

Synthesis, Structure and Reactivity of Homo- and Heterobimetallic Complexes of the General Formula $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{ML}]$ [$\text{LM} = (\text{arene})\text{Ru}, \text{Cp}^*\text{Rh}, \text{Cp}^*\text{Ir}$]

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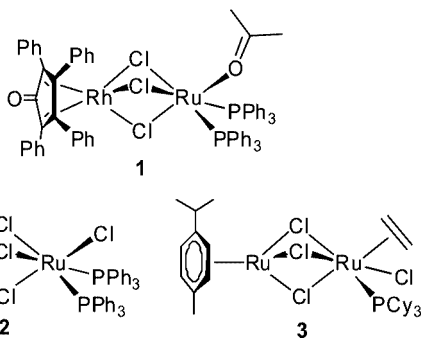
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The homo- and heterobimetallic complexes $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{ML}]$ [$\text{LM} = (\text{C}_6\text{H}_6)\text{Ru}, (\text{cymene})\text{Ru}, (1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)\text{Ru}, \text{Cp}^*\text{Rh}, \text{Cp}^*\text{Ir}$] were prepared by reaction of $[\text{Cp}^*\text{Ru}(\mu\text{-OMe})_2]$ with Me_3SiCl and subsequent addition of $[\text{LMCl}_2]_2$. The complexes $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{cymene})]$ and $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{-IrCp}^*]$ were characterized by single-crystal X-ray analyses. In crossover experiments with $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RuCl}(\text{PPh}_3)_2]$ and $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{Ru}(1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)]$ in CD_2Cl_2 , a dynamic

equilibrium with the complexes $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RuCp}^*]$ and $[(1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{PPh}_3)_2]$ was rapidly established, demonstrating the kinetic lability of the triple chloro bridge. Upon reaction of $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RuCp}^*]$ with benzene, the ionic complex $[\text{Cp}^*\text{Ru}(\text{C}_6\text{H}_6)][\text{Cp}^*\text{RhCl}_3]$ was formed, which was characterized by X-ray crystallography. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Bimetallic complexes, in which two different metal fragments are connected by either two or three halogeno bridges, have been employed as catalyst precursors for ring-opening and ring-closing metathesis reactions,^[1] for the Oppenauer-type oxidation of alcohols,^[2] and for atom-transfer radical reactions.^[3] The heterobimetallic $\text{Rh}^{\text{I}}\text{-Ru}^{\text{II}}$ complex **1**, for example, can be used as an efficient catalyst for the oxidation of secondary alcohols under mild conditions,^[2a] whereas the $\text{Rh}^{\text{III}}\text{-Ru}^{\text{II}}$ complex **2**^[3c] and the $\text{Ru}^{\text{II}}\text{-Ru}^{\text{II}}$ complex **3**^[3a] are among the most active catalysts available for the atom-transfer radical addition of CCl_4 and CHCl_3 to olefins.



The synthesis of mixed, halogeno-bridged complexes can be accomplished by several synthetic routes.^[4] Mixed complexes with two halogeno bridges are most conveniently ob-

tained in metathesis reactions starting from the corresponding homodimeric compounds. Reactions of this kind were first described by the groups of Stone^[5] and Masters^[6] in the 1970s. More recent investigations have shown that this method is quite general.^[7,8] Mixed complexes with three halogeno-bridges can likewise be obtained in metathesis reactions^[9,10] but alternative pathways such as ligand-transfer^[11] or substitution^[3a,3b,12] reactions have also been explored.^[4] The various methods allow the synthesis of a structurally diverse set of homo- and heterobimetallic complexes in relatively short time. This is of interest for the generation of catalyst libraries in combinatorial catalysis.^[3c] In the following, we introduce a new procedure that allows the synthesis of complexes of the general formula $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{ML}]$ [$\text{LM} = (\text{arene})\text{Ru}, \text{Cp}^*\text{Rh}, \text{Cp}^*\text{Ir}$] in excellent yields.

Results and Discussion

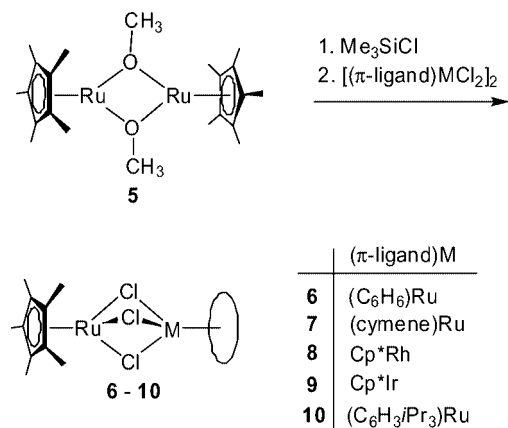
For the synthesis of mixed complexes containing the Cp^*RuCl fragment, the tetrameric complex $[\text{Cp}^*\text{RuCl}]_4$ (**4**) seemed to be well suited as it is known that the chloro bridges of **4** can be easily cleaved.^[13–16] The reaction of **4** with two equivalents of the dimeric half-sandwich complex $[(\pi\text{-ligand})\text{MCl}_2]_2$ was thus expected to give the mixed complex $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{M}(\pi\text{-ligand})]$ in an entropically favored reaction. Complex **4** can be obtained by reduction of $[\text{Cp}^*\text{RuCl}_2]_2$ with LiHBEt_3 ^[14] or with Zn .^[15] Alternatively, it can be obtained by reaction of the methoxy-bridged complex $[\text{Cp}^*\text{Ru}(\mu\text{-OMe})_2]$ (**5**) with Me_3SiCl .^[16] We chose the latter method for our reactions.

For the synthesis of the homo- and heterobimetallic complexes **6–10**, the tetramer **4** was generated in situ by addition of Me_3SiCl to complex **5** in CH_2Cl_2 . Subsequent ad-

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dition of $[(\pi\text{-ligand})\text{MCl}_2]_2$ gave the mixed products **6–10** (Scheme 1). Complex **4** displays a high solubility in a variety of nonpolar organic solvents and even in hydrocarbons such as pentane. It was thus possible to use a slight excess of **5** (1.2 $\times$) with respect to the dimer $[(\pi\text{-ligand})\text{MCl}_2]_2$ because additional **4** could easily be removed by washing with pentane. The homobimetallic product **10**, on the other hand, is itself soluble in pentane. We therefore used a slight excess of $[(1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)\text{RuCl}_2]_2$ (1.2 $\times$) and purified the product **10** by extraction with pentane.



Scheme 1. Synthesis of the complexes **6–10**.

The new complexes **6–10** were characterized by ^1H and ^{13}C NMR spectroscopy and by elemental analysis. In addition, complexes **7** and **9** were analyzed by single-crystal X-ray analysis (Figures 1 and 2, respectively). The crystallographic analyses confirmed that the two metal fragments are connected by three chloro bridges. The planes defined by the π -ligands and the plane defined by the three bridging chloro ligands are nearly parallel to each other. For complex **7**, the distances of the chloro atoms to the Ru atom attached to the cymene π -ligand ($\text{Ru}-\text{Cl} = 2.42\text{--}2.45\text{ \AA}$) are shorter than those to the Ru atom attached to the Cp^* ligand ($\text{Ru}-\text{Cl} = 2.50\text{--}2.56\text{ \AA}$). A likely explanation for this difference is the increased Lewis acidity of the (cymene)- Ru^{2+} fragment compared to the Cp^*Ru^+ fragment. The two Ru atoms in **7** are $3.344(8)\text{ \AA}$ apart from each other. This is longer than what is found for the cationic dimer $[(\text{cymene})\text{-Ru}(\mu\text{-Cl})_3\text{Ru}(\text{cymene})]^+ [\text{Ru}\cdots\text{Ru} = 3.283(3)\text{ \AA}]$.^[17]

In the highly symmetrical dimer **9**, a Cp^*Ru^+ fragment is connected by three chloro bridges to a $\text{Cp}^*\text{Ir}^{2+}$ fragment. As was observed for **7**, the $\text{M}-\text{Cl}$ bond lengths are shorter for the more Lewis-acidic metal fragment: the $\text{Ir}-\text{Cl}$ distances range from 2.41 to $2.45\text{ \AA}$, whereas the $\text{Ru}-\text{Cl}$ distances range from 2.50 to $2.52\text{ \AA}$. Complex **9** is isoelectronic with the mixed-valence $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$ complex $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{-RuCp}^*]$ described by Koelle et al.,^[16a,19] although due to the lack of structural data for the latter a direct comparison was not possible.

The prevalence of polynuclear ruthenium complexes with the $\text{Ru}(\mu\text{-Cl})_3\text{M}$ structural motif suggests that the connection by three chloro bridges is thermodynamically very stable. In fact, it has been shown that some catalysts can be

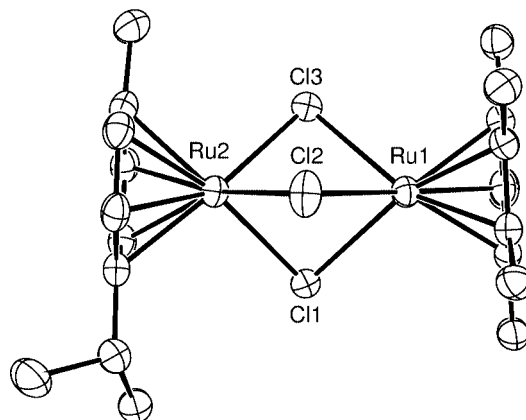


Figure 1. ORTEP^[18] drawing of the molecular structure of **7** in the crystal. The hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: $\text{Ru1}-\text{Cl1}$ $2.5591(13)$, $\text{Ru1}-\text{Cl2}$ $2.5024(14)$, $\text{Ru1}-\text{Cl3}$ $2.5075(14)$, $\text{Ru2}-\text{Cl1}$ $2.4521(13)$, $\text{Ru2}-\text{Cl2}$ $2.4222(13)$, $\text{Ru2}-\text{Cl3}$ $2.4205(13)$; $\text{Ru1}-\text{Cl1}-\text{Ru2}$ $83.70(4)$, $\text{Ru1}-\text{Cl2}-\text{Ru2}$ $85.53(4)$, $\text{Ru1}-\text{Cl3}-\text{Ru2}$ $85.45(4)$, $\text{Cl1}-\text{Ru1}-\text{Cl2}$ $76.70(4)$, $\text{Cl1}-\text{Ru2}-\text{Cl2}$ $80.23(5)$.

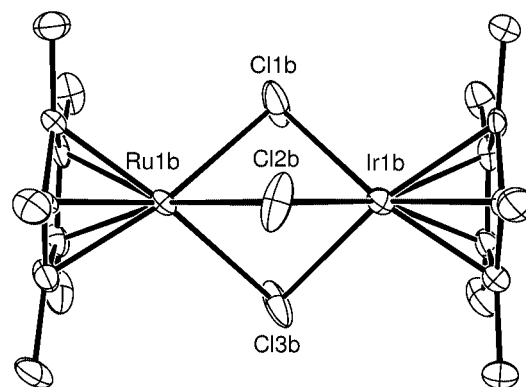


Figure 2. ORTEP^[18] drawing of the molecular structure of **9** in the crystal. Only one of the two crystallographically independent molecules is shown. The hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: $\text{Ru1b}-\text{Cl1b}$ $2.516(3)$, $\text{Ru1b}-\text{Cl2b}$ $2.509(3)$, $\text{Ru1b}-\text{Cl3b}$ $2.523(3)$, $\text{Ir1b}-\text{Cl1b}$ $2.413(3)$, $\text{Ir1b}-\text{Cl2b}$ $2.410(3)$, $\text{Ir1b}-\text{Cl3b}$ $2.428(3)$; $\text{Ru1b}-\text{Cl1b}-\text{Ir1b}$ $85.32(8)$, $\text{Ru1b}-\text{Cl2b}-\text{Ir1b}$ $85.54(8)$, $\text{Ru1b}-\text{Cl3b}-\text{Ir1b}$ $84.86(8)$, $\text{Cl1b}-\text{Ru1b}-\text{Cl2b}$ $77.90(10)$, $\text{Cl1b}-\text{Ir1b}-\text{Cl2b}$ $81.85(11)$.

deactivated by the formation of face-bridged dimers.^[20] In order to investigate the kinetic stability of the bimetallic complexes described above, crossover experiments were performed. Thus, a solution of complex **2** was mixed with a solution of complex **10** (both in CD_2Cl_2) and a ^1H NMR spectrum was recorded immediately after mixing. Apart from signals of the complexes **2** and **10**, the signals of two other complexes were observed (Figure 3). These were identified as the mixed complexes **8** and **11** by comparison with the ^1H NMR spectra of authentic samples (Scheme 2). The time-invariant integrals of the respective signals showed a nearly equimolar distribution of the four species. This suggests that a dynamic equilibrium between the four complexes is rapidly established after the mixing process.

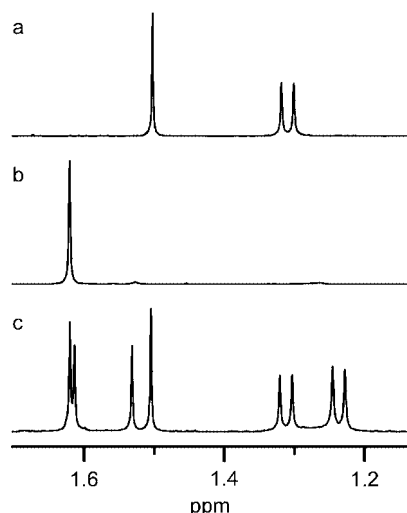
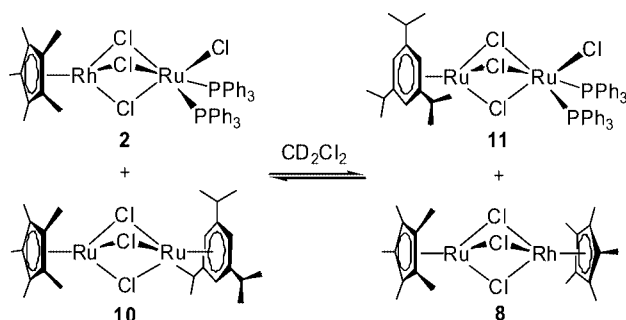


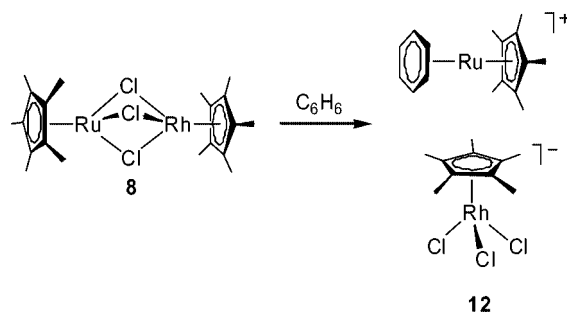
Figure 3. Part of the ^1H NMR spectrum of a) complex **10**, b) complex **2**, and c) an equimolar mixture of complex **2** and **10**, for which the additional signals of the complexes **8** and **11** are visible.



Scheme 2. In solution (CD_2Cl_2), complexes **2** and **10** are in a dynamic equilibrium with complexes **8** and **11**.

The results described above are in agreement with a report by Stephenson et al. in which they show that upon mixing of $[(\text{C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{C}_6\text{H}_6)]^+$ and $[(\text{C}_6\text{H}_6)\text{Os}(\mu\text{-Cl})_3\text{Os}(\text{C}_6\text{H}_6)]^+$, the heterobimetallic complex $[(\text{C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})_3\text{Os}(\text{C}_6\text{H}_6)]^+$ is obtained in equilibrium with the two homobimetallic starting materials.^[21] We have previously shown that the triply bridged complex $[(\text{dcypb})(\text{N}_2)\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{dcypb})]$ reacts rapidly with doubly bridged complexes of the general formula $[\text{LMCl}_2]_2$ [$\text{LM} = (\text{cymene})\text{-Ru}, \text{Cp}^*\text{Rh}, \text{Cp}^*\text{Ir}$] to give the mixed complexes $[(\text{dcypb})\text{-ClRu}(\mu\text{-Cl})_3\text{ML}]$.^[9b] Taken together, these results point to the fact that $[\text{L}_n\text{Ru}(\mu\text{-Cl})_3\text{ML}'_n]$ complexes are generally very labile, despite their apparent thermodynamic stability.

Complexes **6–10** are soluble in a variety of organic solvents such as acetone, THF, CH_2Cl_2 , and Et_2O . The very lipophilic **10** can even be dissolved in pentane. Aromatic solvents, on the other hand, are not suited because of the very high tendency of the Cp^*Ru^+ fragment to form sandwich complexes of the general formula $[\text{Cp}^*\text{Ru}(\text{arene})]\text{-X}$.^[14–16,22] When complex **8** was dissolved in benzene, crystals of the ionic complex $[\text{Cp}^*\text{Ru}(\text{C}_6\text{H}_6)][\text{Cp}^*\text{RhCl}_3]$ (**12**) formed after a few hours (Scheme 3). Larger amounts of **12** could be obtained by slow diffusion of hexane into a solution of **8** in benzene.



Scheme 3. The ionic complex **12** is obtained by reaction of complex **8** with benzene.

The structure of complex **12** was analyzed by single-crystal X-ray analysis (Figure 4). The bond lengths found for the cation $[\text{Cp}^*\text{Ru}(\text{C}_6\text{H}_6)]^+$ ($\text{Ru-C}_{\text{benzene}} = 2.21\text{--}2.22 \text{ \AA}$; $\text{Ru-Cp}^* = 2.18\text{--}2.19 \text{ \AA}$) are very similar to those reported for related $[\text{Cp}^*\text{Ru}(\text{arene})]^+$ complexes.^[22a,22d,23] The corresponding anion $[\text{Cp}^*\text{RhCl}_3]^-$ displays a typical “piano-stool” geometry, with Rh-Cl bond lengths of $2.4114(14)$ and $2.420(2) \text{ \AA}$, respectively. The formation of this anion is rather unusual^[24] given the thermodynamic stability of the $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RhCp}^*]^+$ cation,^[11,25] and underlines the fact that the generation of $[\text{Cp}^*\text{Ru}(\text{C}_6\text{H}_6)]^+$ is the driving force for the reaction.

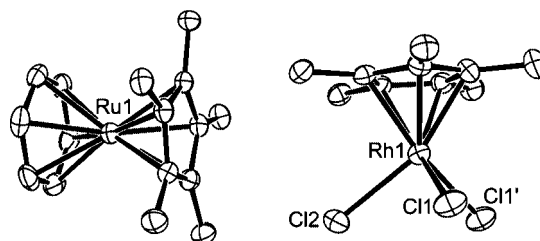


Figure 4. ORTEP^[18] drawing of the molecular structure of **12** in the crystal. The hydrogen atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Rh1-Cl1 $2.4114(14)$, Rh1-Cl2 $2.420(2)$; Cl1-Rh1-Cl2 $90.97(5)$, Cl1-Rh1-Cl1' $91.15(7)$. $^{\circ}$: $x, 1/2 - y, z$.

Conclusions

Bimetallic complexes, in which two different metal fragments are connected by either two or three halogeno bridges, have recently emerged as a promising new class of catalysts.^[1–3] New synthetic routes to generate such complexes are thus highly warranted. In this report, we have described the homo- and heterobimetallic complexes $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{ML}]$ [$\text{LM} = (\text{C}_6\text{H}_6)\text{Ru}, (\text{cymene})\text{Ru}, (1,3,5\text{-C}_6\text{H}_3\text{Pr}_3)\text{Ru}, \text{Cp}^*\text{Rh}, \text{Cp}^*\text{Ir}$]. They can be prepared in excellent yield by reaction of $[\text{Cp}^*\text{Ru}(\mu\text{-OMe})_2]$ with Me_3SiCl and subsequent addition of $[\text{LMCl}_2]_2$. Crossover experiments have demonstrated that these complexes undergo fast scrambling reactions with other triply bridged complexes. The dimers are thus kinetically very labile, a fact which is of importance for possible catalytic applications. In a reaction with benzene, the chloro bridge of the complex $[\text{Cp}^*\text{Ru}(\mu\text{-Cl})_3\text{RhCp}^*]$ is cleaved in a completely asymmet-

ric fashion to give the cation $[\text{Cp}^*\text{Ru}(\text{C}_6\text{H}_6)]^+$ and the anion $[\text{Cp}^*\text{RhCl}_3]^-$. This type of reactivity is unusual for $[\text{L}_n\text{Ru}(\mu\text{-Cl})_3\text{ML}'_n]$ complexes but can be explained by the high intrinsic affinity of the Cp^*Ru^+ fragment for aromatic compounds.

Experimental Section

General: All reactions were performed under an atmosphere of dry dinitrogen. The solvents and Me_3SiCl were distilled from appropriate drying agents and stored under dinitrogen. The complexes $[\text{Cp}^*\text{Ru}(\text{OMe})_2]_2$,^[26] $[(\text{cymene})\text{RuCl}_2]_2$,^[27] $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$,^[28] $[\text{Cp}^*\text{RhCl}_2]_2$,^[29] $[\text{Cp}^*\text{IrCl}_2]_2$,^[29] $[(1,3,5\text{-C}_6\text{H}_3\text{Pr}_3)\text{RuCl}_2]_2$,^[30] and $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_3\text{RuCl}(\text{PPh}_3)_2]$ (**2**)^[2b] were prepared according to literature procedures. An authentic sample of complex **11** was synthesized by mixing equimolar amounts of $[(\text{PPh}_3)_2\text{ClRu}(\mu\text{-Cl})_3\text{Ru}(\text{acetone})(\text{PPh}_3)_2]$ and $[(1,3,5\text{-C}_6\text{H}_3\text{Pr}_3)\text{RuCl}_2]_2$ in CH_2Cl_2 .^[9b] The ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer with the residual protonated solvent as internal standards. All spectra were recorded at room temperature.

General Method for the Synthesis of Complexes 6–9: Me_3SiCl (71 μL , 561 μmol) was added to a solution of $[\text{Cp}^*\text{Ru}(\text{OMe})_2]_2$ (100 mg, 187 μmol) in CH_2Cl_2 (10 mL). After addition of the respective dimer $[(\pi\text{-ligand})\text{MCl}_2]_2$ (156 μmol), the solution was stirred for 20 min. The solvent was then removed in vacuo and the resulting powder was suspended in pentane (10 mL) in order to dissolve the excess of complex $[\text{Cp}^*\text{RuCl}]_4$. The product was isolated by filtration, washed with additional pentane (3×2 mL) and dried under vacuum (yield: 88–96%).

Complex 6: Red powder. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.50 (Cp*), 5.60 (benzene) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 10.4 (CH_3 , Cp*), 70.9 (C, Cp*), 80.5 (benzene) ppm.

$\text{C}_{16}\text{H}_{21}\text{Cl}_3\text{Ru}_2 \cdot 1/6\text{C}_5\text{H}_{12}$ (533.9): calcd. C 37.87, H 4.34; found C 37.96, H 4.51.

Complex 7: Red powder. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a solution of **7** in dichloromethane. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.29 [d, 3J = 7.1 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.51 (s, 15 H, CH_3 , Cp*), 2.18 (s, 3 H, CH_3 , cymene), 2.82 [sept, 3J = 7.1 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 5.21 (d, 3J = 6.0 Hz, 4 H, CH), 5.43 (d, 3J = 6.0 Hz, 4 H, CH) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 10.4 (CH_3 , Cp*), 19.0, 22.4 (CH_3 , cymene), 31.6 [$\text{CH}(\text{CH}_3)_2$], 70.6 (C, Cp*), 77.8, 78.9 (CH, cymene), 95.3, 100.3 (C, cymene) ppm. $\text{C}_{20}\text{H}_{29}\text{Cl}_3\text{Ru}_2$ (577.9): calcd. C 41.56, H 5.06; found C 41.56, H 5.23.

Complex 8: Red powder. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.52 (Cp*Ru), 1.61 (Cp*Rh) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 9.5, 10.5 (CH_3 , Cp*), 70.0 (C, Cp*Ru), 93.6 (d, $^1J_{\text{C,Rh}}$ = 10.1 Hz, C, Cp*Rh) ppm. $\text{C}_{20}\text{H}_{30}\text{Cl}_3\text{RhRu}$ (580.0): calcd. C 41.36, H 5.21; found C 41.51, H 5.26.

Complex 9: Orange powder. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a solution of **9** in a mixture of dichloromethane and hexane (1:9). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.57 (Cp*), 1.58 (Cp*) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 9.5, 10.5 (CH_3), 70.3, 85.2 (C) ppm. $\text{C}_{20}\text{H}_{30}\text{Cl}_3\text{IrRu}$ (670.1): calcd. C 35.85, H 4.51; found C 35.99, H 4.57.

Synthesis of Complex 10: Me_3SiCl (30 μL , 240 μmol) was added to a solution of $[\text{Cp}^*\text{Ru}(\text{OMe})_2]_2$ (43 mg, 80 μmol) in CH_2Cl_2 (5 mL). After addition of $[(\text{C}_6\text{H}_3\text{Pr}_3)\text{RuCl}_2]_2$ (72 mg, 96 μmol), the solution was stirred for 20 min. The solvent was then removed in vacuo and the product was extracted with pentane (2×5 mL). The product was isolated by evaporation of the pentane and drying under vacuum. Yield: 94 mg (92%). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.31 [d, 3J = 7.1 Hz, 18 H, $\text{CH}(\text{CH}_3)_2$], 1.50 (s, 15 H, CH_3 , Cp*), 2.90 [sept, 3J = 7.1 Hz, 3 H, $\text{CH}(\text{CH}_3)_2$], 5.09 (s, 3 H, CH) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 10.5 (CH_3 , Cp*), 22.5 [$\text{CH}(\text{CH}_3)_2$],

Table 1. Crystallographic data for complexes **7**, **9**, and **12**.

	7	9	12
Empirical formula	$\text{C}_{20}\text{H}_{29}\text{Cl}_3\text{Ru}_2$	$\text{C}_{20}\text{H}_{30}\text{Cl}_3\text{IrRu}$	$\text{C}_{26}\text{H}_{36}\text{Cl}_3\text{RhRu}$
Molecular weight [g mol^{-1}]	577.92	670.06	658.88
Crystal size	$0.17 \times 0.12 \times 0.10$	$0.30 \times 0.28 \times 0.11$	$0.19 \times 0.12 \times 0.11$
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$I2/a$	$Pnma$
a [$\text{\AA}$]	11.3160(6)	27.9257(14)	19.069(3)
b [$\text{\AA}$]	17.108(3)	10.6205(3)	12.2265(7)
c [$\text{\AA}$]	11.617(2)	30.1330(14)	11.346(3)
α [$^\circ$]	90	90	90
β [$^\circ$]	100.473(10)	91.031(4)	90
γ [$^\circ$]	90	90	90
Volume [$\text{\AA}^3$]	2211.4(6)	8935.6(7)	2645.2(7)
Z	4	16	4
Density [g cm^{-3}]	1.736	1.992	1.654
Temperature [K]	140(2)	140(2)	140(2)
Absorption coefficient [mm^{-1}]	1.730	6.987	1.510
θ range [$^\circ$]	3.00 to 25.02	3.19 to 25.03	3.25 to 25.03
Index ranges	$-12 \rightarrow 12, -20 \rightarrow 20, -13 \rightarrow 13$	$-33 \rightarrow 33, -11 \rightarrow 11, -35 \rightarrow 35$	$-22 \rightarrow 22, -13 \rightarrow 13, -13 \rightarrow 13$
Reflections collected	13083	24673	16451
Independent reflections	3714 ($R_{\text{int}} = 0.0362$)	7445 ($R_{\text{int}} = 0.0333$)	2352 ($R_{\text{int}} = 0.0444$)
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Max. and min. transmission	0.8179 and 0.6935	0.4376 and 0.2545	0.8633 and 0.7484
Data / restraints / parameters	3714 / 0 / 226	7445 / 0 / 451	2352 / 0 / 152
Goodness-of-fit on F^2	1.114	1.061	1.151
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0365, wR_2 = 0.0880$	$R_1 = 0.0422, wR_2 = 0.0965$	$R_1 = 0.0410, wR_2 = 0.0853$
R indices (all data)	$R_1 = 0.0470, wR_2 = 0.0955$	$R_1 = 0.0522, wR_2 = 0.1001$	$R_1 = 0.0501, wR_2 = 0.0896$
Largest diff. peak/hole [$\text{e \AA}^{-3}$]	0.739 and -0.646	1.778 and -1.723	0.941 and -0.745

32.0 [CH(CH₃)₂], 70.3 (CH), 70.4 (C, Cp*), 106 (C, C₆H₃iPr₃) ppm. C₂₅H₃₉Cl₃Ru₂ (648.1): calcd. C 46.33, H 6.07; found C 46.30, H 6.13.

Exchange Reactions: Complex **10** (5.5 mg, 8.6 μmol) was dissolved in CD₂Cl₂ (500 μL) and a ¹H NMR spectrum of the solution was recorded (400 MHz). A sample of complex **2** (8.7 mg, 8.6 μmol) was analyzed in the same fashion. The two solutions were subsequently mixed and immediately analyzed by ¹H NMR spectroscopy (400 MHz).

Synthesis of Complex 12: Complex **8** (15.0 mg, 25.8 μmol) was dissolved in benzene (2 mL). The resulting mixture was allowed to react for 2 h, after which small crystals of complex **12** could already be observed. Slow addition of hexane (5 mL) by diffusion over 12 h resulted in the formation of crystalline **12**, which was isolated by filtration. Isolated yield: 12.5 mg (73%). The reaction was quantitative, as evidenced by ¹H NMR analysis of the remaining solution. ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.57, 2.07 (Cp*), 6.05 (benzene) ppm. ¹³C NMR (101 MHz, CD₂Cl₂): δ = 9.4, 11.3 (CH₃, Cp*), 87.7 (benzene), 94.4 (d, ¹J_{C-Rh} = 14 Hz, C, Cp*Rh), 97.1 (C, Cp*Ru) ppm. C₂₆H₃₆Cl₃RhRu (658.9): calcd. C 47.39, H 5.51; found C 47.55, H 5.12.

X-ray Crystallography: Details of the crystals and their structure refinement are listed in Table 1; relevant geometrical parameters are given in the respective figure captions. Data collection was performed at 140(2) K on a four-circle goniometer having kappa geometry and equipped with an Oxford Diffraction KM4 Sapphire CCD (**9**) or a mar345 imaging plate detector (**7** and **12**). Data reduction was carried out with CrysAlis RED, release 1.7.0.^[31] An absorption correction was applied to all data sets. Structure solution and refinement were performed with the SHELXTL software package, release 5.1.^[32] The structures were refined using the full-matrix least-squares on *F*² with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the “riding model”.

CCDC-279177 to -279179 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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