5792 *Organometallics* **2005,** *24,* 5792−5794

Syntheses and Structures of the Trinuclear Ruthenium Complexes $[RuCl_2(PAd_2Bu)]_3$ and $[RuCl_2(P^tBu_2Cy)]_3$

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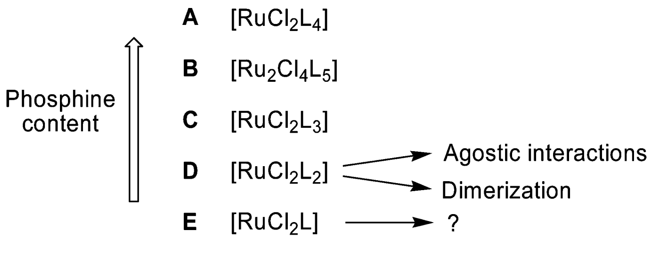
Received July 29, 2005

Summary: The trinuclear ruthenium complexes $[RuCl_2(PAd_2Bu)]_3$ and $[RuCl_2(P^tBu_2Cy)]_3$ have been obtained by reaction of $[(cymene)RuCl_2]_2$ 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] $PMe_2(CH_2Ph)$,[5] and PMe_2Ph,[6] electronically saturated complexes of the formula $[RuCl_2L_4]$ (L = PR_3, PR_2R') (**A**) can be obtained (Scheme 1). The 16-electron complexes $[RuCl_2L_3]$ (**C**) are formed with sterically more demanding ligands such as PPh_3,[2] $P(p\text{-}C_6H_4CH_3)_3$,[7] and $PEtPh_2$.[6] In solution, complexes with the latter ligand are in equilibrium with the dimer $[Ru_2Cl_4(PEtPh_2)_5]$ (**B**).[6] Complexes of the formula $RuCl_2L_2$ (**D**) tend to dimerize via chloro bridges.[8] Using the *ortho*-methyl-substituted phosphine ligand $PPh_2(2,6\text{-}Me_2C_6H_3)$, 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 $[RuCl_2L]_n$ 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.

Scheme 1



The chloro-bridged complexes $[(arene)RuCl_2]_2$ are known to react with PR_3 ligands to give monomeric adducts of the general formula $[(arene)RuCl_2(PR_3)]$.[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-closing[11] and ring-opening olefin metathesis reactions[12] as well as for atom transfer radical addition[13] 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 $[(arene)RuCl_2]_2$, only a partial replacement of the arene was observed and binuclear complexes of the formula $[(arene)Ru(\mu\text{-}Cl)_3RuCl(L)(PCy_3)]$ (L = μ-N_2 or η^2-C_2H_4) were obtained.[13,14a]

In continuation of these studies, we have investigated the reaction of $[(cymene)RuCl_2]_2$[15] with the sterically very demanding phosphine ligands PAd_2Bu and P^tBu_2Cy. These ligands are commercially available[16]

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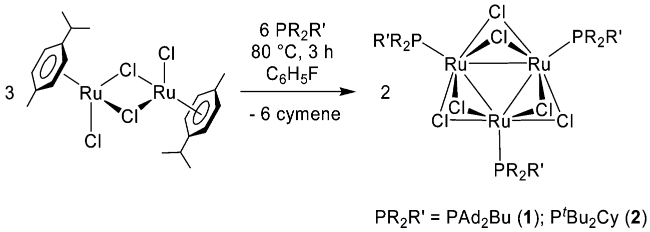
Scheme 2



PR_2R' = PAd_2Bu (**1**); P^tBu_2Cy (**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 [(cymene)$RuCl_2$]$_2$ 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 P^tBu_2Cy 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 [$RuCl_2$(PR_2R')]$_n$. This was confirmed by the results of single-crystal X-ray analyses.[20,21]

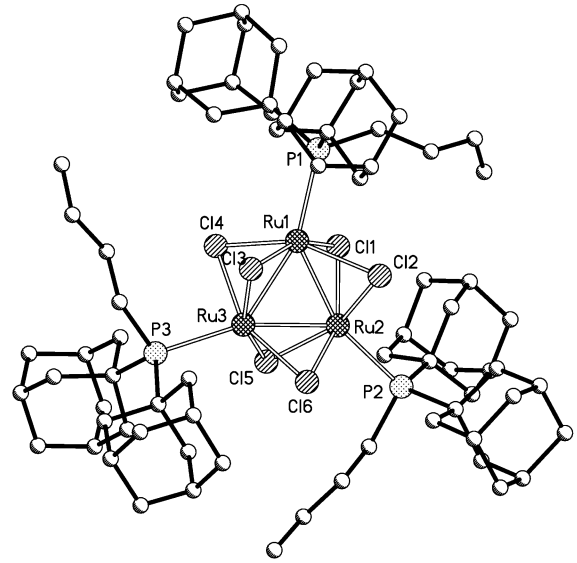


Figure 1. Graphic representation of the molecular structure of **1** in the crystal. The solvent molecules ($CHCl_3$, C_5H_{12}) are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Ru1−Cl1 2.376(3), Ru1−Cl2 2.432(3), Ru1−Cl4 2.361(3), Ru1−Cl3 2.354(3), Ru1−P1 2.463(4), Ru1−Ru2 2.5716(14),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

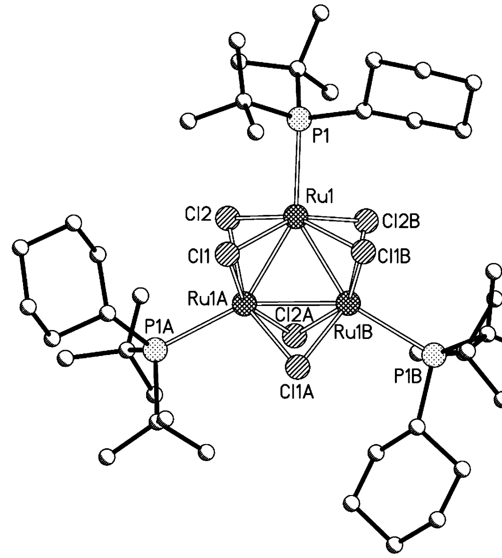


Figure 2. Graphic representation of the molecular structure of **2** in the crystal. The solvent molecule (C_5H_{12}) and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Ru1−Cl1 2.3980(12), Ru1−Cl2 2.3531(12), Ru1−Cl1B 2.3681(12), Ru1−Cl2B 2.4080(12), Ru1−P1 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).

Both complexes have trinuclear structures, in which the three $RuCl_2$(PR_2R') fragments are connected by Ru−Ru bonds and by bridging chloro ligands (Figures 1 and 2). The Ru−Ru distances (Ru−Ru = 2.56−2.58 Å) are indicative of very strong metal−metal interactions. The Ru−Ru bonds in trinuclear hydrido complexes of the general formula [$Ru_3H_3(O)(arene)_3$]$^+$, for example, are approximately 0.2 Å longer (Ru−Ru = 2.74−2.81 Å),[22] and the unsupported Ru−Ru bonds in [$Ru_3(CO)_{12}$] have an average distance of 2.8515(4) Å.[23] As expected for such a compact Ru_3 core, the Ru−Cl bonds are relatively short (Ru−Cl = 2.35−2.43 Å). Dinuclear complexes with the common M(μ-Cl)$_3$Ru binding motif, for comparison, show Ru−(μ-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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[16] The ligands are available from Strem.

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[20] Crystal data for complex **1** × $CHCl_3$ × C_5H_{12}: $C_{78}H_{130}Cl_9P_3Ru_3$, M = 1782.99, orthorhombic, a = 35.121(6) Å, b = 23.608(3) Å, c = 19.039(3) Å, V = 15786(4) Å^3, T = 140(2) K, space group $Aba2$, Z = 8, μ = 0.975 mm^{-1}, 44 821 reflections collected, 13 468 independent reflections, R_{int} = 0.1198, R_1 [$I > 2\sigma(I)$] = 0.0790, wR_2 (all data) = 0.2234.

[21] Crystal data for complex **2** × C_5H_{12}: $C_{47}H_{99}Cl_6P_3Ru_3$, M = 1273.08, rhombohedral, $a = b$ = 14.9378(12) Å, c = 44.142(5) Å, V = 8530.1(14) Å^3, T = 140(2) K, space group $R3c$, Z = 6, μ = 1.183 mm^{-1}, 16 012 reflections collected, 3343 independent reflections, R_{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 PCy_3 or P^iPr_3 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 $[Ru_3Cl_5(PPh_3)_6]^+$ or $[Ru_3Cl_5(L{-}L)_3]^+$ (L−L = BINAP, $(Ph_2P)_2C_6H_4$). But contrary to what is observed for **1** and **2**, they possess a $Ru_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2$ core with two face-capped μ_3-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 PAd_2Bu and $[(cymene)RuCl_2]_2$ 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 "$RuCl_2$" fragment could be used to synthesize **1**, we have investigated the reaction of $[(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2]_2$[27] and $[(cod)RuCl_2]_n$ (cod = cycloocta-1,5-diene)[28] with PAd_2Bu (C_6H_5F, P:Ru = 1.25, 80 °C, 3 h). Neither of the two starting materials gave significant amounts of complex **1**. For $[(cod)RuCl_2]_n$, this was most likely due to its low solubility. For the arene complex $[(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2]_2$, on the other hand, an explanation could be the unfavorable formation of putative intermediate $[(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2(PAd_2Bu)]$ due to steric congestion between the sterically demanding ligands $C_6H_3{}^iPr_3$ and PAd_2Bu.[29]

The complexes **1** and **2** are remarkably stable. Heating solutions of **1** or **2** with 3 equiv of the ligand PPh_3, PCy_3, 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 ^{31}P NMR spectroscopy. Upon addition of bis(diphenylphosphino)ethane (dppe), however, the formation of $[RuCl_2(dppe)_2]$ 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 PAd_2Bu complex **1** was found to be largely inert, whereas for the P^tBu_2Cy complex **2**, a number of unidentified new peaks were observed in the ^{31}P 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 $[RuCl_2(PR_2R')]_3$. The trimers are composed of 12-electron $RuCl_2(PR_2R')$ 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. $[(Arene)RuCl_2]_2$ 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 $[RuCl_2(PR_2R')]_3$ 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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(24) For some selected examples see: (a) Gauthier, S.; Scopelliti, R.; Severin, K. *Helv. Chim. Acta* **2005**, *88*, 435−446. (b) Gauthier, S.; Quebatte, L.; Scopelliti, R.; Severin, K. *Chem. Eur. J.* **2004**, *10*, 2811−2821. (c) Amaroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 3335−3343. (d) Amaroso, D.; Yap, G. P. A.; Fogg, D. E. *Can. J. Chem.* **2001**, *79*, 958−963.

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(29) When the complex $[(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2]_2$ was dissolved together with 2 equiv of PAd_2Bu in CH_2Cl_2 at room temperature, the formation of the monomeric adduct $[(1,3,5\text{-}C_6H_3{}^iPr_3)RuCl_2(PAd_2Bu)]$ could not be observed by ^{31}P NMR spectroscopy. This is in contrast to what was found for $[(cymene)RuCl_2]_2$.