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Synthesis of catalytically active diene and cyclopentadienyl rhodium halide complexes

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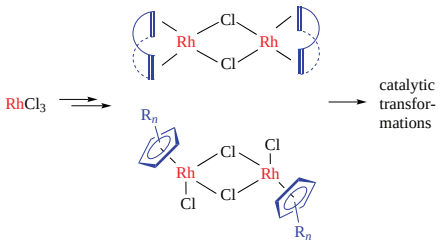
Diene and cyclopentadienyl rhodium halides are very often used as catalysts for various transformations. Herein we analyze the advantages and limitations of classical and more recent synthetic methods for the preparation of these catalysts with a focus on the compounds with chiral ligands.



Keywords: rhodium, catalysis, diene, cyclopentadienyl, half-sandwich complexes, ligand structure.

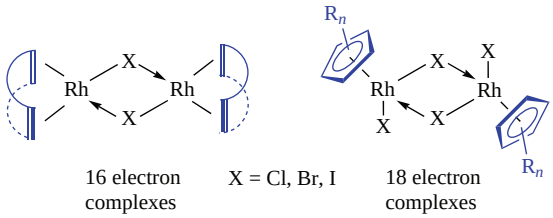
Dedicated with gratitude to the director of the Moscow Chemical Lyceum Sergey E. Semenov in recognition of his enormous contribution to the chemical education in Russia.

Introduction

Modern organic chemistry largely relies on diverse catalytic reactions. Their development often requires the improvement of methods for the synthesis of the corresponding organometallic catalysts. This is especially true for the complexes with fine-tuned chiral ligands, which are often chemically fragile and at the same time more expensive than even platinum metals: compare for example the prices of the ruthenium chloride (*ca*. 10–20 € for 1 g) and one of the cheapest chiral phosphine ligand *R*-BINAP (*ca*. 100–200 € for 1 g). Classical synthetic methods of organometallic chemistry such as heating of metal salts with a large excess of the organic ligands are often not suitable for the preparation of modern catalysts.

Diene and cyclopentadienyl rhodium complexes, *viz*. $[(diene)RhCl]_2$ and $[(cyclopentadienyl)RhCl_2]_2$, are very popular and efficient catalysts for various reactions. Their applications have been recently reviewed,[1–7] but as far as we aware there are no specific reviews on their synthesis (only some general, 30–40 years old reviews briefly cover this topic).[8,9] Here we present such a review, which is focused on practical analysis of recent methods, rather than on comprehensive coverage of all the related papers.

Both the diene and the cyclopentadienyl rhodium complexes typically have the dimeric or oligomeric structures (Scheme 1), in which the halide bridges help the metal centers to achieve stable 16- and 18-electron configuration, respectively. The dimeric structure is usually cleaved during the synthetic and catalytic reactions, although some exceptions have been reported.[10] The nature of halides has only minor influence on reactivity, namely the substitution of iodide ligands proceeds much slower than that



Scheme 1 Typical structures of diene and cyclopentadienyl rhodium halides.

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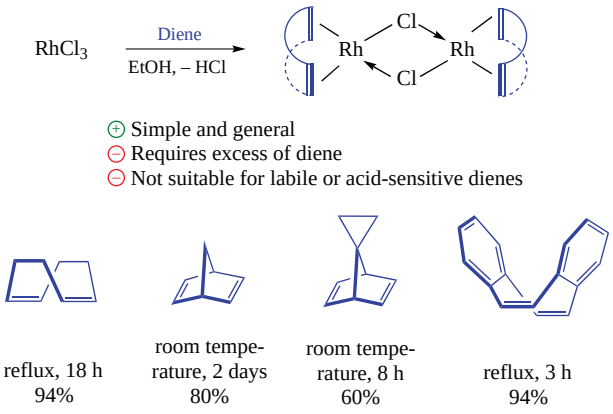
Dmitry S. Perekalin studied chemistry at the Moscow Chemical Lyceum and the Higher Chemical College of the Russian Academy of Sciences. He has received his PhD degree in 2005 and Dr. Sci. degree in 2016 from the A. N. Nesmeyanov Institute of Organoelement Compounds and is currently working in this Institute as a head of the lab. He has been also working as a visiting researcher at the University of Rennes in France, the Harriot-Watt University of Edinburgh in UK, and the Institute of Inorganic Chemistry in the Czech Republic. His research is focused on the synthesis of late-transition metal complexes with potential applications in homogeneous catalysis, photochemistry, and biochemistry.

of chlorides and often requires the help of silver salts such as $AgPF_6$.[11,12] Rhodium(III) complexes $[(cyclopentadienyl)RhCl_2]_2$ are completely stable towards air and moisture, while rhodium(I) complexes $[(diene)RhCl]_2$ are in some cases susceptible to oxidation in solutions,[13] especially if they contain loosely bound diene ligands that can dissociate from the metal.

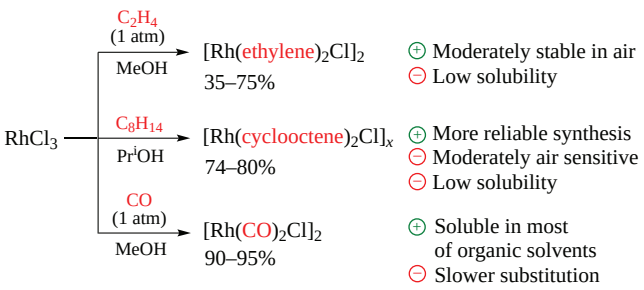
Synthesis of diene rhodium halides

The classical synthesis of $[(diene)RhCl]_2$ complexes is based on refluxing of rhodium chloride with an excess of dienes in ethanol, which acts as a mild reducing agent (Scheme 2).[14] This method is mostly used for the cheap, commercially available dienes such as 1,5-cyclooctadiene (cod)[14] and norbornadiene (nbd),[15] as well as for some more exotic norbornadiene-cyclopropane[16] and dibenzocyclooctatetraene (dbcot).[17] In the case of norbornadienes, the reactions are carried out at room temperature apparently in order to avoid oligomerization of the free ligands. The disadvantages of the method are the use of large amounts of ligands and the formation of HCl in the reaction mixture. This makes it unsuitable for acid-sensitive dienes such as Me_3Si-cyclooctadiene[18] as well as for expensive chiral dienes.



Scheme 2 Classical method for synthesis of diene rhodium halides.

A more delicate synthetic approach is based on the reaction of dienes with complexes containing labile ligands such as $[Rh(ethylene)_2Cl]_2$, $[Rh(cyclooctene)_2Cl]_x$ or $[Rh(CO)_2Cl]_2$ (Scheme 3). These precursors are obtained by the reactions of rhodium chloride with an excess of the olefin or carbon monoxide in some alcohol. The yield of the ethylene complex may vary in a wide range of 35−75% depending on the sample of $RhCl_3$.[19] Sometimes addition of NaOH as HCl scavenger improves the yield of $[Rh(ethylene)_2Cl]_2$. Alternatively, the residual rhodium salts present in the mixture after the synthesis can be converted into the cyclooctadiene complex $[(cod)RhCl]_2$. The synthesis of cyclooctene complex is more reliable, but should be carried out for 5 days at 30 °C. At lower temperatures the reaction is too slow,[20] while at higher temperatures decomposition to metallic rhodium is observed (in particular, we failed to reproduce the reported synthesis at 78 °C).[21] Both olefin complexes have

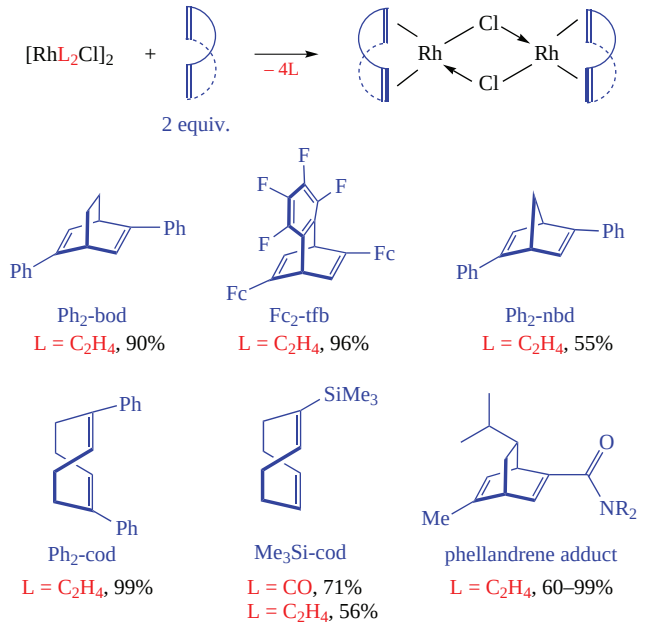


Scheme 3 Synthesis of the labile precursor complexes.

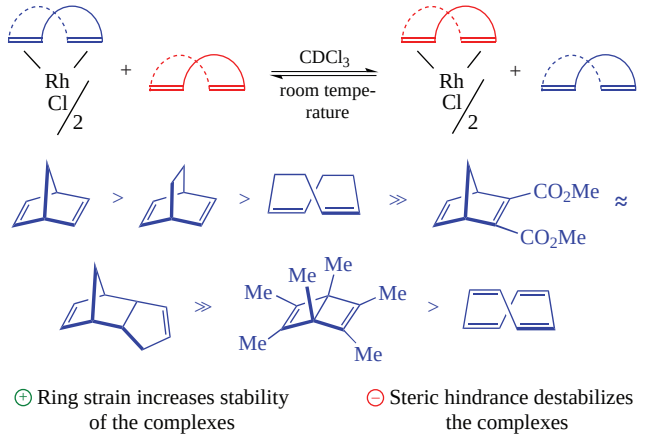
limited thermal stability (best be stored under argon in the fridge) and low solubility in most of organic solvents, which precludes their purification. In contrast, the carbonyl complex[22] $[Rh(CO)_2Cl]_2$ is well soluble[23] and its reactions can be monitored by IR-spectroscopy.

Substitution of olefins or CO by dienes typically proceeds at room temperature within 5–60 min in an almost quantitative yield (Scheme 4). This allows one to generate the catalytically active complexes $[(diene)RhCl]_2$ *in situ*. Many complexes have been prepared this way and isolated in order to obtain structural information using X-ray diffraction analysis. This has been particularly important for complexes with chiral dienes such as substituted dihydrobarrelenes (*e.g.* Ph_2-bod),[24] tetrafluorobenzobarrelenes (*e.g.* Fc_2-tfb),[25] norbornadienes (*e.g.* Ph_2-nbd),[26] cyclooctadienes (*e.g.* Me_3Si-cod,[18] Ph_2-cod[27]), dibenzocyclooctatetraenes (*e.g.* Ph-dbcot),[28] Diels–Alder adducts of natural phellandrene[29] and others.[30] Slower reactions and lower yields are observed for sterically hindered or unstable dienes such as diphenyl-norbornadiene. Interestingly, this method can be used to obtain a rhodium complex even with polymeric cyclooctadiene as a ligand and then convert it into dispersed rhodium nanoparticles.[31]

The strength of the rhodium–diene bond in $[(diene)RhCl]_2$ is an important aspect for catalytic application.[27] It was shown that



Scheme 4 Synthesis of complexes with chiral dienes by the ligand exchange reaction.

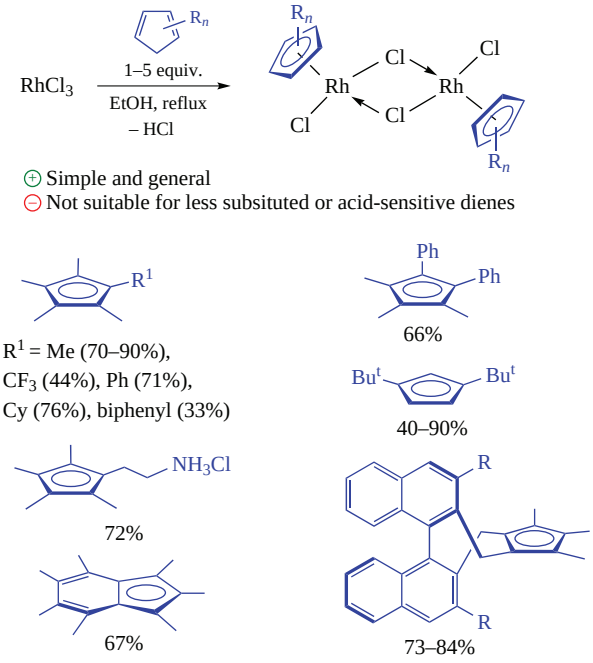


Scheme 5 Ligand exchange reactions that illustrate the relative stability of the complexes.

this bond is stronger for strained dienes such as norbornadiene and weaker for sterically hindered dienes, such as hexamethyl-substituted Dewar benzene (Scheme 5).[32,33] Electron-acceptor substituents apparently have minor destabilization effect.

Synthesis of cyclopentadienyl rhodium halides

As in the case of diene complexes, the classical method for the synthesis of the cyclopentadienyl complexes $[(C_5R_5)RhCl_2]_2$ is based on heating of rhodium chloride with 1–5 equiv. of the corresponding cyclopentadiene in ethanol or isopropanol (Scheme 6). The yields are usually higher when the ligand is used in excess. The products can be purified by crystallization from alcohols or chlorinated solvents (chromatography is usually not suitable). The disadvantages of this method are the use of the excess of the ligands and the formation of HCl, which can polymerize less substituted dienes or react with some sensitive substituents such as Me_3Si.[34] Nevertheless, the method was successfully utilized for the synthesis of complexes

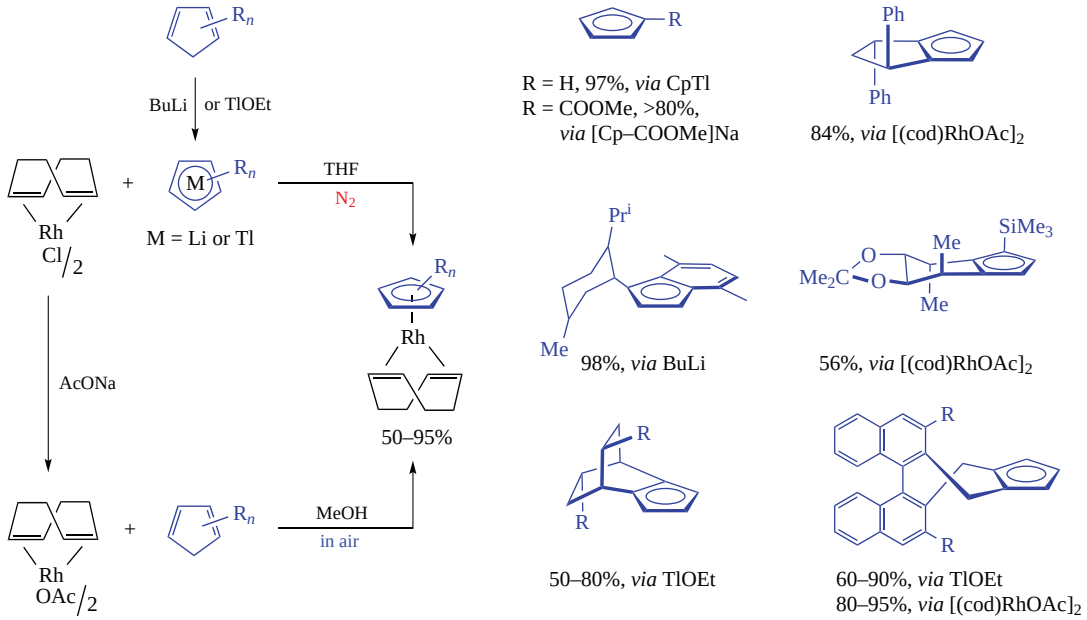


Scheme 6 Synthesis of cyclopentadienyl complexes from $RhCl_3$.

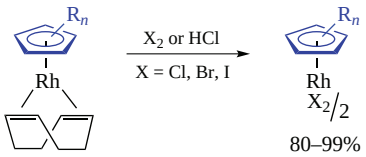
with polysubstituted cyclopentadienyls such as C_5Me_5,[35,36] C_5Me_4Ph,[37] $C_5Me_3Ph_2$,[38] C_5Me_4Cy,[36] $C_5Me_4CF_3$,[39] $C_5Me_4Biphenyl$,[40] $C_5H_3Bu^t_2$,[41,42] $C_5Me_4CH_2CH_2NH_3Cl$,[43] $C_5Me_3(CH_2)_{10}$,[44] the chiral binaphthyl ligands,[45] and some other. The related heptamethylindenyl complex[46] $[(C_9Me_7)RhCl_2]_2$ can be also obtained this way, while similar reactions of $RhCl_3$ with unsubstituted indene or cyclopentadiene give polymeric products with obscure structures.[47]

Another general method for the synthesis of the rhodium(III) complexes $[(C_5R_5)RhX_2]_2$ (X = Cl, Br, I) is based on the initial preparation of the rhodium(I) olefin compounds such as $(C_5R_5)Rh(C_2H_4)_2$ or $(C_5R_5)Rh(cod)$ and their subsequent oxidation with halogens (Schemes 7 and 8). These rhodium(I) complexes are in turn obtained by the reactions of $[(C_2H_4)_2RhCl]_2$ or $[(cod)RhCl]_2$ with lithium, sodium or thallium salts of the cyclopentadienyl anions. The lithium salts are easily generated from the corresponding cyclopentadienes and BuLi, however they sometimes provoke side deprotonation or redox reactions. The thallium salts are obtained from cyclopentadienes and commercially available TlOEt. They are more stable and mild reagents, however they are rather toxic (for TlOAc LD_{50} = 10−30 mg kg^{-1}) and sensitive to light.[48,49] In both variations this method is suitable for variably substituted and acid-sensitive dienes. It was used to prepare rhodium complexes with the unsubstituted cyclopentadienyl,[50,51] indenyl,[52,53] penta-[54] and heptamethyl-indenyl,[55] C_5H_4–COOMe,[56] the chiral binaphthyl[57] and bicyclo[2.2.2]octane[58] derivatives of cyclopentadienyl, and many other ligands.[49,59–61] The yields typically vary from 50 to 90%. The purification of the rhodium(I) complexes can be carried out by column chromatography in hexane, preferably under inert atmosphere.

Recently Cramer *et al*. have developed a new procedure for the high-yield synthesis of compounds $(C_5R_5)Rh(cod)$ from $[(cod)Rh(OAc)]_2$, which does not require preliminary deprotonation of a cyclopentadiene (see Scheme 7).[62] The synthesis is carried out in air and can be used for generation of catalytically active complexes *in situ*. According to DFT calculations, the cyclopentadiene initially coordinates with rhodium and undergoes intramolecular deprotonation by acetate ligand (similar to the carboxylate assisted C–H activation).[63,64] This method was utilized for the preparation of complexes with various chiral ligands including biaryl,[65] binaphthyl,[62,66] and myrtenal[67] derivatives. The typical yields are higher than 80%



Scheme 7 Synthesis of rhodium(I) cyclopentadienyl complexes.

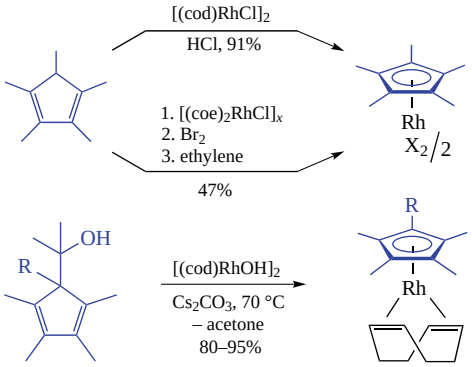


Scheme 8 Synthesis of the complexes $[(C_5R_5)RhX_2]_2$ from $(C_5R_5)Rh(cod)$ intermediates.

and decrease only in the case of sterically hindered dienes (C_5Ph_4H, 58%) or sensitive silyl derivatives (50–60%).

Complexes $(C_5R_5)Rh(cod)$ can act as catalysts themselves. However, they are usually converted into $[(C_5R_5)RhX_2]_2$ by oxidation with halogens or, more rarely, with hydrochloric acid.[68,69] The resulting rhodium(III) complexes are much more stable in air and also insoluble in hydrocarbons, which simplifies their purification. In some cases, formation of polybromide[70] or polyiodides[71,72] was observed; the excess halogens can be removed by ethylene, $Na_2S_2O_3$ or $Na_2S_2O_4$.

There are several other methods for synthesis of cyclopentadienyl rhodium complexes, which are used less often (Scheme 9). In particular, $[(cod)RhCl]_2$ reacts with substituted cyclopentadienes in the presence of concentrated HCl in methanol.[73,74] This procedure sometimes gives better yields (60–95%) and is more reliable than direct synthesis from $RhCl_3$. It is especially useful for the synthesis of the similar iridium complexes $[(C_5R_5)IrCl_2]_2$. Cp*H can also substitute the labile olefin ligands in $[Rh(cyclooctene)_2Cl]_x$ with the following reaction with bromine giving $[Cp^*RhBr_2]_2$ (further bubbling of ethylene is necessary to remove an excess of bromine).[70] Similar method can be used to obtain cyclohexadienyl complexes such as $[(C_6Me_7)RhCl_2]_2$.[75] Finally, compounds $(C_5R_5)Rh(cod)$ can



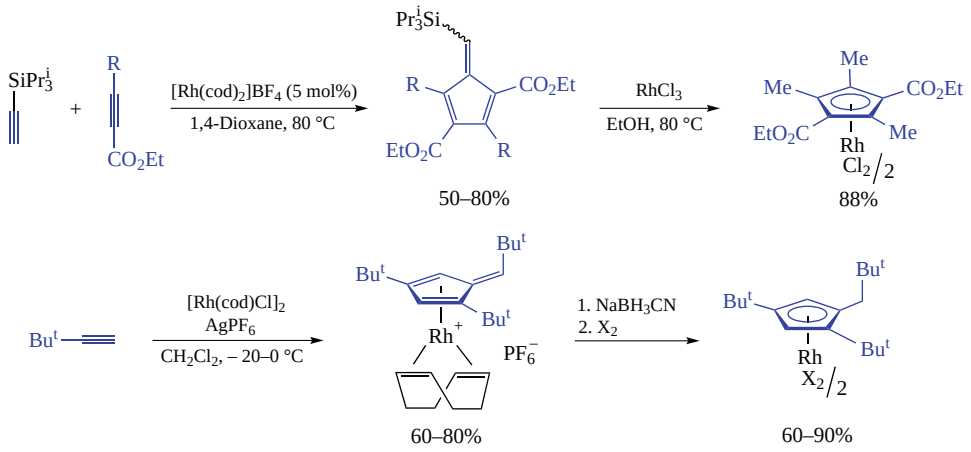
Scheme 9 Less common methods for the synthesis of the complexes $[(C_5R_5)RhX_2]_2$.

be prepared by the reaction of $[(cod)RhCl]_2$ or $[(cod)RhOH]_2$ with pre-synthesized alcohol derivatives of cyclopentadienes.[76]

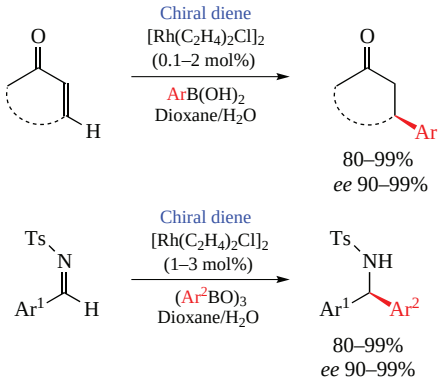
Recently, several methods have been developed for the synthesis of cyclopentadienyl complexes from alkynes *via* fulvene intermediates (Scheme 10). For example, Tanaka *et al.* have synthesized the electron-acceptor fulvenes by catalytic 2+2+1-cross-cyclotrimerization of two molecules of alkynylcarboxylic acid derivatives with Pr^i_3Si-acetylene.[77] The resulting fulvenes can be coordinated by the direct reaction with $RhCl_3$. In a similar way complexes with pendant amide substituents have been obtained from somewhat exotic cyclopropylideneacetamides and 1,6-diynes.[78] We have demonstrated that the bulky fulvene ligand can be assembled directly in the coordination sphere of rhodium by the reaction of $[(cod)RhCl]_2$ with *tert*-butylacetylene[79,80] in the presence of $AgPF_6$ (see also related works).[81,82] Further addition of a hydride and oxidation with halogens provide complexes with planar-chiral cyclopentadienyl ligand $[(C_5H_2Bu^tCH_2Bu^t)RhX_2]_2$. Noteworthy the racemic iodide complex can be separated into pure enantiomers by crystallization of its adduct with L-proline and used in asymmetric catalysis.[83] The main advantage of these methods is the fast assembly of the substituted cyclopentadienyl ring from the commercially available alkynes. However, the possibilities for variation of substituents are limited, because only sterically hindered alkynes form fulvenes. The reaction of rhodium precursors such as $[(cod)RhCl]_2$ with non-hindered internal alkynes usually give arene[84] or cyclobutadiene[85] complexes, while terminal alkynes undergo catalytic trimerization and polymerization.[86]

Typical catalytic reactions

Complexes $[(diene)RhCl]_2$ are commonly used as precursors for generation of catalytically active rhodium(I) phosphine complexes in the reaction mixtures. However, as diene ligand is replaced in this process, such reactions are clearly outside the scope of this review. The most studied catalytic reaction with diene ligand playing a vital role is the asymmetric 1,4-addition of arylboronic acids to unsaturated ketones (Michael acceptors),[2,87] as well as 1,2-addition to tosyl-imines[88–90] (Scheme 11). These reactions tolerate various functional groups, proceed under mild conditions (often in the presence of water) and give the target products with high yields and enantioselectivity (typically 90–99% *ee*). The catalysts are commonly generated *in situ* from $[Rh(ethylene)_2Cl]_2$ and dienes. The catalyst loading can be as low as 0.01%.[91] It is also possible to attach the diene ligand to polymeric support and to reuse the resulting catalyst more than 10 times.[92] The widespread use of these catalytic reactions is limited only by 3–5 step synthesis of the chiral



Scheme 10 Synthesis of the complexes $[(C_5R_5)RhX_2]_2$ from alkynes *via* fulvenes.



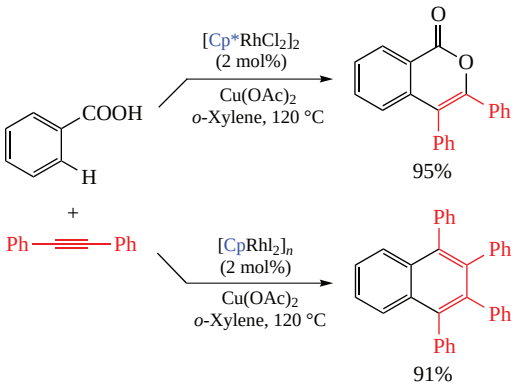
Scheme 11 Typical reactions catalyzed by diene rhodium complexes generated *in situ*.

dienes. The most readily accessible dienes of this type are the Diels–Alder adducts of natural phellandrene and derivatives of acetylene carboxylic acid.[93]

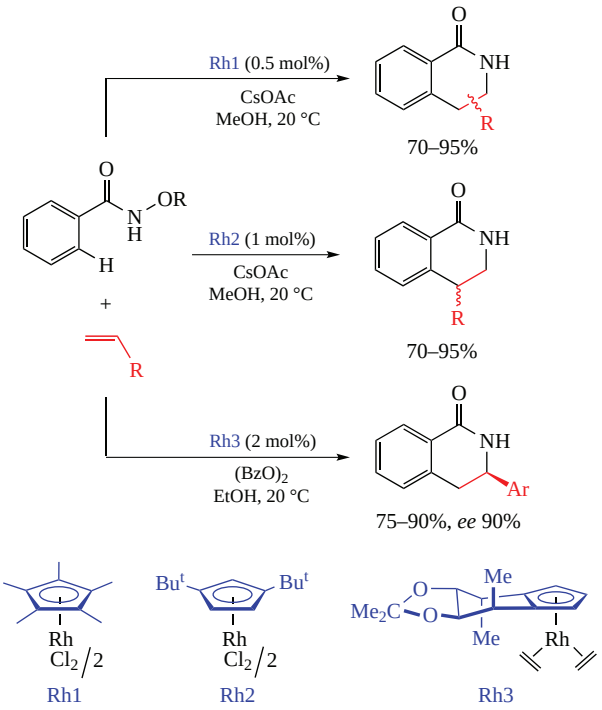
It should be noted that the addition reactions of arylboronic acids have been studied in detail and perhaps do not require substantial further investigation. However, analogous additions of alkyl, vinyl and alkynyl boronic acids are much less explored. Other promising new reactions for the chiral $[(diene)RhCl]_2$ catalysts are transformations of diazo compounds.[94,95]

The cyclopentadienyl rhodium complexes $[(C_5R_5)RhX_2]_2$ are most often used as catalysts for C–H functionalization of aromatic compounds with coordinating, directing groups.[4,96,97] The mechanism of this reaction involves three main steps: (1) coordination of rhodium with a directing group of a substrate, (2) intramolecular activation of the nearest aromatic C–H bond with formation of Rh–C bond, (3) insertion of an electrophile into the newly formed Rh−C bond and final reductive elimination of the metal complex.[63] Such reactions are very versatile and allow one to construct various heterocyclic molecules from simple precursors in one step. The reactions are typically robust and not sensitive to air or water, although they often require rather high temperatures (80−120 °C) and catalyst loading (2–5%). A typical example is the annulation of benzoic acid with alkynes (Scheme 12).[98,99] The cyclopentadienyl ligand of the catalyst plays two important roles: (1) it stabilizes and prevents decomposition of the active species, (2) it determines the regioselectivity of the process. In this particular process, the catalyst $[Cp^*RhCl_2]_2$ provides the substituted isocoumarins, while the unsubstituted analogue $[CpRhI_2]_n$ gives the corresponding naphthalenes.

Another illustration of the influence of the ligand is the reaction of hydroxamic acid derivatives with alkenes (Scheme 13).[63,100] Due to the nature of directing group this reaction proceeds already at room temperature and does not



Scheme 12 Typical C–H functionalization reaction catalyzed by cyclopentadienyl rhodium complexes.



Scheme 13 Influence of the cyclopentadienyl ligand on the regio- and stereoselectivity of the C–H functionalization reactions.

require an external oxidant such as $Cu(OAc)_2$. The classical catalyst $[Cp^*RhCl_2]_2$ in most cases affords a mixture of products, namely 3- and 4-subsituted dihydroisoquinolines.[63] The catalysts $[(C_5H_3Bu^t_2)RhCl_2]_2$ and $[(C_5H_2Bu^t_2CH_2Bu^t)RhCl_2]_2$ with more bulky cyclopentadienyl ligands give only 4-substituted products with high regioselectivity.[101,79] The catalysts with various chiral cyclopentadienyl ligands produce the 3-aryl-substituted dihydroisoquinolines with moderate to excellent stereoselectivity (36−93% *ee*).[62,67,100,102,103]

Despite some progress the rational prediction of the influence of a cyclopentadienyl ligand on activity and selectivity of catalytic C–H functionalization reactions is difficult.[38,104] The synthesis of chiral cyclopentadienyl ligands is also often complicated and time-consuming, although some important improvements have been made in recent years.[58,65,105] Besides, the catalyst loadings are typically rather high (2–5%) and should be lowered for effective large scale application.[106]

Conclusions

To conclude, the methods for the synthesis of catalytically active diene and cyclopentadienyl rhodium halides are quite well developed. The most general method for the diene complexes is the replacement of olefin ligands by diene in $[Rh(ethylene)_2Cl]_2$ or $[Rh(cyclooctene)_2Cl]_x$ intermediates. For the synthesis of cyclopentadienyl complexes, the reaction of $[(cod)Rh(OAc)]_2$ with cyclopentadiene and following oxidation by I_2 is recommended. Both methods can be used to generate catalytically active complexes *in situ*. The main challenge for application of these complexes in catalysis is the development of clear relationship between the ligand structure and the catalyst activity and selectivity.

Acknowledgements

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