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Rhodium-catalyzed transformations of diazo compounds *via* a carbene-based strategy: recent advances

Fatemeh Doraghi, [a] Parsa Baghershahi,[b] Mehran Ghasemi,[c] Mohammad Mahdavi*[a] and Ahmed Al-Harrasi *[c]

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Diazo compounds are known to be good coupling partners in the synthesis of heterocycles, carbocycles and functionalized molecules *via* a rhodium carbene-based strategy. Many heterocyclic and carbocyclic compounds, including isoquinolones and isocoumarins, quinoxalines, indoles, pyrrones, benzothazines, enaminones, benzenes and seven-membered rings, can be constructed using this rhodium-catalyzed system. The reaction mechanism involves C–H activation, carbene insertion and an annulation/functionalization sequence. This review describes the progress made in the last five years in rhodium-catalyzed transformations of diazo compounds as easily accessible precursors in organic chemistry.

1 Introduction

Diazo compounds are an important class of nitrogen-containing compounds that can be used as coupling partners and can be easily accessed from the reaction of cyclic 1,3-diketones and arylsulfonyl azides.[1,2] Polarized diazo compounds form highly reactive carbene species *via* an interaction with the empty orbital of a transition metal. These carbene species can be involved in a broad range of reactions for the construction of complicated fused and spiro polycyclic frameworks as well as multifunctional organic molecules.[3–9]

Several metal salts, including rhodium,[10–23] iridium,[24–26] ruthenium,[27,28] silver,[29] indium,[30] copper[31] and palladium[32] can catalyze the transformations of diazo compounds. Of these transformations, the rhodium-catalyzed C–H activation/annulation of diazo compounds has been extensively investigated. The process includes Rh-carbene formation with N_2

[a]*Endocrinology and Metabolism Research Center, Endocrinology and Metabolism Clinical Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran. E-mail: momahdavi@tums.ac.ir*

[b]*Pharmaceutical and Heterocyclic Chemistry Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran, Iran*

[c]*Natural and Medical Sciences Research Center (NMSRC), University of Nizwa, Nizwa 616, Sulanate of Oman*

Fatemeh Doraghi

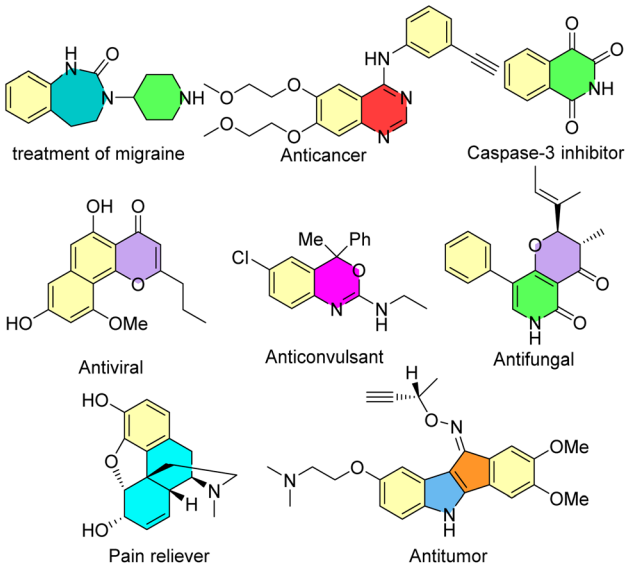
Fatemeh Doraghi received her bachelor's and master's degrees in organic chemistry from Shahid Chamran University, Ahvaz in 2008 and 2014, respectively. She received her PhD degree in organic chemistry from the University of Tehran, Tehran in 2022. During her PhD research, she focused on the development of new synthetic methodologies via transition metals as well as metal-free oxidative coupling reactions. She is currently employed as a researcher at the Endocrinology and Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran.

Parsa Baghershahi

Parsa Baghershahi is currently a second year organic chemistry student at Iran University of Science and Technology, Department of Chemistry. He received his bachelor's degree in practical chemistry from Islamic Azad University Science and Research Branch. He is currently working at the Endocrinology and Metabolism Research Center, Endocrinology and Metabolism Clinical Sciences Institute, Tehran University of Medical Sciences. His field of work and interest is the synthesis of various bioactive organic compounds and new approaches toward the synthesis of complex compounds through catalytic and green methods.

expulsion, the formation of six- and seven-membered rhodacyclic intermediates, and migratory insertion and reductive elimination, which overall can be considered as formal (3 + 2)-, (4 + 1)- or (4 + 2)-cycloadditions. In such reactions, cyclic and acyclic diazo compounds act as a C1, C2, or even C3 synthons. These reactions can be categorized into three groups: (i) Rh-catalyzed C–H insertion/cascade annulation with diazo compounds; (ii) Rh-catalyzed C–C cross-coupling with diazo compounds; and (iii) Rh-catalyzed N–H insertion/annulation.

Many heterocyclic and carbocyclic compounds, such as isoquinolones and isocoumarins, quinoxalines, indoles, pyrrones, benzothazines, enaminones, benzenes and seven-membered rings, can be synthesized *via* the rhodium-carbene strategy.[33,34] Some of these biologically active compounds are shown in Scheme 1.



Scheme 1 Some biologically active compounds which can be synthesized *via* the rhodium-carbene strategy.

However, the rhodium-catalyzed selective activation of unactivated C–H bonds generally requires directing groups (DGs) to resolve the regioselectivity. The increased momentum of the carbene insertion makes diazo compounds versatile building blocks,[35,36] as their uses have expanded to make exciting progress in the field of C–H activation with the help of directing groups (DGs). These directing group strategies fall

Mehran Ghasemi

Mehran Ghasemi received his PhD degree (2020) in Organic Chemistry from Kharazmi University, Tehran, Iran, under the supervision of Dr A. Habibi and Dr F. Jafarpour. He did his postdoctoral research at the University of Tehran (with Dr F. Jafarpour) (2021–2023), Iran. Presently, he is working as an assistant professor at the Natural and Medical Sciences Research Center (NMSRC), University of Nizwa, Oman. His research focuses on the synthesis of organic compounds with biological activities.

Mohammad Mahdavi

Mohammad Mahdavi was born in 1981 in Tehran, Iran. He received his MSc. from the University of Tehran in 2008 and his PhD degree in medicinal chemistry from the Tehran University of Medical Science, Tehran, Iran, in 2016. Since August 2017, he has been with the Endocrinology and Metabolism Research Center, Endocrinology and Metabolism Clinical Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran where he is an Assistant Professor. His current research interests focus on the synthesis of heterocyclic compounds with biological activities.

Ahmed Al-Harrasi

Professor Ahmed Al-Harrasi completed his BSc in chemistry at Sultan Qaboos University (Oman) in 1997 and his MSc and PhD in organic chemistry at the Free University of Berlin in 2002 and 2005, respectively, as a DAAD fellow under the supervision of Prof. Hans-Ulrich Reissig. Soon after his PhD, he was awarded a Fulbright scholarship in 2008 for postdoctoral research in chemical biology for which he joined Prof. Tadhg Begley's group at Cornell University (USA). In 2009, he started his independent research at the University of Nizwa, Oman where he founded the natural and medical sciences research center (NMSRC) working at the frontier between chemistry and biology. He is currently a professor of organic chemistry and a vice chancellor for graduate studies, research and external relations. His research focuses on contributing to a chemical understanding of systems of biological importance and enabling the exploitation of the results for societal benefit.

into two categories: (i) DGs are incorporated into the substrate to aid the site specificity and are then cleaved after activation/functionalization, and (ii) intrinsic DGs in the substrate are used to direct regioselectivity. These DG strategies enhance reaction efficiency and atom economy.

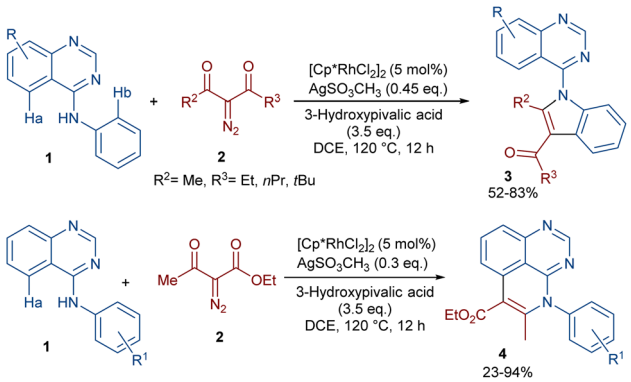
Considering the easy availability and versatility of diazo compounds as carbene sources, and due to the significant role of carbene intermediates in organic chemistry, in this review, we have focused on the progress made in the last five years regarding the transformations of diazo compounds *via* the rhodium-carbene strategy.

2 Rhodium-catalyzed transformations of diazo compounds

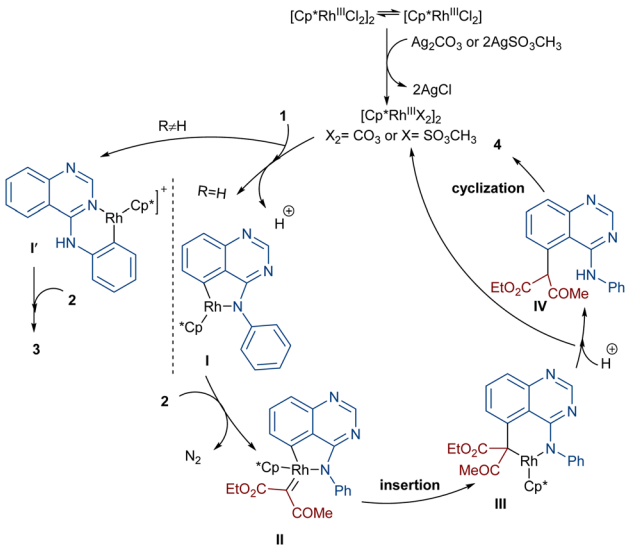
2.1. Synthesis of five-membered rings

In 2020, Dong, Chen and co-workers developed a regioselective strategy for the annulation of 4-anilinoquinazolines with diazo compounds under rhodium catalysis (Scheme 2).[37] It was proposed that the reaction proceeds through a sequence of C–H activation, carbene insertion and intramolecular cyclization. First, the regioselective C(sp^2)–H bond activation of substrate **1** gave a Rh-complex **I**, which in turn coordinated with **2** to generate the Rh-carbene **II** along with the removal of N_2. Through migratory insertion and protonolysis, intermediate **IV** was produced, which underwent intramolecular cyclization to form product **3**. When substrate **1** has steric hindrance due to the substituent at the C6 position, the metal center was coordinated with the nitrogen of the pyrimidine, resulting in a six-membered rhodacycle **I′** instead of **I** (Scheme 3). It should be noted that for the formation of compound **4**, the optimal oxidant was found to be $AgSO_3CH_3$ instead of Ag_2CO_3.

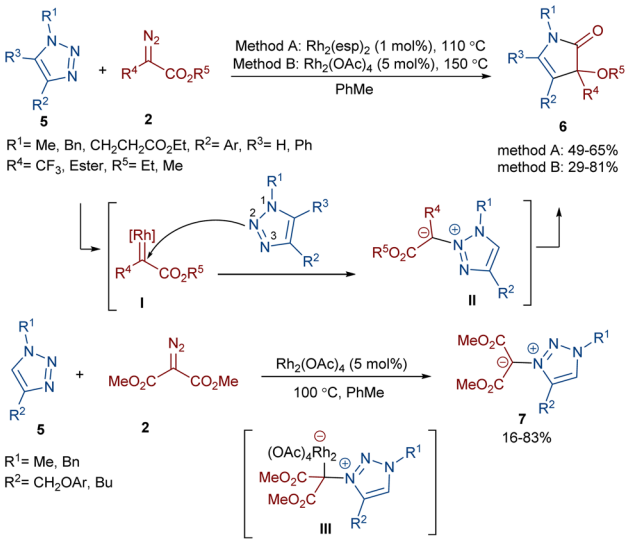
Two different rhodium(II) complexes can catalyze the annulation of diazo esters **2** with 1*H*-1,2,3-triazoles **5** (Scheme 4).[38] In these reactions, various 3-alkoxy-4-pyrrolin-2-one derivatives were constructed in moderate to good yields. First, a Rh-carbenoid intermediate **I** was formed from the diazo ester and Rh(II). When R^2 = aryl, the triazole attacked the electrophilic carbon of **I** through the N2 atom to give the unstable 3,4-dihydro-1,2,4-triazine **II**. It seems that the presence of



Scheme 2 Rh-catalyzed annulation of 4-anilinoquinazolines with diazo compounds.



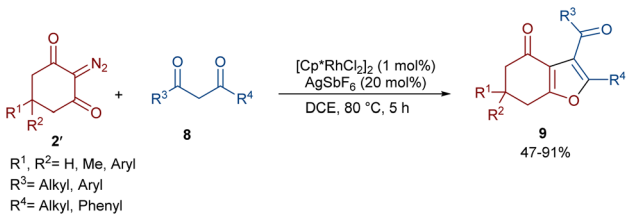
Scheme 3 Catalytic cycle for the Rh-catalyzed annulation of 4-anilinoquinazolines with diazo compounds.



Scheme 4 Rh-catalyzed annulation of diazo esters with 1*H*-1,2,3-triazoles.

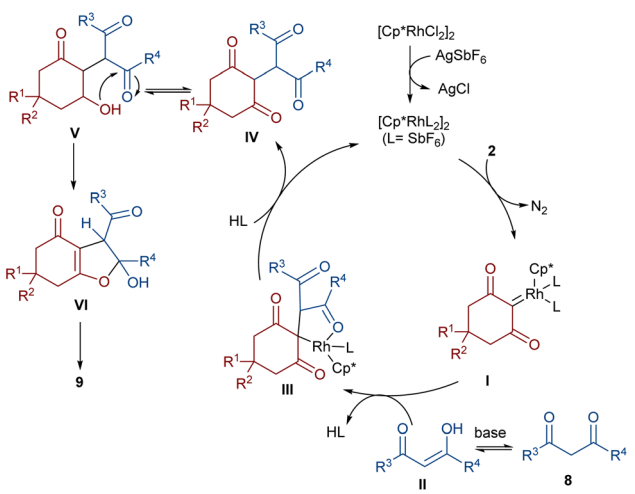
substituents at the C4 position of the triazole shield the N3 center, leading to the regioselective addition of the carbenoid to the N2 center. After that, the pyrrolinone product **6** was obtained *via* the ring contraction of **II** under the influence of rhodium along with the release of N_2. However, if R^2 = alkyl, the attack of the N3 of the triazole on the carbenoid proceeded *via* rhodium intermediate **III** affording 1,2,3-triazol-3-ium ylides **7**. DFT calculations confirmed these results by showing a 3.2 kcal-mol^{-1} decrease in the free energy of complex **III** compared to **II** when R^2 was alkyl not aryl, which is because of the absence of conjugation between the aryl and triazole rings.

In 2021, Shang and co-workers used a rhodium catalyst to make a furan ring *via* the annulation of 2-diazo-1,3-diketones **2**

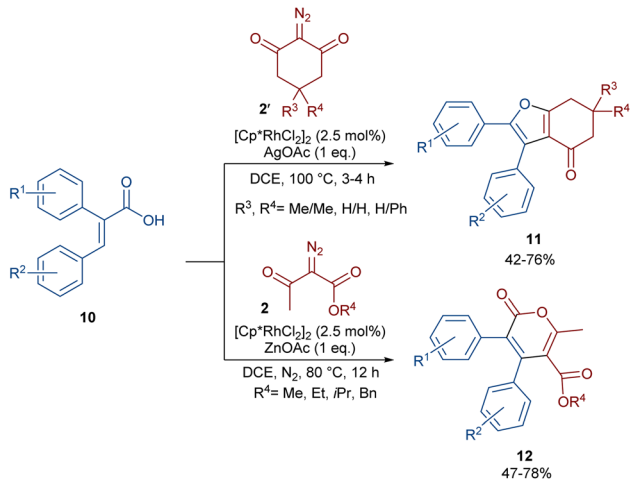


Scheme 5 Rh-catalyzed annulation of cyclic 2-diazo-1,3-diketones with β-keto esters.

with 1,3-dicarbonyl compounds **8** (Scheme 5).[39] The reaction mechanism was rationalized with the help of H/D exchange and kinetic isotope effect (KIE) experiments. The rate-determining step was predicted to be the C–H activation step. A ligand exchange between the pre-catalyst $[Cp^*RhCl_2]_2$ and $AgSbF_6$ occurred to obtain an active catalyst $[Cp^*Rh(SbF_6)_2]_2$, which in turn reacted with **2** to form Rh-carbene **I** with the release of N_2. Meanwhile, the enolization of 1,3-diketones **8** resulted in intermediate **II**, which attacked **I** to form intermediate **III**. Finally, product **9** was achieved through a sequence of protonolysis, enol-ketone tautomerization, intramolecular cyclization and dehydration (Scheme 6). A gram-scale synthesis (0.89 g, 86%) and the post-functionalization of the obtained products in the presence of $N_2H_4 \cdot H_2O$, $NH_2OH \cdot HCl$, or $NaBH_4$ were also performed. Another work on the synthesis of furan structures starting from diazo compounds was reported in 2024 (Scheme 7).[40] By changing some parameters, like additive and temperature in the reactions of *cis*-stilbene acids **10** and 2-diazo-1,3-diketones **2**, Shankaraiah and co-workers could isolate two different annulated products, 6,7-dihydrobenzofuran-4(5*H*)-ones **11** and α-pyrones **12**. Both products were produced *via* a metal carbene strategy, in which two migratory insertions led to dihydrofuran formation. The mechanism involved the formation of the active catalyst from a rhodium pre-catalyst and Lewis acid, followed by the reaction with *cis*-stilbene acid to form rhodacycle **I**. After the formation of carbene **II** from the



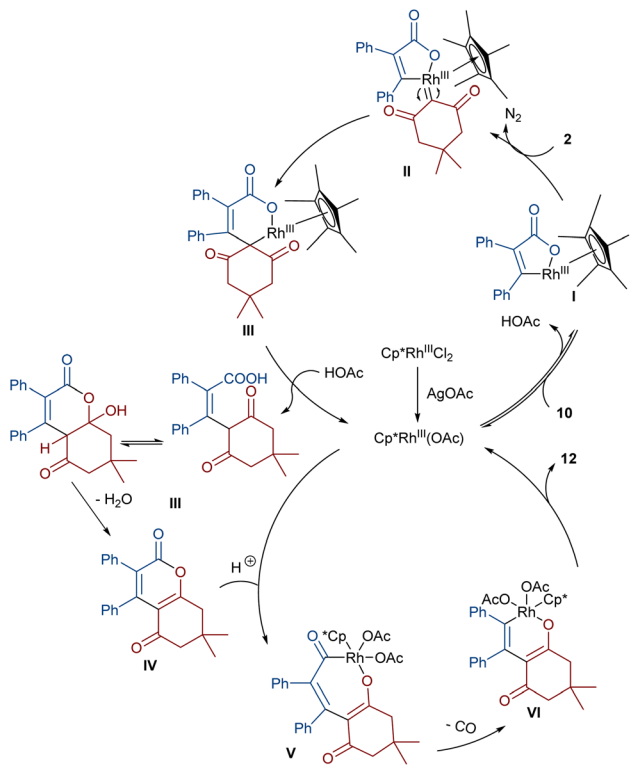
Scheme 6 Possible catalytic cycle for the Rh-catalyzed annulation of cyclic 2-diazo-1,3-diketones with β-keto esters.



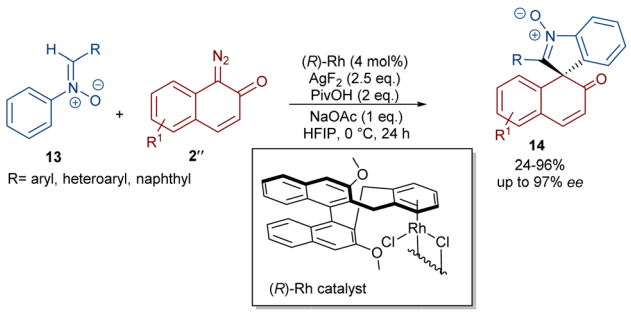
Scheme 7 Rh-catalyzed annulation of *cis*-stilbene acids with diazo compounds.

diazo compounds, and sequential migratory insertion and protonation, intermediate **IV** was furnished. The second migratory insertion of Rh(III) provided intermediate **V** with the removal of CO. Finally, product **12** was furnished *via* reductive elimination (Scheme 8).

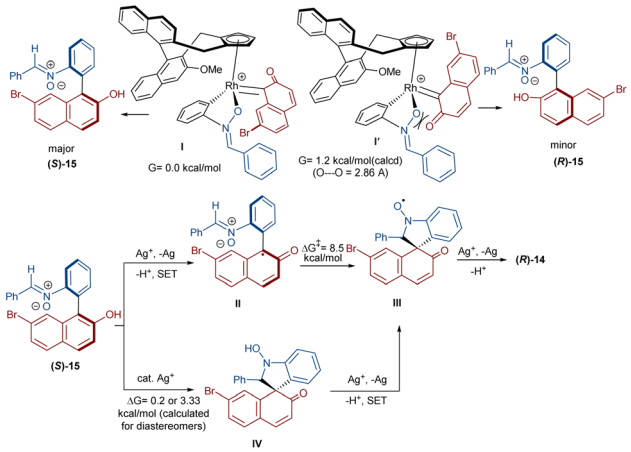
In 2020, Li and his team developed an enantioselective synthesis of spirocyclic compounds **14** from quinone diazides **2″** and nitrones **13** (Scheme 9).[41] The reaction proceeded through the formation of a rhodacyclic intermediate, which



Scheme 8 Possible mechanism for the Rh-catalyzed annulation of *cis*-stilbene acids with diazo compounds.

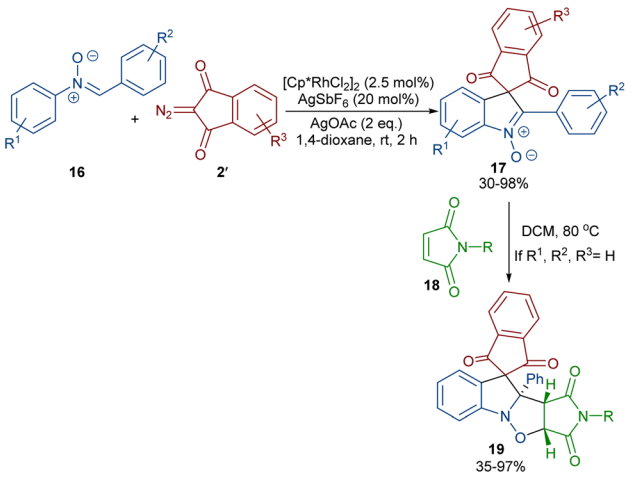


Scheme 9 Rh-catalyzed reaction of diazo compounds and nitrones.

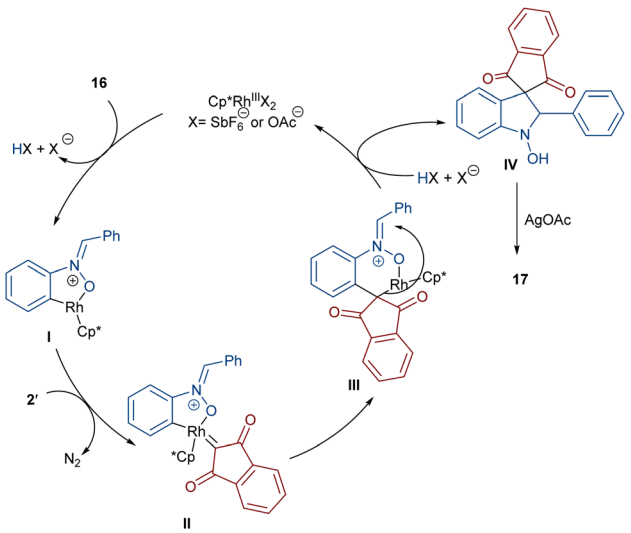


Scheme 10 Rational mechanism for the Rh-catalyzed reaction of diazo compounds and nitrones.

underwent addition of a diazo compound to form a stable biaryl intermediate (*S*)-**15** *via* transition state **I**. With the assistance of Ag(I), single electron transfer (SET) oxidation occurred in **15** to give radical **II**, which rapidly cyclized to generate the more stable nitroxide radical **III**. A second SET process in the presence of Ag(I) led to spiro-cyclic product **14** (Scheme 10). KIE values revealed that the C–H cleavage was not the rate-determining step. In 2023, Guo *et al.* introduced a new strategy for the synthesis of spiro-cyclic indole-*N*-oxides **17** from *N*-aryl nitrones **16** and 2-diazo-1,3-indandiones **2′** (Scheme 11).[42] It was found that the presence of $[Cp^*RhCl_2]_2$, $AgSbF_6$ and AgOAc were all necessary to catalyze this reaction under mild conditions. The reaction proceeded through (4 + 1)-cycloaddition, where the diazo compound acted as a C1 synthon. According to H/D and KIE studies, a possible mechanism was proposed, in which nitrone **16** and Rh produced the five-membered rhodacycle **I**, which then underwent carbene insertion to give the Rh-carbene **II**. Next, through a migratory insertion, **II** was converted to the six-membered rhodacycle **III**, followed by intramolecular nucleophilic addition and protonation to render spiro-cyclic intermediate **IV** along with the regeneration of the Rh(III) species. Finally, **IV** was oxidized by AgOAc to provide product **17** (Scheme 12). Additionally, (3 + 2)-cycloaddition of the obtained product could be carried out with



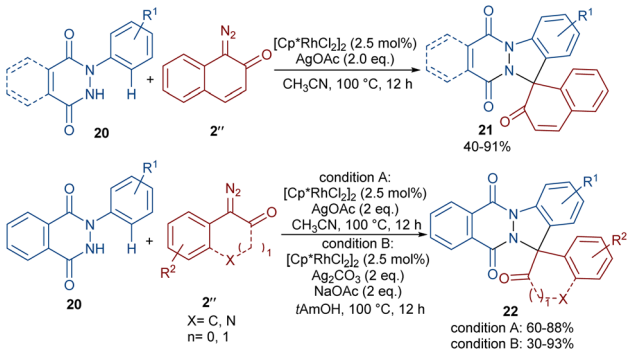
Scheme 11 Rh-catalyzed reaction of *N*-aryl nitrones and 2-diazo-1,3-indandiones.



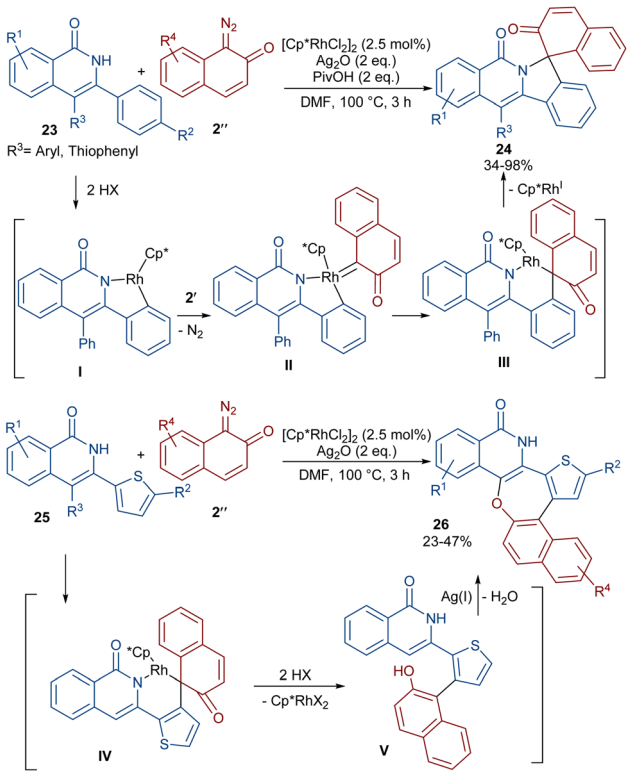
Scheme 12 Proposed mechanism for the Rh-catalyzed reaction of *N*-aryl nitrones and 2-diazo-1,3-indandiones.

maleimides **18** to access biologically active maleimide-fused polycyclic compounds **19** in a diastereoselective manner.

A (4 + 1)-annulation strategy was reported for the construction of spiro-cyclic indazoles **21** (Scheme 13).[43] In this regard, *N*-aryl phthalazine-diones **20** were used as a reagent to react with 1-diazonaphthalen-2(1*H*)-one **2″**. This spiro-annulation involved Rh-catalyzed C–H bond activation, carbene insertion and nucleophilic addition. It is noteworthy that other metal catalysts, such as $[Cp^*IrCl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$, also gave the desired products in 73% and 25% of yields, respectively. Conversely, $[Cp^*Co(CO)I_2]_2$ was not found to be a workable catalyst. A similar (4 + 1)-annulation for the construction of spiro-cyclic compounds under rhodium catalysis was reported by another research team (Scheme 14).[44] In their work, the reaction was carried out using isoquinolones **23** and 1-diazonaphthalen-2(1*H*)-ones **2″** as substrates. The cyclization



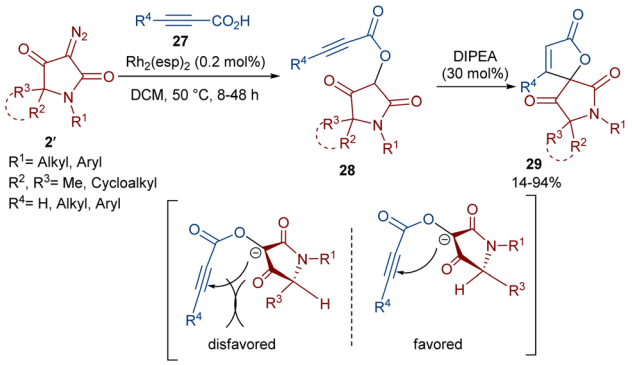
Scheme 13 Rh-catalyzed reaction of *N*-aryl phthalazine-diones and diazo compounds.



Scheme 14 Rh-catalyzed reaction of isoquinolones and diazo compounds.

proceeded through intermediate **I**, where diazo compound **2″** acted as a C1 synthon. Moreover, when 3-(thiophen-2-yl)isoquinolin-1(2*H*)-one **25** was used as a reactant in the reaction with diazonaphthalen-2(1*H*)-ones **2″**, a series of oxepine-fused polycyclic compounds **26** were synthesized *via* (4 + 3)-annulation, in which the diazo compound acted as a C3 synthon and was incorporated in the formation of the six-membered rhodacycle **IV**.

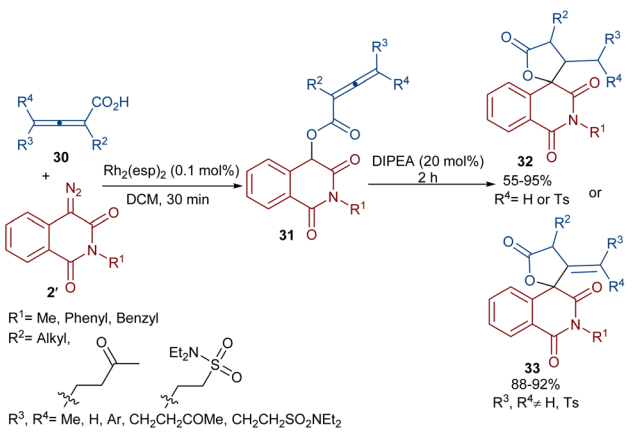
Dar'in *et al.* developed a strategy for the synthesis of spirocyclic products **28** from propiolic acids **27** and a new class of diazo compounds **2′** (Scheme 15).[45] For this purpose, they synthesized the new diazo compounds by the treatment of 3-



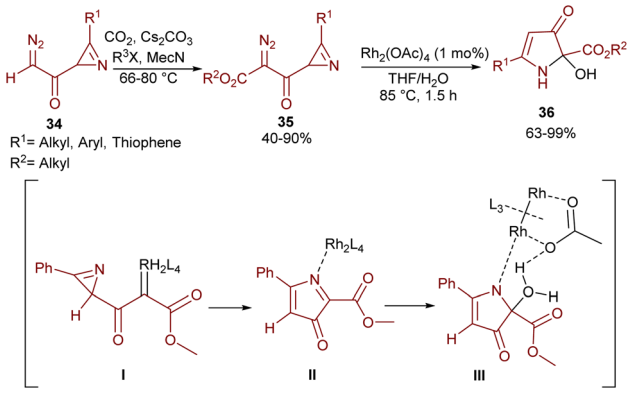
Scheme 15 Rh-catalyzed reaction of propiolic acids and diazo compounds.

methoxy-3-oxopropanoic acid and α-amino acid methyl esters under basic conditions. Through a multi-steps process, they achieved 3-diazotetramic acid substrates **28**. The reaction of the obtained diazo compounds with propiolic acids proceeded through a Rh-catalyzed carbene formation, followed by O–H insertion into the propiolic acids to yield compound **28**. The subsequent base-promoted intramolecular Michael addition from the less hindered side of the molecule furnished the bioactive spirocyclic butenolide products **29** in up to 94% yield. Notably, the position of the hydrogen atom as the R^2 substituent was important in the diastereoselectivity and the formation of the spirocycle. Again, this group could synthesize spiro-cyclic butenolides using heterocyclic diazo compounds **2′** and allenic acids **30** (Scheme 16).[46] Two products **32** and **33** can be produced from adduct **31**, which in turn was generated from the reaction of allenic acid and a diazo compound under rhodium(II) catalysis. It was found that the position of the double bond in β-methylidene furanone **33** is due to a tautomerization process. DFT calculations revealed that **33** with an exocyclic double bond is less thermodynamically stable relative to **32**. Therefore, **33** can be converted into **32** in the presence of a base.

An intramolecular aziridine ring-expansion carbene insertion strategy was reported by Khlebnikov and his team



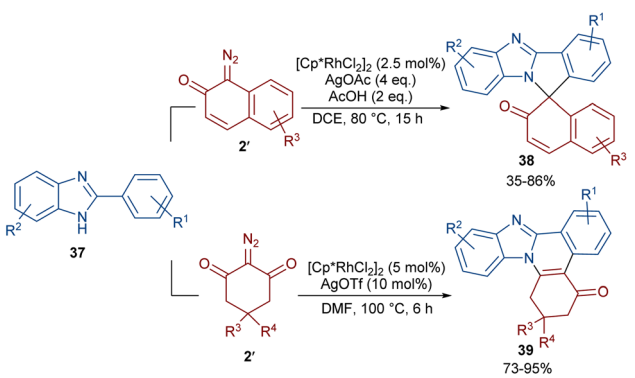
Scheme 16 Rh-catalyzed reaction of allenic acids and diazo compounds.



Scheme 17 Rh-catalyzed intramolecular azirine ring expansion.

(Scheme 17).[47] In this regard, azirinyl-substituted diazodicarbonyl compounds **35** were initially prepared from diazoacetylazirines **34** and then successfully used as substrates in the presence of a rhodium(II) complex to provide 2-hydroxy-3-*oxo*-2,3-dihydro-1*H*-pyrrole-2-carboxylates **36**. The source of the hydroxyl group was found to be water. With the help of DFT calculations, the reaction was suggested to proceed through a Rh-carbenoid intermediate **I**, which under ring-expansion gave pyrrolone complex **II**. Then, the insertion of H_2O into the C–N bond and the liberation of Rh afforded the final product **36**.

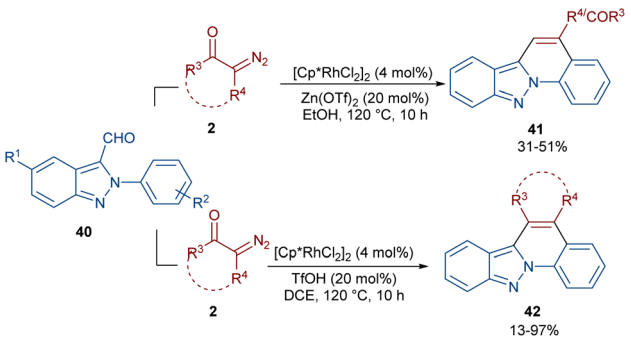
Two (4 + 1) and (4 + 2) annulation methodologies were suggested for the reaction of 2-arylbenzimidazoles **37** with diazo compounds **2** (Scheme 18).[48] Depending on their structure, diazo compounds can act as a C1 and C2 synthon in the cycloaddition with 2-arylbenzimidazoles. The reaction of 2-arylbenzimidazoles with 1-diazonaphthalen-2(1*H*)-one **2″** proceeded through (4 + 1)-cycloaddition to produce spirocyclic benzimidazole-fused isoindole naphthalen-2-ones **38**. This reaction involved C–H activation, Rh-carbene formation, migratory insertion, proto-demetallation and an intramolecular nucleophilic addition of the NH group of the benzimidazole to the carbonyl group, followed by dehydration. Conversely, a (4 + 2)-annulation was involved in the reaction of 2-arylbenzimidazoles and 2-diazocyclohexane-1,3-diones **2′**. In this case, benzimidazole-fused quinolines **39** were obtained *via* Rh-carbene formation, migratory insertion and reductive elimination.



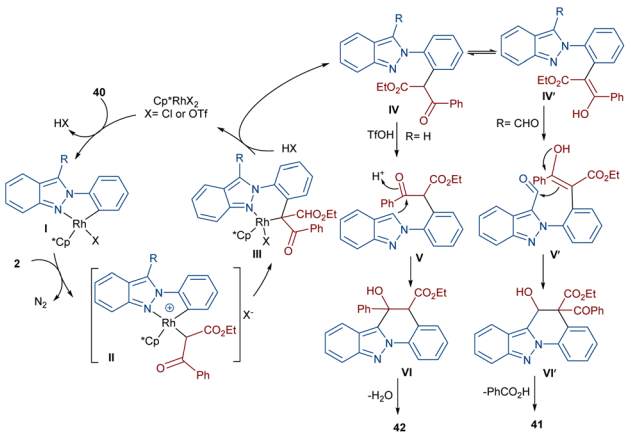
Scheme 18 Rh-catalyzed reaction of 2-arylbenzimidazoles and diazo compounds.

2.2. Synthesis of six-membered rings

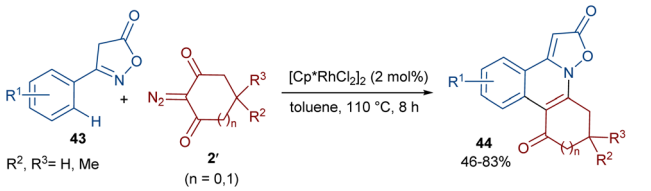
In 2020, Guo *et al.* reported the annulation of 2-aryl-2*H*-indazoles **40** with α-diazo compounds **2** to give a quinolone ring in the presence of the same Rh catalyst (Scheme 19).[49] In this synthetic method, the diazo compound acted as either a C1 or C2 synthon. The use of $Zn(OTf)_2$ as a Lewis acid or TfOH as a Brønsted acid together with $[Cp^*RhCl_2]_2$ as a catalyst can lead to two different indazole derivatives. The reaction started with a Rh(III)-catalyzed indazole-assisted C–H bond activation followed by the coordination with diazo compound **2** to obtain the carbene intermediate **II**. The migratory insertion of **II** yielded a six-membered rhodacycle **III**, which under proto-demetallation gave intermediates **IV** or **IV′**. In this step, when R = H, **IV** moved through an intramolecular C3-nucleophilic addition to deliver a six-membered intermediate **IV**, followed by the H_2O removal to afford product **40**. While, if R = CHO, product **41** was furnished *via* intermediate **IV′** through a regioselective nucleophilic attack of the α-carbon on the carbonyl group to give a six-membered intermediate **VI′**, followed by acid elimination (Scheme 20).



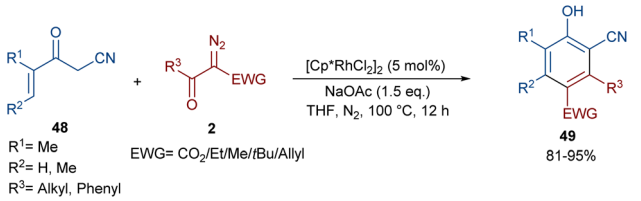
Scheme 19 Rh-catalyzed annulation of 2-aryl-2*H*-indazoles with diazo compounds.



Scheme 20 Possible mechanism for the Rh-catalyzed annulation of 2-aryl-2*H*-indazoles with diazo compounds.



Scheme 21 Rh-catalyzed annulation of 3-arylisoxazolones and cyclic 2-diazo-1,3-diketones.

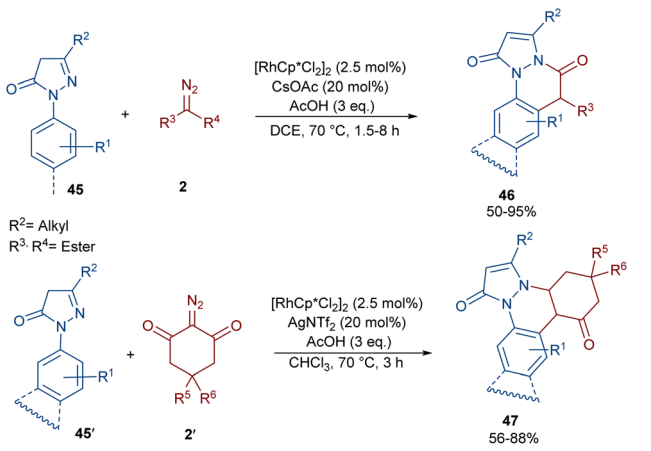


Scheme 23 Rh-catalyzed annulation of diazo compounds with 3-oxopent-4-enenitriles.

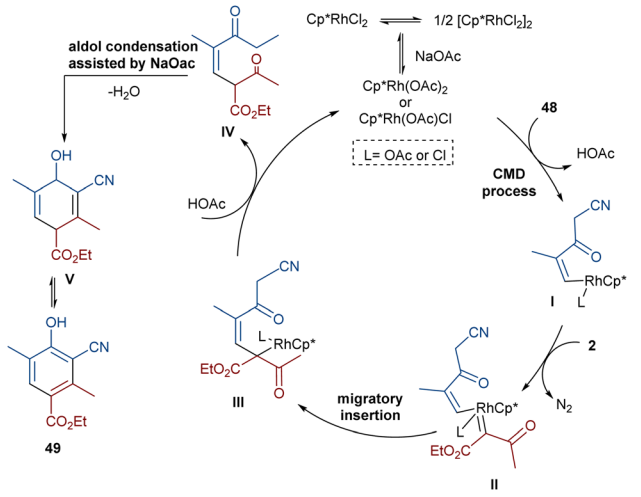
The Shang research team reported the Rh-catalyzed annulation of 3-arylisoxazolones **43** and cyclic 2-diazo-1,3-diketones **2′** (Scheme 21).[50] A wide range of isoxazolo[2,3-*f*]phenanthridines **44** were prepared in the presence of a low catalytic amount of a Rh(III) complex (2 mol%) without any additives. To gain a better understanding of the reaction mechanism, the authors designed H/D exchange and KIE experiments. The results of the H/D exchange showed that the C(sp^2)–H bond activation is fast and no alkenylation occurred on the isoxazol-5(4*H*)-one ring. The following KIE experiments suggested that the C–H activation is the rate-determining step. Thus, the reaction was believed to proceed through sequential Rh-catalyzed C–H activation, Rh-carbene formation, migratory insertion, protonolysis and hydrogen transfer.

Sun and co-workers were able to synthesize a new class of pyrazolone-fused cinnolines **46**, **47** through the annulation of *N*-aryl pyrazolones **45**, **45′** with diazo compounds **2** (Scheme 22).[51] The reaction was reported to involve rhodium-carbene formation, migratory insertion and proto-demetallation. A diverse range of α-diazo esters, α-diazo ketones, phosphate diazo compounds, and cyclic diazo compounds were well tolerated as the carbene precursors, leading to the synthesis of dihydropyrazolo[1,2-*a*]cinnolines **46** and dihydrobenzo[*c*]pyrazolo[1,2-*a*]cinnoline-1,8-diones **47**. Besides *N*-aryl pyrazolones, an *N*-naphthyl pyrazolone also gave the corresponding product in 80% yield. To reveal the synthetic utility of the method, a gram-scale synthesis (1.46, 94%) and further transformation of the products with the Lawesson reagent as well as a hydrolysis reaction were also performed, resulting in 53% and 70% yields, respectively.

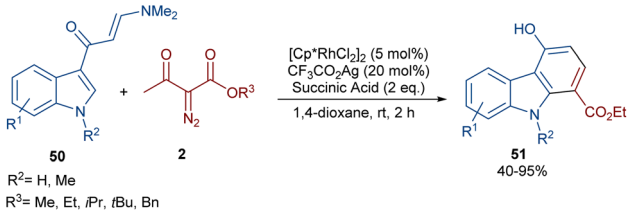
In 2021, Wang and co-workers described a methodology for the (2 + 4)-annulation of diazo compounds with 3-oxopent-4-enenitriles (Scheme 23).[52] A series of multi-functionalized phenols were well synthesized in high to excellent yields. The reaction commenced with the initial formation of the active catalysts, Cp*Rh(OAc)$_2$ or Cp*Rh(OAc)Cl, which participate in the carbonyl-assisted C–H bond cleavage of **48**. The obtained intermediate **I** coordinated with diazo compound **2** to form the Rh-carbene intermediate **II**. Then, migratory insertion of the carbene into the C–Rh bond gave intermediate **III**, which converted to intermediate **IV** through the protonolysis and regeneration of the active Rh catalyst. Subsequently, intramolecular aldol condensation, a double bond shift and aromatization led to product **49** (Scheme 24). It is noteworthy that the base is involved in both the C–H bond activation and the aldol condensation reaction, which justified using a stoichiometric amount of NaOAc. Another synthetic method for the preparation of phenol structures was reported by Liu, Zhou and co-workers (Scheme 25).[53] For this purpose, they used indole-enaminones **50** and diazo compounds **2** in the presence of a rhodium catalyst. This reaction was carried out *via* an unexpected (5 + 1)-cyclization process instead of the more common (4 + 2)-cyclization. First, through a ligand exchange, the active catalyst [Cp*RhX$_2$] was formed, which rapidly reacted with



Scheme 22 Rh-catalyzed annulation of *N*-aryl pyrazolones with diazo compounds.



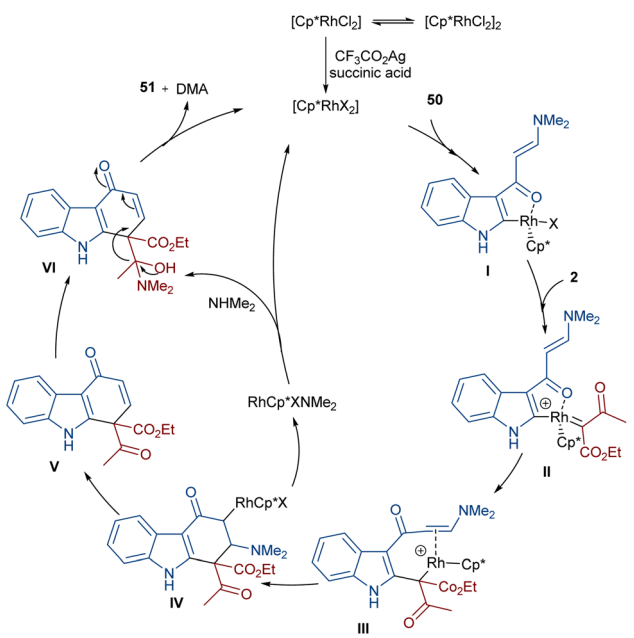
Scheme 24 Possible mechanism for the Rh-catalyzed annulation of diazo compounds with 3-oxopent-4-enenitriles.



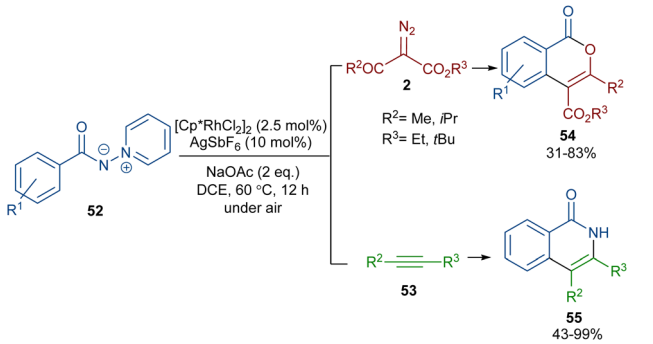
Scheme 25 Rh-catalyzed annulation of indole-enaminones with diazo compounds.

indole-enaminone **50** to form complex **I**. The coordination of α-diazo-β-ketoester **2** to **I** resulted in the formation of rhodium carbene **II**. Sequential intramolecular migratory insertion, and coordination with the alkene bond gave complex **III**. Then, **III** converted to the six-membered cyclic intermediate **IV** *via* migratory insertion and protonolysis, followed by the elimination of the rhodium species to render intermediate **V**. The further elimination of *N*,*N*-dimethylamine led to **VI**. After that, *N*,*N*-dimethylacetamide was removed from **IV** to be aromatized into the desired product **51** (Scheme 26).

When *N*-iminopyridinium ylides **52** were treated with diazo compounds **2** or alkynes **53** in the presence of a Rh(III) catalyst, two different products were obtained (Scheme 27).[54] Isocoumarins **54** were obtained from *N*-iminopyridinium ylides **52** and diazo compounds **2** through Rh-carbene formation, migratory insertion, and lactonization. The *N*-amino pyridine and N_2 molecules were released in this reaction cycle. The replacement of the alkynes **53** as reactants in the reaction with *N*-iminopyridinium ylides **52** yielded isoquinolones **55**. In this reaction, the *N*-iminopyridinium ylide acted as an internal oxidant and directing group. The reaction involved rhodacycle



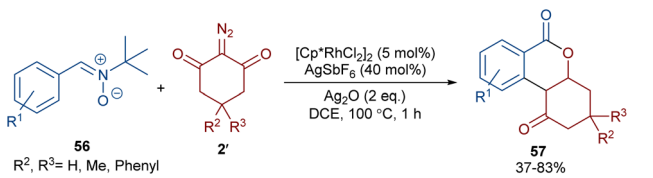
Scheme 26 Catalytic cycle for the Rh-catalyzed annulation of indole-enaminones with diazo compounds.



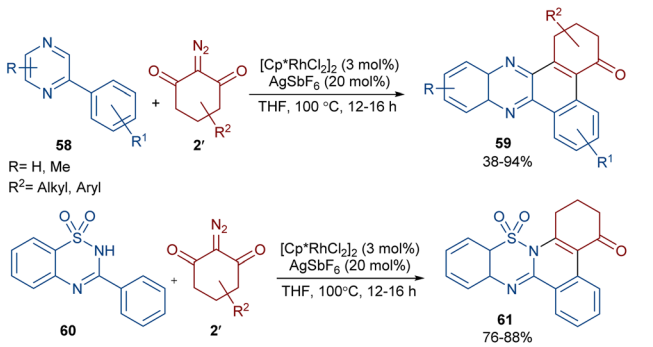
Scheme 27 Rh-catalyzed annulation of *N*-iminopyridinium ylides with diazo compounds and alkynes.

formation, alkyne insertion and proto-demetallation. A similar rhodium catalysis system was utilized for the synthesis of isocoumarins through the reaction of cyclic and acyclic diazo compounds with an enaminone catalyst.[55] In this work, the enaminone assisted C–H coupling with the diazo compounds. Cyclic diazo compounds **2′** and nitrones **56** could also be used for the synthesis of chromenones (Scheme 28).[56] A broad range of nitrones bearing electro-donating and halogen groups at the aryl ring were compatible in the reaction with cyclic diazo compounds. Changing the *tert*-butyl to benzyl group attached to the nitrone *N*-atom also yielded the target product in 45% yield. Only nitrones with electron-withdrawing groups (NO_2 and CO_2H) and 2-diazo-1,3-indandione were not found to be workable.

Reddy and co-workers reported the annulation of cyclic 2-diazo-1,3-diketones **2′** with 2-arylquinoxalines **58** under rhodium(III) catalysis (Scheme 29).[57] A new library of 2,3-



Scheme 28 Rh-catalyzed reaction of nitrones and cyclic diazo compounds.

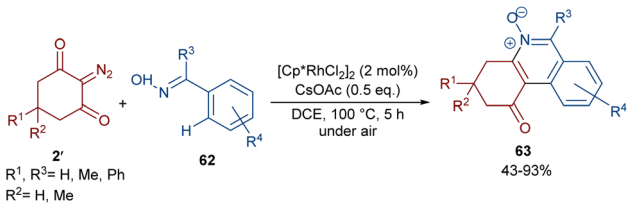


Scheme 29 Rh-catalyzed reaction of 2-arylquinoxalines with cyclic 2-diazo-1,3-diketones.

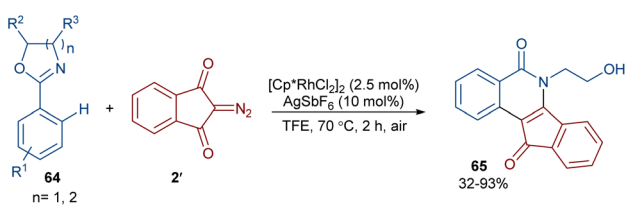
dihydrodibenzo[*a*,*c*]phenazin-4(1*H*)-ones **59** and benzo[5,6][1,2,4]thiadiazino[2,3-*f*]phenanthridin-5(6*H*)-one-10,10-dioxides **61** were constructed through nitrogen atom-assisted *ortho* C–H activation of 2-arylquinoxaline with Rh-carbene insertion, migratory insertion of the Rh-carbene into the Rh–C bond, reductive elimination, and dehydration. A similar pathway was postulated in the case of the 3-aryl-2*H*-benzo[*e*][1,2,4]thiadiazine-1,1-dioxide **60** substrates. Additionally, further transformation of the ketone group of the product into the alcohol or oxime moieties was successful. A similar pathway was suggested for the rhodium-catalyzed preparation of fused isoquinoline *N*-oxides **63** from cyclic 2-diazo-1,3-diones **2′** and aryloximes **62** (Scheme 30).[58] The reaction involved oxime-directed C–H activation in the presence of Rh(III), carbene insertion, migratory insertion and intramolecular cyclization.

2-Diazo-1,3-indandiones **2′** can efficiently react with 2-phenyloxazolines **64** to construct indenoisoquinolinones **65** in the presence of a rhodium(III) catalyst (Scheme 31).[59] This (4 + 2)-annulation reaction proceeded *via* a Rh-carbenoid strategy. Cyclic 1,3-diazo cyclohexanone was also converted to the corresponding product in 72% yield. The gram-scale synthesis of a product (1.29 g, 89%) showed the utility of this method.

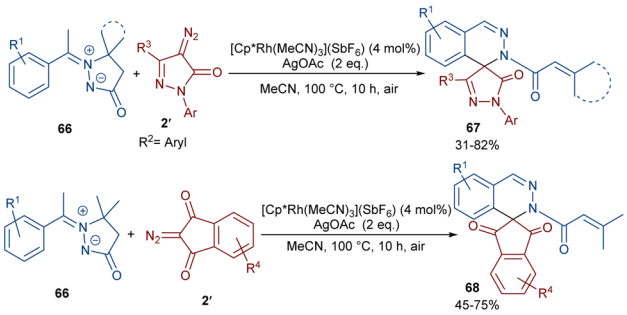
In 2022, Zhang, Fan and co-workers developed the assembly of spirocyclic dihydrophthalazines **67** from aryl azomethine imines **66** with cyclic diazo compounds **2′** (Scheme 32).[60] The reaction seems to proceed through a Rh-catalyzed azomethine imine-assisted cyclometallation, carbene insertion, isomerization and reductive elimination. Again, this group explained that the synthesis of spiro-isoquinoline from diazo compounds could be achieved through the (4 + 1 + 1)-annulation of *N*-aryl amidines with diazo homophthalimides (Scheme 33).[61] The reaction features a broad substrate scope, PEG-600 as a sustainable solvent, O_2 as a green oxidant, and a low reaction temperature. According to the mechanism in Scheme 34, the rhodium-catalyzed amidine-directed *ortho*-C–H bond cleavage



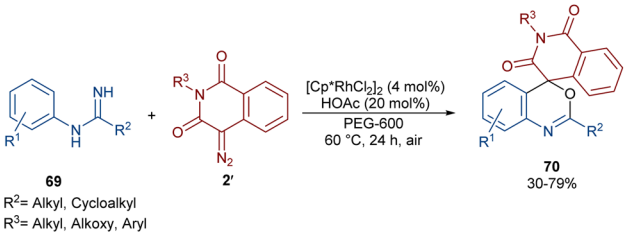
Scheme 30 Rh-catalyzed reaction of cyclic 2-diazo-1,3-diones and aryloximes.



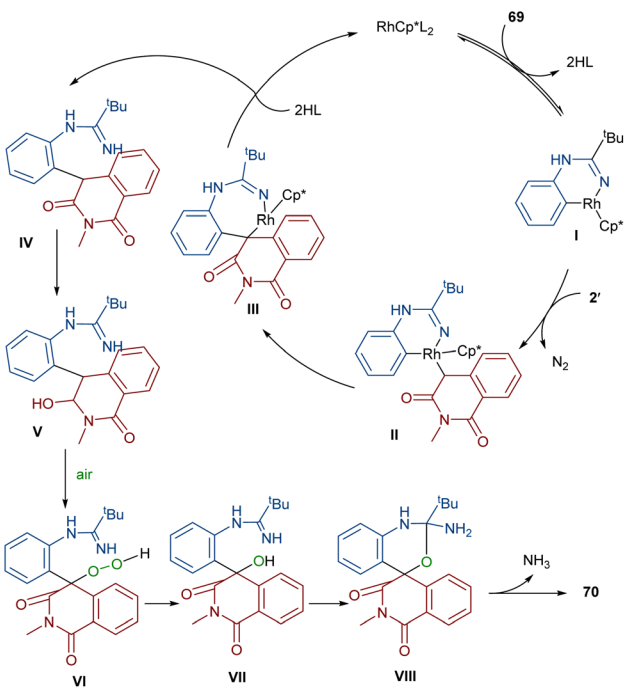
Scheme 31 Rh-catalyzed annulation of 2-diazo-1,3-indandiones and 2-phenyloxazolines.



Scheme 32 Rh-catalyzed annulation of aryl azomethine with diazo homophthalimides.



Scheme 33 Rh-catalyzed annulation of *N*-aryl amidines with diazo homophthalimides.

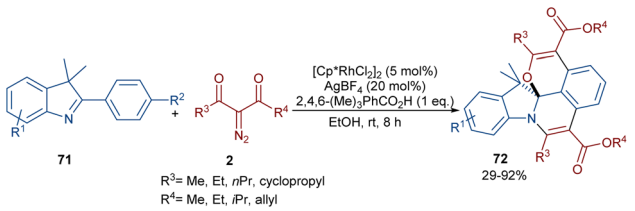


Scheme 34 Plausible mechanism for the Rh-catalyzed annulation of *N*-aryl amidines with diazo homophthalimides.

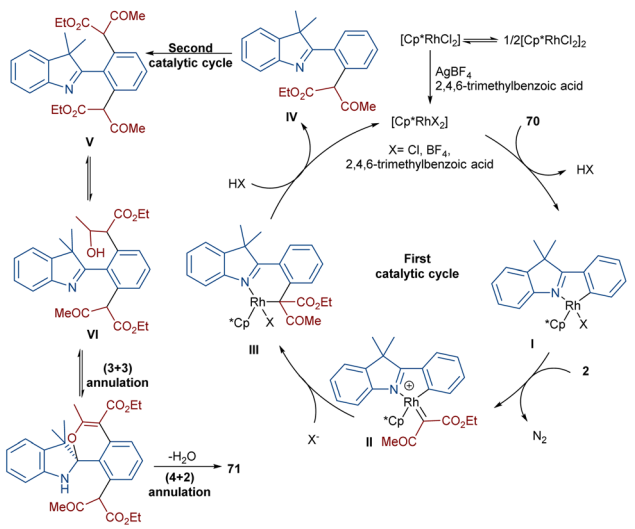
of **69** formed the six-membered rhodacycle **I**, which coordinated with diazo compound **2′** to give Rh-carbene **II**. The carbene migratory insertion into the Rh–C(sp^2) bond yielded intermediate **III**, followed by the protonation to obtain intermediate **IV**

under acidic conditions. Next, the amidine abstracted a benzylic proton from **IV** to afford enolate **V**, followed by oxidation and further protonation towards hydroperoxide species **VI**. In this step, **VI** reacted with reductant **IV** to provide alcohol **VII**, which under an intramolecular nucleophilic attack of the oxygen to the amidine produced intermediate **VIII**. Finally **VIII** removed an ammonia molecule to form product **70**.

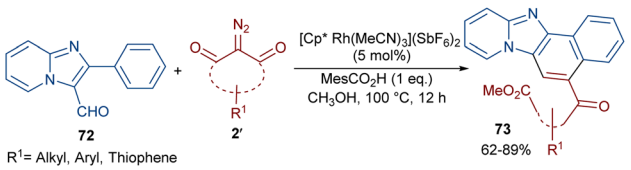
Liu, Zhou and co-workers succeeded in synthesizing a series of highly fused indole heteropolycyclic compounds **71** through an uncommon (3 + 3)- and (4 + 2)-cycloaddition sequence (Scheme 35).[62] For this purpose, they employed 2-phenyl-3*H*-indoles **70** and diazo compounds **2** as the feedstock in the presence of a rhodium(III) catalyst. Interestingly, the diazo compound acted as a C3 synthon in the (3 + 3)-cycloaddition and as a C2 synthon in the (4 + 2)-cycloaddition. The authors proposed a tentative mechanism for this transformation involving the initial C(aryl)–H bond activation of **70** Rh(III) to form the five-membered rhodacycle **I**, followed by interaction with diazo compound **2** to produce the rhodium carbene **II**. Subsequent migratory insertion gave the six-membered rhodacycle **III**, which by further elimination furnished intermediate **IV**. Sequential C–H activation in **IV** yielded the disubstituted indole **V**, which was then converted into enol **VI**. In this step, the hydroxyl group nucleophilically attacked the imino group to obtain spiro intermediate **VII** *via* (3 + 3)-cyclization. Ultimately,



Scheme 35 Rh-catalyzed annulation of 2-diazo compounds and 2-phenyl-3*H*-indoles.



Scheme 36 Tentative mechanism for the Rh-catalyzed annulation of 2-diazo compounds and 2-phenyl-3*H*-indoles.



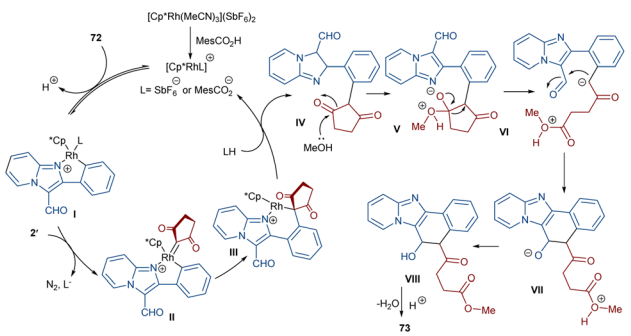
Scheme 37 Rh-catalyzed annulation of 2-diazo compounds and 2-arylimidazo[1,2-*a*]pyridines.

the NH free indole attacked the carbonyl group to yield product **71** along with H_2O elimination *via* (4 + 2)-cyclization (Scheme 36).

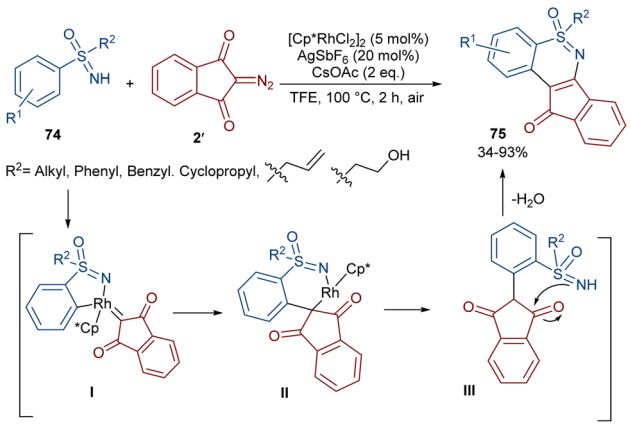
Li *et al.* developed a strategy for the assembly of naphtho[1′,2′:4,5]imidazo[1,2-*a*]pyridines **73** from 2-arylimidazo[1,2-*a*]pyridines **72** and cyclic 2-diazo-1,3-diketones **2′** (Scheme 37).[63] They proposed a carbene insertion/(5 + 1)-annulation pathway, in which the diazo compounds act as a C1 source. First, an active catalyst $[Cp^*RhL]^+$ was formed from the ligand exchange between the Rh catalyst and $MesCO_2H$. Sequential C–H activation, carbene formation, and migratory insertion resulted in the formation of six-membered rhodacycle **III**. Then, **III** underwent protonolysis to give intermediate **IV** and regenerated $[Cp^*RhL]^+$. Next, a retro-Claisen reaction occurred with intermediate **VI**, followed by intramolecular aldol condensation and subsequent dehydrative aromatization under acidic conditions to produce **73** (Scheme 38). The results of the H/D experiments suggested the reversibility of the aryl C(sp^2)–H activation and the KIE values (K_H/K_D = 1.2) showed that the C–H activation may not be rate-limiting step.

The formation of *N*,*S*-heterocyclic compounds from diazo indandiones can be achieved under rhodium catalysis (Scheme 39).[64] Sulfoximide derivatives **74** were utilized as a coupling partner to produce fused tetracyclic indeno-1,2-benzothiazines **75** in up to 93% yield. The reaction involved a five-membered rhodacycle intermediate **I**, which was added to diazo-indandione **2** to generate the rhodium carbenoid **II**. Migratory insertion afforded a six membered rhodacycle **III**, followed by proto-demetallation and dehydration. The gram-scale synthesis of a product (1.35 g, 84%) and the further reduction of the ketone unit to either an alcohol or methylene group demonstrated the utility of this method.

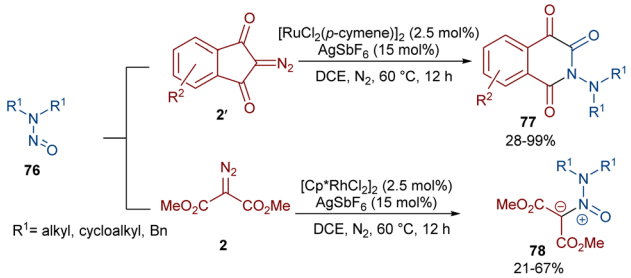
Very recently, the Yan research group disclosed two synthetic strategies including diazo compounds (Scheme 40).[65] They



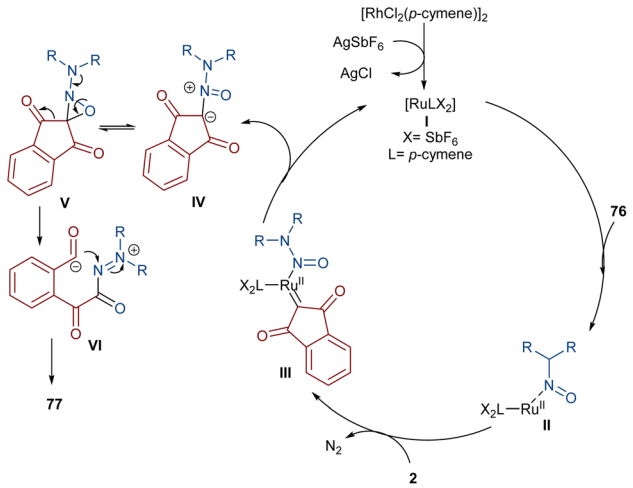
Scheme 38 Plausible mechanism for the Rh-catalyzed annulation of 2-diazo compounds and 2-arylimidazo[1,2-*a*]pyridines.



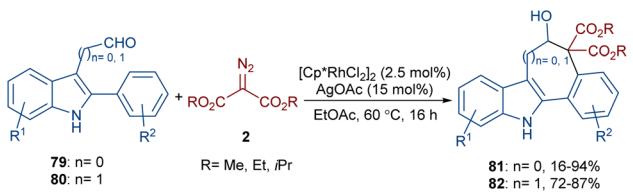
Scheme 39 Rh-catalyzed annulation of diazo compounds and sulfoximides.



Scheme 40 Rh/Ru-catalyzed reaction of cyclic 2-diazo-1,3-diketone, carbodiimide, and 1,2-dihaloethane.



Scheme 41 Possible mechanism for the Ru-catalyzed reaction of cyclic 2-diazo-1,3-diketone, carbodiimide, and 1,2-dihaloethane.



Scheme 42 Rh-catalyzed annulation of 3-aldehyde-2-phenyl-1*H*-indoles with diazo compounds.

treated diazo compounds **2** and *N*,*N*-dialkylnitrosoamines **76** in the presence of the ruthenium and rhodium catalysts. The method delivered a new library of isoquinoline-1,3,4-trione derivatives **77** using diazoindandiones as a carbene synthon in the presence of ruthenium(II) complex, while changing the diazo compound and the catalyst into dimethyl diazomalonate and rhodium(III), respectively, resulted in the formation of nitroso ylide products. The authors proposed a credible mechanism assuming Ru(II) to be the catalyst. Initially, the active catalyst **I** was generated from $[RuCl_2(p\text{-cymene})]_2$ with $AgSbF_6$, and coordinated with *N*,*N*-dialkylnitrosoamine **2** leading to intermediate **II**, which was then added to diazoindandione **2** to form the ruthenium carbene **III** with the removal of N_2. The nitroso ylide **IV** was obtained from the liberation of the active Ru(II) catalyst **I**, followed by conversion to oxaziridine **V**. Then, the cleavage of the N–O and C–C bonds afforded a stable acylazo cation **III**, which following an intramolecular cyclization yielded product **77**. When dimethyl diazomalonate **78** was used as a substrate the reaction ended during the nitroso ylide **VI** step. It was found that two esteric groups stabilized this intermediate (Scheme 41).

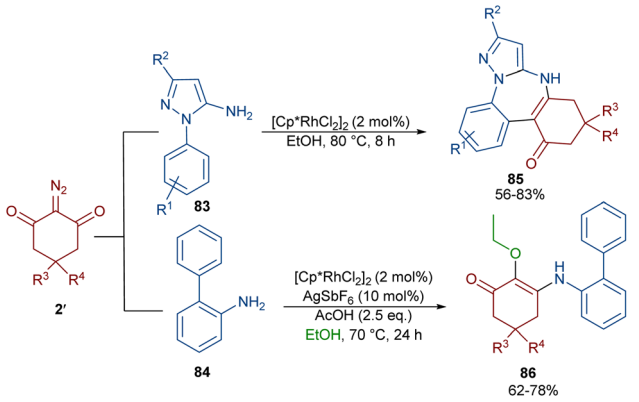
2.3. Synthesis of seven-membered rings

The annulation of 3-aldehyde-2-phenyl-1*H*-indoles **79** and acetaldehyde-2-phenyl-1*H*-indoles **80** with diazo compounds **2** can lead to 5*H*-benzo[*a*]carbazol-6-ols **81** and benzo[6,7]cyclohepta[1,2-*b*]indol-6-ols **82**, respectively (Scheme 42).[66] In this regard, Hu and co-workers employed a combination of rhodium(III) and silver(I) salts in the reaction. Although a rational mechanism was not reported by the authors, they proposed a sequence of C–H activation, carbene insertion, and an aldol-type cyclization. A gram-scale experiment, the oxidation of the alcohol to a ketone group and the elimination of ethanol and CO_2 molecules to give alkenes were also carried out in this work.

Again, Shang and co-workers utilized this Rh complex to assemble benzo[*f*]pyrazolo[1,5-*a*][1,3]diazepines **85** (Scheme 43).[67] For this purpose, they treated 1-aryl-1*H*-pyrazol-5-amines **83** with cyclic 2-diazo-1,3-diketones **2′** under milder reaction conditions. The reaction proceeded through the Rh-catalyzed pyrazole ring-assisted C–H activation, rhodacycle formation, carbene insertion and intramolecular nucleophilic cyclization. However, the use of [1,1′-biphenyl]-2-amine **84** as a substrate in the reaction with diazo compound **2′** led to the uncyclized product **86**. This compound was produced *via* a sequence of 1,1′-insertion, dehydration, and isomerization steps.

2.4. Rhodium-catalyzed functionalization reactions of diazo compounds

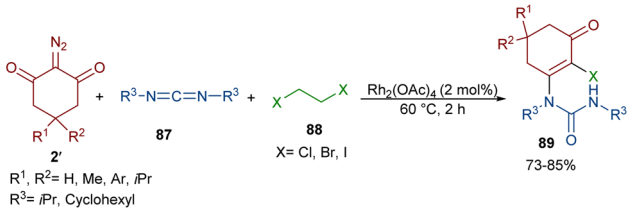
An unsymmetrical reaction between cyclic 2-diazo-1,3-diketone, carbodiimide, and 1,2-dihaloethane derivatives was performed



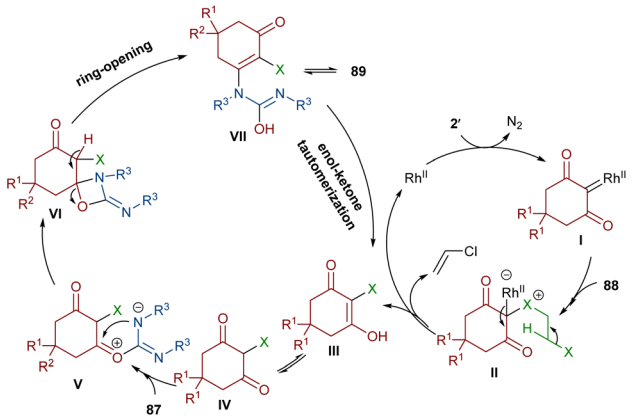
Scheme 43 Rh-catalyzed annulation of 1-aryl-1*H*-pyrazol-5-amines with cyclic 2-diazo-1,3-diketones.

in the presence of a rhodium complex (Scheme 44).[68] In this procedure, urea derivatives were successfully synthesized in good yields. As shown in Scheme 45, the Rh catalyst decomposed diazo compound **2′** into the active Rh-carbene species **I**, which reacted with 1,2-dihaloethanes **88** to provide halonium ylide **II**. Through an intramolecular HCl abstraction in **II**, intermediate **III**, haloethylene and the Rh(II) catalyst were formed. Intermediate **III** can tautomerized with **IV**. This intermediate was then subjected to a nucleophilic attack at the carbonyl oxygen by the carbon of carbodiimide **87** to provide a carbonyl ylide **V**. Subsequent intramolecular nucleophilic addition in **V** gave a four-membered ring intermediate **VI**, which underwent ring-opening and E2 elimination to give intermediate **VII**, followed by an enol-ketone tautomerization to access product **89**. The utility of the reaction was demonstrated by a gram-scale synthesis of the desired product (1.13 g, 83%).

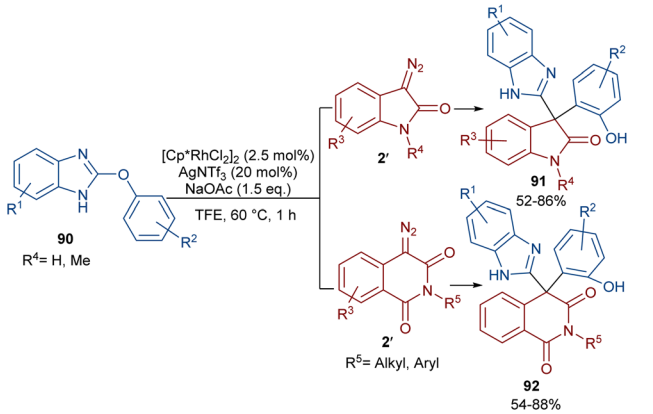
The reaction of 2-phenoxy-1*H*-benzo[*d*]imidazoles with two different diazo compounds can lead to diaryl oxindole or diaryl isoquinolinedione products (Scheme 46).[69] In this context, diazo oxindoles or diazo homophthalimides were used as the diazo compounds, respectively. Interestingly, the reaction did not proceed through the expected Rh-catalyzed C–H/N–H bond metallation and formal (5 + 1)-spiroannulation under these conditions, but resulted in the production of the unexpected unsymmetrical 3,3-diaryl oxindole derivatives **91**. As shown in the mechanism in Scheme 47, Rh-catalyzed NH-assisted C–H bond activation led to rhodacycle **I**, which coordinated with **2′** to



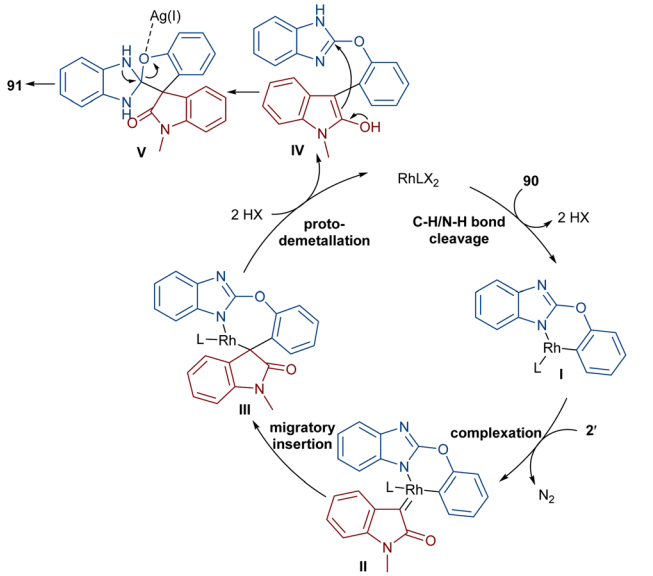
Scheme 44 Rh-catalyzed reaction of cyclic 2-diazo-1,3-diketone, carbodiimide, and 1,2-dihaloethane.



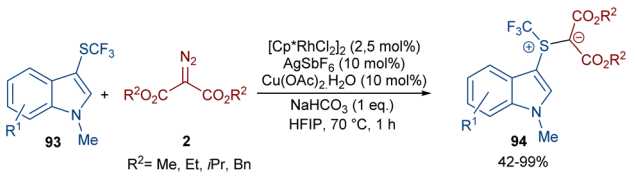
Scheme 45 Possible mechanism for the Rh-catalyzed reaction of cyclic 2-diazo-1,3-diketone, carbodiimide, and 1,2-dihaloethane.



Scheme 46 Rh-catalyzed reaction of 2-phenoxy-1*H*-benzo[*d*]imidazole and diazo compounds.



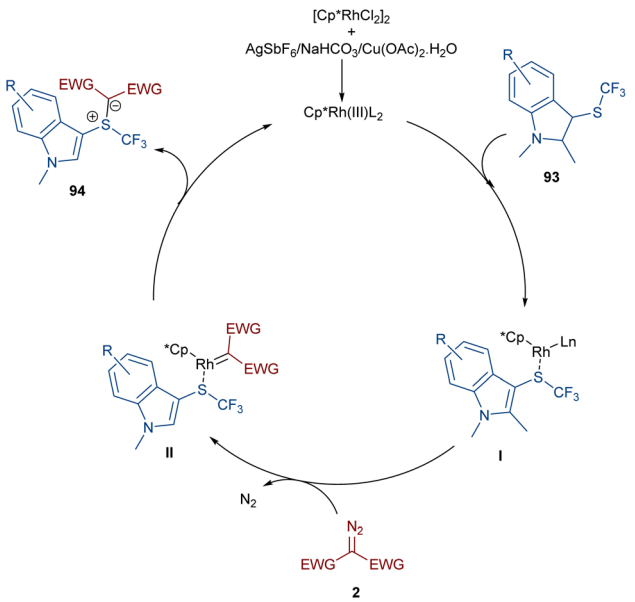
Scheme 47 Catalytic cycle for the Rh-catalyzed reaction of 2-phenoxy-1*H*-benzo[*d*]imidazole and diazo compounds.



Scheme 48 Rh-catalyzed reaction of 1-methyl-3-((trifluoromethyl) thio)-1*H*-indole and diazo compounds.

form Rh-carbene intermediate **II**. The carbene migratory insertion into the C–Rh bond, and subsequent proto-demetallation produced intermediate **IV** along with the release of the Rh(III) catalyst. Then, this cascade process moved through an intramolecular C-nucleophilic addition to form intermediate **V**, which underwent C–O bond cleavage in the presence of the Lewis acidic Ag(I) to furnish product **91**. Moreover, the practicality of this method was shown by the esterification of the alcohol group of the product in 74% and 90% yields and a large-scale synthesis resulting in 1.58 g of product in 89% yield.

A rhodium-carbene approach was proposed for the synthesis of a library of indole-substituted trifluoromethyl sulfonium ylides **94** (Scheme 48).[70] 1-Methyl-3-((trifluoromethyl)thio)-1*H*-indole derivatives **93** reacted with diazo compounds **2** in the presence of a rhodium(III) pre-catalyst, which was converted to an active Cp*Rh(III) catalyst **I** *via* ligand exchange with $AgSbF_6$, $Cu(OAc)_2$, NaOAc, or $NaHCO_3$. The coordination of the sulfur atom of substrate **93** with Rh, and further coordination of diazo compound **2** with the metal center resulted in Cp*Rh(III)-carbenoid intermediate **III** together with the expulsion of N_2. The reductive elimination of **III** afforded product **94** and regenerated the Cp*Rh(III) species (Scheme 49). Some substrates, including diazo compounds containing di-*tert*-butyl, and aryl substituents, were not successfully converted, maybe because of steric hindrance with the Rh complex. Also, a trifluoromethyl sulfide group attached the benzyl or phenyl motifs did not work under these conditions.



Scheme 49 Credible mechanism for the Rh-catalyzed reaction of 1-methyl-3-((trifluoromethyl)thio)-1*H*-indole and diazo compounds.

3 Conclusions

As shown in this review, the reactions of diazo compounds using a rhodium catalyst can be carried out *via* a metal-carbene strategy. Both Rh(III) and Rh(II) catalysts could efficiently catalyze the coupling reaction/annulations of diazo compounds with other reactants *via* the formation of highly active Rh-carbenoid intermediates. The DGs on the coupling substrates played an important role in selectively directing the C–H insertion by the metal. Although most DGs contained nitrogen groups, the use of substrates with poorer coordinating ability, such as oxygen and sulphur groups, should be further investigated. Despite the remarkable progress in the Rh-carbene strategy, various coupling reactants in the reaction with diazo compounds are still unexplored. Since most synthetic methods are reported under harsh reaction conditions, it would be desirable to develop mild and green conditions using organocatalysts in combination with rhodium. In addition, the use of chiral ligands in combination with rhodium catalysis for the synthesis of enantioenriched bioactive molecules could also be attractive in medicinal chemistry.

Data availability

All data associated with this manuscript are available within the article.

Conflicts of interest

There are no conflicts to declare.

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