found: C, 54.34; H, 7.45. C$_{58}$H$_{96}$BO$_{14}$P$_5$Ru requires C, 54.25; H, 7.53%. Λ_M = 57.5 S cm^2 mol^{-1}. IR (KBr) ν/cm^{-1}: 1936 (w) ν(Ru–H). δ_H (CD$_2$Cl$_2$, 25 °C): 8.01–6.70 (m, 25 H, Ph), 4.20–3.50 (m, 28 H, CH$_2$), 1.26 (m, 42 H, CH$_3$), −8.81 to −9.70 (m, 1 H, H$^-$). δ_P (CD$_2$Cl$_2$, 25 °C): ABC$_2$M spin system, δ_M 166.4, δ_A 141.0, δ_B 140.1, δ_C 137.6, J_{AM} = −435.7, J_{BM} = 56.0, J_{CM} = 31.6, J_{AB} = 67.7, J_{AC} = 38.3, J_{BC} = 55.4 Hz).

[Ru(NH$_2$NH$_2$){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 1. An excess of HBF$_4$·Et$_2$O (0.4 mmol, 57 μL) was added to a solution of hydride [RuHL$_5$]BPh$_4$ (0.125 g, 0.1 mmol) in 10 cm^3 of CH$_2$Cl$_2$ cooled to −196 °C and placed under a hydrogen atmosphere. The reaction mixture was brought to room temperature, stirred for 2 h and then, after replacing the H$_2$ atmosphere with argon, an excess of NH$_2$NH$_2$ (1 mmol, 31 μL) was added. The resulting solution was stirred for 20 h and then the solvent was removed under reduced pressure. The oil obtained was triturated with ethanol containing an excess of NaBPh$_4$ (0.2 mmol, 68 mg) giving a white solid, which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥ 60%. (Found: C, 58.35; H, 7.58; N, 1.72. C$_{78}$H$_{119}$B$_2$N$_2$O$_{15}$P$_5$Ru requires C, 58.47; H, 7.49; N, 1.75%. Λ_M = 114.9 S cm^2 mol^{-1}).

[Ru(NH$_2$NH$_2$){PPh(OEt)$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 2. This compound was prepared exactly like the related pentakis(phosphite) complex **1** by reacting the hydride [RuH{PPh(OEt)$_2$}{P(OEt)$_3$}$_4$]BPh$_4$ first with HBF$_4$·Et$_2$O and then with NH$_2$NH$_2$; yield ≥ 65%. (Found: C, 60.39; H, 7.45; N, 1.76. C$_{82}$H$_{119}$B$_2$N$_2$O$_{14}$P$_5$Ru requires C, 60.26; H, 7.34; N, 1.71%. Λ_M = 115.1 S cm^2 mol^{-1}).

[Ru(NH$_2$NH$_2$)$_2${PPh(OEt)$_2$}$_4$](BPh$_4$)$_2$. This complex was obtained in an attempt to prepare the pentakis(phosphite) [Ru(NH$_2$NH$_2$){PPh(OEt)$_2$}$_5$](BPh$_4$)$_2$ following the method reported for the related compounds **1** and **2**. In this case, the known[6a] bis(hydrazine) derivative was obtained as the only isolated product, with a yield of about 75%. (Found: C, 66.12; H, 6.95; N, 3.45. C$_{88}$H$_{108}$B$_2$N$_4$O$_8$P$_4$Ru requires C, 66.21; H, 6.82; N, 3.51%. Λ_M = 114.7 S cm^2 mol^{-1}).

[Os(NH$_2$NH$_2$)L$_5$](BPh$_4$)$_2$ [L = P(OEt)$_3$]. This complex was prepared following the method previously reported.[6c]

[Ru(NH=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 3 and [Os(NH=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 5. A sample of the appropriate hydrazine complex [M(NH$_2$NH$_2$)L$_5$](BPh$_4$)$_2$ (0.16 mmol) was placed in a three-necked 25 cm^3 round-bottomed flask fitted with a solid-addition sidearm containing an equimolar amount of Pb(OAc)$_4$ (0.16 mmol, 71 mg). Dichloromethane (10 cm^3) was added, the solution cooled to −30 °C and Pb(OAc)$_4$ added portionwise over 20–30 min to the cold stirring solution. The solution was then brought to 0 °C, stirred for 10 min and the solvent removed under reduced pressure. The oil obtained was treated at 0 °C with ethanol (2 cm^3) containing an excess of NaBPh$_4$ (0.2 mmol, 68 mg). A white solid slowly separated out, which was filtered and crystallised by dissolving in CH$_2$Cl$_2$ and, after filtration and concentration, by fast precipitation with ethanol; yield ≥ 60%. (Found: C, 58.70; H, 7.47; N, 1.70. C$_{78}$H$_{117}$B$_2$N$_2$O$_{15}$P$_5$Ru **3** requires C, 58.54; H, 7.37; N, 1.75%. Λ_M = 118.4 S cm^2 mol^{-1}. Found: C, 55.38; H, 7.04; N, 1.75. C$_{78}$H$_{117}$B$_2$N$_2$O$_{15}$OsP$_5$ **5** requires C, 55.45; H, 6.98; N, 1.66%. Λ_M = 120.7 S cm^2 mol^{-1}).

[Ru(NH=NH){PPh(OEt)$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 4. This complex was prepared exactly like the related species **3** and **5** by oxidation with Pb(OAc)$_4$ of the starting hydrazine compound **2**; yield ≥ 45%. (Found: C, 60.16; H, 7.30; N, 1.61. C$_{82}$H$_{117}$B$_2$N$_2$O$_{14}$P$_5$Ru requires C, 60.33; H, 7.22; N, 1.72%. Λ_M = 116.9 S cm^2 mol^{-1}).

[Ru(PhN=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 6 and [Os(PhN=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 7. In a three-necked 25 cm^3 round-bottomed flask were placed solid samples of the appropriate hydrides [MHL$_5$]BPh$_4$ (0.1 mmol) and an excess of phenyldiazonium tetrafluoroborate [PhN$_2$]BF$_4$ (0.5 mmol, 96 mg) and the mixture was cooled to −196 °C. Acetone (10 cm^3) was slowly added and the reaction mixture, brought to room temperature, stirred for 4 h. The solvent was removed under reduced pressure giving a brown oil which was treated with ethanol (5 cm^3) containing an excess of NaBPh$_4$ (0.2 mmol, 68 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥ 75%. (Found: C, 60.02; H, 7.35; N, 1.60. C$_{84}$H$_{121}$B$_2$N$_2$O$_{15}$P$_5$Ru **6** requires C, 60.18; H, 7.27; N, 1.67%. Λ_M = 120.3 S cm^2 mol^{-1}. Found: C, 57.01; H, 6.99; N, 1.67. C$_{84}$H$_{121}$B$_2$N$_2$O$_{15}$OsP$_5$ **7** requires C, 57.14; H, 6.91; N, 1.59%. Λ_M = 117.8 S cm^2 mol^{-1}).

[Ru(H$_2$O){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ 8. This complex was obtained in an attempt at crystallisation of the diazene derivative [Ru(NH=NH){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ **3**. In fact, by slow cooling to −25 °C of a saturated solution of **3**, prepared by treating the solid sample (150 mg) with ethanol (8 cm^3) and enough CH$_2$Cl$_2$ to obtain a saturated solution at room temperature, white microcrystals of the aquo-complex **8** were obtained. These crystals were also suitable for X-ray analysis; yield ≥ 80%. (Found: C, 59.11; H, 7.49. C$_{78}$H$_{117}$B$_2$O$_{16}$P$_5$Ru requires C, 58.98; H, 7.42%. Λ_M = 118.2 S cm^2 mol^{-1}).

[Ru(CH$_3$N=NH)(CH$_3$NHNH$_2$){P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 10 and [Ru(CH$_3$N=NH)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 11. These complexes were obtained by oxidation of the [Ru(CH$_3$NHNH$_2$)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ complex[6a] with Pb(OAc)$_4$ in CH$_2$Cl$_2$ at −30 °C following the method used for **3** and **5**. In this case, by reacting 0.2 mmol (0.300 g) of [Ru(CH$_3$NHNH$_2$)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$ with 0.4 mmol (0.177 g) of Pb(OAc)$_4$, a mixture of both compounds **10** and **11** was obtained. Their separation involves the slow cooling to −25 °C of a saturated solution of the mixture prepared at room temperature using as solvent ethanol and enough CH$_2$Cl$_2$ to dissolve the solid. The first solid obtained was the mixed-ligand compound **10** in about 25% yield, while from the mother liquor, after repeated crystallisation, the bis(methyldiazene) **11** was separated in about 10% yield. (Found: C, 59.31; H, 7.48; N, 3.66. C$_{74}$H$_{110}$B$_2$N$_4$O$_{12}$P$_4$Ru **10** requires C, 59.48; H, 7.42; N, 3.75%. Λ_M = 118.5 S cm^2 mol^{-1}. Found: C, 59.42; H, 7.41; N, 3.63. C$_{74}$H$_{108}$B$_2$N$_4$O$_{12}$P$_4$Ru **11** requires C, 59.56; H, 7.29; N, 3.75%. Λ_M = 108.9 S cm^2 mol^{-1}).

Oxidation of [Ru(NH$_2$NH$_2$)$_2$L$_4$](BPh$_4$)$_2$ [L = P(OEt)$_3$ and PPh(OEt)$_2$] and [Os(NH$_2$NH$_2$)$_2${P(OEt)$_3$}$_4$](BPh$_4$)$_2$

Also the oxidation of the bis(hydrazine) complexes[6a,c] was carried out with Pb(OAc)$_4$ at −30 °C, following the method used for the other hydrazine complexes **1**, **2**, [Os(NH$_2$NH$_2$)L$_5$](BPh$_4$)$_2$ and [Ru(CH$_3$NHNH$_2$)$_2$L$_4$](BPh$_4$)$_2$. A typical experiment involves the addition of solid Pb(OAc)$_4$ (0.4 mmol,

Table 1 Crystal data and structure refinement for $[Ru(H_2O)\{P(OEt)_3\}_5](BPh_4)_2$ **8**

Empirical formula	$C_{78}H_{117}B_2O_{16}P_5Ru$
Formula weight	1588.26
Temperature/K	293(2)
Wavelength/Å	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.763(5)
b/Å	16.613(5)
c/Å	18.646(5)
β/°	82.05(5)
Volume/Å^3	4529(2)
Z	2
Absorption coefficient/mm^{-1}	0.318
F(000)	1684
Reflections collected	26755
Independent reflections	18872 [R(int) = 0.0555]
Data/restraints/parameters	18872/6/845
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0948$, $wR2 = 0.2383$
R indices (all data)	$R1 = 0.1649$, $wR2 = 0.2968$

0.177 g) to a cooled solution (−30 °C) of the appropriate bis(hydrazine) complex (0.2 mmol) in CH_2Cl_2. Removal of the solvent at the end of the reaction gave an oil, which was triturated at 0 °C with ethanol (2 cm^3) containing an excess of $NaBPh_4$ (0.4 mmol, 136 mg). The white solid that slowly separated out was filtered and dried under vacuum. The samples contained a mixture of bis(diazene) $[M(NH{=}NH)_2L_4](BPh_4)_2$ and acetate $[M(\kappa^2\text{-}O_2CCH_3)L_4]BPh_4$ complexes, which cannot be separated in pure form. However, in the case of $[Ru(NH{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ **9**, the sample contains the bis(diazene) as the major product (about 60–70%), while in the other cases only little amounts (5–10%) of bis(diazene) are present in the reaction product. For the mixture containing $[Ru(NH{=}NH)_2\{PPh(OEt)_2\}_4](BPh_4)_2$ δ_H (CD_2Cl_2, 20 °C): 16.23, 15.62 (dm, 2 H, NH=NH; $^3J_{HH}$ = 32.0 Hz). For the mixture containing $[Os(NH{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$ δ_H (CD_2Cl_2, 20 °C): 16.63, 16.31 (dm, 2 H, NH=NH).

Crystallography

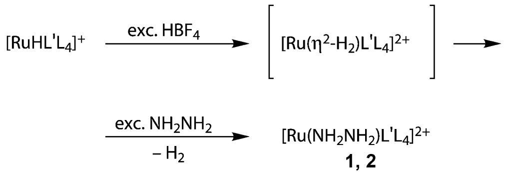
Crystals were air sensitive, a white irregular prism single crystal was sealed in a glass capillary along with some drops of solution. X-Ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with a CCD detector, using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Data collection details are: crystal to detector distance = 5.0 cm, hemisphere mode, time per frame = 30 s, oscillation $\Delta\omega$ = 0.300°. Data reduction was performed up to θ = 28° by the SAINT package[12] and data were corrected for absorption effects by the SADABS[13] procedure. Data collection and refinement results are summarised in Table 1. The crystal suffered a severe merohedral twinning expressed by a mirror plane perpendicular to b, which simulated a $2/m$ Laue symmetry, whilst the actual structure is described in $P\bar{1}$, with α and β close to 90°. The phase problem was solved by direct methods[14] and the structure was refined by full matrix least squares on all F^2 by taking into account the twinning as implemented in Shelxl 97,[15] using the WinGX package.[16] The refinement without considering the twinning was unsuccessful. Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in calculated positions, except for those belonging to the water, located on the Fourier maps. Phenyls were treated as rigid bodies. Use of the Cambridge Crystallographic Database[17] facilities was made for structure discussion. Meaningless electron density residues were left around the metal in the final map.

CCDC reference number 182442.

See http://www.rsc.org/suppdata/dt/b2/b202888n/ for crystallographic data in CIF or other electronic format.

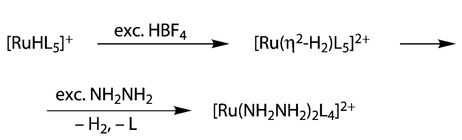
Results and discussion

Hydrazine complexes of ruthenium $[Ru(NH_2NH_2)\{P(OEt)_3\}_5](BPh_4)_2$ **1** and $[Ru(NH_2NH_2)\{PPh(OEt)_2\}\{P(OEt)_3\}_4](BPh_4)_2$ **2** were prepared by reacting the hydride $[RuHL'L_4]BPh_4$ first with an excess of fluoroboric acid and then with hydrazine, as shown in Scheme 1.



Scheme 1 L′ = L = $P(OEt)_3$ **1**; L′ = $PPh(OEt)_2$, L = $P(OEt)_3$ **2**.

Reactions of the pentakis(phosphite)hydride $[RuHL'L_4]^+$ with an excess of HBF_4 gives the η^2-H_2 dihydrogen intermediate $[M(\eta^2\text{-}H_2)L'L_4]^{2+}$ (by ^{1}H NMR), which reacts with NH_2NH_2 to give final hydrazine complexes **1** or **2**. In contrast, the reaction of the hydride $[RuH\{PPh(OEt)_2\}_5]BPh_4$, first with HBF_4 and then with hydrazine, in all conditions afforded the known[6a] bis(hydrazine) complex $[Ru(NH_2NH_2)_2\{PPh(OEt)_2\}_4]^{2+}$, as shown in Scheme 2.



Scheme 2 L = $PPh(OEt)_2$.

In the pentakis(phosphite) $[Ru(\eta^2\text{-}H_2)L_5]^{2+}$ intermediate, hydrazine replaces not only the labile η^2-H_2 ligand, but also one phosphite, giving the bis(hydrazine) species. Attempts to prepare other pentakis(phosphite) hydrazine complexes different from **1** and **2** failed, because the reaction of $[RuHL'L_4]^+$ first with a Brønsted acid and then with an excess of CH_3NHNH_2 or $C_6H_5NHNH_2$ only gave mixtures of solid products not containing the hydrazine ligand. It seems that only the NH_2NH_2 species can bind to the metal centre in the $ML'L_4$ fragment to give stable and isolable derivatives.

Hydrazine complexes **1** and **2** were isolated as white $[BPh_4]$ salts, stable in air and in solutions of polar organic solvents, in which they behave as 2 : 1 electrolytes. Analytical and spectroscopic data (Table 2) support the proposed formulation. The presence of the hydrazine ligand was supported by infrared spectroscopy, which showed the characteristic νNH medium-intensity bands of NH_2NH_2 between 3387 and 3266 cm^{-1}. Further support for the presence of NH_2NH_2 came from ^{1}H NMR spectra, which showed two broad signals at 4.37 and 3.36 ppm (**1**) or at 4.41 and 3.46 ppm (**2**), due to the two NH_2 proton resonances. Integration measurements and homodecoupling experiments confirmed the proposed assignment. In the temperature range between +30 and −80 °C, the $^{31}P\{^1H\}$ NMR spectrum of $[M(NH_2NH_2)L_5]^{2+}$ **1** appeared as an AB_4 multiplet, fitting the proposed formulation (geometry **I**, Fig. 1). In contrast, the spectra of $[Ru(NH_2NH_2)\{PPh(OEt)_2\}\{P(OEt)_3\}_4](BPh_4)_2$ **2** showed a rather complicated pattern, simulated as a set of two systems of types AB_4 and ABC_2M, partly overlapping, and with the parameters listed in Table 2. This result may be interpreted as due to two geometries in solution of the type shown in Fig. 1, with the hydrazine and $PPh(OEt)_2$ ligands in mutually *trans* (**II**) or *cis* (**III**) positions, respectively.

Pentakis(phosphite)hydrazine complexes of both ruthenium **1**, **2** and osmium[6c] $[Os(NH_2NH_2)L_5](BPh_4)_2$ reacted with $Pb(OAc)_4$ at low temperature (−30 °C) with the selective oxidation of the NH_2NH_2 ligand to give 1,2-diazene complexes $[M(NH{=}NH)L_5]^{2+}$ (M = Ru **3**, Os **5**) and $[Ru(NH{=}NH)\{PPh\text{-}$

Table 2 IR and NMR data for ruthenium and osmium complexes

		IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]
Compound		ν/cm^{-1}	Assignment	δ(J/Hz)	Assignment	Spin system	δ(J/Hz)
1	$[Ru(NH_2NH_2)\{P(OEt)_3\}_5](BPh_4)_2$	3368 m	ν(NH)	4.37 s, br	$RuNH_2$	AB_4	δ_A 131.9
		3328 m		4.07 m	CH_2		δ_{AB} 120.9
		3275 w		3.97 qnt			$J_{AB} = 58.3$
		3267 w		3.36 s, br	NH_2		
				1.32 t	CH_3		
				1.27 t			
2	$[Ru(NH_2NH_2)\{PPh(OEt)_2\}\{P(OEt)_3\}_4](BPh_4)_2$	3387 w	ν(NH)	4.41 s, br	$RuNH_2$	AB_4	δ_A 160.7
		3340 w		4.15–3.70 m	CH_2		δ_B 120.4
		3327 w		3.46 q, br	NH_2		$J_{AB} = 50.5$
		3266 w		1.36 t	CH_3	ABC_2M	δ_A 131.5
				1.35 t			δ_B 122.0
				1.33 t			δ_C 120.5
				1.32 t			δ_M 150.4
				1.29 t			$J_{AB} = 55.5$
							$J_{AC} = 61.7$
							$J_{AM} = 48.6$
							$J_{BC} = 63.2$
							$J_{BM} = -475.5$
							$J_{CM} = 54.0$
3	$[Ru(NH{=}NH)\{P(OEt)_3\}_5](BPh_4)_2$			AB_4XY spin syst.	=NH	AB_4	δ_A 129.1
				δ_X 16.76			δ_B 118.3
				δ_Y 15.36			$J_{AB} = 59.3$
				$J_{AX} = 12.4$			
				$J_{AY} = 9.2$			
				$J_{BX} = 1.5$			
				$J_{BY} = 2.6$			
				$J_{XY} = 32.5$			
				4.06 m	CH_2		
				1.37 t	CH_3		
				1.32 t			
4	$[Ru(NH{=}NH)\{PPh(OEt)_2\}\{P(OEt)_3\}_4](BPh_4)_2$			16.74 m	=NH	AB_4	δ_A 158.8
				15.38 m			δ_B 120.5
				3.93 m	CH_2		$J_{AB} = 51.1$
				1.34 t	CH_3	ABC_2M	δ_A 128.8
				1.32 t			δ_B 119.0
				1.31 t			δ_C 118.2
				1.27 t			δ_M 147.3
				1.25 t			$J_{AB} = 53.8$
							$J_{AC} = 65.2$
							$J_{AM} = 45.8$
							$J_{BC} = 61.2$
							$J_{BM} = -460.5$
							$J_{CM} = 52.7$
5	$[Os(NH{=}NH)\{P(OEt)_3\}_5](BPh_4)_2$			A_4BXY spin syst.	=NH	A_4B[e]	δ_A 84.2
				δ_X 16.82			δ_B 63.3
				δ_Y 15.73			$J_{AB} = 40.3$
				$J_{AX} = 1.65$			
				$J_{AY} = 3.85$			
				$J_{BX} = 11.0$			
				$J_{BY} = 7.65$			
				$J_{XY} = 32.2$			
				4.11 m	CH_2		
				4.00 qnt			
				1.37 t	CH_3		
				1.35 t			
6	$[Ru(C_6H_5N{=}NH)\{P(OEt)_3\}_5](BPh_4)_2$			13.72 m[e]	=NH	AB_4[e]	δ_A 133.0
				4.30 m	CH_2		δ_B 121.3
				4.19 qnt			$J_{AB} = 60.4$
				1.40 t	CH_3		
				1.32 t			
7	$[Os(C_6H_5N{=}NH)\{P(OEt)_3\}_5](BPh_4)_2$			14.15 m[e]	=NH	A_4B[e]	δ_A 86.6
				4.35 m	CH_2		δ_B 69.7
				4.11 qnt			$J_{AB} = 41.0$
				1.40 t	CH_3		
				1.34 t			
8	$[Ru(H_2O)\{P(OEt)_3\}_5](BPh_4)_2$			4.07 m	CH_2	AB_4	δ_A 131.7
				2.65 s, br	H_2O		δ_B 119.1
				1.36 t	CH_3		$J_{AB} = 59.5$
				1.32 t			
9	$[Ru(NH{=}NH)_2\{P(OEt)_3\}_4](BPh_4)_2$[f]			16.71 dm	=NH	A_2B_2	δ_A 128.2
				15.83 dm			δ_B 118.1
				$J_{HH} = 32$			$J_{AB} = 60.0$
				4.07 m	CH_2		
				1.37 t	CH_3		
				1.32 t			

Table 2 IR and NMR data for ruthenium and osmium complexes

	IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]
Compound	ν/cm^{-1}	Assignment	δ(J/Hz)	Assignment	Spin system	δ(J/Hz)
10 $[Ru(CH_3N{=}NH)(CH_3NHNH_2)$-$\{P(OEt)_3\}_4](BPh_4)_2$	3347 w	ν(NH)	13.74 m, br	=NH	ABC$_2$[e]	δ_A 128.9
	3304 m		4.64 s, br	RuNH$_2$		δ_B 127.4
	3295 w		4.10 m	CH$_2$		δ_C 118.5
			3.76 s	CH$_3$N=		J_{AB} = 68.7
			3.45 m, br	NH$_{hydrazine}$		J_{AC} = 61.2
			2.65 d	CH$_{3\ hydrazine}$		J_{BC} = 60.1
			1.37 t	CH$_3$		
			1.34 t			
			1.32 t			
11 $[Ru(CH_3N{=}NH)_2\{P(OEt)_3\}_4]$-$(BPh_4)_2$			13.58 m, br	=NH	A$_2$B$_2$	δ_A 129.8
			4.10 m	CH$_2$		δ_B 119.8
			3.81 s	CH$_3$N=		J_{AB} = 61.6
			1.39 t	CH$_3$		
			1.35 t			

[a] In KBr pellets. [b] In CD_2Cl_2 at 25 °C, unless otherwise noted. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In $(CD_3)_2CO$. [f] The sample contains the acetate complex $[Ru(\kappa^2\text{-}O_2CCH_3)\{P(OEt)_3\}_4]BPh_4$.

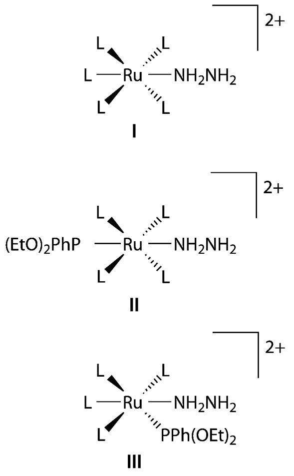
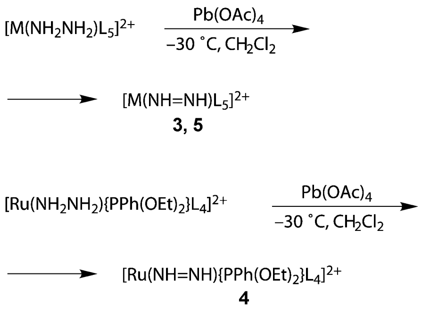


Fig. 1 L = P(OEt)$_3$.



Scheme 3 M = Ru **3**, Os **5**; L = P(OEt)$_3$.

(OEt)$_2$}L$_4$]$^{2+}$ **4**, which were isolated as white solids and characterised (Scheme 3).

It was essential for the successful synthesis of diazene derivatives **3**–**5** to carry out reactions at low temperature (−30 °C) and to use high-purity Pb(OAc)$_4$ (99.99%) in equimolar amounts. Otherwise, mixtures of products not containing the 1,2-diazene complex were obtained. In particular, the use of common Pb(OAc)$_4$ (95%) did not yield pure samples of **3**–**5**, but only mixtures containing small amounts (10–15%) of the diazene complex.

All NH=NH derivatives **3**–**5** are stable as solids, but slowly decompose in solution, losing the diazene ligand. An attempt to crystallise **3** in a mixture of ethanol and dichloromethane as solvent gave aquo-complex $[Ru(H_2O)\{P(OEt)_3\}_5](BPh_4)_2$ **8**, which was isolated and characterised. The H_2O molecule probably comes from the traces of water always present in the common "anhydrous" solvents. In the solution the presence of hydrazine was also detected and confirms the decomposition of free NH=NH.

Diazene complexes **3**–**5** are 2 : 1 electrolytes, and their analytical and spectroscopic data (Table 2) support the proposed formulation. In the low-field region of the ^{1}H NMR spectrum of complex $[Ru(NH{=}NH)L_5]^{2+}$ **3**, two multiplets (Fig. 2) at 16.76 and 15.36 ppm appeared, which were attributed to the two NH protons of a monohapto NH=NH ligand. This pattern is due to coupling with ^{31}P nuclei (AB$_4$ multiplet), as confirmed by simulation of the spectrum using an AB$_4$XY model (X = HA, Y = HB), with the parameters listed in Table 2. The $^3J_{HH}$ value of 32.5 Hz (J_{XY}) also suggested[4d,5] a probable *trans*-NH=NH geometry. The related osmium complex $[Os(NH{=}NH)L_5]^{2+}$ **5**, in the low-field region of the proton spectra, also showed the characteristic A$_4$BXY multiplet of the diazene ligands. In the temperature range between −80 and +30 °C, the ^{31}P{^{1}H} NMR spectra of both complexes **3** and **5** appeared as AB$_4$ or A$_4$B multiplets, fitting geometry **IV** (Fig. 3).

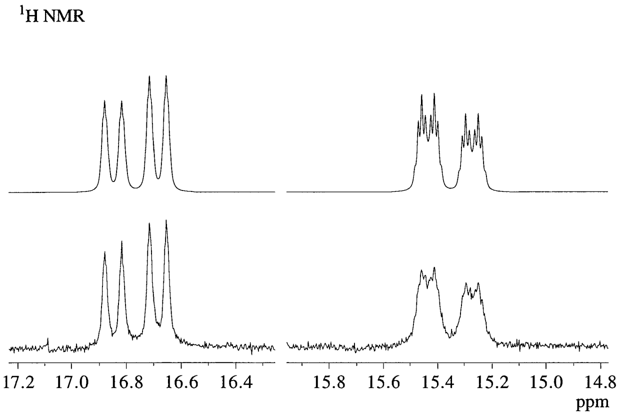
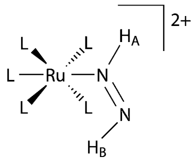


Fig. 2 Observed (bottom) and calculated (top) ^{1}H NMR spectra, in the diazene region, of $[Ru(NH{=}NH)\{P(OEt)_3\}_5](BPh_4)_2$ **3**, in CD_2Cl_2 at 25 °C. The simulated spectrum was obtained using the parameters reported in Table 2.

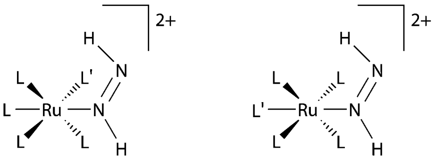
The presence of the diazene ligand was also confirmed in the mixed-phosphite derivative $[Ru(NH{=}NH)\{PPh(OEt)_2\}\{P(OEt)_3\}_4](BPh_4)_2$ **4**, the ^{1}H NMR spectrum of which showed the characteristic =NH multiplet between 17 and 15 ppm (Table 2). In the temperature range between −80 and +30 °C, the ^{31}P{^{1}H} NMR spectrum appeared as a complicated pattern, simulated



IV

Fig. 3 L = P(OEt)$_3$.

as a set of one AB$_4$ and one ABC$_2$M multiplets, partially overlapping. On this basis, and taking into account the ^{31}P spectra of hydrazine precursor **2**, we propose the existence of two isomers of the type shown in Fig. 4 for our complex **4**, containing the NH=NH and PPh(OEt)$_2$ ligands in mutually *cis* (**V**) or *trans* (**VI**) positions, respectively.

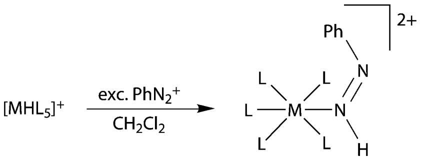


V (*cis*)   **VI** (*trans*)

Fig. 4 L = P(OEt)$_3$, L′ = PPh(OEt)$_2$.

Complexes containing the monodentate 1,2-diazene ligand are very rare,[5] and only one example[5c] of isolable species has been reported for ruthenium and osmium metal centres. Using the pentakis(phosphite) ML$_5$ (or ML′L$_4$) fragment stabilises the NH=NH molecule through coordination, affording stable and isolable species for both Ru(II) and Os(II).

Unfortunately, no other [M(RN=NH)L$_5$]$^{2+}$ diazene complexes besides **3** and **5** could be prepared by oxidation of coordinated hydrazine, owing to the absence of the corresponding precursors. In our hands, hydrazines RNHNH$_2$ different from NH$_2$NH$_2$ could not be coordinated to the ML$_5$ fragment to give stable species. However, taking into account that aryldiazene can also be prepared by insertion of aryldiazonium cations into a M–H bond, we treated the [MHL$_5$]$^+$ (M = Ru, Os) hydrides with the phenyldiazonium cation PhN$_2$$^+BF_4$$^-$ and observed the formation of aryldiazene derivatives [M(PhN=NH)L$_5$]$^{2+}$ (M = Ru **6**, Os **7**) which were isolated as BPh$_4$$^-$ salts and characterised (Scheme 4).



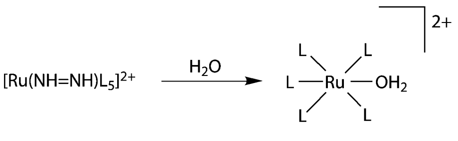
VII
6, 7

Scheme 4 M = Ru **6**, Os **7**; L = P(OEt)$_3$.

The formation of complexes **6** and **7** may indicate that the steric requirement of aryldiazene PhN=NH is lower than that of arylhydrazine PhNHNH$_2$, whose coordination on the ML$_5$ fragment did not take place. Aryldiazene [M(PhN=NH)L$_5$](BPh$_4$)$_2$ derivatives **6** and **7** are stable as solids and in solutions of polar organic solvents, in which they behave as 2 : 1 electrolytes. The presence of the diazene ligand was confirmed by the ^{1}H NMR spectra, which displayed the characteristic high-frequency NH proton resonances at 13.72 (**6**) and 14.15 (**7**) ppm. In the temperature range between −90 and +30 °C, the ^{31}P{^{1}H} NMR spectrum appeared as an AB$_4$ multiplet, fitting the proposed formulation.

Table 3 Selected bond lengths (Å) and angles (°) for [Ru(H$_2$O){P(OEt)$_3$}$_5$](BPh$_4$)$_2$ **8**, with s.u.s in parentheses

Ru–O16	2.219(7)	Ru–P3	2.352(3)
Ru–P4	2.238(3)	Ru–P2	2.356(3)
Ru–P1	2.348(3)	Ru–P5	2.372(3)
O16–Ru–P4	178.3(2)	P1–Ru–P2	88.2(1)
O16–Ru–P1	89.9(2)	P3–Ru–P2	167.7(1)
P4–Ru–P1	91.1(1)	O16–Ru–P5	86.8(2)
O16–Ru–P3	80.7(2)	P4–Ru–P5	92.1(1)
P4–Ru–P3	98.0(1)	P1–Ru–P5	176.6(1)
P1–Ru–P3	91.81(9)	P3–Ru–P5	88.7(1)
O16–Ru–P2	87.0(2)	P2–Ru–P5	90.6(1)
P4–Ru–P2	94.3(1)		



8

Scheme 5 L = P(OEt)$_3$, M = Ru.

Although aryldiazenes **6** and **7** were stable in solution, related 1,2-diazene complexes **3**–**5** slowly decomposed giving aquo-complex [M(H$_2$O)L$_5$]$^{2+}$, probably by substitution of the labile NH=NH ligand with traces of water present in the solvent. In the case of ruthenium, compound [Ru(H$_2$O)L$_5$](BPh$_4$)$_2$ **8** (Scheme 5) was isolated as white microcrystals and characterised spectroscopically (Table 2) and crystallographically (Table 1). The presence of H$_2$O as a ligand in the complex was indicated by the proton NMR signal at 2.65 ppm, and the ^{31}P{^{1}H} spectra confirmed the ML$_5$ fragment.

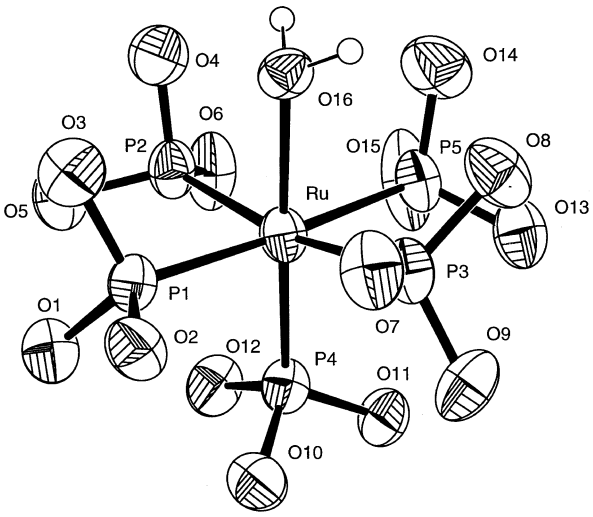
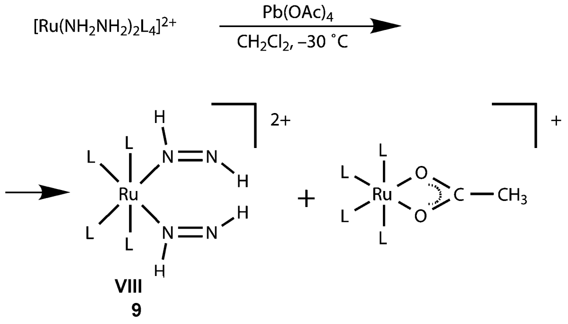


Fig. 5 Perspective view of the solid-state molecular structure of cation [Ru(H$_2$O){P(OEt)$_3$}$_5$]$^{2+}$ **8**$^{2+}$. Anisotropic displacement parameters are at the 50% probability level. Ethoxy groups are omitted for clarity.

The structure and atom labelling of [Ru(H$_2$O){P(OEt)$_3$}$_5$]$^{2+}$ is shown in Fig. 5, and the coordination geometry is summarised in Table 3. The metal coordination is octahedral, with ligand at P4 located *trans* to the water molecule, the remaining phosphites being sterically equivalent to each other. The steric crowding of the bulky phosphite ligands is partly relieved by pushing them towards the water position, thus reducing the width of the *cis* O–Ru–P bond angles, which range between 80.7(2) and 89.9(2)°. The presence of the water ligand also affects the Ru–P4 bond *trans* to it [2.238(3) Å], which is far shorter than the remaining *cis* ones [2.348(3)–2.372(3) Å]. The large *trans* influence of the unique $P(OEt)_3$ ligand is evidenced by the fact that the Ru–O bond is among the longest found in Ru^{2+} water complexes (*e.g.* Ru–O = 2.139 Å in the hexa-aquo cation[18]). There are no intermolecular interactions among non-hydrogen atoms below 3.55 Å in the structure.

Results from oxidation reactions of hydrazine complexes $[M(NH_2NH_2)L_5]^{2+}$ using the new high-purity $Pb(OAc)_4$ (99.99%) prompted us to reinvestigate the oxidation of the bis(hydrazine) complexes $[M(NH_2NH_2)_2L_4]^{2+}$, that were previously studied by us,[6a,c] using low-purity $Pb(OAc)_4$ (95%) as oxidising agent. These earlier reactions did not give diazene complexes, but only acetate derivative $[M(\kappa^2\text{-}O_2CCH_3)L_4]^+$. The reaction was studied in CH_2Cl_2 at −30 °C using high-purity $Pb(OAc)_4$ in a Ru : Pb ratio 1 : 2, and showed that, in the case of $[Ru(NH_2NH_2)_2\{P(OEt)_3\}_4]^{2+}$ it does give a white solid containing a mixture of bis(diazene) $[Ru(NH{=}NH)_2L_4](BPh_4)_2$ **9** and acetate $[Ru(\kappa^2\text{-}O_2CCH_3)L_4]BPh_4$ derivatives, as shown in Scheme 6.



Scheme 6 L = $P(OEt)_3$.

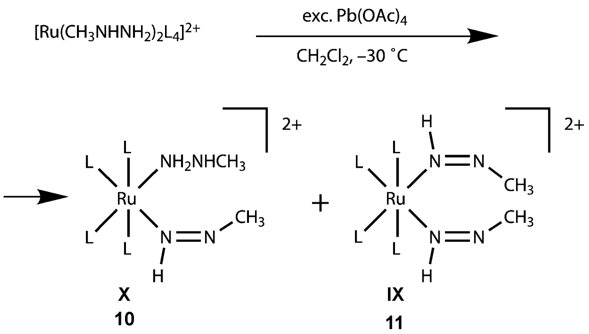
From this mixture, we attempted to separate the diazene complex by fractional crystallisation at low temperature, but the instability in solution of $[Ru(NH{=}NH)_2L_4]^{2+}$ on the one hand, and the comparable solubility of the two complexes on the other, always gave samples containing more products. However, the ^1H NMR spectra of the mixture strongly supports the formation of bis(diazene) **9**, showing two doublets of multiplets at 16.71 and 15.83 ppm, attributed to the two NH protons of the two diazene ligands. The $^3J_{HH}$ value of 32 Hz also suggests[4d,5] a *trans*-NH=NH geometry. The $^{31}P\{^1H\}$ NMR spectra of the oxidation product also shows two A_2B_2 multiplets, due to acetate compound[6a] $[Ru(\kappa^2\text{-}O_2CCH_3)L_4]^+$ and bis(diazene) complex **9**, fitting the proposed formulation. The A_2B_2 pattern also suggests the mutually *cis* positions of the two diazene ligands, as in geometry **VIII**, Scheme 6.

Oxidation of the related $[Ru(NH_2NH_2)_2\{PPh(OEt)_2\}_4](BPh_4)_2$ and $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ derivatives afforded white solids, with ^1H NMR spectra showing diazene signals, probably attributable to bis(diazene) $[M(NH{=}NH)_2L_4](BPh_4)_2$ (M = Ru, Os) complexes. In these cases, however, the predominant species is acetate compound $[M(\kappa^2\text{-}O_2CCH_3)L_4]^+$, with the diazene complex present only in a small amount (from 5 to 10%).

These studies on the oxidation of bis(hydrazine) complexes with high-purity $Pb(OAc)_4$ (99.99%) show that 1,2-diazene complexes can also be formed in these cases, but their stabilisation on the ML_4 fragment is restricted, as compared with related $[M(NH{=}NH)L_5]^{2+}$ derivatives, and does not allow separation of the samples in pure form. However, although substitution of the NH=NH ligand by the acetate ion also takes place using high-purity $Pb(OAc)_4$, a solid sample containing the coordinated 1,2-diazene (**9**) as the predominant species was isolated. In addition, these results confirm our previous hypothesis[6a,c] on the formation of a diazene complex in the oxidation of $[M(NH_2NH_2)_2L_4]^{2+}$ cations, and highlight the importance of the purity of $Pb(OAc)_4$ in determining the nature of the final oxidation products.

On this basis, we extended the oxidation reaction to methylhydrazine complexes $[Ru(CH_3NHNH_2)_2L_4]^{2+}$ and found that, using high-purity $Pb(OAc)_4$ (99.99%), the reaction gives a mixture of bis(methyldiazene) $[Ru(CH_3N{=}NH)_2L_4]^{2+}$ **11** and methyldiazene–methylhydrazine $[Ru(CH_3N{=}NH)(CH_3NHNH_2)L_4]^{2+}$ **10** complexes, which were isolated as BPh_4^- salts and characterised (Scheme 7).

Complexes **10** and **11** were separated by fractional crystallisation into two pale yellow solids, stable in air and in solutions of polar organic solvents, in which they behave as 2 : 1 electrolytes. Analytical and spectroscopic data (Table 2) support the proposed formulation. The ^1H NMR spectrum of bis(methyldiazene) complex **11** shows a slightly broad multiplet at 13.58 ppm, characteristic of the diazene ligand. Beside the signals of phosphite and BPh_4 ion, the spectrum also contains, a singlet at 3.81 ppm, due to the methyl–proton resonance of the methyldiazene group. In the temperature range between −80 and +30 °C, the $^{31}P\{^1H\}$ NMR spectra appear as an A_2B_2 multiplet, fitting the presence of two diazene ligands in a mutual *cis* position (**IX**).



Scheme 7 L = $P(OEt)_3$.

In mixed-ligand complex $[Ru(CH_3N{=}NH)(CH_3NHNH_2)L_4](BPh_4)_2$ **10**, the ^1H NMR spectra show the presence of both nitrogenous ligands. The broad multiplet at 13.74 ppm of the NH proton and the singlet at 3.76 ppm of the methyl resonances confirm the presence of the $CH_3N{=}NH$ ligand, whereas the broad signals at 4.64 and 3.45 ppm, due to NH_2 and NH resonances respectively, and the doublet at 2.65 ppm are diagnostic of the hydrazine group. The ABC_2 multiplet present in the $^{31}P\{^1H\}$ spectra also suggests mutual *cis* position of the hydrazine and diazene ligands in the complex (**X**).

The RuL_4 fragment is therefore able to stabilise both 1,2-diazene and methyldiazene by coordination, affording the related bis(diazene) species, which are very stable, in the case of $CH_3N{=}NH$. Partial substitution was observed with the NH=NH ligand, affording a mixture of diazene (**9**) and acetate $[Ru(\kappa^2\text{-}O_2CCH_3)L_4]^+$ derivatives. However, isolation of solid samples containing diazene complexes of ruthenium was only achieved by using high-purity $Pb(OAc)_4$ (99.99%), and the absence in previous studies[6] of any evidence of these diazene species is probably due to the fact that standard-grade $Pb(OAc)_4$ (95%) was used, which leads to decomposition of diazene derivatives (see ESI).

Acknowledgements

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