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Parallel coordination of hydrazine to diruthenium units: synthesis and molecular structure of the cationic complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)]^{2+}$ and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}$

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Abstract

The dinuclear cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**) reacts in aqueous solution with hydrazine to give the dicationic complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)]^{2+}$ (**2**) and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu^2\text{-}NH_2)]^{2+}$ (**3**). The single-crystal X-ray structure analyses of **2** (tosylate salt) and **3** (triflate salt) reveal both complexes to contain an intact hydrazine ligand coordinated parallel ($\mu_2\text{-}\eta^1,\eta^1$) to the diruthenium backbone, comprising a Ru=Ru double bond (2.69 Å) in **2** and a Ru–Ru single bond (2.85 Å) in **3**. A single crystal of the mixed sulfate-hexafluorophosphate salt of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}N_2H_3)]^{2+}$ (**4**), isolated from the mother liquor of **2**, suggests this hydrazido complex to be an intermediate in the reaction from **2** to **3**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydrazine complexes; Amido complexes; Catonic hexamethylbenzene complexes

1. Introduction

Hydrazine contains two nitrogen atoms, both capable of coordination to transition metal centres by their lone electon pair. In comparison to ammonia, the coordination chemistry of hydrazine is by far less developed. Complexes containing hydrazine have only been reviewed in 1996 [1]. Three coordination modes of the hydrazine ligand have been reported so far: monodentate to one metal ($\mu_1\text{-}\eta^1$), bidentate to one metal ($\mu_1\text{-}\eta^2$), and bismonodentate to two metals ($\mu_2\text{-}\eta^1,\eta^1$) (Scheme 1) [1].

Typical examples for these coordination modes are the complexes $(\eta^5\text{-}C_5H_5)V(CO)_3(\eta^1\text{-}H_2NNH_2)$ (monodentate) [2], $[(\eta^5\text{-}C_5Me_5)WMe_3(\eta^2\text{-}H_2NNH_2)]^+$ (bidentate) [3], $[Mo(CO)_2(S_2CNEt_2)_2]_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)$ (*trans*-bismonodentate) [4], and $[P(MeO)_3]_4Ru_2Cl_3S_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)$ (*cis*-bismonodentate) [5].

However, the parallel $\mu_2\text{-}\eta^1,\eta^1$-coordination of hydrazine to a dinuclear cluster unit, in which the two metal atoms are directly bonded by a metal-metal bond, has not been reported so far [1]. There is only one example of a hydrazine derivative for which the $\mu_2\text{-}\eta^1,\eta^1$-coordination mode of the 1,1-dimethylhydrazine ligand has been observed: $(cod)_2Ru_2Cl_2H_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNMe_2)$ (cod = 1,5-cyclooctadiene), in which the Ru–Ru distance of 2.91 Å clearly suggests a Ru–Ru single bond [6]. In this paper we report our findings of a reactivity study of the cationic dinuclear trihydrido-complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**) towards hydrazine in aqueous solution.

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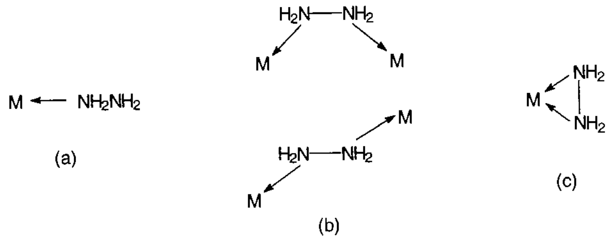


Scheme 1. Bonding modes of hydrazine: (a) monodentate (μ_1-η^1); (b) bismonodentate (μ_1-η^1, η^1, *cis* and *trans*); bidentate (μ_1-η^1).

2. Results and discussion

The reaction of an aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**) with hydrazine results, within 2 days at r.t., in the formation of the dinuclear complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\eta_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)]^{2+}$ (**2**) (Eq.1). The dication **2** can be separated from minor products and unreacted hydrazine by precipitation as salt containing large anions. If the reaction is carried out using the tosylate salt of **1** in a concentrated aqueous solution, the tosylate salt of **2** precipitates during the course of the reaction. Another possiblity is to prepare the sulfate salt of **2** and to precipitate the hexafluorophosphate salt of **2** by addition of NH_4PF_6.

$$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+ (\mathbf{1}) + N_2H_4 + H_2O \longrightarrow$$

$$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^2\text{-}H_2NNH_2)]^{2+} (\mathbf{2}) + H_2 + OH^- \qquad (1)$$

Due to the release of a hydrido ligand, the pH value of the solution increases during the reaction, since the hydride anion reacts with a water molecule to form dihydrogen and hydroxide. Accordingly, an acceleration of the reaction is observed, when the solution is acidified to pH 3, prior to the addition of hydrazine. It turned out to be beneficial to use the starting complex **1** in situ, after its preparation from $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ with $NaBH_4$ in aqueous solution. The borate buffer formed upon hydrolysis of the borohydride reagent prevents the pH of the solution rising above 10, where **2** would be unstable and decompose.

Replacing a formally anionic hydrido ligand in **1** by a neutral hydrazine ligand (to give **2**) implies the increase of the cationic charge by one unity. Since the hydrazine ligand brings in two electrons more than the hydrido ligand, complex **2** should have a Ru=Ru double bond.

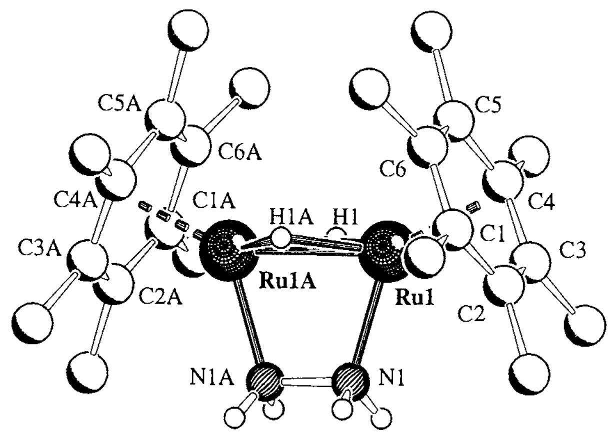


Fig. 1. Molecular structure of complex **2**. The alkyl protons have been omitted for clarity.

The constitution of **2** follows from its spectroscopic and microanalytical data. The ^{1}H-NMR spectra in D_2O and acetone-d_6 reveal **2** to represent a dinuclear hexamethylbenzene-ruthenium complex with two equivalent bridging hydrido ligands (Table 1), but do not show the hydrazine ligand which, however, can be identified in the infrared spectrum (IR data see Section 3). Finally, the microanalytical data of the hexafluorophosphate salt are consistent with the charge of + 2 of cation **2**.

These findings could be confirmed by a single-crystal X-ray structure analysis of the tosylate salt of **2**. Suitable crystals were grown by preparing **2** from $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][p\text{-}CH_3C_6H_4SO_3]$ without stirring the solution. The molecular structure shows **2** to be the first example of a complex containing a μ_2-η^1,η^1-coordinated hydrazine ligand bridging two metal centres held together by a direct metal–metal bond.

The molecular structure of dication **2** is depicted in Fig. 1. Important bond lengths and angles are presented in Table 2. The molecule possesses crystallographic C_2 symmetry, the 2-fold axis bisecting the ruthenium–ruthenium bond and the nitrogen–nitrogen

Table 1
^{1}H-NMR data of complexes **2**, **3**, **4**, **5**, and **6**

Complex	Anion	Solvent	C_6Me_6 (all s, 36H)	Hydrido ligands	*N*-ligands
2	$p\text{-}CH_3C_6H_4SO_3^-$ or SO_4^{2-}	D_2O	2.24	−15.74 (2H)	–
2	PF_6^-	CD_3COCD_3	2.41	−15.49 (2H)	–
3	SO_4^{2-}	D_2O	2.17	−12.97 (1H)	–
3	BF_4^-	CD_3COCD_3	2.32	−12.72 (1H)	5.5 (br)
4	SO_4^{2-} and PF_6^-	D_2O	2.19	−12.38 (1H)	–

bond. It was possible to locate the hydrido ligands. The dication is constructed of two (η^6-C_6Me_6)Ru half-sandwiches. The fragments are linked by two bridging hydrido ligands and a μ_2-η^1,η^1-coordinated hydrazine ligand. The Ru–Ru distance of 2.6925(7) Å is in agreement with a Ru=Ru double bond or a Ru_2H_2 4c–4e interaction.

The hydrazine ligand retains the tetrahedral geometry at the nitrogen atoms upon coordination [Ru(1)–N(1)–N(1A) = 107.22(10)°]. Due to the parallel coordination to the Ru_2 unit, the hydrazine moiety adopts a *cis*-conformation which is unfavourable in the free hydrazine molecule [7]. The N–N bond length of 1.447(7) Å in **2** is as expected for a single N–N bond [8] and unchanged with respect to free hydrazine [9].

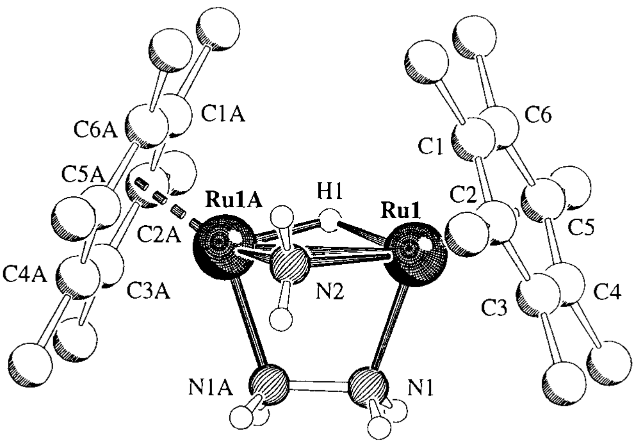


Fig. 2. Molecular structure of complex **3**. The alkyl protons have been omitted for clarity.

$$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^2\text{-}H_2NNH_2)]^{2+}\ (\mathbf{2}) + N_2H_4 + H_2O \longrightarrow$$

$$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^2\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}\ (\mathbf{3}) + H_2 + NH_2OH \qquad (2)$$

Heating the aqueous solution of the sulfate of **2**, prepared in situ, to 100°C for several hours leads to the formation of [(η^6-C_6Me_6)$_2$$Ru_2$($\mu_2$-H)($\mu_2$-$\eta^1$,$\eta^1$-$H_2NNH_2$)($\mu_2$-$NH_2$)]$^{2+}$ (**3**) (Eq. 2). The same product can be obtained directly by heating the aqueous solution of **1** with an excess of hydrazine to the same temperature. Complex **3** can easily be isolated from the aqueous solution by precipitation as the hexafluorophosphate or as the tetrafluoroborate salt. The better solubility of the latter in water predisposes the tetrafluoroborate salt of **3** for further reactions in aqueous solution. The replacement of the μ_2-hydrido ligand (2e) by a μ_2-amido ligand (4e), both formally anionic, in the reaction of **2** to **3** does not affect the cationic charge of the complex, but reduces the Ru=Ru double bond to a Ru–Ru single bond.

Table 2
Selected bond lengths [Å] and angles [°] for **2**

Interatomic distances	
Ru(1)–Ru(1A)	2.6925(7)
Ru(1)–C(1)	2.203(5)
Ru(1)–C(2)	2.200(5)
Ru(1)–C(3)	2.212(5)
Ru(1)–C(4)	2.181(5)
Ru(1)–C(5)	2.234(5)
Ru(1)–C(6)	2.202(5)
Ru(1)–N(1)	2.103(4)
Ru(1)–H(1)	1.80(5)
N(1)–N(1A)	1.447(7)
Angles	
N(1)–Ru(1)–Ru(1A)	84(2)
N(1A)–N(1)–Ru(1)	107.22(10)
Ru(1)–H(1)–Ru(1A)	94.388(6)
H(1)–Ru(1)–H(1A)	84.024(5)
Torsion angle	
N(1)–Ru(1)–Ru(1A)–N(1A)	0.4(3)

The characterization of **3** is based on the spectroscopic and microanalytical data. The ^{1}H-NMR spectra in D_2O and acetone-d_6 show that **3** is a dinuclear hexamethylbenzene-ruthenium complex with one bridging hydrido ligand; a signal at δ 5.5 (br) may be due to the NH_2 ligand (Table 1). The microanalytical data indicate the presence of the amido ligand, which is confirmed by the single-crystal X-ray structure analysis of the triflate salt of **3**. Suitable crystals have been obtained from an aqueous solution of the sulfate salt of **2** with $NaCF_3SO_3$ added.

The molecular structure of dication **3** is depicted in Fig. 2. Important bond lengths and angles are presented in Table 3. The dication consists of two (η^6-C_6Me_6)Ru half-sandwiches which are bridged by a hydrazine ligand, an amido ligand and a hydrido ligand. The molecule possesses crystallographic C_2 symmetry, the 2-fold axis bisecting the ruthenium–ruthenium bond and the nitrogen–nitrogen bond of the hydrazine ligand. The amido and the hydrido ligand have been found to be disordered (occupancy 0.5), both ligands occupy nearly the same positions in space.

In comparison to the structure of complex **2**, the Ru–Ru distance is elongated [2.8555(8) Å in **3**, 2.6925(7) Å in **2**], being in agreement with a Ru–Ru bond or a Ru_2H 3c–2e interaction. The N–N bond length of the hydrazine ligand [1.457(9) Å] as well as the distance Ru1–N1 [2.100(4) Å] are nearly the same as in **2**, despite the reduction of the Ru=Ru double bond to a Ru–Ru single bond. The angle between the plane formed by the ruthenium atoms and the hydrazine nitrogen atoms and the plane formed by the ruthenium atoms and the amido nitrogen atom is almost 90°.

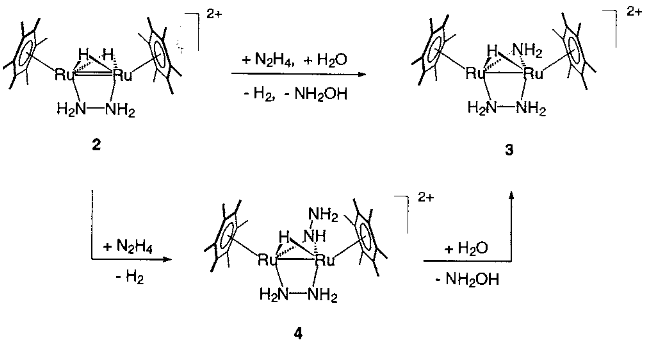
Complex **3** is considerably more stable than **2**. While **3** does not give a reaction with $NaBH_4$, **2** reacts rapidly with $NaBH_4$ in water to give quantitatively $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**). Following this reaction in D_2O by ^1H-NMR gives no hint to intermediates or side products: the spectrum exclusively shows the signals of **2** and **1**.

In the reaction of **2** with excess hydrazine to give **3**, a hydrido ligand is replaced by an amido ligand, although hydrazine is the only nitrogen-containing reagent present in solution. A test reaction under the conditions used in our reaction (100°C, aqueous solution) showed that hydrazine is cleaved with formation of ammonia over a period of 2 days. Nevertheless, it can be demonstrated that the amido complex **3** is not formed by coordination of free ammonia arising from the thermal decomposition of hydrazine, because **2** does not react with ammonia to give **3**.

The isolation of a single crystal of the mixed sulfate-hexafluorophosphate salt of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}N_2H_3)]^{2+}$ (**4**) from the mother liquor of **2** suggests the reaction of **2** with excess hydrazine to **3** to occur via a hydrazido intermediate. Therefore, it can be assumed that the second hydrazine equivalent is first coordinated as μ_2-$NHNH_2$ ligand, after which the N–N bond breaks to give a μ_2-NH_2 ligand (Scheme 2). Unfortunately, all attempts to reproduce the crystallization of the mixed sulfate-hexafluorophosphate salt of **4** failed, giving only the hexafluorophosphate salt of **2**. A preliminary crystal structure analysis [10] of **4** (sulfate-hexafluorophosphate salt; monoclinic, space group A 2/m) confirms the dinuclear structure of **2**. The structure reveals two slightly different independent molecules per asymmetric unit. The Ru–Ru backbone [2.816(2) Å] is bridged by a μ_2-η^1,η^1-N_2H_4 ligand, the N–N axis [1.45(1) Å] being parallel with respect to the metal–metal bond, and by a μ_2-N_2H_3 ligand, the N–N axis [1.46(3) Å] being perpendicular with respect to the ruthenium–ruthenium vector. Due to the poor quality of the crystals, the crystal structure analysis gave a final *R* factor of only 0.1171. The NMR data of **4** (Table 1) are consistent with the crystallographic findings.

Table 3
Selected bond lengths [Å] and angles [°] for **3**

Interatomic distances	
Ru(1)–Ru(1A)	2.85 55(8)
Ru(1)–C(1)	2.190(5)
Ru(1)–C(2)	2.189(6)
Ru(1)–C(3)	2.200(5)
Ru(1)–C(4)	2.204(6)
Ru(1)–C(5)	2.213(7)
Ru(1)–C(6)	2.192(5)
Ru(1)–N(1)	2.100(4)
Ru(1)–N(2)	2.180(8)
Ru(1A)–N(2)	2.249(8)
Ru(1)–H(1)	1.64(7)
N(1)–N(1A)	1.457(9)
Angles	
N(1)–Ru(1)–Ru(1A)	70.45(12)
N(1A)–N(1)–Ru(1)	109.25(13)
Ru(1)–N(2)–Ru(1A)	80.3(3)
Ru(1)–H(1)–Ru(1A)	123.22(1)
Angle between planes	
Ru(1)–N(1)–N(1A)–Ru(1A)/Ru(1)–N(2)–Ru(1A)	89.8(3)



Scheme 2. Proposed mechanism for the formation of the amido ligand from hydrazine in complex **3**.

3. Experimental section

3.1. General

All manipulations were carried out under nitrogen atmosphere, using standard Schlenk techniques. The bidistilled water was degassed and saturated with inert gas prior to use. The organic solvents were refluxed over appropriate desiccants [11], distilled, and saturated with inert gas. The NMR spectra were recorded on a Varian Gemini 200 BB instrument, the treatment of the spectra was done by a Sun Varian station. The IR spectra were recorded on a Perkin-Elmer FTIR 1720X spectrophotometer (4000–400 cm^{-1}) as KBr pellets. Microanalytical data were obtained by the Mikroelementaranalytisches Laboratorium ETH Zürich. The starting material $(\eta^6\text{-}C_6Me_6)_2Ru_2Cl_4$ was synthesized according to the literature procedure [12]. All other reagents were commercially available and were used without further purification.

3.2. Preparation of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**)

A mixture of $(\eta^6\text{-}C_6Me_6)_2Ru_2Cl_4$ (100 mg, 0.150 mmol) and Ag_2SO_4 (94 mg, 0.300 mmol) or Ag(*p*-$CH_3C_6H_4SO_3$) (167 mg, 0.600 mmol) in water (20 ml) was stirred in a Schlenk tube for 1 h in the dark (aluminum foil). During this period the mixture was treated several times with ultrasound (ca. 1 min), until all orange solids were dissolved. After filtration of the silver chloride that precipitated, the yellow solution containing $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ was employed in situ in order to prepare $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (**1**). For this, an aqueous solution of $NaBH_4$ (20 mg, 0.529 mmol, 15 ml H_2O) was added dropwise to the solution of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ (0.300 mmol, 20 ml H_2O). The color turned dark-green upon addition of the first drops, but eventually the solution became dark red. It was filtered in order to remove a fine black precipitate which had formed during the reaction. This aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ was used in situ without further work-up. For this reason, the molar quantities of **1**-given in parentheses-as well as the yields of the new complexes are based on the quantity of $(\eta^6\text{-}C_6Me_6)_2Ru_2Cl_4$ employed.

3.3. Preparation of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)]^{2+}$ (2)

An aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][p\text{-}CH_3C_6H_4SO_3]$ (cation **1**) (0.300 mmol, 60 ml H_2O) was evaporated to dryness and redissolved in water (30 ml). Hydrazine hydrate (80%, 240 ml, 3.95 mmol) was added, the pH value of the solution adjusted to about 5 with diluted sulfuric acid, and the mixture stirred for 2 days at r.t. The reaction mixture was then centrifuged, and the precipitate washed with water (2 × 5 ml). Drying in vacuo gave $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)][p\text{-}CH_3C_6H_4SO_3]_2$ (cation **2**) as a dark red, slightly water-soluble powder (180 mg, 0.199 mmol, 66%).

Addition of hydrazine hydrate (80%, 100 ml, 1.65 mmol) to an aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]_2[SO_4]$ (cation **1**) (0.025 mmol, 15 ml H_2O, pH 3) gave the water-soluble sulfate salt of **2**. ^{1}H-NMR measurements confirmed that after 2 days of stirring, the red solution contained $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)][SO_4]$ (cation **2**), ready to be employed in situ, in spite of the presence of some impurities. Addition of an excess of NH_4PF_6 precipitated selectively the dark red salt $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)][PF_6]_2$ (cation **2**) (13.4 mg, 0.016 mmol, 32%), whereas addition of the tosylate anion did not lead to precipitation of the product at this point. **2** $[PF_6]_2$. Anal. Calcd for $C_{24}H_{42}F_{12}N_2P_2Ru_2$: C, 33.89; H, 4.98; N, 3.29. Found: C, 34.09; H, 4.89; N, 2.97. IR (cm^{-1}): 3315 (m), 3260 (m), ν(N–H), 2930 (w) ν(C–H), 1565 (vw), δ(N–H_{asym}), 1450 (br,w), 1390 (m), ν(C=C), 1070 (m), 1015 (m), ν(C–C).

3.4. Preparation of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}$ (3)

Hydrazine hydrate (80%, 200 ml, 3.29 mmol) was added to an aqueous solution of $[(\eta_6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]_2[SO_4]$ (cation **1**) (0.090 mmol, 40 ml H_2O, pH 3). The solution was heated to 100°C in a closed pressure Schlenk tube for 14 h. After filtration, the product was precipitated by addition of an excess of $NaBF_4$. The mixture was then centrifuged (without nitrogen atmosphere) and the precipitate washed with water (3 ml). Drying in vacuo gave $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)][BF_4]_2$ (cation **3**) as a slightly water-soluble, yellow powder (96.0 mg, 0.128 mmol, 71%). Selective precipitation from the aqueous solution is as well possible with NH_4PF_6, yielding the water-insoluble yellow hexafluorophophate salt of **3** (cation **3**) (52 mg, 0.060 mmol, 33%). **3** [BF4]$_2$. IR (cm^{-1}): 3300 (m), 3220 (m), ν(N–H), 2940 (w) ν(C–H), 1535 (w), δ (N–H_{asym}), 1450 (br, w), 1395 (m), ν(C=C). **3** $[PF_6]_2$. Anal. Calcd for $C_{24}H_{43}F_{12}N_3P_2Ru_2$: C, 33.30; H, 5.01; N, 4.85. Found: C, 33.35; H, 4.92; N, 4.78. IR (cm^{-1}): 3320 (s), 3270 (m), ν(N–H), 2930 (w) ν(C–H), 1535 (w), δ(N–H_{asym}), 1450 (br, m), 1395 (m), ν(C=C), 1070 (m), 1015 (m), ν(C–C).

Heating of a solution of **2** (sulfate) prepared in situ, containing an excess of hydrazine hydrate (cf. 3.2.), to 100°C in a closed pressure Schlenk tube for at least 3 h gave the same product. In order to prepare **3** from isolated **2**, the tosylate salt of **2** (10 mg, 0.011 mmol) and B_2O_3 (23 mg) were dissolved in water (10 ml). Hydrazine hydrate (80%, 30 ml, 0.49 mmol) was then added, and the solution was heated to 100°C in a closed pressure Schlenk tube for 14 h. The work-up was the same as described in the preceding paragraph.

3.5. Crystallization of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}N_2H_3)]_2[SO_4][PF_6]_2$ (cation 4)

Hydrazine hydrate (80%, 100 ml, 1.65 mmol) was added to an aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]_2[SO_4]$ (cation **1**) (0.090 mmol, 40 ml H_2O), and the solution was stirred for 2 days. The solution was then concentrated to about 5 ml by evaporation of the solvent in vacuo. Addition of an excess of NH_4PF_6 precipitated some hexafluorophosphate salt of **2** which was filtered off. Overnight, red crystals of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1,\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}N_2H_3)]_2[SO_4][PF_6]_2$ (cation **4**) formed from the mother liquor. **4** $[SO_4][PF_6]_2$. IR (cm^{-1}): 3315 (w), 3165 (br, w), ν(N–H), 2925 (w) ν(C–H), 1580 (w), δ (N–H_{asym}), 1445 (br, w), 1390 (m), ν(C=C), 1015 (w), ν(C–C).

3.6. X-ray structure determination of complexes 2 and 3

For **2**, the X-ray data were recorded using a Stoe-Siemens AED2 4-circle diffractometer (Mo–K_α

Table 4
Crystallographic and selected experimental data for **2** and **3**

Compound	$[\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_2(\mu_2\text{-}\eta^2\text{-H}_2\text{NNH}_2)]$ $[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2$ (cation **2**)	$[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu^2\text{-H})(\mu_2\text{-}\eta^2\text{-H}_2\text{NNH}_2)(\mu_2\text{-NH}_2)]$ $[\text{CF}_3\text{SO}_3]_2$ (cation **3**)
Formula	$C_{38}H_{56}N_2O_6Ru_2S_2$	$C_{26}H_{43}F_6N_3O_6Ru_2S_2$
Crystal shape	blocks	Needles
Crystal colour	Black–green	Orange–yellow
Crystal size (mm)	0.46 × 0.42 × 0.38	0.65 × 0.20 × 0.08
Crystal system	Monoclinic	Monoclinic
M	903.11	544.56
Space group	C2/c	I2/m
Unit cell dimensions		
a (Å)	19.839(2)	17.520(1)
b (Å)	9.755(2)	11.8708(6)
c (Å)	20.238(2)	17.591(2)
α (°)	90	90
β (°)	91.765(5)	108.995(11)
γ (°)	90	90
V (Å^3)	3915.1(9)	3459.2(5)
Z	4	4
D_{calc} (g cm^{-3})	1.532	1.678
μ(Mo–K$_\alpha$) (mm^{-1})	0.925	1.068
F(000)	1864	1768
θ Scan range (°)	2.01–25.51	2.11–25.87
T (K)	293(2)	293(2)
N standards	2	–
Intensity variation	$<18\%$	–
Reflections measured	3654	13254
Independent reflections	3654	3138
Reflections observed [$I>2\sigma(I)$]	3080	2059
Final R indices [$I>2\sigma(I)$]	$R_1=0.0445$, $wR_2=0.1052$	$R_1=0.0553$, $wR_2=0.0909$
R indices (all data)	$R_1=0.0565$, $wR_2=0.1215$	$R_1=0.0882$, $wR_2=0.0983$
Goodness-of-fit	1.134	1.069
Maximum Δ/σ	-0.104	-2.189
Residual density: maximum, minimum $\Delta\rho$ (eÅ^{-3})	0.722, -1.249	0.473, -1.114

graphite monochromated radiation, $\lambda = 0.71073$ Å; $\omega/2\theta$ scans). Two standard reflections were measured every hour and indicated a certain degree of decomposition (ca. 18%). For **3**, data collection was performed with a Stoe Imaging Plate Diffractometer System (Stoe and Cie, 1995) equipped with a one-circle goniometer and a graphite-monochromator, using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å); 200 exposures (3 min/exposure) were obtained at 70 mm with $0 < \varphi < 200°$ and with the crystal oscillating through 1° in φ, $D_{\min}$–$D_{\max}$ 12.45–0.81 Å. Table 4 summarizes the crystallographic and selected experimental data for **2** and **3**.

The structures were solved using the program SHELXS 86 [13] and refined with SHELXL 93 [14]. The figures were drawn with SCHAKAL [15]. Important bond lengths and angles are given in Table 2 for **2** and in Table 3 for **3**. The hydrido ligands as well as the hydrogen atoms of the hydrazine ligands were located from difference maps and fully refined for both, **2** and **3**. The methyl hydrogens of the hexamethylbenzene ligands and the amido hydrogens in **3** were included in calculated positions and refined as riding atoms using the SHELXL 93 default parameters.

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