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Dirhodium: carbene transformations and beyond

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Dirhodiums, which feature lantern- or paddlewheel-like structures, have emerged as a class of useful catalysts in organic synthesis. Among the transformations catalyzed by dirhodiums, the carbene, with diazo, cyclopropene, hydrazone and triazole as the precursors, and nitrene transfer reactions are dominant and have reached remarkable levels of efficiency and selectivity. Additionally, more and more fascinating properties of dirhodium have been explored and discovered in the past few decades, which has accelerated the applications of dirhodium in organic synthesis. In this review, we aim to showcase these advances in dirhodium-catalyzed transformations. The transformations including cycloisomerization, hetero-Diels–Alder (HDA) reactions, ene reactions, arylation, radical oxidation reactions and C–H activation, *etc.* will be covered. In these reactions, the dirhodiums could not only work as redox-neutral catalysts but also as redox catalysts.

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1. Introduction

As depicted in Scheme 1, dirhodium features a paddlewheel structure defined by four bridging anions about a Rh_2^{4+} core. A formal single bond joins the two rhodium atoms, with a Lewis base or substrate usually coordinated in the axial positions.[1] The common bridging anions include carboxylates and carboxamides, which have demonstrated their wide applications in organic synthesis.[2] Besides, phosphates,[3] 2-aminopyridinates,[4] pyrazolates,[5] *etc.* as the bridging ligands have also been reported.[1b] By adjusting the bridging anions, the catalytic reactivities and selectivities of dirhodiums could be finely tuned.[2a,b,6] Compared with the bridging ligands, the axial ligands were historically considered to play a less important role in catalysis because of their labilities.[7] However, more and more findings have shown that the introduction of axial ligands, like N-heterocyclic carbene and phosphine ligand, was actually an effective strategy to endow the dirhodium with new chemical reactivities.[8] This is because Rh_2(II,II) compounds possess a high degree of potential cooperative and electronic communication between the two rhodium metal sites across the Rh–Rh metal bonds.[1a] In other words, the electronic density and steric hindrance of the terminal rhodium atom are affected by the axial ligand located on the other

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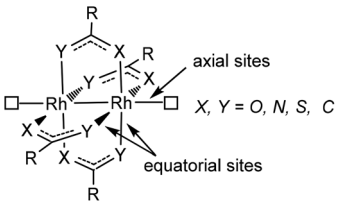
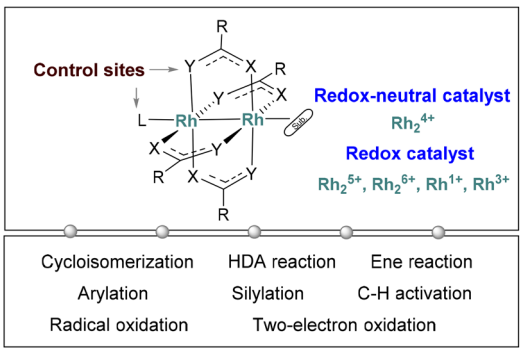


Scheme 1 The structure of dirhodium complex.

rhodium *via* the Rh–Rh bond, which demonstrates the characteristic of dirhodium as a bimetallic complex.

From the viewpoint of synthetic applications, the past few decades have witnessed a rapid growth of dirhodium chemistry, which provided a vast array of efficient and practical methodologies for organic synthesis.[9] Above all, the dirhodium compounds are well-known for their outstanding performances in carbene and nitrene transfer reactions, such as X–H (X = C, Si, B, N, O, S, P) insertion,[10] cyclopropanation,[11] cyclopropenation,[12] ylide transformations[13] and C–H amination.[14] With the employment of chiral dirhodiums or achiral dirhodiums combined with organocatalysts, the corresponding asymmetric versions have also been achieved in many cases.[15] Among these, the dirhodium acted as the efficient catalyst for the generation of dirhodium carbene,[16] with diazo,[10a,d,11,13a,17] cyclopropene,[18] hydrazone[15a,19] and triazole[20] as the carbene precursors, which will not be covered in the review. On the other hand, the dirhodium-catalyzed nitrene transfer reaction has emerged as one of the most important and effective nitrogen-atom transfer methods, providing a large number of nitrogen-containing molecules, on which there are a lot of discussions and these will not be involved in this review for the limited space.[2c,14,21] The preparative methods and classification of dirhodium have also been well summarized previously.[1b] However, other quite meaningful and inspiring chemical reactivities of dirhodium have also been discovered but less discussed.[2b] Therefore, we will focus on these dirhodium-catalyzed organic reactions, in which dirhodium carbene-involved reactions are partly included but not limited. This review will cover reactions including cycloisomerizations, hetero-Diels–Alder (HDA) reactions, ene reactions, arylation, C–H activation, silylation, radical or two-electron oxidation reactions, *etc.* (Scheme 2). In these reactions, the roles of dirhodium could be classified as redox-neutral catalyst (the oxidation state of the dirhodium is Rh_2^{4+}) and redox catalyst (the dirhodium could be oxidized to Rh_2^{5+} and Rh_2^{6+} or dissociates to the monomer Rh^{1+} or Rh^{3+}). Besides, the reaction scopes and mechanistic rationales are discussed. We hope this review will demonstrate the great potential of dirhodium in organic synthesis and inspire explorations of wider applications and further modifications of the dirhodium structure.



Scheme 2 The roles and applications of dirhodium in organic synthesis.

Shifa Zhu

Shifa Zhu is a professor of Chemistry at the South China University of Technology. He received his Bachelor's degree from Hunan University in 2001. He obtained his Ph.D. from the Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, in 2006, under the supervision of Prof. Shizheng Zhu. After two years' postdoctoral training with Prof. X. Peter Zhang from 2007–2008 at the University of South Florida, he returned to China and joined the South China University of Technology (SCUT) in 2009 and started his independent research. His current research interests mainly focus on alkyne chemistry.

2. Dirhodium as a redox-neutral catalyst

One of the most recognized and widespread applications of dirhodium is in carbene chemistry, in which the dirhodiums are generally neutral dinuclear complexes and serve as redox-neutral catalysts.[2b] With the development of carbene chemistry, more and more precursors of carbene have sprung up.[19a,22] Notably, in addition to frequently used precursors, such as diazo, cyclopropene and triazole, the easily available and operationally safe alkyne could also be activated by dirhodium to generate carbene, although with limited types.[15a,19b] The cycloisomerizations of enyne, diyne, enynone and azaenyne are efficient to afford dirhodium carbene species, which could be trapped inter- and intramolecularly to give a collection of functionalized chiral molecules. Besides, the dirhodiums work nicely as redox-neutral catalysts in the HDA reaction, ene reaction, arylation and silylation. These transformations provide efficient accesses to synthesize pivotal molecules.

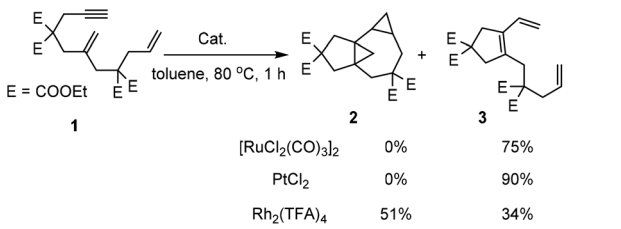
2.1 Dirhodium in enyne and diyne cycloisomerizations

Enyne cycloisomerization reactions represent a class of processes which provide a unique method to get carbo- and heterocyclic compounds from simple linear substrates, with the complexity improved swiftly.[23] The reports of dirhodium as the carbophilic catalyst in enyne cycloisomerization date back to the year of 1998. Murai and coworkers found that $Rh_2(TFA)_4$ showed comparable reactivities with $[RuCl_2(CO)_3]$ and $PtCl_2$ (Scheme 3).[24] Various substrates could be well activated at 80 °C and gave the corresponding products in relatively low to moderate yields. Especially, when the ene–ene–yne **1** was employed, the target product of bicyclopropanation **2** could be produced only under the catalysis of dirhodium. These reactions highlight the uniqueness of dirhodium as the catalyst. In 2008, the same group also described that $Rh_2(TFA)_4$ could be employed in the skeleton reorganization of 1,6- and 1,7-enyne with good catalytic activity.[25]

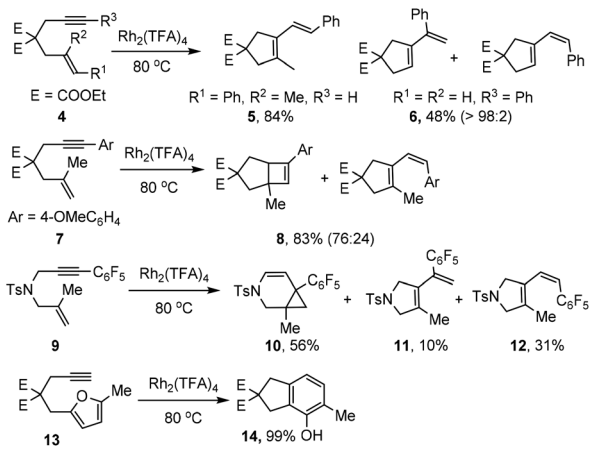
Later, Chatani and coworkers conducted a systematic investigation on dirhodium-catalyzed enyne cycloisomerization (Scheme 4).[26] After various achiral dirhodium catalysts were screened, they found that the more electrophilic dirhodiums were necessary for the transformations of enynes. $Rh_2(OAc)_4$ and $Rh_2(O_2CC_7H_{15})_4$ showed no reactivity, but $Rh_2(TFA)_4$ and $Rh_2(O_2CC_4F_7)_4$ could be the right catalysts to give the corresponding products successfully. As shown in Scheme 4, $Rh_2(TFA)_4$ was competent to participate in a diversity of transformations of enynes and the reaction pathway depended on the substitution mode of the substrates. Notably, when the alkene moiety of the enyne was replaced by furan, the phenol **14** could be obtained in quantitative yield.

Despite the excellent work on dirhodium-catalyzed cycloisomerization, the weak alkynophilicity of dirhodium impedes its further development because of the fact that electron-poor $Rh_2(TFA)_4$ and a high temperature were required in the previous reports.[24–26] As a result, asymmetric variants have not been reported until recent work reported by Zhu's group in 2020. With the enynal **15** as the substrate, they introduced a synergetic effect to achieve the activation of enyne, that is, the electron-withdrawing activation and the C–H···O interaction (Scheme 5).[27] In this way, the substrate **15** could be catalyzed successfully to give **16** selectively by both the achiral dirhodium $Rh_2(OPiv)_4$ and the chiral one $Rh_2(S\text{-BTPCP})_4$. Of particular note was that the reaction could be conducted at 0.1 mol% catalyst loading under mild conditions. Up to 99% yield and 94% ee were observed. Actually, when the dirhodium was replaced with other excellent carbophilic catalysts, such as $PtCl_2$, PPh_3AuNTf_2, *etc.*, the reactions hardly worked, which underlined the possible unique activation mode between the substrate and the dirhodium. To figure out the activation mechanism, they conducted detailed DFT calculations and control experiments, which supported the synergetic activation of electron-withdrawing activation and C–H···O interaction. In addition, the formyl group could also serve as a useful handle for further manipulations besides acting as the activation group.

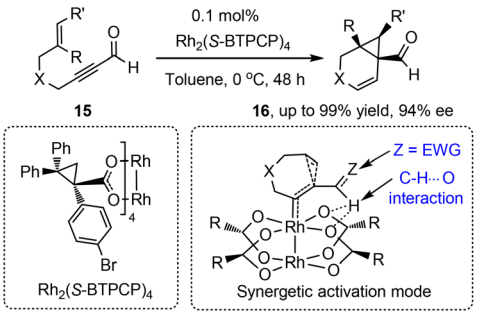
In 2021, Zhu and coworkers extended the synergetic catalytic system to the desymmetric cycloisomerization of diyne (Scheme 6).[28] With $Rh_2(R\text{-PTAD})_4$ as the catalyst, the first asymmetric cycloisomerization of 1,6-diyne was achieved. In this transformation, the formyl group of **17** could be perfectly incorporated into the furan moiety of products **18** and aza-quaternary carbon centres were constructed with good enantioselectivities (up to 98% ee). To gain more information on the mechanism, they succeeded in getting the single crystal of alkyne–dirhodium complexes **17-A**, the data of which supported the hydrogen bonding interactions. Moreover, detailed



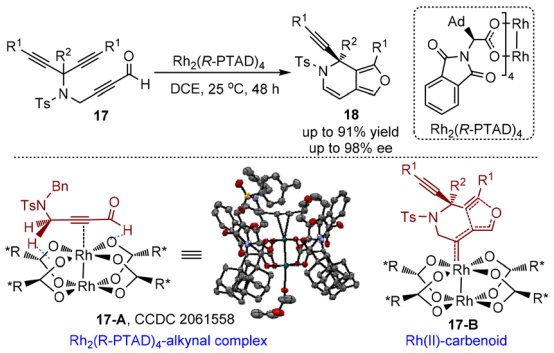
Scheme 3 The cycloisomerization of ene–ene–yne catalyzed by dirhodium.



Scheme 4 Examples of enyne cycloisomerization catalyzed by dirhodium.



Scheme 5 The enantioselective cycloisomerization of enyne catalyzed by $Rh_2(S\text{-BTPCP})_4$.



Scheme 6 The enantioselective desymmetric cycloisomerization of diyne catalyzed by Rh_2(*R*-PTAD)$_4$.

control experiments and DFT calculations were convincing to show that the reaction underwent the following processes: a concerted and energetically favorable [3 + 2] cycloaddition, the formation of the key Rh–carbene intermediate **17-B** and a 1,2-H shift.

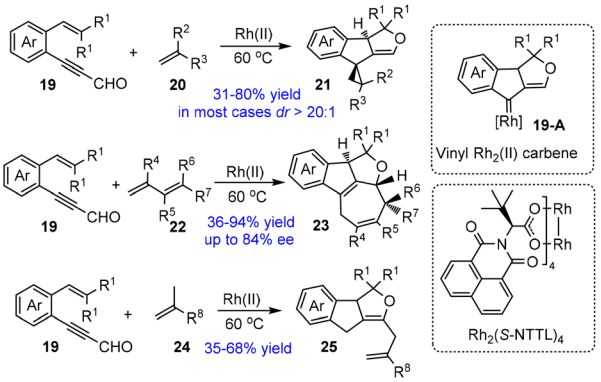
In 2022, they further demonstrated that the easily available benzo-enynal **19** could be catalyzed by dirhodium to generate the rare endocyclic donor–donor vinyl carbene **19-A** (Scheme 7).[29] This sterically encumbered dirhodium carbene could be intercepted by a diverse range of alkenes, such as styrenes **20**, dienes **22** and α-methyl styrenes **24**, to give a collection of polycyclic heterocycles. Mechanistic studies revealed that the 1,1-disubstituted enynal was the prerequisite for the formation of the vinyl dirhodium carbene intermediate and the formal allylation products **25** originated from a combined C–H functionalization/Cope rearrangement[30] and subsequent 1,3-H shift which was confirmed by rigorous deuterium experiments. These reactions could also be conducted with enantioselective versions. With Rh_2(*S*-NTTL)$_4$ as the catalyst, moderate to good ee values could be obtained.

2.2 Dirhodium in enynone and azaenyne cycloisomerizations

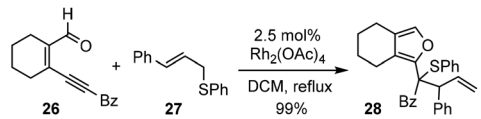
As a result of the driving force of aromatization for the formation of furan, enynone is a highly reactive substrate to be catalyzed by the weak alkynophilic dirhodium to give dirhodium carbene, followed by a series of carbene transfer reactions.[15a,19b,31] Remarkably, in many cases, the generated dirhodium carbene belongs to the type of donor/donor carbene and could be nicely engaged in asymmetric carbene transfer reactions.[15a,19b]

In 2003, Uemura and coworkers demonstrated that enynone **26** could be transformed into furyl dirhodium carbene under the catalysis of $Rh_2(OAc)_4$, followed by an efficient Doyle–Kirmse reaction at reflux temperature with the formation of **28** in 99% yield (Scheme 8).[32] Later, they found that the furyl dirhodium carbene intermediate generated from terminal enynone **29** could also be trapped efficiently by a diverse array of different substituted alkenes (Scheme 9).[33]

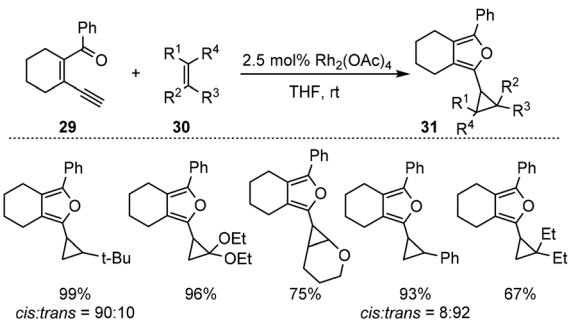
In addition to the above carbene transfer reactions, the generated furyl dirhodium carbene could also be engaged in X–H insertion; the trapping reagents included alcohol, amine, thioalcohol, silane and even 1,3-cyclohexadiene (Scheme 10).[34] Notably, the enynones substituted with electron-deficient groups could generate carbenes with stronger electrophilicities for the ensuing carbene transfer reactions.



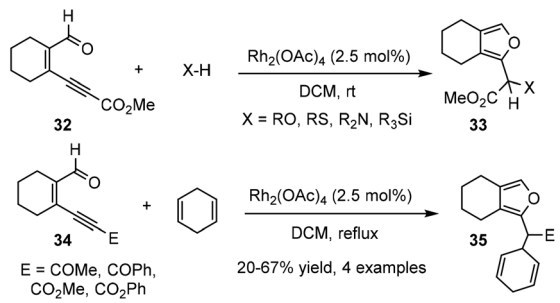
Scheme 7 The cascaded cycloaddition of enyne and alkenes catalyzed by dirhodium.



Scheme 8 The Doyle–Kirmse reaction of enynone catalyzed by $Rh_2(OAc)_4$.



Scheme 9 The cyclopropanation of enynone catalyzed by $Rh_2(OAc)_4$.



Scheme 10 The X–H insertion of furyl dirhodium carbene.

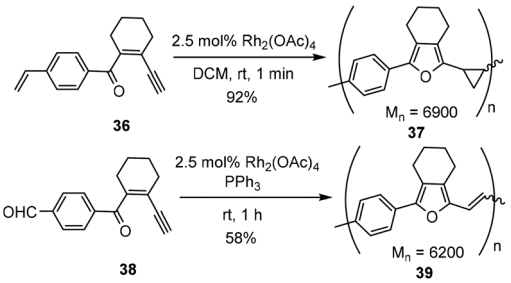
Uemura and coworkers then took advantage of the dirhodium-catalyzed enynone-involved cyclopropanation and Wittig-type condensation to give furylcyclopropane-containing polymers **37** and furfurylidene-containing polymers **39** in 92% and 58% yield (Scheme 11).[35] The number-average molecular weight could be up to 6900 and 6200, respectively.

In addition to enynone, the azaenyne **40** and thioenyne **43** were also suitable substrates to be activated by dirhodium even with possible interference by the competent coordination of nitrogen and sulfur atoms.[36] The corresponding dirhodium carbenes were perfectly involved in cyclopropanation reactions at room temperature (Scheme 12). If furan and thiophene were added instead, ring-opening would occur to give corresponding dienes.

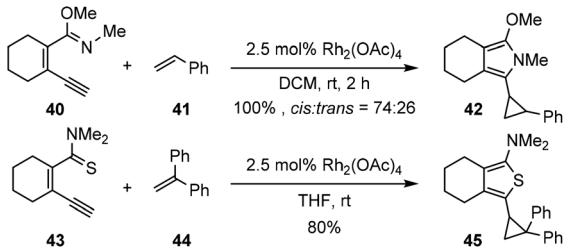
In 2016, Zhu's group found that the dirhodium carbene generated from enynone **46** could be perfectly engaged in aziridination, providing easy access to the polysubstituted aziridines **48** with good *trans*/*cis* ratios (>20 : 1 for most cases) and up to 90% yield (Scheme 13).[37] Besides, this protocol is appealing for the salient features, including mild conditions, wide substrate scope and high atom efficiency. The obtained aziridines **48** were good 1,3-dipoles for the synthesis of 2,5-dihydropyrroles and 1,2,4-triazolidines.

Additionally, 2-furyl dirhodium carbene could be intercepted by external terminal alkynes, giving the furan derivatives **50** and **51**, whose ratio depended on the electronic nature of the substituent groups on the alkynyl terminal of enynone (Scheme 14).[38] When enynones bearing an electron-withdrawing group or alkyl group were employed, complete selectivity for **50** was observed. When the reaction conditions were adjusted sightly, cyclopropene **52** was obtained in a limited time while the starting material was not completely consumed. Higher conversions at longer reaction times led to the appreciable formation of the furan derivatives. Hence, the cyclopropene was considered as the intermediate, which experienced subsequent ring-opening processes to give the products **50** and **51**.

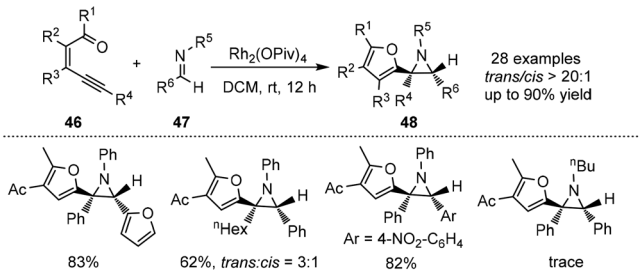
In the same year, Zhu and coworkers reported an interesting proton/metal-catalyzed tandem benzofuran annulation/carbene transfer reaction for the synthesis of diversified benzofuryl-substituted cyclopropanes and cycloheptatrienes (Scheme 15).[39] In the presence of a Brønsted acid, *o*-hydroxylbenzyl alcohol (*o*-HBA) **53** could be transformed into the key intermediate *o*-quinone methide (*o*-QM) **53-A**, which was activated by dirhodium to give the benzofuryl dirhodium carbene



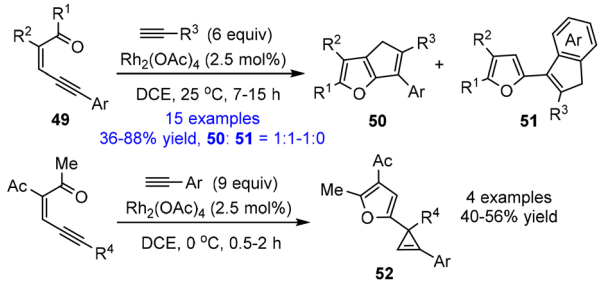
Scheme 11 Dirhodium-catalyzed reactions for the synthesis of polymers.



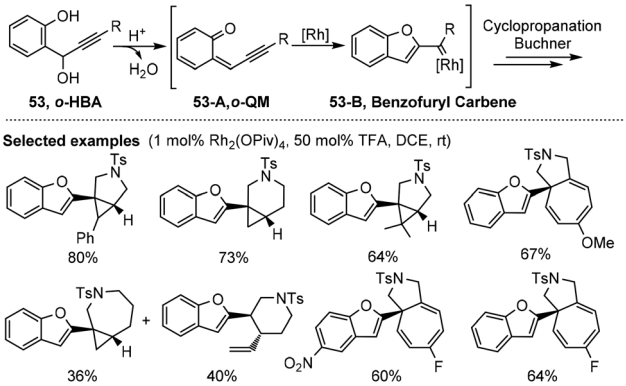
Scheme 12 Dirhodium-catalyzed cyclopropanation of azaenyne and thioenyne.



Scheme 13 The aziridination of furyl dirhodium carbene.



Scheme 14 Dirhodium-catalyzed carbene transfer to alkynes.



Scheme 15 The proton/dirhodium-catalyzed tandem benzofuran annulation/carbene transfer reaction.

53-B. These reaction processes were proposed on the basis of DFT calculations and mechanistic studies. Then the ensuing intramolecular cyclopropanations and Büchner reactions occurred efficiently with good compatibilities for various substituted alkenyls and phenyls. The enantioselective version was also investigated and the ee could reach up to 83%.

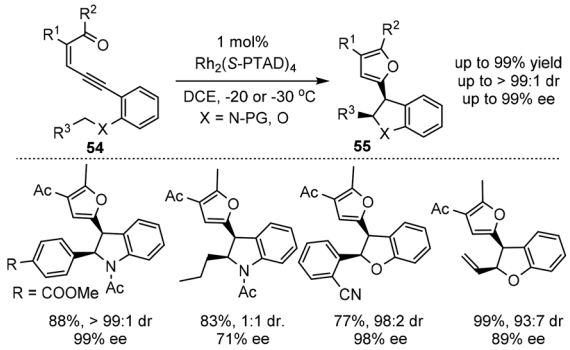
After that, tremendous efforts were made to realize the enantioselective transformations to meet the increasing needs of chiral molecules by employing the powerful chiral dirhodium catalysts. In 2016, Zhu's group reported the first asymmetric sp^3 C–H insertion enabled by donor–donor furyl dirhodium carbene (Scheme 16).[40] The optimal reaction conditions were at −20 or −30 °C in dichloroethane with Rh_2(*S*-PTAD)$_4$ as the optimal catalyst. Excitingly, these C–H insertion reactions were so robust that up to 99% yield, >99 : 1 dr and 99% ee could be obtained.

When the allyl was embedded in enynone, the competitive reactions of cyclopropanation and C–H insertion would occur. It was found that the chemoselectivity could be controlled by employing different catalytic systems.[41] The chiral dirhodium Rh_2(*S*-PTAD)$_4$ was selectively suitable for the cyclopropanation, giving rise to cyclopropane-fused tetrahydroquinoline derivatives **57** in excellent yields with greater than 99 : 1 chemoselectivity and up to 97% ee, whereas Ru^{II}/Pybox preferred C–H insertion to produce vinyl-substituted dihydroindoles **58** with greater than 20 : 1 chemoselectivity and up to greater than 99% ee (Scheme 17).

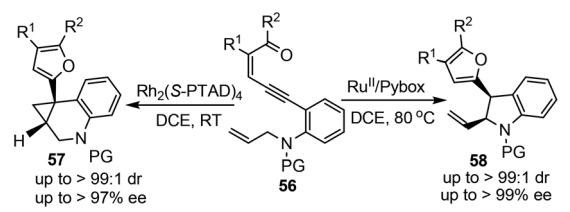
Furthermore, the key intermediate furyl dirhodium carbene could also participate in the enantioselective intramolecular aromatic substitution and Büchner reaction.[42] Excellent yields (up to 99%) and outstanding enantioselectivities (up to >99% ee) could be achieved under the catalysis of Rh_2(*S*-BTPCP)$_4$ (Scheme 18). It is interesting that furyl-substituted chiral cyclohepta[*b*]benzofurans bearing a substituent at the C^4 position on the cycloheptatrienes underwent racemization with or without light. Accordingly, a diradical-involved mechanism was put forward to elucidate the racemization.

Organic silicon- and boron-containing compounds are often found in biomedicines and materials and they are also crucial building blocks due to their rich chemical reactivities.[43] In 2017, Zhou, Zhu and coworkers developed an efficient Rh-catalyzed B–H bond insertion reaction with enynones **63** as the precursors, providing chiral boranes **64** in excellent yields and good enantioselectivities (Scheme 19).[44] Importantly, these chiral boranes could be easily transformed into widely used borates and diaryl methanol compounds without loss of optical purity. Mechanistically, the kinetic experiments and DFT calculations showed that the formation of metal carbene was the rate-limiting step while the B–H insertion was a fast and concerted process.

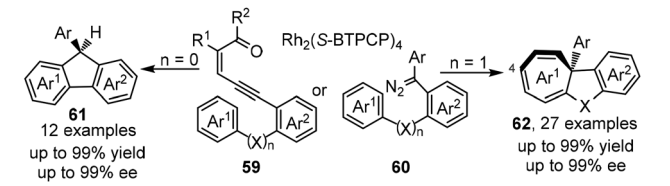
After two years, they further demonstrated that the dirhodium carbene generated from enynone could be utilized for the synthesis of chiral organosilicons (Scheme 20).[45] Both the yields and enantioselectivities could be up to 98% under the catalysis of Rh_2(*S*-BTPCP)$_4$ or Rh_2(*S*-*tert*PTTL)$_4$. This reaction had a good compatibility for a diversity of enynones, including an alkyl-substituted one which is inclined towards a 1,2-H



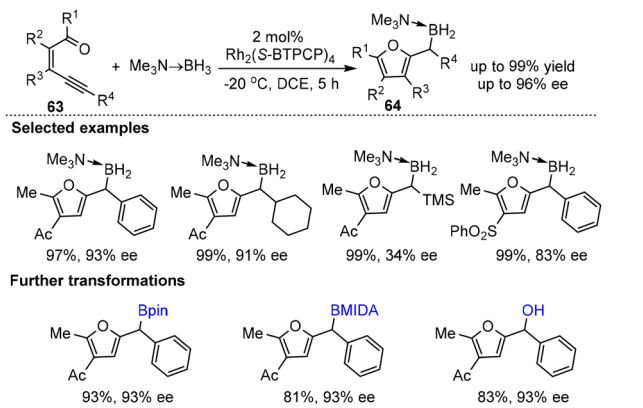
Scheme 16 The asymmetric C–H insertion of furyl dirhodium carbene.



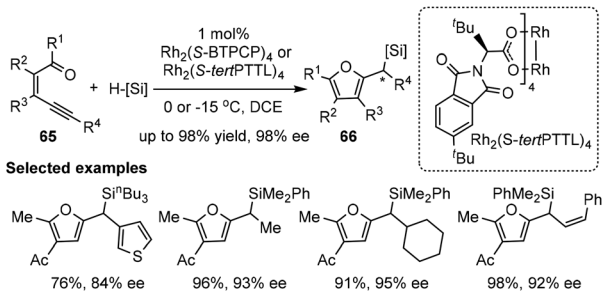
Scheme 17 The chemoselective transformations of furyl carbene.



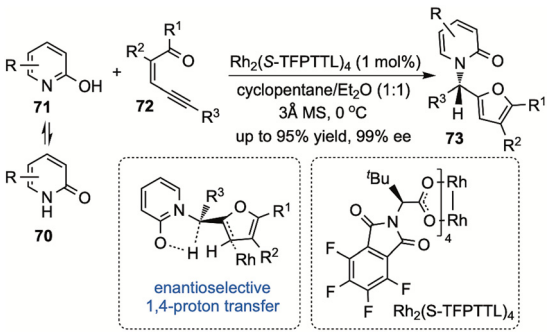
Scheme 18 The enantioselective aromatic substitution and Büchner reaction of furyl dirhodium carbene.



Scheme 19 The enantioselective B–H insertion of furyl dirhodium carbene.



Scheme 20 The enantioselective Si–H insertion of furyl dirhodium carbene.



Scheme 22 The formal N–H insertion of furyl dirhodium carbene.

shift. Importantly, this example represents the first asymmetric Si–H insertion with alkyne as the carbene precursor. In contrast to B–H insertion, Si–H insertion rather than the formation of dirhodium carbene was the most likely rate-determining step according to the mechanistic studies. Recently, Chen *et al.* reported a dirhodium metal–organic cage that could also be a good catalyst for Si–H and B–H insertion with enynones as the carbene precursors.[46] Importantly, the catalyst could be recovered easily by simple centrifugation and reused for ten runs without a significant loss in activity, which promotes the utilization rate of the valuable precious metal rhodium.

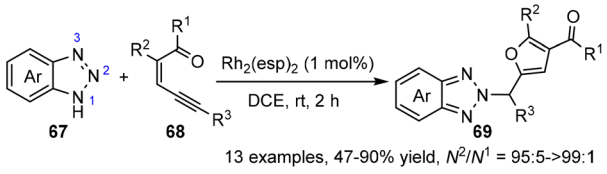
In 2018, a dirhodium-catalyzed and enynone-involved highly selective N^2 alkylation of benzotriazoles was achieved by Sun and coworkers (Scheme 21).[47] In the presence of $Rh_2(esp)_2$, the enynones **68** generated dirhodium carbenes, which reacted with the benzotriazoles **67** to undergo cross-coupling reactions to give **69** with good selectivities. Unlike the traditional mechanism of carbene insertion into X–H bonds, this work was considered to involve a formal 1,3-proton shift from the N^1 to carbene carbon atom, which was consistent with the DFT calculations.

Later, the same group reported a chemo- and enantioselective formal N–H insertion of 2-pyridones **70** with enynones **72** as the donor–donor carbene precursors.[48] This protocol constitutes the first formal N–H insertion of donor–donor carbene. $Rh_2(S\text{-TFPTTL})_4$ gave the best results in the mixed solvent of cyclopentane and Et_2O, and up to 95% yield and 99% ee were obtained. The reaction mechanism, including enantioselective pyridinium ylide formation and sequential 1,4-proton transfer, was verified by DFT calculations and control experiments (Scheme 22).

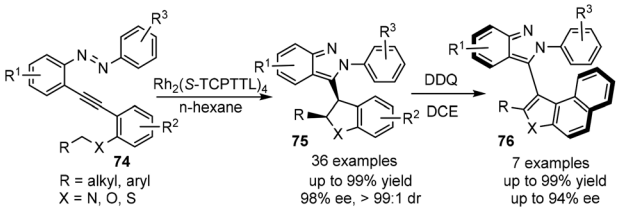
Azaenyne could also act as a good precursor of donor–donor–carbene to participate in the dirhodium-catalyzed carbene transfer reactions. But these reactions were highly challenging because of its inherent strong background reaction leading to racemate formation and the high capability of coordination of the nitrogen atom resulting in catalyst deactivation. By taking advantage of the tether effect and cap modulation, the azaenynes **74** were favorably converted into centrally chiral isoindazole derivatives **75** with up to 99 : 1 dr, 99 : 1 er, and 99% yield under the activation of 2 mol% $Rh_2(S\text{-TFPTTL})_4$.[49] The obtained products **75** could be oxidized by DDQ to access diverse enantiomerically enriched atropisomers **76** bearing two five-membered heteroaryls (Scheme 23).

In addition to the two-component reactions, dirhodium could also exert its important value in muti-component reactions. Sun and coworkers reported a novel metal-organo relay-catalysed three-component reaction of enynones **77**, *N*-hydroxyanilines **78** and diazo compounds **79**, giving polysubstituted β-lactams **81** with good diastereoselectivities.[50] It was supposed that a sequential reaction of Rh-catalyzed imine formation, Wolff rearrangement and benzoylquinine-catalyzed Staudinger cyclization was involved (Scheme 24).

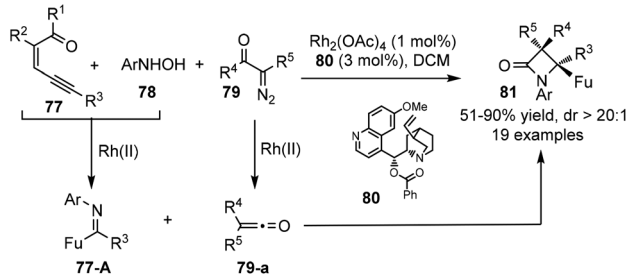
Recently, an elegant three-component reaction of enynal **82**, alcohol **83** and imine **84** was reported by Xu, Hu and coworkers.[51] It should be mentioned that the enynals substituted with ester groups were easier for forming the furyl dirhodium carbene and making it possible to form the key enolate **82-A** and enol intermediate **82-B** (Scheme 25). The intermediate **82-B** would react with imine under the catalysis of CPA **85**, affording chiral α-furyl-β-amino carboxylate derivatives **86** with excellent selectivities and wide substrate scopes. This protocol



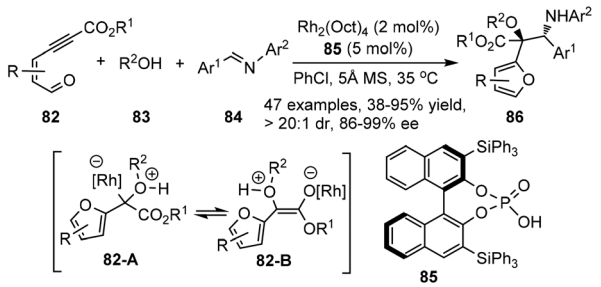
Scheme 21 The cross-coupling reaction of enynones and benzotriazoles.



Scheme 23 The C–H insertion of dirhodium carbene with azaenynes as the precursors.



Scheme 24 The formation of β-lactams *via* metal–organo relay catalysis.

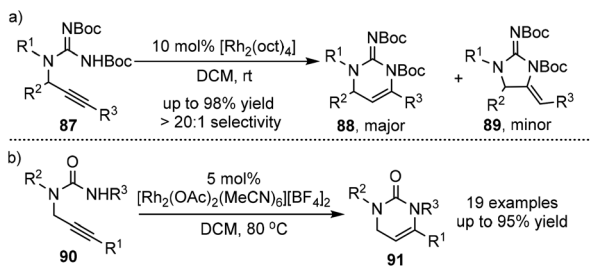


Scheme 25 Three-component reaction of enynal with alcohol and imine catalyzed by dirhodium and CPA.

provides an expeditious route to obtain highly functionalized furan derivatives with adjacent quaternary and tertiary stereocenters.

2.3 Dirhodium in other transformations of alkynes

In addition to the above noticeable transformations, there are some inconspicuous but fascinating reports on the transformations of alkynes activated by dirhodium. In 2011, Looper and coworkers were surprised to find the dirhodium(II) carboxylate $Rh_2(Oct)_4$ with poor π-Lewis acidity was able to catalyze the 6-*endo-dig* selective hydroamination of propargylguanidines **87** at room temperature (Scheme 26a).[52] Surprisingly, the reaction was much faster when an electron-deficient alkyne was used than an electron-donating one. However, this catalytic system was inapplicable in the hydroamination of propargyl ureas **90.** No reaction was detected when $Rh_2(Oct)_4$ was used even at an elevated temperature. To this end, they synthesized more Lewis-acidic cationic Rh(II) complexes $[Rh_2(OAc)_2(MeCN)_6][BF_4]_2$, which were able to catalyze the hydroamination of propargyl ureas **90** in a 6-*endo* fashion to give **91** at 80 °C with up to 95% yield (Scheme 26b).[53]



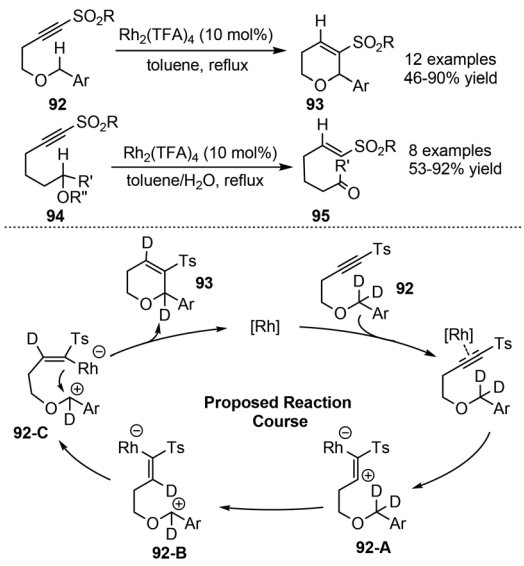
Scheme 26 Dirhodium(II)-catalyzed hydroaminations of propargylguanidines and propargyl ureas.

Another example was reported by Urabe and coworkers in 2009.[54] They found a new isomerization reaction from benzyl alkynyl ethers **92** to dihydropyrans **93** and an intramolecular redox reaction from alkynyl ethers **94** to ketoolefins **95.** Both of them were catalyzed by $Rh_2(TFA)_4$ and the alkyne was substituted with the sulfonyl group. With the help of deuterium-labelled reactions, they proposed a reasonable mechanism, in which dirhodium was coordinated to the alkyne to afford a cationic carbon at the β-position to the Ts group **92-A**. Then the cationic carbon grabbed the hydrogen α to the ether, giving a zwitterionic intermediate **92-B**, which underwent ring closure to afford the final products **93** (Scheme 27).

2.4 Dirhodium in HDA and ene reactions

The hetero-Diels–Alder (HDA) reactions of carbonyl compounds with conjugated dienes are an important methodology for the synthesis of heterocycles.[55] At the early stage, the HDA reaction was one of the most successful applications of dirhodium(II) as a redox-neutral catalyst, a Lewis acid to be precise. The chiral dirhodium catalyst excelled in these reactions, allowing for the ready constructions of a collection of optically active oxygen-incorporated six-membered rings. Significantly, this methodology has been applied to the total synthesis of natural products. With the development of dirhodium, other related applications, including aldol reactions, [2 + 2]-cycloaddition, 1, 3-dipole cycloaddition and ene reactions were established successively.

The seminal work on HDA reactions was covered by Doyle and coworkers in 2001.[56] The cycloaddition of Danishefsky's



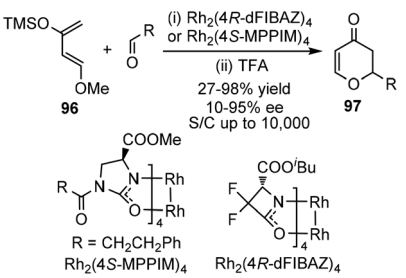
Scheme 27 Dirhodium-catalyzed isomerization and intramolecular redox reaction of sulfonyl group substituted alkynyl ethers.

diene **96** with an equivalent amount of *p*-nitrobenzaldehyde was employed as the template reaction to evaluate the effectiveness of dirhodium. The chiral carboxamidate and carboxylate dirhodium complexes were applied in this reaction to give the corresponding products after the addition of trifluoroacetic acid. However, Rh_2-(4*S*-MPPIM)$_4$ gave better results (82% yield, 95% ee) than other dirhodium complexes including dirhodium(II) carboxamidates with enhanced Lewis acidities and dirhodium(II) carboxylates (Scheme 28). Nevertheless, a significant electronic influence on enantiocontrol was observed, and the ee values increased when electron-deficient aldehydes were employed. There were also large variations in yields (27–98%) and enantioselectivities (10–95%) for different substrate combinations. In spite of these, the substrate-to-catalyst (S/C) ratio could reach up to 10 000. Kinetically, these reactions showed first-order dependence on the aldehyde and diene, and there was a variable dependence on the catalyst.[57]

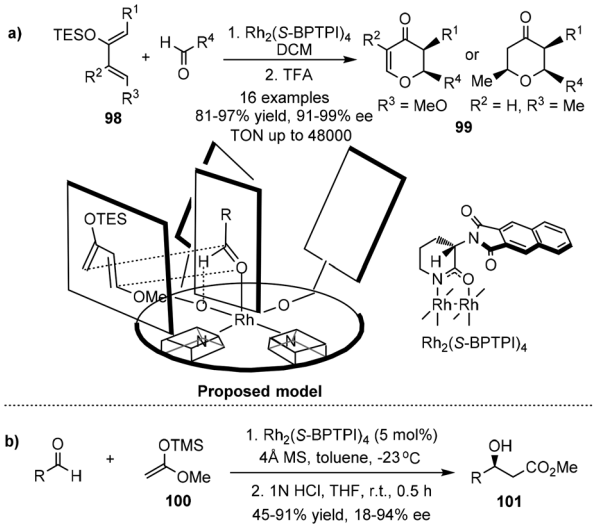
To tackle the challenges in terms of the floating enantioselectivity for different substates, Hashimoto's group developed a new dirhodium carboxamidate complex Rh_2(*S*-BPTPI)$_4$ that incorporated (*S*)-3-(benzene-fused-phthalimido)-2-piperidinonate as the chiral bridging ligand.[58] This newly-designed catalyst proved to be a more general and highly efficient catalyst for *endo*- and enantioselective HDA reactions (Scheme 29a). Danishefsky's dienes as well as monooxygenated dienes **98** were suitable to react with a diverse range of aldehydes, resulting in **99** in up to 97 yield, 99% ee and 48 000 turnover numbers. A stereochemical model is presented in Scheme 29a, in which a favorable hydrogen bond between the formyl hydrogen atom and the carboxamidate oxygen atom is allowed. Moreover, Rh_2(*S*-BPTPI)$_4$ was proved useful in enantioselective Mukaiyama aldol reactions although with less efficiency and a narrow substrate scope (Scheme 29b).[59]

Under the catalysis of Rh_2(*S*-BPTPI)$_4$, enantioselective HDA reactions could also proceed smoothly between 4-aryl-2-silyloxy-1,3-butadienes **102** and phenylpropargyl aldehyde derivatives, giving the exclusively *cis*-2,6-disubstituted tetrahydropyran-4-ones **103** (Scheme 30).[60] Using this methodology as the key step, the asymmetric synthesis of (−)-centrolobine was achieved in 41% overall yield for seven steps and the first asymmetric synthesis of (−)-de-*O*-methylcentrolobine was completed in 39% overall yield for eight steps.

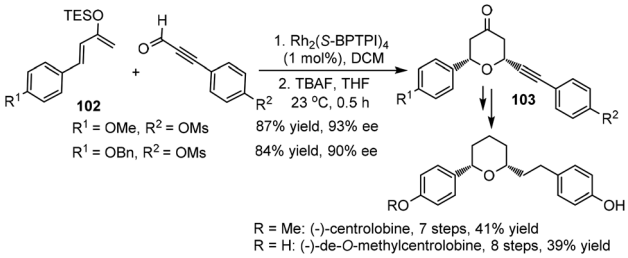
Soon after, the first catalytic asymmetric HDA reaction between 2-aza-3-silyloxy-1,3-butadienes **104** and aldehydes was realized by Hashimoto and coworkers (Scheme 31a).[61] Rh_2(*S*-BPTPI)$_4$ was the optimal catalyst to give all-*cis*-substituted 1,3-oxazinan-4-ones 105 with up to 99% yield and 97% ee in an exclusive *endo* mode after work-up with methanol. This methodology was extensible to the asymmetric HDA reaction between 3-*tert*-butyldimethylsilyloxy-1-dimethylamino-1,3-pen-



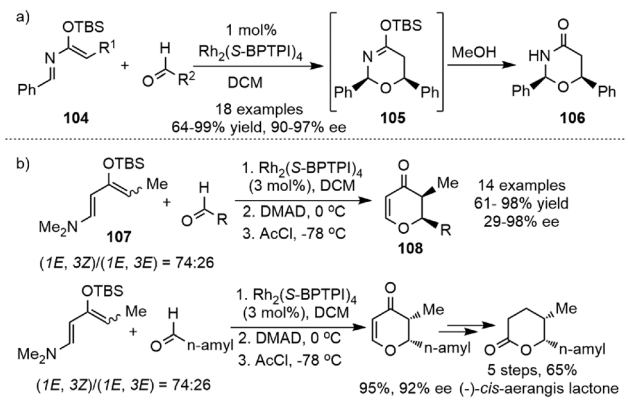
Scheme 28 Dirhodium-catalyzed HDA reactions.



Scheme 29 The Rh_2(*S*-BPTPI)$_4$-catalyzed HDA reaction.



Scheme 30 The Rh_2(*S*-BPTPI)$_4$-catalyzed HDA reaction of 4-aryl-2-silyloxy-1,3-butadienes and phenylpropargyl aldehyde derivatives.



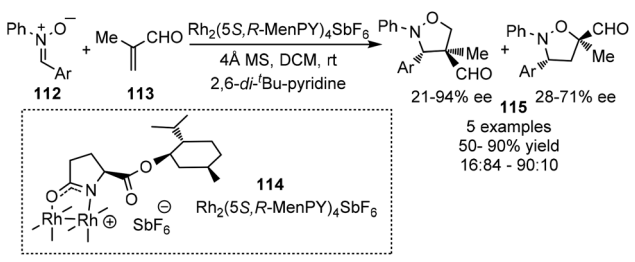
Scheme 31 The dirhodium-catalyzed HDA reaction between 2-aza-3-silyloxy-1,3-butadienes or 4-methyl-substituted Rawal's dienes and aldehydes.

tadiene (4-methyl-substituted Rawal's diene) **107** and aldehydes with up to 98% ee and perfect diastereoselectivity (Scheme 31b).[62] The utility of this catalytic protocol was demonstrated by Hashimoto and coworkers in an asymmetric synthesis of the (-)-*cis*-aerangis lactone.[62]

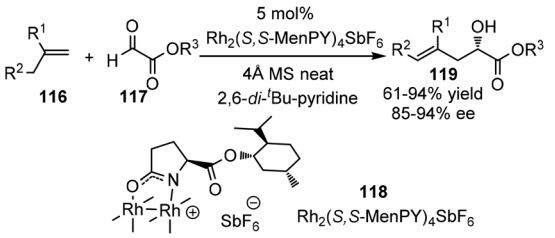
In fact, dirhodium was also an efficient catalyst for the intermolecular [2 + 2]-cycloaddition reaction between trimethylsilylketene **109** and ethyl glyoxylate **110** with the cooperation of quinine, which was postulated to react with ketone to form ammonium ketene enolate and resulted in a shorter reaction time and possible better selectivity.[63] This [2 + 2]-cycloaddition occurred in 87% yield and 99% ee with the employment of a chiral dirhodium(II) azetidinone-ligated catalyst $Rh_2(4S\text{-MEAZ})_4$ (Scheme 32). This example represents the first intermolecular [2 + 2]-cycloaddition reaction between ethyl glyoxylate and trimethylsilylketene catalyzed by dirhodium(II).

Although dirhodium is powerful in the HDA and [2 + 2] cycloaddition, however, the Lewis acidity of dirhodium(II) carboxamidates is low compared with that of other Lewis acids,[64] and chiral dirhodium(II) carboxamidates showed no catalytic activity in suitable Diels–Alder, ene, and many other dipolar cycloaddition reactions. From this point of view, Doyle and coworkers prepared cationic Rh^{II}/Rh^{III} counterparts to address this issue.[65] This more Lewis acidic dirhodium was believed to increase the closeness of association of the catalyst with the Lewis bases, increasing the reaction rate and enhancing the enantiocontrol. They found that dirhodium(II) carboxamidates could be oxidized facilely to the corresponding Rh^{II}/Rh^{III} salts by nitrosonium salts, whose structure was confirmed by the crystal structure. These cationic chiral dirhodium carboxamidates **114** formed *in situ* could be successfully used in 1,3-dipolar cycloaddition between nitrones **112** and enals **113** to form isoxazolidines **115** (Scheme 33).

Scheme 32 The enantioselective [2 + 2] cycloaddition catalyzed by $Rh_2(4S\text{-MEAZ})_4$ with quinine as cocatalyst.



Scheme 33 The enantioselective 1,3-dipolar cycloaddition between nitrones and enals catalyzed by $Rh_2(5S,R\text{-MenPY})SbF_6$.



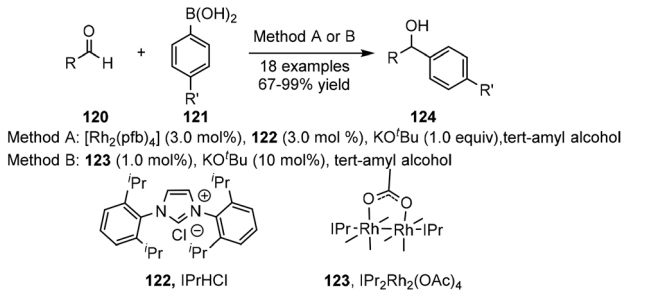
Scheme 34 The enantioselective carbonyl–ene reaction catalyzed by $Rh_2(S,S\text{-MenPy})SbF_6$.

Benefiting from the enhanced Lewis acidity of chiral cationic dirhodium(II,III) carboxamidates, Doyle and coworkers further reported an enantioselective carbonyl-ene reaction of 1,1-disubstituted alkenes **116** with glyoxylate esters **117**, giving the homoallylic alcohol products **119** in 61–94% yield and 85–94% ee (Scheme 34).[66]

2.5 Dirhodium in the arylation of aldehyde

Diaryl methanols have received much attention and become important synthetic targets because they are key structural skeletons in a diversity of biologically active compounds.[67] The arylation of aldehydes is one of the most powerful methods to construct them,[67] in which few Rh_2(II)-catalyzed examples have been established as a result of the introduction of axial additives, such as N-heterocyclic carbene (NHC) and phosphine ligands. These findings provide complementary ways to obtain diaryl methanols, and also unveil a new reaction mode for dirhodium(II) complexes.

In 2007, Gois and coworkers reported a dirhodium–NHC complex-catalyzed arylation of aldehydes.[68] It was found that, in contrast to the lack of reaction under the conditions of $Rh_2(OAc)_4$, the dirhodium–NHC complex prepared *in situ* could improve the results dramatically in the synthesis of diaryl methanols **124** from aldehyde **120** and boric acid **121** (Scheme 35). A 37% yield could also be obtained by using PPh_3 as the axial ligand. Conditions screening showed that $Rh_2(pfb)_4$ and the protic solvent *tert*-amyl alcohol was the best combination with **122**, giving the product **124** in 67–99% yields. Moreover, the complex with two axial NHCs **123** was also effective in catalyzing the reaction while one of the NHCs



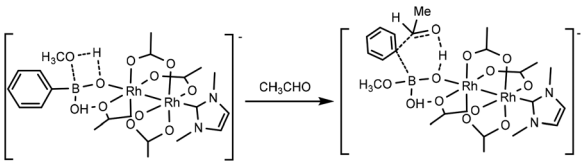
Scheme 35 Arylation of alkyl and aryl aldehydes catalyzed by dirhodium–NHC complexes.

dissociated from the complex during the reaction. This methodology had a noteworthy tolerance to functional groups, although it was slightly sensitive to electronic effects. Further theoretical and structural studies confirmed that the mono-complex was the most active catalyst in the arylation of alkyl aldehydes.[69] The axial NHC ligands result in a longer Rh–Rh bond due to the σ-donation from the carbene lone pair electrons to the Rh–Rh antibonding orbital and the NHC could act as an electron buffer, releasing excess electron density on the $Rh_2(OAc)_4$ core due to coordination of the second axial ligand. Besides, they may also provide steric protection to stabilize the catalyst. Instead, no obvious reaction was observed when boronate ester was used in place of boronic acid. These results coupled with DFT calculations showed that the hydrogen-bonding network between dirhodium, aldehyde and boric acid and solvent (alcohol) was the fundamental element for the reaction (Scheme 36).[69]

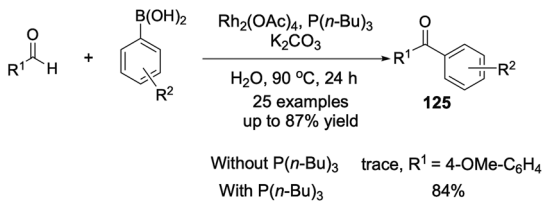
Although it seems that the NHC ligands are too far away to control the arylation of aldehyde which occurs on the other rhodium, Ma *et al.* found that moderate enantioselectivities (28–52% ee) could be observed when the bulky planar chiral imidazolium salts derived from [2.2]paracyclophane were employed.[70]

Apart from the NHC, phosphine ligands could also be coordinated to the axial position to activate the other side Rh of the dirhodium. In 2014, Wang and coworkers reported a cross-coupling reaction of aryl aldehydes and arylboronic acids in neat water, giving ketones **125** as the products in up to 87% yield (Scheme 37).[71] The reaction was proposed to occur through a cascade process involving the dirhodium-catalyzed addition of the boronic acid to the aldehyde followed by dehydrogenative oxidation. The fine-tuning effect and the conical shape of the opposite axial phosphine ligands across the Rh–Rh bond could be the main reasons accounting for the results. Later, they provided a detailed insight for the mechanism with the arylation of isatin derivatives **126** as the template reaction. Analysis of the crystal structure data showed that the net σ-donation from the axial phosphine ligand to the Rh–Rh bond was the result of the electron-donating ability and the steric profile. In this context, the σ-donation effect of strong σ-donor P(*t*-Bu)$_3$ was similar to the aryl phosphane ligand PPh_3, but the complex with P(*t*-Bu)$_3$ coordinated to the rhodium had a long Rh–P bond distance, which facilitated the substitution of one of the axial phosphane ligands by the arylboronic acid.[72] Therefore, the P(*t*-Bu)$_3$ behaved better than PPh_3 in this reaction (Scheme 38).

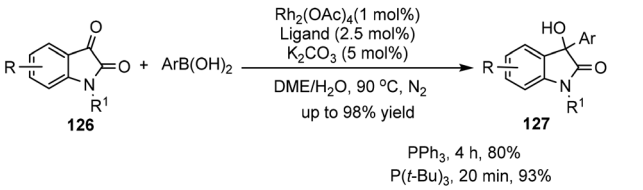
Using phosphine-ligated dirhodium(II) acetate as the catalyst, Wang and coworkers further realized the synthesis of aryl alkyl ketones by the cascaded reactions of α,β-unsaturated aldehydes with arylboronic acids (Scheme 39).[73] The reaction was proved to undergo the aforementioned arylation process and the subsequent isomerization process. They found that the length of the Rh–P bond was an important factor affecting the catalytic reactions. A shorter Rh–P bond favored the isomerization process. The mechanism of the two-step catalytic cycle was proposed as in Scheme 39. The aldehyde **128** and phenylboronic acid **129** were catalyzed by the Rh_2(II) catalyst to form a six-membered ring transition state mediated by hydrogen bonding to give the alcohols. The isomerization process could be interpreted as that the oxygen atom of the alcohols coordinates axially with the rhodium atom, followed by dissociation of the bridging ligand through a four-membered ring



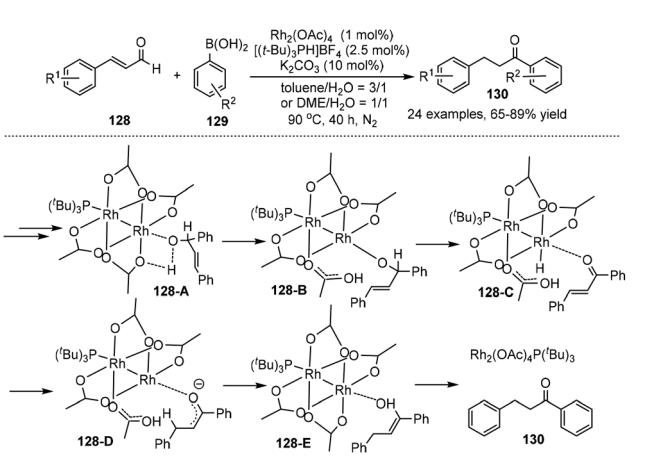
Scheme 36 The hydrogen-bonding network in arylation catalyzed by dirhodium–NHC complexes.



Scheme 37 Arylation of aldehydes catalyzed by dirhodium and P(*n*-Bu)$_3$.



Scheme 38 Arylation of isatin derivatives catalyzed by dirhodium and P(*t*-Bu)$_3$.



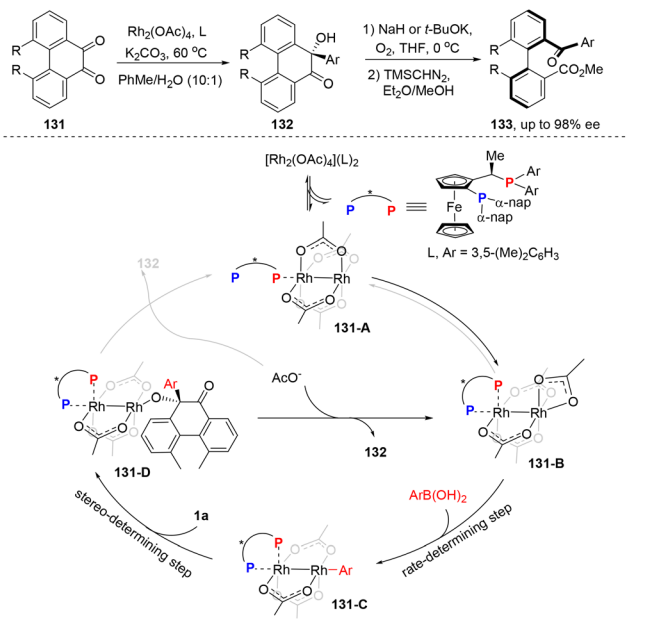
Scheme 39 Dirhodium-catalyzed cascaded arylation and isomerization process.

transition state. The β-H elimination and 1,4-addition of the Rh-hydride to the ketene then occur to afford **128-D**. Afterwards, the dissociated acetoxy ligand coordinates with the rhodium atom to regenerate $Rh_2(OAc)_4$ with the formation of axially coordinated enols **128-E**. Finally, the enols dissociate from the $Rh_2(OAc)_4$ during tautomerism to give the products **130**.

Recently, Gu and coworkers achieved the highly asymmetric arylation of phenanthrene-9,10-diones **131** with arylboronic acids using the combination of $Rh_2(OAc)_4$ and phosphine with a chiral environment at the bridging site as the catalyst (Scheme 40).[74] Notably, the obtained α-hydroxyl ketone **132** could be transformed into axially chiral biaryls **133** *via* a newly developed oxidative ring-opening reaction. Detailed mechanistic studies were conducted to reveal the reaction process and the catalytic species. Based on the results of NMR, UV–vis spectra and X-ray photoelectron spectroscopy (XPS) analysis, **131-B** was assumed to be the key catalytic species, in which the two arms of the phosphine ligand act as axial and bridging ligands respectively, the dinuclear structure was reserved and the oxidation state was still +2. Additionally, in contrast to the reaction mechanism proposed by Gois and coworkers, the rate-determining step transmetalation instead of the hydrogen-bonding network was involved, which was supported by the kinetic investigations.

2.6 Dirhodium in silylation reactions

The transition-metal-catalyzed silylations of alkenes or alkynes, including hydrosilylation, dehydrosilylation and silylformylation *etc.*, are appealing strategies for the synthesis of silanes and vinylsilanes, which are crucial building blocks in the preparation of biologically active molecules and functional materials.

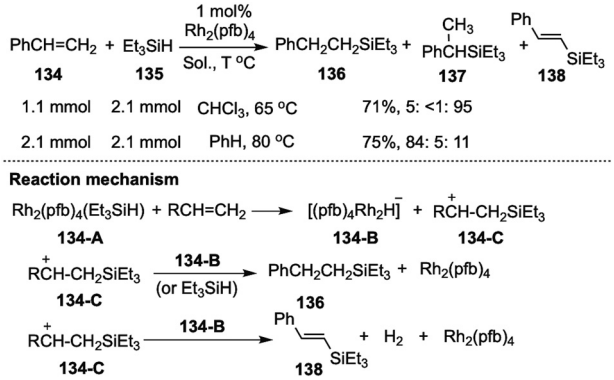


Scheme 40 Dirhodium-catalyzed highly enantioselective arylation.

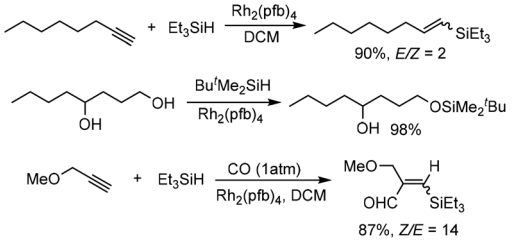
Doyle and coworkers reported a series of discoveries on dirhodium-catalyzed silylation reactions. Under the catalysis of 1 mol% $Rh_2(pfb)_4$, the styrene **134** underwent silylation and a subsequent elimination or reduction to give products **136–138** (Scheme 41).[75] The selectivity depended on the ratio of alkene and silane and the reaction conditions. An ionic process is proposed in Scheme 41; the silane or rhodium hydride **134-B** promoted hydrogenation of cationic intermediate **134-C** takes place to give **136**, while the rhodium hydride **134-B** could also facilitate the elimination of **134-C** to give the product **138**.

The $Rh_2(pfb)_4$-catalyzed reactions were also expanded to the hydrosilylation of alkynes,[76] silane alcoholysis[77] and silylformylations[78] (Scheme 42). In addition, these findings highlighted the importance of the electrophilicity of these complexes in determining their activities and selectivities in hydrosilylation and silylformylation. In addition, although carbon monoxide gas was typically used in dirhodium-catalyzed carbonylation, it was also found that formic acid could serve as more practical carbonyl source to circumvent the highly toxic and explosive CO gas.[79]

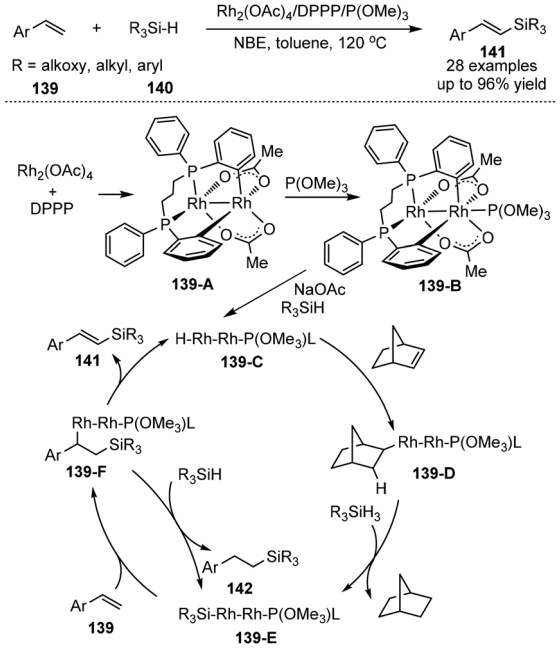
In 2021, Zhang and coworkers demonstrated that the combination of $Rh_2(OAc)_4$, DPPP and $P(OMe)_3$ in the presence of norbornene (NBE) could be nicely employed in the dehydrosilylation of vinylarenes (Scheme 43).[80] A wide range of vinylarenes **139** and tertiary silanes **140** were compatible. Moreover, the mechanistic studies were more appealing. DPPP coordinated to $Rh_2(OAc)_4$ to form a stable and rigid complex **139-**



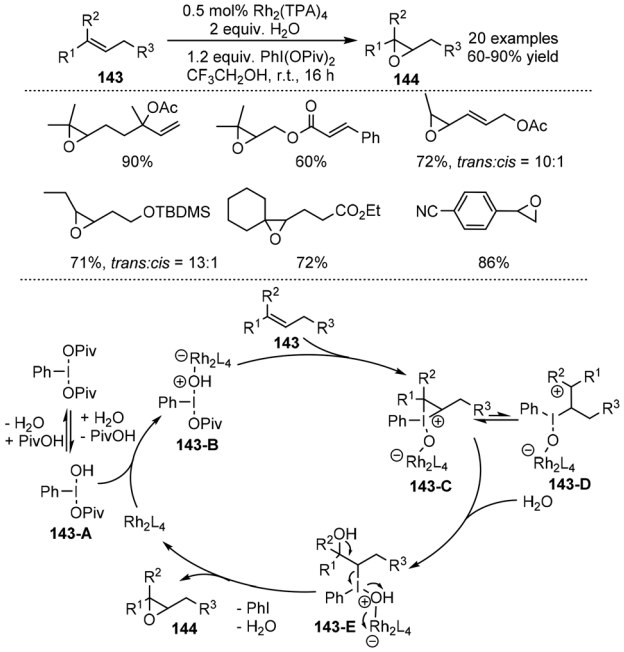
Scheme 41 Dirhodium(II)-catalyzed hydrosilylation of alkenes.



Scheme 42 Dirhodium-catalyzed hydrosilylation, silane alcoholysis and silylformylations.



Scheme 43 Dirhodium(II)-catalyzed dehydrosilylation of vinylarenes.



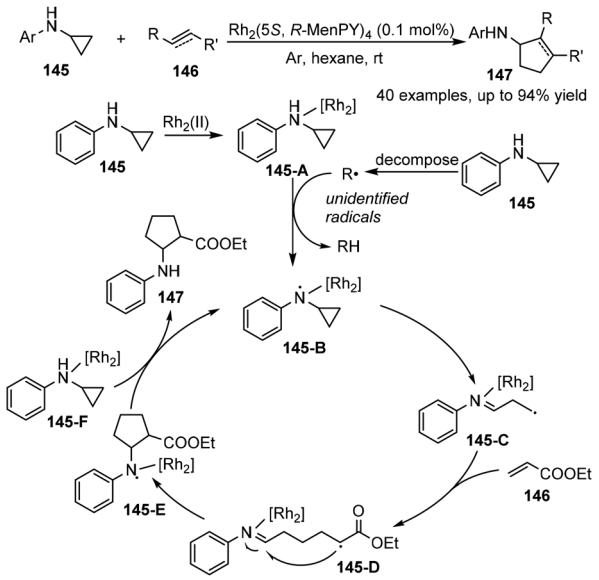
Scheme 44 Dirhodium-catalyzed alkene epoxidation.

A, in which the phosphine atoms of the DPPP were coordinated to one of the rhodium atoms, and the other was bonded with the phenyl of each phosphine by *ortho*-metalation while the $P(OMe)_3$ was then ligated to the orthometalated rhodium atom at the axial position to generate **139-B**. These above coordination and bonding modes were confirmed by the X-ray crystal diffraction of the corresponding crystal. These complexes were the active species to generate Rh–H **139-C** and subsequent Rh–[Si] species **139-E**. In addition, control experiments revealed that the norbornene served as the hydrogen acceptor, which inserted into the **139-C** followed by reaction with silane to give Rh–[Si] species **139-E**. Then the alkene **139** reacted with **139-E** by migratory insertion and subsequent β-H elimination to give the final dehydrosilylation product **141**. Sometimes, a small amount of hydrosilylation product **142** could also be observed, which was attributed to the σ-bond metathesis between **139-F** and silane, but the dehydrosilylation process was more favorable for the crowded steric structure of dirhodium(II) complex **139-F**.

2.7 Miscellaneous reactions

In addition to the abovementioned applications of dirhodium as a Lewis acid, there are some unclassified but meaningful transformations reported. Dirhodium(II) complexes and iodine (III) oxidants could usually be a good combination in nitrene chemistry.[2c] However, in 2018, Dauban and coworkers found serendipitously that the dirhodium(II) complex could serve as a Lewis acid species to be engaged in alkene epoxidation in the presence of iodine(III) oxidants and 2 equivalents of water (Scheme 44).[81] A diversity of substituted alkenes **143** were feasible to be oxidized to give **144** with up to 90% yield. Mechanistically, the possible involvement of radicals was excluded and a reasonable mechanism with dirhodium(II) as the Lewis acid was proposed in Scheme 44. The water works as a ligand to exchange with the OPiv of the $PhI(OPiv)_2$ firstly to afford the iodine(III) species **143-A**. Then the dirhodium reacts with **143-A** to generate the zwitterionic intermediate **143-B**, which reacts with the alkene **143** to produce the cyclic iodonium **143-C**. It undergoes sequential nucleophilic substitution with water to give the epoxide **144** with iodobenzene and water as by-products and the dirhodium(II) complex is regenerated. In some cases, isomerization was also observed, which could be rationalized by a hypothetical equilibrium between the intermediate **143-C** and the carbocationic species **143-D**.

In the same year, Wang and coworkers found that the dirhodium could also coordinate with nitrogen atom of *N*-arylaminocyclopropane to decrease the bond-dissociation energy (BDE) of the N–H bond, thus facilitating the formation of *N*-centered radicals. Based on this, they reported a dirhodium-catalyzed [3 + 2] cycloaddition reaction between *N*-arylaminocyclopropane **145** and alkenes or alkynes derivatives **146** (Scheme 45).[82] This protocol exhibited a wide substrate scope. UV/vis spectral analysis showed that the oxidative state of Rh_2(II,II) did not change. A reasonable reaction process is presented in Scheme 45. The aminocyclopropane **145** decomposes to generate unidentified radicals, which abstract an H atom from the Rh_2(II,II) regulated **145** and the N-centered radical **145-B** is generated. Then the cyclopropane undergoes ring-opening to generate radical **145-C**, which is captured by external alkene **146** to produce **145-D**. An intramolecular radical addition then occurs to yield **145-E**. After a hydrogen atom transfer course, the product **147** is obtained with the N-centered radical **145-B** regenerated. It is worthwhile to mention that the obtained products were optically inactive,

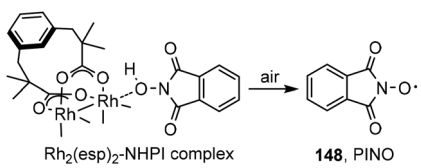


Scheme 45 Dirhodium(II)-catalyzed [3 + 2] cycloaddition of the *N*-arylaminocyclopropane with alkene or alkyne derivatives.

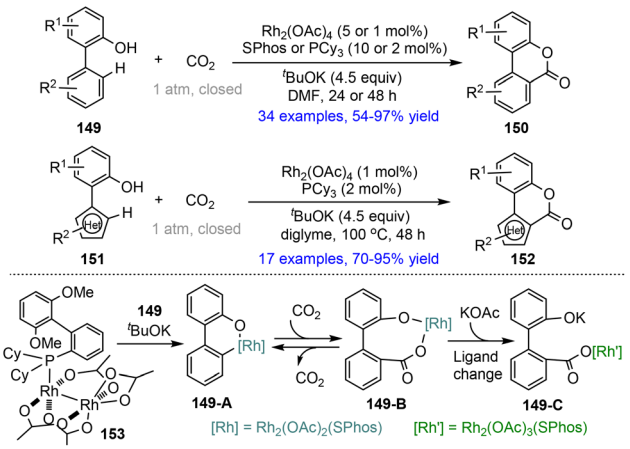
though a chiral catalyst $Rh_2(5S,R\text{-MenPY})_4$ was employed. Therefore, the reaction mechanism and enantioselective control are waiting for further in-depth investigations.

There was a similar case that happened to dirhodium(II)/*N*-hydroxyphthalimide (NHPI)-mediated allylic and benzylic oxidations, in which the $Rh_2(esp)_2$ could decrease the BDE of O–H in NHPI, facilitating phthalimide-*N*-oxyl radical (PINO) **148** formation.[83] The PINO then could be engaged in an allylic and benzylic oxidation of alkene with ambient air as the oxidant (Scheme 46).

In 2018, a ligand-enabled site-selective aryl C–H carboxylation under atmospheric pressure of CO_2 catalyzed by $Rh_2(OAc)_4$ was disclosed by Li and coworkers (Scheme 47).[84] The combination of $Rh_2(OAc)_4$ and SPhos or PCy_3 or NHC showed good reactivities and selectivities. It is worth mentioning that the reaction took place on the less nucleophilic phenyl group, overriding the site selectivity of a Kolbe–Schmitt type reaction. A wide range of benzene rings **149** and heterocycles **151** (five-membered heterocycles for most cases) were compatible to give the products in 54–97% yields. Detailed mechanistic studies showed that the SPhos and $Rh_2(OAc)_4$ were formed into complex **153** initially. Then a reversible chelation-assisted aryl C–H bond activation occurred with the assistance of a base, followed by a reversible insertion with



Scheme 46 Dirhodium(II)-catalyzed PINO formation.

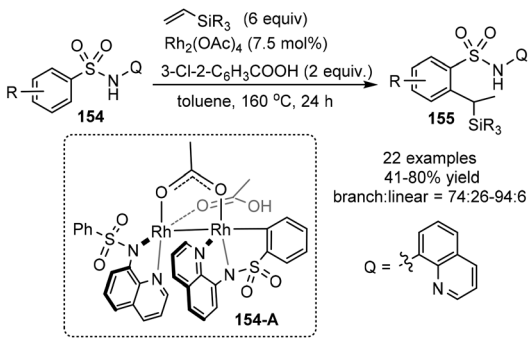


Scheme 47 Dirhodium(II)-catalyzed aryl C–H carboxylation with CO_2.

CO_2 to generate **149-B**. Subsequently, the **149-B** underwent a ligand change and protonolysis to give the final product **150**. Therefore, the reaction was a redox-neutral process. Nevertheless, whether other valent Rh species were involved was still unclear. This innovative strategy could also be extended to the aryl C–H carboxylation of 2-pyridylphenols and imidazo[1,2-*a*]pyridine with good efficiency.[85]

In 2020, Chatani's group reported a Rh(II)-catalyzed C–H alkylation of aryl sulfonamides **154** with vinylsilanes using 8-aminoquinoline as the directing group (Scheme 48).[86] The branched alkylation products **155** were obtained with good selectivities. On the basis of the mechanistic experiments, a di-8-aminoquinoline-chelated perpendicular metallacycle species **154-A** was proposed as the key intermediate. The origin of good branch-selectivity was further elucidated by detailed DFT calculations.[87] The metallacycle species **154-A**, in which the linear-selective migratory insertion transition state was destabilized for steric interactions between the silicon group and the acetic acid ligand, was presented.

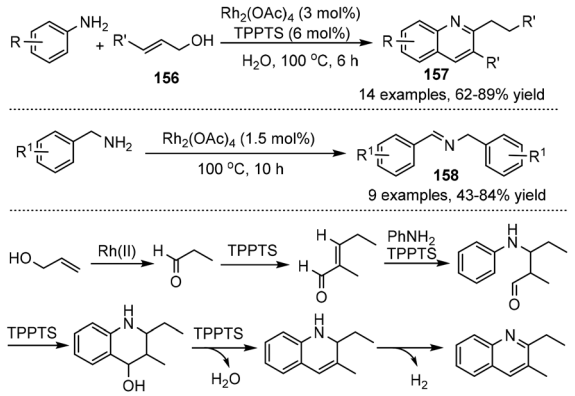
Quinolines are a crucial class of structural frameworks in biologically active molecules.[88] In 2015, Bhanage and coworkers found that the quinolines **157** could be synthesized from anilines and allyl alcohol **156** using $Rh_2(OAc)_4$ and tri-



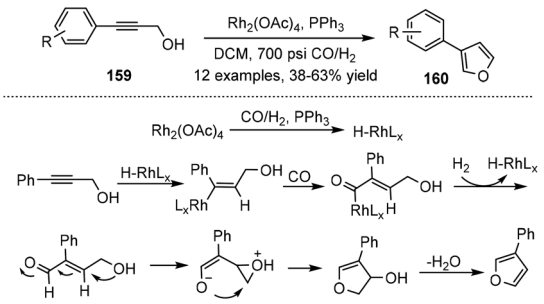
Scheme 48 Dirhodium(II)-catalyzed branch-selective C–H alkylation of aryl sulfonamides.

phenylphosphine trisulfonate sodium salt (TPPTS) as the catalysts in a simple but efficient manner (Scheme 49).[89] Remarkably, this reaction was conducted in water and the catalyst could be recycled up to five runs without much loss in its catalytic activity. Mechanistically, dirhodium hydride-mediated isomerization of allyl alcohol to the corresponding propanal was involved. Based on this, the self-condensation of benzyl amine to provide the corresponding imine **158** was also disclosed.

The furan ring widely exists in natural products and pharmaceutical molecules.[90] In 2005, Alper's group demonstrated a straightforward route to obtain the 3-substituted furans **160** *via* the dirhodium-catalyzed regioselective hydroformylation of phenyl propargylic alcohols **159** (Scheme 50).[91] The reaction proceeded in an atmosphere of CO/H_2 with PPh_3 as the indispensable ligand to give the 3-phenyl furans in 38–63% yields. A plausible mechanism for this transformation is outlined in Scheme 50, in which a dirhodium hydride species is formed in the presence of PPh_3 and CO/H_2. Then the dirhodium hydride species adds to the propargylic alcohol in a *cis* fashion and the regioselectivity could be attributed to the possible weak H-bonding interaction between dirhodium hydride species and alcohol. Carbonyl insertion and cyclization with the elimination of a water molecule then occur to produce the target product 3-substituted furans **160**.



Scheme 49 Dirhodium-catalyzed synthesis of quinolines and imine.



Scheme 50 Rh(II)-catalyzed hydroformylation of propargylic alcohol.

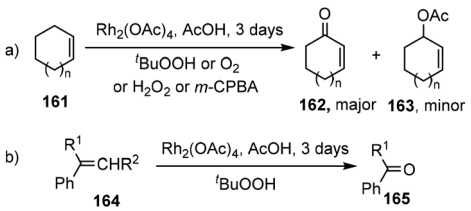
3. Dirhodium as a redox catalyst

As mentioned above, dirhodium has undoubtedly demonstrated powerful competence as a redox-neutral catalyst. These related transformations are typically conducted in mild conditions with high atom-economy. Importantly, the enantioselective versions have been achieved in many cases. In contrast, dirhodium could also be engaged in redox reactions, such as radical or two-electron oxidation, diamination, or redox C–H activation. Oxidants, like peroxy-*tert*-butanol (*tert*-butyl hydroperoxide), *N*-fluorobenzenesulfonimide (NFSI), high-valent idoine reagents, allylic esters and benzene halides were typically employed. In these reactions, the roles of bridging and axial ligands were underlined. Maybe due to a lack of in-depth understanding of the reaction mechanism, asymmetric reactions with dirhodiums as the redox catalysts were rarely reported.

3.1 Dirhodium in radical oxidation and diamination

Under a suitable oxidant, like *tert*-butyl hydroperoxide, NFSI and high valent idoine reagents, dirhodium(II) could be oxidized into a Rh_2(II,III) intermediate, typically with a radical species ligated on the axial position. This Rh_2(II,III) species could be engaged in value-added oxidation reactions, such as allylic/benzylic oxidation, which provides a straightforward and efficient route to obtain the oxidation products in mild conditions. Besides, the key Rh_2(II,III) species also play crucial roles in aromatic azidation reactions and diamination reactions of alkenes or alkanes, allowing the rapid synthesis of various nitrogen-containing compounds. The wide applications of dirhodiums benefit from their structural modification, that is, the improvement of bridging ligands and the introduction of axially additives.

In 1982, Uemura and coworkers reported that under the conditions of $Rh_2(OAc)_4$, acetic acid and oxidizing agents, such as *t*-BuOOH, O_2, H_2O_2 or *m*-CPBA, cyclic olefins **161** could be transformed into enones **162** and allylic acetates **163**, and enones **162** were predominant (Scheme 51a).[92] Moreover, this catalytic system could also be employed in selective carbon–carbon double bond fission (Scheme 51b). However, the reaction efficiency and selectivity needs to be improved for most cases. When a radical scavenger such as 6-*t*-butyl-*o*-cresol or hydroquinone was added, the reaction was hardly affected. Therefore, the reaction was considered to proceed *via* an ionic pathway based on the radical trapping experiments, but maybe

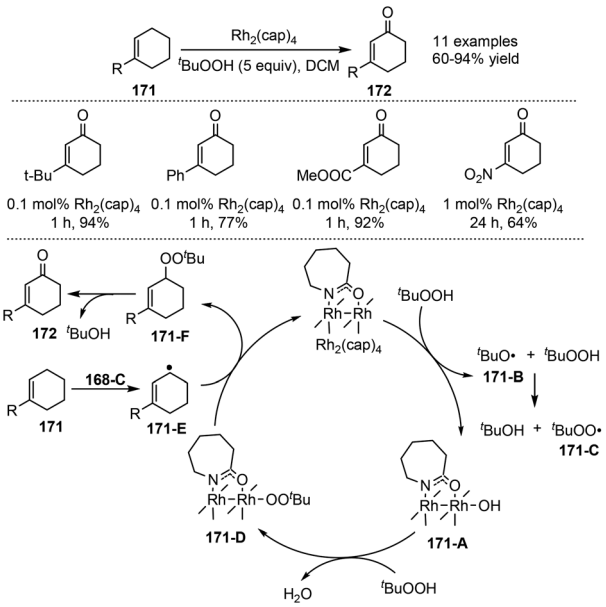


Scheme 51 The seminal work of $Rh_2(OAc)_4$-catalyzed oxidation reaction.

2 mol% radical scavenger was not enough to draw this conclusion.

Soon afterwards, Doyle *et al.* found that $Rh_2(OAc)_4$ could also be used as the catalyst for autooxidations of hydrocarbons at room temperature and under atmospheric oxygen conditions (Scheme 52).[93] Under these conditions, cyclohexadiene **166** could be oxidized into *p*-cymene **167** in 96% yield after 22 h, and could be further oxidized into the corresponding alcohol **168** with an additional 18 days. The alcohol was probably arising from the decomposition of hydroperoxide species catalysed by dirhodium. A free radical pathway was proposed for the autooxidation process. Furthermore, the combination of dirhodium and oxidant was applicable to the oxidation of the allylic and benzylic alcohols **169** (Scheme 53).[94] However, for the unactivated primary and secondary alcohols, this protocol was ineffective.

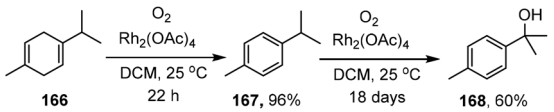
Although $Rh_2(OAc)_4$ was found to be a feasible catalyst in the chemical oxidation, it always suffered long reaction times, a narrow substrate scope and low efficiency. With the development of dirhodium catalysts, an exceptional catalyst for allylic oxidation was discovered by Doyle *et al.* in 2004 (Scheme 54).[95] Under the condition of only 0.1 mol% $Rh_2(cap)_4$ and K_2CO_3, various representative olefins **171** were rapidly converted to enones **172** with good selectivities. The reversible oxidation at 55 mV (in CH_3CN, *vs.* Ag/AgCl) corresponding to the Rh_2^{4+}/Rh_2^{5+} redox couple of $Rh_2(cap)_4$, compared with $Rh_2(OAc)_4$ (1170 mV), was considered to be main cause for the high efficiency. Based on the UV-visible spectrum, and reaction phenomenon, a reasonable reaction mechanism constituting a redox chain catalytic cycle was proposed in Scheme 54. $Rh_2(cap)_4$ undergoes 1-electron oxidation in the presence of *tert*-butyl hydroperoxide to form a Rh_2^{5+} species **171-A** and tertbutyloxygen radical **171-B**. This radical **171-B** then reacts with *tert*-butyl hydroperoxide to give tertbutyl peroxy radical **171-C**, which is capable of selective hydrogen atom abstraction to produce allyl radical **171-E**. On the other hand, the OH-ligated dirhodium **171-A** reacts with *tert*-butyl hydroperoxide to generate tertbutyl peroxy-ligated dirhodium **171-D** whose metal-



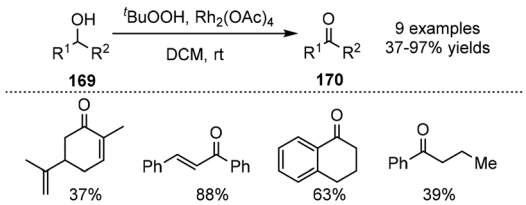
Scheme 54 Allylic oxidation of alkenes catalyzed by $Rh_2(cap)_4$.

bound peroxide is transferred to the allyl radical center to produce the mixed peroxide **171-F** and the Rh_2^{4+} is regenerated. Finally, the rapid decomposition of **171-F** yields the enone **172**. Notably, the base was envisioned to promote the conversion of allylic *tert*-butyl peroxy ethers **171-F** to carbonyl compounds **172**.

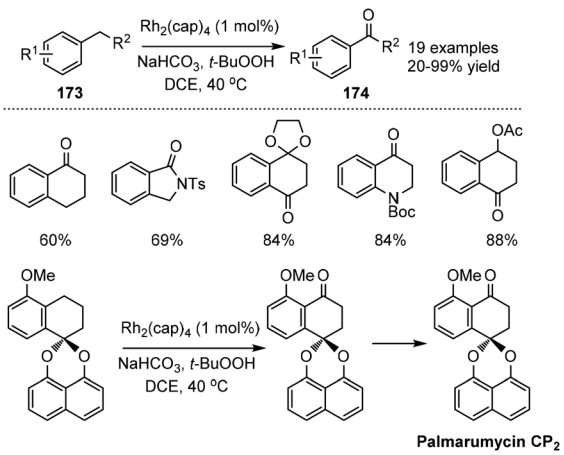
In addition to the allylic oxidation, $Rh_2(cap)_4$ was also an efficient catalyst for benzylic oxidation in the presence of *tert*-butyl hydroperoxide and base (Scheme 55).[96] Systematic investigations revealed that $NaHCO_3$ was the best base. Interestingly, an action of the base being a mediator for *tert*-butyl peroxy ether intermediates to carbonyl compounds was excluded by control experiments and the role of the base was still elusive. A diverse selection of substrates **173**, such as *N*-protected tetrahydroquinolines, chroman and 1-acetoxy-



Scheme 52 Rhodium(II) acetate-induced autooxidation.



Scheme 53 Oxidation of alcohols catalyzed by $Rh_2(OAc)_4$ using *tert*-butyl hydroperoxide.



Scheme 55 Benzylic oxidation catalyzed by $Rh_2(cap)_4$.

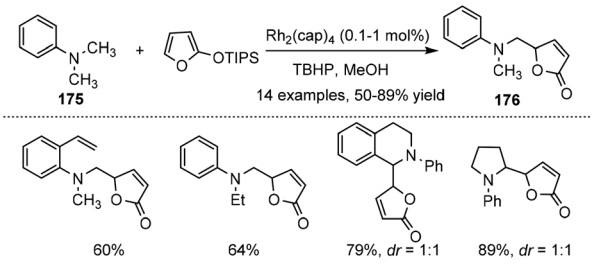
tetrahydronaphthalene *etc.*, were facilely converted to carbonyl compounds **174** in 20–99% yields. With this method, a formal synthesis of Palmarumycin CP_2 was also achieved.

After the allylic and benzylic oxidation, in 2006, Doyle and coworkers found that $Rh_2(cap)_4$ could be further utilized in an oxidative Mannich reaction, which allowed for the formation of valuable aminoalkyl butenolides **176** from readily available amines **175** using 2-triisopropoxysiylfuran to intercept the possible iminium ion intermediate (Scheme 56).[97] This oxidative Mannich reaction was proved feasible for a diverse collection of amine substrates, giving the product **176** in 50–89% yields. Noteworthy examples included an amine containing a proximal olefin as well as *N*-phenyl tetrahydropyrrole.

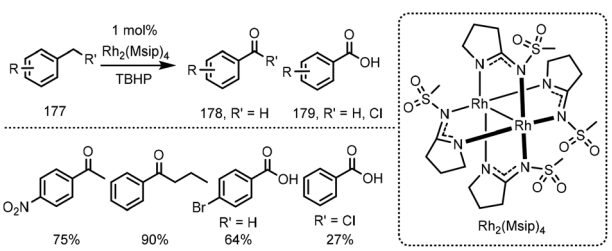
Inspired by the N,O-ligated dirhodium(II) complexes and their high efficiency in the oxidation of benzylic and allylic C–H bonds, Lu *et al.* prepared a new class of dirhodium(II) tetraamidinates, which mainly appear to be a (3, 1) geometry.[98] Among these, $Rh_2(Misp)_4$ showed good catalytic reactivity in benzylic oxidation with *tert*-butyl hydroperoxide (*tert*-butyl hydroperoxide) as the oxidant in water. The oxidation of electron-deficient arylalkanes was also viable in this catalytic system (Scheme 57). Some of the results were comparable to the $Rh_2(cap)_4$-catalyzed examples. Notably, the substrate **179** of benzyl chloride or toluene led to the formation of benzoic acid. Cyclic voltammetry measurements showed that the reversible one-electron oxidation of $Rh_2(Msip)_4$ occurs at $E_{1/2}$ = 570 mV, which was much higher than for $Rh_2(cap)_4$ ($E_{1/2}$ = 55 mV). These results implied that an extreme tendency for one-electron oxidation was not a precondition for $Rh_2(Msip)_4$ in catalytic benzylic oxidation.

In addition to changing the bridging ligands of dirhodium, introducing axial ligands also could induce electronic and structural changes, so as to improve the catalytic activities of the dirhodium complexes. In 2007, Jang and coworkers introduced a new dirhodium tetraacetate involving N-heterocyclic carbene **181** into the allylic oxidation, giving the carbonyl compounds in 18–57% yields (Scheme 58).[99] Importantly, this complex showed improved reactivity over $Rh_2(OAc)_4$ in the allylic oxidation (57% *vs.* 9%). X-ray crystallography showed that the Rh–Rh distance was elongated as a result of the electron donor axial ligand of NHC. Afonso and coworkers later further showed that the mono-NHC-ligated $Rh_2(OAc)_4$ displayed lower oxidation potential values than $Rh_2(OAc)_4$.[100] In other words, the introduced NHC ligands promote the oxidation of the complex and enhance the catalytic ability towards the allylic and benzylic oxidation reactions. They also concluded that NHC was a much stronger electron donor than pyridine, acetonitrile or isocyanide. Moreover, comparing with the well-established $Rh_2(cap)_4$, the reactions conducted with $Rh_2(OAc)_4$(IPr) are less exothermic and release lower amounts of oxygen.

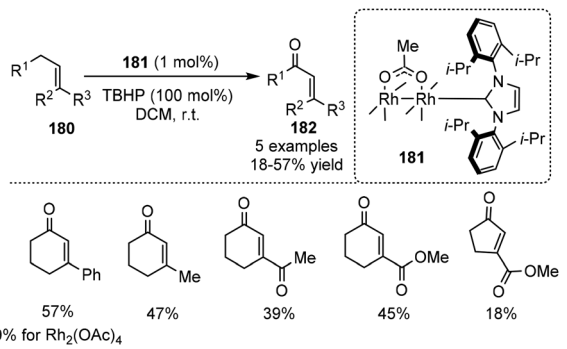
However, Wang and coworkers surprisingly found that the Du Bois catalyst $Rh_2(esp)_2$, with a high half-wave potential (1130 mV) similar to that of $Rh_2(OAc)_4$ (1170 mV), could also act as an excellent catalyst (0.1 mol%) in allylic and benzylic oxidation without comprising the reaction time (Scheme 59a).[101] Unlike $Rh_2(cap)_4$, which was considered to be the most efficient one for their low oxidation potential $E_{1/2}$ of 11 mV, the outstanding performance of $Rh_2(esp)_2$ was elucidated to be that the Rh_2(II,II) species was the resting state in $Rh_2(esp)_2$-catalyzed reactions, which was less prone to decom-



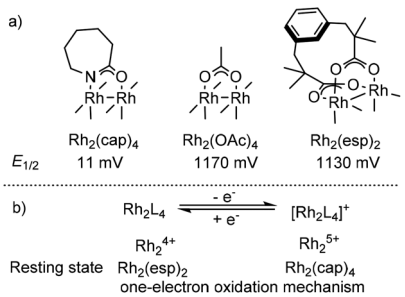
Scheme 56 The oxidative Mannich reaction catalyzed by $Rh_2(cap)_4$.



Scheme 57 Benzylic oxidation catalyzed by $Rh_2(Msip)_4$.



Scheme 58 Dirhodium–NHC complex-catalyzed allylic oxidations.



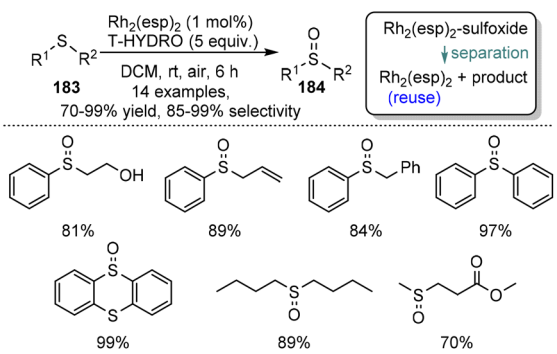
Scheme 59 Half-wave potential of dirhodium(II) catalysts and the discussion of the resting state.

posing compared with Rh_2(II,III) as the resting state in $Rh_2(cap)_4$-catalyzed oxidation (Scheme 59b). Besides, the bridging ligand of $Rh_2(esp)_2$ was also relevant to its high performance when comparing the results for $Rh_2(OAc)_4$. This protocol offers a new method to improve the catalyst efficiency besides lowering the oxidation potentials of dirhodium complexes.

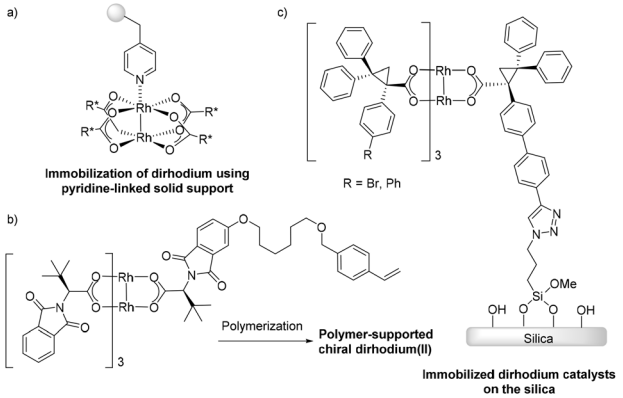
$Rh_2(esp)_2$ could also be applied to catalyze the selective sulfoxidation with *tert*-butyl hydroperoxide as the oxidant (Scheme 60).[102] A range of organic sulfides **183** were applicable with good selectivities and excellent yields. Relatively speaking, sulfides bearing electron-withdrawing substituents required longer reaction times for good conversion. Interestingly, the dirhodium catalyst precipitated as a $Rh_2(esp)_2$-sulfoxide complex, from which the catalyst could be separated and reused. Besides, the precipitated $Rh_2(esp)_2$-sulfoxide complexes could also be collected and directly reused to catalyze the sulfoxidation reactions without obvious loss of activity. To recover the $Rh_2(esp)_2$ catalyst from a homogeneous solution, a Merrifield resin functionalized with a pyridine group also proved helpful.[103]

Indeed, rhodium is a very expensive noble metal and the cost for dirhodium catalysts cannot be ignored. Therefore, methods for improving the catalyst turnover number (TON) and recovering dirhodium for reprocessing are highly desired. To solve this problem, Davies, Hashimoto, Jones and coworkers developed some feasible approaches to immobilize the catalyst on a support material, such as noncovalent immobilization technology (pyridine coordination with no derivatization of the chiral ligands necessary),[104] polymerization of dirhodium(II)-complex-containing monomer[105] and click reactions between alkyne-containing dirhodium with an azide-functionalized silane on the silica support[106] (Scheme 61). In addition to the advantage of excellent recyclability, the immobilized dirhodium catalysts could also exhibit good reactivities and selectivities.

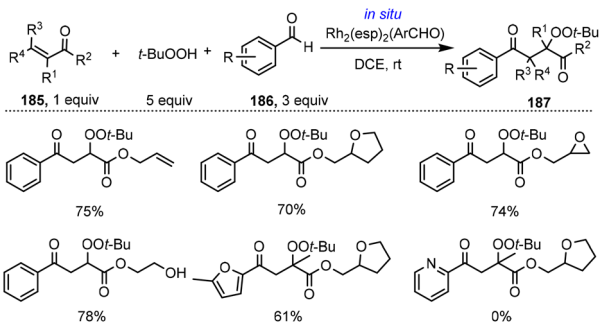
To broader the application of dirhodium(II) as the 1-electron reactant, Wang and coworkers developed a three-component oxidative coupling of α,β-unsaturated esters **185** with aryl aldehydes **186** and *tert*-butyl hydroperoxide catalyzed by $Rh_2(esp)_2$ to generate β-peroxyketones **187**, which potentially works in the synthesis of epoxides, biologically important natural products (Scheme 62).[107] The reaction intermediates



Scheme 60 Oxidation of sulfides catalyzed by $Rh_2(esp)_2$.



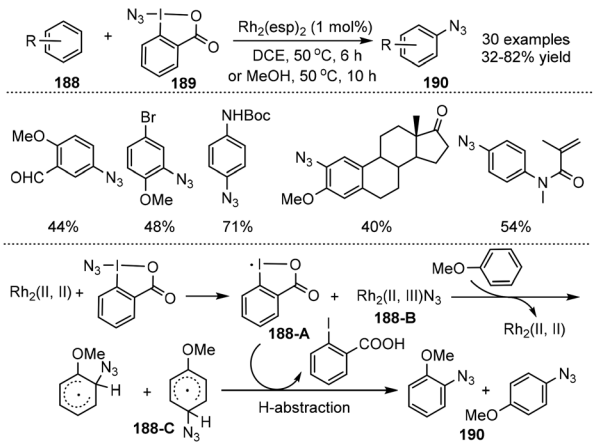
Scheme 61 Methods to improve the recyclability of dirhodium.



Scheme 62 Rh(II)-catalyzed carbonylation peroxidation of α,β-unsaturated esters.

were investigated by UV/vis spectra. This showed that besides being reactants, aryl aldehydes **186** could also coordinate to the dirhodium axially, inhibiting the free ligated $Rh_2(esp)_2$ to be the predominant species to protect the catalyst from deactivation. Moreover, the excess aryl aldehyde played an important role in avoiding catalyst deactivation by reducing the inactive $Rh_2(esp)_2Cl$ species. The unique structure of $Rh_2(esp)_2$ also played a critical role in maintaining the catalyst reactivity.

Organic azides are ubiquitous intermediates in the synthesis of nitrogen-containing compounds;[108] therefore, developing efficient methods to synthesize them is of great importance. In 2018, Wang *et al.* described a selective aromatic azidation reaction catalyzed by dirhodium(II), and Zhdankin's reagent **189** served as the azide source (Scheme 63).[109] In this transformation, the reactive functional groups, such as alkenyl, formyl and halogen *etc.*, were all compatible, giving the aryl azides **190** in 32–82% yields. The observed selectivity was similar to that of the aromatic electrophilic substitution reaction. The UV/vis, infrared and ^{1}H NMR spectra, coupled with the MS data, supported the existence of Rh_2(II,III)N_3 species **188-B**. Based on the mechanistic studies, the tentative process is proposed in Scheme 63; the weak I–N_3 is induced to cleave by the Rh_2(II,II), producing a 2-iodobenzoxyl radical **188-A** and Rh_2(II,III)N_3 **188-B**, which reacts with the arene to give the azidated radical **188-C** with the release of Rh_2(II,II). The



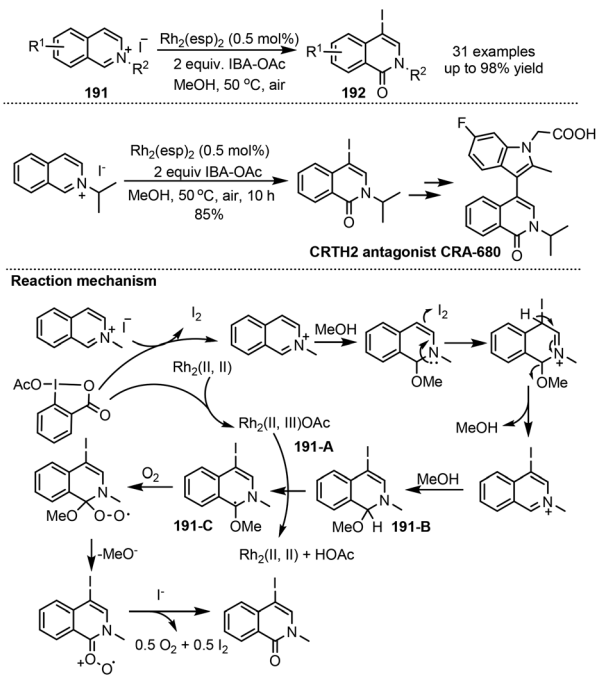
Scheme 63 Dirhodium(II)-catalyzed azidation of arenes.

radical **188-A** then abstracts the hydrogen from radical **188-C** to give the product **190** and the by-product 2-iodobenzoic acid. This one-electron oxidative process was also supported by the later study on the azidation of electron-rich aromatic aldehydes using phenyliodine(III) bis(trifluoroacetate) (PIFA) as the oxidant and $TMSN_3$ as the azide source.[110]

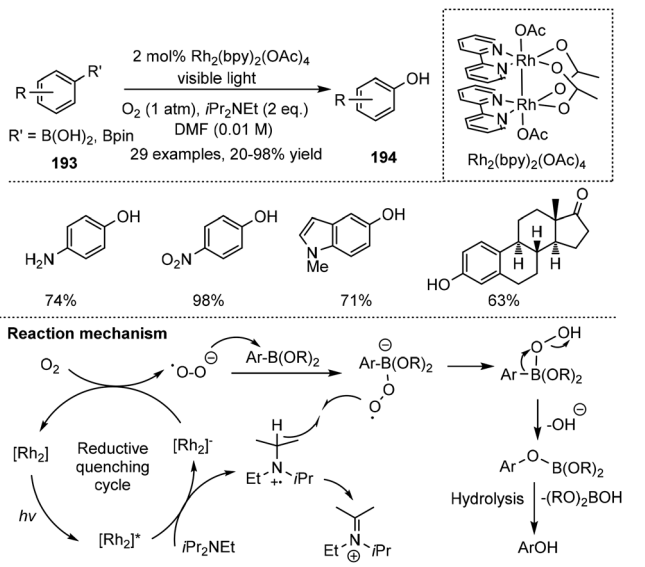
$Rh_2(esp)_2$ could also be used as one-electron reactant in the 1,3-bisfunctionalization of isoquinolinium iodide salts (Scheme 64).[111] In this transformation, readily available isoquinolinium iodide salts **191** could undergo iodination/oxidation under aerobic conditions to give 4-iodoisoquinolin-1(2*H*)-ones **192** with up to 98% yield. Notably, this synthetic method was proved viable for the gram-scale synthesis of a key intermediate in the synthesis of the CRTH2 antagonist CRA-680.[112] Mechanistically, in the presence of IBA-OAc, the $Rh_2(esp)_2$ was oxidized to generate the $Rh_2(esp)_2OAc$ **191-A**, which abstracted a hydrogen atom from hemiaminal-type intermediate **191-B** to form radical **191-C**.

When dirhodium was decorated with light-absorbing ligands, it could be applied in photoredox catalysis for organic synthesis. In 2020, Chuang and coworkers reported the first example of visible light-promoted aerobic oxidation reactions with the dipyridyl bridged dirhodium catalyst (Scheme 65).[113] The arylboronic acids **193** could be oxidized to phenols **194** in 20–98% yields under aerobic conditions. Reaction mechanism studies revealed that the excited Rh_2(II,II) acted as an oxidant, which was reduced to $[Rh_2]^-$ by iPr_2NEt. The formed $[Rh_2]^-$ could be oxidized by oxygen into $[Rh_2]$ to complete the catalytic reductive quenching cycle. Meanwhile, the oxygen was converted to a superoxide radical anion, which was able to engage in the subsequent arylboronic acid hydroxylation. Moreover, this catalytic system could be extended to other oxidation reactions, such as the oxidation of fluorene to fluorenone, *in situ* oxidation of iodide to promote iodolactonization and bromination of guaiacol.

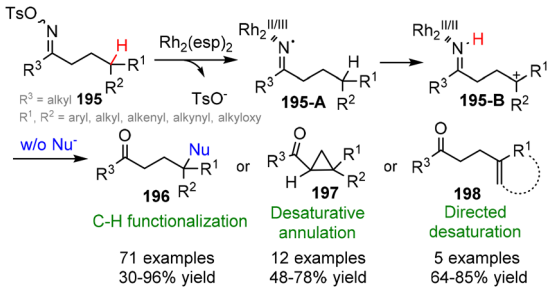
Recently, Munnuri and coworkers found that dirhodium(II) could also be engaged in the single electron transfer (SET) process with *O*-tosyloximes **195** to generate imino dirhodium (II,III) radical **195-A**, which underwent subsequent C(sp^3)–H activation to give carbocation **195-B** (Scheme 66).[114] The intermediate **195-B** was exploited for an agile trichotomy of challenging transformations: (1) remote C–H functionalization in the presence of a diverse variety of nucleophiles, such as alcohol, acyl silanes and ethers *etc.*, to afford **196**; (2) desaturative annulation to generate cyclopropane **197**; and (3) directed desaturation to give olefins **198**.



Scheme 64 Synthesis of 4-iodoisoquinolin-1(2*H*)-ones catalyzed by dirhodium.



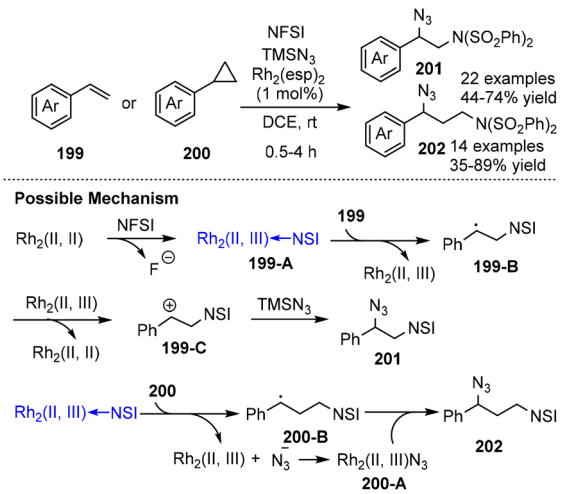
Scheme 65 Aerobic hydroxylation of arylboronic acids with dirhodium (II).



Scheme 66 Dirhodium-catalyzed C(sp^3)–H functionalization, desaturative annulation and desaturation.

In addition to the chemical oxidation reactions, a series of elegant works on dirhodium-catalyzed amination reactions were also reported by Wang and coworkers by virtue of the cooperation of dirhodium and NFSI. These results showed the untapped potential of dirhodium(II) in C–H amination reactions in addition to the well-known transformations of dirhodium nitrenoids.[2c] In 2021, they reported 1,2- and 1,3-diamination reactions of styrene **199** and phenylcyclopropane **200** with NFSI and $TMSN_3$ as the nitrogen sources, giving the corresponding products **201** and **202** in moderate to good yields (Scheme 67).[115] Different from the classical dirhodium-involved nitrene transfer reactions, UV-visible spectroscopy and further mechanistic studies showed the dirhodium(II,II) was oxidized by NFSI to dirhodium(II,III)NSI **199-A**, which underwent a radical addition on the alkene to give benzylic radical **199-B**. This radical was then oxidized to give carbon cation **199-C**, which was captured by the azide anion to give the product **201**. However, when it comes to phenylcyclopropane **200**, the situation become different for a higher oxidation potential of the radical **200-B** on account of a weaker induction effect, whereas the Rh_2(II,III)N_3 **200-A** was capable of oxidizing the intermediate **200-B** to the corresponding carbon cation.

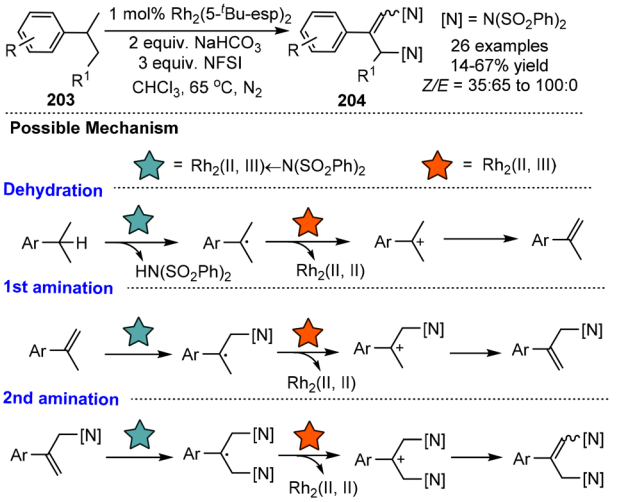
Afterwards, the same group described the successful application of the catalytic system on the C(sp^3)–H 1,3-diamination



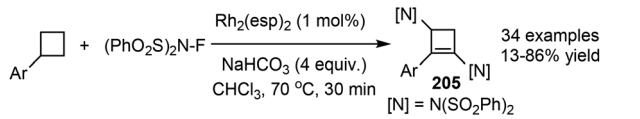
Scheme 67 Dirhodium(II)-catalyzed diamination reaction.

of easily available cumene derivatives **203** (Scheme 68).[116] In this protocol, the NFSI not only served as the nitrogen source, but also worked with Rh_2(II,II) as the oxidant to abstract the hydrogen from the cymene, so that the process of cymene to styrene was accomplished. That is, the reaction underwent iterative radical polar crossover and desaturation activation. On the whole, the reaction mechanism includes three cycles, *i.e.*, dehydration, 1st amination and 2nd amination. With this strategy, they also developed an efficient direct diamination protocol for arylcyclobutanes (Scheme 69)[117] and the desaturative [3 + 2] tandem cyclization of arylcycloalkanes with β-dicarbonyls (Scheme 70).[118]

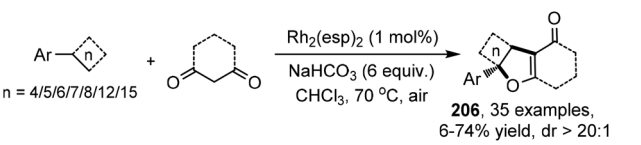
In the course of research, Wang and coworkers also found an interesting one-step route for allylic 1,3-diamination (Scheme 71).[119] The isomers of the alkenes **207** and **208**, one terminal and the other internal, could all be transformed into the same product **209** in 27–88% yields under the conditions of $Rh_2(esp)_2$ and NFSI. The reaction mechanism was clarified



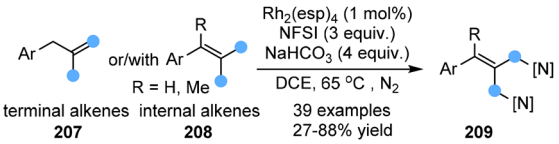
Scheme 68 C(sp^3)–H 1,3-diamination of cumene derivatives catalyzed by dirhodium(II).



Scheme 69 C(sp^3)–H diamination of arylcyclobutanes catalyzed by dirhodium(II).



Scheme 70 Desaturative [3 + 2] tandem cyclization of arylcycloalkanes with β-dicarbonyls.



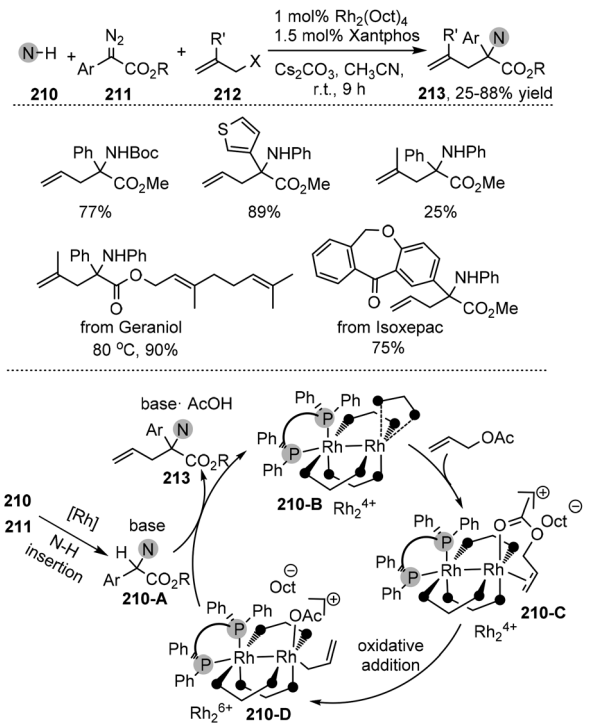
Scheme 71 Dirhodium(II)-catalyzed allylic 1,3-diamination.

by radical capture experiments, deuterated reactions and intermediates verification experiments. The radical polarity crossover for terminal alkenes and the activation of allylic C–H bonds followed by radical cross-coupling for internal alkenes were proposed to be the key processes.

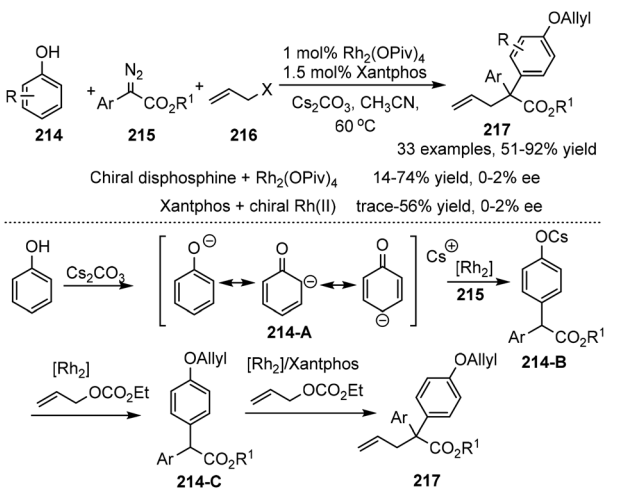
3.2 Dirhodium in two-electron oxidative addition

In addition to the radical oxidation reactions, the dirhodium catalyst could also be involved in two-electron oxidative addition, although usually unfavorable.[120] To achieve this process, effective regulations of ligands and axial additives are usually required. In 2021, Wang and Peng and coworkers disclosed a novel relay carbene insertion and allylic alkylation process under the catalysis of dirhodium/Xantphos, providing a straightforward way to synthesize allylated α-quaternary α-amino acid derivatives **213** in 25–88% yields (Scheme 72).[121] A wide range of amines, diazo compounds and allylic compounds were suitable. Besides, this protocol was also applicable to the late-stage functionalization of complex architectures. Notably, the bidentate ligand Xantphos was highlighted and indispensable. It was supposed that the electron density at the $[Rh_2]^{4+}$ core was increased for the chelation of the σ-donation of Xantphos, making the Rh_2(II) more susceptible to oxidation addition by an allylic substrate. Although detailed mechanistic investigations were conducted, the exact mechanism was still unclear. A tentative mechanism was proposed in Scheme 72. A common dirhodium-catalyzed N–H insertion of diazo compound **211** and amine **210** occurs to give the intermediate **210-A**. The Xantphos coordinates to dirhodium to form catalytic species **210-B**, which undergoes oxidation addition to give a $[Rh_2]^{6+}$ allylic intermediate **210-D** *via* substrate-ligated **210-C**. In the presence of a base, the subsequent nucleophilic attack takes place to give the product **213** and the Xantphos-$[Rh_2]$ is recycled.

Under a similar catalytic system, a multicomponent reaction of free phenols, diazoesters and allylic carbonates could also occur, providing a wide range of phenol derivatives in 51–92% yields, at which a quaternary carbon center and a useful allylic unit are situated (Scheme 73).[122] Interestingly, a distinctive reactivity of *para*-selective C–H rather than O–H insertion was observed. However, the catalytic asymmetric version still remains a challenging task as the best result was only 2% ee for various combinations of Rh_2(II) and diphosphine in the preliminary attempt. Based on extensive mechanistic studies, a possible reaction pathway was proposed in Scheme 73. In the presence of a base, the phenol **214** is transformed into phenolate salt **214-A** of which the aromatic ring possessed an enhanced nucleophilic ability. Then a *para*-selective C–H functionalization occurs to give **214-B**, followed by *O*-allylation under the catalysis of $[Rh_2]$ or $[Rh_2]$/Xantphos to afford the intermediate **214-C**. Finally, $[Rh_2]$/Xantphos-catalyzed allylic alkylation takes place to give the products **217**. The outstanding catalytic system was also further extended to the synthesis of diverse 3-acyl-3-allyl oxindole derivatives from easily available *N*-aryl-α-diazo-β-keto amides and allylic compounds.[123]



Scheme 72 Dirhodium(II)-catalyzed relay carbene insertion and allylic alkylation of amine.



Scheme 73 Dirhodium(II)-catalyzed relay carbene insertion and allylic alkylation of phenol.

3.3 Dirhodium in C–H activation

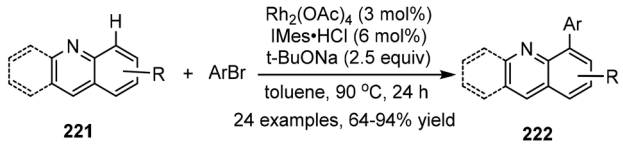
Transition metal-catalyzed C–H activation has proved to be one of the most effective and economical strategies to construct various C–C and C–heteroatom bonds to synthesize complex molecules.[124] Compared with other transition metals, like palladium and ruthenium *etc.*, examples of dirhodium(II)-catalyzed C–H activation are much less reported. The reported examples have shown some applications of dirhodium in arylation, hydroacylation, dehydrogenative silylation, and alkylation.

In 2009, a dirhodium/N-heterocyclic carbene catalyzed intermolecular arylation of sp^2 and sp^3 C–H bonds was introduced by Chang and coworkers. 1.5 mol% $Rh_2(OAc)_4$, 3 mol% IMesHCl and 5 mol% PCy_3 resulted in the arylation of **218** to give benzo[*h*]quinoline **220** in 98% yield at 80 °C (Scheme 74).[125] The reaction conditions were much milder than for other metal species.[126] This protocol features a high degree of functional group compatibility. Both the pyridyl, pyrazolyl, or oxazyl group and imino moiety could serve as the directing group efficiently. Mechanistically, the NHC was coordinated to one Rh of the dirhodium, while the PCy_3 was coordinated to the other. The PCy_3 was assumed to stabilize the Rh–NHC species and would be released during the reaction. In addition, they envisioned that the rhodium metal centre was operative between Rh^{II}–Rh^{IV} in the redox process.

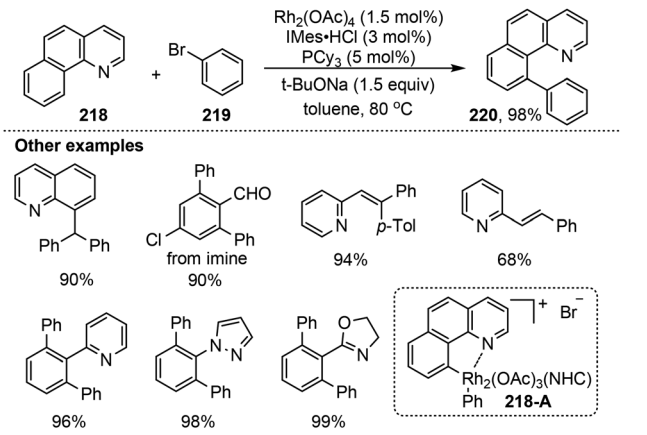
Two years later, they further demonstrated the application of Rh–NHC in the arylation of quinolines **221** (Scheme 75).[127] This method was suitable for the regioselective arylation of quinoline derivatives at the 8-position and exhibited a wide substrate scope. In these cases, the NHC played an important role in promoting the oxidation addition process. However, the structures of the active catalytic species, bimetallic or monomeric, are still waiting for identification. In the same year, Chang group also established a delicate catalytic system, based on dirhodium and N-heterocyclic carbene (NHC), for the *O*-arylation of aryl bromides.[128]

In 2016, Kobayashi and coworkers demonstrated that a combination of $Rh_2(OAc)_4$/dppp and $Sc(OTf)_3$ could serve as a highly effective catalyst system for ketone hydroacylation (Scheme 76).[129] A high turnover number was observed (up to 400). It is worthwhile to mention that when the chiral diphosphine ligand DuanPhos was employed, the asymmetric version could be accomplished in 50% yield and 80% ee. As for the reaction mechanism, the reaction processes likely included the oxidation of Rh by aldehyde, Rh–H insertion of the carbonyl group and reductive elimination (Scheme 76). The $Sc(OTf)_3$ acted as a Lewis acid to coordinate to the aldehyde to facilitate the oxidative addition process. A disproportionation of Rh(II) to give Rh(I) was regarded as unlikely based on the results using $[Rh(C_2H_4)_2Cl]_2$ and AgOAc as the catalysts instead. Interestingly, Lee's group has reported that without the phosphine ligand and Lewis acid, the $Rh_2(OAc)_4$ could catalyze the hydroacylation reaction between aldehydes **225** and azodicarboxylates **226** (Scheme 77).[130] But the reaction was proposed to be a radical-mediated process based on the radical-trapping experiments. Further research on the mechanism needs to be studied.

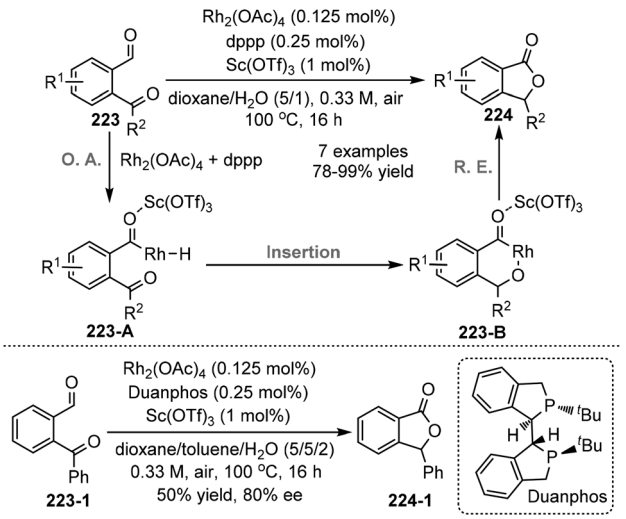
Shortly afterwards, by taking advantage of the P-chelated and directed role on dirhodium and norbornene (NBE) as a hydrogen acceptor, Shi and coworkers developed an efficient route to establish a library of P-ligand-containing different steric and electronic silyl groups using commercially available phosphines **228** and silanes (Scheme 78).[131] This method features a broad substrate scope and no need for an external



Scheme 75 Rh(NHC)-catalyzed direct and selective arylation of quinolines at the 8-position.

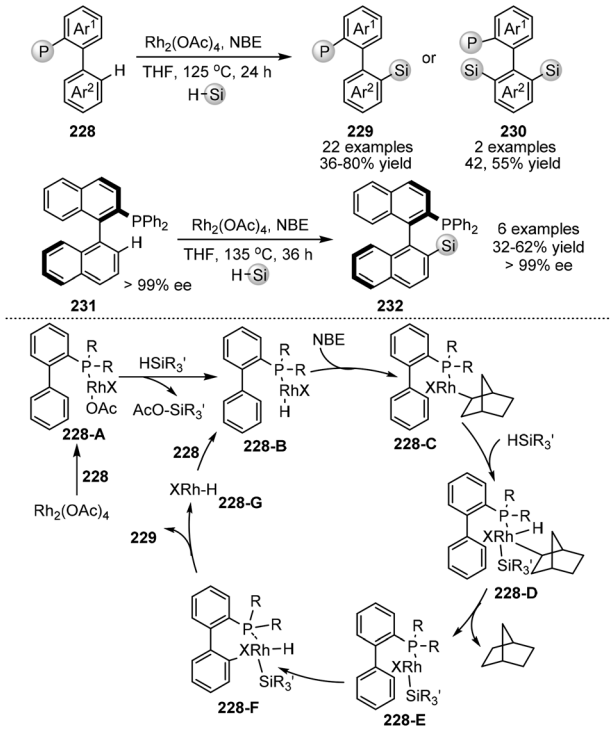


Scheme 74 Dirhodium/NHC catalyzed intermolecular arylation of sp^2 and sp^3 C–H bonds.



Scheme 76 Lewis acid-assisted dirhodium(II) catalyzed ketone hydroacylation.

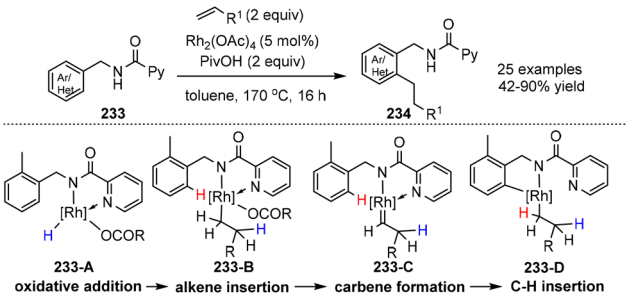
Scheme 77 Dirhodium(II) catalyzed hydroacylation of azodicarboxylates.



Scheme 78 Dirhodium-catalyzed dehydrogenative silylation of biaryl-type monophosphines with hydrosilanes.

ligand. Moreover, the binaphthalene-based axial chiral monophosphine ligands **231** were also applicable to give **232** with no erosion of ee. The obtained silyl-substituted axial chiral ligand **232** had been proved powerful in the palladium-catalyzed asymmetric Suzuki coupling reactions. The mechanistic processes include that $Rh_2(OAc)_4$ coordinates to the phosphine to form **228-A**, which undergoes transmetalation with silane to deliver Rh-hydride species **228-B**. Rh–H addition to NBE then takes place to give **228-C**. Oxidative addition of silane with **228-C** forms **228-D**, which undergoes reductive elimination to produce **228-E**. Subsequently, **228-E** undergoes C–H activation to form rhodacycle **228-F**, which proceeds via reductive elimination to produce product and Rh–H **228-G**. This Rh–H species **228-G** then chelates with another phosphine, producing the **228-B** complex to complete the catalytic cycle.

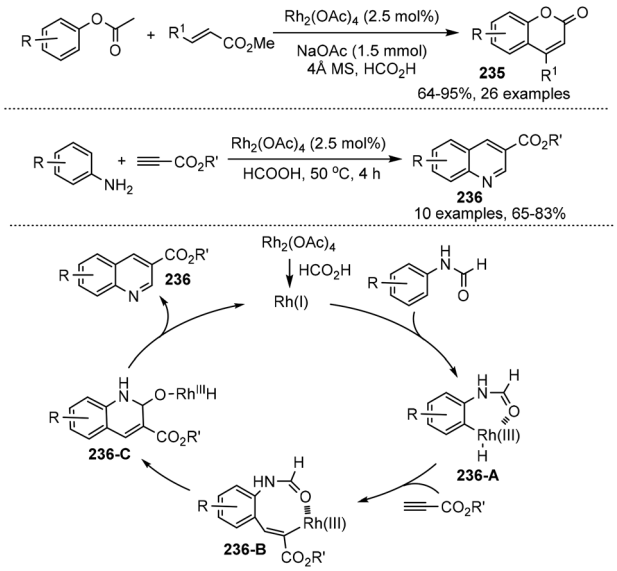
Not long ago, the same group found that $Rh_2(OAc)_4$ could also be employed in the C–H alkylation of benzylamines with alkenes (Scheme 79).[132] Both picolinamide as well as other heterocycles such as a thiophene-derived amine were amen-



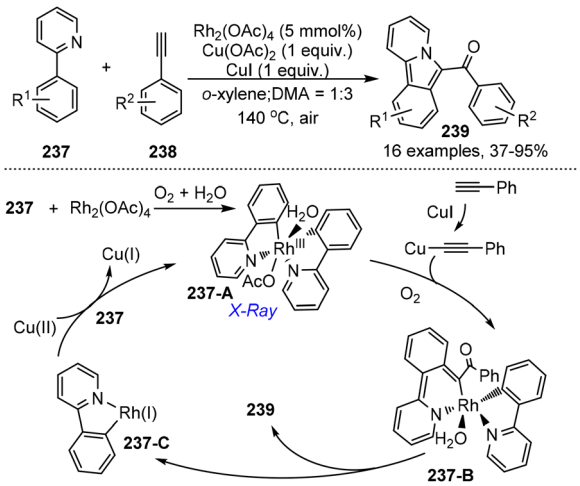
Scheme 79 Rh(II)-catalyzed C–H alkylation of benzylamines with alkenes.

able for use as the directing group. The conditions of Rh(I) as the catalyst also worked well, but were inferior in the substrate scope investigation. Besides, the Rh(I)-catalyzed reactions could be conducted under flow conditions, in which the yields were higher than in a batch process. However, the flow process was not suitable for Rh(II) because of solubility issues. After a series of deuterium-labelling experiments, this reaction was proposed to undergo several key processes, including oxidative addition, alkene insertion, carbene formation, C–H insertion and reductive elimination (Scheme 79).

Actually, the dirhodium(II) could also be reduced to Rh(I) species *in situ* to participate in the C–H activation. Sudalaia and coworkers disclosed that with $Rh_2(OAc)_4$ as catalyst and formic acid as reducing agent, *ortho* C–H bonds of phenolic acetates and arylamines were able to be successfully activated, providing rhodacycle intermediates **236-A** (Scheme 80). Subsequent migratory insertions of alkynic esters and acrylates occurred to provide coumarin derivatives **235** and quinoline carboxylates **236** with high yields and excellent regioselectivities.[133] Credibly, the formation of Rh(I) species was



Scheme 80 Rh(II)-catalyzed C–H activation with formic acid as reducing agent.



Scheme 81 Rh(II)-catalyzed direct oxidative C–H acylation.

proved by the UV-visible spectra and cyclic voltammetry studies.

Additionally, dirhodium(II) was able to be oxidized to Rh(III) species, but the binuclear structure was destroyed under the harsh conditions, which was confirmed by X-ray studies of **237-A**. which has been utilized in the synthesis of pyrido[2,1-*a*] isoindoles in moderate to excellent yields with 2-arylpyridines and terminal alkynes as the starting materials (Scheme 81).[134] The real active species of Rh(III) **237-A** had been isolated and characterized by X-ray crystallography, which reacted with a copper complex to furnish complex **237-B** in the presence of oxygen. Reductive elimination then occurred followed by the release of Rh(I) species to give the target products **239**. The Rh (I) was then oxidized by Cu(II) to regenerate Rh(III) to be involved in the next catalytic cycle.

4. Conclusion

With the development of dirhodium catalysts, the dirhodiums have been successfully engaged in a wide collection of reactions, including cycloisomerization, hetero-Diels–Alder reactions, ene reactions, arylation, silylation, radical or two-electron oxidation reactions, C–H activation, *etc*., providing a number of efficient routes to construct functionalized molecules. In these reactions, the dirhodium displays its unique characteristics as a redox catalyst, Lewis acid and carbophilic catalyst. From the perspective of the regulatory mechanism, the catalytic properties of dirhodium could be tuned both by adjusting the bridge ligands and axial ligands. Typically, the coordination of axial ligands usually results in a decreased electrophilicity, a lower oxidation potential and a tuned selectivity, whereas the higher valent rhodium species obtained by the oxidation of dirhodium(II) allow increasing electrophilicity. In addition, the introduction of hydrogen-bonding between the substrate and the dirhodium also offers another helpful strategy. These wonderful findings have greatly expanded the versatility of dirhodium and will shed light on the catalyst design and application.

Nevertheless, this field is still waiting for further development. Although great progress has been made in the studies of the reaction mechanisms, many of these are still elusive, especially for the structural changes of the catalytically active species during the reaction. Besides, in addition to carbene and nitrene transfer reactions, examples of dirhodium in enantioselective reactions are still lacking, especially in the redox reactions. In-depth mechanism studies will also provide more insights and solutions to solve this issue. Moreover, as we all know, rhodium is precious and expensive. To achieve a high turnover number and high efficiency has always been our target. Also, to find practical and convenient means for the recovery and reuse of dirhodium could be another complementary route. In summary, we are convinced that more fabulous properties of dirhodium will be disclosed, which will demonstrate their powerful applications in organic synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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