ACS Catalysis

Review

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Fine Tuning of Dirhodium(II) Complexes: Exploring the Axial Modification

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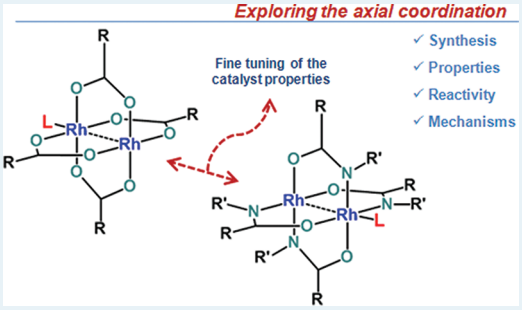
ABSTRACT: Over the years, dirhodium(II) complexes have had an important role in the synthesis of numerous complex organic molecules because many useful transformations are mediated by this unique family of complexes. The recognized success of this class of catalysts relies on their bimetallic structure. They have a Rh−Rh bond, two axial ligands, and four bridging ligands responsible for controlling the catalyst electrophilicity and, in some cases, provide a mechanism for inducing asymmetry. The modification of the bridge ligand structure has been the main strategy to prepare new complexes, whereas the axial ligands have been considered to have a less important role in catalysis. This concept is changing, and over the past decade, the axial ligand modification was proven to be a valuable and simple strategy to prepare new complexes and achieve new reactivities. In this review a comprehensive overview of this topic is presented, with a particular focus on the changes induced by the axial coordination on the complex properties and reactivity.



KEYWORDS: *dirhodium(II), axial ligands, mixed valence dimers, reactivity tuning, N-heterocyclic carbenes*

1. INTRODUCTION

About 40 years of intensive research in dirhodium(II) chemistry has allowed the discovery of valuable methodologies that have been successfully applied in synthetic organic chemistry. Among these, carbene and nitrene insertions in C−H bonds (also O−H, N−H, and S−H for carbenes), cyclopropanations, cyclopropenations, cycloadditions, and reactions with nitrenoids have attracted considerable attention and have been extensively reviewed.[1−28] A possible explanation for these developments lies in their unique capability for clean formation of metal-carbene species from diazo compounds (as compared with Cu or Ru catalysts), which is linked to their stable lanternlike structures. The development of simple methods for ligand exchange for catalyst modification also boosted their applications in catalysis.

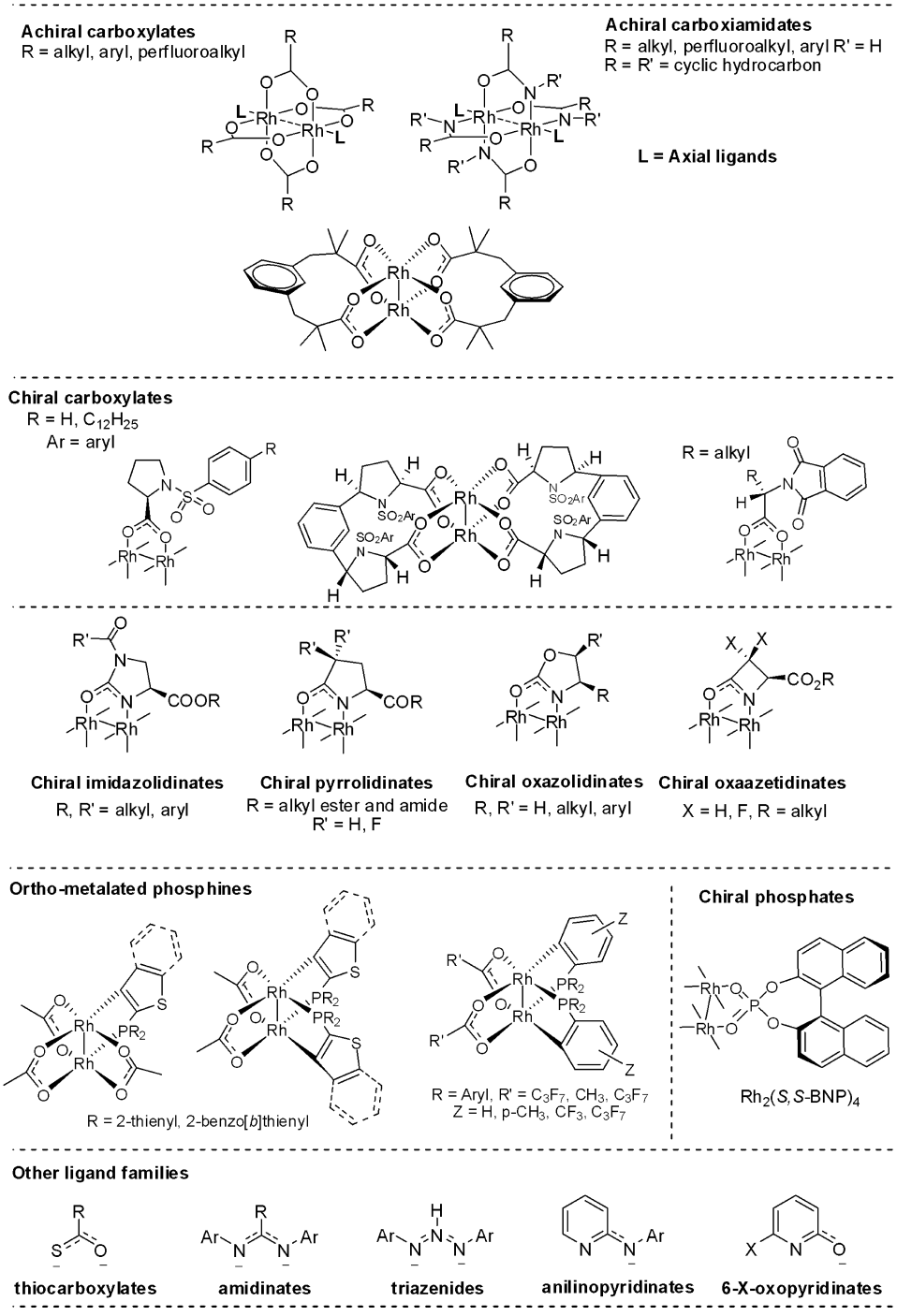
Dirhodium(II) complexes are bimetallic compounds with one metal−metal bond, four bridge ligands, and two axial ligands displayed in an octahedral geometry conferring a lanternlike structure.[9] The presence of a Rh−Rh single bond plays a crucial role in the performance of these complexes in the formation and reactivity of metallocarbenes and metallonitrenes when compared with other transition metals (such as copper and ruthenium).[29] Any electronic alteration in the metal atom where the carbene or nitrene is being formed is compensated by the second metal atom.[30]

The discovery of simple and efficient methods to introduce new bridge ligands in dirhodium(II) dimers boosted the application of these complexes as racemic or chiral catalysts and adds further insights into their role in catalysis. The most widely applied method for the introduction of new bridge ligands consists in refluxing bidentate ligands with dirhodium tetraacetate in the presence of a base. On the basis of this approach, several bidentate bridge ligands that can coordinate to the rhodium cations by oxygen, nitrogen, carbon, sulfur or phosphorus atoms were applied in several combinations. Despite all possible types of bidentate ligands that can be used and were, in fact, used, to prepare new families of dirhodium dimers, carboxylates and carboxamidates are among the most studied ones (Scheme 1).[5,7−9,14−16,31−35]

Different bridge ligands coordinated to rhodium will donate distinct degrees of charge to the metal. Consequently, it is possible to control the electronic profile of the catalyst by changing these ligands. In other words, it is possible to tune the complex reactivity and selectivity by changing the nature of the bridge ligand. This strategy has been extensively explored in the literature by several groups. A clear example of this is the

Received: November 18, 2011
Revised: January 27, 2012
Published: January 30, 2012

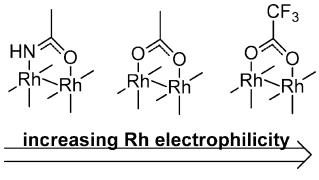
Scheme 1. Structural Diversity of Dirhodium(II) Complexes



increased elecrophilicity of the rhodium center when using perfluorobutyrate bridging ligands, compared with the lower electrophilicity of the rhodium center in complexes with amides (Scheme 2). Ligands such as amides generate catalysts that are less reactive in reactions involving diazo compounds than carboxylates but are more likely to be more selective, providing higher levels of the thermodynamic controlled products.[1,3,6−8,15,16] The reactivity of carboxamidate catalysts can be further increased by using strained oxaazetidinates ligands (Scheme 1), increasing the length of the Rh−Rh bond.[2]

The two axial positions of dirhodium dimers are electrophilic and are often occupied by solvent molecules that establish

Scheme 2. Relationship between Bridge Ligand and Rhodium Electrophilicity

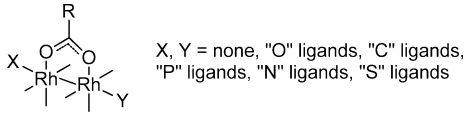


weaker bonds with the rhodium centers when compared with the bridge coordination.[36] These labile ligands are easily displaced by the substrates in the reaction vessel, and their role

dx.doi.org/10.1021/cs200597a | ACS Catal. 2012, 2, 370−383

in catalysis has been somehow overlooked. Nevertheless, several studies disclosed in the literature described the axial coordination of nitrogen, oxygen, carbon, and phosphorus adducts with rhodium(II) dimers (Scheme 3). The coordination of such ligands requires a smoother protocol compared with reactions of bridge ligand exchange because the coordination is instantaneous due to the electrophilic character of the parent rhodium(II) complex.[9,34,35,37]

Scheme 3. Structural Diversity of Rhodium(II) Carboxylates

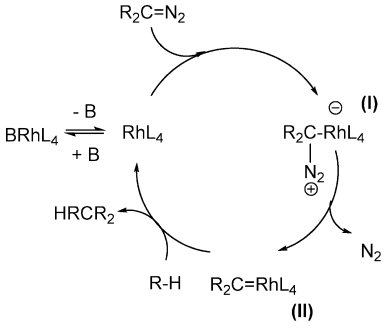


Interestingly, some of the most recent developments in this area of chemistry are concerned with the development of alternative strategies to tune the reactivity of rhodium(II) complexes without changing the bridge ligands. Therefore, this review aims to provide the first critical overview on these new exciting developments.

2. GENERATION OF METALLOCARBENES FROM DIAZO COMPOUNDS

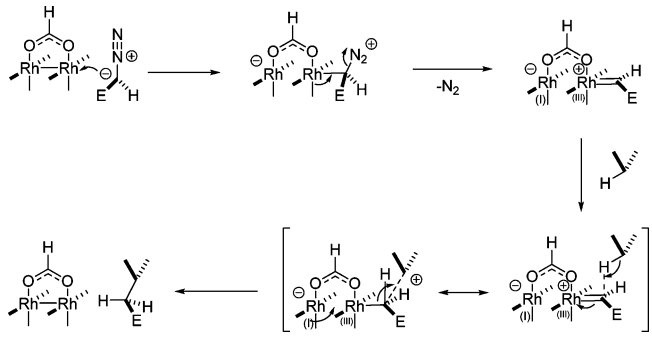
The most well-known catalytic application of dirhodium(II) dimers is the generation of metallocarbenes from diazo compounds, which can undergo C−H bond and heteroatom-H insertion, cyclopropanations, and dipolar ylide cycloaddition. The mechanism of cyclopropanation[2,17,19,38−40] and C−H insertion[11,41−45] has been the subject of several theoretical studies. Today, the generally accepted mechanism for the C−H insertion transformation starts by a solvent (B) decomplexation from the catalyst axial positions, followed by a nucleophilic attack of the diazo compound on the metal generating ylide (I), which upon nitrogen extrusion provides the metallocarbenoid (II). Then an electrophilic attack from the metallocarbene to an electron-rich C−H bond (substrate R−H) furnishes the product, regenerating the catalyst (Scheme 4).[8]

Scheme 4. Mechanism Proposed for R−H Insertion Reactions in Diazo Compounds



The catalytic cycle described was studied in more detail by Nakamura and co-workers using a hybrid DFT functional (B3LYP) and involves only two steps: carbene coordination promoting nitrogen extrusion (the rate-limiting step[43]), and C−H insertion.[41,42] In the first step, the diazo compound coordination into the rhodium leads to a small stabilization of the system. Further approximation of the carbene to the rhodium together with back-donation from the metal induces nitrogen extrusion, furnishing the metallocarbene intermediate (II). In the reaction of methyl diazoacetate with methane in the presence of dirhodium tetraformate, the transition state for the formation of the metallocarbene requires 16.7 kcal/mol and was described as a very late transition state. In the second step, two events are accomplished in a concerted but non-synchronous 3-members-centered mechanism. In the first event, a hydride transfer from the alkane to the carbon atom of the carbene occurs, and in the second event the formation of a new C−C bond with regeneration of the Rh−Rh bond takes place (Scheme 5).

Scheme 5. Mechanism Proposal for the Intermolecular Insertion of Methyl Diazoacetate in Propane



The proposed mechanism considers that only one of the two rhodium atoms works as a carbene binding site throughout the reaction.[46,47] The second rhodium atom acts as a mobile ligand for the first one to enhance the electrophilicity of the carbene moiety and to facilitate the cleavage of the rhodium−carbon bond.[41,42] This communication and compensation between the two rhodium centers were also found in Drago and Tanner's early findings. In 1979, they determined the enthalpy and kinetics for formation of mono and bis adducts of a dirhodium(II) tetrabutyrate complex with several Lewis bases.[36,48] As depicted in Table 1, the equilibrium constants decrease considerably for the formation of the 2:1 adduct. These observations suggest that the coordination of a ligand to one of the Rh atoms affects the electrophilicity of the other Rh atom and, therefore, the reactivity of the whole complex.

Table 1. Thermodynamic Data for Forming 1:1 and 2:1 Base Adducts of Dimeric Rhodium(II) Butyrate in Benzene Solution

Lewis base	K_1	K_2	$-\Delta H_{1:1}$ kcal mol^{-1}	$-\Delta H_{2:1}$ kcal mol^{-1}
acetonitrile	1.7×10^3	27	5.1	8.3
pyridine	1.6×10^8	2.4×10^4	11.2	11.2
piperidine	10^9	6×10^4	13.2	12.5
tetrahydrothiophene	1.7×10^7	1.9×10^4	11.0	10.3
DMSO	1.1×10^5	5.5×10^2	6.6	6.5

Indeed, the most important ligand that should be considered is the reaction solvent, and in fact, it has a deep impact on the reaction outcome. Solvents with poor coordinative capabilities (dichloromethane or 1,2-dichloroethane) were observed to be the most efficient, although solvents that coordinate into dirhodium complexes, such as acetonitrile or tetrahydrofuran, can partially or totally inhibit the generation of the metallocarbene.[6,7,46,47,49−51] The extent by which a solvent molecule

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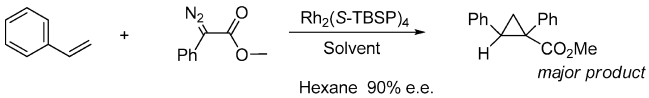
can inhibit this type of reactions was studied in detail by Pirrung and co-workers.[46,47] The Michaelis–Menten (MM) kinetics were studied for dirhodium(II) carboxylate-catalyzed carbenoid reactions, and it was discovered that many reactions mediated by these complexes obey saturation MM kinetics. The authors also disclosed that axial ligands, such as acetonitrile, inhibit these transformations by a mixed kinetic inhibition mechanism in which the ligand can bind both to the free complex and to the catalyst–substrate complex. Another important conclusion of this study was that the active catalyst uses only one of its two coordination sites at a time for catalysis.

The Jessop group demonstrated the effect of supercritical and liquid solvents on the enantioselectivity of asymmetric cyclopropanation of styrene with $Rh_2((S)\text{-TBSP})_4$. The enantioselectivity was found to be dependent on both the dielectric constant (the more polar, the lower the ee that was obtained) and the coordinating ability of the solvent. As seen previously, coordinative solvents such as acetonitrile or THF depleted the rate of cyclopropanation (Scheme 6). Interestingly, in these solvents, the enantioselectivity of the cyclopropanes obtained was superior to that expected if only their dielectric constant were taken into consideration (compare acetonitrile with dichloromethane).[50]

Scheme 6. Solvent Effect in the Enantioselectivity of Styrene Cyclopropanation with $Rh_2((S)\text{-TBSP})_4$

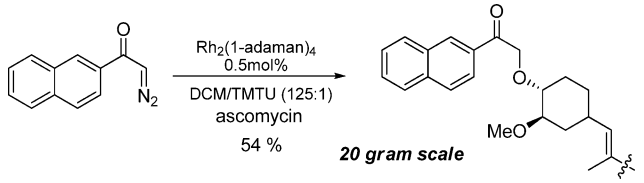


Hexane	90% e.e.
CH_2Cl_2	67% e.e.
THF	81% e.e.
CH_3CN	73% e.e.
DMF	69% e.e.
$scCO_2$	84% e.e.

In 2000, Nelson and co-workers from Merck Laboratories in their pivotal work found that other Lewis bases (cosolvents) can be used to tune the properties of dirhodium(II) catalysts. They were interested in studying the possibility of using intermolecular O–H insertion reactions to achieve the synthesis of macrolactams with potential immunosuppressive activity. However, they found that the application of traditional dirhodium(II) catalysts with different steric hindrance and electronic properties resulted only in unselective reactions with low yields (25–36%). The utilization of mild coordinative cosolvents such as tetramethyl urea, Hünig's base, *N,N*-diethyl aniline, and 2,4,6-trimethylpyridine resulted in improvements on the reaction selectivity. It was disclosed that the concentration of the cosolvent can have a deep impact on the reaction outcome. As an example, no reaction took place when using a 1:1 mixture of tetramethylurea (TMTU) and dichloromethane; meanwhile, a ratio of 1:125 (DCM/TMTU) resulted in improved yields (Scheme 7).

The steric hindrance of the cosolvent also influenced the reaction outcome. Although with *N,N*-dimethylacetamide, no reaction took place, with the utilization of the bulkier *N,N*-dimethylpivalamide, the diazoketone insertion was immediate. The diazo insertions were more sensitive to the amount and nature of the additive, as opposed to the steric bulk of the rhodium ligands. Simply changing the ligand (e.g., octanoate to adamantoate) did not significantly alter the insertion reaction. In parallel, diisopropyl ethyl amine can also be added as a cosolvent to improve the yields of O–H insertion using only

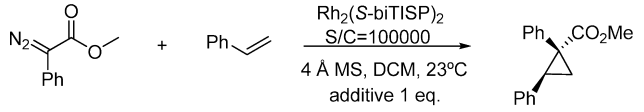
Scheme 7. Additive Influence of Tetramethylurea in O–H Insertion Reactions



equimolar amounts of alcohol. The authors did not provide any rationalization for such improvements other than acknowledging that cosolvents could coordinate in the axial positions of dirhodium(II) dimers. However, there is evidence that electronic and steric effects of the cosolvents can differently influence dirhodium(II) catalysts, possibly by axial coordination.[52]

Davies et al. found that methyl benzoate could not only improve the enantioselectivity of styrene cyclopropanation with methyl 1-phenyldiazoacetate but also allow the utilization of very low amounts of catalyst, S/C = 100 000, with high efficiency (Scheme 8). At the time, the authors were not sure of the additive's role; however, the possibility of its coordination to the carbenoid or to the other rhodium center was considered.[53]

Scheme 8. Additive Effect in Activity of $Rh_2((S)\text{-biTISP})_2$ in Cyclopropanation Reactions with Diazo Compounds



none	42h, 82%, 65% ee
$PhCO_2Me$	28h, 85%, 83% ee
TMTU	>36h, 48%, 74% ee
DIPEA	>36h, 5%

Charette and co-workers found that $TfNH_2$ and DMAP could also be used as additives to moderately improve the chiral induction in cyclopropanation reactions using diazo compounds possessing two acceptor groups.[54,55] The additive's degree of success was highly dependent in the diazo substrate and reaction temperature. $TfNH_2$ and DMAP have been shown to be optimal with $Rh_2((S)\text{-NTTL})_4$ and $Rh_2((S)\text{-TCPTTL})_4$, respectively, suggesting a correlation between the additive and the corresponding symmetry of the metallocarbene intermediate. The role of $TfNH_2$ remains undisclosed. Regarding the temperature effect, DMAP impacted the diasterioselectivity only at temperatures around −50 °C, at which point spectroscopic evidence suggested its axial complexation, under the reaction conditions (1 equiv relative to rhodium catalyst). The enantioselectivity improvements disclosed could be explained in two ways on the basis of axial coordination. The coordination onto the stereoselective reactive site lacking catalyst could not only modify its electronic properties but also alter the spatial arrangement of the chiral bridge ligands. Of course, a decrease in the reactivity was observed when using DMAP as an additive.[56]

Recently, Ball et al. took advantage of the axial coordination of triphenylphosphite to enhance the enantioselectivity of a bis-peptide rhodium(II) complex in silane insertion reactions on diazo compounds, despite a decreased reaction rate (Scheme 9). The authors studied several axial additives to increase the

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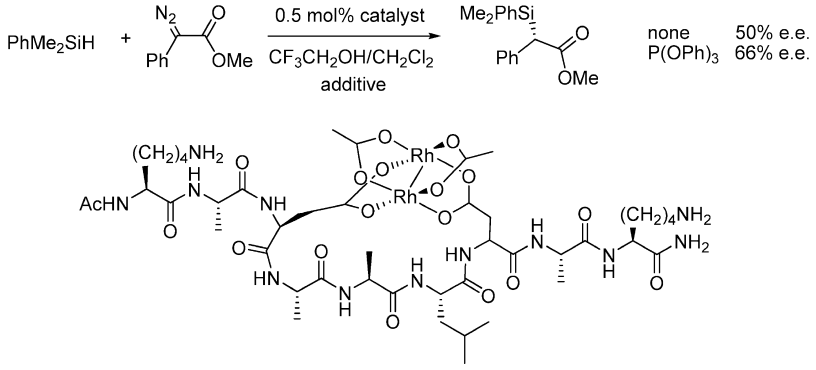
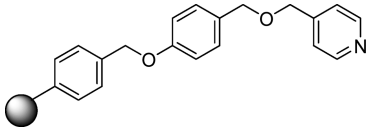
Scheme 9. Positive Impact on the Enantioselectivity by Axial Coordination of Triphenylphosphite in Dirhodium(II) Complex



enantioselectivity (phosphines, phosphites, tertiary amines, nitriles hydroxylamines, and DMSO), but only triphenylphosphite produced any good result. Furthermore, the phosphite was found to bind with equal affinity to both rhodium centers, despite being nonchemically equivalent. These observations suggested that the improvement on enantioselectivity could be explained by steric effects. In fact, the authors observed chemical shifts of some aspartate protons upon phosphite coordination, suggesting the hypothesized alterations in the peptide structure and dynamics.[50]

Davies et al. identified that axial positions of dirhodium(II) catalysts could be used to coordinate these complexes into polymeric resins bearing pyridine moieties. The aim was to achieve the reutilization of expensive chiral rhodium catalysts. The authors had chosen Argopore-Wang resins (highly cross-linked macroporous polystyrene) because pyridine residues can be easily installed and can be used in a large number of solvents. This support was combined with several chiral dirhodium(II) complexes and evaluated in cyclopropanation and C−H insertion reactions in diazo compounds (Scheme 10). The authors found that the levels of enantioselectivity were

Scheme 10. Polymeric Support for Dirhodium(II) Chiral Complexes Immobilization



not affected by the presence of the support. However, as an example, when $Rh_2((S)\text{-biTISP})_2$ was tested in cyclopropanations, a decreased activity was observed, perhaps as a result of axial pyridine coordination and partial inhibition. The immobilization mechanism remains unclear, but empirical evidence points toward that it could be due to a combination of pyridine coordination and an encapsulation effect within the polystyrene matrix. It is possible to achieve immobilization of rhodium species in Argopore resins modified without pyridine residues, but the immobilization loading is superior when such a residue is available.[57−60]

In 1999, the Lahuerta and Pérez-Prieto groups published the preparation of novel dirhodium(II) complexes with orthometalated phosphine ligands. The ligands studied in this work had one dangling group that was found to coordinate onto the axial position of the rhodium, furnishing a quite different complex compared with the one obtained if no dangling group was present (Scheme 11). In this way, catalysts **1** and **2** cannot be directly compared with **3** in the intramolecular cyclopropanation reaction studied. However, in the presence of a methoxide moiety, no catalysis occurred, but with chlorine, about 53% of product was obtained. The inhibition effect was more pronounced for the methoxy coordination than for the weaker Lewis base chlorine.[61,62] If a pendant alkyl hydroxyl group is used, higher temperatures (100 °C) are required to achieve catalysis so as to have hydroxyl group decoordination from the axial position.[63]

Two years later, Arduengo and Snyder isolated the first dirhodium(II) dimer with one *N*-heterocyclic carbene coordinated in the axial position.[64] Upon coordination of tetramethylimidazolidene, the Rh−Rh bond was elongated by 0.05 Å, and the rhodium−carbon bond became 2.06 Å long. A shorter rhodium−ligand bond indicates that the ligand coordinates more strongly to the dirhodium(II) complex. Hence, methylene is a stronger ligand than tetramethylimidazolidene, and this last one is stronger than water (Table 2). The rhodium−rhodium bond becomes weaker and longer with coordination of stronger ligands because it involves a σ^* orbital from the dirhodium complex.[48]

On the basis of this theoretical data, the authors expected that the axial coordination of tetramethylimidazolidene would have a significant impact on the parent complex reactivity. To test this hypothesis, the $Rh_2(OPiv)_4(ITM)$ was applied in diazo decomposition reactions: C−H insertions and ylide cycloadditions. Interestingly, this catalyst furnished the same

Scheme 11. Intramolecular Cyclopropanation with Dirhodium(II) Complexes with Orthometalated Phosphine Ligands

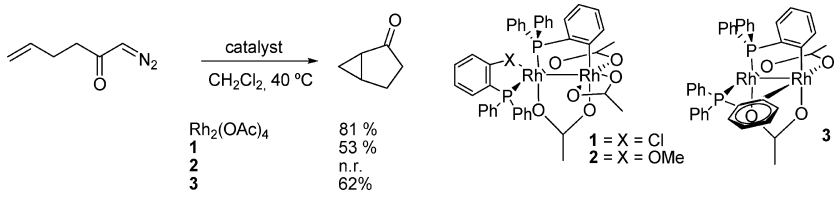


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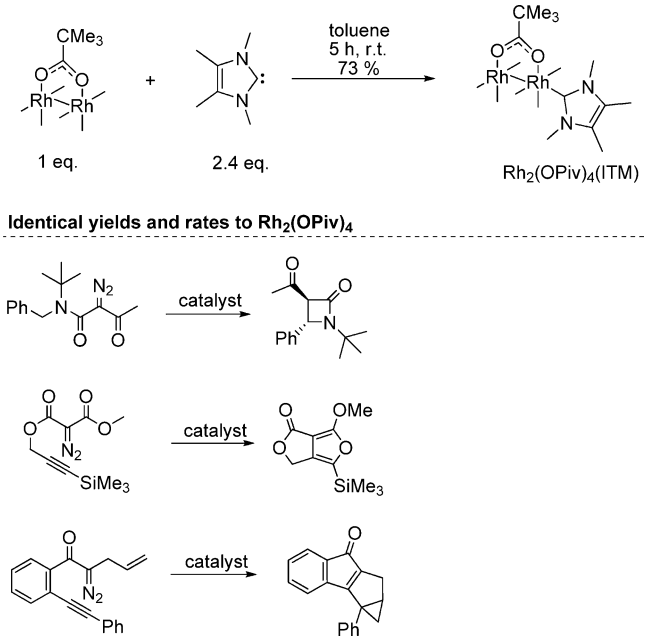
Table 2. Relevant Bond Distances, Natural Charges and Bond Ligation Orders for Several Dirhodium Complexes with and without Axial Ligands

complex	Rh−Rh, *d* (Å)	Rh_1−L, *d* (Å)
$Rh_2(OAc)_4$[a,65]	2.37	
$Rh_2(OAc)_4{\cdot}2H_2O$[b,42]	2.38	2.40
$Rh_2(O_2CH)_4(=CH_2)$[a,42]	2.48	1.91
$Rh_2(OPiv)_4(ITM)$[b,64]	2.42	2.06

[a]DFT calculations performed at the B3LYP/VDZP level of theory. [b]X-ray structure.

products and the same yields as the parent dirhodium tetrapivalate (Scheme 12).

Scheme 12. The First NHC−Rh(II) Complex Developed: Synthesis and Reactivity



The authors rationalized that the complex displayed low stability under the reaction conditions, and therefore, the reactions were most likely catalyzed by the parent dirhodium(II) complex after displacement of the axial tetramethylimidazolidene ligand. On the basis of this precedent, Gois et al. anticipated that using more stereo-demanding *N*-heterocyclic carbene ligands, such as *N*,*N*-(2,6-diisopropylphenyl)-imidazolidene (IPr), it would be possible to overcome this lack of stability by improving the protection to the Rh center (Scheme 13).

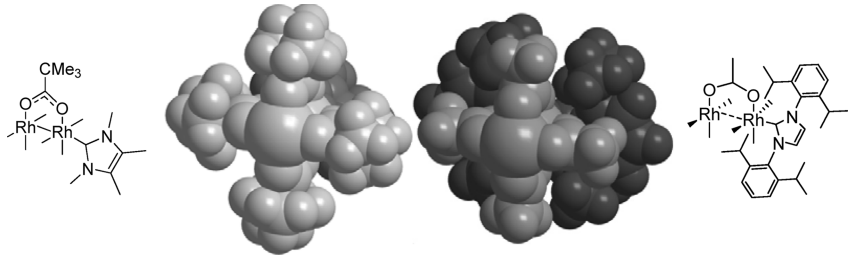
The authors prepared different complexes bearing one or two NHC ligands coordinated onto the dirhodium(II) axial positions: $Rh_2(OAc)_4(IPr)_2$ **4**, $Rh_2(tfa)_4(IPr)_2$ **5**, $Rh_2(OAc)_4(SIPr)_2$ **6**, $Rh_2(OAc)_4(IPr)$ **7**, and $Rh_2(OAc)_4(SIPr)$ **8**. They found that despite that the ITM ligand formed a stronger bond with rhodium (Rh−C_{ITM} = 2.08, Wiberg index = 0.44[64] vs Rh−C_{Ipr} = 2.17, Wiberg index = 0.38[65]), IPr furnished a more stable complex that was isolated using standard chromatographic techniques.[66,67] The higher stability displayed by this complex enabled the evaluation of the NHC axial ligand influence over the C−H insertion reaction of diazo compounds.[65,68] Generally, the cyclization of diazo acetamides catalyzed by NHC−dirhodium(II) complexes **7** and **8** proceeded at a considerably slower rate than when using the parent complex $Rh_2(OAc)_4$. This reflected a less favorable nucleophilic attack by the diazo compound onto the NHC−diRh (II) complex as a result of the increased electron density of the terminal Rh center in **7** and **8**, according to Pirrung's[46,47] and Nakamura's[41,42] studies.

Interestingly, the introduction of an axial ligand IPr or SIPr also led to alterations in the reaction selectivity. Typically, diazo compounds such as diazoacetamide **9** afford the γ-lactam isomer with $Rh_2(OAc)_4$,[69,70] although when the reaction was performed in the presence of complexes **7** and **8**, along with the β-lactam, a new decarbonylated product **12** was isolated (Scheme 14). The conversion of other diazoacetamides catalyzed by **8** generally afforded the expected lactams without forming the decarbonylated product, suggesting the importance of the diazoacetamide structure for the decarbonylation pathway.

As a result, the formation of product **12** was explained on the basis of a (a) stepwise or a (b) concerted Wolff rearrangement from the uncatalyzed diazo decomposition (Scheme 15) or via a (c) mechanism based on the metallocarbene decoordination from the rhodium center (Scheme 15).[65] The first two pathways assume that the degree of catalysis inhibition is high and allows the background thermal Wolff rearrangement. In mechanism c, it is considered that the electronic pushing effect exerted by the NHC ligand contributes to the formation of the free reactive carbene. It is worth mentioning that thermal Wolff rearrangements with migration with nitrogen fragments are rare.[71]

An alternative method to tune the reactivity of dirhodium dimers was developed by Dikarev's group. This method introduces important modifications since the authors were able to prepare complexes in which one of the rhodiums was replaced by a bismuth atom. The heterobimetallic complex

Scheme 13. Structures of $Rh_2(OPiv)_4(ITM)$ (left) and $Rh_2(OAc)_4(IPr)$ (right)[a]



[a]The NHC ligand is darkened on the space fill representations.

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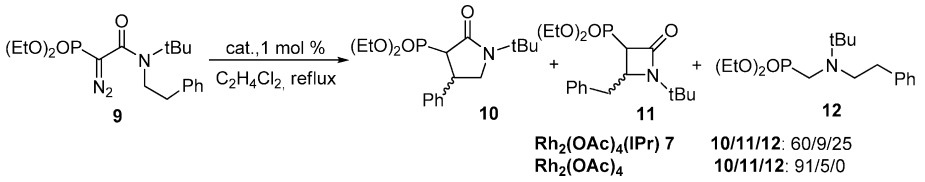
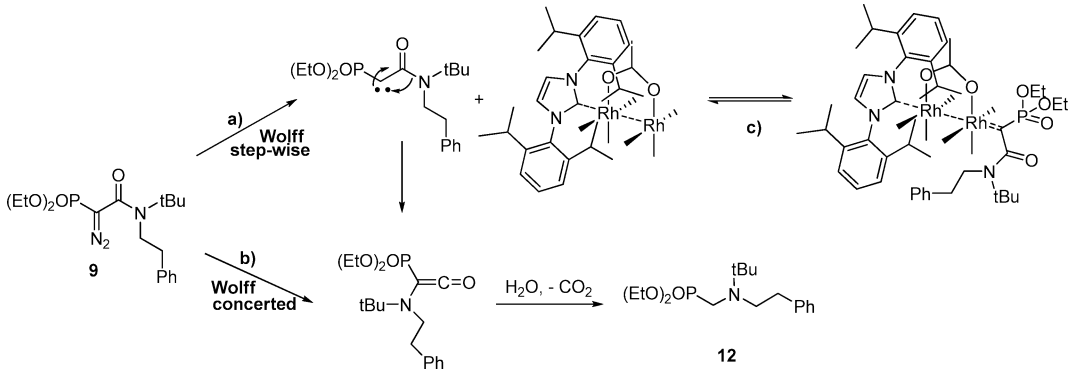
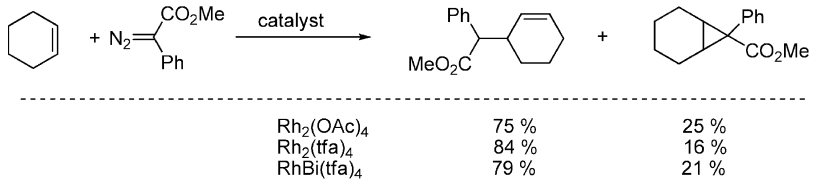
Scheme 14. Intramolecular C−H Insertion Catalyzed by NHC−Dirhodium(II) Complexes



Scheme 15. Possible Mechanistic Pathways Leading to Product 12



Scheme 16. Catalytic Comparison between $RhBi(O_2CCF_3)_4$ and $Rh_2(O_2CCF_3)_4$



$RhBi(O_2CCF_3)_4$ was prepared by a sublimation/deposition procedure and features a Rh−Bi bond with 2.55 Å (bond order ∼ 1). Interestingly, in the solid state, the oxygen from the bridge ligand coordinates to another complex molecule only in the rhodium center. In fact, even with diethyl ether, coordination on bismuth was always absent. The complex possesses only one-end Lewis acidity.[72,73]

Davies's and Dikarev's groups studied the effect in catalysis of the substitution of rhodium by bismuth. They found that the rhodium−bismuth bond was able to catalyze diazo decomposition reactions: cyclopropanations and C−H insertions. For instance, the catalyst $RhBi(O_2CCF_3)_4$ effectively catalyzed cyclopropanation and C−H insertion reactions on cyclohexene as well as reactions involving ylide intermediates with selectivities identical to $Rh_2(O_2CCF_3)_4$ (Scheme 16). However, qualitatively it was observed that this catalyst was less reactive than the dirhodium complex. Quantitative studies were performed with the heterometallic complex $BiRh(O_2CCF_3)_3(O_2CCH_3)$. Even though this complex was less effective than $RhBi(O_2CCF_3)_4$, it was also found to be ∼1600 times less reactive than its homometallic analogue $Rh_2(O_2CCF_3)_3(O_2CCH_3)$ in the reaction of methyl phenyldiazoacetate with cyclohexene.[44]

The excellent ability for dirhodium complexes to catalyze reactions involving formation of carbene and nitrene species is related to their unique stability and electronic communication along their metal−metal single bond.[7,30] To evaluate if the same property was found in the Rh−Bi complex, the authors conducted DFT calculations to gain further insight into the mechanism. Immediately, it is noticeable that the rhodium linked to bismuth is less positive than when linked to other rhodium. This observation demonstrates that linkage to bismuth reduces the rhodium electrophilicity, and is expected that the rate-limiting step becomes more difficult. In fact, the calculations demonstrated that when using $RhBi(O_2CH)_4$, the rate-limiting step energy barrier was higher when compared with $Rh_2(O_2CH)_4$ (8 kcal/mol higher), explaining the decreased reactivity. An analysis of rhodium's and bismuth's charge along the reaction coordinate showed that the rhodium−bismuth bond has the same flexibility as the rhodium−rhodium bond.[44] The substitution of one rhodium with a bismuth atom had a similar impact on the reactivity relative to the dirhodium parent complex as the coordination of IPr into the axial position.

3. EXPANDING DIRHODIUM(II) CHEMISTRY

As seen in the previous section, the coordination of an axial ligand or exchange of one rhodium with a bismuth atom introduced new reactivities and selectivities. The possibility to perform a fine-tuning of the complex properties could open new, exciting avenues for new reaction profiles.

3.1. Arylation of Aldehydes with Boronic Acids. The first successful example of the application of *N*-heterocyclic carbenes with dirhodium(II) complexes dates to 2001. The findings that arylations of aldehydes with boronic acids were best run with sterically hindered and strongly basic ligands attracted the attention of Fürstner et al. and encouraged the application of this family of ligands in this transformation.[74] The best results were obtained with IMes when generated in

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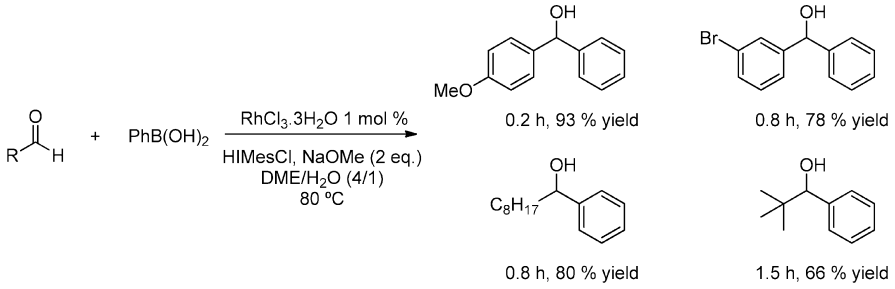
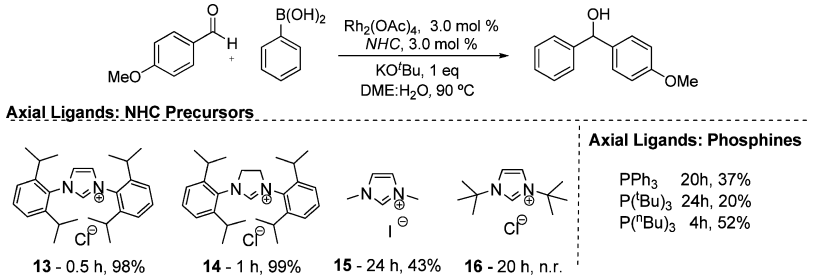
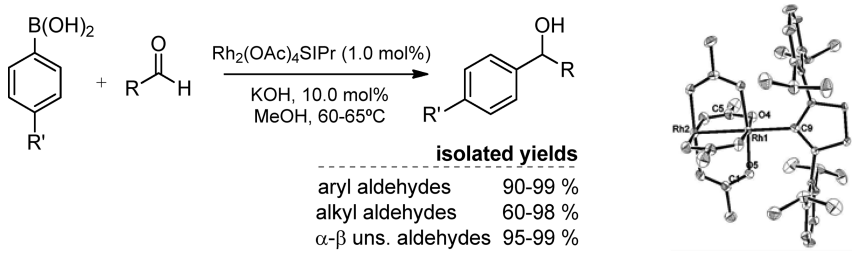
Scheme 17. Substrate Scope for the Arylation of Aldehydes Catalyzed by a Rh(III)/NHC System



Scheme 18. Axial Ligand Screening in the Arylation of Aldehydes Using Boronic Acids



Scheme 19. Substrate Scope in the Arylation of Aldehydes with $Rh_2(OAc)_4(SIPr)$ and X-ray Structure for $Rh_2(OAc)_4(SIPr)$



situ via deprotonation of HIMesCl, using $RhCl_3 \cdot 3H_2O$ as precatalyst (1 mol %, Scheme 17).

In addition to a variety of rhodium(I) precatalysts, $[Rh(OAc)_2]_2$ was also successfully employed; however, it was found to have inferior catalytic ability compared with $RhCl_3 \cdot 3H_2O$. The study was continued with rhodium(III) catalysts, and no further information was given regarding the utilization of dirhodium(II) tetraacetate. This observation captured the attention of Gois et al. because this type of reactivity, using $[Rh(OAc)_2]_2$, was described in this work for the first time.[2,6,7,21,36,48]

Gois et al. studied in more detail the arylation of aldehydes with boronic acids using different rhodium(II) complexes and several potential axial ligands, such as NHCs and phosphines (Scheme 18).[66,67,75] Considering the results disclosed, the presence of either phosphines or NHC ligands was necessary to observe catalytic activity. For this system, NHCs were much superior to phosphines, although the reaction efficiency dramatically depended on steric effects. IPr and SIPr NHCs provided the best results in combination with dirhodium(II) tetraacetate, whereas the use of ItBu (*t*-butyl N-substituent) afforded no product at all.

This difference in reactivity was clarified by the X-ray analysis of complex $Rh_2(OAc)_4(IPr)_2$ and DFT calculations, which revealed that the coordination of the IPr ligand results in a perfect structural match between the NHC and the dirhodium complex. This arrangement, in which the isopropyl groups of the NHC fit between the complex OAc bridges while the carbene ring remains in an eclipsed conformation confers a higher stability to the complex.[67] Finally, comparing the $Rh_2(OAc)_4(IPr)_2$ and $Rh_2(OAc)_4(PPh_3)_2$ complexes[76] revealed a longer Rh−Rh bond in the first case due to the σ-donation from the carbene lone pair to the complex Rh−Rh antibonding orbital associated with a very reduced π-back-bonding.[76,77]

In the course of this study, the authors showed that the presynthesized Rh(II)/NHC complexes, bearing one or two axial IPr or SIPr ligands, could be used as catalysts in this transformation. More importantly, it was also demonstrated that these complexes could be quantitatively recovered from the reaction and reused without loss of activity. The arylation of aromatic and aliphatic aldehydes with aromatic and vinylic boronic acids proceeded smoothly under relatively mild reaction conditions (1 mol % of catalyst, 10 mol % of base at 60 °C; Scheme 19), and the transformation was shown to be quite selective for the 1,2-arylation of vinyl aldehydes.[66] More recently, it was demonstrated that it is possible to perform the arylation of aromatic and aliphatic aldehydes in the presence of ketones and 3,4-unsaturated ketones using Rh(II)/NHC complexes as catalysts.[75]

Regarding the mechanism of the aldehyde arylation with boronic acids, Hayashi et al. proposed for the rhodium-catalyzed 1,4-addition of organoboronic acids a mechanism involving the transmetalation of the aryl group from boron to rhodium, followed by addition to the substrate.[78] Mechanistic

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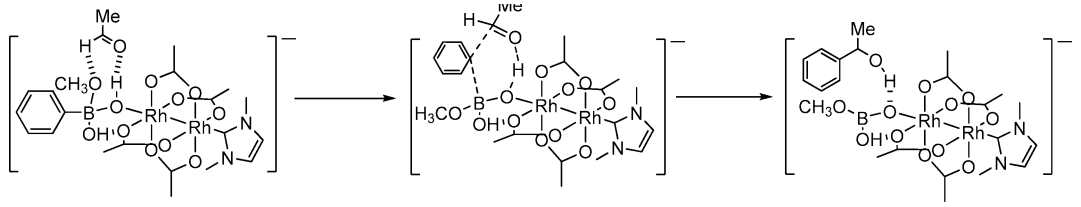
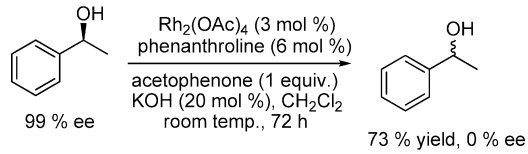
Scheme 20. Mechanistic Proposal for Aldehyde Arylation with Rh(II)/NHC Complexes



studies undertaken at Hartwig's group for 1,2-addition of boronic acids to aldehydes are in good agreement with a proposal by Hayashi et al.[79,80] Gois and co-workers did not find evidence for this type of transmetalation processes; therefore, they proposed an alternative mechanistic pathway by which the activation of the boronic acid occurs via an "ate" complex stabilized by a structured network of hydrogen bonds with the Rh(II)/NHC complex (Scheme 20).

The enantioselective aldehyde arylation using chiral dirhodium dimers (see Scheme 1) and several nonchiral N-heterocyclic carbenes was also attempted without any success.[75] Related to this, the authors reported that under certain reaction conditions, arylmethanols were being racemized by this catalytic system; however, this work was not the first to describe racemization of arylmethanols using dirhodium tetraacetate (and a ligand). In 1996, Williams et al. had described this same transformation, using $Rh_2(OAc)_4$/phenanthroline as the catalytic system in the presence of 1 equiv of acetophenone and 20 mol % of potassium hydroxide (Scheme 21).[81] At the time, no information was provided regarding the

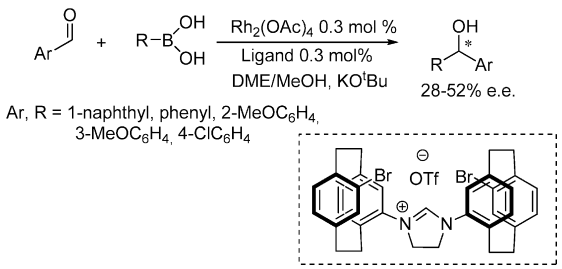
Scheme 21. Racemization of Aryl Methanols with Rh_2OAc_4/Phenanthroline



type of active catalyst in this transformation. However, it is known that diamine ligands such as phenanthroline have the ability to coordinate to dirhodium(II) dimers, opening acetate bridges and destroying the lantern-like structure.[9,34,35]

Later, Ma's group was able to achieve this goal by using chiral NHC ligands and a nonchiral rhodium(II) source.[82] The enantiomeric excesses described in this work reached 52% ee (Scheme 22). The authors do not comment on the mechanism

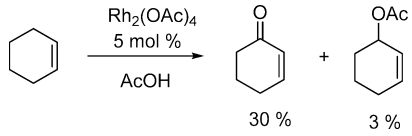
Scheme 22. Chiral Planar [2.2]-Paracylophane-Based Imidazolidiniums Applied in Enantioselective Aldehyde Arylation with Rhodium Tetraacetate (up to 52% ee)



of chiral induction in their catalytic system. There is a possibility that the chiral ligand is too bulky to be accommodated in the axial positions of dirhodium dimers with lanternlike structure. Furthermore, the possibility of disproportion to Rh(I) and Rh(III) or, alternatively, the opening of a bridge ligation cannot be excluded.

3.2. Oxidations. Rhodium(II) tetracarboxylates have been used in the allylic oxidation of cyclohexene since 1982. Uemura and Patil left a mixture of cyclohexene/*tert*-butyl hydroperoxide (TBHP) 1/1 to react in the presence of dirhodium tetraacetate in acetic acid for 3 days, after which the formation of 30% of cyclohexenone and traces of cyclohexenyl acetate (Scheme 23)

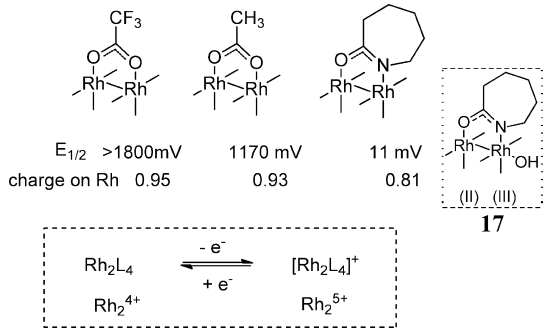
Scheme 23. First Example of Rhodium(II) Catalysis for Allylic Oxidation of Alkenes



was disclosed.[83] Twenty years later, Moody et al. described the application of the same catalyst in the oxidation of allylic and benzylic alcohols to ketones.[84]

More recently, it was observed that dirhodium(II) carboxamidates have a much lower oxidation potential than dirhodium(II) carboxylates.[2,85] The cyclic voltammetry data collected for $Rh_2(cap)_4$ showed a reversible oxidation at 55 mV (in CH_3CN, vs Ag/AgCl) corresponding to the Rh_2^{4+}/Rh_2^{5+} redox couple. Moreover, $Rh_2(cap)_4$ readily engages using a 1-electron oxidation mechanism ($E_{1/2}$ = 11 mV, Scheme 24).

Scheme 24. Half-Wave Potential for Dirhodium Tetrafluoroacetate, Dirhodium Tetraacetate and Dirhodium Tetracaprolactamate[a]



[a]Charges obtained with DFT calculations performed at the B3LYP/631LAN level of theory.[65]

Very differently, $Rh_2(OAc)_4$ displays an $E_{1/2}$ of 1170 mV and for that reason has limited activity in the allylic oxidation of olefins. The decrease in the oxidation potentials accompanies

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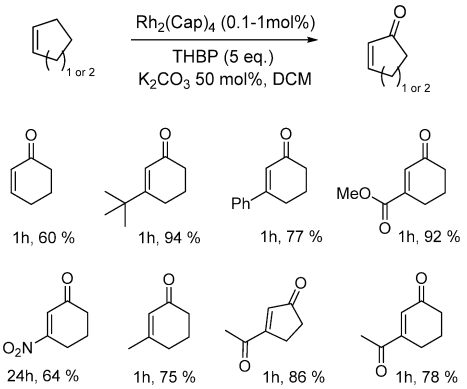
the decrease in the electrophilicity of the rhodium moiety and also a decrease in the rhodium's positive charge.

Not surprisingly, dirhodium tetracaprolactamate was shown to react with TBHP with a color shift from light blue to red, indicative of a mono-oxidation of the complex and formation of a Rh_2^{5+} complex (**17** is the proposed structure).

This family of complexes was shown to catalyze the oxidation of benzylic,[86] propargylic,[87] and allylic positions[85,88,89] and tertiary alkyl amines to imines.[90] For comparison purposes, herein only the work of alkene allylic oxidation, in which the authors show that dirhodium caprolactamate was a very good catalyst for the allylic oxidation of cyclic alkenes at low catalyst loadings of 0.1−1 mol % in the presence of base (potassium carbonate; Scheme 25) will be described. The presence of base

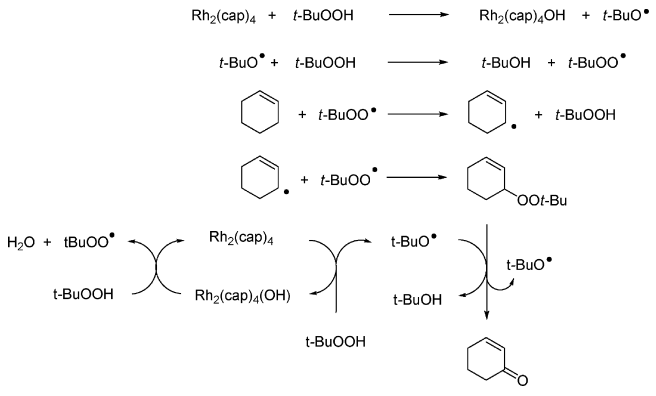
Scheme 25. Substrate Scope of the Oxidation Reaction



was found essential to increase the oxidation efficiency; namely, in the reduction of the allylic peroxides formed to the ketone. Regarding cyclohexene, nothing is described regarding the formation of such peroxides, and the lower yield was attributed to the volatility of the cyclohexenone. This methodology was successfully extended to the allylic oxidation of steroids.[88]

The mechanistic pathway for the $Rh_2(cap)_4$-mediated allylic oxidation is outlined in Scheme 26 using cyclohexene as the

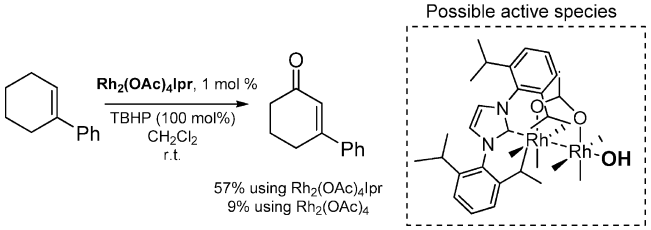
Scheme 26. Proposed Mechanism for Allylic Oxidation with Dirhodium Caprolactamate



model olefinic substrate.[89] Initial oxidation occurs between TBHP and $Rh_2(cap)_4$ to form the oxidized dirhodium(II,III) intermediate and the *tert*-butoxy radical that, in turn, abstracts a hydrogen atom from TBHP at a rate that is much faster than hydrogen atom abstraction from the allylic position of the alkene.[91,92] The *tert*-butylperoxy radical undergoes selective hydrogen atom abstraction from the hydrocarbon substrate, a process that is well documented and universally accepted.[93] Capture of the allyl radical by the *tert*-butylperoxy radical forms the mixed peroxide that is susceptible to *tert*-butoxy radical-catalyzed disproportionation.

In these contributions was clearly demonstrated the effect of bridge ligand electronic properties, which can greatly affect the oxidation potential of rhodium dimers. Meanwhile, we have seen that the coordination of axial N-heterocyclic ligands can also decrease the electrophilicity of the reactive rhodium. Therefore, it was expectable that complexes such as $Rh_2(OAc)_4IPr$ would be catalytically active in these oxidations. In fact, Jang et al. observed that the axial coordination of an IPr onto $Rh_2(OAc)_4$ resulted in a significant change of the electrochemical properties of this complex.[94] The $Rh_2(OAc)_4IPr$ exhibited a quasi-reversible oxidation/reduction wave corresponding to the Rh_2^{4+}/Rh_2^{5+} redox couple with a 120 mV cathodic shift. Under the same conditions, $Rh_2(OAc)_4$ displays an irreversible one-electron oxidation/reduction behavior. On this basis, $Rh_2(OAc)_4IPr$ was shown to be a competent catalyst in the allylic oxidation of double bonds using TBHP, as depicted in Scheme 27.

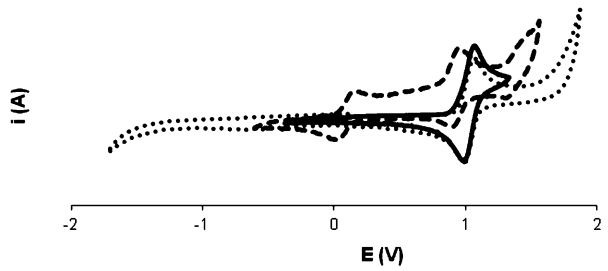
Scheme 27. Allylic Oxidation Catalyzed by $Rh_2(OAc)_4IPr$ Reported by Jang et al.



The authors also studied the effect of phosphine axial coordination.[95] They found that the coordination of triphenylphosphine resulted in an anodic shift (80 mV), and tri-4-methoxyphenylphosphine displayed a cathodic shift of 100 mV. These catalysts where found considerably inferior compared with the complex with IPr, being only sluggishly more effective than $Rh_2(OAc)_4$. This result is in agreement with Gois observations in the arylation of aldehydes.

Gois et al. found that the coordination of a second NHC in the axial position can further drop the first oxidation potential, showing a second reversible oxidation wave (Scheme 28). The

Scheme 28. Cyclic Voltammeters of $Rh_2(OAc)_4SIpr$ (····), $Rh_2(OAc)_4Ipr$ (—) and $Rh_2(OAc)_4Ipr_2$ (----)



works of the Jang and Gois group demonstrate that the axial position can be used to introduce ligands that can alter the oxidation potential of rhodium carboxylates, improving their

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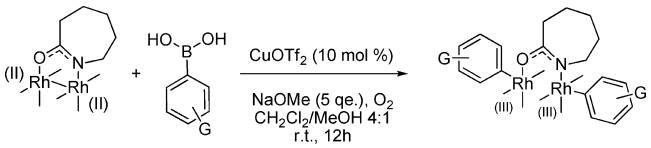
catalytic abilities in oxidation reactions of alkenes. More interestingly, the effect of axial coordination introduces smaller electronic alterations compared with bridge coordination, allowing a fine-tuning of oxidation capabilities.

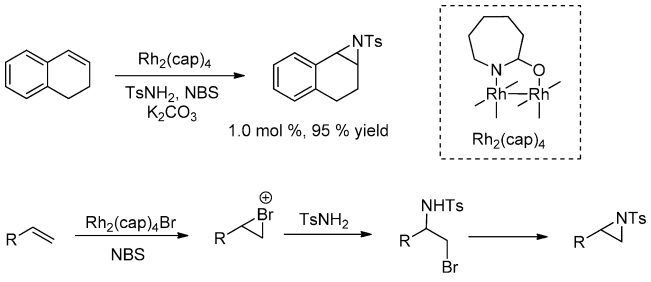
The coordination of halogens was conducted by Doyle's group in dirhodium tetracaprolactamate. The introduction of an axial halogen was done by oxidizing one rhodium center to rhodium(III) with *N*-chloro succinimide rather than by ligand coordination.[86,96] Complete oxidation of both rhodium centers to Rh (III) was achieved by reacting the same complex with sodium tetraphenyl borate in the presence of a copper(I) catalyst and oxygen.[97] The same type of complexes can be obtained using aryl boronic acids instead of sodium tetraphenyl borate. This allows the preparation of dirhodium(III) complexes with aromatic axial ligands with different substituents (Scheme 29).[98,99]

Scheme 29. Oxidation of Dirhodium Tetracaprolactamate



Taking advantage of this knowledge, the authors described a mild, efficient, and selective aziridination protocol of olefins catalyzed by dirhodium(II) caprolactamate [$Rh_2(cap)_4 \cdot 2CH_3CN$]. The use of *p*-toluenesulfonamide ($TsNH_2$), *N*-bromosuccinimide (NBS), and potassium carbonate readily afforded aziridines in isolated yields of up to 95% under considerably mild conditions with as little as 0.01 mol % $Rh_2(cap)_4$ (Scheme 30). Aziridine formation occurs through

Scheme 30. Application of Dirhodium Caprolactamate As an Efficient Catalyst for Alkene Aziridination

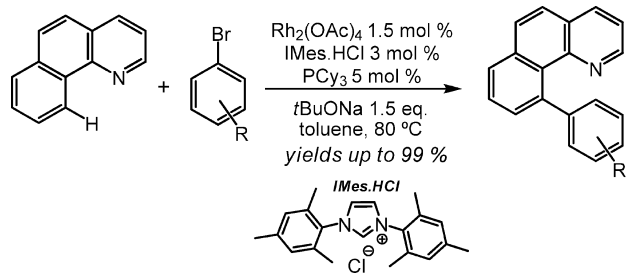


Rh_2^{5+}-catalyzed aminobromination of alkenes and subsequent base-induced ring closure. The Rh_2^{5+} species involved in the catalytic cycle is believed to have one bromide in the axial position, introduced by oxidation of the Rh(II) center.[96]

In this section, it was disclosed how the axial coordination can enhance the catalytic properties of dirhodium(II) carboxylates. In contrast, Doyle has shown that a modification of the oxidation state of dirhodium tetracaprolactamate can allow this catalyst to be used in aziridination reactions.

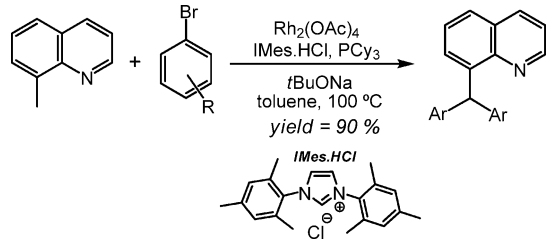
3.3. Direct Activation of C−H Bonds. The direct activation of C−H bonds as an alternative to traditional cross-coupling methodologies has recently become the center of intense research.[100−107] Chang et al. reported another interesting application of NHC−dirhodium(II) complexes. They were successfully used in the direct intermolecular arylation of sp^2 and sp^3 C−H bonds via a chelation-assisted approach, as shown in Scheme 31. This methodology uses an in situ approach using rhodium tetraacetate and IMes·HCl as catalyst precursors.[108]

Scheme 31. Direct Intermolecular Arylation of sp^2 and sp^3 C−H Bonds via a Chelation Assisted Approach Reported by Chang et al.



During the catalytic system optimization, the authors pointed out several results that are very interesting. For instance, the substitution of IMes by IPr leads to no catalysis. Furthermore, with the addition of tricyclohexylphosphine, the catalytic system was considerably more efficient; however, in the absence of IMes, the phosphine alone cannot trigger any catalysis. Even more interesting, when $Rh_2(OAc)_4$/IMes·HCl was substituted with pregenerated $Rh_2(OAc)_4$IMes, the reaction became less efficient. The most striking example of this work, due to its inherent difficulty, is the possibility to activate a benzylic sp^3 C−H bond. Although it requires 100 °C, the activation is very successful, reaching 90% yield (Scheme 32). This methodology uses milder experimental conditions as

Scheme 32. Benzylic C−H Bond Activation for Benzylation



compared with other catalytic systems with Pd, Fe, Ni, and Ru.[100−105]

The authors proposed that in the beginning of the reaction, a precatalyst, **I**, consisting of two distinct axial ligands, IMes and PCy_3, was formed. The coordination of substrate in the axial position (**III**) occurs after decoordination of the phosphine from the precatalyst. Subsequently, a proton abstraction by the action of sodium *tert*-butoxide takes place, affording a five-membered metallacycle intermediate, **IV**, upon release of one molecule of anionic acetate ligand.

This means that one acetate bridge is broken down during the catalytic cycle. Oxidative addition of bromobenzene in the Rh(II) center generates a chelated cationic rhodium species, **V**, which upon reductive elimination and reassociation of one acetate ligand generates the arylated product and the catalyst [(NHC)$Rh_2(OAc)_4$] **II** (Scheme 33). The authors considered that the role of added phosphine could be to stabilize catalytically active species.

Recently, this methodology was extended to regioselective arylation of the 8-position of quinolines, thus reinforcing the

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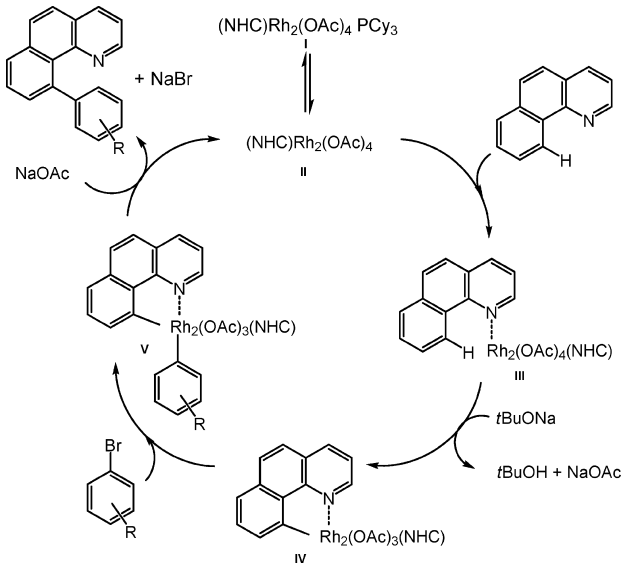
Scheme 33. Mechanism Proposal for the Direct Intermolecular Arylation of sp^2 and sp^3 C−H Bonds via a Chelation-Assisted Approach



proposed pathway. For quinolines, the most efficient protocol requires the utilization of a double amount of catalyst (in the absence of phosphine) as compared with benzo[*h*]quinolines (Scheme 34). Because of geometry constraints, a distinct activation of quinoline's 8-position was suggested.[109]

4. CONCLUSION

Over 40 years, researchers have used bridge ligands to tune the catalytic properties of dirhodium(II) dimers. However, in the last 10 years, several strategies have appeared in the literature that allow one to tune the properties of the rhodium(II) centers by coordination of axial ligands. So far, the coordination of phosphines, phosphites, *N*-heterocyclic carbenes in the axial positions, and exchange of rhodium by bismuth (in the dimers) have been the unique strategies to decrease the electrophilicity of dirhodium dimers and tune their reactivity. As an alternative, the change of oxidation state allows increasing such electrophilicity. On the basis of these strategies, alterations of selectivity in diazo decomposition reactions and allylic oxidations and disclosed new reactivities for rhodium(II) chemistry (C−H functionalization, aziridinations and arylation of aldehydes) were observed. An important part of this critical review relies in the rationalization of the works herein described, on the basis of the mechanistic insights provided. The aim of this review is to provide an overview of this emerging field of research and further boost its development.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Fundação para a Ciência e Tecnologia and FEDER (PTDC/QUI-QUI/099389/2008; SFRH/BPD/73932/2010) are thanked for their financial support.

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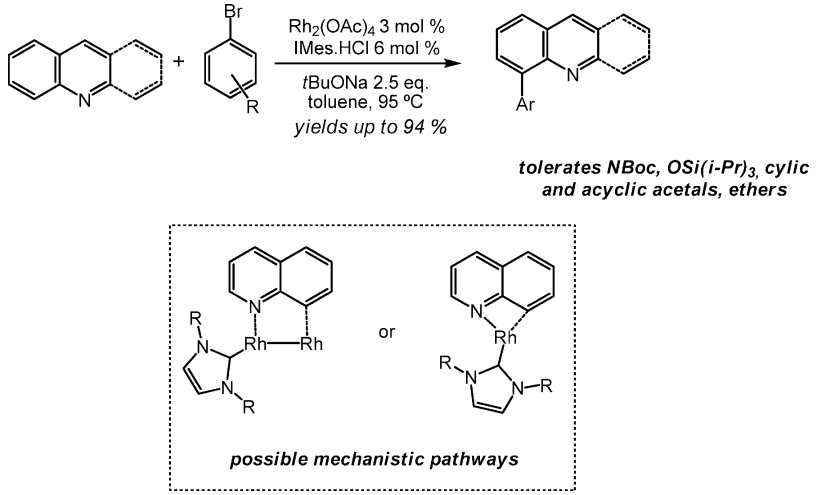
Scheme 34. Arylation of 8-Position of Quinolines



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