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Dinuclear (Arene)ruthenium Hydrido Complexes: Synthesis, Structure, and Fluxionality of $(C_6Me_6)_2Ru_2H_3(BH_4)$

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In aqueous solution, the cationic complex $[(C_6Me_6)Ru(H_2O)_3]^{2+}$ reacts with sodium borohydride to give the known dinuclear cation $[(C_6Me_6)_2Ru_2H_3]^+$ (**1**$^+$), which can be isolated as the hexafluorophosphate salt. Under biphasic conditions (water/diethyl ether), **1**$^+$ reacts with additional sodium borohydride to afford the neutral dinuclear hydrido complexes $(C_6Me_6)_2Ru_2H_4$ (**2**) and $(C_6Me_6)_2Ru_2H_3(BH_4)$ (**3**), which are extracted into the organic phase. The solid-state structure of **3** has been solved by a single-crystal X-ray structure analysis. It contains a single-bonded ruthenium−ruthenium backbone with one μ-hydride and two terminal hydrides; the BH_4 bridge is bonded through two H atoms to the two ruthenium atoms. In solution, two independent fluxional processes can be distinguished by variable-temperature ^1H NMR spectroscopy, one of which involves the bridging and the terminal hydrido ligands and the other the coordinated and the noncoordinated H atoms of the BH_4 bridge. In addition, deuteration experiments reveal that the terminal hydrides and the μ-hydrides at the Ru atoms as well as the boron-bound hydrides of the BH_4 ligand undergo complete hydride scrambling, a process that is slow with respect to the NMR time scale.

The chemistry of water-soluble organometallic complexes is a relatively new area of research which has attracted steadily increasing interest.[1−4] Organometallic aqua complexes combining the features of both organometallic complexes (given by the soft organic ligand) and classical Werner-type complexes (given by the hard aqua ligands) at the same metal center, open up the prospect of new reactivity patterns in organometallic chemistry.[5]

We are interested in the chemistry of cationic aqua−arene complexes of ruthenium(II), $[(\eta^6\text{-arene})Ru(H_2O)_3]^{2+}$, which represent these ambivalent features. They were proposed as promising synthons as long ago as 1981[6] but have nevertheless only sporadically been the object of synthetic studies.[7−12] Recently we have shown that these complexes give rise to a range of di-, tri-, and tetranuclear hydrido clusters upon reaction with molecular hydrogen, the nature of the products depending crucially on the substituents at the arene ligand.[13−15]

However, the hexamethylbenzene derivative $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ was not as reactive toward molecular hydrogen in aqueous solution as the other derivatives studied. We therefore investigated the reactivity of this bulky complex toward other hydridic reagents. In addition to molecular hydrogen, the water-soluble sodium borohydride is a promising reagent for reactions in aqueous solution or biphasic systems. In this paper we report on neutral (arene)ruthenium hydrido complexes obtained from the reaction of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ with sodium borohydride in mono- and biphasic aqueous solution.

Results and Discussion

Reaction of $[(C_6Me_6)Ru(H_2O)_3]^{2+}$ with $NaBH_4$ in Water. The reaction of triaqua(hexamethylbenzene)ruthenium(II), $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$, employed as the sulfate or tosylate salt, with sodium borohydride in aqueous solution is very complex. With 1.5 equiv of $NaBH_4$, the known[16] dinuclear complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]^+$ (**1**$^+$) is formed (Scheme 1). Cation **1**$^+$, easily isolated from the aqueous solution as the hexafluorophosphate salt, has already been reported by Bennett *et al.*, who had obtained it by three different routes.[16,17] The method described here is more convenient, since it gives higher yields and allows an easier workup.

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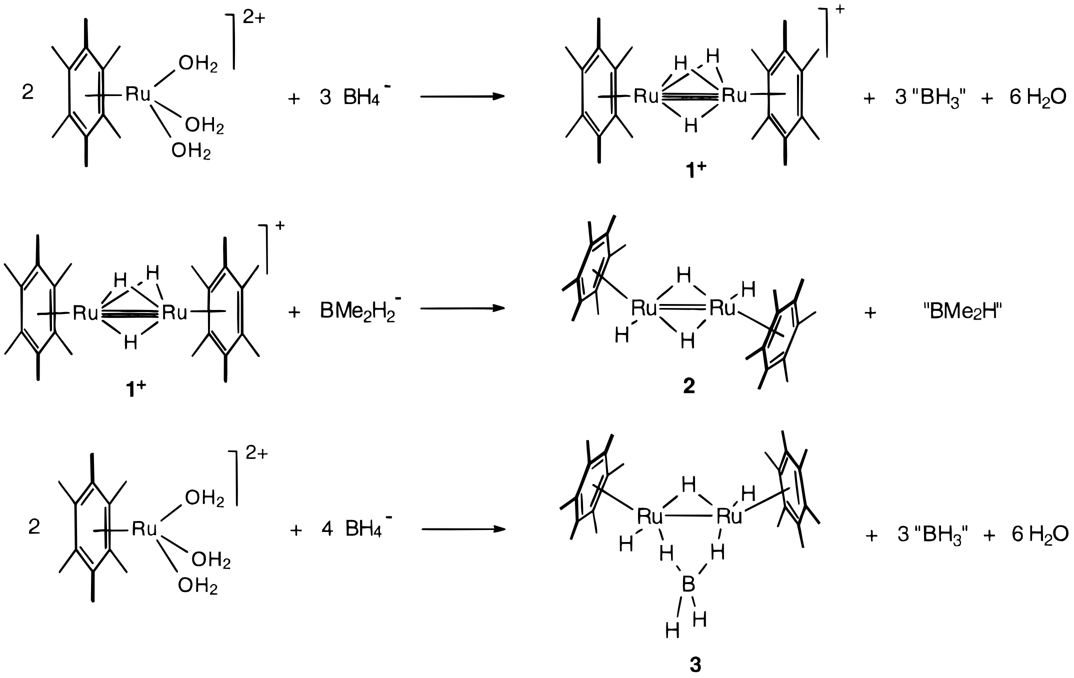
Scheme 1. Synthetic Routes to Complexes 1^+, 2, and 3



Treatment of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ with a larger excess of $NaBH_4$ (>4 equiv) gives rise to several neutral hydrido species containing the (hexamethylbenzene)ruthenium fragment. They are extracted into the organic phase, when the reaction is carried out in a biphasic system consisting of water and diethyl ether. Two of these species can be prepared more selectively by using the hydrido complex $\mathbf{1}^+$ instead of the aqua complex $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$. These two compounds turned out to be the new hydrido complexes $(\eta^6\text{-}C_6Me_6)_2Ru_2H_4$ (**2**) and $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3(BH_4)$ (**3**), which have been characterized by spectroscopic and analytical data and, for **3**, also by a single-crystal X-ray structure analysis.

Complex **2** represents the first neutral hydrido complex of an (arene)ruthenium moiety without a further stabilizing ligand, whereas complex **3** contains the borohydride ligand in a very rare coordination mode. Both complexes are very air-sensitive and thermally unstable. Due to their high sensibility and their similar solubility and crystallization properties, it was not possible to separate them from the mixture. Therefore, we had to develop specific synthetic routes for **2** and **3**.

Preparation of $(C_6Me_6)_2Ru_2H_4$ (2). The formation of **2** in a pure form has been achieved by using $LiBMe_2H_2$ as the hydride donor (Scheme 1). The addition of this reagent to a suspension of the hexafluorophosphate of $\mathbf{1}^+$ in hexane, followed by addition of water, gives **2** (without **3**), the excess reagent being hydrolyzed and dissolved by the water. The violet compound **2** is isolated by filtration, extraction with benzene, and evaporation of the solvent.

Thus, by choosing $LiBMe_2H_2$ instead of $NaBH_4$ as the hydride donor, the sole formation of **2** can be attained. Interestingly, a whole series of other hydride donor reagents, such as $LiAlH_4$, NaH, $KB[CH(CH_3)C_2H_5]_3H$, $NaB(O_2CCH_3)_3H$, $NaBH_3CN$, and alcohols in basic solution, failed to give this formally simple addition of one hydride ligand to form **2**.

Preparation of $(C_6Me_6)_2Ru_2H_3(BH_4)$ (3). The orange complex **3** is obtained by direct reaction of an aqueous solution of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ with a large excess (about 20 equiv) of solid sodium borohydride (Scheme 1). A brown solid is precipitated during the vigorous reaction. After washing of this precipitate with methanol, extraction with tetrahydrofuran, and evaporation of the solvent, **3** is obtained in pure form.

The use of methanol as a washing solvent was found to be crucial, because **3** and contaminates which also precipitate from the aqueous solution have the same solubility in most organic solvents. However, while **3** is unaffected by methanol, the contaminates react with the alcohol with formation of methanol-soluble products.

Complex **3** is also accessible by reaction of $\mathbf{1}^+$ with BH_4^- or by reaction of **2** with $BH_3\cdot THF$. Both reactions are important in understanding the interrelations of the different (hexamethylbenzene)ruthenium hydrido complexes; synthetically they are less interesting, since the direct method employing $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ is considerably more convenient.

Characterization and Variable-Temperature ^{1}H NMR Analysis of $(C_6Me_6)_2Ru_2H_4$ (2). The constitution of **2** was concluded from the ^{1}H NMR (Table 1), infrared, and microanalytical data, in comparison to the known (mesitylene)osmium analogue.[18] The solid-state infrared spectrum (KBr pellet) is in accordance with the assumption of two terminal hydrido ligands and two bridging hydrido ligands in **2**: the absorption of the terminal Ru−H bonds shows up at 1875 cm^{-1}, while a broad band at 1185 cm^{-1} can be assigned to the Ru−H−Ru bridges.

A preliminary crystal structure analysis[19] of a single crystal of **2** (triclinic, space group $P\bar{1}$), obtained by diffusion of hexane into a tetrahydrofuran solution of the complex at −30 °C, confirms the dinuclear structure of **2**, with a $Ru_2(\eta^6\text{-}C_6Me_6)_2$ backbone: The molecule possesses crystallographic C_i symmetry, the center of inversion lying between the two ruthenium atoms. The

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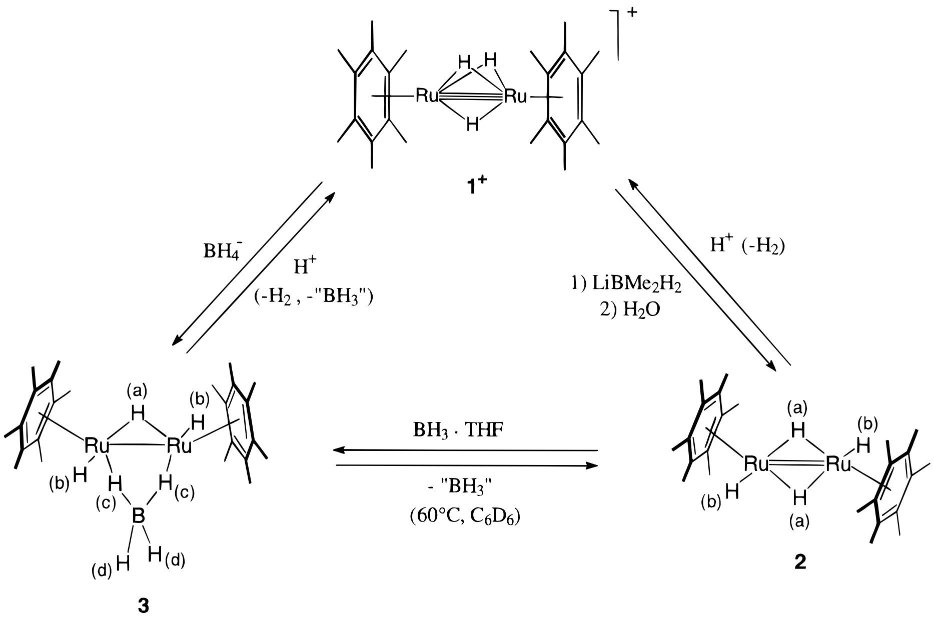
Table 1. ^1H NMR Data for Complexes 1^+, 2, 3, and 4

	η^6-C_6**Me**$_6$	hydride region	
		ambient temp	low temp
1^+ (sulfate)[a]	2.27	−16.41 (s)	
1^+ (chloride)[b]	2.31	−16.09 (s)	−16.27 (s)[i]
1^+ (hexafluorophosphate)[c]	2.38	−15.99 (s)	
2[d]	2.08	−9.2 (br)	−1.52 (t, J = 7.4 Hz, 2H, H_b)
			−17.18 (t, J = 7.4 Hz, 2H, H_a)[e,f,i]
3[d]	2.05	−12.4 (br, 4H)	+3.2 (br, 2H, H_d)
		−18.4 (br, 1H)	−11.74 (s, 2H, H_b)
			−13.4 (br, 2H, H_c)
			−18.36 (s, 1H, H_a)[e,f,g]
4[e]	2.07	−11.37 (s)	−10.14 (s, 1H, H_{br})
			−11.88 (s, 2H, H_t)[h]

[a] D_2O. [b] CD_2Cl_2. [c] Acetone-d_6. [d] Benzene-d_6. [e] Toluene-d_8. [f] Cf. assignment in Scheme 2. [g] −60 °C. [h] −70 °C. [i] −80 °C.

Scheme 2. Interrelations of Complexes 1^+, 2, and 3



Ru−Ru distance is 2.68 Å, which would be in accordance with a formal metal−metal double bond or a Ru_2H_2 four-center−four-electron interaction. Due to the poor quality of the unstable crystals, the crystal structure analysis, however, was not good enough for an unambiguous localization of the hydrogen atoms.

The ^1H NMR spectrum (200 MHz) of **2** in benzene-d_6 at ambient temperature shows—besides the large hexamethylbenzene singlet at δ 2.08—a broad signal in the hydride region (δ −9.2). When the temperature is lowered (in toluene-d_8), the resonance broadens into the base line, while the hexamethylbenzene resonance remains unaffected. At −80 °C two new hydride signals of equal intensities appear, a downfield triplet at δ −1.52 (terminal hydrides b) and an upfield triplet at δ −17.18 (J = 7.4 Hz) (bridging hydrides a) (Table 1; for the assignments cf. Scheme 2). These data can be explained with a rapid site exchange of the terminal and the bridging hydrido ligands at ambient temperature. At low temperatures this dynamic process is frozen with respect to the NMR time scale, giving rise to two different resonances, which exhibit the expected hydrogen−hydrogen coupling pattern.

Crystal Structure of $(C_6Me_6)_2Ru_2H_3(BH_4)$ (3). Suitable crystals of **3** have been obtained by diffusion of hexane into a tetrahydrofuran solution of the compound at −30 °C. The structure reveals that **3** is the second example containing a μ-η^2-coordinated borohydride ligand, the first example of this type being the analogue $(\eta^5\text{-}C_5Me_5)_2Ir_2H_3(BH_4)$, isolated by Bergman's group.[20]

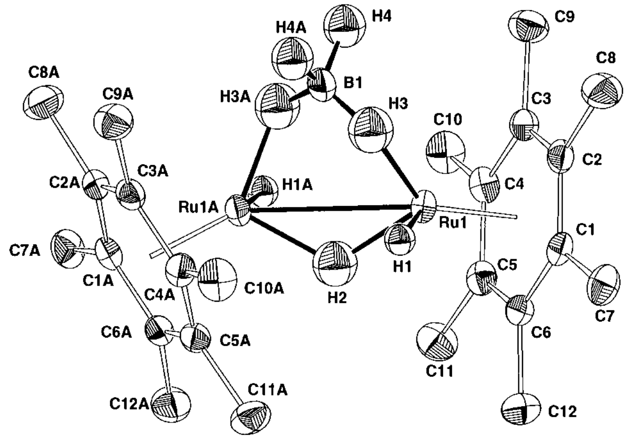


Figure 1. ORTEP drawing of $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3BH_4$ (**3**).

The molecular structure of **3** is depicted in Figure 1. Important bond lengths and angles are presented in Table 2. The molecule possesses crystallographic C_2 symmetry, the 2-fold axis passing through atoms B(1) and H(2) and bisecting the Ru−Ru bond. It was possible to locate all hydrogen atoms from difference maps; the

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Table 2. Selected Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 3, with Esd's in Parentheses

Interatomic Distances			
Ru(1)−Ru(1A)	2.895(1)	Ru(1)−H(1)	1.46(3)
Ru(1)−C(1−6)	1.72(1)	Ru(1)−H(2)	1.68(3)
Ru(1)−C(1)	2.202(3)	Ru(1)−H(3)	1.69(3)
Ru(1)−C(2)	2.220(3)	B(1)−H(3)	1.24(4)
Ru(1)−C(3)	2.284(3)	B(1)−H(4)	1.13(4)
Ru(1)−C(4)	2.294(3)	H(4)−H(9B)	2.74(8)
Ru(1)−C(5)	2.224(3)	H(4)−H(9C)	2.75(8)
Ru(1)−C(6)	2.202(3)	H(4)−H(9F)	2.19(3)
Ru(1)−B(1)	2.406(4)		
Bond Angles			
Ru(1A)−Ru(1)−H(1)	86(1)	B(1)−Ru(1)−H(3)	29(1)
Ru(1A)−Ru(1)−H(2)	31(2)	Ru(1A)−Ru(1)−H(3)	70(1)
H(4)−B(1)−H(3)	124(2)	Ru(1)−B(1)−H(3)	41(2)
B(1)−Ru(1)−H(1)	91(1)	Ru(1)−B(1)−Ru(1A)	74.0(2)
B(1)−Ru(1)−Ru(1A)	53.02(8)		
Torsion Angles			
H(1)−Ru(1)−Ru(1A)−H(1A)	−172(2)		
H(3)−Ru(1)−Ru(1A)−H(3A)	55(3)		
Dihedral Angles between Planes			
H(3)−B(1)−H(3A)/Ru(1)−Ru(1A)−H(2)	40(2)		
H(3)−B(1)−H(3A)/H(4)−B(1)−H(4A)	65(3)		
C(1−6)/C(1A−6A)	35.6(1)		

ruthenium hydrides and the boron hydrides have been fully refined.

The molecule is constructed of two (η^6-C_6Me_6)Ru half-sandwiches, each ruthenium being additionally coordinated by a terminal hydrido ligand. The fragments are linked by a bridging hydride and a bridging borohydride. The Ru−Ru distance of 2.895(1) Å is in agreement with a single metal−metal bond, which should better be interpreted in terms of a Ru_2H three-center−two-electron bond.

The planar hexamethylbenzene rings in **3** are not symmetrically bound to the ruthenium atoms. Instead, the distances of the ring carbon atoms to Ru(1) increase in pairs from C(1)/C(6) to C(3)/C(4) (Table 2). This can be explained by the steric strains between the borohydride ligand and the methyl groups of the arene ligand. Accordingly, the distances between the terminal hydrogen atoms of the borohydride ligand and some hydrogen atoms of the disordered methyl group at C(9) are quite short (H(4)−H(9B), 2.738(79) Å; H(4)−H(9C), 2.745(79) Å; H(4)−H(9F), 2.193(34) Å). These distances are near to or even within the sum of the van der Waals contact radii of two hydrogen atoms (2.4 Å).

The borohydride fragment has lost its tetrahedral structure upon coordination. Thus, the H(4)−B(1)−H(3) angle (124(2)°) is considerably larger than the expected value of 109.5°, and the angle between the plane formed by H(3), H(3A), and B(1) and the plane formed by H(4), H(4A), and B(1) (65(3)°) is quite different from the theoretical value of 90°. Furthermore, it is tilted toward the Ru−Ru backbone in such a way that the plane formed by Ru(1), H(2), and Ru(1A) and the plane formed by B(1), H(3), and H(3A) are inclined one to another by an angle of 40(2)°.

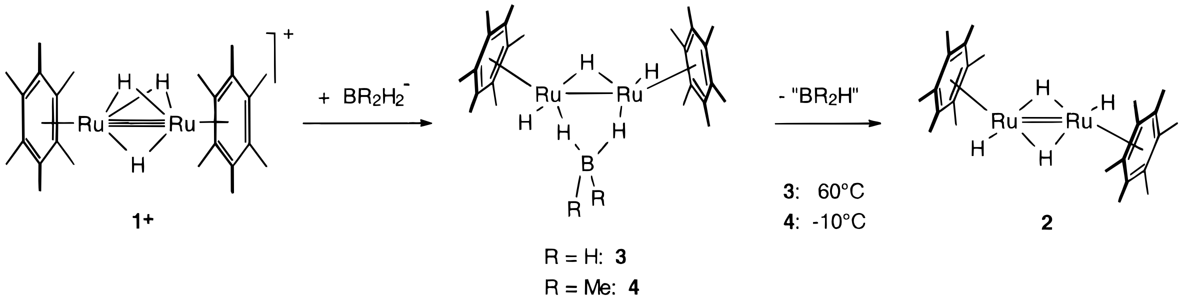
All B−H distances lie well within the range of covalent bonds, though the distances of the metal−boron bridging hydrides are longer than those of the terminal ones. In (η^5-C_5Me_5)$_2Ir_2H_3(BH_4)$,[20] by contrast, Bergman *et al.* found the distances between the boron atom and the hydrogen atoms bridging the boron−iridium bond to be far longer than is required for a covalent bond (1.77(8) Å). They considered this finding to be the main reason for the strong distortion of the borohydride moiety upon coordination. We have found the corresponding distances in **3** (1.24(4) Å) to lie within the range of a covalent bond, the borohydride moiety being nevertheless strongly distorted as stated previously. This leads us to the conclusion that the distortion of the BH_4 moiety in both complexes is the result of the unusual coordination mode of the borohydride fragment bridging two metal centers; the steric demands of the (η^5-C_5Me_5) and the (η^6-C_6Me_6) ligands, respectively, may also play a role.

Variable-Temperature ^{1}H NMR Analysis of (C_6Me_6)$_2Ru_2H_3(BH_4)$ (3). In contrast to the known complex (η^5-C_5Me_5)$_2Ir_2H_3(BH_4)$,[20] the ^{1}H NMR spectrum of which stays unchanged over the temperature range from −80 to 25 °C, complex **3** shows a fluxional behavior in the variable-temperature ^{1}H NMR spectra (Table 1). The large hexamethylbenzene singlet shows up at δ 2.05 (benzene-d_6) and remains unaffected by temperature changes. In the hydride region two very broad signals of intensity ratio 4:1 are observed at ambient temperature. When the temperature is lowered (in toluene-d_8), the large downfield resonance (δ −12.4) is resolved into two resonances. At −60 °C it gives rise to a singlet (δ −11.7), which is due to the terminal hydrido ligands b (assignment in Scheme 2) and to a still broadened signal (δ −13.4), which is attributed to the hydrides linking the ruthenium atoms and the boron atom (c). The upfield signal (δ −18.4) sharpens to a singlet upon cooling. It is assigned to the hydrido ligand bridging the Ru−Ru bond (a). The resonance due to the terminal hydrogen atoms of the borohydride ligand (d) could be located downfield of TMS as a very broad peak even at −60 °C (δ +3.2). Decoupling of the ^{11}B resonance led to a considerable sharpening of both hydride resonances c and d, thus confirming their assignment as being bound to the boron atom and, moreover, indicating that their broadness can be explained by a fast relaxation process induced by the quadrupolar moment of the neighboring ^{11}B nucleus. The hydrogen−hydrogen couplings of the hydrido ligands a and b could not be resolved, the coupling constants being too small.

In order to further analyze this dynamic behavior, we heated a benzene-d_6 solution of **3** up to 60 °C, in steps of 10 °C. Due to the thermal instability of the compound, a further rise in temperature was not possible. The results reveal two independent fluxional processes, one involving the terminal and the bridging hydrido ligands a and b and the other involving the coordinated and the noncoordinated hydrogen atoms of the borohydride ligand, c and d. Thus, at 40 °C the resonances of the hydrides a and b coalesce, whereas the resonances of the hydrogen atoms c can still be detected as a very broad signal (δ −13.4). At 60 °C, the hydrides a and b give rise to only one very broad signal (δ −14.0), while the signal of hydrides c is now broadened into the base line.

This interpretation is confirmed by the variable-temperature measurements of **3** in CD_2Cl_2, which could be performed in spite of a partial decomposition to [(η^6-C_6Me_6)$_2Ru_2(\mu$-$H)_3$]$^+$ (**1**$^+$) and [(η^6-C_6Me_6)$_2Ru_2(\mu$-$H)_2(\mu$-$Cl)$]$^+$. At −40 °C the same picture as in toluene-d_8 at

Scheme 3. Reactivity Analogies of Complexes 3 and 4



−60 °C is obtained. Comparing the broadness of the resonances as the temperature was lowered gradually to −95 °C showed that the resonances of the hydrides b (δ −12.67) and a (δ −18.52) did not change any more, while the resonance of the hydrogen atoms c (δ −14.47) still sharpened. This sharpening can be explained by the slowing down of the fluxional process of the borohydride ligand, since the effect of the quadrupolar moment of the ^{11}B nucleus upon cooling would instead lead to a further broadening of the signal.

The two independent fluxional processes proposed for **3** in order to account for the variable-temperature ^{1}H NMR spectra have been observed separately in other complexes: a hydride exchange within a coordinated BH_4 unit has been reported for many complexes containing η^1-, η^2-, and η^3-coordinated BH_4 ligands,[21] and ligand-site exchange between terminal and bridging hydrido ligands has, for instance, been reported for $[(C_5Me_5)_2Ir_2(PMe_3)_2H_2(\mu\text{-}H)]PF_6$[22] and for $(C_5Me_5)Ru(\mu\text{-}SiEt_2H)_2(\mu\text{-}H)RuH(C_5Me_5)$.[23]

However, in **3** both independent fluxional processes are superimposed by an overall site exchange of all hydrides (a−d), which is slow in relation to the NMR time scale but can be verified chemically. Thus, after addition of [PPN][BH_4] to the hexafluorophosphate salt of deuterated **1**$^+$, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}D)_3][PF_6]$, in acetone-$d_6$ at −80 °C and warming to 20 °C for 5 min, the ^{1}H NMR spectrum at −80 °C reveals all hydride positions in complex **3** formed to be equally deuterated. This result can only be interpreted by a complete hydride scrambling of all positions a−d in **3**.

Interrelation Study of the Complexes $[(C_6Me_6)_2Ru_2(\mu\text{-}H)_3]^+$ (1$^+$), $(C_6Me_6)_2Ru_2H_4$ (2), and $(C_6Me_6)_2Ru_2H_3(BH_4)$ (3). The interrelations of **1**$^+$, **2**, and **3** are shown in Scheme 2. The preparation of **3** by addition of BH_4^- to **1**$^+$ is easily accomplished by use of $NaBH_4$ or [PPN][BH_4] in tetrahydrofuran or acetone. Immediate formation of the product can be observed by the fast color change from red to orange. The ^{1}H NMR spectrum shows that **1**$^+$ is totally transformed into **3** without formation of any side products. The formal addition of one hydride anion to **1**$^+$ in order to give **2**, however, has not been achieved, but this transformation can be realized indirectly by addition of $LiBMe_2H_2$ and consecutive hydrolysis with water.

Complex **3** is accessible from **2** by reaction of **2** in hexane solution with BH_3·THF. Abstraction of BH_3 from **3** to go back to **2** proved to be difficult: the usual BH_3 abstractors[24] such as triethylamine and dimethyl sulfide failed to transform **3** into **2**. This reaction could only be achieved thermally by heating a benzene-d_6 solution of **3** to 60 °C: after 10 min about 20% of **3** is transformed into **2**, as shown by the NMR spectrum. After 1 h the hexamethylbenzene signal of **2** is already larger than that of **3**, but now the spectrum also shows the signal of uncoordinated hexamethylbenzene, indicating thermal decomposition of the complexes.

Finally, both **2** and **3** give hydride abstraction with formation of H_2 when treated with Brønsted acids. Thus, **1**$^+$ is formed by treatment of either **2** or **3** in a biphasic system consisting of hexane and water which is acidified with sulfuric acid. However, the borohydride complex **3** is more stable than the hydrido complex **2**: while **2** already reacts at pH 4, **3** gives the reaction only at pH 2.

As the preparation of pure $(\eta^6\text{-}C_6Me_6)_2Ru_2H_4$ (**2**) (free of **3**) was only achieved by using $LiBMe_2H_2$ instead of $NaBH_4$, it was interesting to study the course of the reaction. Upon addition of $LiBMe_2H_2$ to a suspension of the hexafluorophosphate salt of **1**$^+$ in hexane, an only sparingly hexane-soluble yellow product is formed, which hydrolyzes then with water to give **2**. In order to characterize this intermediate **4**, the yellow solid was filtered off and dissolved in toluene-d_8; it is only relatively stable at low temperatures (below −10 °C) or with an excess of $LiBMe_2H_2$ present in the solution. The proton NMR spectrum of this solution suggests **4** to be $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3(BMe_2H_2)$, a complex analogous to **3**.

At −70 °C, the spectrum shows two hydride signals in a 1:2 ratio (δ −10.14 [s, 1H] and δ −11.88 [s, 2H]) and a singlet for the coordinated hexamethylbenzene ligands at δ 2.07. Above −40 °C only one hydride resonance is observed (δ −11.37), which sharpens with increasing temperature; this is consistent with an exchange process of terminal and bridging hydrido ligands. Unfortunately, the two bridging hydrogen atoms of the BMe_2H_2 ligand could not be detected in the NMR spectrum, presumably due to the ^{11}B quadrupolar moment, and the signals of the two methyl groups appeared as badly resolved signals centered at around δ 1 that were difficult to interpret. Thus, the interpretation of the intermediate **4** as being $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3(BMe_2H_2)$ is not without ambiguity.

However, the most convincing argument for the structure proposed for **4** is its chemical behavior in comparison to **3** (Scheme 3). Both complexes are formed from the hexafluorophosphate salt of **1**$^+$ with the appropriate borohydride anion, and both lose the borane unit "BR_2H" upon warming. The molecular structure

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of **3** reveals repulsive interactions of the terminal hydrogen atoms of the BH_4 ligand with the methyl groups of the hexamethylbenzene ligand (see above). Obviously, this repulsion must be considerably more important in **4**, which contains the bulkier methyl substituents instead of hydrogen atoms, thus explaining the higher thermal instability of **4** toward loss of a borane unit.

Experimental Section

General Considerations. All manipulations were carried out under a nitrogen or argon 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,[25] distilled, and saturated with inert gas. The NMR spectra were recorded on a Varian Gemini 200 BB instrument and the $^1H\{^{11}B\}$ and ^{11}B NMR spectra of **3** on a Bruker AMX 600. The IR spectra were recorded on a Perkin-Elmer FTIR 1720 X 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.[26] $LiBMe_2H_2$ was partially purchased from Aldrich (no longer available) and partially prepared according to a literature procedure.[27,28] All other reagents were commercially available and were used without further purification.

Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$. A slightly modified procedure with respect to the published method[8] was used: 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) in water (20 mL) is stirred in a Schlenk tube for 1 h in the dark (aluminum foil). During this period the mixture is treated several times with ultrasound (~1 min) until all orange solids are dissolved. After filtration of the silver chloride that precipitated, the yellow solution can be employed *in situ* (0.300 mmol). Instead of silver sulfate, other silver salts such as silver nitrate or silver tosylate can be used as well in stoichiometric amounts to remove the chloro ligands from the starting complex.

Synthesis of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]^+$ (1^+). An aqueous solution of $NaBH_4$ (20 mg, 0.529 mmol, 15 mL of H_2O) is added dropwise to a solution of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3][SO_4]$ (0.300 mmol, 20 mL of H_2O). The mixture turns dark green upon addition of the first drops, but eventually the solution becomes dark red. It is filtered in order to remove a fine black precipitate which is formed during the reaction. This aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]_2[SO_4]$ can be used *in situ*, or alternatively, $\mathbf{1}^+$ can be isolated as the hexafluorophosphate salt. In this case, an aqueous solution of ammonium hexafluorophosphate (50 mg, 0.307 mmol, 2.5 mL of H_2O) is added, upon which a brown solid precipitates immediately. This precipitate is filtered off, washed with water (2 × 3 mL), and dried *in vacuo*. Yield of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3][PF_6]$: 88 mg, 0.127 mmol, 85%. Anal. Calcd for $C_{24}H_{39}F_6PRu_2\cdot H_2O$: C, 41.61; H, 5.97. Found: C, 41.67; H, 5.65. IR (cm^{-1}): 2930 (w), ν(C—H); 1445 (br, m), 1390 (m), ν(C═C); 1070 (m), 1010 (m), ν(C—C); 840 (vs), ν(P—F); 560 (s), δ(P—F).

The deuterated complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}D)_3][PF_6]$ is prepared by the same procedure, using $NaBD_4$ as the reagent and D_2O as the solvent.

Reaction of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^{2+}$ with $NaBH_4$. An aqueous solution of $NaBH_4$ (24 mg, 0.634 mmol, 15 mL of H_2O) is added dropwise with vigorous stirring to a biphasic system consisting of an aqueous solution of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3][SO_4]$ (0.150 mmol, 15 mL of H_2O) and diethyl ether (25 mL). The organic phase turns red during the reaction, while the aqueous phase becomes slightly yellow. The mixture is filtered in order to remove the fine black precipitate that is formed during the reaction; then the organic phase is separated from the aqueous one. The ether is evaporated and the product mixture dried *in vacuo*. ^1H NMR (C_6D_6; δ): 2.17, 2.14, 2.08, 2.05, 2.03 (all s, $C_6\mathbf{Me_6}$); −9.2 (br), −10.52 (s), −12.4 (br), −12.67 (s), −13.80 (s), −18.4 (br).

Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]^+$ (1^+) with $NaBH_4$. An aqueous solution of $NaBH_4$ (15.5 mg, 0.410 mmol, 12 mL of H_2O) is added dropwise with vigorous stirring to a biphasic system consisting of an aqueous solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3]_2[SO_4]$ (sulfate salt of $\mathbf{1}^+$ in 25 mL of H_2O; prepared from 0.150 mmol of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3][SO_4]$) and diethyl ether (30 mL). The organic phase turns deep red during the reaction, while the aqueous phase becomes slightly yellow. The mixture is stirred for 1 h, the color of the organic phase turning from red to violet. After filtration, the organic phase is separated from the aqueous one. The solvent is evaporated and the product mixture dried *in vacuo*. ^1H NMR (C_6D_6; δ): 2.08, 2.05, (both s, C_6Me_6); −9.2 (br), −12.4 (br), −18.4 (br).

Synthesis of $(\eta^6\text{-}C_6Me_6)_2Ru_2H_4$ (2). A hexane solution of $LiBMe_2H_2$ (0.5 M, 1.3 mL, 0.65 mmol) is added to a suspension of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3][PF_6]$ (hexafluorophosphate of $\mathbf{1}^+$) in hexane (40 mg, 0.058 mmol, 4 mL of hexane). A yellow suspension is formed which is stirred for 30 min and treated several times with ultrasound (~1 min). Addition of water (3 mL) at 0 °C gives rise to gas evolution, while the suspension turns red-violet. After 30 min of stirring at ambient temperature, the hexane phase is evaporated *in vacuo*; then, 1 mL of hexane is added to the aqueous suspension in order to wash off hexane-soluble impurities from the sparingly hexane-soluble product. After some stirring, the violet precipitate is filtered off and washed with water (1 mL) and hexane (1 mL). Extraction with benzene and evaporation of the solvent gives pure **2** as a violet solid (10 mg, 0.019 mmol, 33%). Crystals of **2** are obtained by diffusion of hexane into a tetrahydrofuran solution of the compound at −30 °C. Anal. Calcd for $C_{24}H_{40}Ru_2$: C, 54.32; H, 7.60. Found: C, 54.10; H, 7.53. IR (cm^{-1}): 2915 (vs), ν(C—H); 1875 (m), ν(Ru—H); 1455 (br, m), 1385 (s), ν(C═C); 1185 (br, w), ν(Ru—H—Ru); 1070 (m), 1010 (m), ν(C—C); 800 (w), 550 (w), 535 (w).

Synthesis of $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3(BH_4)$ (3). An aqueous solution of $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3][SO_4]$ (0.300 mmol, 20 mL of H_2O) is added at once to solid $NaBH_4$ (200 mg, 5.29 mmol) in a 250 mL Schlenk frit. After evolution of gas and strong foaming, the rather vigorous reaction gives rise to a brown precipitate. The almost colorless aqueous solution is suctioned off and the precipitate washed successively with water (3 × 6 mL) and with methanol (3 × 3 mL), dried *in vacuo* for 1 h, and then extracted with tetrahydrofuran (3 × 3 mL). Evaporation of the solvent and drying *in vacuo* gives **3** as an orange solid (25 mg, 0.046 mmol, 31%). Crystals of **3** are obtained by diffusion of hexane into a tetrahydrofuran solution of the compound at −30 °C. Anal. Calcd for $C_{24}H_{43}BRu_2$: C, 52.94; H, 7.96. Found: C, 53.00; H, 7.52. $^{11}B\{^1H\}$ NMR (δ): −9.9 (br) (−60 °C, external reference $BF_3\cdot Et_2O$). IR (cm^{-1}): 2910 (s), ν(C—H); 2355 (s), 2250 (w), $\nu(B—H_t)$; 1935 (s), $\nu(Ru—H_t)$; 1440 (br, m), 1385 (vs), ν(C═C); 1070 (m), 1010 (m), ν(C—C); 1130 (m), 945 (m), δ(B—H); 770 (m).

Identification of $(\eta^6\text{-}C_6Me_6)_2Ru_2H_3(BMe_2H_2)$ (4). A hexane solution of $LiBMe_2H_2$ (0.5 M, 0.5 mL, 0.25 mmol) is added to a suspension of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu\text{-}H)_3][PF_6]$ (hexafluorophosphate of $\mathbf{1}^+$) in hexane (15 mg, 0.022 mmol, 3 mL of hexane). The yellow suspension formed is stirred for 30 min and treated several times for ~1 min with ultrasound. The precipitate is then filtered off at −40 °C, using a Schlenk frit equipped with a cooling mantle, washed with hexane (2 × 1 mL), and dried *in vacuo* for 10 min. Thereupon, it is extracted

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Table 3. Crystallographic and Selected Experimental Data

compd	$(\eta^6\text{-}C_6Me_6)_2Ru_2H_3BH_4$ (**3**)
formula	$C_{24}H_{43}BRu_2$
cryst shape	thin plates
cryst color	orange
cryst size/mm	0.46 × 0.38 × 0.06
crystal syst	monoclinic
M_r	544.56
space group	$C2/c$
a/Å	15.428(5)
b/Å	8.430(3)
c/Å	19.038(5)
α/deg	90
β/deg	112.09(3)
γ/deg	90
V/Å^3	2294.3(13)
Z	4
D_c/(g cm^{-3})	1.576
μ(Mo Kα)/mm^{-1}	1.323
F(000)	1120
θ scan range/deg	2.3−30
T/K	183(2)
N standards	2
intensity variation/%	1.5
no. of rflns measd	6900
no. of indep rflns	3336
R_{int}	0.0444
no. of rflns obsd ($I > 2\sigma(I)$)	2780
final R indices ($I > 2\sigma(I)$)	R1 = 0.0350, wR2 = 0.0763
R indices (all data)	R1 = 0.0451, wR2 = 0.0836
goodness of fit	1.038
max Δ/σ	−0.265
residual density: max, min $\Delta\rho$/(e Å^{-3})	+1.476, −1.023

directly into the NMR tube with cold toluene-d_8 (−70 °C). The ^{1}H NMR spectrum is recorded immediately at −70 °C.

Reaction of 2 and 3 with Sulfuric Acid. Dilute sulfuric acid (pH ~4) is added to solutions of **2** and **3** in hexane. After vigorous stirring of the biphasic system, the pH value of the aqueous phase is determined, and the ^{1}H NMR spectra of the organic phase and the aqueous phase are taken in order to confirm the product distribution. Then, some drops of sulfuric acid of pH ~1 are added, and the product distribution is analyzed as before. The procedure is repeated, until the starting complex **2** (or **3**) is completely transformed into **1**$^+$, which is found in the aqueous phase as the sulfate salt. The reaction can also be followed by the color change of the solutions. It is accompanied by the evolution of H_2 gas. The transformation takes places at pH ~4 for **2** and at pH ~2 for **3**.

X-ray Structure Analysis of 3. X-ray data were recorded using a Stoe-Siemens AED2 four-circle diffractometer (Mo Kα graphite-monochromated radiation, λ = 0.710 73 Å; ω/θ scans). Table 3 summarizes the crystallographic and selected experimental data. An empirical absorption correction using ψ-scans was applied (T_{max} = 0.5631; T_{min} = 0.4399). The structure was solved using the program SHELXS 86[29] and refined with SHELXL 93.[30] Figure 1 was drawn with ZORTEP[31] (thermal ellipsoids, 50% probability level). Important bond lengths and angles are given in Table 2. The ruthenium hydrides and the hydrogens bound to boron were located from difference maps and were fully refined; the methyl hydrogens were included in calculated positions and refined as riding atoms using the SHELXL 93 commands AFIX 127 for the disordered (C(8), C(9), C(10)) and AFIX 137 for the idealized methyl groups (C(7), C(11), C(12)).

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Supporting Information Available: Listings of crystal data and structure refinement details, positional and thermal parameters, bond distances and angles, and least-squares planes for **3** (9 pages). Ordering information is given on any current masthead page.

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