

A Surprising Reaction of Trimethylphosphane with the Unsaturated Diruthenium Complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$: Synthesis and Molecular Structure of the Cations $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3]^+$ and $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_2(\mu_2\text{-H})(\text{H})_2]^+$

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Whereas aromatic or aliphatic phosphanes undergo cleavage of the P–C bond in the reaction with $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ to give phosphido-bridged diruthenium cations of the type $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PR}_2)(\mu_2\text{-H})_2]^+$, trimethylphosphane surprisingly yields the substitution product $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3]^+$ (**1**), as well as the racemic intermediate $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_2(\mu_2\text{-H})(\text{H})_2]^+$ (**2**), in the form

of the tetrafluoroborate salts. In complex **2**, the hydrido ligands are fluxional in solution, as shown by variable-temperature ^1H NMR spectroscopy. Cation **1** reacts with *p*-bromothiophenol to give the complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_3\text{-}(\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4)\text{-S})(\mu_2\text{-H})_2]^+$ (**3**), isolated as the tetrafluoroborate salt.

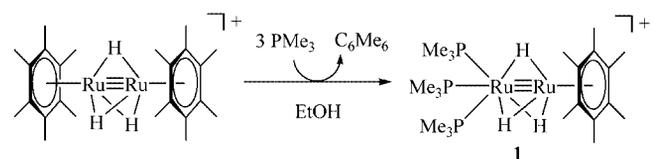
Introduction

Tertiary phosphanes are without any doubt among the most important ligand systems used in organometallic chemistry or in molecular catalysis.^[1] The cleavage of the carbon–phosphorus bond has been observed in numerous cases, essentially by reacting metal carbonyl complexes with aromatic phosphanes.^[2] Recently, we found that trisubstituted (aliphatic or aromatic) phosphanes, PR_3 , undergo facile P–C bond cleavage with the unsaturated complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ to give the phosphido-bridged complexes $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PR}_2)(\mu_2\text{-H})_2]^+$.^[3] In the reaction of triphenylphosphane with $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ to give $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PPh}_2)(\mu_2\text{-H})_2]^+$, we were able to isolate an intermediary complex containing a bridging phenyl ligand, $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PPh}_2)(\mu_2\text{-Ph})(\mu_2\text{-H})_2]^+$, and to perform a single-crystal X-ray structure analysis of the tetrafluoroborate salt. In the reaction of trialkylphosphanes with $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ to give $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PR}_2)(\mu_2\text{-H})_2]^+$ ($\text{R} = n\text{Oct}, n\text{Bu}$), we were able to show that the reaction produces the corresponding olefins (*n*-octene or *n*-butene) and not the expected alkanes. This suggests that the P–C bond cleavage in trialkylphosphanes at the diruthenium centre occurs by $\beta\text{-H}$ elimination from the alkyl group. In order to confirm this hypothesis, we de-

cidated to study the reaction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ with trimethylphosphane, in which $\beta\text{-H}$ elimination is impossible.

Results and Discussion

The reaction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ with PMe_3 indeed does not yield the expected complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-PMe}_2)(\mu_2\text{-H})_2]^+$, but surprisingly leads to the formation of the cation $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3]^+$ (**1**), in which one of the two hexamethylbenzene ligands has been replaced by three trimethylphosphane ligands. Cation **1** is obtained in 28% yield and it can be isolated as the tetrafluoroborate salt (Scheme 1). The substitution of an $\eta^6\text{-arene}$ ligand at a ruthenium atom by three phosphane ligands has been observed so far for benzene,^[4] toluene^[5] and *p*-cymene^[6] ligands, but never for the strongly bound $\eta^6\text{-C}_6\text{Me}_6$ ligand.



Scheme 1. Synthesis of **1**.

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The single-crystal X-ray structure analysis of **[1][BF₄]**, crystallised by slow diffusion of diethyl ether in a concentrated acetone solution of **[1][BF₄]**, reveals for cation **1** the presence of three bridging hydrido ligands coordinated to

the two ruthenium atoms, one ruthenium atom being coordinated to an $\eta^6\text{-C}_6\text{Me}_6$ ligand and the other one to three PMe_3 ligands. The molecular structure of cation **1** is shown in Figure 1.

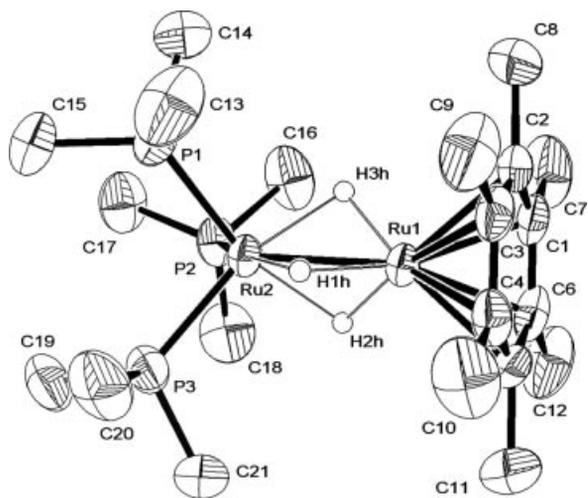


Figure 1. Molecular structure of cation **1** (ORTEP drawing of **1** at the 50% probability level with hydrogen atoms and tetrafluoroborate anion omitted for clarity).

The Ru–Ru distance [2.4934(6) Å] is within the range of a ruthenium–ruthenium triple bond.^[7] The replacement of a hexamethylbenzene ligand by three PMe_3 ligands does not significantly affect the geometrical parameters of the $\text{Ru}_2(\mu_2\text{-H})_3$ backbone as compared to $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$.^[7b] The three independent Ru–P lengths (ca. 2.258 Å) are comparable to those found in $[\text{Ru}_2(\text{PMe}_3)_6(\mu_2\text{-H})_3]^+$.^[8] In the ^1H NMR spectrum the nine methyl protons give rise to a broad signal, each carbon atom of the three equivalent PMe_3 ligands can be differentiated in the ^{13}C NMR spectrum (i.e. $\delta = 24.59, 24.69$ and 24.79 ppm). This is probably due to the steric hindrance of the methyl groups (see Figure 2) and suggests a restricted rotation of the three PMe_3 ligands, which gives rise to three independent signals in the ^{13}C NMR spectrum.

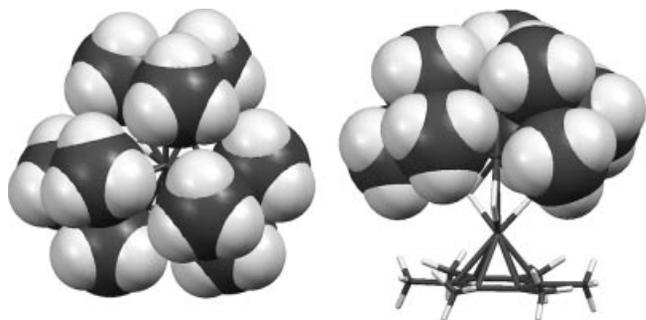
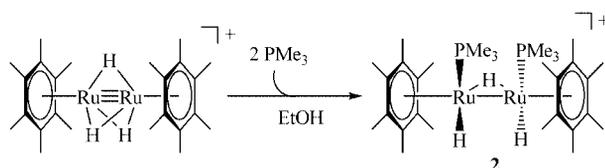


Figure 2. Mixed van der Waals and capped sticks representation of **1** with hydrogen atoms.

The molar ratio of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ and PMe_3 in the synthesis of **1** is critical: Although the stoichiometry of the reaction requires 3 equiv. of PMe_3 (see Scheme 1), the reaction must be carried out with an excess of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{BF}_4]$.

The best yield (28%) is obtained with 2.5 equiv. of PMe_3 , 3 equiv. or more leads to decomposition. In order to shine light on this strange observation, we carried out the reaction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ with 2 equiv. of PMe_3 in ethanol at room temperature. In this case, the reaction quantitatively gives the cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_2(\mu_2\text{-H})(\text{H})_2]^+$ (**2**), in which both hexamethylbenzene are still present (Scheme 2). Cation **2** can be considered as an intermediate in the formation of cation **1** (see below), and its conversion with PMe_3 into **1** is accompanied by the formation of mononuclear complexes, mainly $[(\eta^6\text{-C}_6\text{Me}_6)\text{-Ru}(\text{PMe}_3)_2\text{H}]^+$.^[9] This explains why any local excess of trimethylphosphane has to be avoided for the synthesis of **1**.



Scheme 2. Synthesis of **2**.

The single-crystal X-ray structure analysis of $[\mathbf{2}][\text{BF}_4]$, crystallised by slow diffusion of diethyl ether in a concentrated acetone solution of $[\mathbf{2}][\text{BF}_4]$, reveals for cation **2** only one hydrido bridge, each ruthenium atom being coordinated also to a terminal hydride, an $\eta^6\text{-C}_6\text{Me}_6$ ligand and a PMe_3 ligand. The molecular structure of cation **2** is shown in Figure 3.

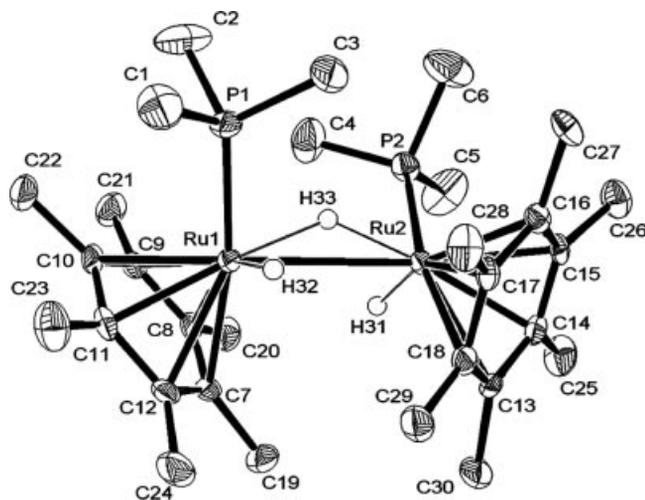


Figure 3. Molecular structure of cation **2** (ORTEP drawing of **2** at the 50% probability level with hydrogen atoms and tetrafluoroborate anions omitted for clarity).

The two C_6Me_6 arene ligands are not parallel to each other, and the angle between the C_6Me_6 planes is $56.6(2)^\circ$. Accordingly, to reduce the steric hindrance, the phosphorus atoms adopt a staggered conformation, the P1–Ru1–Ru2–P2 torsion angle being 67.79° (Figure 3). Interestingly, in **2**, the Ru–Ru distance [3.2230(8) Å] is very long. As the electron count of 34 e suggests a formal metal–metal single bond, this would be the longest Ru–Ru bond observed in a dinuclear complex. In the absence of DFT calculations,

however, the question of metal–metal bonding interaction remains a debatable point.

At room temperature, no hydride resonances can be observed in the ^1H NMR spectrum of $[2][\text{BF}_4]$, which suggests a fluxional behaviour of the hydrido ligands. This is confirmed by variable-temperature NMR experiments down to $-40\text{ }^\circ\text{C}$ (Figure 4). At $0\text{ }^\circ\text{C}$, two badly-defined signals centred at $\delta = -13.00$ and -25.25 ppm appear, which sharpen at $-40\text{ }^\circ\text{C}$, to give a doublet of doublets at $\delta = -13.10$ ppm [dd, $^2J_{(\text{H,H})} = 7.6$ Hz, $^2J_{(\text{H,P})} = 51.8$ Hz, 2 H], which corresponds to the two terminal hydrides, and a triplet of triplets at -25.24 ppm [tt, $^2J_{(\text{H,H})} = 7.6$ Hz, $^2J_{(\text{H,P})} = 23.4$ Hz, 1 H], which is assigned to the bridging hydride in the ^1H NMR spectra.

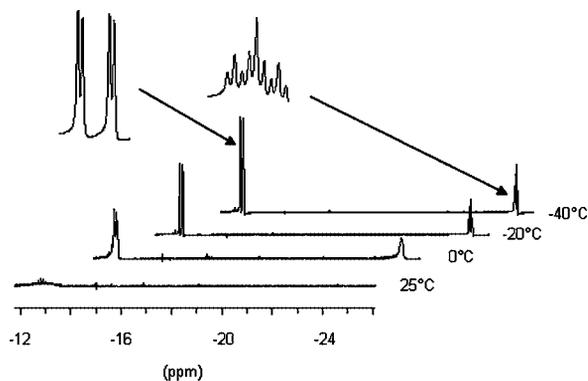
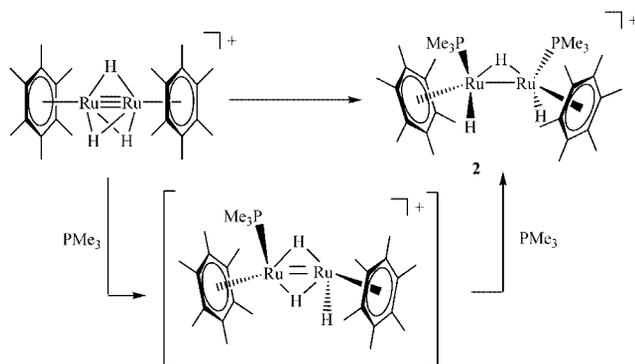


Figure 4. Variable ^1H NMR temperature for $[2][\text{BF}_4]$ in $[\text{D}_6]$ acetone.

The two ruthenium atoms in **2** are stereogenic, the crystal structure analysis of $[2][\text{BF}_4]$ reveals a racemic mixture of the (*R,R*) and the (*S,S*) enantiomers, the *meso* (*R,S*) isomer being absent. This observation shows that the addition of the trimethylphosphane ligands to $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ occurs diastereospecifically.

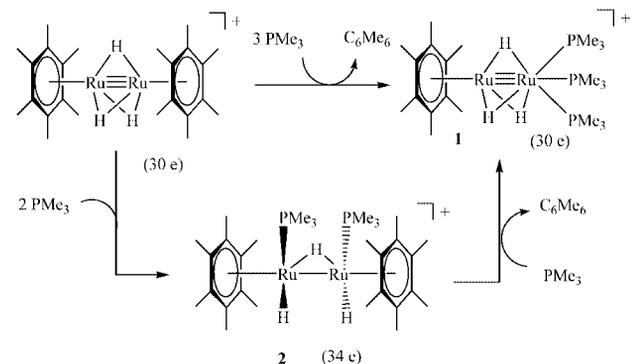
This can be explained by step-wise attack of the two PMe_3 molecules: In the first step, one PMe_3 molecule coordinates to one ruthenium atom, which forces the two hexamethylbenzene ligands to adopt a tilted geometry in the *trans* configuration with respect to each other, and pushes one of the three hydrido ligands from a bridging into a terminal position at the second ruthenium atom, in an *anti* configuration with respect to the PMe_3 ligand. In the second step, the next PMe_3 molecule enters the complex coordinating to the second ruthenium atom, *trans* with respect to the $\eta^6\text{-C}_6\text{Me}_6$ ligand, which pushes a second hydrido ligand from a bridging into a terminal position. As the coordination of the first trimethylphosphane ligand does not favour the (*R*) or (*S*) enantiomers, the racemic mixture is obtained (Scheme 3). Alternatively, an intermediate containing a bridging trimethylphosphane ligand may be considered.^[10]

At $80\text{ }^\circ\text{C}$ in the presence of PMe_3 (0.1 equiv.), cation **2** converts into cation **1** with liberation of one equivalent of hexamethylbenzene (10% yield), which suggests **2** to be an intermediate in the reaction between $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ and PMe_3 to give **1** (Scheme 4). However, no evidence



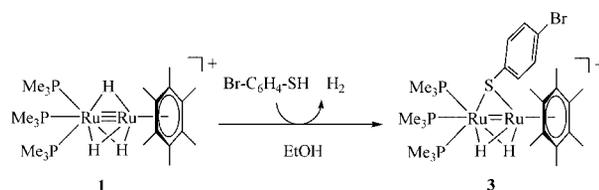
Scheme 3. Mechanistic proposal for the diastereospecific addition of two PMe_3 ligands to $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$.

for the direct transfer of one PMe_3 ligand from one ruthenium atom to the other one in **2** to give **1**, could be obtained.



Scheme 4. Mechanistic hypothesis for the synthesis of **1**.

In order to study the reactivity of unsaturated complex **1** (**30 e**), we reacted **1** with *p*-bromothiophenol given that the parent cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ (**30 e**) reacts with *p*-bromothiophenol to give $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\{\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4\text{-S})\}(\mu_2\text{-H})_2]^+$ and $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\{\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4\text{-S})\}_2(\mu_2\text{-H})]^+$.^[11] Indeed, complex **1** reacts in refluxing ethanol with *p*-bromothiophenol to give, with elimination of molecular hydrogen, the thiolato-bridged derivative $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_3\{\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4\text{-S})\}(\mu_2\text{-H})_2]^+$ (**3**), isolated as the tetrafluoroborate salt (Scheme 5) in 45% yield. Unlike the reaction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ with *p*-bromothiophenol, analogous complex **1** gives only the monosubstituted product even with a large excess (10 equiv.) of *p*-bromothiophenol, probably for steric reasons.



Scheme 5. Synthesis of **3**.

The two hydrido ligands in **3** are not equivalent due to the tetrahedral geometry of the sulfur atom, which gives rise to two signals in the hydride region ($\delta = -14.29$ and -15.48 ppm) in the ^1H NMR spectrum.

Conclusions

In conclusion, we studied the reactivity of the unsaturated cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ toward trimethylphosphane, which shows that even the strongly bound $\eta^6\text{-C}_6\text{Me}_6$ ligand can be replaced by three trimethylphosphane ligands in $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ to give $[(\eta^6\text{-C}_6\text{Me}_6)\text{-Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3]^+$ (**1**). A possible intermediate $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_2(\mu_2\text{-H})(\text{H})_2]^+$ (**2**), obtained as a racemic mixture of both (*R,R*) and (*S,S*) enantiomers, has been isolated by reacting $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ and trimethylphosphane at room temperature.

Experimental Section

General Remarks: All manipulations were carried out in an inert atmosphere of nitrogen by using standard Schlenk techniques. All solvents were degassed with nitrogen prior to use. Silica gel (type G) used for preparative thin-layer chromatography was purchased from Macherey–Nagel GmbH. Trimethylphosphane solution (1 M) in thf was purchased from Aldrich. The dinuclear trihydrido complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{BF}_4]$ was synthesised by a previously described method.^[12] Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded with a Bruker 400 MHz spectrometer and ESI mass spectra were recorded at the University of Fribourg by Prof. Titus Jenny. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva.

Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3][\text{BF}_4]$ (1**) $[\text{BF}_4]$:** In a pressure Schlenk tube, $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{BF}_4]$ (100 mg, 0.16 mmol) was dissolved in ethanol (20 mL, puriss.) and a solution of trimethylphosphane (1 M) in thf (0.4 mmol, 0.4 mL) was then added. The resulting solution, which turned red after a few minutes, was stirred at 80 °C for 18 h. The reaction mixture was then cooled to room temperature, and the solvent was evaporated under reduce pressure. The resulting orange-red solid was purified by preparative thin-layer chromatography on silica (acetone/dichloromethane, 1:10). The pure product was extracted with acetone from the main orange band and evaporation of the solvent gave **1** $[\text{BF}_4]$. Yield: 30 mg, 0.044 mmol (28%). ^1H NMR (400 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = -13.24$ (q, $^2J_{(\text{H,P})} = 4.5$ Hz, hydride), 1.51 [br., 27 H, $\text{P}(\text{CH}_3)_3$], 2.46 [s, 18 H, $\text{C}_6(\text{CH}_3)_6$] ppm. $^{13}\text{C}\{^31\text{P}, ^1\text{H}\}$ NMR (100 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = 18.05$ [$\text{C}_6(\text{CH}_3)_6$], 24.59 [$\text{P}(\text{CH}_3)_3$], 24.79 [$\text{P}(\text{CH}_3)_3$], 24.89 [$\text{P}(\text{CH}_3)_3$], 93.53 [$\text{C}_6(\text{CH}_3)_6$] ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = 18.69$ (s) ppm. MS (ESI): $m/z = 597$ [$\text{M} + \text{H}]^+$. $\text{C}_{21}\text{H}_{48}\text{BF}_4\text{P}_3\text{Ru}_2$ (682.47): calcd. C 36.95, H 7.08; found C 36.88, H 7.02.

Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\text{PMe}_3)_2(\mu_2\text{-H})(\text{H})_2][\text{BF}_4]$ (2**) $[\text{BF}_4]$:** In a pressure Schlenk tube, $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{BF}_4]$ (100 mg, 0.16 mmol) was dissolved in ethanol (20 mL, puriss.) and a solution of trimethylphosphane (1 M) in thf (0.33 mmol, 0.33 mL) was added. The resulting solution, which turns red after a few minutes, was stirred at room temperature for 18 h. The solvent was evaporated to dryness under reduced pressure. The red solid was washed with diethyl ether (3 \times 60 mL), dissolved in acetone, and filtered

through celite under an inert atmosphere by using a Mülheim apparatus. The solvent was then evaporated to dryness to give quantitatively **2** $[\text{BF}_4]$ (115 mg, 0.15 mmol). ^1H NMR (400 MHz, $[\text{D}_6]$ -acetone, -40 °C): $\delta = -25.24$ (tt, $^2J_{(\text{H,H})} = 7.6$ Hz, $^2J_{(\text{H,P})} = 23.4$ Hz, 1 H, hydride), -13.10 (dd, $^2J_{(\text{H,H})} = 7.6$ Hz, $^2J_{(\text{H,P})} = 51.8$ Hz, 2 H, hydride), 1.40 [d, $^2J_{(\text{H,P})} = 9.16$ Hz, 18 H, $\text{P}(\text{CH}_3)_3$], 2.28 [s, 36 H, $\text{C}_6(\text{CH}_3)_6$] ppm. $^{13}\text{C}\{^31\text{P}, ^1\text{H}\}$ NMR (100 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = 18.14$ [$\text{C}_6(\text{CH}_3)_6$], 23.45 [d, $^1J_{(\text{P-C})} = 32$ Hz, $\text{P}(\text{CH}_3)_3$], 99.26 [$\text{C}_6(\text{CH}_3)_6$] ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, $[\text{D}_6]$ -acetone, 25 °C): $\delta = 8.61$ (s) ppm. MS (ESI): $m/z = 681$ [$\text{M}]^+$ (and decomposition signals). $\text{C}_{30}\text{H}_{57}\text{BF}_4\text{P}_2\text{Ru}_2$ (768.66): calcd. C 46.87, H 7.47; found C 46.94, H 7.39.

Conversion of **2 into **1**:** In a pressure Schlenk tube, $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{BF}_4]$ (100 mg, 0.16 mmol) was dissolved in ethanol (20 mL, puriss.) and a solution of trimethylphosphane (1 M) in thf (0.34 mmol, 0.34 mL) was added. The resulting red solution was stirred at room temperature for 18 h. The solution containing **2** $[\text{BF}_4]$ was heated at 80 °C for 8 h, and the solvent was then evaporated to dryness under reduce pressure. The resulting orange-red solid was purified by preparative thin-layer chromatography on silica (acetone/dichloromethane, 1:10). The product was extracted with acetone from the main orange band and evaporation of the solvent gave **1** $[\text{BF}_4]$. Yield: 11 mg, 0.016 mmol (10%).

Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3\{\mu_2\text{-}(p\text{-Br-C}_6\text{H}_4)\text{-S}\}(\mu_2\text{-H})_2][\text{BF}_4]$ (3**) $[\text{BF}_4]$:** $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}_2(\text{PMe}_3)_3(\mu_2\text{-H})_3][\text{BF}_4]$ (30 mg, 0.044 mmol) and *para*-bromothiophenol (26.6 mg, 0.14 mmol) were dissolved in ethanol (25 mL, puriss.), and the red solution was heated at reflux for 18 h. After cooling to room temperature, the solvent was evaporated to dryness, and the red solid was washed with diethyl ether (3 \times 40 mL). The red solid was purified by preparative thin-layer chromatography on silica (acetone/dichloromethane, 1:10). The product was extracted with acetone from the main orange fraction and evaporation of the solvent gave the pure product. Yield: 18 mg, 0.02 mmol (45%). ^1H NMR (400 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = -15.48$ (m, 1 H, hydride), -14.29 (m, 1 H, hydride), 1.14 [d, $^2J_{(\text{H,P})} = 9.0$ Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 1.47 [d, $^2J_{(\text{H,P})} = 9.4$ Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 1.69 [d, $^2J_{(\text{H,P})} = 8.7$ Hz, 9 H, $\text{P}(\text{CH}_3)_3$], 2.22 [s, 18 H, $\text{C}_6(\text{CH}_3)_6$], 7.48 (br., 4 H, *H*-Ar) ppm. $^{13}\text{C}\{^31\text{P}, ^1\text{H}\}$ NMR (100 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = 17.75$ [$\text{C}_6(\text{CH}_3)_6$], 21.64 [$\text{P}(\text{CH}_3)_3$], 21.92 [$\text{P}(\text{CH}_3)_3$], 22.01 [$\text{P}(\text{CH}_3)_3$], 22.31 [$\text{P}(\text{CH}_3)_3$], 24.03 [$\text{P}(\text{CH}_3)_3$], 24.32 [$\text{P}(\text{CH}_3)_3$], 94.97 [$\text{C}_6(\text{CH}_3)_6$], 121.53 (*C*-Br), 132.67 (*C*-Ar), 133.11 (*C*-Ar), 146.25 (*C*-S) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, $[\text{D}_6]$ acetone, 25 °C): $\delta = 10.89$ (dd, $^2J_{(\text{H,P})} = 28$ Hz, $^2J_{(\text{H,P})} = 32$ Hz), 12.68 (dd, $^2J_{(\text{H,P})} = 32$ Hz, $^2J_{(\text{H,P})} = 43$ Hz), 16.40 (dd, $^2J_{(\text{H,P})} = 30$ Hz, $^2J_{(\text{H,P})} = 44$ Hz) ppm. MS (ESI) $m/z = 783$ [$\text{M} + \text{H}]^+$. $\text{C}_{27}\text{H}_{51}\text{BBrF}_4\text{P}_3\text{Ru}_2\text{S}$ (869.53): calcd. C 37.29, H 5.91; found C 37.34, H 5.94.

X-ray Crystallography: Crystals of **1** $[\text{BF}_4]$ and **2** $[\text{BF}_4]$ were mounted on a Stoe Image Plate Diffraction System equipped with a ϕ circle goniometer by using Mo- K_α graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 1.0 and 1.5°, respectively, 2θ range from 2.0–26°, $D_{\text{max}}/D_{\text{min}} = 12.45/0.81$ Å. The two structures were solved by direct methods by using the program SHELXS-97.^[13] Refinement and all further calculations were carried out by using SHELXL-97.^[14] The H-atoms were included in calculated positions and treated as riding atoms with the use of the SHELXL default parameters. The non-H atoms were refined anisotropically by using weighted full-matrix least-square on F^2 . Crystallographic details are summarised in Table 1. Figure 1 and Figure 3 (ORTEP^[15] drawing) show the labelling scheme for **1** $[\text{BF}_4]$ and **2** $[\text{BF}_4]$. Figure 3 is drawn with MERCURY.^[16]

Table 1. Crystallographic and selected experimental data for [1][BF₄] and [2][BF₄].

	[1][BF ₄]	[2][BF ₄]
Chemical formula	C ₂₁ H ₄₈ BF ₄ P ₃ Ru ₂	C ₃₀ H ₅₇ BF ₄ P ₂ Ru ₂
Formula weight	682.45	768.64
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Crystal colour and shape	Red block	Orange block
Crystal size	0.25 × 0.20 × 0.20	0.30 × 0.22 × 0.12
<i>a</i> [Å]	9.379(2)	14.612(3)
<i>b</i> [Å]	12.812(3)	15.260(3)
<i>c</i> [Å]	26.127(5)	15.000(3)
β [°]	95.40(3)	94.03(3)
<i>V</i> [Å ³]	3125.6(12)	3336.4(12)
<i>Z</i>	4	4
<i>T</i> [K]	293(2)	173(2)
<i>D_c</i> [g cm ⁻³]	1.450	1.528
μ [mm ⁻¹]	1.151	1.042
Scan range [°]	4.46 < 2 θ < 51.90	3.82 < 2 θ < 52.12
Unique reflections	6084	6462
Reflections used	3454	3857
[<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> _{int}	0.0622	0.0760
Final <i>R</i> indices	0.0297, <i>wR</i> ₂ 0.0525	0.0344, <i>wR</i> ₂ 0.0620
[<i>I</i> > 2 σ (<i>I</i>)] ^[a]		
<i>R</i> indices (all data)	0.0730, <i>wR</i> ₂ 0.0578	0.0740, <i>wR</i> ₂ 0.0670
Goodness-of-fit	0.755	0.798
Max, Min $\Delta\rho/e$ [Å ⁻³]	0.596, -0.492	0.870, -0.731

[a] Structures were refined on F_o^2 : $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

CCDC-615022 (1)[BF₄] and CCDC-615023 (2)[BF₄] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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