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Syntheses and structures of homo- and heterobimetallic, chloro-bridged complexes containing the $RuCl_3(AsPh_3)_n$ fragment ($n = 1, 2$) ☆

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Abstract

The reaction of $[RuCl_3(AsPh_3)_2(MeOH)]$ with the dimeric complexes $[(cod)RhCl]_2$, $[(ppy)RhCl]_2$ (ppy = cyclometalated 2-phenylpyridine), $[(cymene)RuCl_2]_2$ and $[Cp^*MCl_2]_2$ (M = Rh, Ir) has been investigated. The structure of the resulting products was shown to depend on the reaction partner. Whereas for the rhodium complexes $[(cod)RhCl]_2$ and $[(ppy)RhCl]_2$, heterobimetallic compounds with two halogeno-bridges were found, the reactions with the halfsandwich complexes $[(cymene)RuCl_2]_2$ and $[Cp^*MCl_2]_2$ gave triply bridged products with concomitant formation of mononuclear $[(\pi\text{-ligand})MCl_2(AsPh_3)]$ side products. The new complexes were all characterized by single crystal X-ray analysis.

Keywords: Heterobimetallic complex; Organometallic complex; Ruthenium; Rhodium; Iridium

Complexes, in which two different metal fragments are connected by halogeno-bridges, have recently emerged as a promising new class of catalysts. The Rh^{III}–Ru^{II} complex **1**, for example, was shown to display a very high activity for the ring opening metathesis polymerization of 1,5-cyclooctadien (Fig. 1) [1,2]. The structurally related Rh^{III}–Ru^{II} complex **2** is able to efficiently catalyze the oxidation of secondary alcohols using 2-butanone as the oxidation agent [3] and the Rh^{I}–Ru^{II} complex **3** was shown to be a very active and robust catalyst for the atom transfer radical addition of CCl_4 to olefins [4].

Mixed, halogeno-bridged complexes are accessible by a variety of synthetic methods [5]. For the synthesis of compounds with *two* halogeno-bridges, a metathesis reaction using the corresponding homobimetallic complexes was found to be the most versatile and easy method. Reactions of this kind were first described by the groups of Stone [6] and Masters [7] but more detailed investigations, which demonstrate the potential of this method, have been published only recently [8,9]. For the synthesis of mixed complexes with *three* halogeno-bridges, several routes were found to give good results. Initial studies showed that the solvent-stabilized complexes $[(CO)_3Re(thf)Br]_2$ [10] and $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(acetone)(PPh_3)_2]$ [3] are well suited starting materials. These investigations were recently expanded and numerous other compounds have been identified, which allow to generate mixed complexes with three halogeno-bridges in a very efficient way [11]. So far, investigations in this area have focused on diamagnetic complexes. In the following, we show that halogeno-bridged complexes containing a Ru^{III} fragment can be obtained in reactions of $[RuCl_3(AsPh_3)_2(MeOH)]$ (**4**) with dimeric complexes of Ru^{II}, Rh^{I}, Rh^{III} and Ir^{III}.

The complex $[RuCl_3(AsPh_3)_2(MeOH)]$ (**4**) can be synthesized from $RuCl_3 \times H_2O$ and $AsPh_3$ [12]. It contains a weakly bound methanol ligand which is easily replaced by other ligands. This is supported by exchange reactions with acetone [12] and by electrochemical data which suggest that upon dissolving **4** in CH_2Cl_2,

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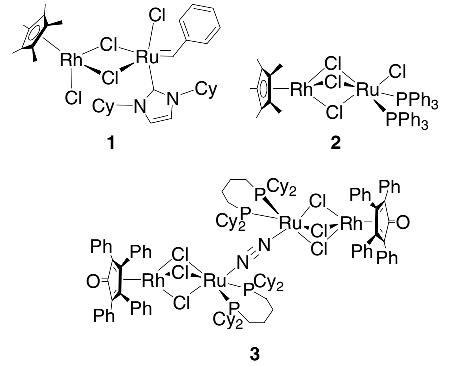
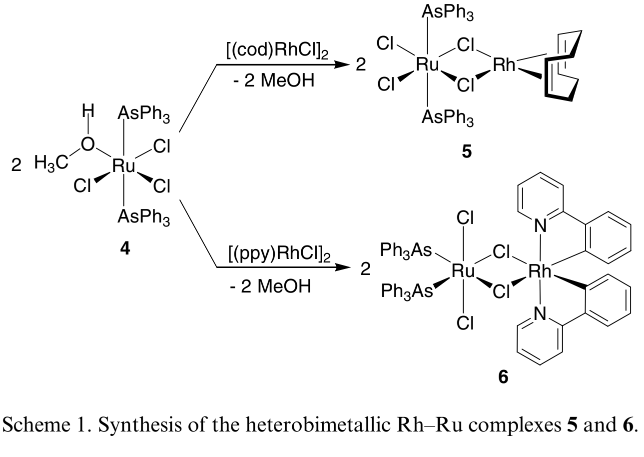


Fig. 1. Heterometallic Rh(μ-Cl)$_n$Ru complexes, which have found applications as catalysts in metathesis reactions (**1**), oxidation reactions (**2**) and atom transfer radical additions (**3**).

methanol is spontaneously liberated to give the dimer [$Ru_2Cl_6(AsPh_3)_4$] [13]. In order to obtain heterobimetallic Rh–Ru complexes, we have investigated the reaction of **4** with the Rh^I complex [(cod)RhCl]$_2$ [14] and the Rh^{III} complex [(ppy)RhCl]$_2$ (ppy = cyclometalated phenylpyridine) [15] (Scheme 1). The reactions were performed in CH_2Cl_2 and the resulting products **5** and **6** were crystallized from benzene/pentane or from CH_2Cl_2/pentane. The new complexes were characterized by elemental analyses and by single crystal X-ray analyses [16,17]. In both cases, heterobimetallic Rh–Ru complexes were obtained. To the best of our knowledge, they represent the first structurally characterized complexes with Ru^{III}(μ-Cl)$_2$Rh connections.

For complex **5**, a square planar (cod)Rh^I fragment is coordinated via two chloro-bridges to an octahedral Ru^{III} fragment. The two $AsPh_3$ ligands are positioned *trans* to each other and are aligned in an almost perfect linear fashion (Fig. 2). The bond lengths of the two metals to the bridging chloro-ligands are all very similar (Rh–Cl1/2 = Ru–Cl1/2 = 2.39 ± 0.02 Å) and slightly longer than what is found for the two terminal chloro-ligands (Ru–Cl3/4 = 2.32 ± 0.01 Å). Significant metal–metal interactions can be ruled out due to a Rh–Ru distance of 3.53 Å. The Ru(μ-Cl)$_2$Rh unit is slightly bent with a dihedral angle between the normals of the planes defined by Ru1, Cl1, Cl2 and Rh1, Cl1, Cl2 of 11.2°. The overall structure of **5** is similar to that of the complex [(cod)Rh(μ-Cl)$_2$Ir(P*i*Pr_3)$_2H_2$] [18] described by Werner et al.: as for **5**, a (cod)Rh^I fragment is connected via two chloro-bridges to an octahedral M^{III} fragment with donor ligands in *trans* configuration.



Scheme 1. Synthesis of the heterobimetallic Rh–Ru complexes **5** and **6**.

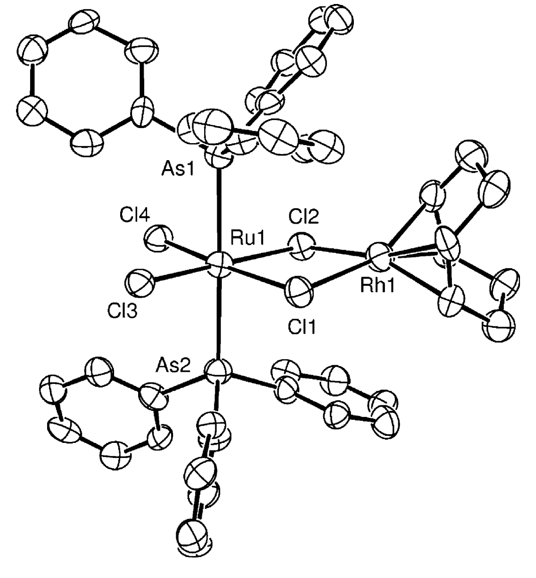


Fig. 2. ORTEP [19] representation of the molecular structure of **5** in the crystal. The hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Rh1–Cl1 2.395(4), Rh1–Cl2 2.373(4), Ru1–Cl1 2.411(4), Ru1–Cl2 2.388(4), Ru1–Cl3 2.328(4), Ru1–Cl4 2.307(4), Ru1–As1 2.4710(18), Ru1–As2 2.4798(18); As1–Ru1–As2 178.93(6).

Complex **6** also consists of a Rh fragment, which is connected by two chloro-bridges to an octahedral Ru^{III} fragment. But contrary to what is observed for **5**, the arsine ligands are now in *cis* position to each other (Fig. 3). This rearrangement is most likely the result of the increased steric requirements of the octahedral (ppy)$_2$Rh fragment, which make a *trans* geometry energetically less favorable. With 2.527(4) Å and 2.551(4) Å, the Rh^{III}–Cl bond lengths of complex **6** are significantly longer than what was found for the Rh^I–Cl bond lengths of complex **5**. As it is expected for a complex with two $AsPh_3$ ligands in *cis* position, the octahedral geometry around the Ru^{III} center is slightly distorted with As1–Ru1–As2 = 105.24(7)°.

In reactions of **4** with the chloro-bridged halfsandwich complex [(cymene)$RuCl_2$]$_2$ [20], a mixture of two products was obtained (Scheme 2). They show a very different solubility in acetone and can thus be separated. The soluble complex was identified by NMR spectroscopy to be the monomeric [(cymene)$RuCl_2(AsPh_3)$]. The second product was found to be the mixed-valence, triply bridged complex **7** as evidenced by single crystal X-ray analysis [17,21]. A reaction of this kind was not unexpected since it was known that one $AsPh_3$ ligand in

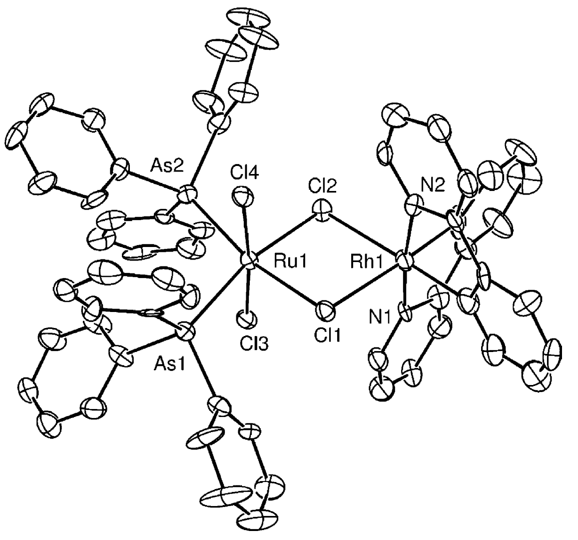
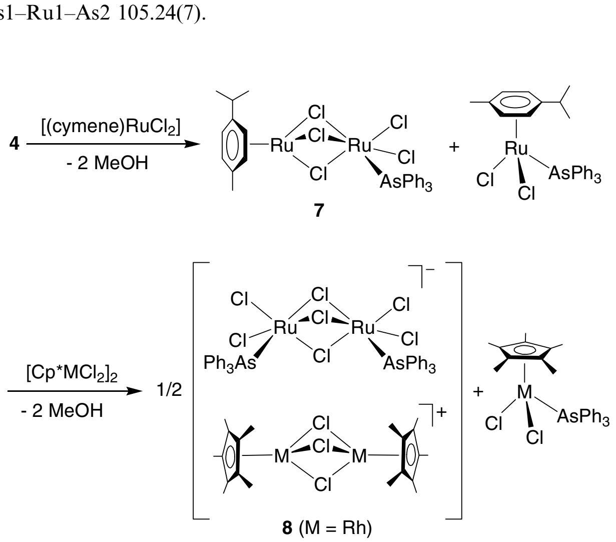


Fig. 3. ORTEP representation of the molecular structure of **6** in the crystal. The hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Rh1–N1 2.038(13), Rh1–N2 2.013(11), Rh1–Cl1 2.527(4), Rh1–Cl2 2.551(4), Ru1–Cl1 2.437(4), Ru1–Cl2 2.419(4), Ru1–As1 2.4876(18), Ru1–As2 2.4729(18), Ru1–Cl3 2.315(4), Ru1–Cl4 2.328(4); N1–Rh1–N2 173.2(5), Cl3–Ru1–Cl4 174.79(14), As1–Ru1–As2 105.24(7).



Scheme 2. Synthesis of the complexes **7**–**9**.

4 can easily be replaced [12]. Furthermore, a similar ligand transfer has been observed for reactions of $[(cymene)RuCl_2]_2$with ruthenium carbene complexes of the general formula $[RuCl_2(PR_3)_2(CHR')]$ [1,2] and for the reaction with $[RuCl_2(dppb)(PPh_3)]$ (dppb = 1,4-bis-diphenylphosphinobutane) [3].

The molecular structure of complex **7** is shown in Fig. 4. The (cymene)Ru^{II} fragment is connected by three chloro-bridges to the octahedral Ru^{III} fragment containing one $AsPh_3$ ligand. As it was found for **5** and **6**, the Ru–Cl bond lengths to the terminal chloro-ligands are shorter than the Ru–Cl distances of the bridging chloro-ligands. A few mixed-valence $Ru^{II}(\mu\text{-}Cl)_3Ru^{III}$ complexes with AsR_3 ligands have been described [22] but complex **7** appears to be the first one containing an arene π-ligand.

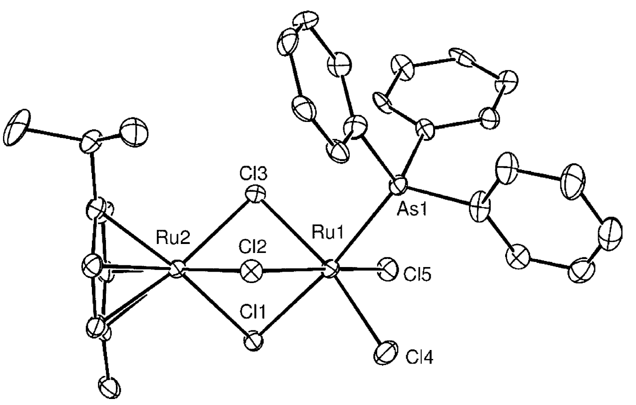


Fig. 4. ORTEP representation of the molecular structure of **7** in the crystal. The hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Ru2–Cl1 2.450(4), Ru2–Cl2 2.457(4), Ru2–Cl3 2.460(4), Ru1–As1 2.418(2), Ru1–Cl1 2.501(4), Ru1–Cl2 2.428(4), Ru1–Cl3 2.436(4), Ru1–Cl4 2.310(4), Ru1–Cl5 2.302(4); As1–Ru1–Cl1 172.57(11), As1–Ru1–Cl4 95.39(13).

Reactions with the dimeric halfsandwich complexes $[Cp^*MCl_2]_2$ (M = Rh, Ir) [23] were thought to proceed in a fashion similar to what was found for $[(cymene)RuCl_2]_2$. And indeed, the monomeric complexes $[Cp^*MCl_2(AsPh_3)]$ were obtained as side products (Scheme 2). But contrary to what was observed for **7**, the other species containing a Cp*M fragment were not the expected heterobimetallic complexes $[Cp^*M(\mu\text{-}Cl)_3RuCl_2(AsPh_3)]$ but the isomeric ionic complexes **8** and **9** [24]. This was confirmed for both complexes by a single crystal X-ray analysis [17,25].

The structural data for the complexes **8** (Fig. 5) and **9** (not shown) are very similar. The complexes contain the dimeric anion $[(AsPh_3)Cl_2As(\mu\text{-}Cl)_3AsCl_2(ASPh_3)]$ and the dimeric cation $[Cp^*M(\mu\text{-}Cl)_3MCp^*]$. Both, the anion [26] as well as the cation [27], have been described previously (although only together with other counter ions) and the bond length and angles found for **8** and **9** are within the expected range. At present, we have no explanation of why complex **7** forms a neutral dimer, whereas an ionic complex is found for **8** and **9**. It is conceivable, however, that the neutral and the isomeric ionic forms are energetically very similar as it was found for the mixed, bromo-bridged complex $[(CO)_3Re(\mu\text{-}Cl)_3Ru(cymene)]$ [10].

In summary, we have described the syntheses and the structures of five new chloro-bridged complexes containing the $Ru^{III}Cl_3(AsPh_3)_n$ (n = 1,2) fragment. The new compounds were obtained in reactions of $[RuCl_3(AsPh_3)_2(MeOH)]$ with the dimeric complexes $[(cod)RhCl]_2$, $[(ppy)RhCl]_2$, $[(cymene)RuCl_2]_2$ and $[Cp^*MCl_2]_2$ (M = Rh, Ir). The structure and the geometry of the resulting products was shown to depend to a

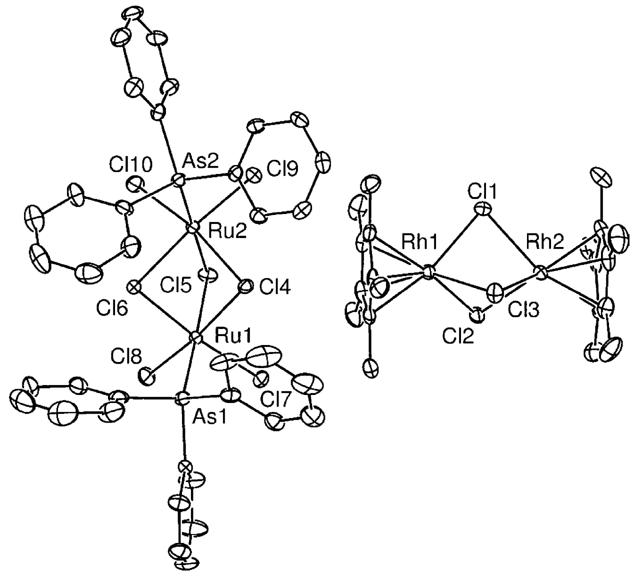


Fig. 5. ORTEP representation of the molecular structure of **8** in the crystal. The hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Ru1–As1 2.4212(7), Ru2–As2 2.4161(7), Ru1–Cl4 2.4093(12), Ru1–Cl7 2.3182(12), Ru2–Cl10 2.3060(12), Ru2–Cl4 2.4222(12), Rh1–Cl1 2.4703(14), Rh1–Cl2 2.4723(13), Rh1–Cl3 2–4520(12), Ru1···Ru2 3.1367(6), Rh1···Rh2 3.1989(6); As1–Ru1–Cl5 176.15(4); Cl6–Ru1–Cl7 173.35(5).

large extent on the reaction partner. For applications in homogeneous catalysis, the heterobimetallic Rh–Ru complexes **5** and **6** appear to be of special interest.

Supplementary material

An experimental section including detailed synthetic procedures and elemental analyses is available from the authors on request. CCDC 232760–CCDC 232764 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

References

[1] T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W. Herrmann, Angew. Chem., Int. Ed. 38 (1999) 2416–2419.

[2] (a) For other mixed, halogeno-bridged complexes, which are able to catalyze metathesis reactions see: B. De Clercq, F. Verpoort, Adv. Synth. Catal. 344 (2002) 639–648;
  (b) A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, Chem. Eur. J. 7 (2001) 4811–4820;
  (c) A. Fürstner, A.F. Hill, M. Liebl, J.D.E.T. Wilton-Ely, Chem. Commun. (1999) 601–602;
  (d) E.L. Dias, R.H. Grubbs, Organometallics 17 (1998) 2758–2767.

[3] A.C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, Eur. J. Inorg. Chem. (2001) 685–691.

[4] L. Quebatte, R. Scopelliti, K. Severin, Angew. Chem., Int. Ed. 43 (2004) 1520–1524.

[5] For an overview see: K. Severin, Chem. Eur. J. 8 (2002) 1515–1518.

[6] M.I. Bruce, M.Z. Iqbal, F.G.A. Stone, J. Organomet. Chem. 40 (1972) 393–401.

[7] (a) A.A. Kiffen, C. Masters, J.P. Visser, J. Chem. Soc., Dalton Trans. (1975) 1311–1315;
  (b) C. Masters, J.P. Visser, J. Chem. Soc., Chem. Commun. (1974) 932–933.

[8] (a) E. Corradi, N. Masciocchi, G. Pályi, R. Ugo, A. Vizi-Orosz, C. Zucchi, A. Sironi, J. Chem. Soc., Dalton Trans. (1997) 4651–4655;
  (b) J.D. Scott, R.J. Puddephatt, Organometallics 5 (1986) 1253–1257;
  (c) H.C. Clark, G. Ferguson, V.K. Jain, M. Parvez, Inorg. Chem. 25 (1986) 3808–3811;
  (d) H.C. Clark, G. Ferguson, V.K. Jain, M. Parvez, Inorg. Chem. 24 (1985) 1477–1482.

[9] (a) M. Öhm, A. Schulz, K. Severin, Eur. J. Inorg. Chem. (2000) 2623–2629;
  (b) K. Polborn, K. Severin, J. Chem. soc., Dalton Trans. (1999) 759–764;
  (c) K. Polborn, K. Severin, Eur. J. Inorg. Chem. (1998) 1187–1192;
  (d) K. Severin, K. Polborn, W. Beck, Inorg. Chim. Acta 240 (1995) 339–346.

[10] A.C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, J. Chem. Soc., Dalton Trans. (2000) 2960–2963.

[11] S. Gauthier, L. Quebatte, R. Scopelliti, K. Severin, Chem. Eur. J. (2004) in press.

[12] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945–956.

[13] R. Contreras, G.A. Heath, A.J. Lindsay, T.A. Stephenson, J. Organomet. Chem. 179 (1979) C55–C60.

[14] G. Giordano, R.H. Crabtree, Inorg. Synth. 28 (1990) 88–90.

[15] S. Sprouse, K.A. King, P.J. Spellane, R.J. Watts, J. Am. Chem. Soc. 106 (1984) 6647–6653.

[16] Crystal data for $\mathbf{5}\times C_6H_6$: $C_{50}H_{48}As_2Cl_4RhRu$, $M_r = 1144.50$, monoclinic, space group $P2_1/c$, $a = 18.841(8)$, $b = 12.562(4)$, $c = 20.343(6)$ Å, $\alpha = 90°$, $\beta = 111.79(4)°$, $\gamma = 90°$, $V = 4471(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.700$ g cm^{-3}, $\mu = 2.450$ mm^{-1}, $T = 140(2)$ K, 26,552 reflections collected, 7874 independent reflections, $R_{int} = 0.1001$, Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0879$, $wR_2 = 0.2391$. Crystal data for $\mathbf{6}\times 2$ CH_2Cl_2: $C_{60}H_{50}As_2Cl_8N_2RhRu$, $M_r = 1436.44$, monoclinic, space group $P2_1/c$, $a = 13.0860(13)$, $b = 28.510(3)$, $c = 16.261(17)$ Å, $\alpha = 90°$, $\beta = 104.349(9)°$, $\gamma = 90°$, $V = 5877.8(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.623$ gcm^{-3}, $\mu = 2.059$ mm^{-1}, $T = 140(2)$ K, 33,754 reflections collected, 9841 independent reflections, $R_{int} = 0.1409$, Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.1099$, $wR_2 = 0.2609$.

[17] Data reduction and cell refinement was performed with CrysAlis RED 1.6.9 (Oxford Diffraction Ltd., Abingdon, Oxfordshire, OX14 1 RL, UK, 2002). Absorption correction was applied to all data sets using an empirical method. All structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the riding model with $U_{iso} = a^{*}U_{eq}(C)$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others, C is the parent carbon atom). Space Group Determination, structure refinement and geometrical calculations were carried out on all structures with the SHELXTL software package, release 5.1 (G.M. Sheldrick, University of Göttingen, 1997; Bruker AXS, Inc., Madison, Wisconsin, 53719, USA, 1997).

[18] H. Werner, O. Nürnberg, J. Wolf, Z. Anorg. Allg. Chem. 627 (2001) 693–698.

[19] ORTEP 3 for Windows version 1.076. L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.

[20] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74–78.

[21] Crystal data for $\mathbf{7} \times CHCl_3$: $C_{29}H_{30}AsCl_8Ru_2$, $M_r = 939.19$, triclinic, space group $P\bar{1}$, $a = 9.6173(13)$, $b = 13.192(2)$, $c = 14.665(2)$ Å, $\alpha = 115.081(16)°$, $\beta = 94.563(12)°$, $\gamma = 92.857(12)°$, $V = 1672.2(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.865$ g cm^{-3}, $\mu = 2.545$ mm^{-1}, $T = 140(2)$ K, 10,010 reflections collected, 5155 independent reflections, $R_{int} = 0.0764$, Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0820$, $wR_2 = 0.2249$.

[22] (a) M.P. De Araujo, O.M. Porcu, A.A. Batista, G. Olivia, D.-H.F. Souza, M. Bonfadini, O.R. Nascimento, J. Coord. Chem. 54 (2001) 81–94;
  (b) G.A. Heath, A.J. Lindsay, T.A. Stephenson, D.K. Vattis, J. Organomet. Chem. 233 (1982) 353–358;
  (c) R. Contreras, G.G. Elliot, R.O. Gould, G.A. Heath, A.J. Lindsay, T.A. Stephenson, J. Organomet. Chem. 215 (1981) C6–C10.

[23] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228–230.

[24] Equimolar amounts of $[(Cp^*)MCl_2]_2$ and $[RuCl_3(AsPh_3)_2(MeOH)]$ were heated for 30 min at 80 °C. The products precipitate from the reaction mixture if benzene (**8**) or propylbenzene (**9**) is used as the solvent.

[25] Crystal data for **8**: $C_{56}H_{60}As_2Cl_{10}Rh_2Ru_2$, $M_r = 1645.34$, triclinic, space group $P\bar{1}$, $a = 10.7154(6)$, $b = 14.1944(10)$, $c = 20.0355(12)$ Å, $\alpha = 91.732(5)°$, $\beta = 96.701(5)°$, $\gamma = 90.966(5)°$, $V = 3024.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.807$ g cm^{-3}, $\mu = 2.590$ mm^{-1}, $T = 140(2)$ K, 18,368 reflections collected, 9365 independent reflections, $R_{int} = 0.0289$, Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0242$, $wR_2 = 0.0497$. Crystal data for **9**: $C_{56}H_{60}As_2Cl_{10}Ir_2Ru_2$, $M_r = 1823.92$, triclinic, space group $P\bar{1}$, $a = 10.7713(7)$, $b = 14.2400(10)$, $c = 20.0868(14)$ Å, $\alpha = 91.732(6)°$, $\beta = 96.698(6)°$, $\gamma = 90.626(6)°$, $V = 3058.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.981$ g cm^{-3}, $\mu = 6.368$ mm^{-1}, $T = 140(2)$ K, 17,797 reflections collected, 9434 independent reflections, $R_{int} = 0.0282$, Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0290$, $wR_2 = 0.0776$.

[26] M.P. De Araujo, S.L. Queiroz, A.A. Batista, E.H. Panepucci, G. Olivia, E.E. Castellano, Trans. Met. Chem. 27 (2002) 110–114.

[27] (a) M. Valderrama, M. Scotti, P. Campos, R. Sariego, K. Peters, H.G. von Schnering, H. Werner, New J. Chem. 12 (1988) 633;
  (b) K. Umakoshi, K. Murata, S. Yamashita, K. Isobe, Inorg. Chim. Acta 190 (1991) 185–191;
  (c) I. Ara, J.R. Berenguer, E. Eguizábal, J. Forniés, E. Lalinde, A. Martín, Eur. J. Inorg. Chem. (2001) 1631–1640.