

Heterometallic bromo-bridged complexes with a $\text{Re}(\text{CO})_3$ fragment

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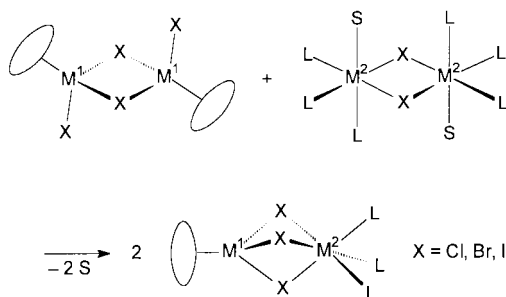
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Heterobimetallic complexes in which half-sandwich complexes of ruthenium(II), rhodium(III) and iridium(III) are connected by three bromo-bridges to $\text{Re}(\text{CO})_3$ have been prepared from metathesis reactions of $[\text{RuBr}(\mu\text{-Br})\text{-}(\text{arene})]_2$ (arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Et}_3$ -1,3,5 or *p*-cymene) or $[\text{MBr}(\mu\text{-Br})\text{Cp}^*]_2$ ($\text{M} = \text{Rh}$ or Ir) with $[\text{Re}(\mu\text{-Br})(\text{CO})_3\text{-}(\text{C}_4\text{H}_8\text{O})]_2$. The crystal structures of $[(\text{arene})\text{Ru}(\mu\text{-Br})_3\text{Re}(\text{CO})_3]$ (arene = C_6H_6 or $\text{C}_6\text{H}_3\text{Et}_3$ -1,3,5) and $[\text{Cp}^*\text{M}(\mu\text{-Br})_3\text{-}\text{Re}(\text{CO})_3]$ ($\text{M} = \text{Rh}$ or Ir) have been determined by X-ray analysis. In solution all complexes were shown to be in a dynamic equilibrium with isomeric ionic compounds of the general formula $[\text{M}_2(\mu\text{-Br})_3(\pi\text{-ligand})_2][\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]$ ($\text{M} = \text{Ru}$, Rh or Ir). The solid state structures of $[\text{Ru}_2(\mu\text{-Br})_3(\text{C}_6\text{H}_3\text{Et}_3\text{-}1,3,5)_2][\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]$ and $[\text{Ru}_2(\mu\text{-Br})_3\text{-}(p\text{-MeC}_6\text{H}_4\text{Pr}^t)][\text{Re}_2(\mu\text{-Br})_3(\text{CO})_6]$ are described.

Introduction

In previous publications we have shown that metathesis reactions of symmetrical halogeno-bridged complexes can be used to synthesize asymmetric complexes in which different metal centres are connected by two halogeno-bridges.¹ Compounds of this kind are of special interest as catalyst precursors. Chloro-bridged complexes, for example, in which cyclopentadienyl rhodium fragments are bound to ruthenium carbene complexes are among the most active catalysts for olefin metathesis known to date.²

Recently, we have expanded our investigations to asymmetric complexes with *three* halogeno-bridges. Although homodimeric complexes with three halogeno-bridges are often found for complexes of the late transition metals, heterobimetallic complexes of this kind are very rare.³ We have described the synthesis of homo- and hetero-dinuclear $(\mu\text{-Cl})_3$ complexes with RuCl_2L_2 fragments ($\text{L} = \text{PR}_3$ or alkene), some of which are remarkably active catalysts for the Oppenauer-type oxidation of secondary alcohols.⁴ Based on these results we suggest that asymmetric complexes with three halogeno-bridges can generally be obtained in metathesis reactions given that one partner has an additional halogeno ligand and the other a potentially free co-ordination site (Scheme 1). In this

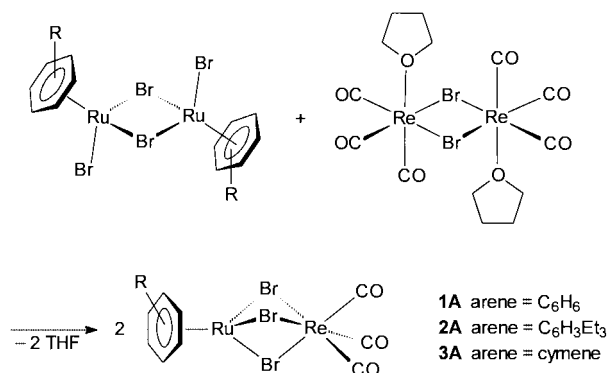


Scheme 1 General method to synthesize heterometallic complexes with three halogeno-bridges: "S" represents a free co-ordination site or a labile ligand, the circle a π ligand such as η^6 -arene or η^5 -cyclopentadiene.

paper we show that this reaction scheme is well suited for the generation of heteronuclear complexes with $\text{Re}(\text{CO})_3$ fragments.

Results and discussion

$[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})]_2$ is a useful starting material for the synthesis of various $\text{Re}(\text{CO})_3$ complexes under mild conditions.⁵ The THF ligand as well as the bromo-bridge are known to be labile. We therefore anticipated that $[\text{Re}(\mu\text{-Br})(\text{CO})_3\text{-}(\text{C}_4\text{H}_8\text{O})]_2$ should be an ideal candidate for the synthesis of heterobimetallic complexes⁶ according to Scheme 1. In a first experiment we have treated $[\text{RuBr}(\mu\text{-Br})(\text{C}_6\text{H}_6)]_2$ with $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})]_2$ in dichloromethane (Scheme 2). After



Scheme 2 Synthesis of the $\text{Ru}^{\text{II}}\text{-Re}^{\text{I}}$ complexes **1A–3A**.

2 h the (arene)Ru complex had dissolved indicating that a reaction had occurred.⁷ After work-up and crystallisation from THF red crystals of complex **1A** were obtained. The crystals are stable in air and display moderate to low solubility in organic solvents. The infrared spectrum of **1A** shows a strong band at 2032 cm^{-1} and a strong, broad band at 1906 cm^{-1} indicating the presence of a *fac*- $\text{Re}(\text{CO})_3$ fragment. The expected bimetallic structure with three bromo-bridges was confirmed by the result of a single crystal analysis (Fig. 1).⁸

The molecule contains a crystallographic mirror plane defined by Ru1, Br1 and Re1. The geometry around the rhenium atom can be described as distorted octahedral with C–Re–C angles close to the ideal 90° and Br–Re–Br angles of 80.2° . The Re–Br bond lengths (2.63 and 2.62 \AA) are slightly larger than the Ru–Br bond lengths (2.58 and 2.56 \AA). Similar Ru–Br bond distances were found for the symmetrical bromo-bridged complex $[\text{Ru}_2(\mu\text{-Br})_3(\text{AsMe}_3)_6][\text{CF}_3\text{SO}_3]$.⁹ The two

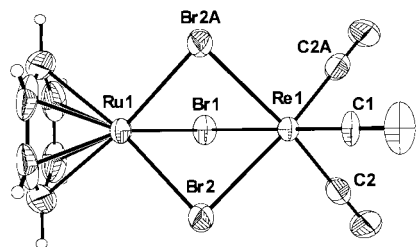


Fig. 1 Molecular structure of complex **1A** in the crystal. The solvent molecule is omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–Br1 2.576(2), Re1–Br1 2.630(2) and Re1–C1 1.840(14); Ru1–Br1–Re1 82.18(5), C1–Re1–Br1 172.7(4), C1–Re1–C2 89.6(4), Br1–Re1–Br2 80.21(4) and Br1–Ru1–Br2 82.46(5).

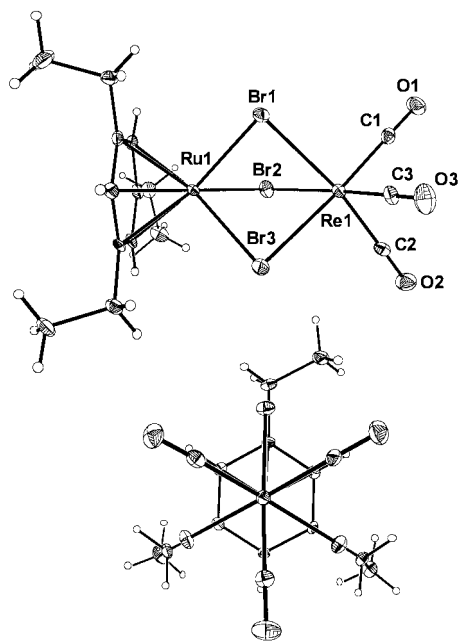


Fig. 2 Top: molecular structure of complex **2A** in the crystal. Selected bond lengths [Å] and angles [°]: Ru1–Br1 2.565(1), Re1–Br1 2.626(1) and Re1–C1 1.917(7); Ru1–Br1–Re1 82.50(2), C1–Re1–Br3 176.0(2), C1–Re1–C2 89.7(3), Br1–Re1–Br2 79.51(3) and Br1–Ru1–Br2 81.82(3). Bottom: view along the Re–Ru axis highlighting the pseudo- C_3 symmetry.

metal atoms are 3.42 Å apart from each other making metal–metal interactions unlikely.

In an analogous fashion the Ru^{II}–Re^I complexes **2** and **3** were synthesized (Scheme 2). Upon crystallisation of **2** two sorts of crystals with different shapes were obtained which could be separated manually. The elemental analyses for the two kinds were very similar and consistent with the formula [ReRu(Br)₃(C₆H₅Et₃-1,3,5)(CO)₃]. Nevertheless the infrared spectra and the melting points were different. Fortunately we were able to determine the solid state structure in both cases by X-ray diffraction.

Remarkably, complex **2** crystallises in two significantly different structures **2A** and **2B**. That of **2A** shows the expected geometry: the (arene)Ru fragment is co-ordinated *via* three bromo-bridges to the Re(CO)₃ fragment (Fig. 2). The bond lengths and angles of **2A** are very similar to what was observed for **1A**. The ethyl groups of the arene ligand adopt a staggered conformation with respect to the carbonyl ligands. Overall, the complex shows a local pseudo C_3 symmetry. The solid state structure of **2B**, on the other hand, is comprised of the dimeric cation [Ru₂(μ-Br)₃(C₆H₅Et₃-1,3,5)₂]⁺ (Fig. 3) and the dimeric anion [Re₂(μ-Br)₃(CO)₆][−] (Fig. 4). Chloro-bridged ruthenium complexes of the general formula [Ru₂(μ-Cl)₃(arene)₂]⁺ have been previously described.¹⁰ The Ru atoms in **2B** are 3.40 Å apart from each other. As expected this distance is longer than

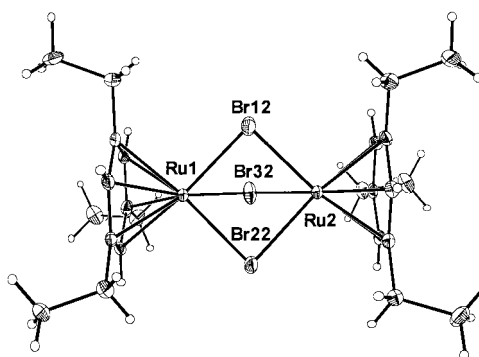


Fig. 3 Molecular structure of the cation of complex **2B** in the crystal. Selected bond lengths [Å] and angles [°]: Ru1–Br12 2.552(1), Ru2–Br12 2.554(1), Ru1–Br22 2.567(1) and Ru2–Br22 2.569(1); Ru1–Br12–Ru2 83.40(2), Ru1–Br22–Ru2 82.83(2) and Br12–Ru1–Br22 80.61(2).

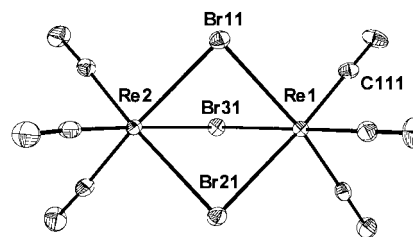


Fig. 4 Molecular structure of the anion of complex **2B** in the crystal. Selected bond lengths [Å] and angles [°]: Re1–C111 1.892(6) and Re1–Br11 2.645(1); C111–Re1–C211 90.4(3), C111–Re1–Br11 95.5(2), Re1–Br11–Re2 81.58(2) and C111–Re1–Br21 175.1(2).

what was found for the related chloro complexes (3.28–3.29 Å).¹⁰ A Ru–Ru bond as was proposed for the mixed-valence complexes [Ru(μ-Br)₃Br₂L₄] (L = PMe₂Ph or AsMe₂Ph)¹¹ can be excluded. Ionic compounds with the anion [Re₂(μ-Br)₃(CO)₆][−] in combination with other complex cations such as [Re(μ-Br)Cp*₂(CO)₄]⁺,¹² [Re(C₆H₅CH₃)(CO)₃]⁺¹³ and [ReBrCp*(CO)₃]⁺¹⁴ have structurally been characterised. In all cases the geometry can be described as two face-sharing octahedra with three bridging bromo ligands.

If crystals of complex **2B** are dissolved in CDCl₃ the ¹H NMR spectrum shows two sets of signals the relative ratio of which is 2 : 1. This result suggests that in solution the two isomers **2A** and **2B** form a dynamic equilibrium. Further evidence for the existence of such an equilibrium was obtained by MS experiments (desorption electron impact mode, DEI). If the ionic compound **2B** is dissolved in dichloromethane a peak for the neutral heterobimetallic species **2A** at *m/z* = 774 is observed. A similar spectrum is obtained from complex **2A**.

For complex **3** only one type of crystal was obtained. The structure in the solid state was shown to be the isomeric form **B** by X-ray diffraction. This is consistent with the infrared spectrum which displays bands at 2021 and 1906 cm^{−1}, similar to what was observed for **2B**. For the neutral complexes **1A** and **2A** bands at higher wavenumbers ($\nu_{A_1}(\text{CO})$ 2032 and 2031 cm^{−1}) were recorded as is expected because of reduced back donation. The structural parameters found for the cation of **3B** resemble those of complex **2B** (Fig. 5). The two isopropyl groups adopt approximately a *trans* configuration.

Contrary to what was observed for complex **2**, crystals of **3B** dissolved in CDCl₃ show only one set of signals in the ¹H NMR spectrum. Upon addition of a few drops of CD₃OD, however, a second set of signals can be noticed. We assume that in chloroform the neutral isomer **3A** is the dominant species, whereas in a more polar solvent mixture like CDCl₃–CD₃OD the ionic form **3B** is also present. This was confirmed by MS experiments. In chloroform the isomer **A** can be detected (DEI mode), in *p*-nitrobenzyl alcohol the ions of isomer **B** (+FAB and −FAB mode). Similar results were obtained in MS experi-

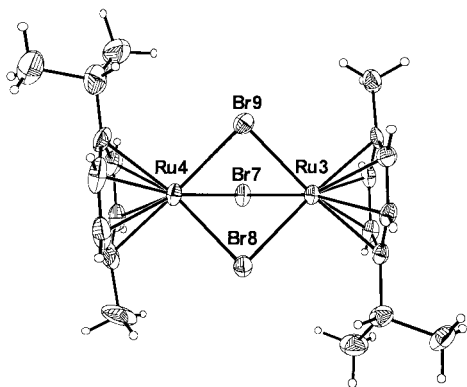


Fig. 5 Molecular structure of the cation of complex **3B** in the crystal. Selected bond lengths [Å] and angles [°]: Ru4–Br7 2.50(1), Ru4–Br8 2.570(2), Ru3–Br7 2.543(1) and Ru3–Br8 2.576(1); Br7–Ru3–Br8 81.08(4) and Ru4–Br8–Ru3 82.55(4).

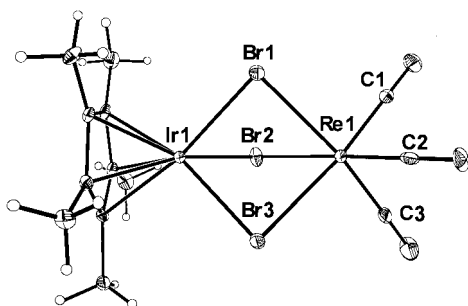
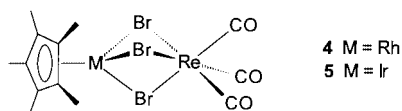


Fig. 6 Molecular structure of complex **5** in the crystal. Selected bond lengths [Å] and angles [°]: Ir1–Br1 2.573(1), Re1–Br1 2.648(1) and Re1–C1 1.894(7); Br1–Ir1–Br2 82.80(3), Br1–Re1–C3 172.3(3), C1–Re1–Br1 95.6(2), Br2–Re1–Br1 79.78(2) and Ir1–Br1–Re1 82.33(2).

ments with **1A** indicating that the ionic isomer **1B** can also be stabilised in polar solvents.

We were interested whether bromo-bridged complexes of other metals are also suited to undergo a metathesis reaction with $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$. Therefore we have investigated the reaction of $[\text{MBr}(\mu\text{-Br})\text{Cp}^*]_2$ ($\text{M} = \text{Rh}$ or Ir) with equimolar amounts of the rhenium complex in dichloromethane. In both cases crystals of the complexes **4** and **5** can be obtained in



good yields simply by adding benzene and slow evaporation of the solvent mixture in air.

The structure of complex **5** was determined by single crystal X-ray diffraction. As for **1A** and **2A** a neutral heterobimetallic complex with three bromo-bridges is observed (Fig. 6). The geometry around the rhenium atom is similar to what was observed for **1A** and **2A**. The bond length of the iridium atom to the bridging bromide atom (2.57 Å) is the same as in $[\text{IrBr}(\mu\text{-Br})\text{Cp}^*]_2$.¹⁵ The crystal structures of the complexes **4** and **5** are isotypical showing nearly identical bond lengths and angles. Their ¹H NMR spectra (CDCl_3) reveal the presence of two different isomers the relative ratio of which is 10:4 (**4**) and 10:3 (**5**). In view of the fact that cationic complexes of the formula $[\text{Cp}^*\text{M}(\mu\text{-Br})_3\text{MCp}^*]^+$ ($\text{M} = \text{Rh}$ or Ir) are known¹⁶ we assume that in solution an equilibrium between neutral and ionic isomers as observed for **1–3** exists.

Conclusion

We have shown that bromo-bridged (arene) Ru^{II} , CpRh^{III} and $\text{Cp}^*\text{Ir}^{\text{III}}$ complexes undergo metathesis reactions with $[\text{Re}$

$(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$ to give heterobimetallic complexes. In solution a dynamic equilibrium with isomeric ionic complexes is observed. Apparently the two isomers are energetically very similar which is reflected by the fact that for complex **2** crystals of both isomers have been isolated. In accordance with our previous study the results described above confirm that metathesis reactions are well suited to synthesize heterobimetallic complexes with three bridging halogeno ligands. The reaction outlined in Scheme 1 appears to be rather general and we therefore expect that new, presently unknown complexes can be prepared in a similar manner. We are currently investigating the scope and the limitations of this synthetic methodology as well as applications of asymmetric halogeno-bridged complexes in homogeneous catalysis.

Experimental

General remarks

The complexes $[\text{RuCl}(\mu\text{-Cl})(p\text{-MeC}_6\text{H}_4\text{Pr}^i)]_2$,¹⁷ $[\text{RuCl}(\mu\text{-Cl})(\text{C}_6\text{H}_3\text{Et}_3\text{-1,3,5})]_2$ ¹⁸ and $[\text{MCl}(\mu\text{-Cl})\text{Cp}^*]_2$ ($\text{M} = \text{Rh}$ or Ir)¹⁹ were prepared according to published procedures and converted into the bromo complexes by treatment with KBr in water– CHCl_3 . Literature procedures were used to prepare $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$ ²⁰ and $[\text{RuBr}(\mu\text{-Br})(\text{C}_6\text{H}_6)]_2$.²¹ The NMR spectra were recorded on a JEOL EX 400 or a GSX 270 spectrometer with the solvent as the internal standard. If two isomers were detected the signals of the dominant species were labelled with “A”. The molecular weights were determined with a JEOL MStation JMS 700 mass spectrometer.

Preparations

Complex 1. $[\text{RuBr}(\mu\text{-Br})(\text{C}_6\text{H}_6)]_2$ (34 mg, 50 μmol) and $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$ (42 mg, 50 μmol) in CH_2Cl_2 (10 ml) were stirred for 12 h. After removal of the solvent under reduced pressure the product was dissolved in THF and crystallised by slow mixing (vapour diffusion) with pentane. Red crystals. Yield: 50 mg (69%). mp > 250 °C. IR (KBr): 2032 (CO), 1906 (br) cm^{-1} (CO). ¹H NMR (400 MHz, CDCl_3): δ 5.83 (C_6H_6). MS (DEI): $m/z = 690$. Found: C 18.33, H 1.45. Calc. for $\text{C}_9\text{H}_6\text{Br}_3\text{-O}_3\text{ReRu-0.5THF}$: C 18.22, H 1.39%.

Complex 2. $[\text{RuBr}(\mu\text{-Br})(\text{C}_6\text{H}_3\text{Et}_3\text{-1,3,5})]_2$ (42 mg, 50 μmol) and $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$ (42 mg, 50 μmol) in CH_2Cl_2 (8 ml) were stirred for 1 h. The clear orange solution was layered with pentane. After one week orange crystals had formed. Yield: 52 mg (71%). mp > 250 (**2A**), 149–151 °C (**2B**). IR (KBr): (**2A**) 2031 (CO), 1928 (sh) (CO) and 1904 (CO); (**2B**) 2021 (CO), 1911 (sh) (CO) and 1898 cm^{-1} (CO). ¹H NMR (400 MHz, CDCl_3): δ 1.31 (t, ³ $J = 7$, CH_3 , A), 1.32 (t, ³ $J = 7$, CH_3 , B), 2.59 (q, ³ $J = 7$ Hz, CH_2 , A + B), 5.23 (s, CH, B) and 5.25 (s, CH, A). MS (DEI): $m/z = 774$. Found: C 23.69, H 2.34. Calc. for $\text{C}_{15}\text{H}_{18}\text{-Br}_3\text{O}_3\text{ReRu}$: C 23.30, H 2.35%.

Complex 3. The synthesis was performed analogously to that of complex **2** using $[\text{RuBr}(\mu\text{-Br})(p\text{-MeC}_6\text{H}_4\text{Pr}^i)]_2$. Orange crystals. Yield: 37 mg (50%). mp 125–127 °C. IR (KBr): 2021 (CO) and 1906 (br) cm^{-1} (CO). ¹H NMR (270 MHz, CDCl_3): δ 1.31 [d, ³ $J = 7$, 6 H, $\text{CH}(\text{CH}_3)_2$], 2.29 (s, 3 H, CH_3 , cymene), 2.82 [s, ³ $J = 7$, 1 H, $\text{CH}(\text{CH}_3)_2$], 5.44 (d, ³ $J = 5$, 2 H, CH) and 5.60 (d, ³ $J = 5$ Hz, 2 H, CH). ¹H NMR (300 MHz, CD_3OD): δ 1.29 [d, ³ $J = 7$, 6 H, $\text{CH}(\text{CH}_3)_2$], 2.22 (s, 3 H, CH_3 , cymene), 2.81 [s, ³ $J = 7$, 1 H, $\text{CH}(\text{CH}_3)_2$], 5.63 (d, ³ $J = 6$, 2 H, CH) and 5.85 (d, ³ $J = 6$ Hz, 2 H, CH). MS (DEI): $m/z = 746$. Found C 21.05, H 1.92. Calc. for $\text{C}_{13}\text{H}_{14}\text{Br}_3\text{O}_3\text{ReRu}$: C 20.95, H 1.89%.

Complex 4. $[\text{RhBr}(\mu\text{-Br})\text{Cp}^*]_2$ (40 mg, 50 μmol) and $[\text{Re}(\mu\text{-Br})(\text{CO})_3(\text{C}_4\text{H}_8\text{O})_2]$ (42 mg, 50 μmol) in CH_2Cl_2 (10 ml) were stirred at room temperature. After 1 h benzene (10 ml) was added and the stirring stopped. Red crystals formed upon slow

Table 1 Crystallographic data for complexes **1A**, **2A**, **2B**, **3B**, **4** and **5**

	1A	2A	2B	3B	4	5
Empirical formula	C ₂₁ H ₁₈ Br ₃ O ₃ - ReRu	C ₁₅ H ₁₈ Br ₃ O ₃ - ReRu	C ₃₀ H ₃₆ Br ₆ O ₆ - Re ₂ Ru ₂	C ₂₆ H ₂₈ Br ₆ O ₆ - Re ₂ Ru ₂	C ₁₃ H ₁₅ Br ₃ O ₃ - ReRh	C ₁₃ H ₁₅ Br ₃ IrO ₃ Re
Molecular weight	845.35	773.29	1546.58	1490.58	748.09	837.39
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>Pnma</i>	<i>P1</i>	<i>P2₁/n</i>	<i>P1</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	11.896(3)	8.9917(9)	15.3340(11)	9.6067(13)	9.6576(8)	9.7123(7)
<i>b</i> /Å	11.297(3)	10.5637(11)	15.1881(9)	12.8694(14)	14.8986(17)	14.9342(10)
<i>c</i> /Å	18.236(8)	10.9076(11)	17.0439(10)	16.152(4)	12.3079(10)	12.2606(10)
<i>a</i> °		111.142(11)		77.44(2)		
<i>β</i> °		91.800(12)	91.680(8)	78.986(15)	90.434(10)	90.574(10)
<i>γ</i> °		96.043(12)		71.207(11)		
<i>V</i> /Å ³	2450.6(14)	958.26(17)	3967.7(4)	1829.4(5)	1770.7(3)	1778.3(2)
<i>Z</i>	4	2	4	2	4	4
<i>T</i> /K	295(2)	200(3)	200(3)	295(2)	200(3)	200(3)
<i>μ</i> /mm ⁻¹	10.461	13.362	12.908	13.993	14.535	21.022
Reflections collected	4056	8528	36602	5940	16749	11649
Independent reflections	2019 (<i>R</i> _{int} = 0.0351)	4211 (<i>R</i> _{int} = 0.0527)	9483 (<i>R</i> _{int} = 0.0555)	5702 (<i>R</i> _{int} = 0.0203)	4233 (<i>R</i> _{int} = 0.0557)	3421 (<i>R</i> _{int} = 0.1013)
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>) (all data)]	0.0405, 0.0683 0.0713, 0.0840	0.0339, 0.0803 0.0415, 0.0829	0.0266, 0.0557 0.0468, 0.0594	0.0409, 0.1039 0.0540, 0.1133	0.0257, 0.0547 0.0374, 0.0566	0.0286, 0.0715 0.0341, 0.0730

evaporation of the solvent. Yield: 62 mg (83%). mp > 250°C. IR (KBr): 2032 (CO) and 1907 (br) cm⁻¹ (CO). ¹H NMR (270 MHz, CDCl₃): δ 1.80 [s, Cp*, B] and 1.83 [s, Cp*, A]. MS (DEI): *m/z* = 748. Found: C 20.99, H 2.04. Calc. for C₁₃H₁₅Br₃O₃ReRh: C 20.87, H 2.02%.

Complex 5. The synthesis was performed analogously to that of complex **4** using [IrBr(μ-Br)Cp*]₂. Orange crystals. Yield: 68 mg (81%). mp > 250 °C. IR (KBr): 2030 (CO) and 1911 (br) cm⁻¹ (CO). ¹H NMR (270 MHz, CDCl₃): δ 1.82 [s, Cp*, B] and 1.73 [s, Cp*, A]. MS (DEI): *m/z* = 838. Found C 18.82, H 1.77. Calc. for C₁₃H₁₅Br₃IrO₃Re: C 18.65, H 1.81%.

Crystal structure analyses

The structures of the complexes **2A**, **2B**, **4** and **5** were determined with a Stoe IPDS diffractometer, those of **1A** and **3B** with an Enraf-Nonius diffractometer (Table 1). Structure solution was performed by direct methods using SIR 97²² (**2A**, **2B**, **4** and **5**) and SHELXS 97 or SHELXS 86.²³ Refinement: full-matrix least squares on *F*² (SHELXL 97, SHELXL 93).²³ For the hydrogen atoms a riding model was employed. Complex **1A** co-crystallises with two molecules of benzene. For **3B** there are two independent cations one of which contains a disordered 2-propyl group.

CCDC reference number 186/2097.

See <http://www.rsc.org/suppdata/dt/b0/b004262p/> for crystallographic files in .cif format.

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