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Dirhodium(II,II) Paddlewheel Complexes

Radim Hrdina*[a]

This minireview summarizes synthetic approaches towards homoleptic dirhodium(II,II) paddlewheel complexes with the general formula Rh_2A_4. These complexes have found numerous applications in a wide range of chemical research and industry as catalysts, detectors, enzymatic inhibitors or building blocks for molecular scaffolds. In organic synthesis they are commonly used to transfer electron-deficient species, they act as Lewis acids to activate unsaturated bonds, serve as hydrogenation catalysts and participate in oxidation/reduction processes. Dirhodium paddlewheel complexes are composed of the Rh-Rh backbone and four bridging anions, which surround the core. According to the application, the electrochemical potential of the Rh atom can be modulated, as can the geometry and physical and chemical properties of the metal complex. Dirhodium complexes can be prepared in one step from basic inorganic precursors or by post-functionalization of the paddlewheel structures.

1. Introduction

Dirhodium(II,II) paddlewheel complexes with the general formula Rh_2A_4 (Figure 1) are compounds consisting of a Rh-Rh backbone and four bridging anions, which surround this core. The reported bridging anions from which homoleptic dirhodium complexes are built up include amidinates, 2-aminopyridinates, carboxamidates, carboxylates, phosphinates, phosphates, pyrazolates, 2-oxo-pyridinates, triazenides and thioanalogs (replacing the oxygen) of such bidentate ligands (overview in section 6). These complexes are widely used in many industrial applications and in academic research, specifically in hetero- and homogeneous catalysis of organic reactions,[1] material science,[2] life sciences,[3] medicine,[4] analytical chemistry,[5] structural inorganic chemistry[6] and theoretical chemistry.[7]

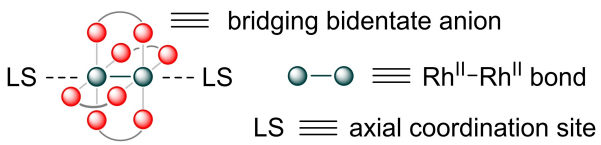

Figure 1. Schematic representation of dirhodium(II,II) paddlewheel complexes.

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2. Structure of dirhodium(II,II) complexes

2.1. Symmetry of dirhodium(II,II) paddlewheel complexes

Dirhodium(II,II) tetraacetate **2** was the first binuclear rhodium paddlewheel compound whose structure was confirmed by X-ray crystallography.[8] The four bridging anions (acetates) are arranged around the Rh-Rh core in such a way that the structure resembles lantern or paddlewheel. These two words are now used to describe binuclear complexes with such an anion arrangement (Figure 2). Dirhodium tetraacetate represents the most symmetrical complex (besides dirhodium formate **K2**, Figure 12, section 6) in this class of compounds. All other dirhodium complexes with structurally different bridging ligands either belong to the same point group D_{4h} or the number of operations of symmetry in the described complex is reduced.

2.2. Properties of dirhodium(II,II) paddlewheel complexes

The formal oxidation state of each rhodium atom in dirhodium tetraacetate and generally in this class of complexes is +2. The distance between two rhodium atoms is in the range of 2.35–2.55 Å according to the nature of the bridging ligand and of the

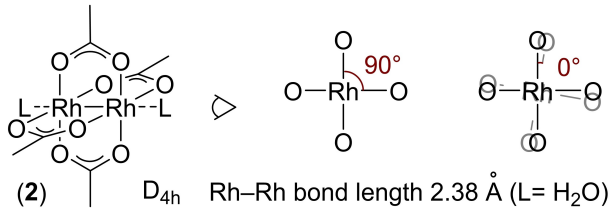
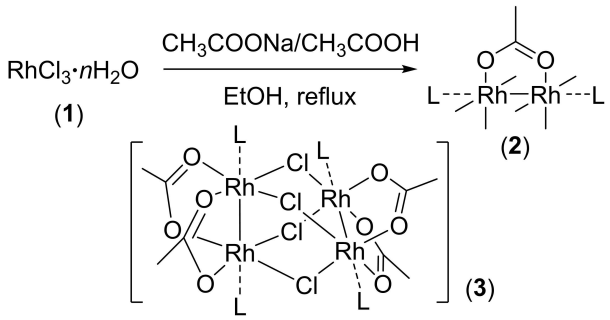
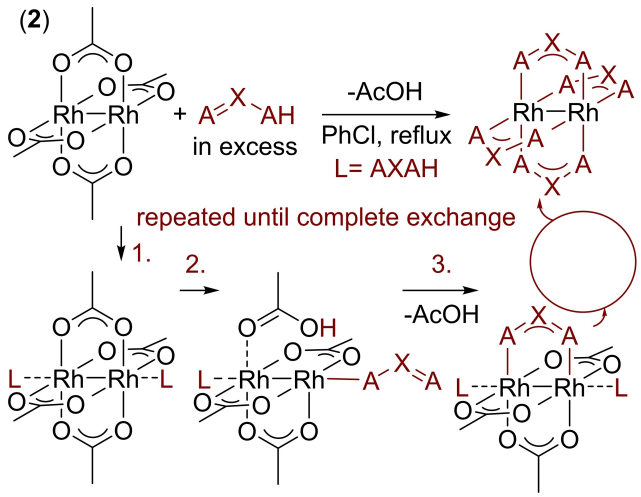


Figure 2. Structure of dirhodium(II,II) tetraacetate (Rh_2OAc_4) **2**. L = ligand coordinating through a dative bond to Lewis acidic rhodium atom. The length of the rhodium-rhodium bond is sensitive to the nature of ligand L and can vary in the range of 2.38 to 2.52 Å. The torsion angle around the rhodium-rhodium bond may be nonzero in case of complexes with other bridging ligands.

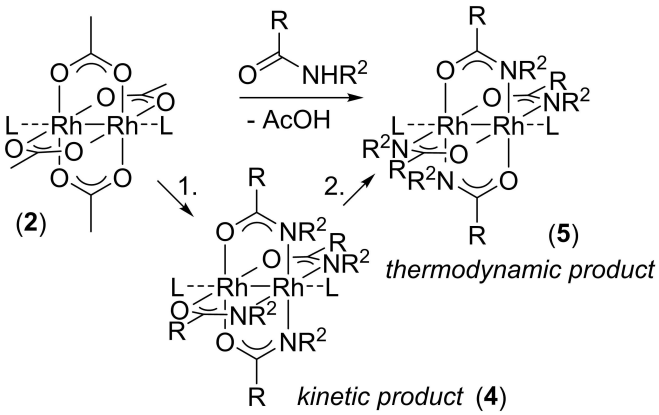


Scheme 1. Synthesis of dirhodium tetraacetate **2** from rhodium trichloride **1** through intermediate structure **3**. L = EtOH or H_2O. (Depiction of homoleptic complexes with plain lines as in the case of compound **2** appears in literature and is used in this review as well.)

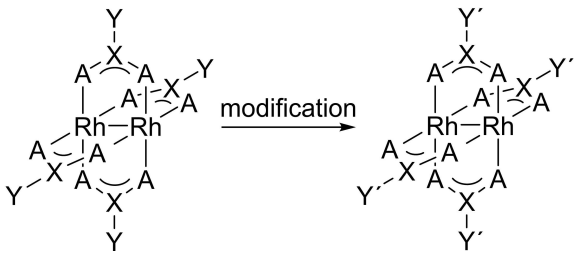


Scheme 2. Dirhodium tetraacetate **2** as model starting material for ligand exchange reactions. The ligand exchange proceeds in three consecutive steps. Coordination of the ligand (AXAH) in axial position of the dirhodium complex, protonation of the acetate bridging ligand and finally release of acetic acid accompanied by formation of a new bridge. This sequence of steps is repeated until all ligands are exchanged for new ones.

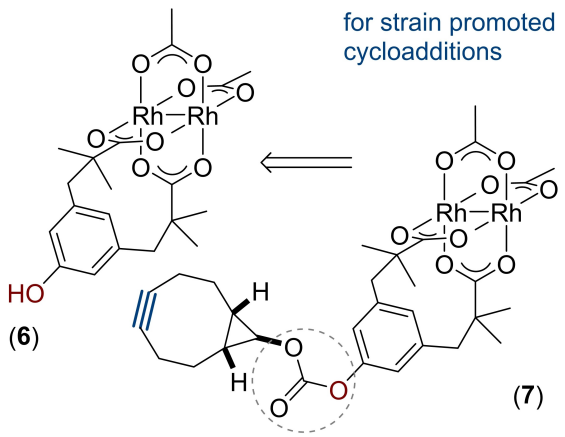
Radim Hrdina obtained his Ph.D. degree in 2007 at Charles University in Prague in the group of Martin Kotora. Afterwards he joined the group of Peter R. Schreiner at Justus-Liebig University as Alexander-von-Humboldt fellow. After two years, he moved to University of Geneva to join the group of Jérôme Lacour. Since 2014 till 2019 he has been a "habilitand" at Justus-Liebig University in Giessen. 2019 he completed the habilitation process with the thesis "Functionalization of bridged cycloalkanes" and was awarded the title of Privatdozent. His research interests include synthesis of organic compounds, development of artificial enzyme-like complexes, organo-, semi-metal-, transition-metal-catalysis and C–H functionalization of alkanes.



Scheme 3. Kinetically controlled formation of isomer **4** in the ligand exchange reaction of dirhodium acetate **2** with *N*-substituted carboxamides (R = *C*-substituent) or carbamates (R = *N*-substituent) and subsequent rearrangement of **4** to thermodynamically most stable product **5**. L = $RCONHR_2$. Removal of acetic acid can be described as irreversible process. Typically, the acetic acid is removed from the reaction mixture or the new ligand is in huge excess to the starting material that the acetic acid does not participate in ligand exchange processes.

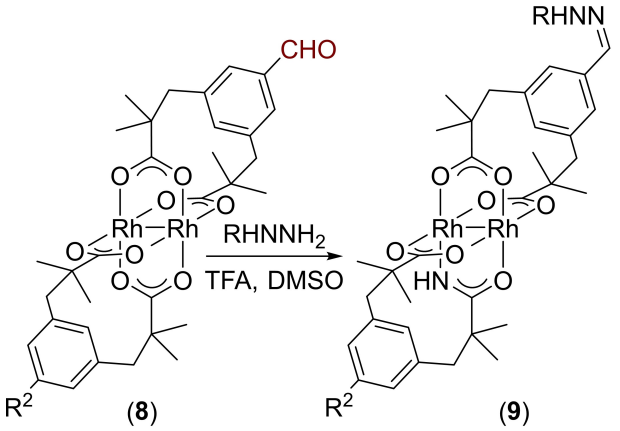


Scheme 4. Dirhodium(II,II) paddlewheel complexes as starting materials in organic reactions, *i.e.* modifications of organic ligand without changing the lantern structure of the metal complex.

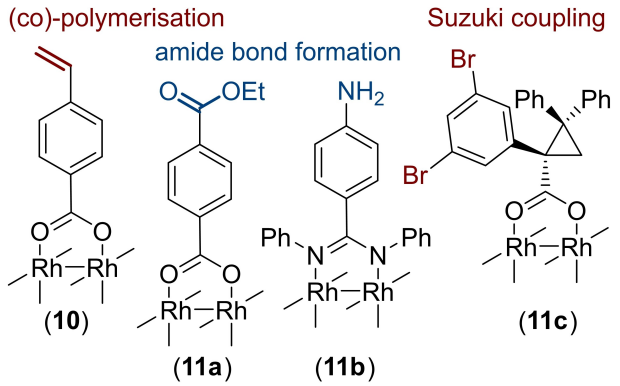


Scheme 5. Dirhodium(II,II) complex **7** was designed for click reactions with organic azides. Carbonate formation was the key post-functionalization reaction to connect dirhodium complex **6** with an organic moiety.

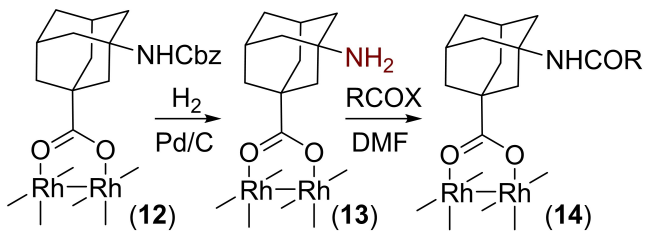
axial ligand (for example, if the axial ligand is water then the Rh-Rh bond length in Rh_2A_4 for A = ^{t}BuCOO is 2.37 Å, for A = CH_3COS is 2.55 Å; for Rh_2OAc_4 **2** with water as an axial ligand is



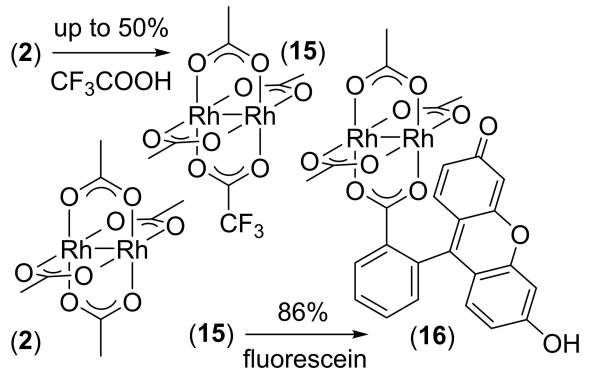
Scheme 6. Dirhodium complex **8** containing carbonyl group was designed for condensation reactions with organic hydrazines to get highly substituted complexes **9**. R^2 = H, COOH; R = biotin, maleimide, folic acid, Hoechst dye.



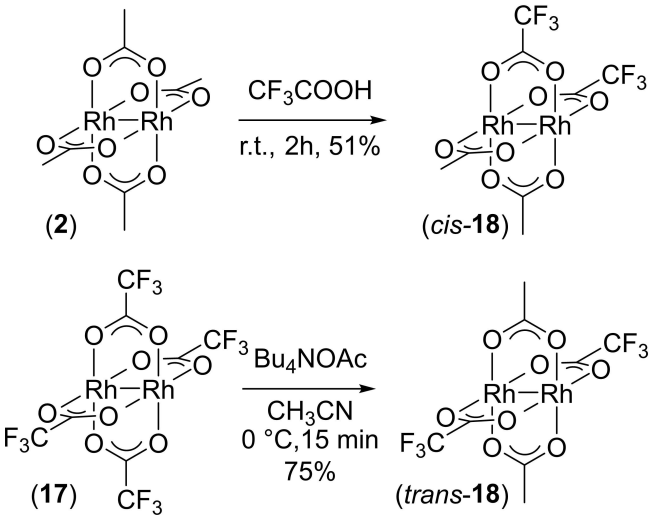
Scheme 7. Synthesis of complex **10** with terminal double bond designed for addition reactions or (co)-polymerizations. Complexes **11 a** and **11 b** were designed for transesterification reactions and amidations. Complex **11 c** was designed for Suzuki reaction with boronic acids (C–C coupling).



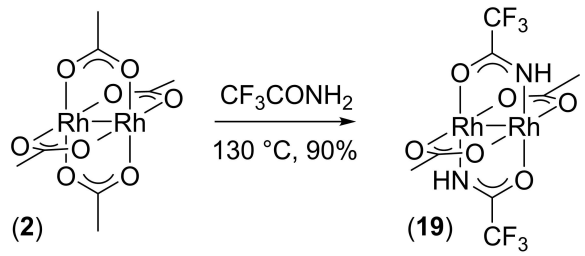
Scheme 8. Design of dirhodium(II,II) complex **13** with free amino group for the attachment of functional groups *via* amide bond formation towards poly- functional complexes **14**. These complexes found application as nitrene transfer catalysts in site-selective amination reactions.



Scheme 9. Formation of heteroleptic complex **16** by formal exchange of one bridging acetate ligand for fluorescein. The synthesis was performed by the preparation of the intermediate complex **15** and subsequent exchange of the labile trifluoroacetate ligand.

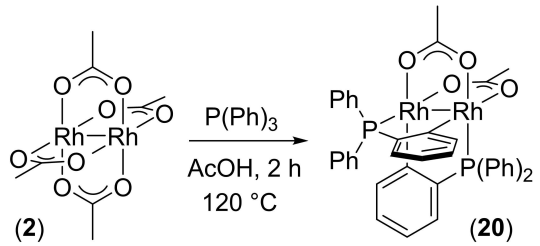


Scheme 10. Preparation of heteroleptic complexes, geometric isomers *cis*-**18** and *trans*-**18** from suitably chosen starting materials **2** and **17**.

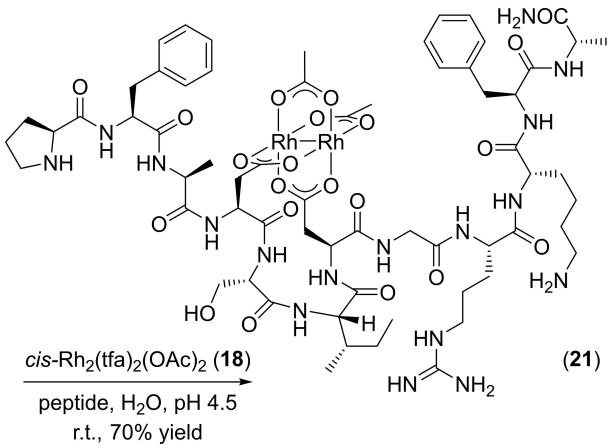


Scheme 11. Heteroleptic complexes with ligands containing different bridging atoms (O, N). Out of four different geometric isomers the *trans*-complex **19** was formed exclusively.

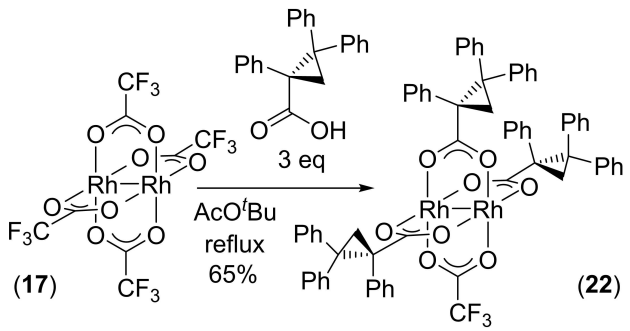
2.38 Å, with Et_2NH as an axial ligand is 2.40 Å).[9] The rhodium-rhodium bond is described according to the analytical data,[10] diamagnetism[11] and electronic spectra[12] as a single bond.[13] The unusual strength of this metal-metal single bond is explained by orbital mixing of the rhodium atom with the bridging ligands.[14] Both rhodium atoms have free coordination site in the axis of the Rh-Rh bond. The color of the complex and other electronic properties strongly depend on the ligand in this axial position. For example, if the axial ligand in the molecule of rhodium tetraacetate is water then the complex is green, if the axial ligand is ammonia then the complex is red.[15] Excited state properties such as life time, optical transition



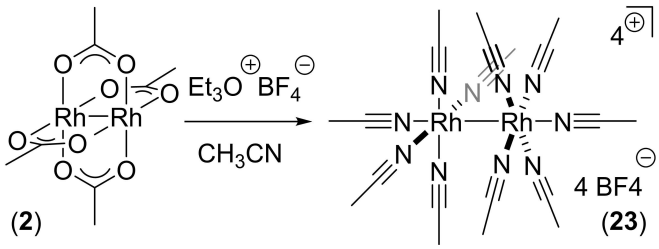
Scheme 12. Synthesis of heteroleptic complex *via* twofold Friedel-Crafts reaction of dirhodium(II,II) acetate with triphenyl phosphine. *Cis*-isomer **20** was formed exclusively and isolated.



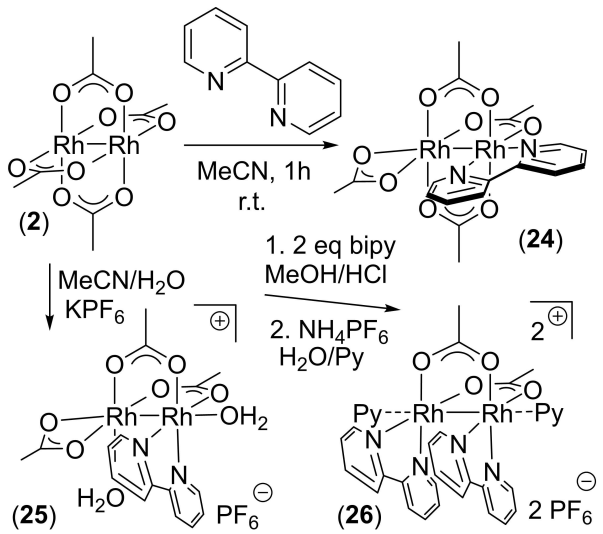
Scheme 13. Synthesis of dirhodium based metallo-peptide **21** used for modulating of the peptide chain structure.



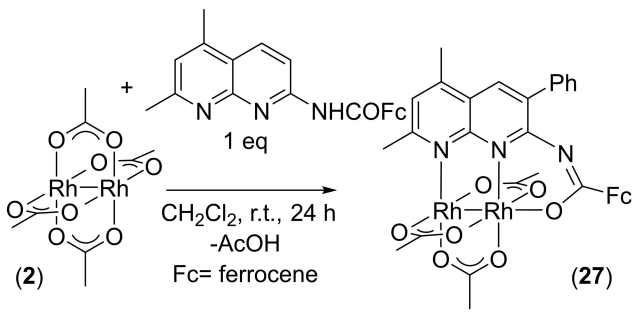
Scheme 14. Synthesis of heteroleptic complex **22** from **17** *via* threefold ligand exchange. Presumably, the steric effect of the ligand limits the number of exchanges.



Scheme 15. Irreversible removal of acetate ligands of complex **2** using alkylating agent in the presence of acetonitrile or other nitrogen containing ligand leads to the formation of dirhodium(II,II) complexes **23** without any bridging ligand.

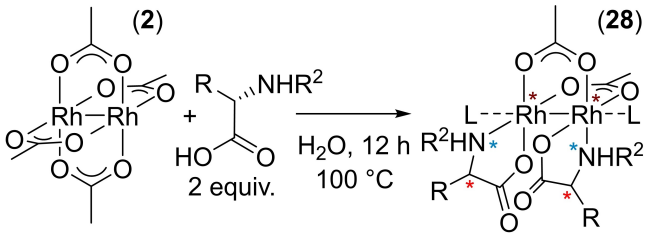


Scheme 16. Disruption of lantern structure of rhodium acetate **2** with 2,2′-bipyridine ligand under different reaction conditions.

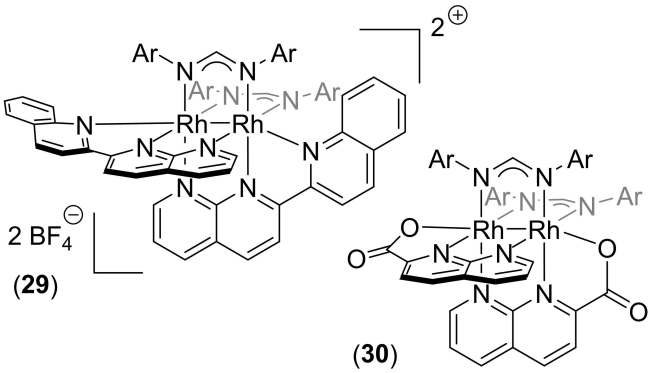


Scheme 17. Ligand exchange of bridging acetate for 2-amido-1,8-naphthyridine derived ligand in the molecule of dirhodium acetate **2** to form complex **27**.

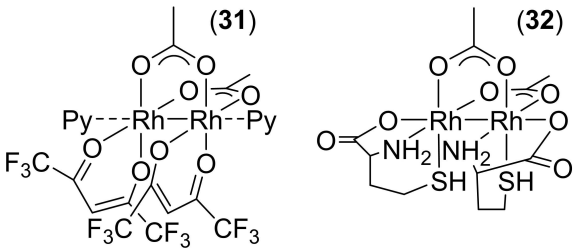
frequency and energy transfer of dirhodium carboxylates are independent of the axial ligand.[16] The dirhodium paddlewheel complex with a sterically demanding bridging carboxylate ligand (Figure 17, **P9**) was prepared to demonstrate that the axial positions can be blocked for intermolecular ligation.[17] The bridging anion can be also designed to contain moiety for intramolecular axial ligation.[18] The distance between the Rh atom and the axial ligand L is in the range between 2.2–2.5 Å and these values are typically listed. Bridging anions influence properties of the complex electronically and determine the resulting spatial shape of the complex.[19] The most frequent bridging anions are carboxylates[20] and carboxamidates,[21] accessibility of these as enantiopure starting materials allows the preparation of chiral dirhodium complexes that can be used for enantioselective processes.[22] The axial electrophilic site of the rhodium atom is exploited in catalysis[23] especially for transfer of electron deficient species such as carbenes or



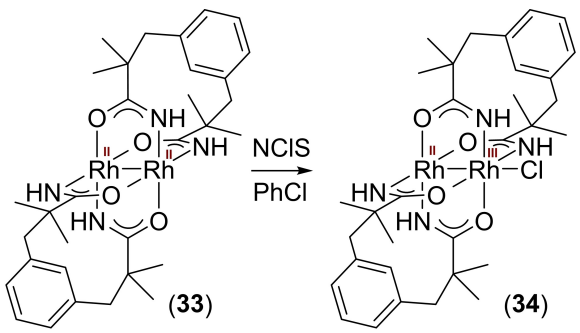
Scheme 18. Replacement of two acetate ligands in the complex **2** for chiral enantiopure *N*-substituted α-amino acid. Thermodynamically the most stable diastereomer is formed exclusively. L = H_2O.



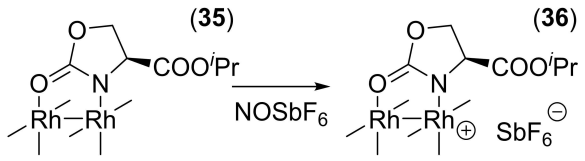
Scheme 19. Neutral **30** and cationic **29** complexes of 1,8-napthyridine derivatives.



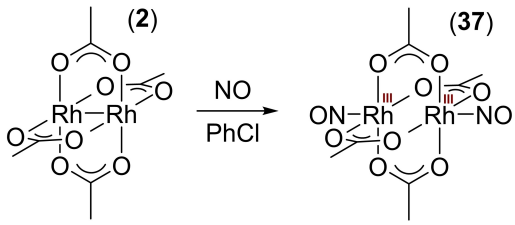
Scheme 20. Disruption of lantern structure with ligands containing also other heteroatoms than nitrogen as hexafluoroacetylacetonate complex **31** and methionine complex **32** (studied in context of cytotoxicity of dirhodium compounds exposed to physiological conditions).



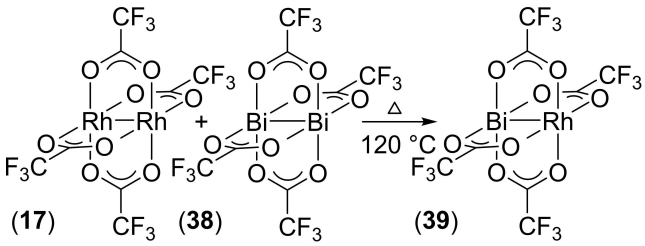
Scheme 21. Oxidation of dirhodium complex **33** by *N*-chlorosuccinimide. Complex **34** exhibits remarkable TON's as nitrenoid transfer catalyst in intramolecular C–H amination reactions.



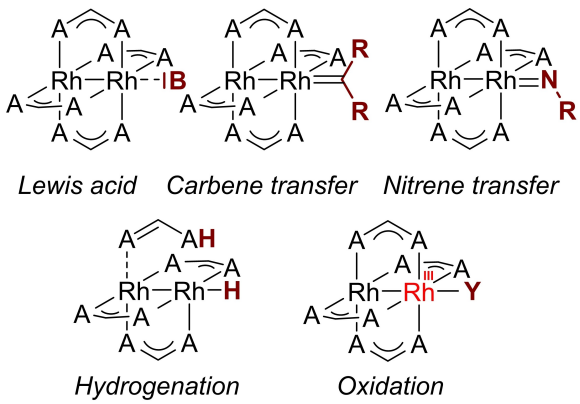
Scheme 22. Oxidation of dirhodium(II,II) paddlewheel complex **35** by nitrosyl hexafluoroantimonate to dirhodium(II,III) cationic complex **36**. This complex is used as Lewis acidic catalyst in enantioselective [2 + 3] cycloaddition reactions.



Scheme 23. Oxidation of dirhodium tetraacetate **2** by NO, cleavage of rhodium-rhodium bond. The distance of rhodium atoms in complex **37** is 2.52 Å.

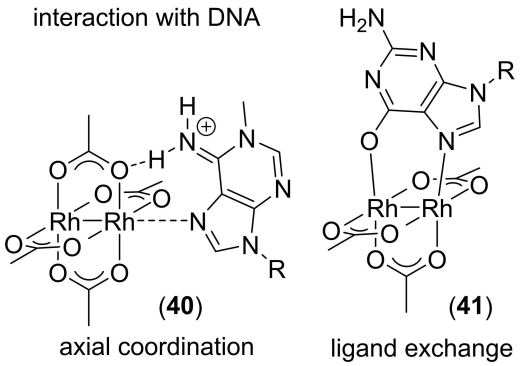


Scheme 24. Synthesis of Rh-Bi heterometallic paddlewheel complex **39** by heating of stoichiometric mixture of $Rh_2(OOCCF_3)_4$ and $Bi_2(OOCCF_3)_4$ in glass ampoule.

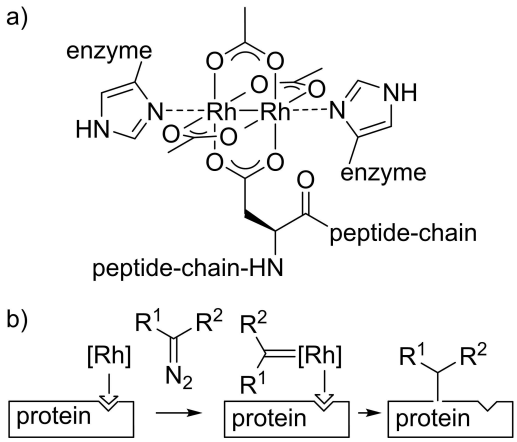


Scheme 25. Important intermediates relevant for applications in catalysis were confirmed, with the exception of the intermediate splitting molecular hydrogen, which is here just proposed.

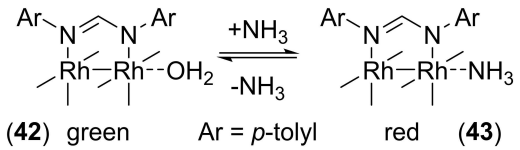
nitrenes. The electron donating ability of the bridging anions influence stabilization of the electron deficient ligated species in axial position through the metal back bonding and thus



Scheme 26. Interaction of dirhodium tetraacetate **2** with DNA.



Scheme 27. Dirhodium(II,II) peptide complexes developed for (a) reversible binding or for (b) covalent marking of peptides.



Scheme 28. Detectors based on the change of properties during axial ligand exchange. An example, complex **42** is green, complex **43** is red.

modulate its reactivity.[24] Electron deficiency of the rhodium atom can be correlated with the oxidation potential of the complex and these values are recorded for model complexes from individual categories (e.g., $E_{1/2}$ for $Rh_2(OAc)_4 = 1.02$ V in DCM, for Rh_2(caprolactamate)$_4 = 0.05$ V in CH_3CN).[25] Lewis acidic properties of the complexes are also exploited in other fields of catalysis or in different applications. For example, axial ligands with two nucleophilic sites can be used to connect dirhodium complexes into the coordination polymer networks.[26]

All bridging anions can be exchanged for different bridging anions and new homoleptic complexes are described. Exchange of one, two or three bridging anions with a structurally different bridging anion leads to the formation of heteroleptic complexes. The bridging anion can be composed of two same binding atoms (O, N, P, C, S) or the atoms are different. If the two binding atoms are not equivalent (chemically, or due to symmetry of the ligand) then it gives rise to the formation of geometric isomers. The ratio of such isomers reflects the kinetics of the ligand exchange, thermodynamic stability of resulting complexes and physical properties as solubility of the individual isomeric complexes.

3. Syntheses of dirhodium(II,II) complexes

3.1. From rhodium trichloride

Rhodium trichloride **1** is the main inorganic precursor for the preparation of dirhodium(II,II) paddlewheel complexes (Scheme 1). Rhodium acetate **2** was one of the first complexes prepared using the following method: A mixture of rhodium chloride, sodium acetate, acetic acid and ethanol is refluxed under inert gas to obtain dirhodium acetate.[27] Rhodium carboxylates of stronger acids as for example trifluoroacetic acid are prepared directly from corresponding sodium salts in ethanol.[28] It has been deduced that ethanol serves as reducing agent in this synthesis. This reaction was proven to proceed through intermediate **3** $Rh_4(\mu\text{-}Cl)_4(\mu\text{-}OAc)_4$, which was isolated and fully characterized.[29] This method is used for the preparation of dirhodium (II) paddlewheel complexes in cases when the educt (organic acid) is not soluble in organic solvents. Rhodium hydroxide can be also used for the synthesis of rhodium paddlewheel complexes, but the yields are lower due to formation of rhodium metal.[15]

3.2. Bridging ligand exchange

The majority of homoleptic dirhodium complexes are prepared by the bridging ligand exchange from dirhodium tetraacetate **2**. Dirhodium(II,II) tetrakis(trifluoroacetate) **17** was the first compound synthesized using this method.[15] The general procedure is following: The ligand, organic acid, which is loaded in an excess is refluxed in high boiling solvents such as toluene or chlorobenzene with the rhodium acetate **2**. During the reaction the releasing acetic acid is continuously removed (distilled off) from the reaction mixture to shift the equilibrium towards the new complex. The ligand exchange proceeds in three formal steps.[30] Coordination of the new ligand to the dirhodium complex in axial position, disruption of the bridge, *i.e.* protonation of the acetate ligand and subsequent release of acetic acid accompanied by bridging ligand replacement. This process continues until all four acetates are replaced for a new ligand (Scheme 2). The ligand exchange leads to the mixture of isomers, if the bridging ligand contains two different binding atoms or the ligand is not symmetrical. The ratio of isomers can be changed according to the reaction conditions (kinetic *versus* thermodynamic control of the ligand exchange reaction). The kinetics of the exchange reaction is dominated by the trans-effect (*i.e.*, labilization of the exchanging ligand due to electron

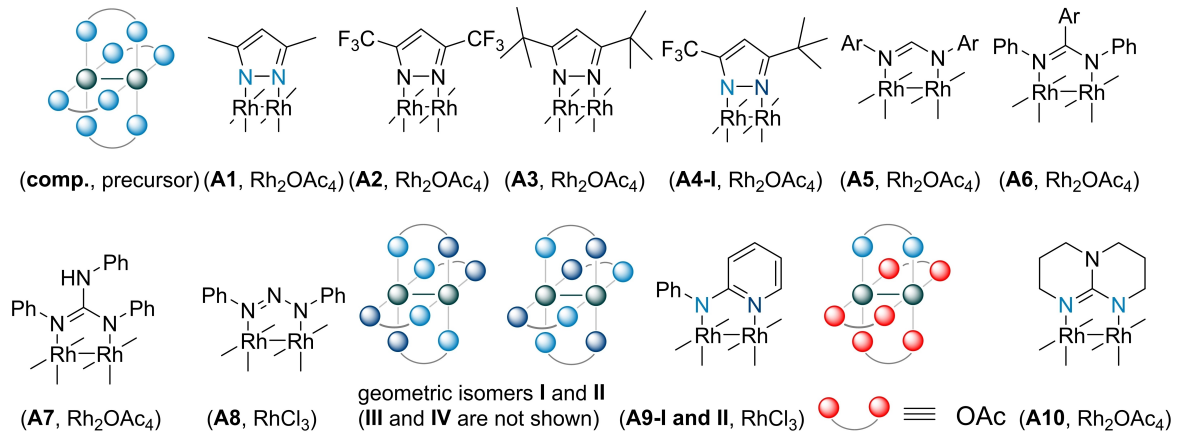


Figure 3. Dirhodium(II,II) complexes containing *N,N'*-bridging ligands: **A1**,[124] **A2**,[125] **A3**,[125] **A4**,[125] **A5**: Ar=Ph,[126] **A5**: Ar=C_6H_4-(*p*-CF_3, *p*-Cl, *p*-OCH_3, *m*-OCH_3),[127] **A5**: Ar = $C_6H_{3/4}$-(*p*-Me, *m*-Me, *m*-Cl, *m*-CF_3, 3,4-Cl_2, 3,5-Cl_2),[25] A5: Ar=C_6H_4-(*p*-F, *p*-Me, *o*-F, *o*-Me),[109] **A6**: Ar=C_6H_4(*p*-Br, *p*-NH_2, *p*-tethered Ru complex by amide bond),[40] **A6**: Ar = *p*-Py,[128] **A7**,[127] **A8**,[129] **A9**,[130] **A10**.[131]

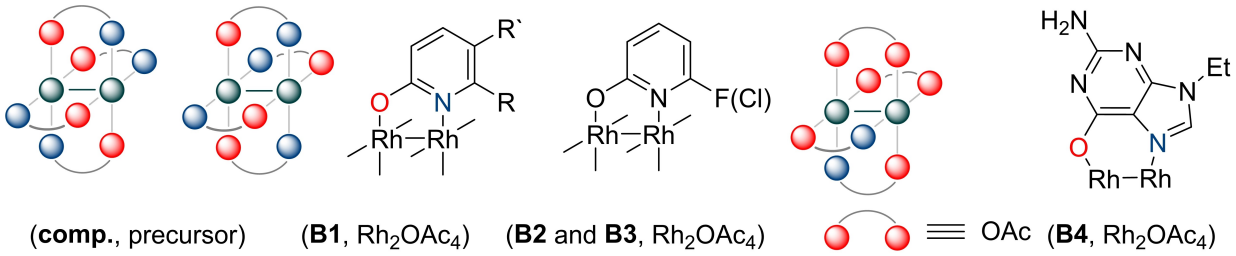


Figure 4. Dirhodium(II,II) complexes containing *N,O*-bridging ligands: **B1** R = Me, R' = H,[132] **B1** R = CHMeEt, R' = H,[133] **B1** R = H, R′ = COOMent,[133] **B2** (F),[134] **B3** (Cl),[134] **B4**.[118]

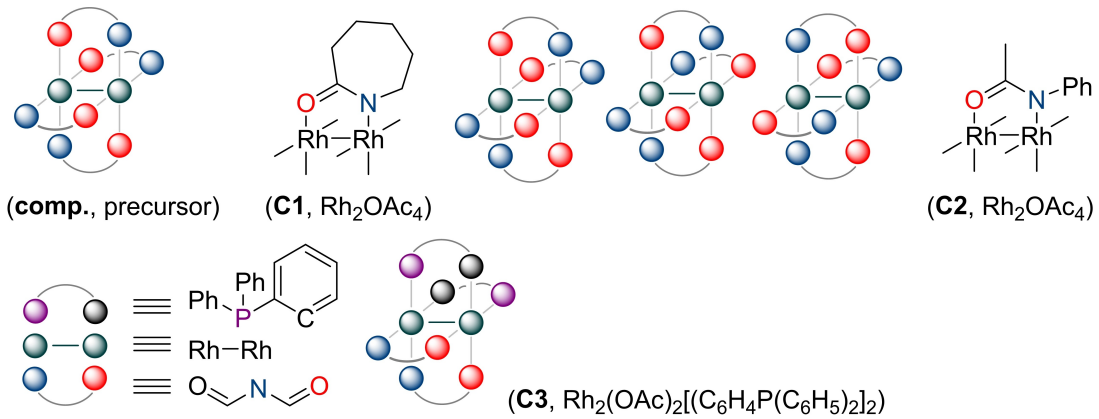


Figure 5. Dirhodium(II,II) complexes containing *N,O*-bridging ligands: **C1**,[135] **C2**,[136] **C3**.[137]

donation of the bridging ligand atom in *trans* position on the same rhodium atom).

This phenomenon is reflected in the syntheses of dirhodium (II,II) tetrakiscarboxamidates, carbamates and other complexes containing (*N,O*)-bridging ligands, since nitrogen is stronger σ-donor than oxygen (Scheme 3). In some cases, the trans-effect can be used to control the number of ligand exchanges for the selective formation of heteroleptic complexes (section 4.1). If the reaction conditions allow reversible exchange of ligands, which is very often the case, the thermodynamically more stable complexes are formed and typically only the major isomer is isolated and described as **5** or the mixture of geometric isomers is obtained and the preparative separation of these complexes follows (Scheme 3).[31]

There is only one report, in which the authors succeeded in isolating the kinetic product 4 in the class of (*N,O*)-bridging ligand containing dirhodium complexes (the bridging ligand is in this case a carbamate derivative E5 (Figure 12).[32]

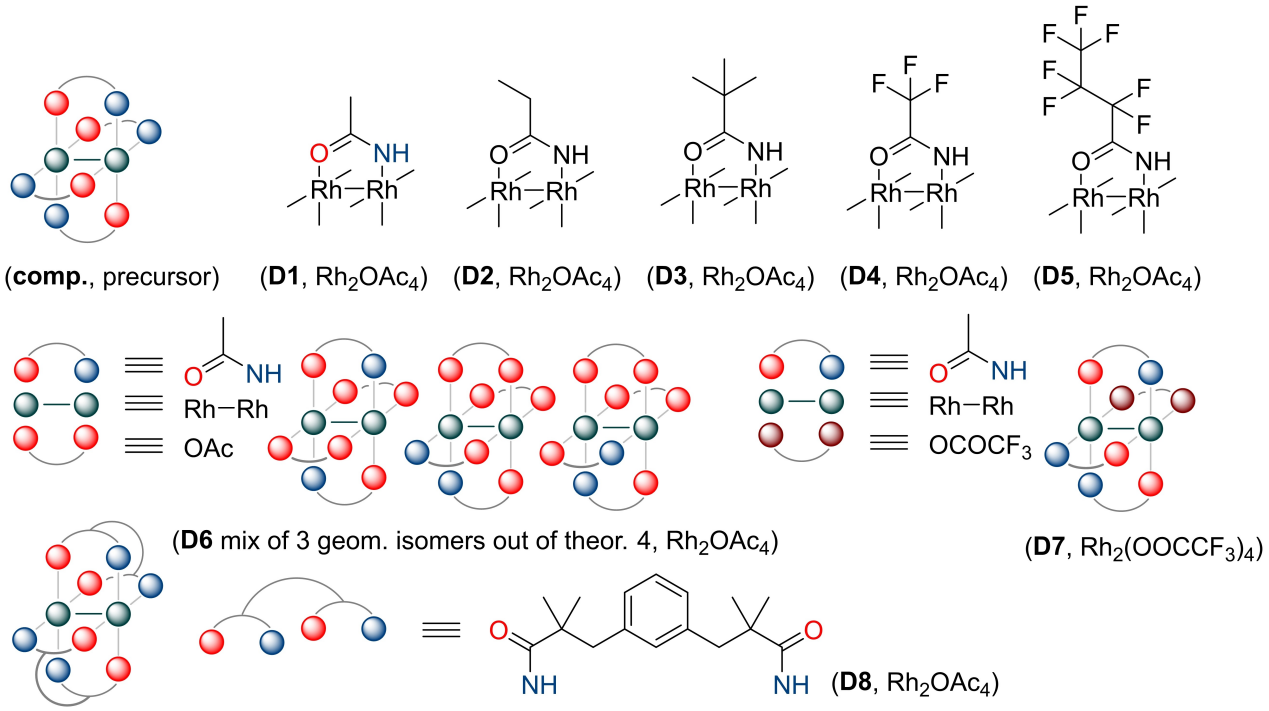


Figure 6. Dirhodium(II,II) complexes containing *N,O*-bridging ligands (achiral amidates derived from $RCONH_2$): **D1**,[138] **D2**,[139] **D3**,[140] **D4**,[141] **D5**,[142] **D6** (heteroleptic complexes with various acetamide/acetate ratio described, [138] **D7** (heteroleptic complexes with various acetamide/trifluoroacetate ratio described),[143] **D8**.[60]

Ligand exchange reactions can be performed in water as a solvent, in such cases rhodium carbonate $Na_4Rh(CO_3)_4$ is typically used as a starting material.[33]

3.3. Functionalization of the organic part of the complex

Dirhodium(II,II) complexes are relatively stable in mild acidic or basic media, which can be exploited for post-functionalization reactions and purification of resulting complexes by methods commonly used in organic chemistry such as column chromatography on silica gel. Post-functionalization of rhodium complexes, *i.e.* the direct modification of the organic part of the complex enables implementation of functional groups that are not tolerated by the ligand exchange procedures mentioned in section 3. Either these functional groups degrade during the ligand exchange process or they hinder the ligand exchange. A further advantage of post-functionalization reactions is the late stage structural modification, which speeds up the synthesis of a broad variety of desired complexes. So far only few methods have been developed to decorate dirhodium paddlewheel complexes with additional functional groups by covalent bond formation reaction directly on the organic part of the dirhodium complex (Scheme 4).

Complex **6** with unprotected hydroxyl group was prepared by ligand exchange method from *cis*-dirhodium diacetate di (trifluoroacetate) complex **18** (Scheme 5). Complex **6** was isolated and used as a starting material in the carbonate formation reaction. This reaction enabled to connect the dirhodium paddlewheel complex **6** with the organic moiety containing strained carbon-carbon triple bond to form complex **7**.[34] Huisgen cycloaddition of azides with reactive alkynes, also called strain promoted azide-alkyne cycloaddition (SPAAC),[35] is a frequently used "click" reaction for various conjugations, for example of metal complexes with proteins. In another work complex **6** was used as starting material to prepare biotinylated complex (connected through the hydroxyl group), which was then embedded within streptavidin enzyme variant to form artificial metalloenzyme. This metalloenzyme was used for enantioselective carbene transfer reactions.[36]

Complex **8** with a free carbonyl group was developed to implement new functionalities *via* hydrazone bond formation with hydrazine derivatives.[37] Hydrazone bond formation proceeds at mild acidic conditions at room temperature and is also commonly used to connect various (bio)-molecules. In this case, dirhodium complex **8** was connected with derivatives of biotin, maleimide, folic acid and Hoechst dye to form substituted complexes **9** (Scheme 6).

Complex **10** with terminal carbon-carbon double bond was prepared by ligand exchange from dirhodium tetrakis trifluoroacetate **17**.[38] Replacement of trifluoroacetate group, the ligand exchange proceeds at low temperatures under which terminal double bonds do not degrade. The resulting complex **10** was isolated and used for (co)-polymerization reactions to immobilize the dirhodium complex on solid support and use in heterogeneous catalysis. Complex **11a** with an ethylcarboxylate group served as precursor for amidation reaction with benzylic amines, which were connected to solid polymer support

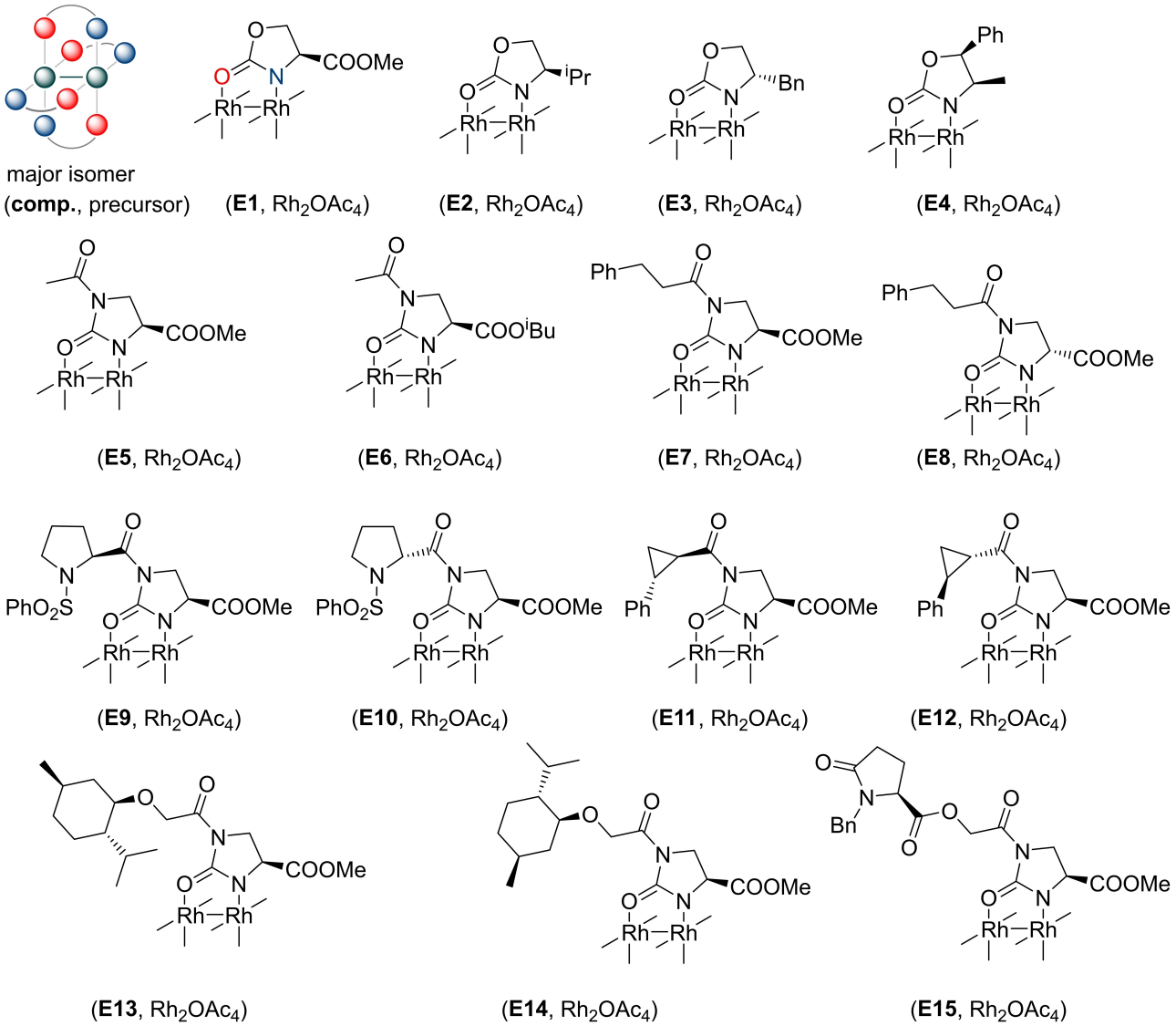


Figure 7. Dirhodium(II,II) complexes containing *N,O*-bridging ligands (carbamates and ureates): **E1**,[144] **E2**,[133] **E3**,[145] **E4**,[133] **E5**,[146] **E6**,[147] **E7**,[148] **E8**,[148] **E9**,[149] **E10**,[149] **E11**,[149] **E12**,[149] **E13**,[150] **E14**,[150] **E15**.[150]

(Scheme 7).[39] Complex **11 a** was prepared by ligand exchange from dirhodium acetate **2**. Complex **11 b** (Scheme 7) was prepared by palladium catalyzed Hartwig-Buchwald amination using benzophenonimine as a coupling reagent from the corresponding bromo-derivative (**A6**, Figure 3), which was prepared by ligand exchange from rhodium acetate **2**. Complex **11 b** was used for the connection of Ru(II) complexes *via* covalent amide bond. Resulting heterometallic compounds are studied as potential photo-active devices for hydrogen production from water.[40] Complex **11 c** (Scheme 7) was designed for C–C coupling reactions with boronic acid derivatives.[41] The resulting bulky complexes served as catalysts for carbene transfer reactions in the C–H functionalization of alkanes.

Complex **12** was prepared by ligand exchange from dirhodium tetraacetate **2** and *N*-protected adamantane based artificial γ-amino acid. Hydrogenolysis of the Cbz protecting group with hydrogen catalyzed by Pd/C was performed to prepare complex **13** with sterically shielded free amino group. This complex is configurationally stable, can be isolated and was post-functionalized *via* amide bond formation using activated organic esters or organic isocyanates.[42] Dirhodium lantern complexes of amino acids, in which the unprotected amine group is not sterically shielded are not bench stable and undergo structural (in this work unspecified) rearrangements to different type of complexes (Scheme 8).

4. Reactivity of dirhodium(II,II) complexes

4.1. Formation of heteroleptic paddlewheel complexes

The exchange of one, two or three bridging ligands of the homoleptic dirhodium complex leads to the formation of heteroleptic complexes. Selected examples are ordered by the

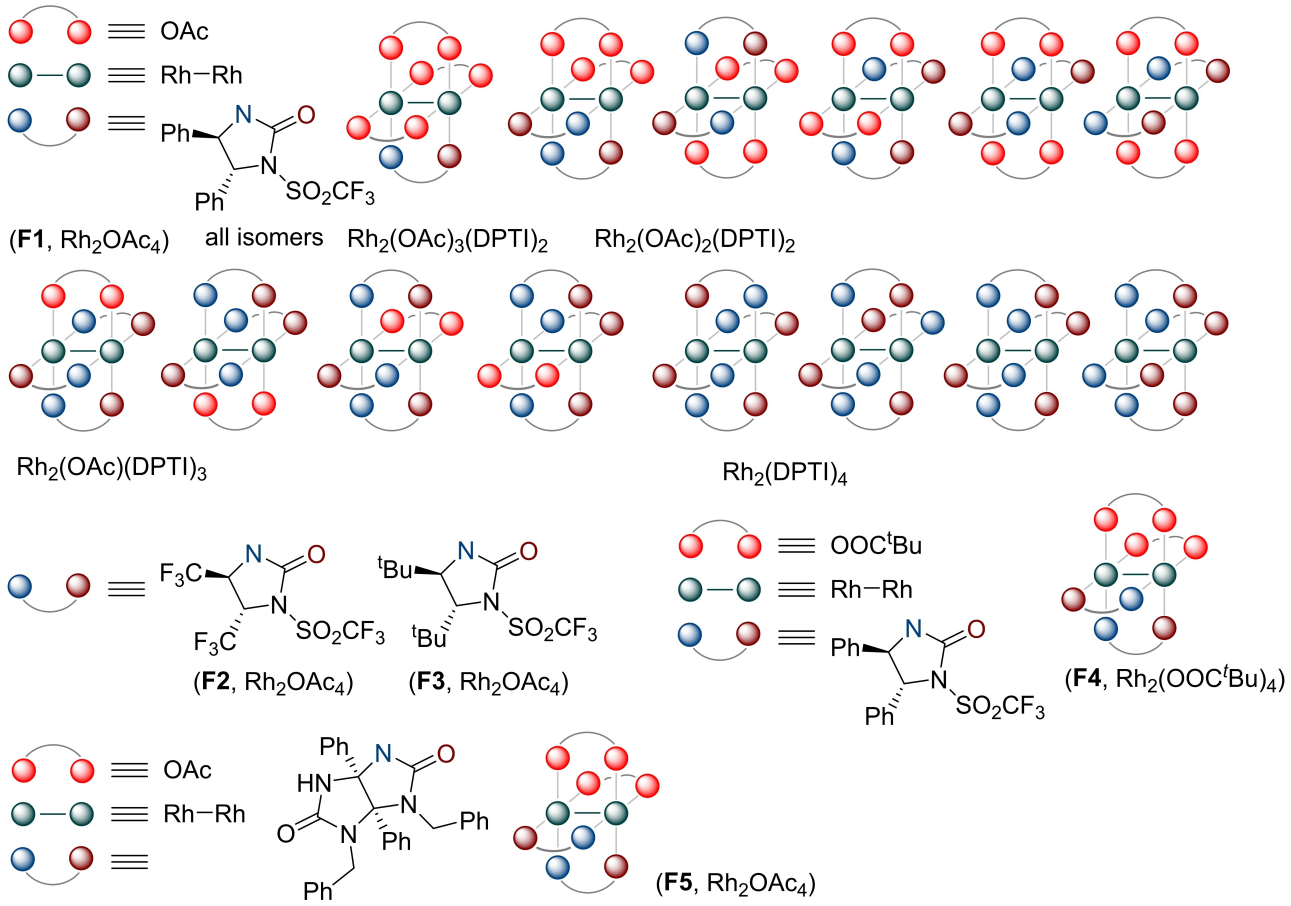


Figure 8. Dirhodium(II,II) complexes containing *N,O*-bridging ligands (ureates): **F1**,[151] **F2**,[152] **F3**,[151] **F4**,[153] **F5**.[154]

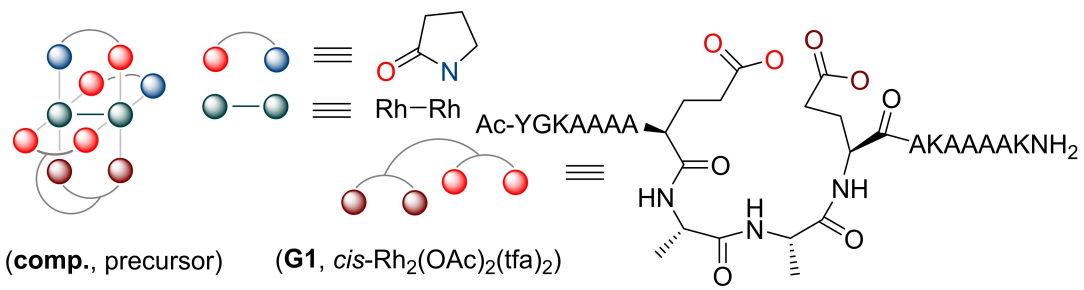


Figure 9. Dirhodium(II,II) complexes containing *N,O*-bridging ligands (amidates): **G1**.[155]

number of ligand exchanges. Partial ligand exchanges are difficult to control and typically lead to a mixture of complexes. Desired complexes, according to their properties, can be separated by crystallization, chromatography on silica-gel, HPLC or using other separation techniques.

The replacement of one bridging ligand (acetate) for the ligand with similar binding properties (carboxylate) is synthetically the most difficult task as demonstrated on the preparation of complex **16**.[43] A direct ligand exchange from dirhodium tetraacetate **2** would lead to a statistical mixture of heteroleptic complexes. To solve this problem complex **15** with labile sacrificial trifluoroacetate group was prepared first and then this group was replaced by the new ligand in 86% yield (Scheme 9). The yield of the *mono*-substituted complex **15** is unfortunately not reported in the literature. If two ligands significantly differ in bridging ability/stabilization of ligand rhodium bond then there is a possibility to control the exchange process. The dominance of the trans-effect in kinetic controlled ligand exchange reactions was demonstrated in the targeted preparation of heteroleptic complexes *cis*-**18** and *trans*-**18**.[44] The twofold ligand exchange of acetate for trifluoroacetate starting from dirhodium tetraacetate **2** leads to the formation of *cis*-geometric isomer **18**, while starting from

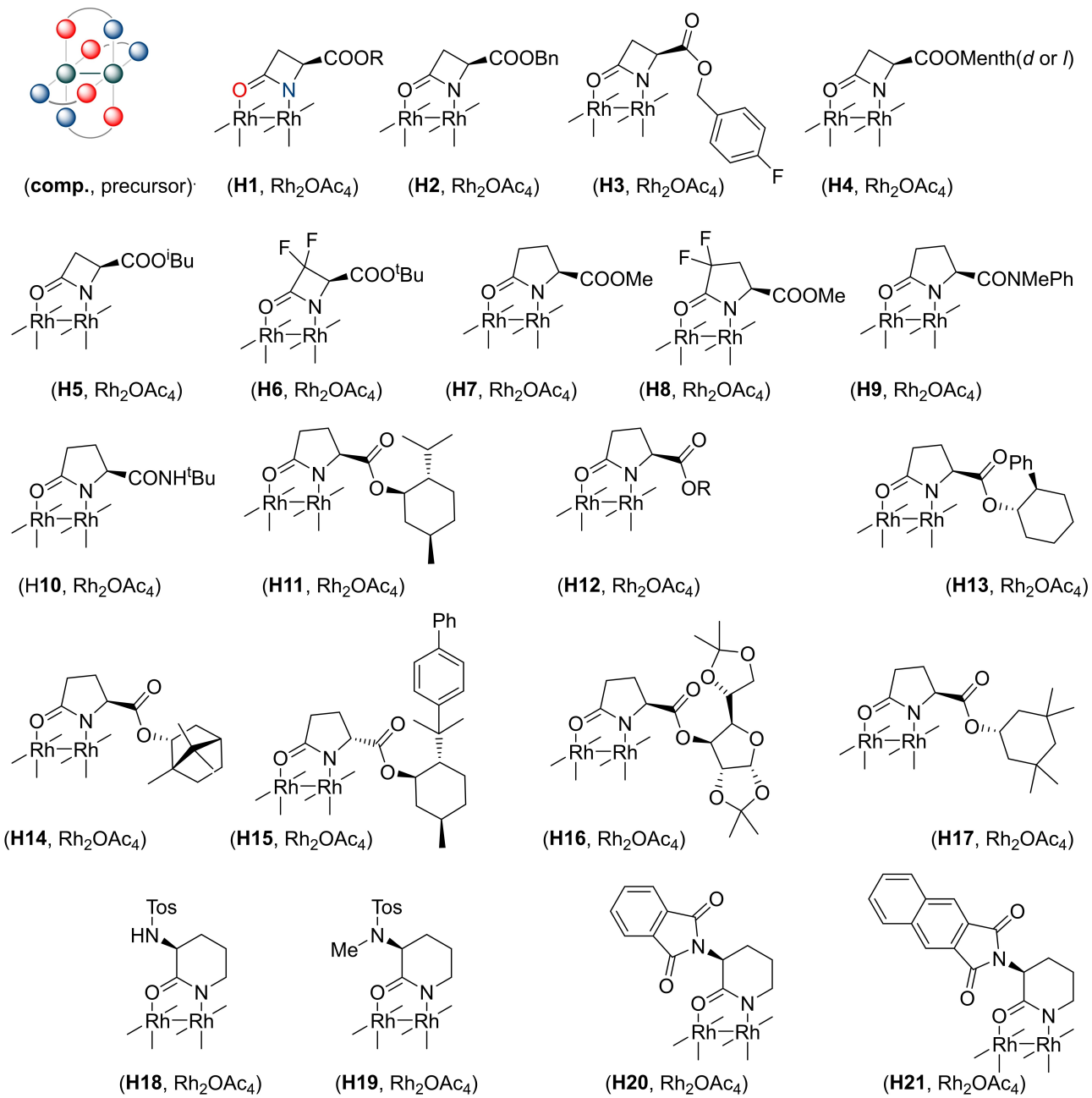


Figure 10. Dirhodium(II,II) complexes containing *N,O*-bridging ligands (chiral amidates): **H1**: R = Me, $CH_2{}^tBu$, cyclohexyl,[156] **H2**,[157] **H3**,[158] **H4** (OMenth = menthol),[159] **H5**,[157] **H6**,[160] **H7**,[161] **H8**,[160] **H9**,[162] **H10**,[162] **H11**,[62] **H12**: R = cyclohexyl, cyclooctyl, 2-adamantyl,[77] **H13**,[162] **H14**,[162] **H15**,[162] **H16**,[162] **H17**,[162] **H18**,[163] **H19**,[164] **H20**,[165] **H21**.[165]

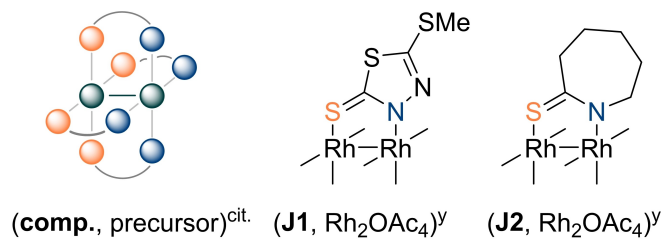


Figure 11. Dirhodium(II,II) complexes containing *N,S*-bridging ligands: **J1**,[166] **J2**.[167]

dirhodium tetrakis(trifluoroacetate) **17** leads to the formation of *trans*-isomer **18** (Scheme 10).

An example that demonstrates the combination of kinetic and thermodynamic effects is the synthesis of heteroleptic complex $Rh_2(OAc)_2(HNCOCF_3)_2$ **19**. Exclusive formation of one isomer (out of four geometrical isomers) of heteroleptic complex **19** in high 90% yield was observed when Rh_2OAc_4 **2** was refluxed at 130 °C in CF_3CONH_2 as solvent for one day. In this case the partial exchange of two acetate ligands leads to the product with carboxamidate bridges *trans* to each other (trans-effect) and thermodynamically more stable is the isomer

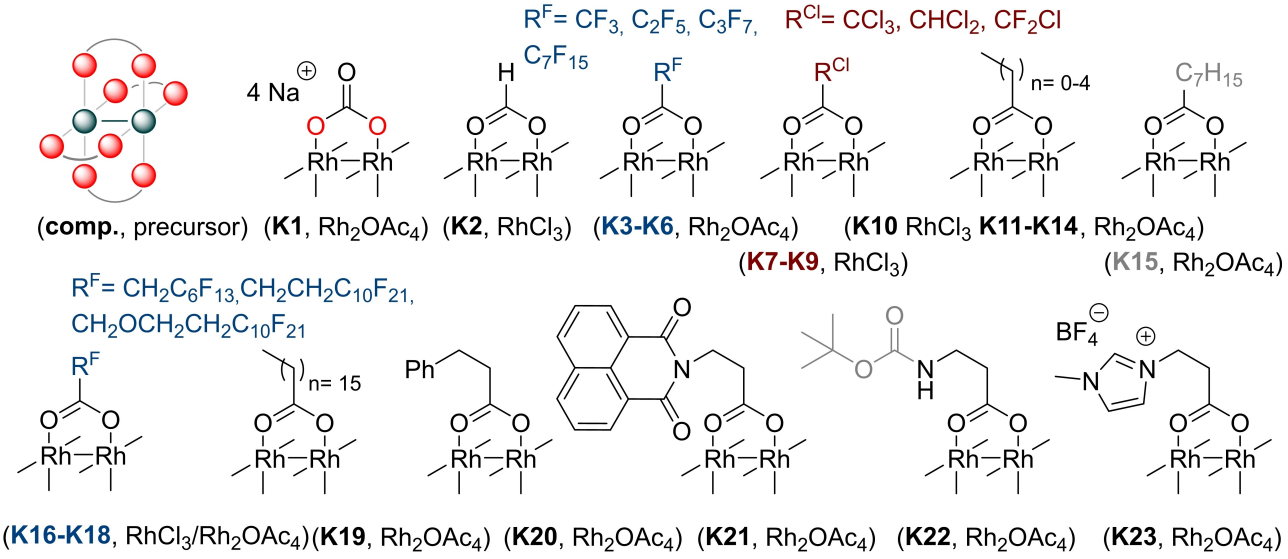


Figure 12. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive $OOCCH_2R$ and fluorinated analogues: **K1**,[168] **K2** (the first complex in the history of dirhodium(II,II) paddlewheel complexes),[169] **K3**,[15] **K4**,[170] **K5**,[171] **K6**,[172] **K7**,[28] **K8**,[28] **K9**,[28] **K10**,[8] **K11**,[173] **K12**,[173] **K13**,[173] **K14**,[173] **K15**,[174] **K16**,[175] **K17**,[175] **K18**,[175] **K19**,[170] **K20**,[176] **K21**,[177] **K22** (including the complex as Boc deprotected salt),[178] **K23**.[179]

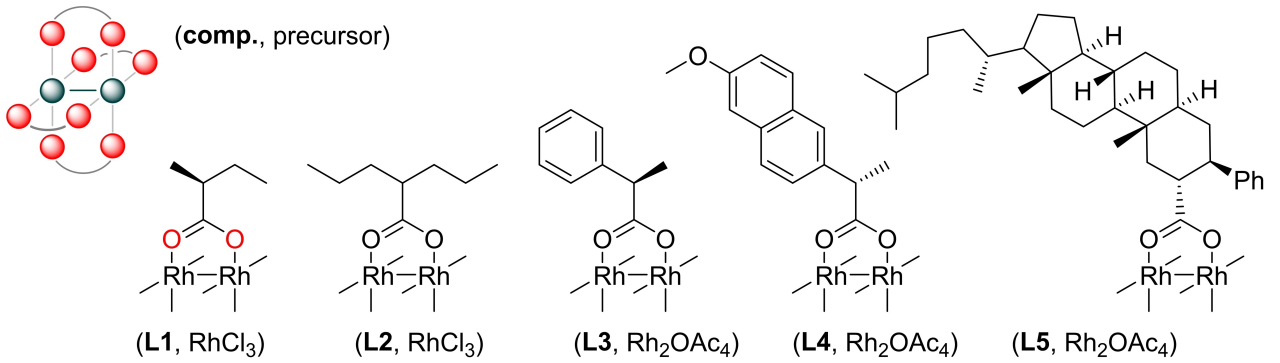


Figure 13. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHRR': **L1**,[180] **L2**,[181] **L3**,[182] **L4**,[182] **L5**.[183]

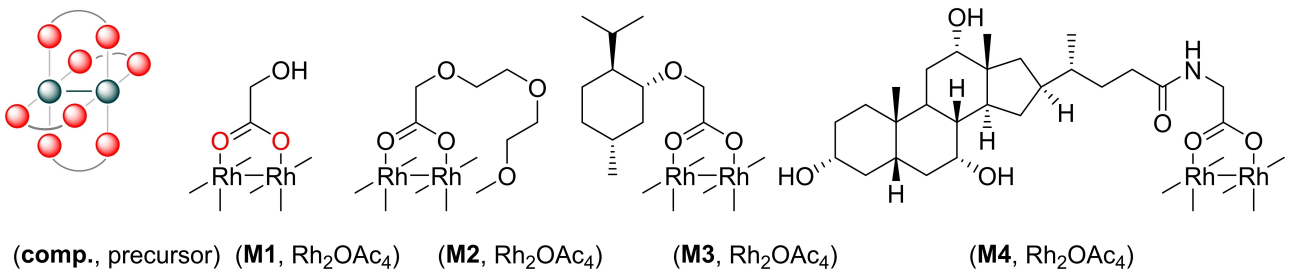


Figure 14. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive $OOCCH_2Het$; Het = heteroatom: **M1**,[111] **M2**,[184] **M3**,[182] **M4**.[182]

with C_i symmetry. Carboxamidate ligands are *trans* to each other in the complex framework and nitrogen atoms do not share the same rhodium atom in the complex **19** (Scheme 11).[45]

Heteroleptic complexes can vary in nature of bridging heteroatoms (C, N, O, P, S) as demonstrated on the reaction of rhodium acetate **2** with triphenylphosphine (Scheme 12):[46] Twofold Friedel-Crafts reaction leads to the formation of paddlewheel complex **20** bridging Rh-Rh bond through carbon and phosphorus atoms. Only one geometric isomer **20** is formed in this reaction.

The synthesis of heteroleptic complexes with three different ligands was demonstrated on the preparation metallo-peptide **21**.[47] Precursor for this exchange reaction was the *cis*-complex

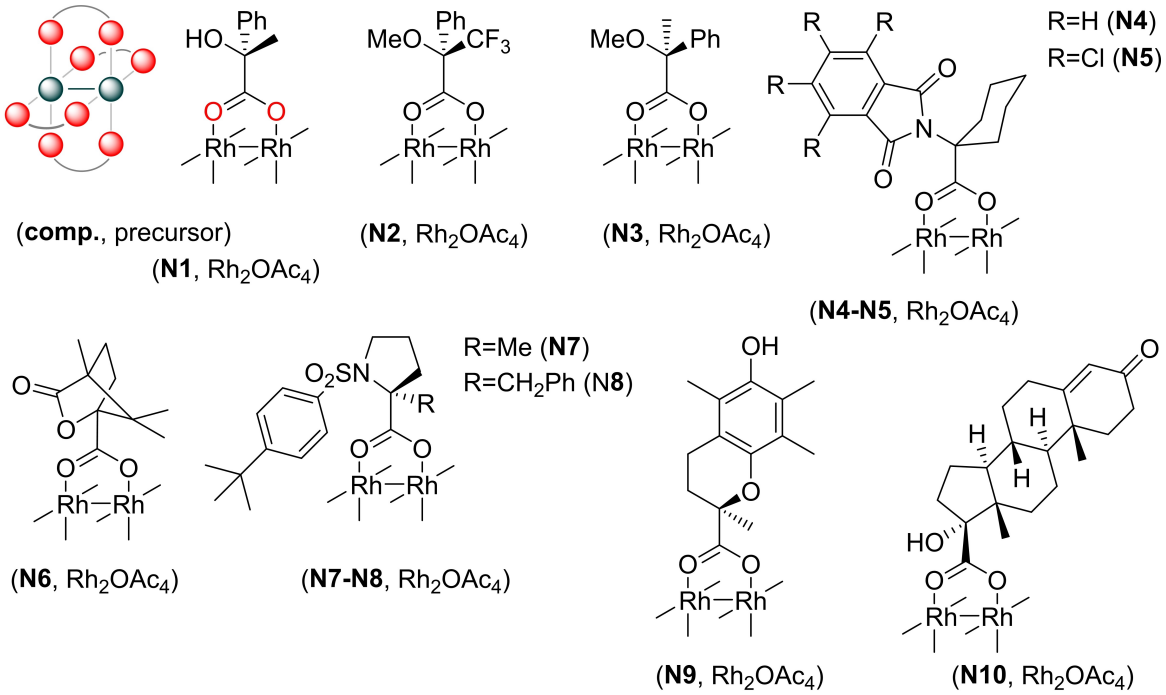


Figure 15. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCRR'Het; Het = heteroatom, R,R' = alkyl or aryl: **N1**,[182] **N2**,[5] **N3**,[182] **N4**,[185] **N5**,[186] **N6**,[187] **N7**,[188] **N8**,[188] **N9**,[182] **N10**.[182]

18, with labile (weaker trans-effect) trifluoroacetate bridging ligands. Exchanging carboxylates of the peptide precursor are chemically different, which leads to the formation of geometric isomers. Desired isomer **21** was separated using HPLC (Scheme 13).

Presumably, steric factors enabled to partially control the threefold exchange of trifluoroacetate ligand for the bulky carboxylate in the synthesis of heteroleptic dirhodium complex **22**. The 65% yield of the desired complex under stated conditions is remarkably high (Scheme 14).[48]

To the best of my knowledge, dirhodium(II,II) complexes with four different bridging ligands have not been reported so far.

4.2. Disruption of the lantern structure

Nitrogen coordinates strongly to the rhodium atom, which leads to the formation of structurally different complexes. One heteroatom containing molecules coordinate in the axial position of the dirhodium paddlewheel complexes as a dative ligand. If the removal of the bridging ligand is irreversible (Scheme 15) as demonstrated with triethyloxonium tetrafluoroborate, which alkylates the acetate, then compounds as acetonitrile form square planar complexes around each of the rhodium atom and coordinate also in the axis of rhodium-rhodium bond.[49] This type of dirhodium(II,II) "wheel" complexes as **23** lacking μ-bridging ligands can be formed also with other compounds as porphyrins,[50] imine[51] or oxime derivatives.[52] The rhodium-rhodium bond in such complexes is much weaker and can be thermally broken.

Compounds containing two spatially separated heteroatoms can bind two molecules of dirhodium complexes and form supramolecular structures keeping the paddlewheel framework. Two or more heteroatoms in proximity (1,1' or 1,2-substituted) containing ligands as naphthyridines, phenanthrolines, bipyridines and other can disrupt the lantern structure and form new complexes with different geometries. For example 2,2'-bipyridine breaks the lantern structure by binding to one atom of rhodium to form complex **24** with three bridging acetates and one non-bridging (Scheme 16).[53] The same ligand under different exchange conditions can remove one acetate completely while forming complex **25**.[53] Ligand exchange reaction with two equivalents of 2,2'-bipyridine leads to the formation of complex **26**.[54]

Generally, bridging type of complexation is denominated μ, complexation to one atom is denominated κ, for contiguous atoms then η. The kappa convention is used together with μ when it is necessary to specify which central atoms are bridged, and through which donor atoms. Compound with three heteroatoms can be designed that both types of ligation occur within the same ligand as exemplified on the preparation of complex **27** (Scheme 17).[55] The binding of the nitrogen containing ligands can be bridging or the bidentate ligand can bind to each atom of rhodium separately.

If the two binding atoms are different or if the bidentate ligand is not symmetrical then the resulting complex of type **28** is chiral as the rhodium atom becomes stereogenic. If the ligand itself is chiral that means it contains stereogenic element then

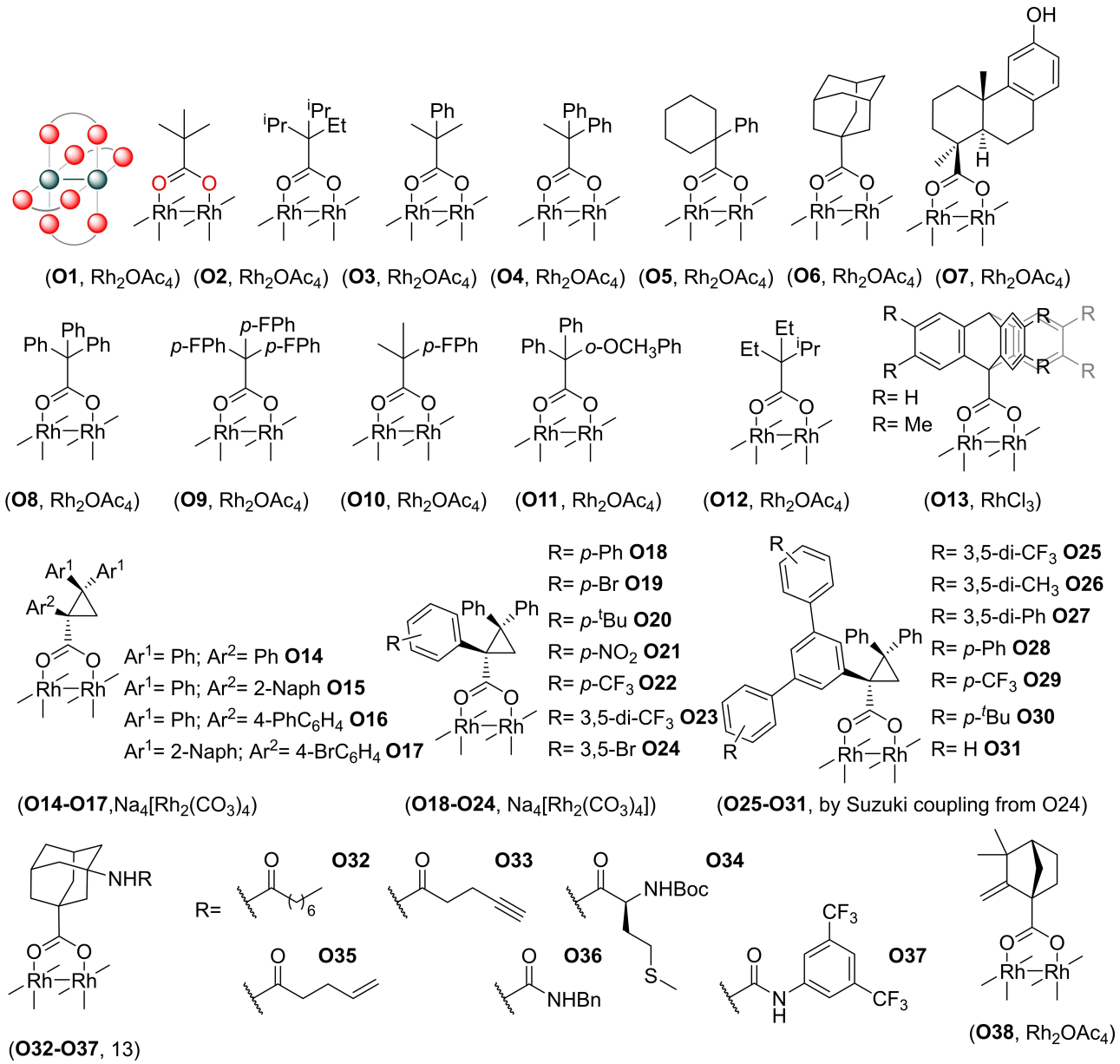


Figure 16. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCR^{1}R^{2}R^3: **O1**,[189] **O2**,[190] **O3**,[190] **O4**,[191] **O5**,[185] **O6**,[192] **O7**,[193] **O8**,[191] **O9**,[194] **O10**,[194] **O11**,[194] **O12**,[194] **O13**: R = H,[195] R = Me,[196] **O14**,[197] **O15**,[197] **O16**,[197] **O17**,[197] **O18**,[41] **O19**,[41] **O20**,[41] **O21**,[41] **O22**,[41] **O23**,[41] **O24**,[41] **O25**,[41] **O26**,[41] **O27**,[41] **O28**,[41] **O29**,[41] **O30**,[41] **O31**,[41] **O32**,[42] **O33**,[42] **O34**,[42] **O35**,[42] **O36**,[42] **O37**,[42] **O38**.[182]

the diastereomers are formed. If the nitrogen atom is substituted then the complexation hinders the inversion on the nitrogen and this atom is also stable stereogenic center. Interestingly, in the case of *N*-substituted enantiopure α-amino acids only one isomer of the dirhodium complex **28** was formed and isolated (Scheme 18). The absolute configuration of resulting complexes was determined using ECD, VCD and NMR spectroscopy.[56]

Various homoleptic or heteroleptic complexes are used as precursors for the ligand exchange reactions. Five- and six-membered rhodium containing rings are formed preferentially. The ligand exchange can lead to the formation of neutral complexes as **30** or cationic complexes as **29** with non-coordinating anion (Scheme 19).[57]

Complexes **29**, **30** and related derivatives are now tested and applied as photosensitizers for water splitting to generate molecular hydrogen.[57]

The disruption of lantern structure can occur also with ligands containing other heteroatoms than nitrogen. Examples of complexes with hexafluoro acetylacetonate ligand **31**[58] and with racemic amino acid methionine **32**[59] are shown in Scheme 20.

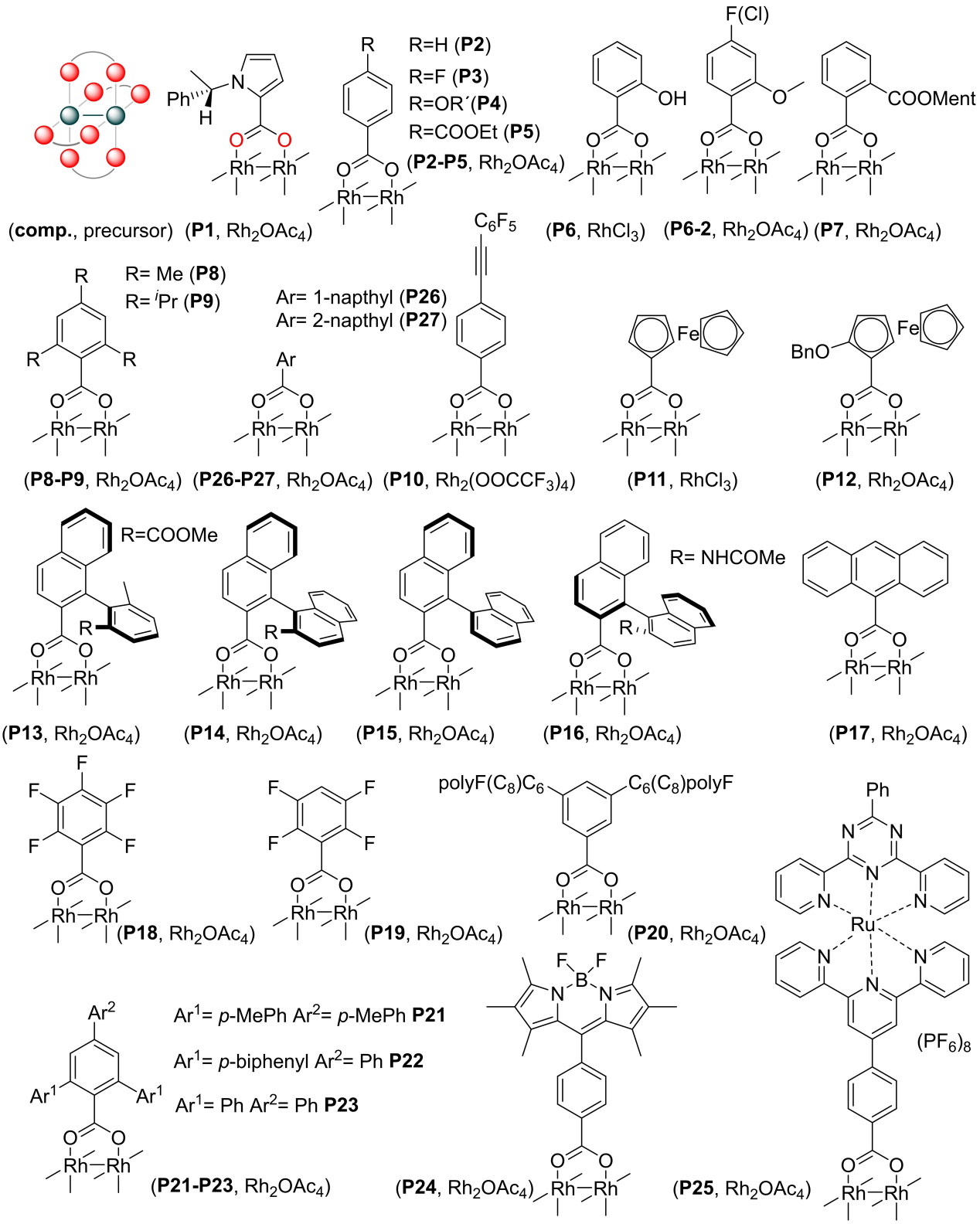


Figure 17. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCAr: **P1**,[182] **P2**,[198] **P3**,[24] **P4** R' = Me,[199] **P4** R' = C_9H_{19}, R' = $C_{13}H_{27}$,[200] **P5**,[39] **P6**,[201] **P6-2** (Cl),[202] **P6-2** (F),[203] **P7**,[182] **P8**,[204] **P9**,[17] **P10**,[205] **P11**,[206] **P12**,[207] **P13**,[208] **P14**,[208] **P15**,[208] **P16**,[209] **P17**,[194] **P18**,[210] **P19**,[211] **P20**,[212] **P21**,[213] **P22**,[213] **P23**,[213] **P24**,[214] **P25**,[215] **P26**,[273] **P27**.[273]

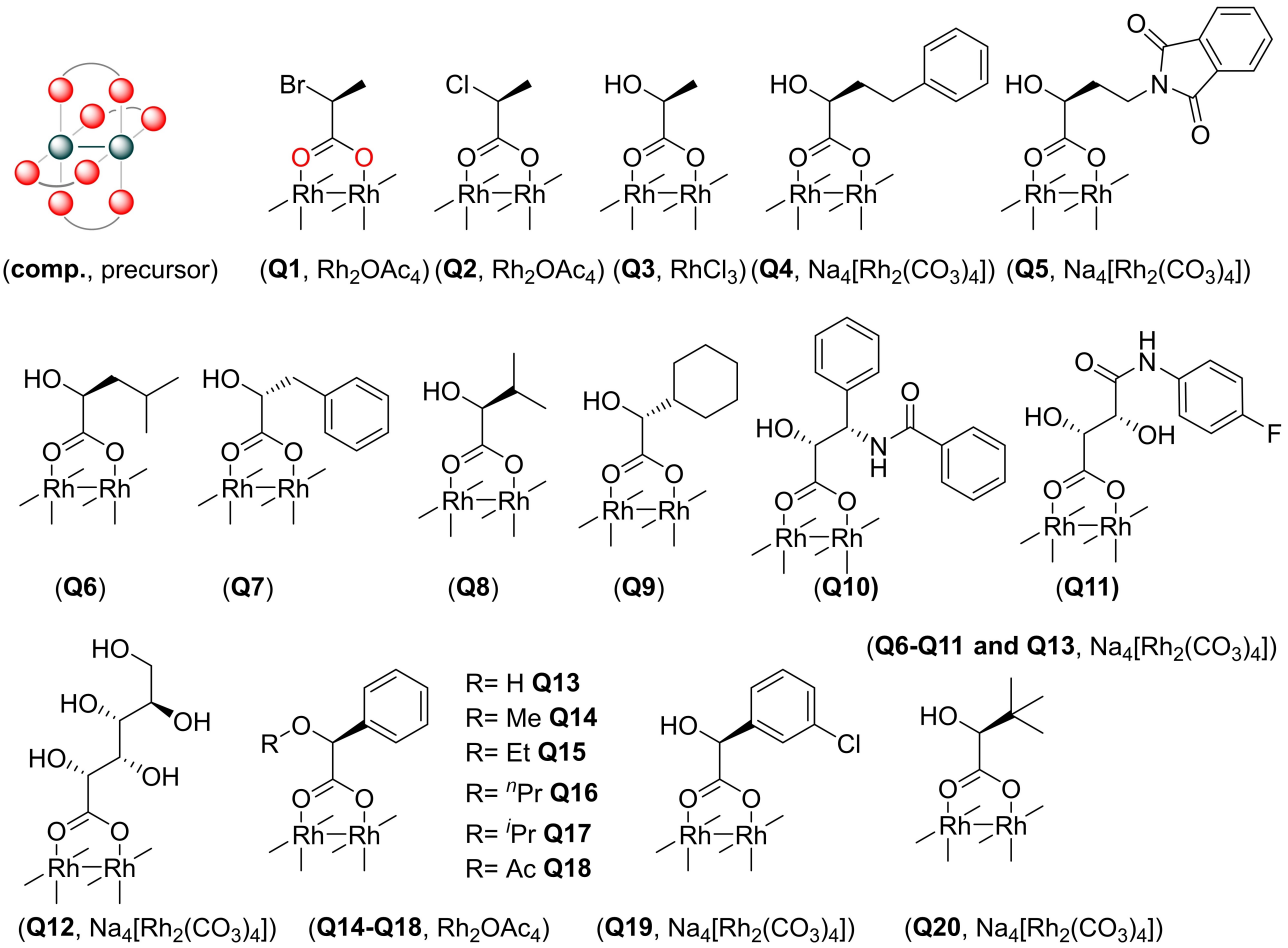


Figure 18. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHHetR; Het = oxygen or halogen, R = alkyl or aryl: **Q1**,[216] **Q2**,[189] **Q3**,[180] **Q4**,[182] **Q5**,[182] **Q6**,[182] **Q7**,[182] **Q8**,[182] **Q9**,[182] **Q10**,[182] **Q11**,[182] **Q12**,[182] **Q13**,[217] **Q14**,[187] **Q15**,[182] **Q16**,[182] **Q17**,[182] **Q18**,[182] **Q19**,[182] **Q20**.[182]

4.3. Oxidation of rhodium atom in paddlewheel complexes

Oxidants in stoichiometric amounts to the dirhodium complex can remove electron from one of the rhodium atom and form complexes, which are highly Lewis acidic.

Complexes with *O,N*-bridging ligands such as **34**[60] or **36**[61] are stable and can be prepared, whereas the isolation of dirhodium (II,III) complexes with *O,O'*-bridging ligands has not been reported. The excess of an oxidant leads to the cleavage of the rhodium-rhodium bond and further transformations. The anion either binds to the rhodium atom in axial position like chloride in complex **33** (Scheme 21) or does not coordinate as in the case of **36** with hexafluoroantimonate and other non-coordinating anions as hexafluorophosphate or tetrafluoroborate (Scheme 22).

Chiral dirhodium(II,III) complexes can be used as Lewis acid catalysts for example as in enantioselective [2 + 3] cycloaddition reactions[61] or hetero-Diels-Alder reactions.[62]

4.4. Rhodium-rhodium bond cleavage

The use of two equivalents or an excess of an oxidant can lead to the cleavage of the metal-metal bond keeping the paddlewheel structure of bridging ligands. The complex **37** was prepared by oxidation of dirhodium tetraacetate **2** by NO gas. The structure was confirmed by X-ray crystallography showing significantly prolonged distance between rhodium atoms (2.52 Å) and computationally (Scheme 23).[63] Another protocol employing Cu(II) catalyst, arylboronic acid as an substrate and oxygen as an oxidant demonstrates that the Rh-Rh bond can be cleaved irreversibly to form stable *bis*-aryl-dirhodium(III) tetrakis carboxamidate complexes.[64]

There are number of oxidative procedures, which lead to the formation of monomeric Rh(III) complexes from dirhodium complexes, one example is the reaction of dirhodium acetate **2** with arylsulfinic acid under aerobic conditions, which leads to the formation of $Rh(O_2SAr)_3$.[65]

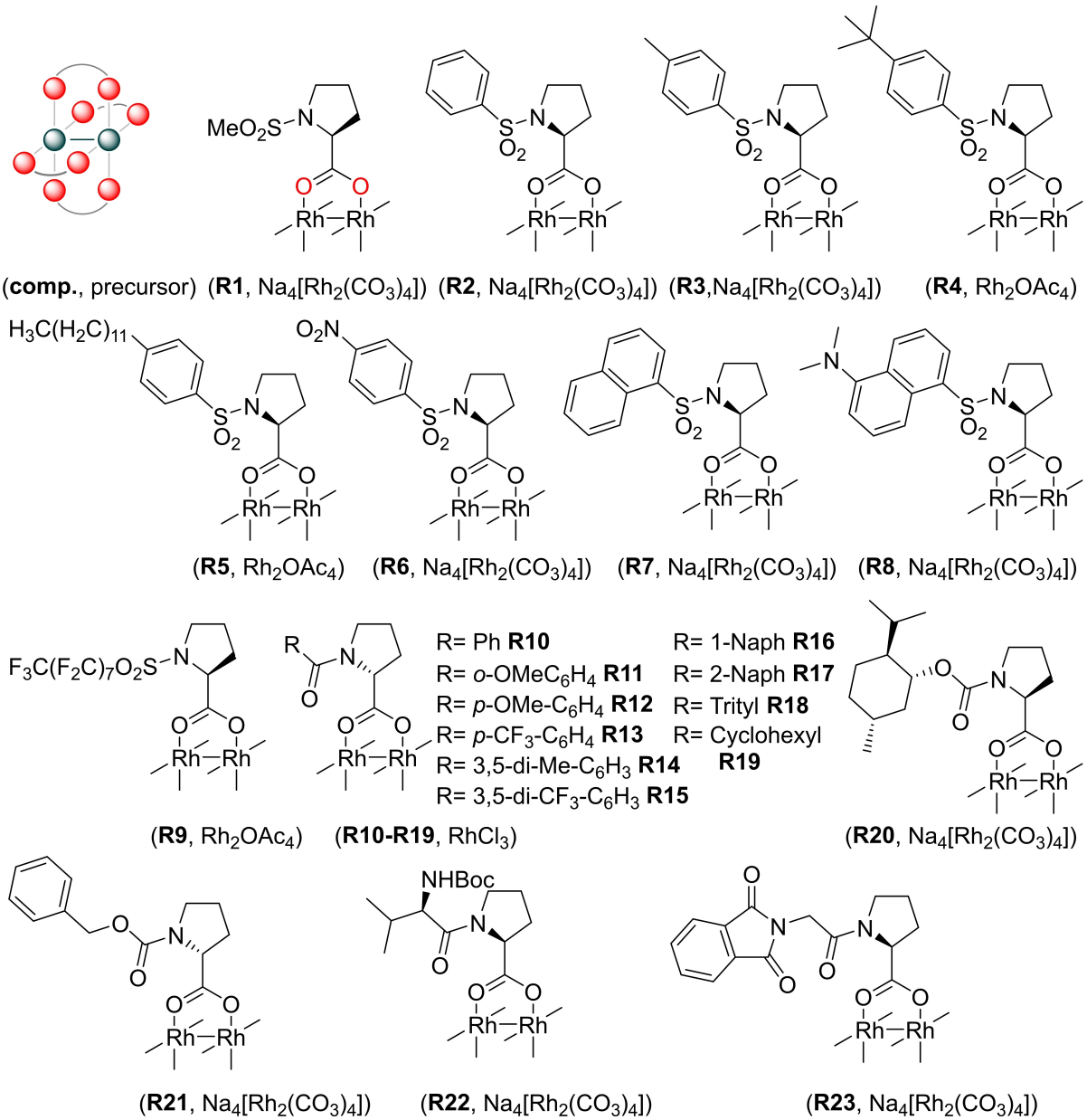


Figure 19. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHHetR; Het = nitrogen, R = alkyl or aryl (proline derivatives): **R1**,[218] **R2**,[219] **R3**,[220] **R4**,[221] **R5**,[222] **R6**,[182] **R7**,[223] **R8**,[182] **R9**,[224] **R10**,[225] **R11**,[225] **R12**,[225] **R13**,[225] **R14**,[225] **R15**,[225] **R16**,[225] **R17**,[225] **R18**,[225] **R19**,[225] **R20**,[223] **R21**,[182] **R22**,[182] **R23**.[182]

4.5. Replacement of one Rh atom by Bi in paddlewheel complexes

Heating a stoichiometric mixture of two bimetallic complexes dirhodium tetrakis(trifluoroacetate) **17** and dibismuth tetrakis-(trifluoroacetate) **38** leads to the formation of heterometallic complex bismuth-rhodium tetrakis(trifluoroacetate) **39** with lantern structure of bridging ligands (Scheme 24).[66] The synthesis of this complex **39** was developed in solution to increase the yield of the transformation.[67] Complex **39** is used as starting material for the preparation of various Bi-Rh paddlewheel complexes by ligand exchange reactions (Figure 26).[68] Such complexes are used in catalysis and their reactivity is compared with dirhodium(II,II) analogs to study the effect of metal-metal interactions.[69] The enhanced electrophilicity of the rhodium atom in Bi-Rh paddlewheel complexes (due to interaction between 4*d* orbitals of rhodium and 6*p* orbitals of Bi, also resulting in reduced π-back bonding to the species bound in axial position) can lead in some cases to different reaction outcomes as demonstrated on the catalyzed insertion of carbenes into the molecule of dichloromethane.[70]

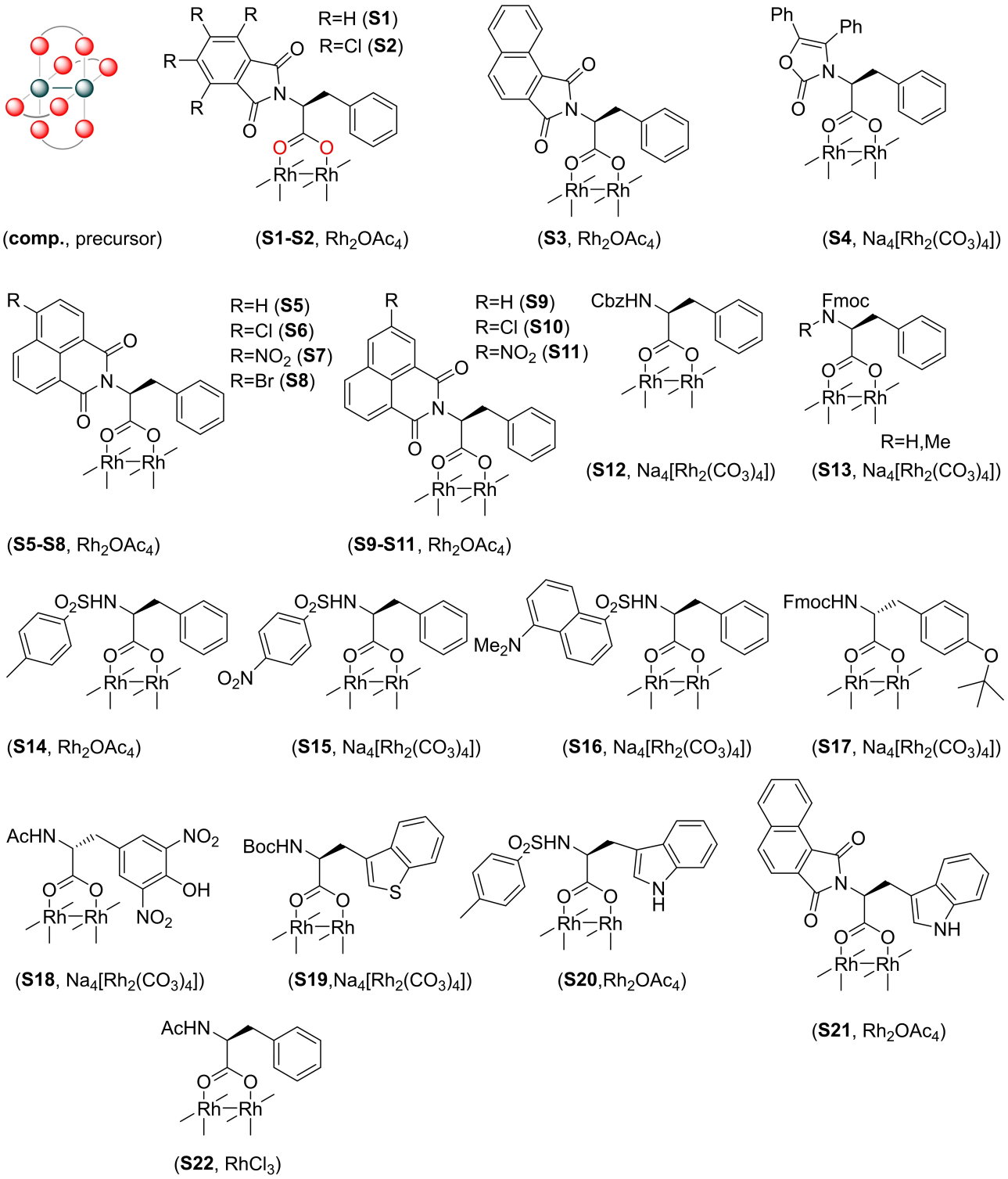


Figure 20. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHHetR; Het = nitrogen, R = alkyl or aryl (α-amino acid derivatives): **S1**,[226] **S2**,[206] **S3**,[227] **S4**,[223] **S5**,[228] **S6**,[229] **S7**,[229] **S8**,[229] **S9**,[228] **S10**,[229] **S11**,[229] **S12**,[182] **S13**,[182] **S14**,[33] **S15**,[230] **S16**,[182] **S17**,[182] **S18**,[182] **S19**,[182] **S20**,[231] **S21**,[227] **S22**.[180]

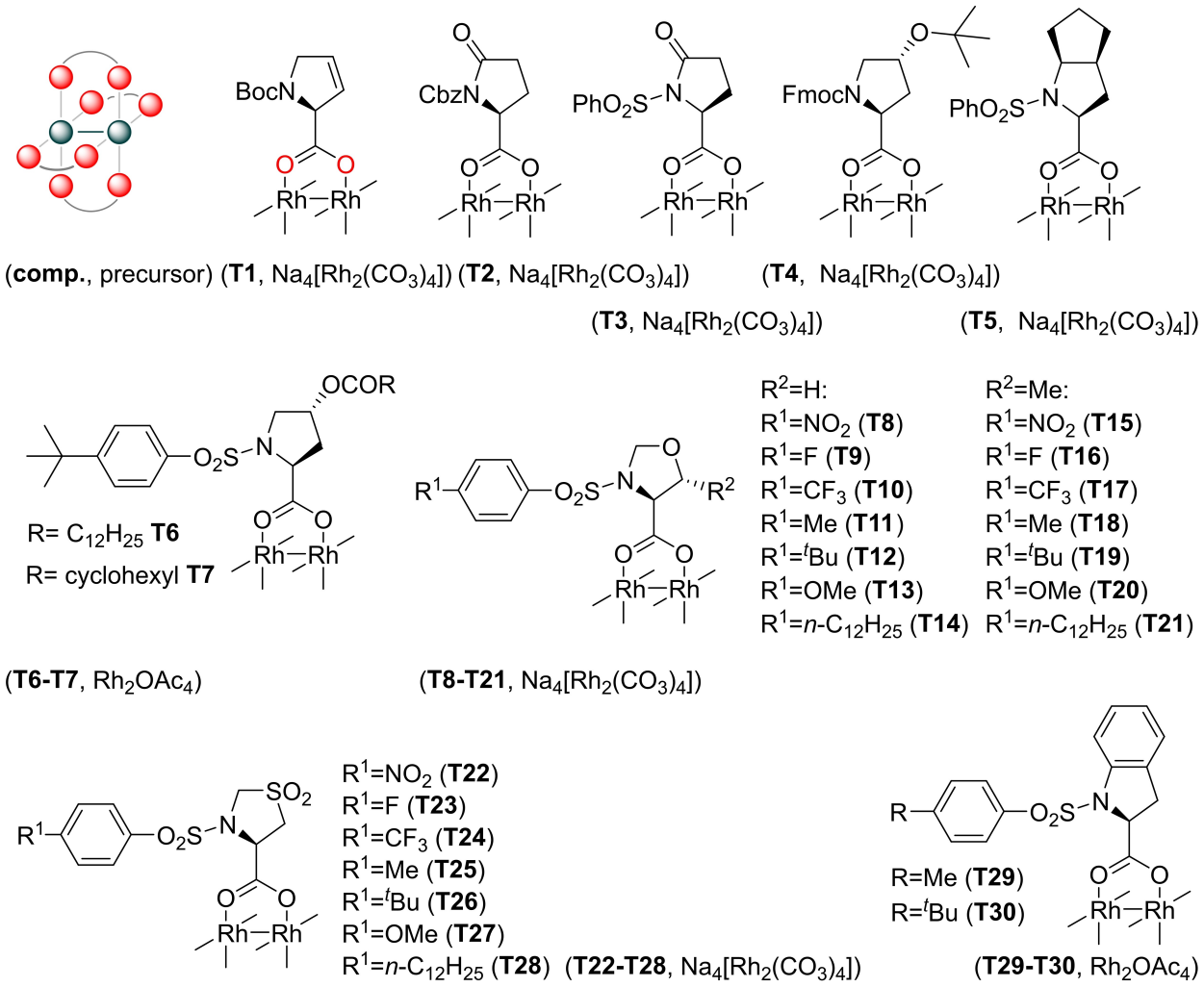


Figure 21. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHHetR; Het = nitrogen, R = alkyl or aryl (cyclic α-amino acid derivatives): **T1**,[182] **T2**,[182] **T3**,[232] **T4**,[182] **T5**,[223] **T6**,[233] **T7**,[233] **T8**,[234] **T9**,[234] **T10**,[234] **T11**,[234] **T12**,[234] **T13**,[234] **T14**,[234] **T15**,[234] **T16**,[234] **T17**,[234] **T18**,[234] **T19**,[234] **T20**,[234] **T21**,[234] **T22**,[234] **T23**,[234] **T24**,[234] **T25**,[234] **T26**,[234] **T27**,[234] **T28**,[234] **T29**,[235] **T30**.[235]

5. Applications of dirhodium(II,II) complexes

5.1. Catalysts of organic reactions

Dirhodium complexes (chiral or achiral) are used as homogeneous catalysts or can be immobilized for heterogeneous catalysis. Immobilization platform is provided by achiral polymer or by chiral peptide of enzymatic cavity.[36] Immobilization is typically performed through axial ligation to one of the rhodium atoms.[71] The second rhodium atom then serves as the site of action. Immobilization can be also achieved *via* connection through the bridging ligand[72] and then the reactivity of both rhodium atoms can be further modulated as mentioned in previous section 4. Another possibility is the formation of polymeric networks using tetradentate bridging ligands and the application in heterogeneous catalysis (e.g., based on terephthalic acid).[73]

Dirhodium(II,II) paddlewheel complexes (Scheme 25) serve as Lewis acid catalysts (e.g. for activation of enynes,[74] boronic acids[75]). Catalytic properties of the dirhodium paddlewheel complexes can be tuned also by axial ligation of one of the rhodium atom.[76] The acidity can be increased by oxidation of one of the rhodium atom to cationic dirhodium (II,III) complexes, which are also used as catalysts of organic transformations (carbonyl ene reactions,[77] dipolar cycloadditions,[61] hetero-Diels-Alder reactions[62]).

The most frequent application of dirhodium(II,II) complexes is the transfer of electron deficient species as carbenes[78] or nitrenes[79] on organic substrates. Rhodium-carbenoids can be generated from various precursors as diazo compounds,[80] cyclopropenes,[81] enynals/enynones[82] or substituted triazols.[83] Rhodium-carbynoid was recently generated from hypervalent iodo-derivative containing diazo moiety and its reactivity was studied in the reaction with alkenes.[84] Rhodium-nitrenoids are typically generated from imidoiodinanes, which are prepared *in situ* by oxidation of amides using hypervalent iodine compounds or by decomposition of azides[85] or by α-elimination reactions.[86] Transfer of rhodium-carbenoids/nitre-

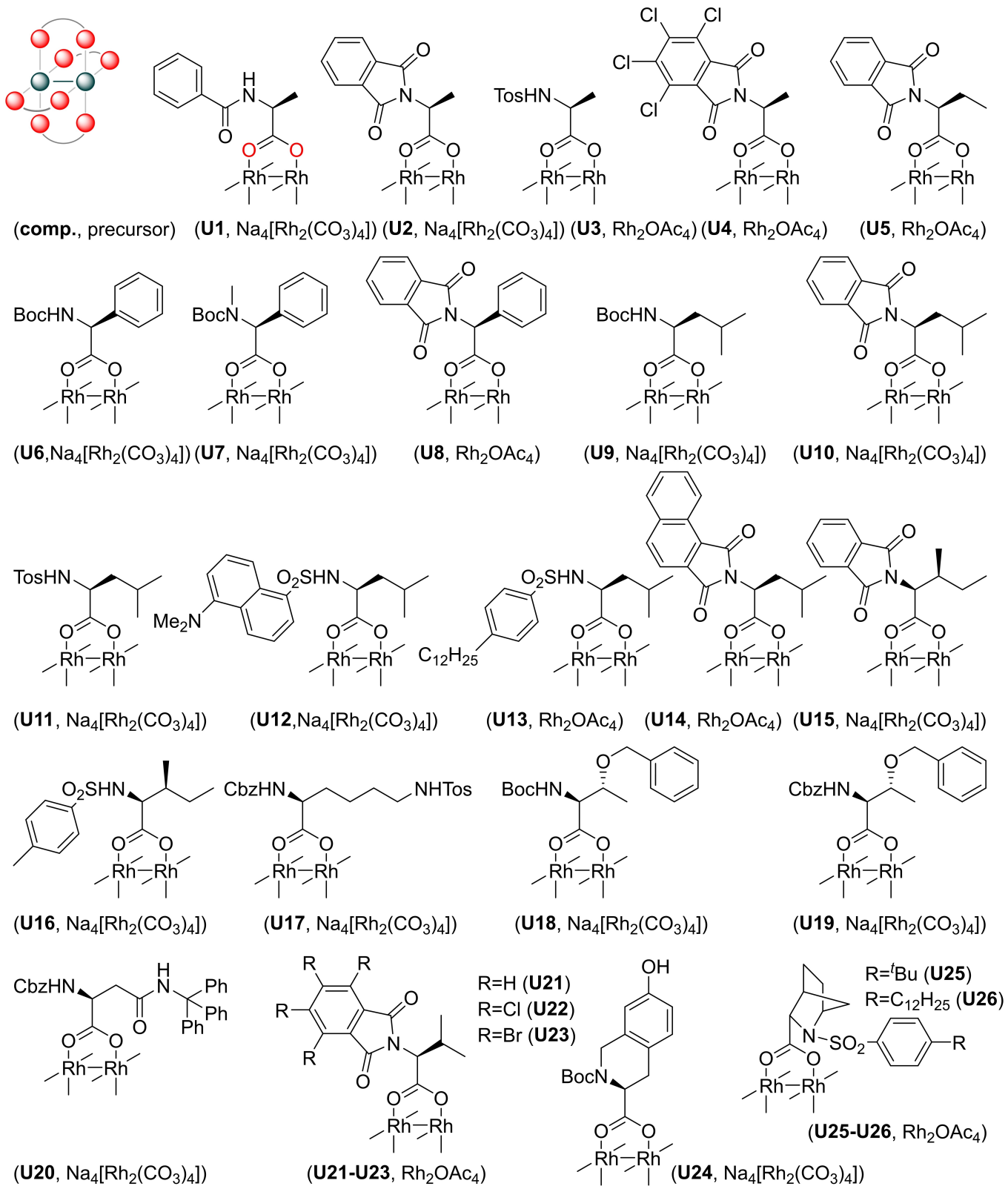


Figure 22. Dirhodium(II,II) complexes containing *O*,*O*'-bridging ligands with structural motive OOCCHHetR; Het = nitrogen, R = alkyl or aryl (α-amino acid derivatives): **U1**,[182] **U2**,[182] **U3**,[231] **U4**,[206] **U5**,[218] **U6**,[182] **U7**,[182] **U8**,[231] **U9**,[182] **U10**,[182] **U11**,[182] **U12**,[182] **U13**,[230] **U14**,[227] **U15**,[182] **U16**,[182] **U17**,[182] **U18**,[182] **U19**,[182] **U20**,[182] **U21**,[182] **U22**,[236] **U23**,[105] **U24**,[182] **U25**,,[237] **U26**.[238]

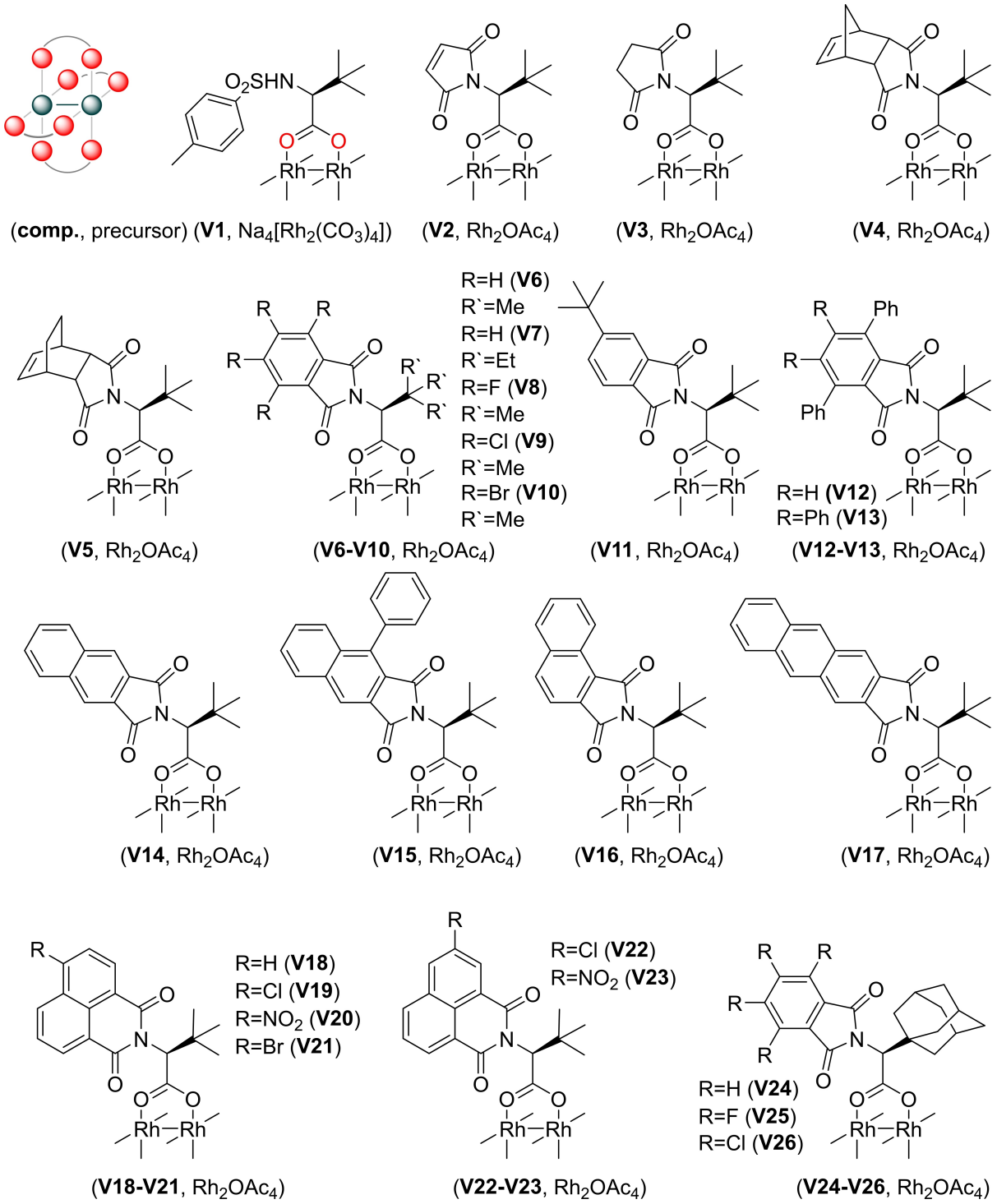


Figure 23. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOCCHHetR; Het = nitrogen, R = tertiary substituent: **V1**,[230] **V2**,[231] **V3**,[231] **V4**,[239] **V5**,[239] **V6**,[240] **V7**,[241] **V8**,[236] **V9**,[242] **V10**,[243] **V11**,[239] **V12**,[244] **V13**,[245] **V14**,[246] **V15**,[239] **V16**,[227] **V17**,[231] **V18**,[235] **V19**,[247] **V20**,[247] **V21**,[247] **V22**,[229] **V23**,[229] **V24**,[248] **V25**,[249] **V26**.[248]

noids on organic educts results in (singlet-like) C–H functionalizations (amination reactions[87]/ alkylations[88]),[89] insertion reactions to unsaturated bonds (aziridinations[90]/ cyclopropanations[91]/ cylopropenations[92]), insertion reactions to Si–H bonds,[93] insertion reactions to other heteroatom-H bonds,[94] ylide formations[95] with heteroatoms (oxygen,[96] nitrogen,[97] sulfur[98]) and subsequent ylide transformations (intramolecular rearrangements[99] or intermolecular condensation reactions[100]) to the final natural or artificial products.[101]

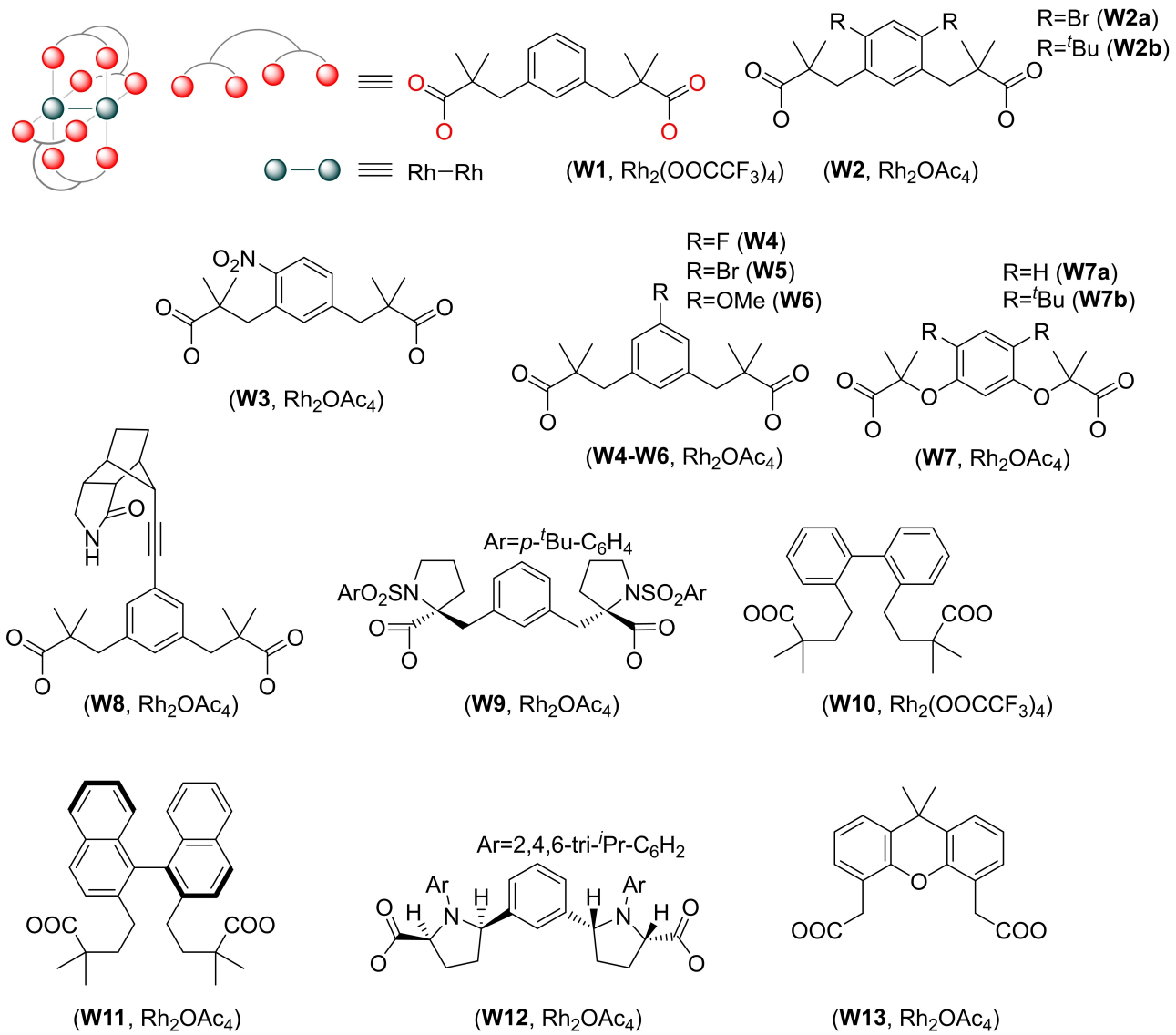


Figure 24. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive OOC-spacer-COO: **W1**,[250] **W2**,[251] **W3**,[252] **W4**,[253] **W5**,[254] **W6**,[252] **W7a** R = H,[255] **W7b** R = ^{t}Bu,[256] **W8**,[257] **W9**,[188] **W10**,[258] **W11**,[258] **W12**,[71] **W13**.[259]

Intermediates relevant to carbene transfer processes, *i.e.* diazo derivative[102] as ligand in axial position of dirhodium complex, and dirhodium complex coordinating carbene, were isolated and confirmed by X-ray structural analysis.[103] Dirhodium nitrenoid intermediate proposed in many theoretical studies has recently been trapped in crystalline matrix and described.[104] Heteroleptic dirhodium complexes for highly enantioselective processes start to appear.[105] Dirhodium compounds can be used as catalysts for hydrogenation of alkenes[106] (such reactions were proposed to proceed *via* heterolytic splitting of hydrogen by the dirhodium complex) or can be used as catalysts for transfer hydrogenations[107], dynamic kinetic resolution of alcohols, DKR of homoallylcarboxylic acids[108] or as catalysts in other processes as hydroformylation of alkenes[109,274] or reduction of CO_2 with silanes.[110] Photochemical and thermal evolution of molecular hydrogen from water[111] can be catalyzed with dirhodium paddlewheel complexes with electron withdrawing carboxylate ligands.[112] Rh(II) to Rh(III) redox transitions of dirhodium complexes are used in reduction/oxidation processes (e.g. sulfide oxygenations catalyzed by $Rh_2(esp)_2$ (**W1**, Figure 24)[275] or allylic oxidations of alkenes with hydrogen peroxide as an oxidant catalyzed by caprolactam dirhodium complex (**C1**, Figure 5)[113] or by $Rh_2(esp)_2$ (**W1**, Figure 24)).[276]

5.2. Bio-medical applications

Rhodium does not occur in any of the known natural biological processes.[3] The use of rhodium for medicinal applications dates back to 1958, when interactions of rhodium (I) complexes with the protein casein were studied.[114] Later rhodium (II)

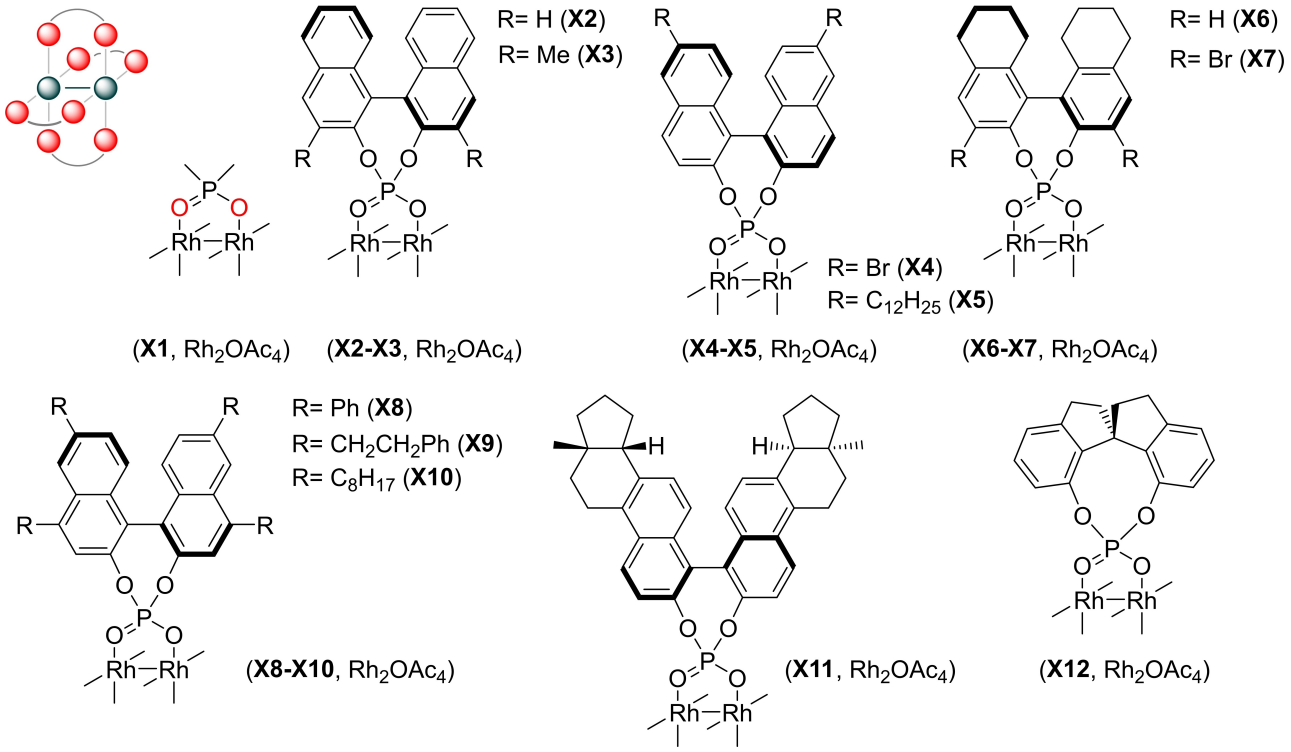


Figure 25. Dirhodium(II,II) complexes containing *O,O'*-bridging ligands (phosphinate or phosphate derivatives): **X1**,[260] **X2**,[19] **X3**,[261] **X4**,[261] **X5**,[261] **X6**,[262] **X7**,[262] **X8**,[263] **X9**,[263] **X10**,[263] **X11**,[261] **X12**.[264]

complexes, specifically dirhodium(II,II) tetracarboxylates together with other transition metal complexes that act as cisplatin were tested as anti-tumor agents,[115] but their toxicity prevented their use for cancer treatment at that time.[116]

It has been found that rhodium paddlewheel complexes bind to the DNA bases[117] *via* axial ligation site **40** and in some cases the bridging ligand is replaced by the nucleic base (guanine) to form complexes like **41** (Scheme 26).[118] Various heteroleptic complexes as **16** (Scheme 9) containing the fluorescent ligands were prepared from homoleptic structures to assess the intracellular fate of dirhodium complexes in living organisms.[119] Rhodium tetracarboxylates quench the fluorophores in their vicinity, i.e. complex **16** does not emit visible light. After the induced ligand "loss" (fluorescein in case of complex **16**) in the studied medium the released fluorophore is the molecule that is then detected as emitter.

Dirhodium-peptide complexes, which exploit the Lewis acidity of both rhodium atoms, were developed to study the structural properties of enzymatic peptides. Either "passively", by reversible binding of e.g. two histidine units in axial position of the dirhodium complex (Scheme 27, a)[43] or "actively" serving as (carbene/nitrene)-transfer catalyst by labelling the protein with a specific organic compound (Scheme 27, b).[120]

5.3. Molecular detectors

Devices for the detection of small molecules/gases such as carbon monoxide,[121] ammonia,[122] nitrogen oxide[123] and other heteroatomic compounds are based on the change of complex physical properties upon ligation of detected molecule in the axial position of the dirhodium complex. For example, conductivity can be measured in case of complexes coated on semi-conductive materials.[121] The molecules can be also detected by simple visual inspection as the colour of the dirhodium complexes changes dramatically with different axial ligands (Scheme 28).[9]

6. Overview of Rh_2A_4 paddlewheel complexes

An overview of bridging ligands *(to the best of my search)* used for the syntheses of homoleptic dirhodium(II,II) paddlewheel complexes from their first report in 1960 to 2019 is listed. Selected heteroleptic complexes are not completely covered. They were mentioned because some special bridging ligands appear only in heteroleptic complexes, e.g. 2-phenyl-phosphines or guanidine derivatives, or because they serve as an example for the formation of geometric isomers, which often complicate the isolation of one desired complex. Citation in figures refers to the first preparation of the complex with depicted bridging ligand or to the described synthesis with spectral characterization of the complex containing depicted

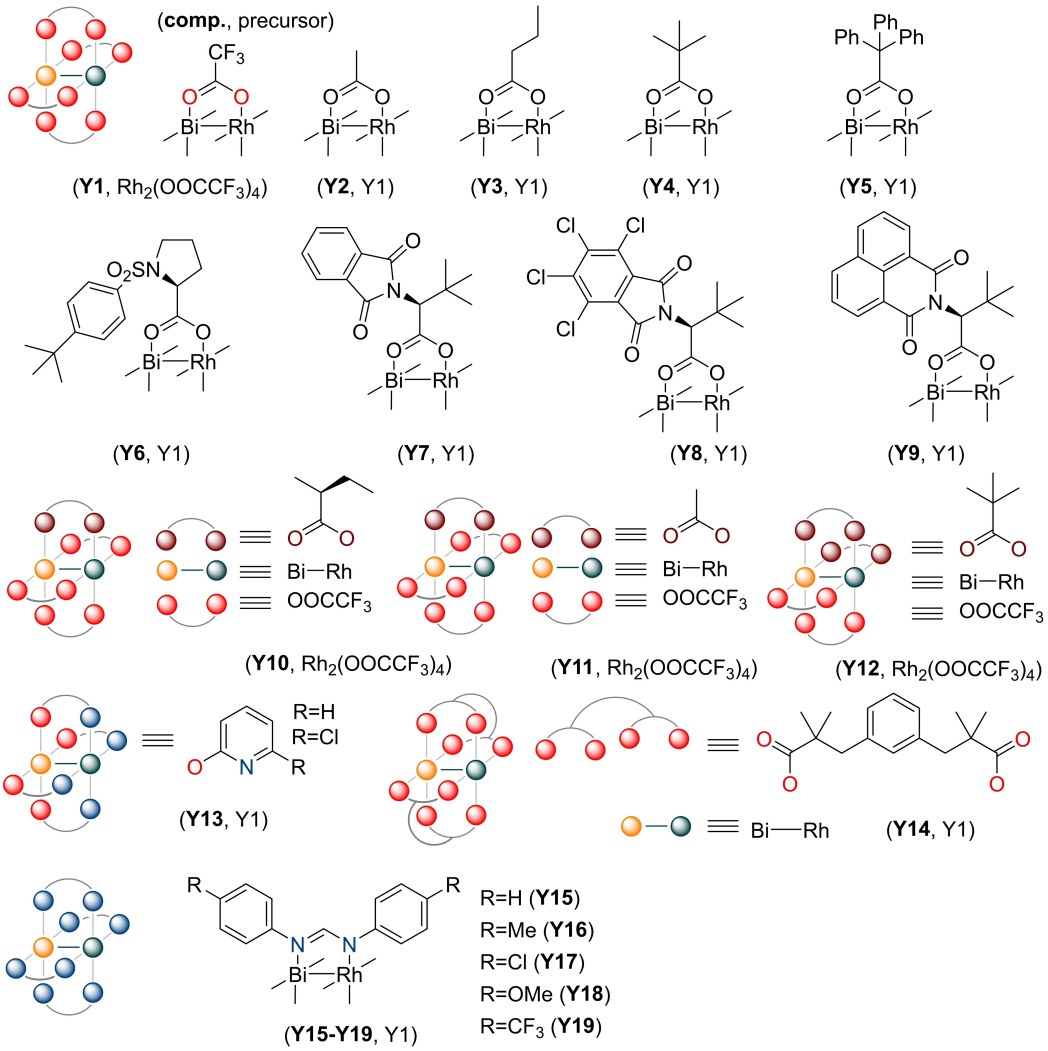


Figure 26. Bismuth-rhodium(II,II) paddlewheel complexes: **Y1**,[265] **Y2**,[266] **Y3**,[266] **Y4**,[266] **Y5**,[266] **Y6**,[267] **Y7**,[68] **Y8**,[68] **Y9**,[68] **Y10**,[268] **Y11**,[268] **Y12**,[268] **Y13**,[269] **Y14**,,[266] **Y15**,[270] **Y16**,[270] **Y17**,[270] **Y18**,[270] **Y19**.[270]

bridging ligand. Citations do not cover syntheses of complexes with the same bridging ligand, but different axial ligation L. Geometric isomers are visualized by means of a ball stick image with the color code. The isolated isomer described is shown (this does not guarantee that it is the only isomer formed in the reaction or the main isomer). In many cases the ratio between major and minor isomer(s) is not mentioned in the corresponding publication. The absolute configuration of chiral ligands is shown, enantiomeric complexes are omitted. This overview is intended for quick orientation in the literature and does deal with the properties of individual complexes.

6.1. *N,N'*-Bridging ligands

6.2. Figure 3 shows dirhodium(II,II) complexes containing *N,N'*-bridging ligands.

6.2. *N,O*-Bridging ligands

See Figure 4, Figure 5, Figure 6, Figure 7, Figure 8, Figure 9, and Figure 10 for dirhodium(II,II) complexes containing *N,O*-bridging ligands.

6.3. *N,S*-Bridging ligands

Figure 11 depicts dirhodium(II,II) complexes containing *N,S*-bridging ligands.

6.4. *O,O'*-Bridging ligands

The figures below present an overview of dirhodium(II,II) complexes containing *O,O'*-bridging ligands with structural motive $OOCCH_2R$ and fluorinated analogues (Figure 12), OOCCHRR' (Figure 13), $OOCCH_2Het$; Het = heteroatom (Fig-

ure 14), OOCCRR'Het; Het = heteroatom, R,R' = alkyl or aryl (Figure 15), $OOCCR^1R^2R^3$ (Figure 16), OOCAr (Figure 17), OOCCHHetR; Het = oxygen or halogen (Figure 18), OOCCHHetR; Het = nitrogen, R = alkyl or aryl (proline derivatives) (Figure 19), OOCCHHetR; Het = nitrogen, R = alkyl or aryl (α-amino acid derivatives) (Figure 20), OOCCHHetR; Het = nitrogen, R = alkyl or aryl (cyclic α-amino acid derivatives) (Figure 21), OOCCHHetR; Het = nitrogen, R = alkyl or aryl (α-amino acid derivatives) (Figure 22), OOCCHHetR; Het = nitrogen, R = tertiary substituent (Figure 23), and OOC-spacer-COO (Figure 24). Figure 25 shows phosphinate or phosphate derivatives of dirhodium(II,II) complexes containing *O,O'*-bridging ligands.

6.5. Bridging ligands in heterobimetallic Bi-Rh paddlewheel complexes

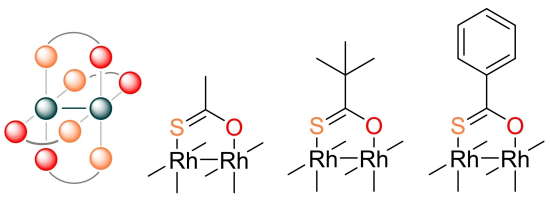
See Figure 26 for bismuth-rhodium(II,II) paddlewheel complexes.

6.6. *O,S*-Bridging ligands

Figure 27 shows dirhodium(II,II) complexes containing *O,S*-bridging ligands.

7. Conclusion

The soft nucleophilicity of the rhodium atom at the core of the dirhodium paddlewheel complexes is exploited in a variety of applications. The broad applicability of these complexes, ranging from homogeneous catalysis to advanced materials, is the driving force for their structural modifications. The optimization of known processes, the search for new applications and curiosity lead to the development of new homoleptic complexes with elaborated organic bridging and axial ligands as well as heteroleptic complexes combining the features of individual ligands in one complex. Interestingly, dirhodium(II,II) complexes with four different bridging ligands are not yet known. The stability of dirhodium(II,II) complexes with bridging ligands against mild oxidants, reductants, acidic or basic media resembles to certain degree to the stability of organic compounds. This feature allows to use methods of organic chemistry for structural modifications and for the purification of the final complexes. We are witnessing the boom of this field, which will bring a variety of new poly-functional complexes and exciting applications.



(**Z1**, $Rh_2(OOCH)_4$ (**Z2**, Rh_2OAc_4) (**Z3**, $Rh_2(OOCH)_4$)

Figure 27. Dirhodium(II,II) complexes containing *O,S*-bridging ligands: **Z1**,[271] **Z2**,[272] **Z3**.[198]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Bidentate ligands · Bridging ligands · Paddlewheel complexes · Post-functionalization · Rhodium

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