

Syntheses and Structures of the Trinuclear Ruthenium Complexes $[\text{RuCl}_2(\text{PAd}_2\text{Bu})]_3$ and $[\text{RuCl}_2(\text{P}^t\text{Bu}_2\text{Cy})]_3$

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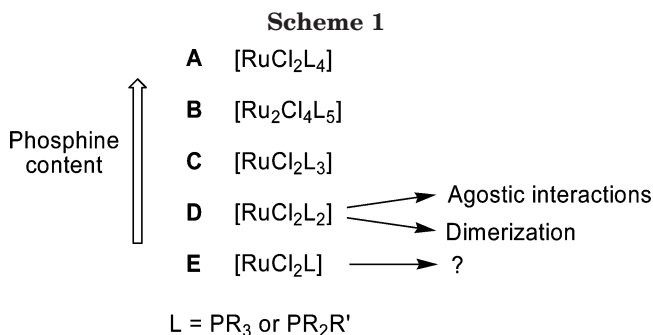
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Summary: The trinuclear ruthenium complexes $[\text{RuCl}_2(\text{PAd}_2\text{Bu})]_3$ and $[\text{RuCl}_2(\text{P}^t\text{Bu}_2\text{Cy})]_3$ have been obtained by reaction of $[(\text{cymene})\text{RuCl}_2]_2$ with 2 equiv of the respective phosphine. Crystallographic analyses show that the three metal fragments are connected by strong Ru–Ru bonds and bridging chloro ligands.

Neutral ruthenium(II) chloro complexes with monodentate phosphine ligands are key starting materials in organometallic synthesis^{1,2} and catalysis.^{2,3} With small phosphine ligands such as PMe_3 ,⁴ $\text{PMe}_2(\text{CH}_2\text{Ph})$,⁵ and PMe_2Ph ,⁶ electronically saturated complexes of the formula $[\text{RuCl}_2\text{L}_4]$ ($\text{L} = \text{PR}_3$, $\text{PR}_2\text{R}'$) (**A**) can be obtained (Scheme 1). The 16-electron complexes $[\text{RuCl}_2\text{L}_3]$ (**C**) are formed with sterically more demanding ligands such as PPh_3 ,² $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$,⁷ and PETPh_2 .⁶ In solution, complexes with the latter ligand are in equilibrium with the dimer $[\text{Ru}_2\text{Cl}_4(\text{PETPh}_2)_5]$ (**B**).⁶ Complexes of the formula RuCl_2L_2 (**D**) tend to dimerize via chloro bridges.⁸ Using the *ortho*-methyl-substituted phosphine ligand $\text{PPh}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$, however, it was possible to stabilize a monomeric 14-electron complex of type **D**.⁹ In this case, two agostic interactions between the methyl groups and the ruthenium center were observed. The formal removal of another phosphine ligand would lead to the hypothetical 12-electron complexes RuCl_2L (**E**). These complexes are expected to form aggregates in order to increase the coordination number of the metal, but to the best of our knowledge, complexes of the type $[\text{RuCl}_2\text{L}]_n$ have not been described so far. In the following, we report the synthesis and the structures of two first examples of this class of compounds.

The chloro-bridged complexes $[(\text{arene})\text{RuCl}_2]_2$ are known to react with PR_3 ligands to give monomeric adducts of the general formula $[(\text{arene})\text{RuCl}_2(\text{PR}_3)]$.¹⁰



When sterically demanding phosphine ligands are employed, the arene π -ligand can subsequently be cleaved off by photochemical or thermal activation. The resulting ruthenium complexes have been employed as catalysts for ring-closing¹¹ and ring-opening olefin metathesis reactions¹² as well as for atom transfer radical addition¹³ and polymerization reactions.¹⁴ So far, there is only very limited knowledge about what type of complexes are formed after cleavage of the π -ligand. When 1 equiv of PCy_3 was employed with respect to the dimer $[(\text{arene})\text{RuCl}_2]_2$, only a partial replacement of the arene was observed and binuclear complexes of the formula $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{L})(\text{PCy}_3)]$ ($\text{L} = \mu\text{-N}_2$ or $\eta^2\text{-C}_2\text{H}_4$) were obtained.^{13,14a}

In continuation of these studies, we have investigated the reaction of $[(\text{cymene})\text{RuCl}_2]_2$ ¹⁵ with the sterically very demanding phosphine ligands PAd_2Bu and $\text{P}^t\text{Bu}_2\text{Cy}$. These ligands are commercially available¹⁶

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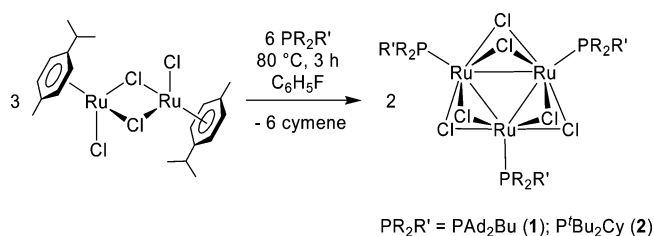
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Scheme 2



and have mainly been used in Pd-catalyzed reactions.^{17,18} The organometallic chemistry in connection with ruthenium, on the other hand, has just started to be explored.¹⁹ As the solvent for our reactions, we decided to use fluorobenzene, which is chemically inert and has a low tendency to form π -complexes. When a solution of $[(\text{cymene})\text{RuCl}_2]_2$ and 2 equiv of the respective phosphine was heated for 3 h at 80 °C, the complexes **1** and **2** were formed in excellent yield (Scheme 2). The PAd_2Bu complex **1** precipitates from solution, whereas the $\text{P}^t\text{Bu}_2\text{Cy}$ complex **2** is obtained after evaporation of the solvent and washing with pentane.

The complexes were analyzed by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The data confirmed that the cymene ligand has been cleaved off. A single peak in the ^{31}P NMR spectra was observed. The elemental analysis was in agreement with structures of the formula $[\text{RuCl}_2(\text{PR}_2\text{R}')_n]_n$. This was confirmed by the results of single-crystal X-ray analyses.^{20,21}

Both complexes have trinuclear structures, in which the three $\text{RuCl}_2(\text{PR}_2\text{R}')$ fragments are connected by Ru–Ru bonds and by bridging chloro ligands (Figures 1 and 2). The Ru–Ru distances ($\text{Ru–Ru} = 2.56\text{--}2.58$ Å) are indicative of very strong metal–metal interactions. The Ru–Ru bonds in trinuclear hydrido complexes of the general formula $[\text{Ru}_3\text{H}_3(\text{O})(\text{arene})_3]^+$, for example, are approximately 0.2 Å longer ($\text{Ru–Ru} = 2.74\text{--}2.81$ Å),²² and the unsupported Ru–Ru bonds in $[\text{Ru}_3(\text{CO})_{12}]$ have an average distance of 2.8515(4) Å.²³ As expected for such a compact Ru_3 core, the Ru–Cl

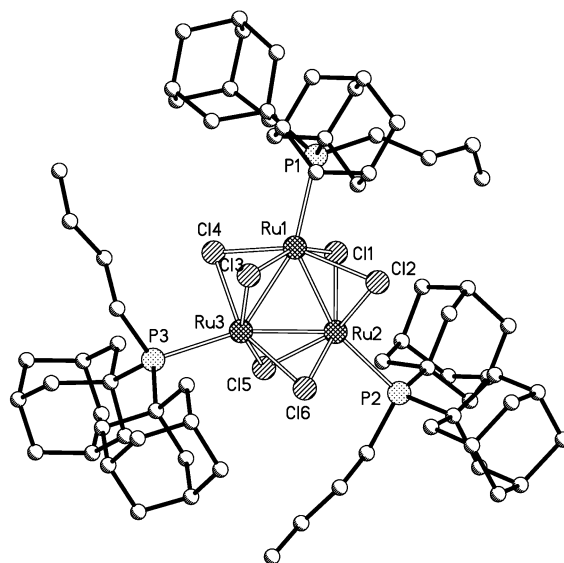


Figure 1. Graphic representation of the molecular structure of **1** in the crystal. The solvent molecules (CHCl_3 , C_5H_{12}) are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Ru1–Cl1 2.376(3), Ru1–Cl2 2.432(3), Ru1–Cl4 2.361(3), Ru1–Cl3 2.354(3), Ru1–P1 2.463(4), Ru1–Ru2 2.5716(14), Ru2–Ru3 2.5834(14), Ru1–Ru3 2.5649(14); Cl1–Ru1–Cl2 82.56(12), Cl4–Ru1–Cl2 154.15(13), Cl2–Ru1–P1 96.20(12).

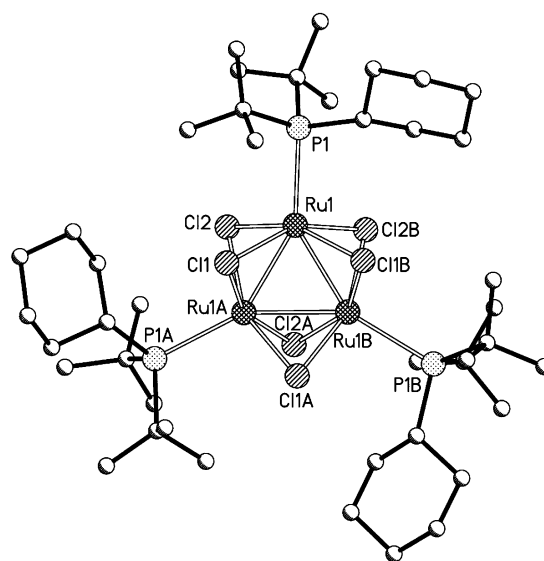


Figure 2. Graphic representation of the molecular structure of **2** in the crystal. The solvent molecule (C_5H_{12}) and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Ru1–Cl1 2.3980(12), Ru1–Cl2 2.3531(12), Ru1–Cl1B 2.3681(12), Ru1–Cl2B 2.4080(12), Ru1–P1 2.5028(13), Ru1–Ru1B 2.5693(7); Cl1–Ru1–Cl2 84.15(4), Cl1B–Ru1–Cl2 157.09(5), Cl2–Ru1–P1 102.78(4).

bonds are relatively short ($\text{Ru–Cl} = 2.35\text{--}2.43$ Å). Dinuclear complexes with the common $\text{M}(\mu\text{-Cl})_3\text{Ru}$ binding motif, for comparison, show Ru–($\mu\text{-Cl}$) distances in the range of 2.50 ± 0.05 Å.²⁴ The Ru–P bonds in **1** and **2**, on the other hand, are relatively long: with an average length of 2.49 Å, they are longer than what is

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(20) Crystal data for complex **1** $\times \text{CHCl}_3 \times \text{C}_5\text{H}_{12}$: $\text{C}_{78}\text{H}_{130}\text{Cl}_9\text{P}_3\text{Ru}_3$, $M = 1782.99$, orthorhombic, $a = 35.121(6)$ Å, $b = 23.608(3)$ Å, $c = 19.039(3)$ Å, $V = 15786(4)$ Å³, $T = 140(2)$ K, space group $\text{Ab}a2$, $Z = 8$, $\mu = 0.975 \text{ mm}^{-1}$, 44 821 reflections collected, 13 468 independent reflections, $R_{\text{int}} = 0.1198$, $R_1 [I > 2\sigma(I)] = 0.0790$, wR_2 (all data) = 0.2234.

(21) Crystal data for complex **2** $\times \text{C}_5\text{H}_{12}$: $\text{C}_{47}\text{H}_{98}\text{Cl}_6\text{P}_3\text{Ru}_3$, $M = 1273.08$, rhombohedral, $a = b = 14.9378(12)$ Å, $c = 44.142(5)$ Å, $V = 8530.1(14)$ Å³, $T = 140(2)$ K, space group $R3c$, $Z = 6$, $\mu = 1.183 \text{ mm}^{-1}$, 16 012 reflections collected, 3343 independent reflections, $R_{\text{int}} = 0.0537$, $R_1 [I > 2\sigma(I)] = 0.0323$, wR_2 (all data) = 0.0698.

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typically found for Ru(II) complexes with sterically demanding PCy₃ or PⁱPr₃ ligands (Ru–P = 2.40 ± 0.05 Å).²⁵

Trinuclear ruthenium complexes, which contain exclusively chloro and phosphine ligands, have been characterized before.²⁶ These cationic complexes have the formula [Ru₃Cl₅(PPh₃)₆]⁺ or [Ru₃Cl₅(L–L)₃]⁺ (L–L = BINAP, (Ph₂P)₂C₆H₄). But contrary to what is observed for **1** and **2**, they possess a Ru₃(μ₂-Cl)₃(μ₃-Cl)₂ core with two face-capped μ₃-chloride atoms and Ru–Ru distances of more than 3.21 Å.

To investigate in more detail the parameters that are of importance for the formation of complex **1**, we have performed a number of additional experiments. When the temperature of the reaction was reduced from 80 to 60 °C, no precipitation was observed after 3 h, indicating that the thermal activation is essential. Complex **1** remained the dominant reaction product when the stoichiometry between PAd₂Bu and [(cymene)RuCl₂]₂ was increased to P:Ru = 2:1. Using substoichiometric amounts of phosphine (P:Ru = 0.5), however, the precipitation of an unidentified compound of low solubility was observed. To determine whether other precursors for the “RuCl₂” fragment could be used to synthesize **1**, we have investigated the reaction of [(1,3,5-C₆H₃ⁱPr₃)RuCl₂]₂²⁷ and [(cod)RuCl₂]_n (cod = cycloocta-1,5-diene)²⁸ with PAd₂Bu (C₆H₅F, P:Ru = 1.25, 80 °C, 3 h). Neither of the two starting materials gave significant amounts of complex **1**. For [(cod)RuCl₂]_n, this

was most likely due to its low solubility. For the arene complex [(1,3,5-C₆H₃ⁱPr₃)RuCl₂]₂, on the other hand, an explanation could be the unfavorable formation of putative intermediate [(1,3,5-C₆H₃ⁱPr₃)RuCl₂(PAd₂Bu)] due to steric congestion between the sterically demanding ligands C₆H₃ⁱPr₃ and PAd₂Bu.²⁹

The complexes **1** and **2** are remarkably stable. Heating solutions of **1** or **2** with 3 equiv of the ligand PPh₃, PCy₃, or 1,3-diaminopropane in toluene at 70 °C for 1 h did not lead to any significant decomposition of the trinuclear structure as evidenced by ³¹P NMR spectroscopy. Upon addition of bis(diphenylphosphino)ethane (dppe), however, the formation of [RuCl₂(dppe)₂] was observed, regardless of the stoichiometry. When toluene solutions of **1** and **2** were heated for 1 h to 70 °C under an atmosphere of CO, the PAd₂Bu complex **1** was found to be largely inert, whereas for the PⁱBu₂Cy complex **2**, a number of unidentified new peaks were observed in the ³¹P NMR spectrum together with a dominant peak for the starting material **2**. The nature of these products was not investigated further.

In summary, we have described the syntheses and the structures of two complexes of the general formula [RuCl₂(PR₂R')]₃. The trimers are composed of 12-electron RuCl₂(PR₂R') fragments, which aggregate by formation of Ru–Ru bonds and μ-Cl bridges. The resulting clusters are remarkably stable, as evidenced by attempted addition reactions with P- and N-donor ligands and with carbon monoxide. [(Arene)RuCl₂]₂ complexes in combination with sterically demanding phosphine ligands are frequently used for the in-situ generation of electronically unsaturated Ru-catalysts.^{11–14,19} So far, there is only very limited knowledge about what kind of complexes are formed after cleavage of the arene ligand. The possibility that chemically inert complexes of type [RuCl₂(PR₂R')]₃ can be generated in such reactions should be considered in future investigations.

Supporting Information Available: Synthetic procedures and analytical data for the complexes **1** and **2** as well as crystallographic data in CIF format. This material is available free of charge on the Internet at <http://pubs.acs.org>.

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(29) When the complex [(1,3,5-C₆H₃ⁱPr₃)RuCl₂]₂ was dissolved together with 2 equiv of PAd₂Bu in CH₂Cl₂ at room temperature, the formation of the monomeric adduct [(1,3,5-C₆H₃ⁱPr₃)RuCl₂(PAd₂Bu)] could not be observed by ³¹P NMR spectroscopy. This is in contrast to what was found for [(cymene)RuCl₂]₂.

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