Chiral Dirhodium Catalysts: A New Era for Asymmetric Catalysis

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Abstract: The catalysis by dirhodium paddlewheel complexes has been an area of immense interest and extensive study over the past three decades - not only because most of the catalysts are highly stable to heat, moisture and ambient atmosphere but also for the asymmetric induction in the ylide generation. In this review, we attempt to provide an overview on the general preparation method for most homogeneous chiral dirhodium(II) catalysts that have appeared to date and their recent applications in asymmetric catalysis with iodonium ylides as carbenoid precursors.

Keywords: Dirhodium catalysts, Asymmetric catalysis, Stereoselrctive reactions, Enantioselectivity, Homogenous catalysts, Chiral catalysts.

1. INTRODUCTION

Driven by the demands of the pharmaceutical industry and other applications such as agricultural chemicals, flavors, fragrances, and materials, the need for chiral compounds, often as single enantiomers, has recently increased greatly. Historically, enantiomerically enriched compounds were produced either by chemical transformation of an enantiomerically enriched precursor - derived directly or indirectly from nature's chiral pool - or by an equimolar combination of the two enantiomers. Nevertheless, these approaches have harsh shortcomings: while the former requires stoichiometric quantities of a suitable precursor, the latter yields only up to 50% of the desired enantiomer [1]. Asymmetric catalysis, which consists of metal complexes with chiral ligands, has vital possible merits over these older procedures since a single molecule of the chiral catalyst can return many equivalents of molecules of the chiral product for ending catalyst molecule. Making an effective transition metal catalyst is a challenging process involving interdisciplinary research that merges organic, inorganic, organometallic and biomimetic chemistry, as it requires designing and synthesizing chiral ligands; preparing appropriate substrates, catalyst precursors, and metal-ligand complexes; and searching for ideal reaction conditions. A number of approaches, varying from combinatorial synthesis of modular systems to balanced design of structurally novel ligand frameworks can, therefore, be tackled so as to develop new and efficient chiral ligands with due consideration of steric, electronic, and conformational properties.

The scope of asymmetric catalysis has grown to encompass a wide range of other reactions due to the increasing availability and reproduction of methodologies for producing enantiomerically enriched organic compounds [2]. Ideally, a practical asymmetric catalyst is inexpensive and readily available in both enantipure forms whilst providing high yields and enantioselectivities for a broad range of substrates in different reactions. A large number of complexes have been synthesized and many of these complexes have been studied and used in catalysis [3-18]. The catalysis by dirhodium paddlewheel complexes has been an area of immense interest and extensive study over the past three decades - not only because most of the catalysts are highly stable to heat, moisture and ambient atmosphere but also for the asymmetric induction in the ylide generation [3-19].

The development of dirhodium paddlewheel catalysts has been primarily concerned with the modification of the electronic and/or steric properties of the ligands [20]. The ease with which simple modification of the bridging groups on the catalyst brings about dramatic reactivity changes makes these dirhodium complexes desired compared to mononuclear copper or palladium counterparts.

The design of a catalytic system that leads to high enantioselectivity has become a challenging goal in chemical synthesis. This review attempts to provide an overview on the general preparation method for most homogeneous chiral dirhodium(II) catalysts that have appeared to date and their recent applications in asymmetric catalysis with iodonium ylides as carbenoid precursors. The dement rationale for the enantioinduction with these chiral dirhodium(II) catalysts is reported within this review.

2. CHIRAL DIRHODIUM CATALYSTS

2.1. Preparations and Characterization

2.1.1. Dirhodium Carboxylate Complexes

Dirhodium tetracarboxylate complexes (such as dirhodium(II)tetraformate monohydrate, $[Rh_2(O_2CH)_4(H_2O)]$ were first discoverd by Chernyaev *et al.* [21] in 1960 when they heated rhodium(III) chloride under reflux in neat formic acid. Consequently, the design and synthesis of chiral carboxylic acids, which serve as the ligands of the catalysts, led to the development of new chiral rhodium(II) carboxylate complexes. From these findings, Schchelokov *et al.* [22,23] in 1981 used (*S*)-mandelic acid, RCO_2H (R = (*S*)-CH(OH)Ph), as a chiral carboxylic acid to prepare the dirhodium tetrakis-(*S*)-mandalate complex **1**, $Rh_2(O_2CR)_4$ and their adducts (Fig. **1**). The catalyst was prepared by the reaction of the dirhodium carbonate complex $Na_4Rh_2(CO_3)_4.2.5H_2O$ with (*S*)-mandelic acid in water under refluxed for 1 hour. In 1986, Pruchnik and co-workers prepared the *R* enantiomer of this catalyst either by following the same procedure for the preparation of *S* enantiomer or by the reaction of $RhCl_3.3H_2O$, (*R*)-mandelic acid, and sodium ethoxide in EtOH at reflux temperature under argon for 1 hour [24].

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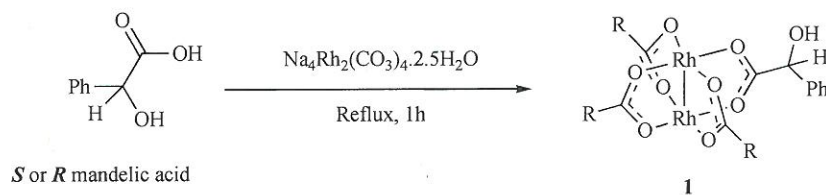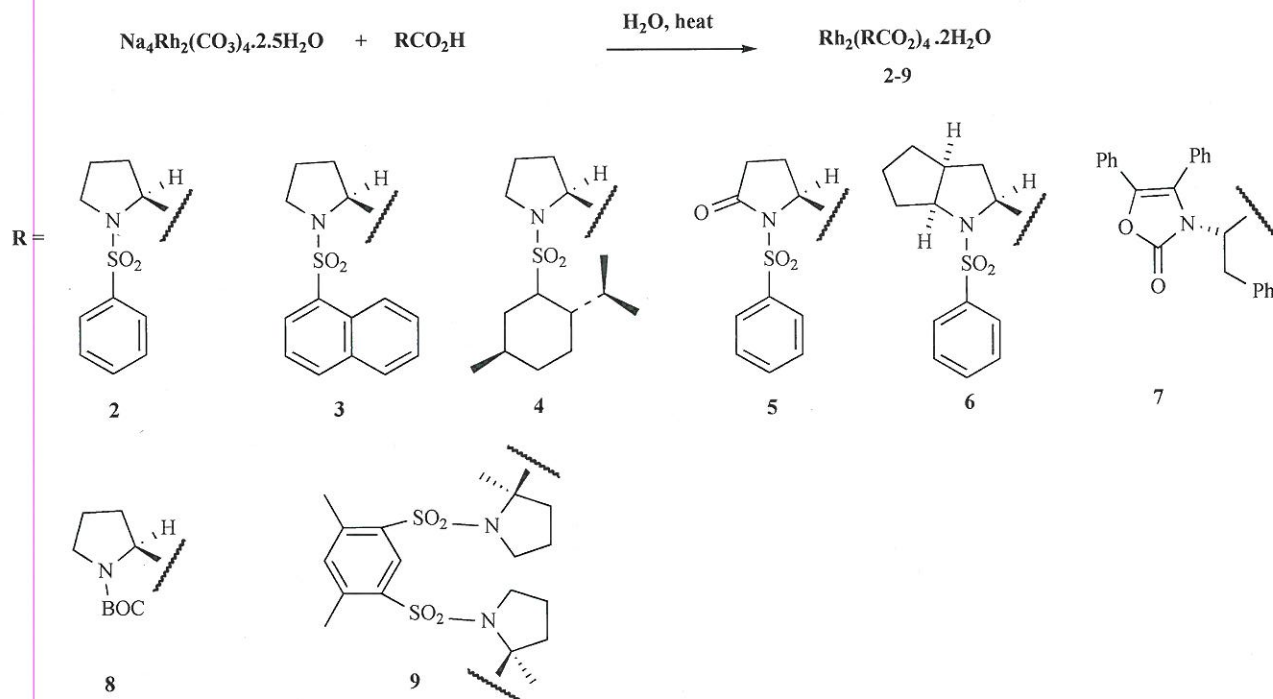
Fig. (1). Synthesis of dirhodium complex **1**.

$$Na_4Rh_2(CO_3)_4 \cdot 2.5H_2O \quad + \quad RCO_2H \xrightarrow{\quad H_2O, \text{ heat} \quad} Rh_2(RCO_2)_4 \cdot 2H_2O$$
$$\text{2-9}$$

R =

2   **3**   **4**   **5**   **6**   **7**

8   **9**

Fig. (2). Synthesis of dirhodium complexes **2-9** derived from L-Proline.

Pruchnik and co-workers have further reported, in the same context, the preparation of the dihalobis(1,1-*O*-phenanthroline)-*μ*-bis((*S*)-mandelato)dirhodium(II)-tetrahydrate, $Rh_2(O_2CR)_2(1,1\text{-}O\text{-phen})_2 X_2$ (X = Cl, Br, I), and dihalobis(2,2'-dipyridyl)-*μ*-bis((*S*)-mandelato)dirhodium(II)-tetrahydrate, $Rh_2(O_2CR)_2(2,2'\text{-dipyridyl})_2 X_2$ (X = Cl, Br, I), from the reaction of **1** with either phenanthroline or 2,2'-bipyridyl, respectively, in presence of NaX in EtOH under N_2 at reflux for 2 hours. The produced catalysts have been characterized by using infrared and electronic spectral analysis. Yet, the catalytic activity of these complexes has not been studied.

In 1986, as well, not only did Cotton *et al.* [25] prepare [Rh_2{(*S*)-mandelate}_4(EtOH)_2] using another method via the reaction of $RhCl_3 \cdot 3H_2O$ and (*S*)-mandelic acid in water/dimethylformamide at 80 °C for 6 hours, but also, he repared [Rh_2{(*R*)-*α*-methoxy-*α*-phenylacetate}_4·(THF)_2] via the reaction of $RhCl_3 \cdot 3H_2O$ and (*R*)-*α*-methoxy-*α*-phenylacetic acid in water/EtOH at refluxed temperature for 1 hour. The structures of the two catalysts were determined by X-ray crystallography which illustrated that either two ethanol or THF molecules are bonded to the rhodium cental axial positions and prevents the complex from making intermolecular interactions as observed for [Mo_2{(*R*)-mand}_4.2THF] [26]. The case of the (*S*)-manadelate catalyst, each (*S*)-manadelate ligand has internal hydrogen-bonds between the hydroxyl on C_α group and one of the coordinated carboxyl oxygen atoms. There is no observed internal hydrogen bonding in case of the second catalyst in which a methoxy group is used instead of a hydroxyl group.

There are different categories of dirhodium carboxylate depending on the type of ligand. The main classes of these are detailed below.

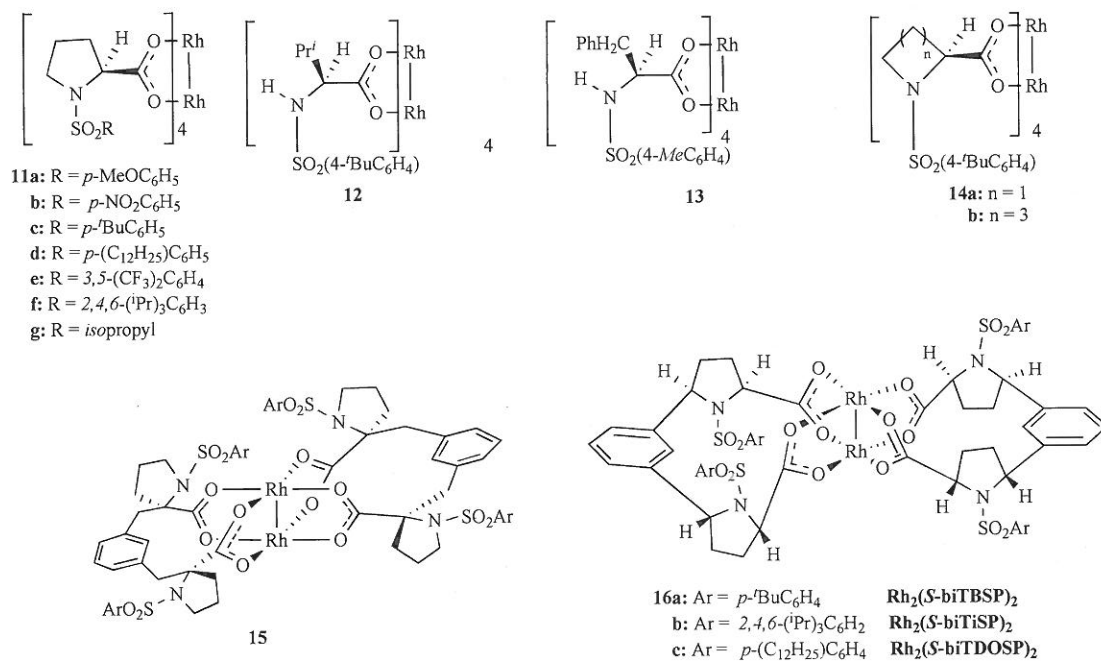### 2.1.1.1. L-Proline Derived Dirhodium Complexes

M. A. McKervey *et al.* [27-30] reported the preparation of a new chiral dirhodium carboxylate complexes derived from L-proline (**2-9**). The catalysts were prepared by ligand exchange in which the sodium salts of rhodium carbonates were exchanged with the appropriate *N*-substituted-sulphonyl-L-prolinate ligand (Fig. **2**) [30].

The catalysts was found to have a good levels of enantioselectivity in intramolecular C-H insertion reactions of *α*-diazocarbonyl compounds (**8**) as shown in Fig. (**3**) [30].

After that, Davies *et al.* [31] reported the preparation of a series of catalysts via high temperature ligand exchange between rhodium(II) acetate and a chiral carboxylic acid [32] mainly derived from prolinate derivatives (**11a-g**, **15** and **16**), acyclic derivatives (**12** and **13**), the azetidinecarboxylate (**14a**), and the picolinate (**14b**) as shown in Fig. (**4**).

The catalytic activity of such complexes have been examined for the intermolecular cyclopropanation reaction of vinyl diazoacetate **17** and styrene **18**, giving a very high *ee* up to 98% in dichloromethane as shown in Table **1** [33,34].

Furthermore, Berilsson and Anderson prepared a rigid dirhodium carboxylate complex (Fig. **5**) derived from (1*S*,3*R*,4*R*)-2-(*p-tert*-butylphenylsulphonyl)-2-aza-bicyclo[2.2.1]heptane-3-carboxy-

Rh$_2$L$_4$	%9	%10
2	97	3
3	96	4
4	96	4
5	82	18
6	97	3
7	90	10
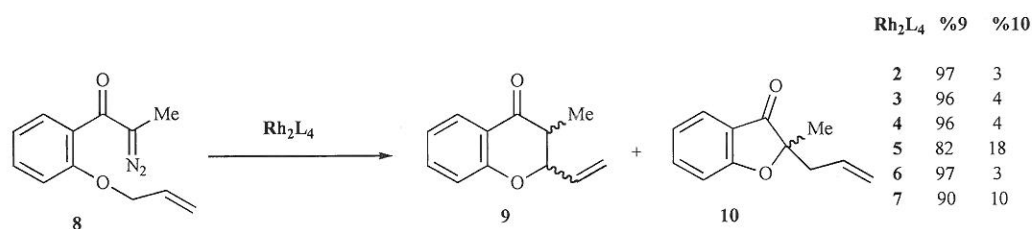
Fig. (3). Intramolecular C-H insertion reactions of α-diazocarbonyl compounds **8** with catalysts **2-7**.

11a: R = p-MeOC$_6$H$_5$
b: R = p-NO$_2$C$_6$H$_5$
c: R = p-^{t}BuC$_6$H$_5$
d: R = p-(C$_{12}$H$_{25}$)C$_6$H$_5$
e: R = $3,5$-(CF$_3$)$_2$C$_6$H$_4$
f: R = $2,4,6$-(^{i}Pr)$_3$C$_6$H$_3$
g: R = isopropyl

12

13

14a: n = 1
b: n = 3

15

16a: Ar = p-^{t}BuC$_6$H$_4$ **Rh$_2$(S-biTBSP)$_2$**
b: Ar = $2,4,6$-(^{i}Pr)$_3$C$_6$H$_2$ **Rh$_2$(S-biTiSP)$_2$**
c: Ar = p-(C$_{12}$H$_{25}$)C$_6$H$_4$ **Rh$_2$(S-biTDOSP)$_2$**

Fig. (4). Structure of Davies complexes **11-16**.

Table 1. Intermolecular Cyclopropanation Reaction of Vinyl Diazoacetate 17 and Styrene 18
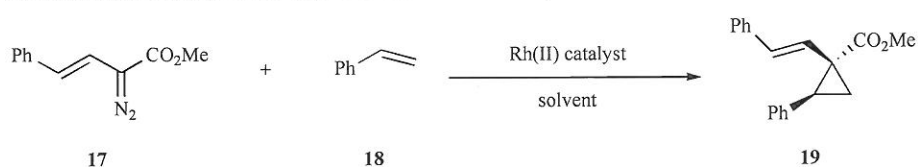
Solvent	Temerature °C	% *ee* of the product		
		11d	**15**	**16b**
n-Hexane	25	90 (R,R)	56 (S,S)	74 (S,S)
CH$_2$Cl$_2$	25	74 (R,R)	59 (S,S)	90 (S,S)
CH$_2$Cl$_2$	-50	88 (R,R)	83 (S,S)	98 (S,S)

lic acid using the ligand exchange method [35] with Rh$_2$(OAc)$_4$ in chlorobenzene as a solvent. The catalysts were fully characterized by NMR, Mass spectrometery, and CHNS analysis. The complex activity has been examined for asymmetric cyclopropanation of alkenes with vinyl and phenyl-diazoester giving a high enantioselectivities up to 92% [36].

In 2001, Hodgson *et al.* [7] reported the preparation of two analogues of the McKervey and Betrilsson catalysts by applying the Callot method [35]. Again, the catalysts were fully characterized by NMR, Mass spectrometery, and CHNS analysis. It has been reported that these catalysts achieve moderate enantioselectivities in the cycloaddition reaction of 2-diazo-3,6-diketoester **23** (Fig. **6**).

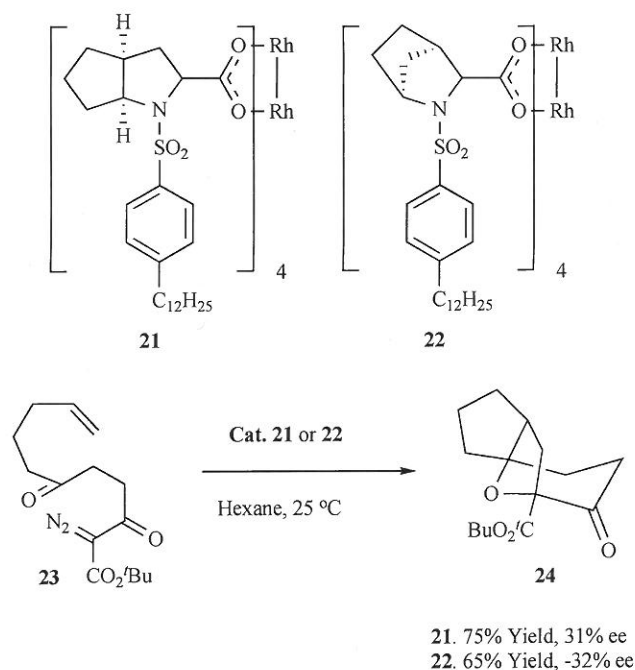**20**
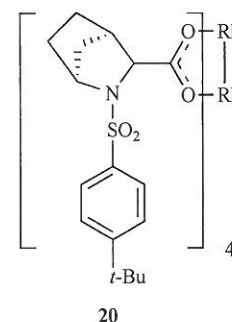
Fig. (5). Structure of complex **20**.

reactive chiral face and an unreactive achiral face for Rh(II) catalysts with proline-derived ligands such as $Rh_2(DOSP)_4$ **11d** and $Rh_2(TBSP)_4$ **11c**, along with the new Rh(II)-HYP catalysts. The catalysts gave good yields of up to 78% and up to 90% *ee* in intermolecular C-H insertion and cyclopropanation reactions of methyl phenyldiazoacetate with either admantane **29** or styrene **18**, respectively (Fig. **7**).

2.1.1.2. Phthalimide Derived Dirhodium Carboxylate Complexes

Hashimoto and Ikegami group [19-24] have developed a new family of homochiral rhodium(II) carboxylate complexes (**32-34**) that are derived from enantiomerically pure *N*-protected amino acids by the reaction of the corresponding ligands with $Rh_2(OAc)_4$ according to Callot method (Fig. **8**) [35]. Combustion analysis, ^{1}H-NMR and X-ray crystal structure were used in catalysts characterization [38,39].

The catalysts **33** and **34** have been trialed in the asymmetric oxonium ylide-[2,3]sigmatropic rearrangement with the diazocarbonyl compound **35** and dimethyl acetylene dicarboxylate (DMAD) using $CF_3C_6H_5$ as a solvent and have been found to have moderate *ee* as shown in Fig. (**9**) [40].

M. A. McKervey *et al.* [40] synthesized the new chiral dirhodium(II) carboxylate complex **38**, which has phthlidomide nucleus, from $Rh_2(OAc)_4$ by an exchange reaction with the appropriate ligand according to Callot method (Fig. **10**) [35]. The catalytic activity of **38** was tested for enantioselective intramolecular C-H insertion of α–diazo-β-keto esters and it offered the corresponding optically active cyclopropane derivatives in up to 46% *ee* [41].

21　　**22**

Cat. 21 or 22

Hexane, 25 °C

23　$CO_2{}^tBu$　→　**24**

21. 75% Yield, 31% ee
22. 65% Yield, -32% ee

Fig. (6). Cycloaddition reaction of 2-diazo-3,6-diketoester **23**.

In the work of Bonge *et al.* [37], a three new chiral Rh(II) catalysts with 4-hydroxyproline-derived ligands were synthesized by using the high temperature ligand exchange method [32] with $Rh_2(OAc)_4$ (Fig. **7**). The characterization of such catalysts pinpointed that Rh(II) catalysts exist in an all-up conformation with a

Trans　　　　***Cis***

1 R = $C_{12}H_{25}$　　　**2** R = $C_{12}H_{25}$
　　　　　　　　　　　3 R = Cyclohexyl

29

25: 56 (92% *ee*)
26: 65 (90% *ee*)
27: 67 (93% *ee*)

30

Ph CO_2Me
N_2
28

Cat. 25-27
i-hexane, r.t., 1h

18

25: 76 (84% *ee*)
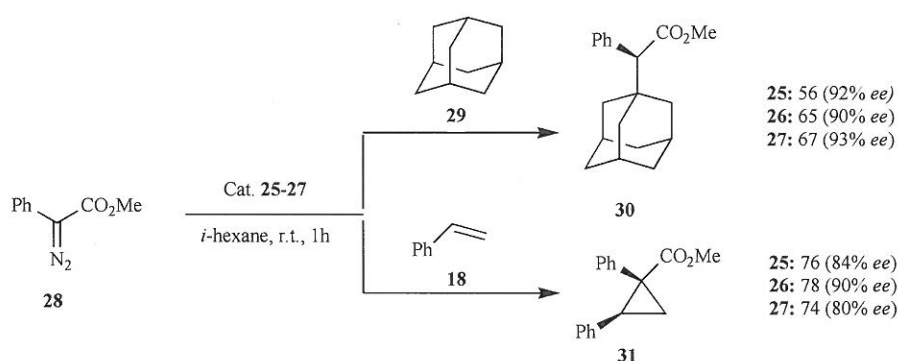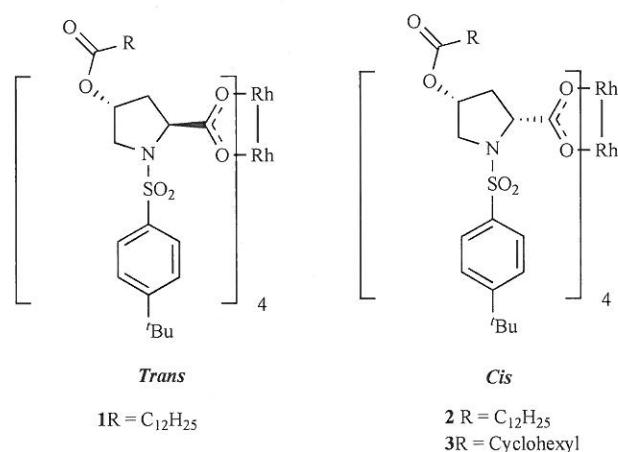**26**: 78 (90% *ee*)
27: 74 (80% *ee*)

31

Fig. (7). Intermolecular C-H insertion and cyclopropanation reactions of methyl phenyldiazoacetate with either admantane **29** or styrene **18**.

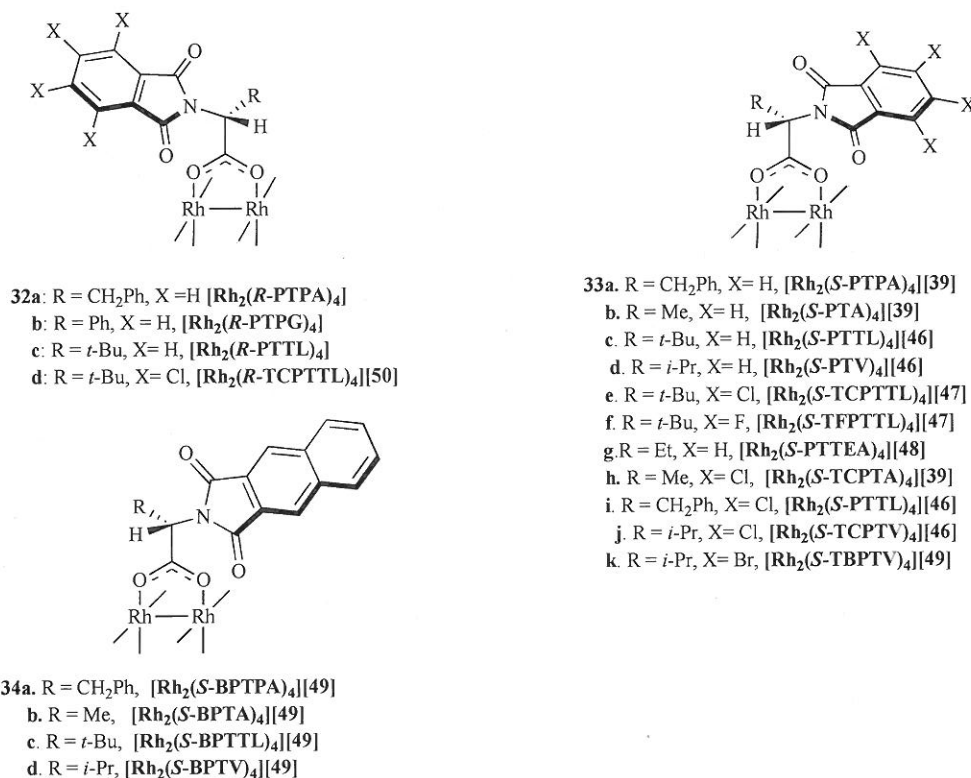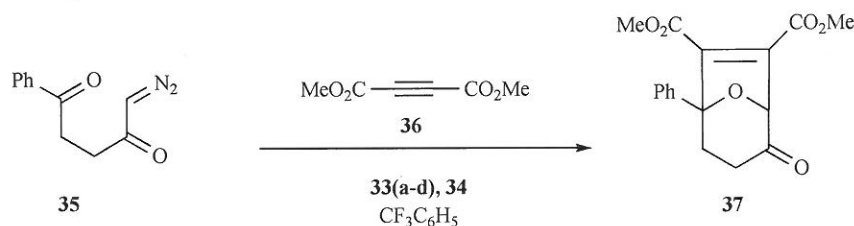**32a**: R = CH₂Ph, X =H [**Rh₂(*R*-PTPA)₄**]
b: R = Ph, X = H, [**Rh₂(*R*-PTPG)₄**]
c: R = *t*-Bu, X= H, [**Rh₂(*R*-PTTL)₄**]
d: R = *t*-Bu, X= Cl, [**Rh₂(*R*-TCPTTL)₄**][50]

33a. R = CH₂Ph, X= H, [**Rh₂(*S*-PTPA)₄**][39]
b. R = Me, X= H, [**Rh₂(*S*-PTA)₄**][39]
c. R = *t*-Bu, X= H, [**Rh₂(*S*-PTTL)₄**][46]
d. R = *i*-Pr, X= H, [**Rh₂(*S*-PTV)₄**][46]
e. R = *t*-Bu, X= Cl, [**Rh₂(*S*-TCPTTL)₄**][47]
f. R = *t*-Bu, X= F, [**Rh₂(*S*-TFPTTL)₄**][47]
g.R = Et, X= H, [**Rh₂(*S*-PTTEA)₄**][48]
h. R = Me, X= Cl, [**Rh₂(*S*-TCPTA)₄**][39]
i. R = CH₂Ph, X= Cl, [**Rh₂(*S*-PTTL)₄**][46]
j. R = *i*-Pr, X= Cl, [**Rh₂(*S*-TCPTV)₄**][46]
k. R = *i*-Pr, X= Br, [**Rh₂(*S*-TBPTV)₄**][49]

34a. R = CH₂Ph, [**Rh₂(*S*-BPTPA)₄**][49]
b. R = Me, [**Rh₂(*S*-BPTA)₄**][49]
c. R = *t*-Bu, [**Rh₂(*S*-BPTTL)₄**][49]
d. R = *i*-Pr, [**Rh₂(*S*-BPTV)₄**][49]

Fig. (8). Structure of Hashimoto complexes **32-34**.

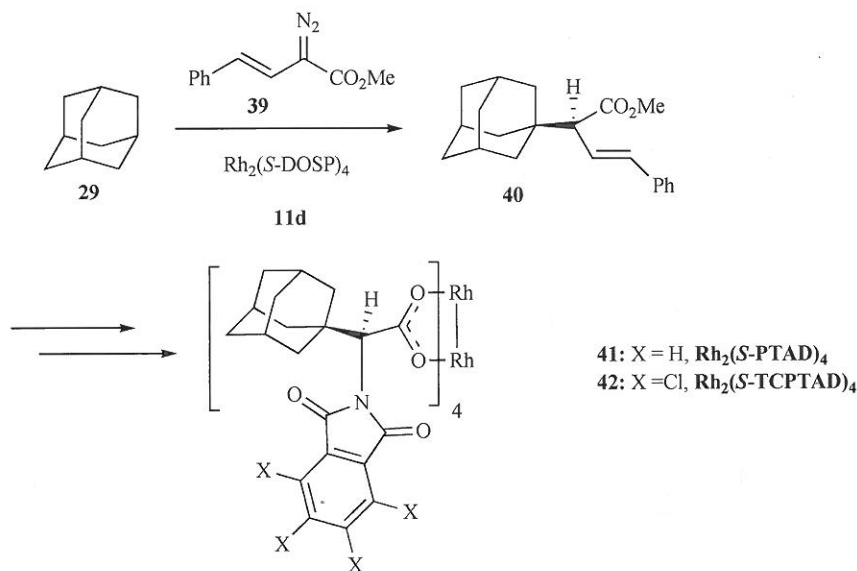| entry	Rh(II) Catalyst	Yield %	*ee* %
1	[Rh₂(*S*-PTPA)₄]	81	60
2	[Rh₂(*S*-PTA)₄]	79	61
3	[Rh₂(*S*-PTV)₄]	79	59
4	[Rh₂(*S*-PTTL)₄]	80	69
5	[Rh₂(*S*-BPTPA)₄]	81	82
6	[Rh₂(*S*-BPTA)₄]	79	83
7	[Rh₂(*S*-BPTV)₄]	79	90
8	[Rh₂(*S*-BPTTL)₄]	83	65

Fig. (9). Enantioselective intermolecular 1,3-dipolar cycloaddition reaction of α-diazoketone **35** with DMAD **36** catalyzed by Rh(II) complexes **33a-d** and **34**.

38
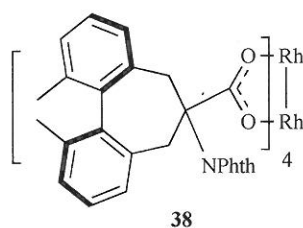
Fig. (10). Structure of complex **38**.

Davies *et al.* [41] synthesized the new dirhodium tetracarboxylate complex **41** and **42** derived from *N*-phthaloyl admanylglycine which is considered as an effective chiral catalyst for both inter and intramolecular C-H amination reactions. The complexes have been prepared by the catalytic reaction of admantyl with diazoester compound in the presence of Rh₂(*S*-DOSP)₄ **11d** followed by a series of steps to obtain the desired complexes (Scheme **1**).

These catalysts also have been tested under Che-Du Bois conditions in which the nitrine precursors are generated *in situ* (Fig. **11**).

Scheme 1.

41: X = H, **Rh₂(S-PTAD)₄**
42: X =Cl, **Rh₂(S-TCPTAD)₄**

95% Yield, 94% *ee*

72% Yield, 88% *ee*
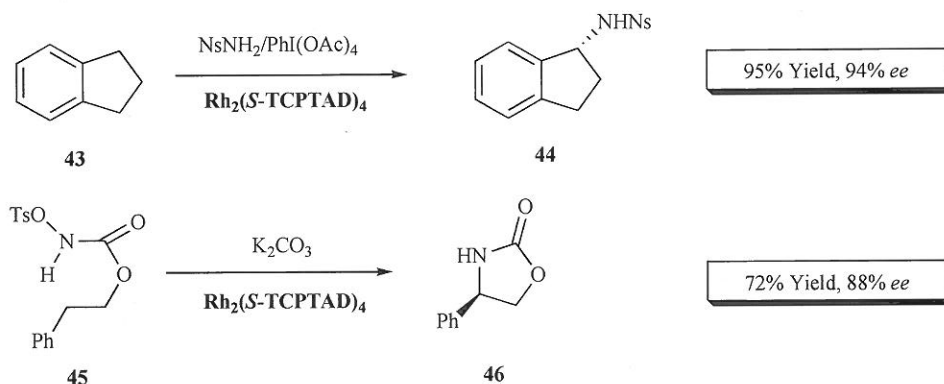
Fig. (11). Rh₂(S-TCPTAD)₄-Catalyzed Intermolecular C-H Amination.

2.1.1.3. Naphthalodimide Derived Dirhodium Carboxylate Complexes

McKervey and coworkers [27,29,30] have presented the synthesis of a series of new chiral dirhodium carboxylate complexes **47** and **48** that are derivatives from either substituted or unsubstituted (*S*)-*N*-naphtholyl amino acids by refluxing Rh₂(OAc)₄ with the corresponding ligand in chlorobenzene for 24 hours. The catalysts have been used for the one-pot asymmetric cyclopropanation of olefins with CH acidic reagents through intermediate phenyliodonium ylides to afford cyclopropane derivatives in up to 98% *ee*, especially for the catalyst [Rh₂(*S*-4-Br-NTTL)₄], **48d** (Fig. **12**) [42].

In 1992, McKervey *et al.* [29,40] prepared a series of homochiral Rh(II) acetate complexes by using the reaction of Rh(II) carbonate (Na₄Rh₂(CO₃)₄) with the corresponding carboxylic acids (**52-60**) (Scheme **2**) to give the corresponding product in a good yield.

Hashimoto and Ikegami group [38,39] developed a new family of homochiral rhodium(II) carboxylate complexes (**61** and **62**) by the reaction of the corresponding ligands with Rh₂(OAc)₄ according to Callot method (Fig. **13**) [35]. The combustion analysis and X-ray crystal structure was used to characterize the catalysts.

In 1996, Moody *et al.* [43,44] reported the synthesis of various chiral dirhodium carboxylate complexes (**63-67**) derived from phthalate half esters and 1-substituted pyrroles (Fig. **14**). The cata-

lysts have been examined for the asymmetric Si-H insertion reaction of methyl diazophenylacetate with dimethylphenylsilane that gave a highest level of enantiocontrol approaching 50%.

Abduhijleh *et al.* [45] synthesized the dirhodium(II) tetra(μ-valproate) complex Rh₂(valp)₄ **68**, and its bis-adducts with theophylline, Rh₂(valp)₄(ThH)₂ **71**, or caffeine, Rh₂(valp)₄(Caf)₂ **72**, which have been synthesized and characterized by elemental analysis, IR, UV-Vis, magnetic moment, ¹H and ¹³C NMR spectroscopic techniques (Scheme **3**). Spectral data for the complexes are consistent with a dinuclear structure as found for rhodium(II) tetracarboxylate adducts. Theophylline and caffeine bases in complexes **71** and **72**, respectively, have been found to be axially coordinated to rhodium(II) atoms through the sterically hindered N-9 site. This was confirmed by X-ray crystal structure analyses of such complexes. The catalytic activity of these complexes has not yet been studied.

2.1.2. Dirhodium Carboxamidate Complexes

Chiral dirhodium(II) catalysts derived from enantiomerically pure α-carboxamidates ligands were initially developed by Doyle and co-workers [7,32-41,46-50]. Later on, the range of complexes has been expanded to include a greater diversity of a variety of ligands (**73-83**) (i.e., Pyrrolidinone, oxazolidinones, imidiazolidinone, and azetidinone) and ligand substituents. The general method
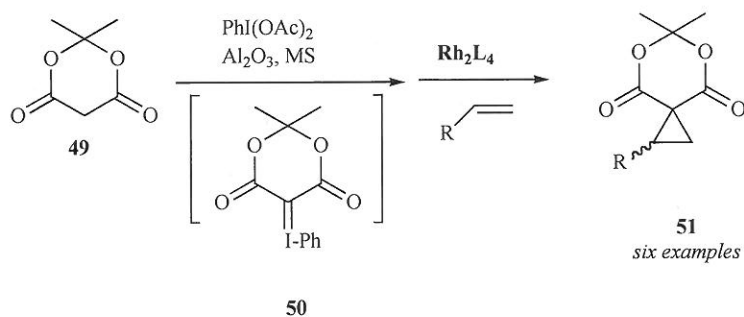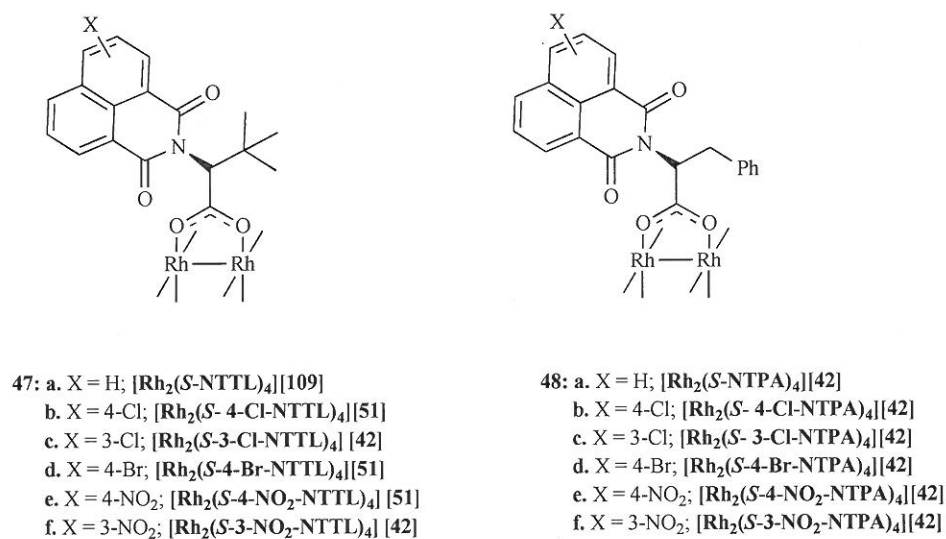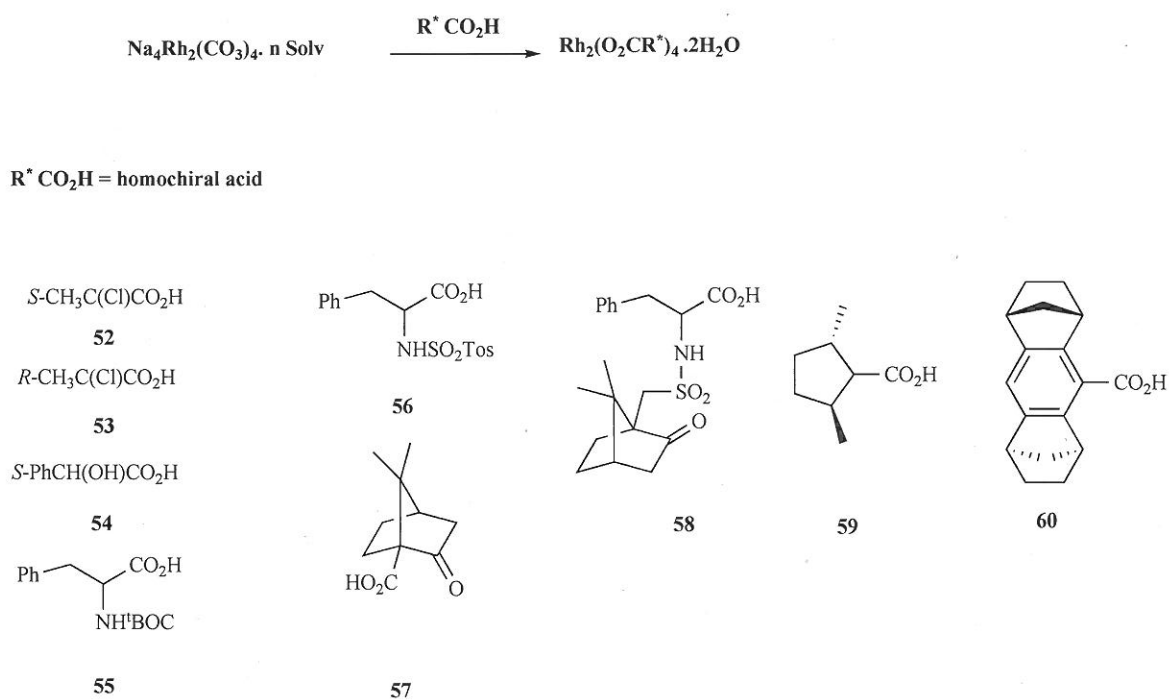
47: a. X = H; [**Rh₂(*S*-NTTL)₄**][109]
   b. X = 4-Cl; [**Rh₂(*S*- 4-Cl-NTTL)₄**][51]
   c. X = 3-Cl; [**Rh₂(*S*-3-Cl-NTTL)₄**] [42]
   d. X = 4-Br; [**Rh₂(*S*-4-Br-NTTL)₄**][51]
   e. X = 4-NO₂; [**Rh₂(*S*-4-NO₂-NTTL)₄**] [51]
   f. X = 3-NO₂; [**Rh₂(*S*-3-NO₂-NTTL)₄**] [42]

48: a. X = H; [**Rh₂(*S*-NTPA)₄**][42]
   b. X = 4-Cl; [**Rh₂(*S*- 4-Cl-NTPA)₄**][42]
   c. X = 3-Cl; [**Rh₂(*S*- 3-Cl-NTPA)₄**][42]
   d. X = 4-Br; [**Rh₂(*S*-4-Br-NTPA)₄**][42]
   e. X = 4-NO₂; [**Rh₂(*S*-4-NO₂-NTPA)₄**][42]
   f. X = 3-NO₂; [**Rh₂(*S*-3-NO₂-NTPA)₄**][42]

Fig. (12). Cyclopropanation reaction of **49** catalyzed by complexes **47** and **48**.

R*CO₂H = homochiral acid

Scheme 2.

47: a. X = H; **[Rh₂(*S*-NTTL)₄][109]**
   b. X = 4-Cl; **[Rh₂(*S*- 4-Cl-NTTL)₄][51]**
   c. X = 3-Cl; **[Rh₂(*S*-3-Cl-NTTL)₄][42]**
   d. X = 4-Br; **[Rh₂(*S*-4-Br-NTTL)₄][51]**
   e. X = 4-NO₂; **[Rh₂(*S*-4-NO₂-NTTL)₄][51]**
   f. X = 3-NO₂; **[Rh₂(*S*-3-NO₂-NTTL)₄][42]**

48: a. X = H; **[Rh₂(*S*-NTPA)₄][42]**
   b. X = 4-Cl; **[Rh₂(*S*- 4-Cl-NTPA)₄][42]**
   c. X = 3-Cl; **[Rh₂(*S*- 3-Cl-NTPA)₄][42]**
   d. X = 4-Br; **[Rh₂(*S*-4-Br-NTPA)₄][42]**
   e. X = 4-NO₂; **[Rh₂(*S*-4-NO₂-NTPA)₄][42]**
   f. X = 3-NO₂; **[Rh₂(*S*-3-NO₂-NTPA)₄][42]**
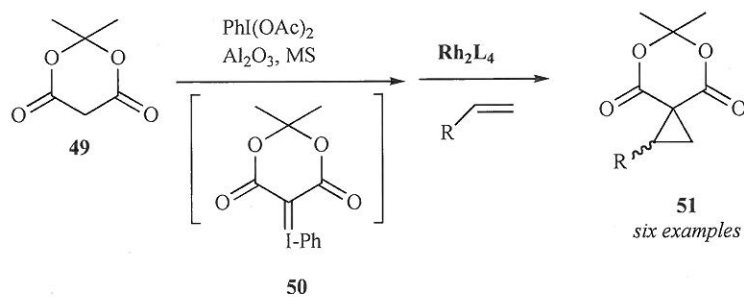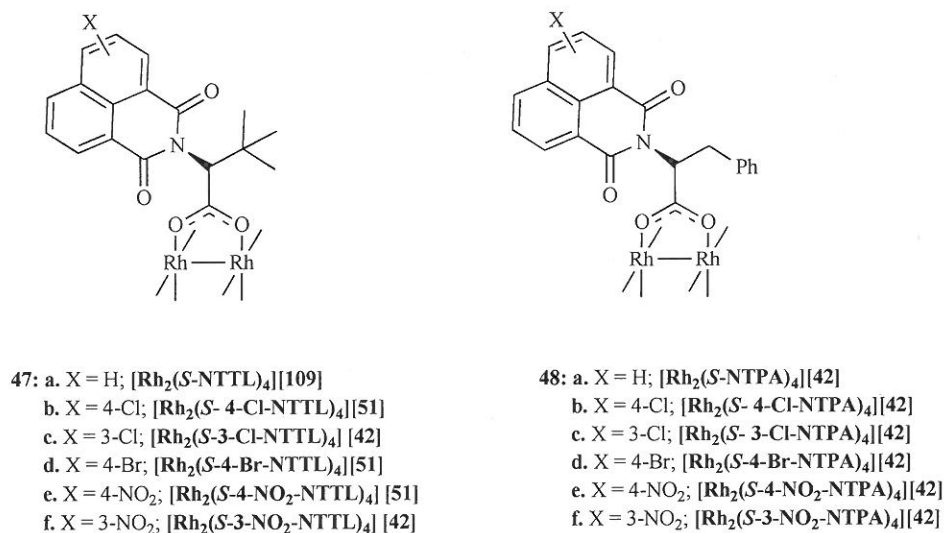
Fig. (13). Structure of complexes **61** and **62**.

Rh₂(menthylphthalate)₄

63

Rh₂(camphanate)₄

64

Rh₂(camphene-1-carboxylate)₄

65

Rh₂[1-(1-phenylethyl)pyrole-2-carboxylate]₄

66

Rh₂(MTPA)₄

67
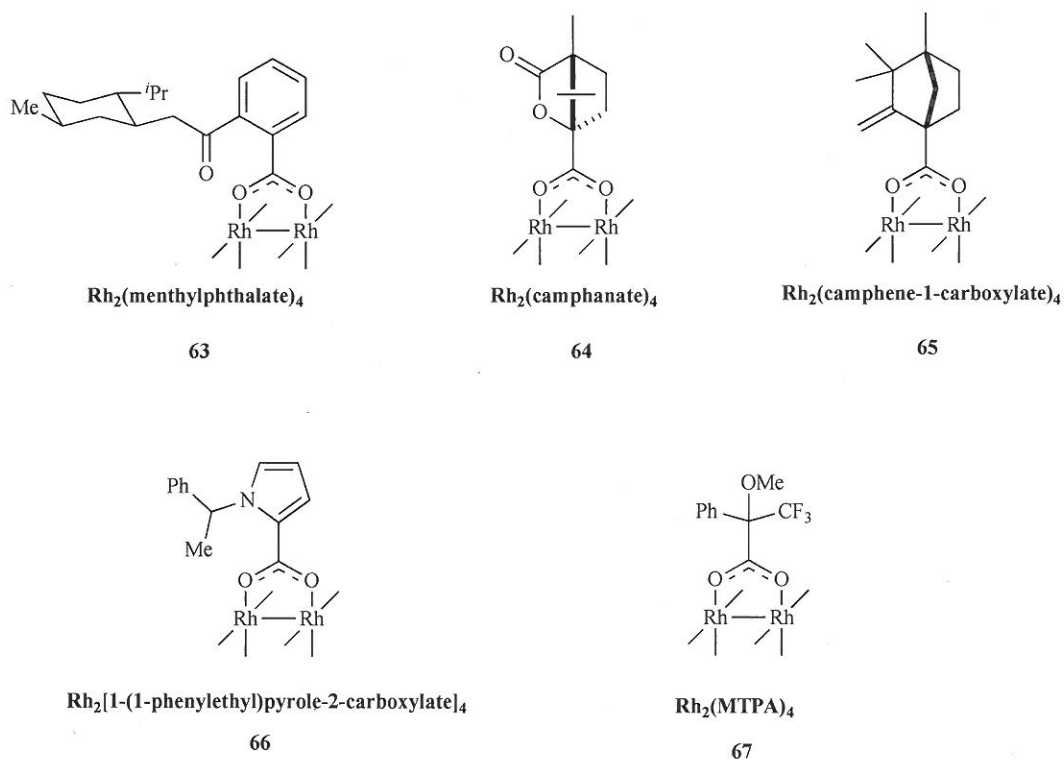
Fig. (14). Structure of Moody complexes **63-67**.
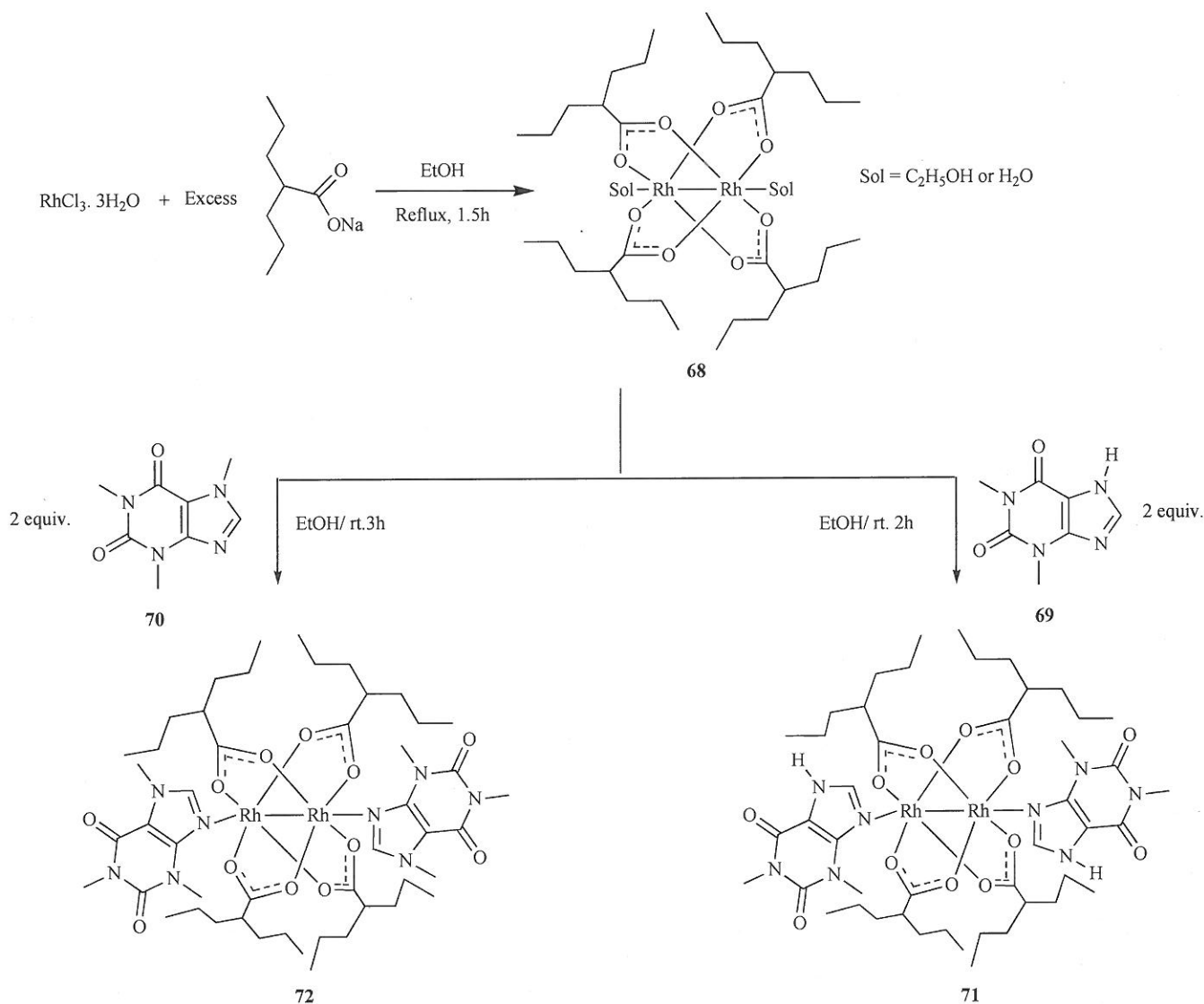
Scheme 3.

for the preparation of such catalysts is, again, the ligand exchange methodology in which the acetate groups of rodium Acetate were exchanged with the corresponding ligand in refluxing chlorobenzene under nitrogen (Fig. **15**).

The structure characterization of the dirhodium(II) carboxamidate catalysts revealed that the chiral ligands are arranged around the dirhodium(II) nucleus so that the two nitrogen and the two oxygen are bonded to each rhodium in which the two nitrogen atoms are having a *cis*-orientation (C_2-symmetry; alignment of ligands in the $\alpha,\alpha,\beta,\beta$-arrangement) [46,51]. The catalytic activity of these dirhodium carboxamidate complexes has been checked in different metal-carbene transfer reactions such as intramolecular allylic cyclopropanation reactions [52], intermolecular cyclopropanation reactions of diazoester and olefins [53], intramolecular C-H insertion reactions [52], Oxonium ylide-[2,3]sigmatropic rearrangement [54], and Lewis acid catalyzed hetero Diels-Alder reactions [55]. The catalysts gave high yield with moderate to excellent *ee* especially for intramolecular allylic cyclopropanation reaction (Scheme **4**).

In addition to what precedes, Doyle *et al.* have reported the synthesis of the dirhodium(II) carboxamidate catalyst [Rh$_2$(1,6-

BPGlyc)$_2$(NCMe)$_2$], derived from 1,6-Bis-(*N*-benzyl)-diphenylglycoluril **96** as a new μ-NCO ligand architecture. The catalyst was prepared in 46% yield via ligand exchange of [Rh$_2$(OAc)$_4$] with the 1,2-diphenylglycoluril ligand (Fig. **16**). The structure of the complex has been fully charecterized by ^{1}H, ^{13}C NMR, IR, UV and X-ray crystal structure which proved that the catalyst is existing in the *cis*-(1,3) form [56,57].

[Rh$_2$(1,6-BPGlyc)$_2$(OAc)$_2$(NCMe)$_2$] was examined in intermolecular cyclopropanation of diazoesters with styrene and it was found that the *cis/trans* selectivity in the formation of **97** was closer to dirhodium(II) methyl 2-oxopyrrolidine-5-carboxylate, [Rh$_2$(5*S*-MEPY)$_4$], than the electronically related [Rh$_2$(4*S*-MPPIM)$_4$]. The formation of *E/Z* **98** was observed in a 4:1 product ratio of **98:97** and a 1:1 *E/Z*-selectivity of **98**. The cis/trans selectivity of the formation of **31** is basically unchanged by **96** in comparison to the results for both dirhodium(II) carboxylates and carboxamidates except that **96** is more reactive than [Rh$_2$(5*S*-MEPY)$_4$] (Fig. **17**).

The Hashimoto group have put forward the preparation of new dirhodium(II) carboxamidate complexes which are derived from (*S*)-3-(benzene-fused-phthalimido)-2-piperidinonate as chiral bridging ligands by using the ligand exchange method with Rh$_2$(OAc)$_4$
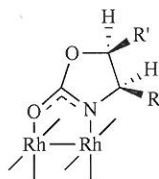
$$Rh_2(OAc)_4 \ + \ 4\,L^*H \ \xrightarrow[\text{Reflux}]{\text{PhCl}} \ Rh_2L^*_4 \ + \ 4AcOH$$

73-83
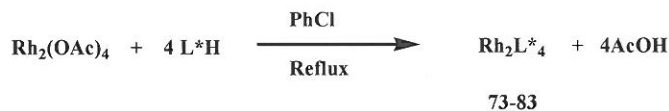
Dirhodium(II) catalysts derived from chiral pyrrolidinates:
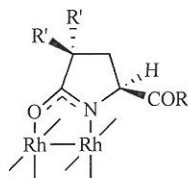
73a: [Rh₂(5S-MEP)₄], R = OMe , R' = H [53]
  b: [Rh₂(5S-NEPY)₄], R = OCH₂CMe₃, R' = H [148]
  c: [Rh₂(5S-DMAP)₄], R = NMe₂, R' = H [149]
  d: [Rh₂(5S-ODPY)₄], R = O(CH₂)₁₇CH₃, R' = H [150]
  e: [Rh₂V5S-dFMEPY)₄], R = OMe, R' = F [151]

Dirhodium(II) catalysts derived from chiral oxazolidinates:

74a: [Rh₂(4S-IPO)₄], R = ᶦPr , R' = H [53]
  b: [Rh₂(4S-BNOX)₄], R = Bn, R' = H [53]
  c: [Rh₂(4S-MPOX)₄], R = Me, R' = Ph [152]
  d: [Rh₂(4S-PHOX)₄], R = Ph, R' = H [153]
  e: [Rh₂(4S-MEOX)₄], R = R' = H [154]
  f: [Rh₂(4S-THREOX)₄], R =H, R' = Me [154]

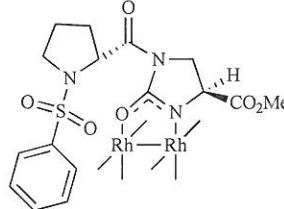Dirhodium(II) catalysts derived from chiral imidizolidinates:
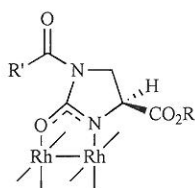
75a: [Rh₂(4S-MACIM)₄], R = R' = Me [155]
  b: [Rh₂(4S-MPAIM)₄], R = Me, R' = Bn [155]
  c: [Rh₂(4S-MPPIM)₄], R = Me, R' = PhCH₂CH₂[155]
  d: [Rh₂(4S-MBOIM)₄], R = Me, R' = Ph [52]
  e: [Rh₂(4S-MCHIM)₄], R = Me, R' = cyclohexyl-CH₂[52]
  f: [Rh₂(4S-EPPIM)₄], R = Et, R' = PhCH₂CH₂ [157]
  g: [Rh₂(4S-BPPIM)₄], R = ᵗBu, R' = PhCH₂CH₂ [157]
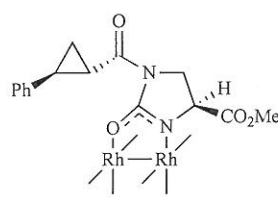
76
[Rh₂(4S,2'S,3'S-MCPIM)₄] [158]
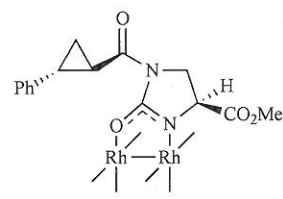
77
[Rh₂(4S,2'R,3'R-MCPIM)₄] [158]

78
[Rh₂(4S,2'R-BSPIM)₄] [158]
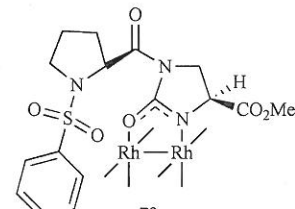
79
[Rh₂(4S,2'S-BSPIM)₄] [158]
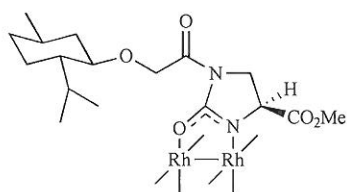
80
[Rh₂(4S-MLMIM)₄] [156]
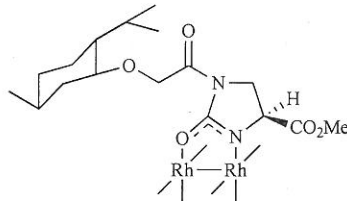
81
[Rh₂(4R-MLMIM)₄] [156]
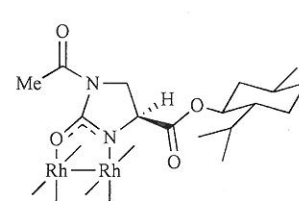
82
[Rh₂(1'R,2'R,5S,4S-MNACIIM)₄] [156]

Dirhodium(II) catalysts derived from chiral 2-oxaazetidinates
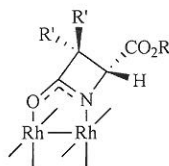
83a: [Rh₂(4*S*-IBAZ)₄], R = ʹBu, R' = H [159]
  b: [Rh₂(4*S*-BNAZ)₄], R = Bn, R' = H [159]
  c: [Rh₂(4*S*-MEAZ)₄], R = Me, R' = H [159]
  d: [Rh₂(4*S*-NEPAZ)₄], R = CH₂CMe₃, R' = H [151]
  e: [Rh₂(4*S*-CHAZ)₄], R = cyclohexyl-CH₂, R' = H [151]
  f: [Rh₂(4*R*-dfIBAZ)₄], R = ʹPr, R' = F [151]
  g: [Rh₂(4*R*-dfCHAZ)₄], R = cyclohexyl-CH₂, R' = F [151]
  h: [Rh₂((*S*,*S/R*)-MENTHAZ)₄], R = *S/R*-menthyl, R' = H [160]
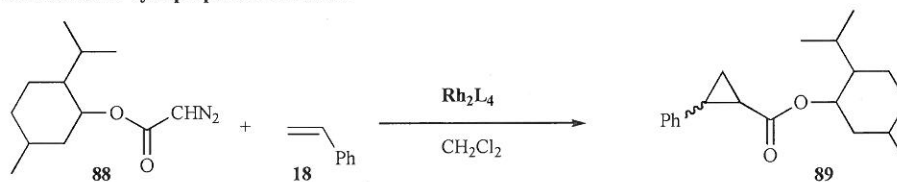
Fig. (15). Structure of Doyle complexes **73-83**.

Intramolecular allylic cyclopropanation reaction
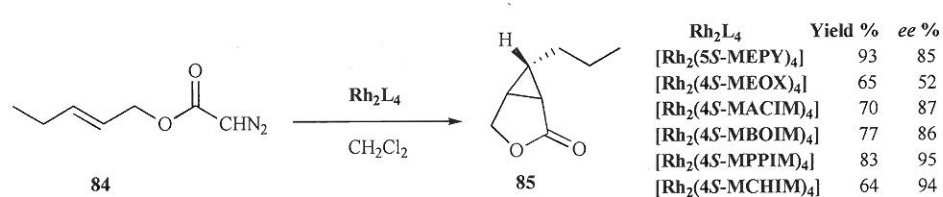
Rh₂L₄	Yield %	*ee* %
[Rh₂(5*S*-MEPY)₄]	93	85
[Rh₂(4*S*-MEOX)₄]	65	52
[Rh₂(4*S*-MACIM)₄]	70	87
[Rh₂(4*S*-MBOIM)₄]	77	86
[Rh₂(4*S*-MPPIM)₄]	83	95
[Rh₂(4*S*-MCHIM)₄]	64	94

Intramolecular C-H insertion reaction

Rh₂L₄	Yield %	*ee* %
[Rh₂(5*S*-MEPY)₄]	62	91
[Rh₂(4*S*-MEOX)₄]	65	92
[Rh₂(4*S*-MACIM)₄]	58	78
[Rh₂(4*S*-MBOIM)₄]	56	73
[Rh₂(4*S*-MPPIM)₄]	50	92
[Rh₂(4*S*-MCHIM)₄]	63	94
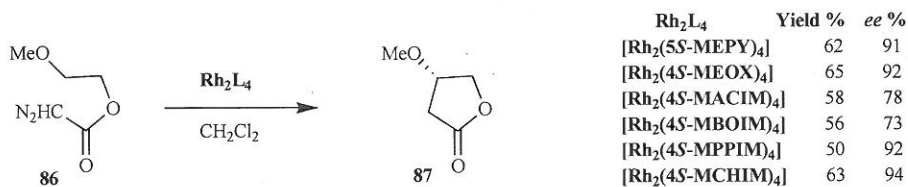
Intermolecular cyclopropanation reaction

Rh₂L₄	Yield %	*ee* % trans	*ee* % cis
Rh₂(OAc)₄	82	5 (1*R*,2*R*)	13 (1*R*,2*S*)
Rh₂(4S-IPOX)₄	55	34 (1*R*,2*R*)	56 (1*R*,2*S*)
Rh₂(4S-BNOX)₄	56	34 (1*R*,2*R*)	63 (1*R*,2*S*)
Rh₂(4R-IPOX)₄	51	4 (1*S*,2*S*)	25 (1*S*,2*R*)
Rh₂(5S-MEPY)₄	47	56 (1*S*,2*S*)	79 (1*S*,2*R*)

Oxonium ylide/[2,3]sigmatropic rearrangement

N₂CHCO₂Et / CH₂Cl₂

Rh₂[4(*S/R*)-MEOX]₄

91a: 15 (94% *ee*)   **91b:** 85 (98% *ee*)

Lewis acid catalyzed hetero-Diels Alder

1. Rh₂[4*S*-MPPIM]₄
2. TFA

82 (95% *ee*)
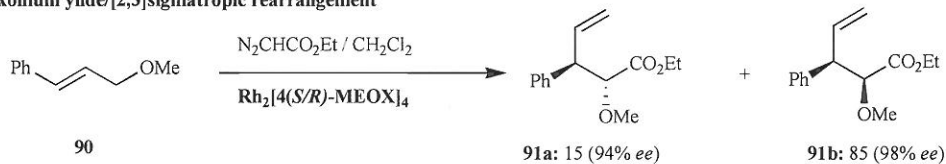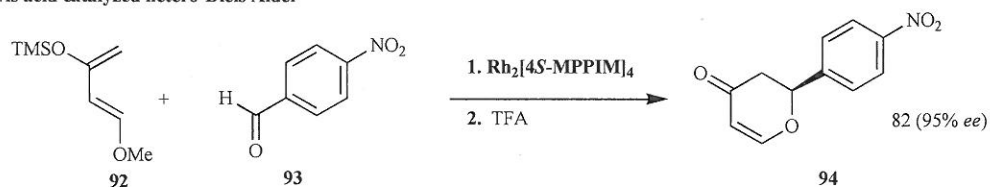
Scheme 4.
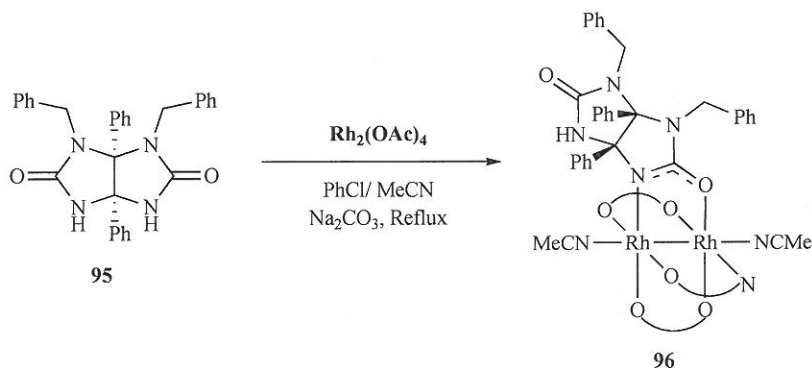
Fig. (16). Synthesis of complex **96**.

97: R = H, R' = Et
31: R = Ph, R' = Me

(E/Z)-**98** R = H, R' = Et
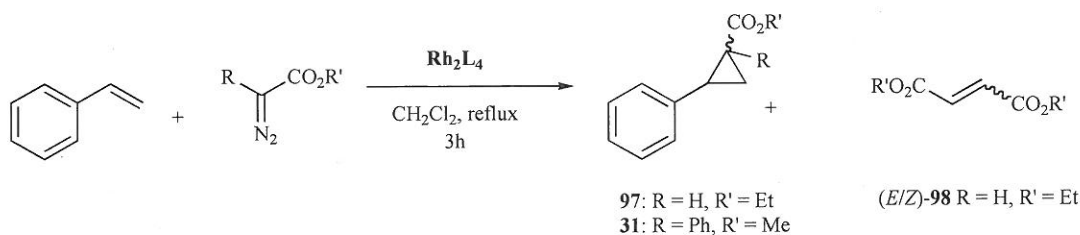
Entry	Rh$_2$L$_4$	% Yield(*cis:trans*)	
		31	97
1	[Rh$_2$(4S-MPPIM)$_4$]	64 (74:26)	66 (97:3)
2	[Rh$_2$(5S-MEP4)$_4$]	59 (46:54)	59 (97:3)
3	[Rh$_2$(1,6-BPGlyc)$_2$(OAc)$_2$(NCMe)$_2$]	43 (47:53)	43 (99:1)
4	[Rh$_2$(OAc)$_4$]	93 (38:62)	69 (98:2)

Fig. (17). Catalytic cyclopropanation of styrene with diazoesters.

99. [Rh$_2$(S-PTPI)$_4$]   **100. [Rh$_2$(S-BPTPI)$_4$]**

101

102

83-97% Yield
69-96% *ee*

6 examples

Fig. (18). Enantioselective hetero-Diels–Alder reactions.

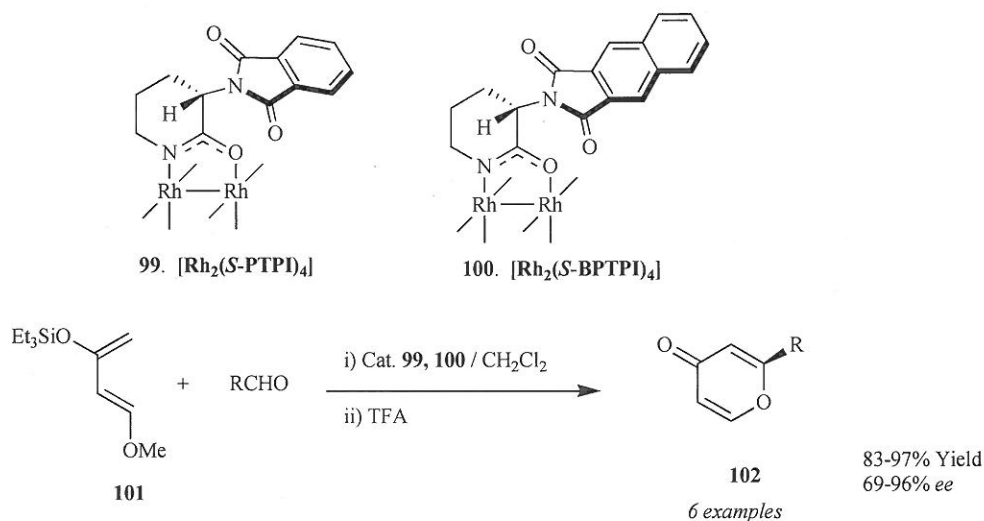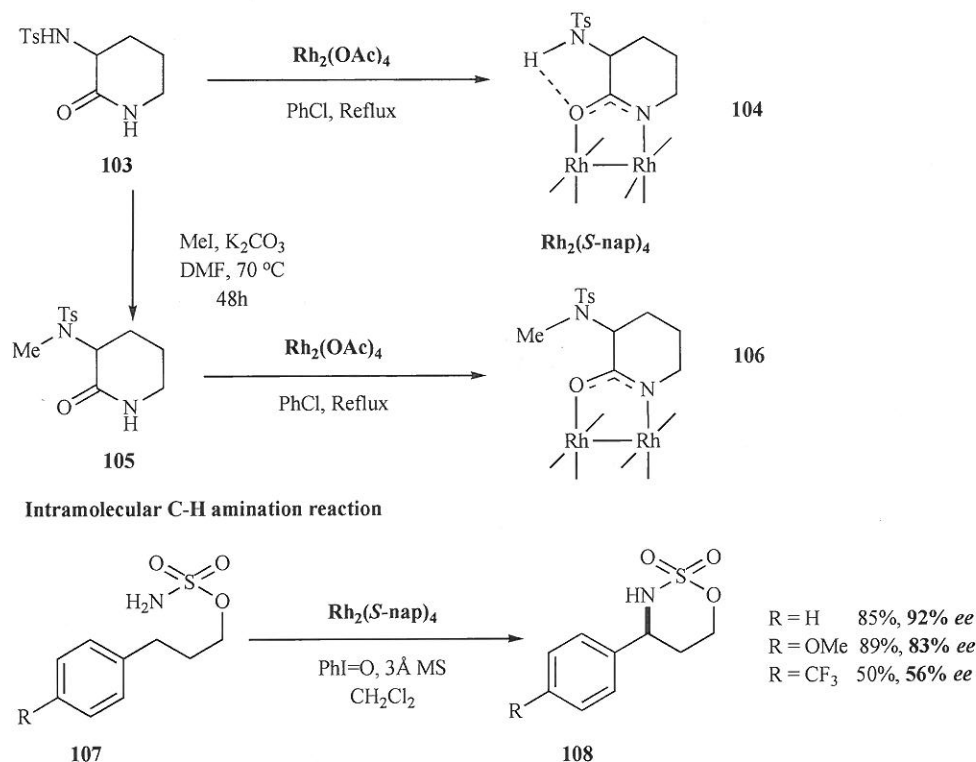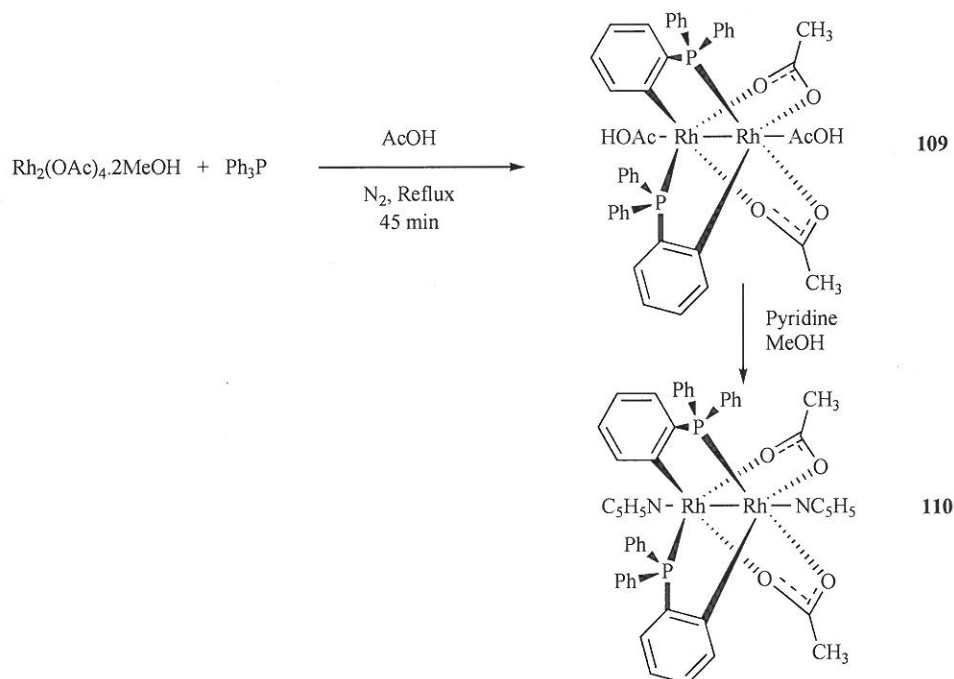(Fig. **18**) [58,59]. The catalysts structure turned out to have a C$_2$-like symmetry in which the benzene-fused-phthalimido groups are aligned in a "down-down-up-up" $\alpha,\alpha,\beta,\beta$ arrangement. The catalysts have been applied as a chiral Lewis acid catalysts for enantioselective hetero-Diels–Alder reactions between different aldehydes and 1-methoxy-3-(triethylsilyloxy)-1,3-butadiene (6 examples) which provided excellent yields with up to 96% *ee*.

In 2008, Zalatan and Du Bois [60] presented the preparation of novel chiral carboxamidate dirhodium catalysts resulting from chiral valerolactams, Rh$_2$(S-nap)$_4$ **104**, and its *N*-methylated analogue **106** via ligand exchange as shown in Scheme 5. The ongoing reason to design such catalysts was the poor enantiomeric induction (0-20% *ee*) of dirhodium tetracarboxylate complexes derived from α-amino acids for enantioselective synthesis of cyclic sulfamate

Intramolecular C-H amination reaction

R = H   85%, **92%** *ee*
R = OMe 89%, **83%** *ee*
R = CF$_3$ 50%, **56%** *ee*

Scheme 5.

Fig. (19). Synthesis of *ortho*-metalated complexes **109** and **110**.

esters by an asymmetric C-H amination reaction of the prochiral sulfamate ester [61].

2.1.3. Ortho-Metalated Dirhodium(II) Complexes

Cotton and co-workers [62] introduced a new class of dirhodium(II) complexes with a backbone chirality which is derived from two *ortho*-metalated phenyl phosphines ligands and two carboxylate ligands, Rh$_2$(OAc)$_2$(pc)$_2$ (pc: *ortho*-metalated aryl phosphine) **109**, having a head-to-tail arrangement (i.e., the

phosphine ligands are oriented opposite each other). The *ortho*-metalated phosphine dirhodium(II) complexes and their adduct have been prepared from thermal reaction of Rh$_2$(OAc)$_4$ and aryl phosphines followed by addition of pyridine in methanol to give the bis(pyridine) adduct **110** with the molecular formula [Rh$_2$(OAc)$_2${(C$_6$H$_5$)$_2$P(*O*-1-C$_6$H$_4$)}$_2$.(C$_5$H$_5$N)$_2$] as shown in Fig. (**19**). All complexes were characterizied by X-ray crystallography [63].
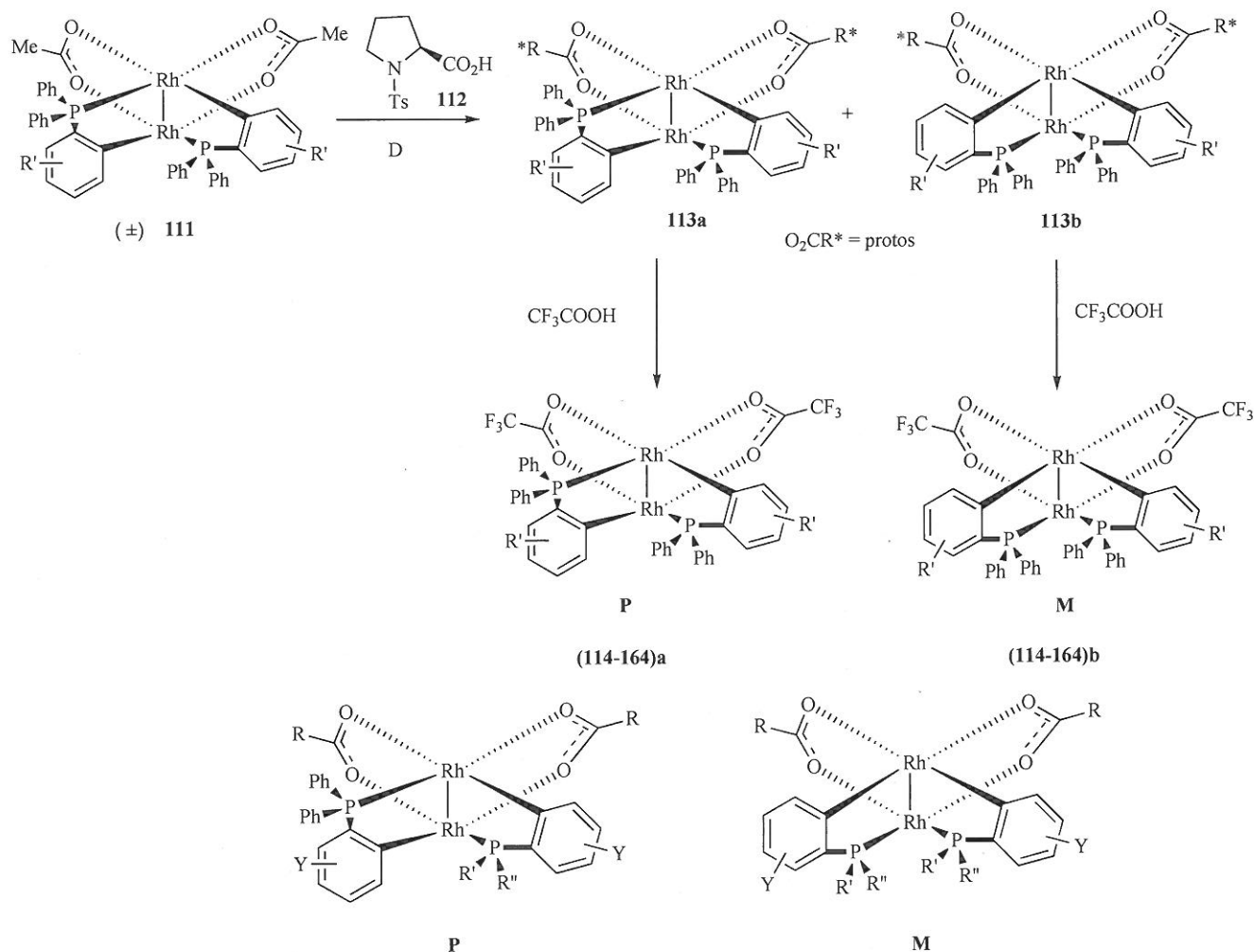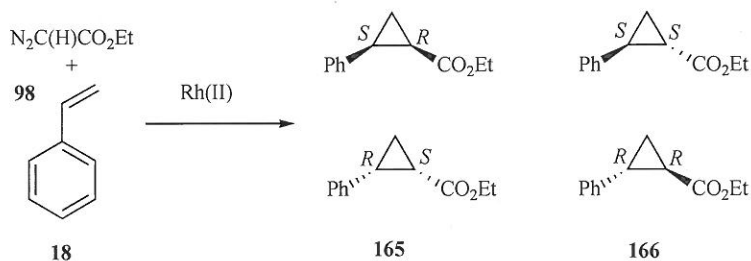
Scheme 6.

Fig. (20). Catalyzed Cyclopropanation of Styrene with Ethyl Diazoacetate.

Cotton's method [62] for the synthesis of a new family of chiral dirhodium(II) compounds with *ortho*-metalated aryl phosphine ligands with several substituent patterns (**114-164**) has been used and further explored by Francisco Estevan and co-workers [64-73]. Estevan *et al.* isolated the pure enantiomers via conventional resolution methods (the racemic mixture of the compound [Rh$_2$(OAc)$_2${(O-C$_6$H$_4$)P(C$_6$H$_5$)$_2$}.(AcOH)$_2$] was transformed into two diastereoisomers by replacing the acetate groups with *N*-(4-Methylphenylsulfonyl)-(L)-proline (Scheme **6**) [74,75]. All catalysts were characterized by NMR, CHNS analysis and most of them were characterized by X-ray crystal structure determination.

The formed complexes **114-164** were examined for intramolecular cyclization and intramolecular C-H insertion reactions of α-diazo ketones, giving up to 95% *ee*, and up to 73% *ee*, respec-

tively. In addition, the chiral catalysts were tested in the standard reaction of asymmetric cyclopropanation of styrene **18** with ethyl diazoacetate **98**, presenting up to 80% yields with 91% *ee* (Fig. **20**) [76].

Moreover, Estevan and co-workers [77,78] have reported the synthesis of new *ortho*-metalated dirhodium catalysts from the reaction of tri(2-thienyl)phosphine **167** [77], with dirhodium acetate in refluxing toluene for 1 hour. The single crystal X-ray crystal structure revealed that the thienyl ring for the bis-cyclometalated product is arranged in either a head-to-tail (H-T, **170**) or a head-to-head (H-H, **168**) configurations (Fig. **21**). The catalytic activity of catalysts **169** and **170** have been examined for the catalyzed reaction of methyl 2-diazoundecanoate **171**, which exhibits competition between β-elimination and 1,5-C-H insertion reactions. Both cata-
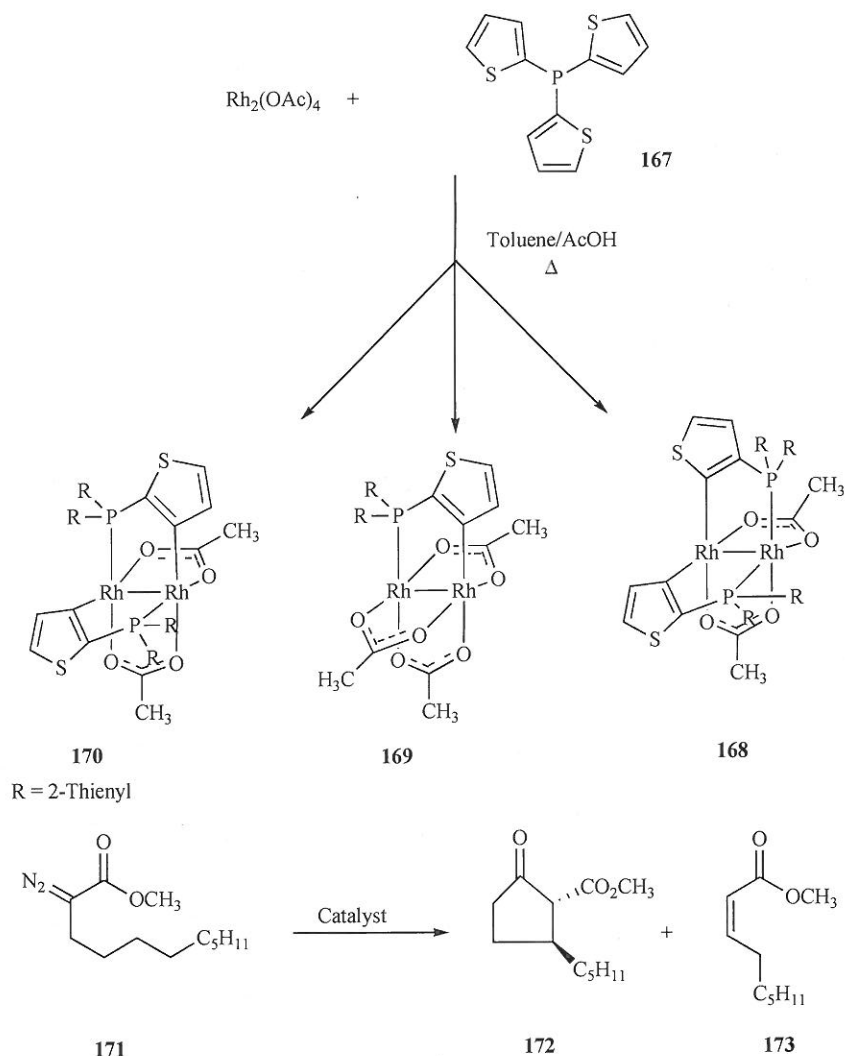
Fig. (21). Synthesis of complexes **168**, **169** and **170** and their applications.
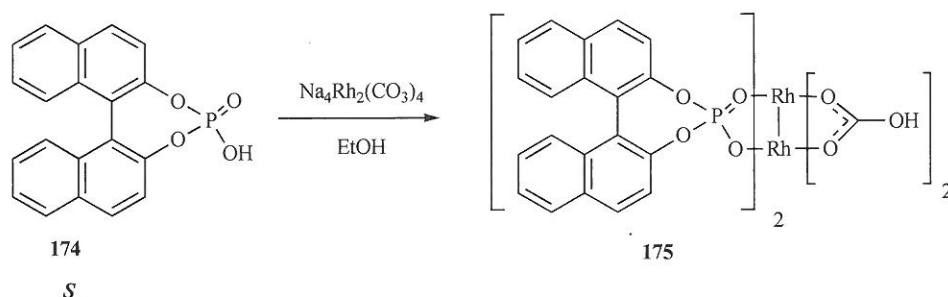

Fig. (22). Synthesis of dirhodium phosphonate catalyst **175**.

lysts have provided 17% yield for cyclization reaction and 83% for 1,5-C-H elimination reaction at room temperature.

2.1.4. Dirhodium Phosphonate Catalysts

The dirhodium(II) paddlewheel complexes based on optically active phosphine ligands were developed in 1992 by McKevery and co-workers [79] when they prepared a mixed ligand system of homochiral Rh(II) complex, $[Rh_2(HCO_3)_2\{(+)-PhOS\}_2.5H_2O]$ **175**, via the reaction of $[Na_4\{Rh_2(CO_3)_4\}.2H_2O]$ [80] with $(S)-(+)-1,1'-$ binaphtyl-2,2'-diyl hydrogen phosphate **174**, (+)-PhOSH [81,82], in ethanol at room temperature (Fig. **22**).

Catalyst **175** was tested for different reaction types like 2,3-sigmatropic rearrangement which is considered the first example in this period, C-H insertion and aromatic cyclization reactions as shown in Fig. (**23**).

Also, in 1992, Pirrung and Zhang [32] provided the preparation of the dirhodium tetrakisbinaptholphosphate $[Rh_2(R-BNP)_4]$ **183** catalyst by ligand exchange with dirhodium acetate $[Rh_2(OAc)_4]$. The substituted analogues at either 3,3'-positions [83,84] or 6,6'-positions [85-88] in the binaphtholyl ring were carried out by the same method through the ligand exchange of $[Rh_2(OAc)_4]$ with the
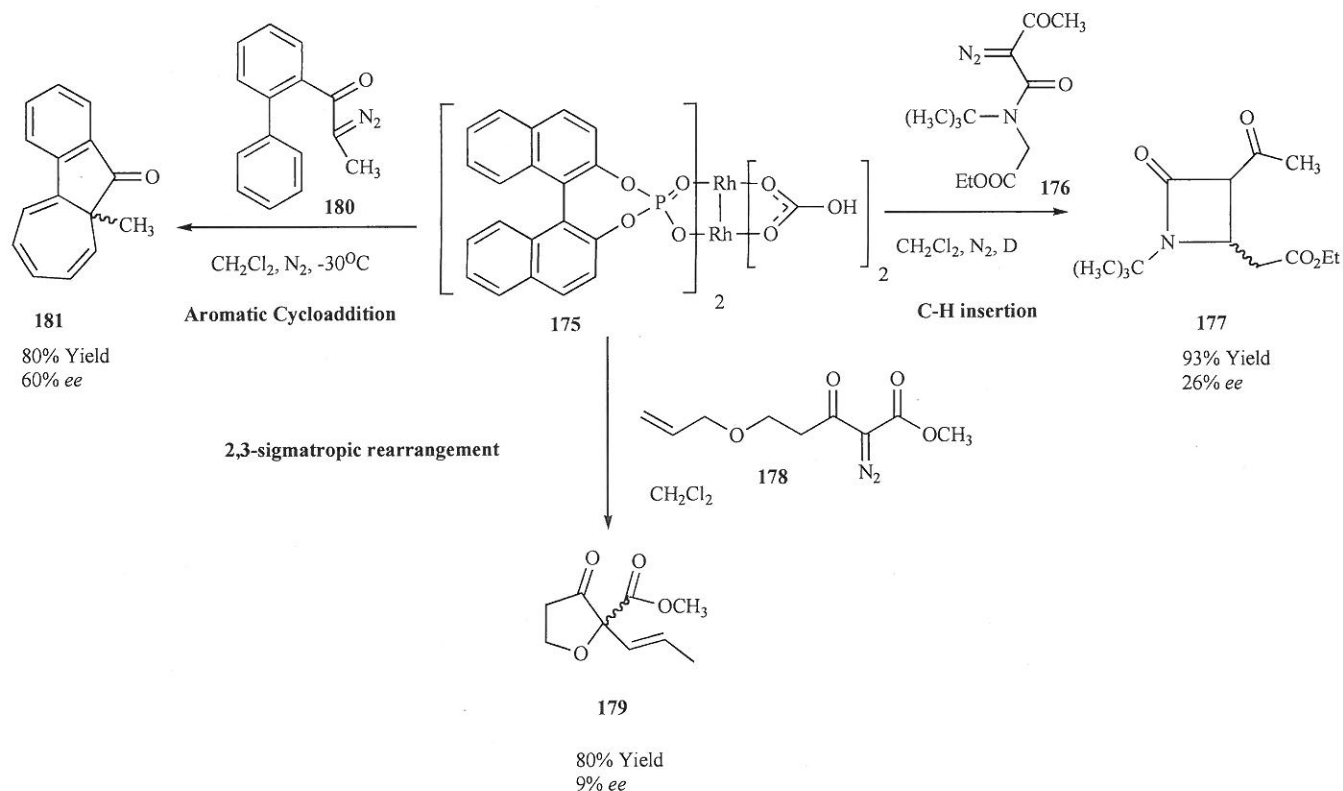
Fig. (23). Application of complex **175**.

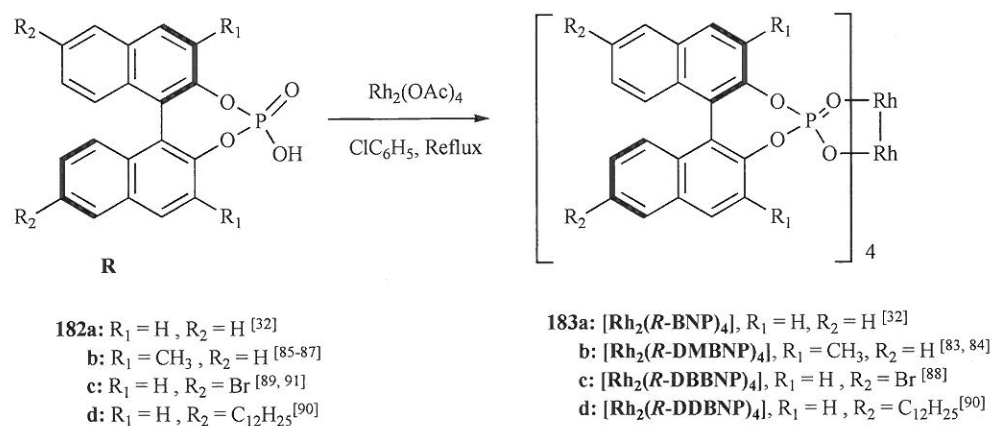**Fig. (24).** Synthesis of complex **183**.

182a: $R_1 = H$, $R_2 = H$ [32]
b: $R_1 = CH_3$, $R_2 = H$ [85-87]
c: $R_1 = H$, $R_2 = Br$ [89, 91]
d: $R_1 = H$, $R_2 = C_{12}H_{25}$ [90]

183a: **[Rh₂(*R*-BNP)₄]**, $R_1 = H$, $R_2 = H$ [32]
b: **[Rh₂(*R*-DMBNP)₄]**, $R_1 = CH_3$, $R_2 = H$ [83, 84]
c: **[Rh₂(*R*-DBBNP)₄]**, $R_1 = H$, $R_2 = Br$ [88]
**d:** **[Rh₂(*R*-DDBNP)₄]**, $R_1 = H$, $R_2 = C_{12}H_{25}$ [90]

corresponding substituted binaphtholhydrogen phosphate ligands [88-91] (Fig. **24**).

Hodgson, Stupple and co-workers [7] continued their work and reported the preparation of novel catalysts derived from bis-steriodal binaphthol (i.e., bis-isoequilenine), [Rh₂{(*R,S*)-biep}₄] **185a** and [Rh₂{(*S,S*)-biep}₄] (biep: bisisoequileninephosphate) **185b** through the ligand exchange method as demonstrated in the literature [35] (Fig. **25**).

The catalytic activity of the dirhodium(II) phosphonate catalysts **183** and **185** have been studied in the enantioselective 1,3-dipolar cycloaddition of 2-diazo-3,6-diketoester **186** as shown in Table **2**. The most significant catalyst has been discovered to be Rh₂(*R*-DDBNP)₄ as it contains *n*-dodecyl groups in its backbone that increase the solubility in addition to increasing the activity of the catalytic reaction.

Recently, bis(diethylphosphina)methane (depm, Et₂PCH₂Pet₂) was used as a new bridging ligand for the synthesis of a series of dirhodium complexes, starting from *trans*-[Rh₂Cl₂ (CO)₂(depm)₂]. The reduction of this chloro complex in aqueous KOH under an atmosphere of CO produced the neutral tricarbonyl complexes [Rh₂ (CO)₃(depm)₂]. Protonation of these tricarbonyl complexes by triflic acid (HOTf) or Brookhart's acid (HBArF₄) yielded the hydride bridged tricarbonyl complex [Rh₂ (CO)₃(*μ*-H)(depm)₂][X]. Reaction of [Rh₂ (CO)₃(depm)₂] with methyl triflate yielded the methyl complex [Rh₂(CH₃)(CO)₃(depm)₂][OTf] at below -20°C which upon warming to above -20°C results in a migrating insertion to yield an acetyl bridged species [Rh₂(CO)₂(*μ*-C(CH₃)O)(depm)₂] [OTf] [92] (Scheme **7**).

The catalytic activity for such complexes were examined for geminal C-H activation of α-olefines.
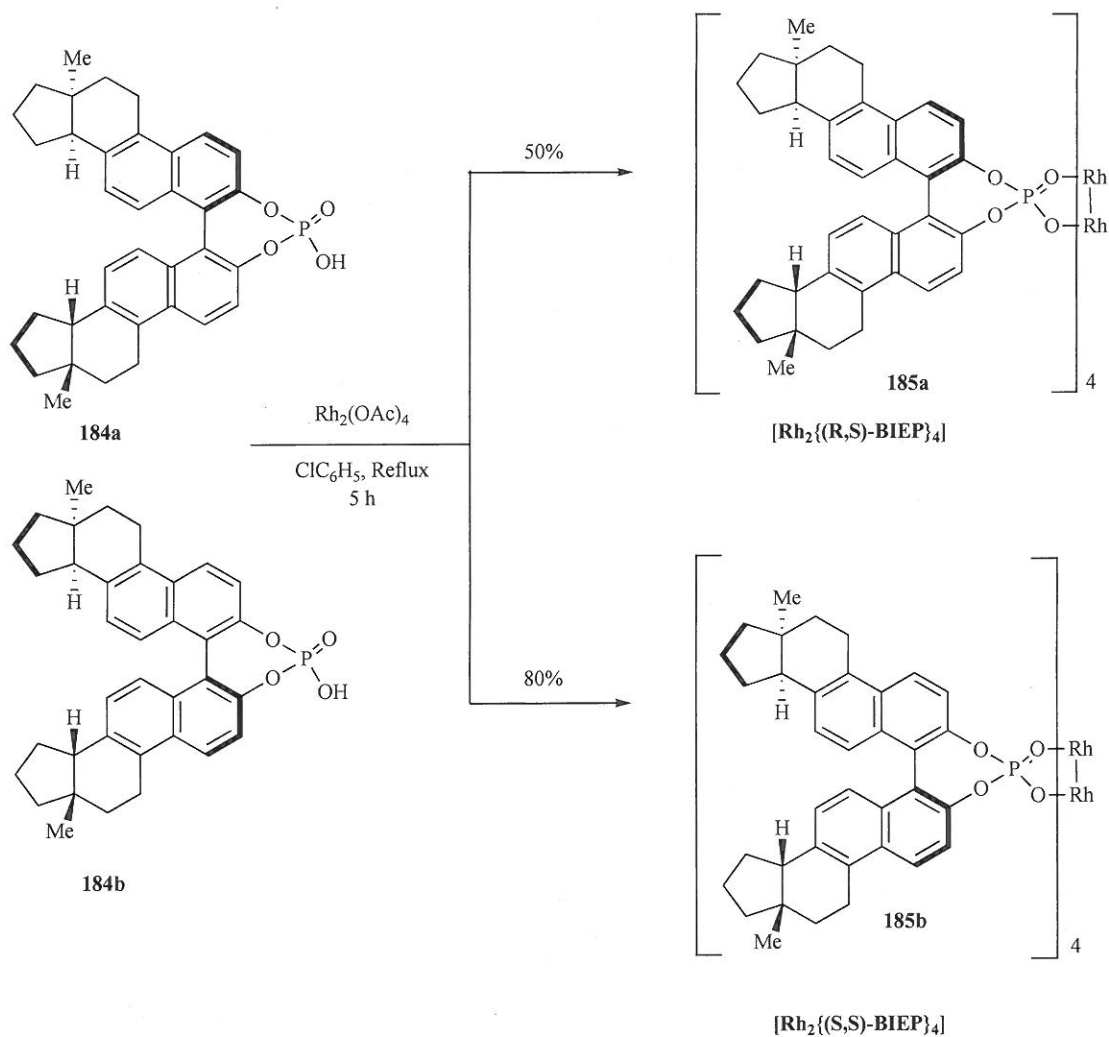
Fig. (25). Synthesis of complexes **185a** and **185b**.

Table 2. Intramolecular C-H Insertion Reaction of 186 catalyzed by 183 and 185
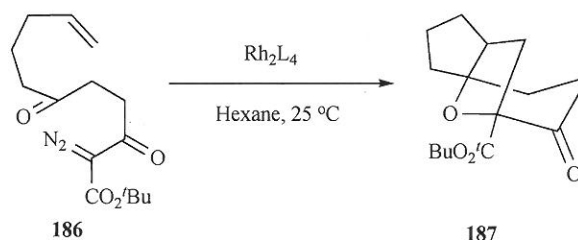
Rh$_2$L$_4$	Yield %	*ee* %
[Rh$_2$(*R*-BNP)$_4$]	65	64
[Rh$_2$(*R*-DMBNP)$_4$]	0	0
[Rh$_2$(*R*-DBBNP)$_4$]	34	66
[Rh$_2$(*R*-DDBNP)$_4$]	76	81
[Rh$_2${(*R,S*)-BIEP}$_4$]	65	75
[Rh$_2${(*S,S*)-BIEP}$_4$]	66	77
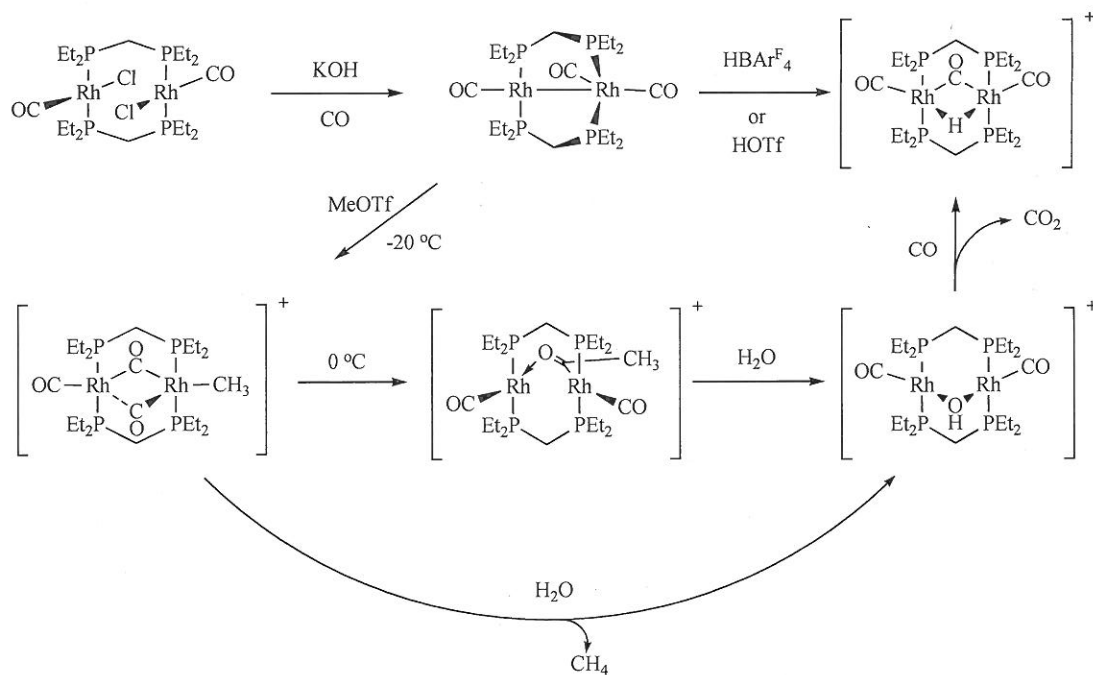
Scheme 7.

2.1.5. Axial Ligands Modification of Dirhodium Complexes

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 ligands modification was proven to be a valuable and simple strategy to prepare new complexes and achieve new activities. A comprehensive overview about this point was reviewed by Trindade *et al.* [93] with a particular focus on the changes induced by the axial coordination on the complex properties and reactivity.

2.2. Conformational Elucidation

Knowing the structure of a compound helps in understanding its different properties and its reactivity behavior during a reaction. In the past, different spectroscopic techniques were used to elucidate the structure of compounds but these techniques were not effective. X-ray crystal structure analysis has not been possible for many catalysts as, in most cases, it was impossible to obtain suitable crystals. Recently, synchrotron X-ray crystallography has allowed samples, only a few microns in size, to be analyzed. This technique has impressive advantages over lab-based X-ray crystallography as: it works on smaller sample amount allowing trace analysis, it works on samples with weak signals including poorly crystalline samples and samples containing light elements and it have a shorter measurement time due to the rapid throughput in principle allowing real-time monitoring of processes *in situ*. In the case of rhodium catalysts, a number of structures have recently been elucidated by the use of either advanced spectroscopic analysis or by crystal structure determination of Lewis base adducts.

2.2.1. Advanced Spectroscopic Analysis

In 2009, several reports were published elucidating the structures of chiral tetracarboxylate Rh(II) catalysts and models accounting for their activity were proposed. Fox *et al.* [94] reported that the Hashimoto complex $Rh_2(S\text{-}PTTL)_4$ **33c** which exists in the shape of a chiral crown conformation where the four *N*-phthaloyl groups

exist in an all-up symmetry conformation ($\alpha,\alpha,\alpha,\alpha$ conformer) and the tertiary butyl groups exist on the other face. Furthermore, they reported that this chiral cavity, shrouded by the *N*-phthaloyl groups, was responsible for the catalyst chemoselectivity, enantioselectivity, and diastereoselectivity in intermolecular cyclopropanation reactions as the reaction takes place in the crown cavity of the catalyst. On the other hand, the other *tert*-butyl encapsulation kept the rhodium axial coordination site deem crowded for reactivity to occur. This finding was investigated by DFT calculation.

Charette *et al.* [95] reported that the *N*-phthaloyl tetracarboxylate Rh(II) catalysts **33a-d** are fluxional in solution by undergoing a process that involves the rotation of one or more phthaloyl group to flip the aryl units between axial binding sites. This was on the basis of NOE correlations between the side chain protons and the phthaloyl aromatic carbons of the adjacent ligand and it was confirmed by VT NMR experiments. In the case of chlorinated *N*-phthaloyl complexes **33e,h-j**, where the halogen is attached to the phthaloyl ring, there is no observed interaction between the *N*-tetrachlorophthaloyl aromatic carbons and either *t*-Bu protons or the α-protons, suggesting that the all-up conformation is maintained in solution.

Ghanem, Gardiner and co-workers [42] published the first X-ray structure of a *N*-naphthaloyl chiral Rh(II) complex $Rh_2(S\text{-}NTTL)_4$ **47a**, using synchrotron X-ray diffraction which revealed that the catalyst structure is also having an $\alpha,\alpha,\alpha,\alpha$ conformation with a reasonably square chiral crown cavity formed by the *N*-naphthaloyl unit serving as a model that accounts for the 4-Br substituted analogue **47d**. These complexes have greatly improved enantioselectivity through the cavity rim steric impedance due to the greater rigidity of the cavity corners accounting for the enhanced catalytic selectivity (see the graphical abstract). Different conformations that exists for each of these adducts that, notably, shows an inequivalent axial coordination sites unlike both reported by Hashimoto [38] and Fox [96] for $[Rh_2(S\text{-}PTPA)_4(4\text{-}t\text{-}BuC_5H_4)_2]$ and $[Rh_2(S\text{-}PTPA)_4(NCMe)_2]$ adducts, respectively, showing that these catalysts exhibited an $\alpha,\alpha,\beta,\beta$ conformation.
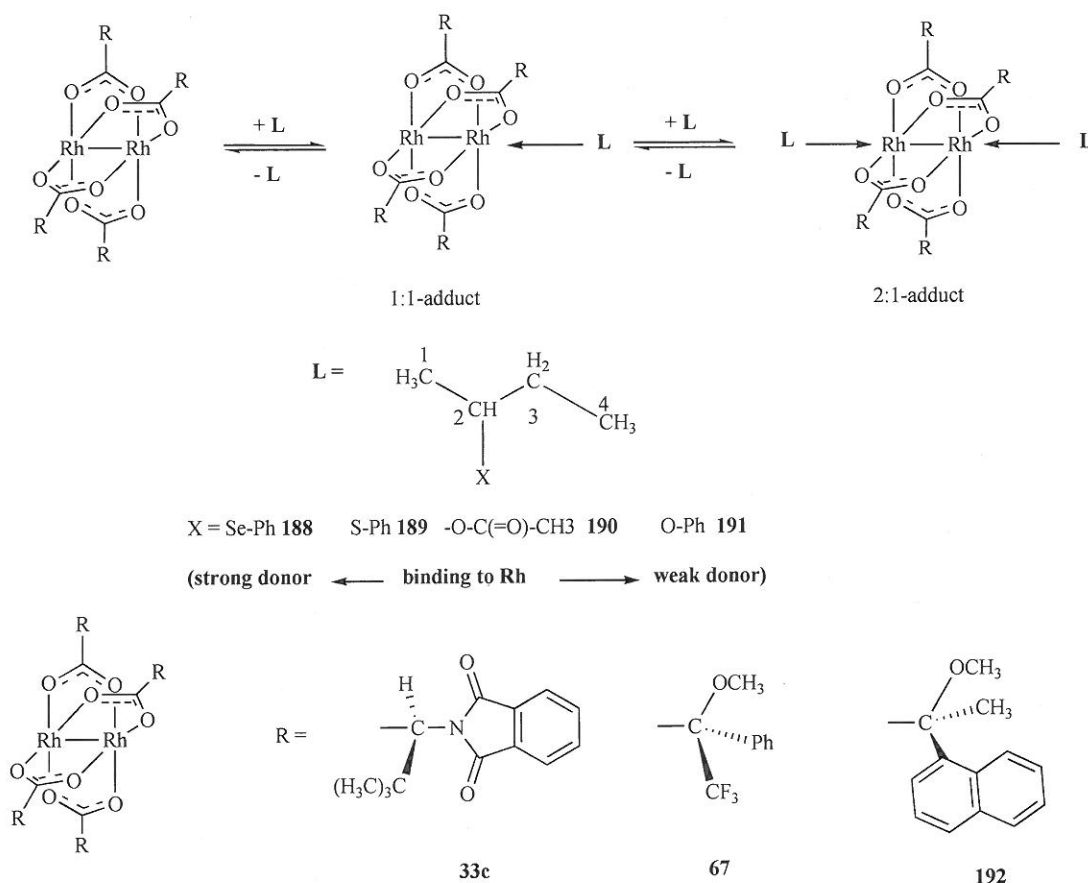
Fig. (26). Structure of dirhodium tetracarboxylate complexes used.

2.2.2. Elucidation by Formation of Adducts

Duddeck and co-workers [97] have studied the effect of using 2-butyl derivatives (Se-Ph, S-Ph, -O-C(=O)-CH₃, and O-Ph) as ligands for various enantiopure dirhodium tetracarboxylate complexes to form adducts aiming to gain further insight into the complexation mechanisms of these ligands through their NMR properties (i.e., "dirhodium method") as shown in Fig. (26) [98-100].

Duddeck *et al.* studied the formation of these adducts on Hashimoto complex, dirhodium tetrakis[(*S*)-*N*-phthaloyl-tert-leucinate] (**33c**; [Rh₂{(*S*)-PTTL}₄]) [47], dirhodium tetra-(*R*)-α-methoxy-α-(trifluormethyl)-phenylacetate, Mosher complex (**67**; [Rh₂{(*R*)-1-MTPA}₄]) [100], dirhodium tetrakis[(*S*)-2-methoxy-2-(1-naphthyl)propionate] and Harada complex (**192**; [Rh₂{(*S*)-Mα NP}₄]) [101]. They found that if the strong ligands involved **188** and **189**, the chiral enantiopure dirhodium complex with four Mα NP acids residues **192** would show somewhat better enantioresolving properties (diastereomeric dispersion, *δν*) than **67** which was employed in their previous studies. They also found that, in contrast to **67**, the complex **192** failed with weak ligands (e.g., **190** and **191**). So, **192** could not be regarded as a generally applicable auxiliary. Moreover, both complexes **192** and **33c** seem to fail with phosphane ligands because they produce broad NMR signals at room temperature due to coalescence phenomena indicating a reduced adduct formation energy.

Further studies have been carried out to investigate this effect and its reason through studying the binding modes of stereoisomeric 2-butylphenylsulfoxides in the adducts formed with Mosher complex (Fig. **27**). These studies found that all stereoisomers of the 2-butylphenylsulfoxides **193a** and **194a** and their *p*-substituted

derivatives **193b–1e** and **194a-2e** (X = F, Br, NO₂, and OCH₃) were synthesized. Absolute configurations were assumed from the commercial enantiopure 2-butanols used as starting materials, by X-ray diffraction and by polarimetry. Preferred .conformations were determined by density functions and second-order Møller–Plesset calculations. Oxygen atoms dominate in the adduct formation equilibria of 2-butylsubstituted sulfoxides and the chiral dirhodium complex **67** although the sulfur atom is, in principle, the stronger donor and this is due to steric shielding of the sulfur atom produced by the aromatic ring and the secondary 2-butyl substituent. Enantiomeric differentiation of sulfoxides is easily accomplished by the dirhodium experiment, i.e., recording the NMR spectra in the presence of an equimolar amount of **67**. Complex formation shifts (*Δδ*) and diastereomeric dispersion effects (*δν*) differed in the dirhodium experiment for nonracemic mixtures of sulfoxides when compared with the pure enantiomers and this did not affect the efficiency of the dirhodium experiment [102].

Mattiza *et al.* [103] also checked thirteen enantiopure paddle-wheel-shaped dirhodium tetrakiscarboxylate complexes **13**, **32b**, **33b-c**, **34c**, **47a**, **67**, **192**, and **198-202** for their efficiency in the dirhodium method (Fig. **28**); the differentiation between enantiomers was done on the bases of ¹H{¹H} NOE experiments and X-ray diffraction. Adducts of each complex have been examined with five different test ligands representing all relevant donor properties from strong (phosphane) to very weak (ether). Only one of them, the dirhodium complex with four axial (*S*)-*N*-2,3-naphthalene dicarboxylate-*tert*-leucinate groups **34c**, has shown significantly better results for all ligands than the conventional [Rh₂(*R*-MTPA)₄] **67** complex with four axial Mosher acid anion residues which are usu-

(R_S, R_C) like **193** (S_S, S_C) (R_S, S_C) unlike **194**

195   **196**   **197**

	a	b	c	d	e
X =	H	F	Br	NO_2	OCH_3
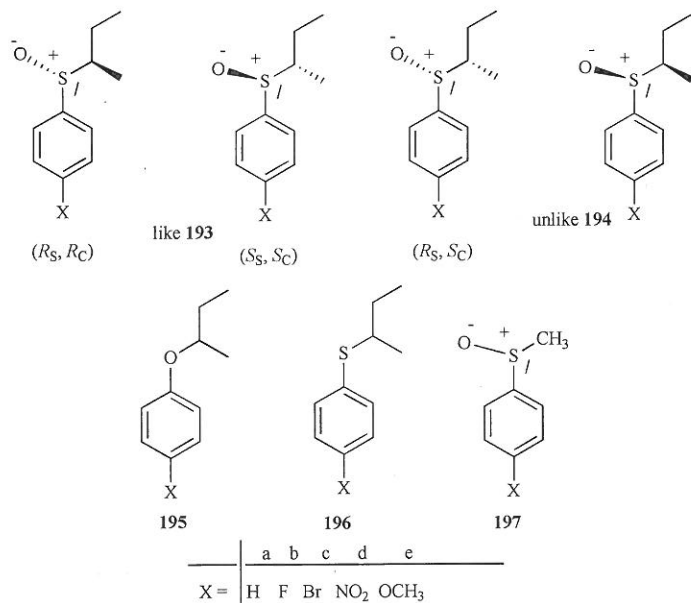
Fig. (27). The Structure of ligands that bind with dirhodium complex **67**.

R =

33c   **67**   **192**

198   **13**   **198**

33b   **32b**   **33c**

200   **201**   **34c**

47a   **202**

Ligands:

X = Se-Ph **188**   S-Ph **189**   -O-C(=O)-CH₃ **190**   O-Ph **191**   PPh₂

Fig. (28). Structure of dirhodium tetracarboxylate complexes and the ligands investigated.
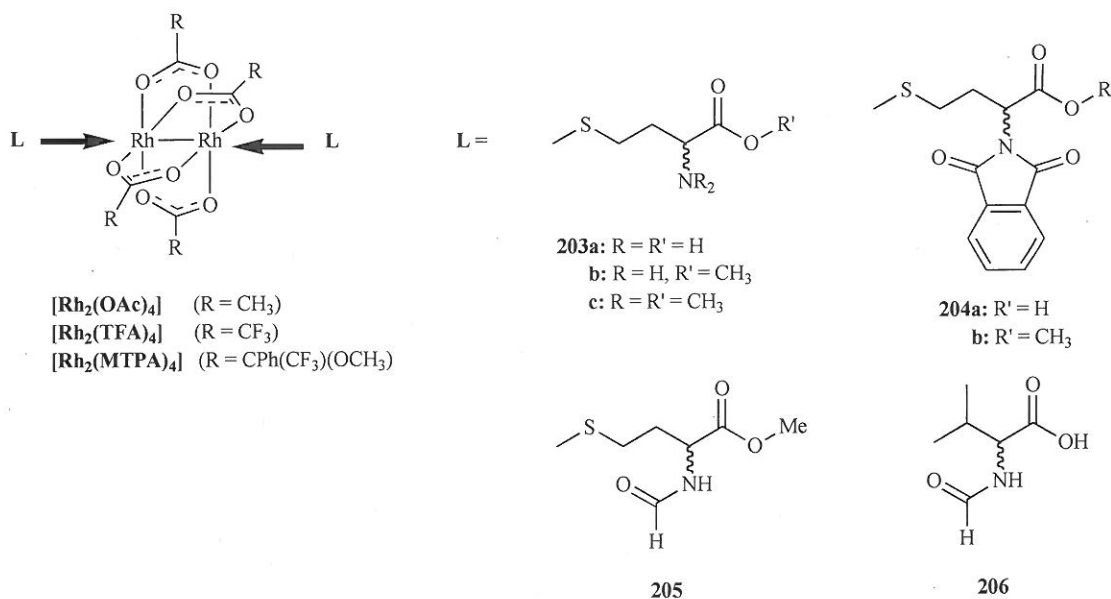
Fig. (29). Dirhodium salts and ligands studied. The arrows mark are able to bound the axial positions of the dirhodium salts where the organic ligands.

Fig. (30). Dimeric Dirhodium(II) tetracarboxylates and amines used as ligands.

ally used as a chiral auxiliary. Both complexes **67** and **34c** are recommended as chiral auxiliaries for the dirhodium method as they enhance the dispersion effects $(\delta v)^*$. On contrast, in case of complex **32b** it reduces the dispersion effect value (δv); as a consequence, this complex is unqualified to be used as a chiral auxiliary.

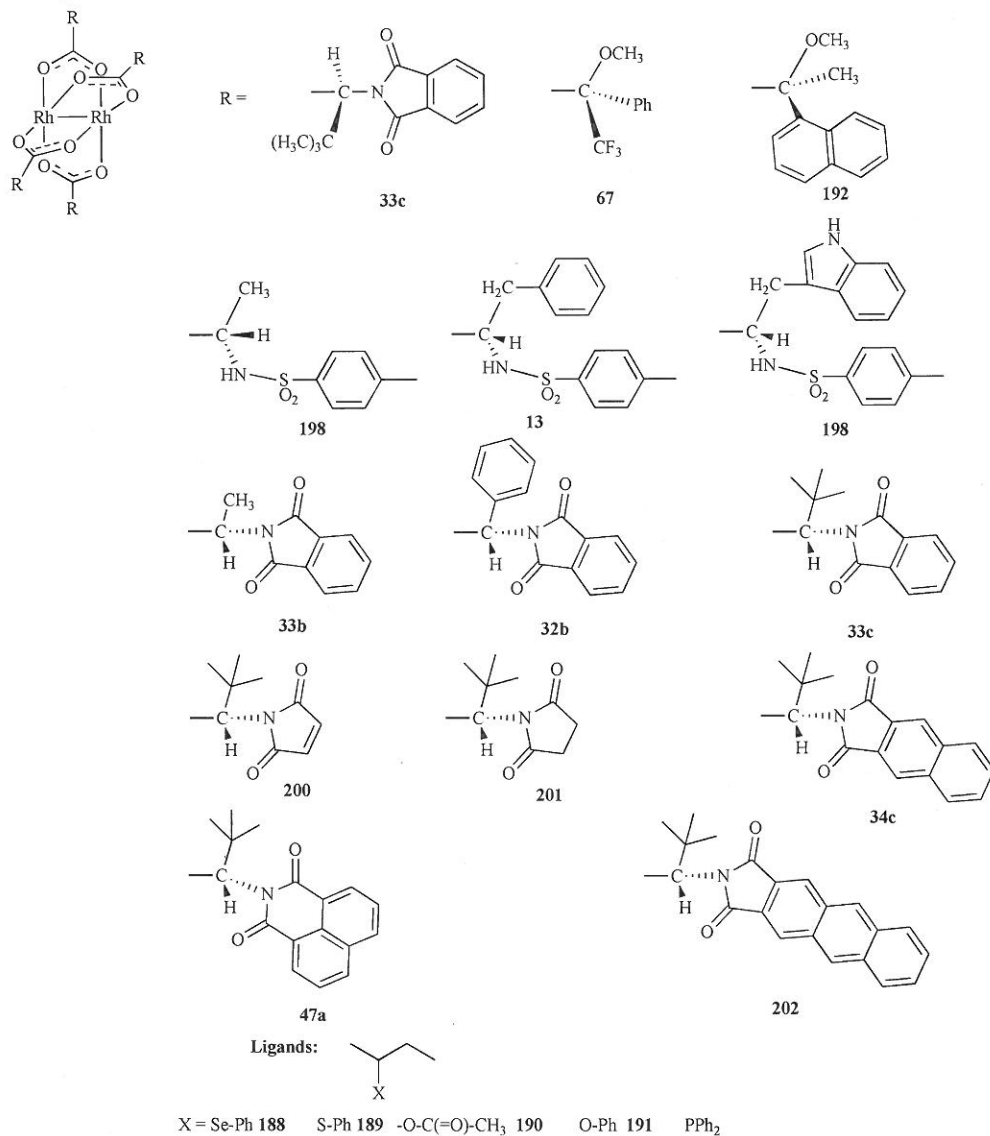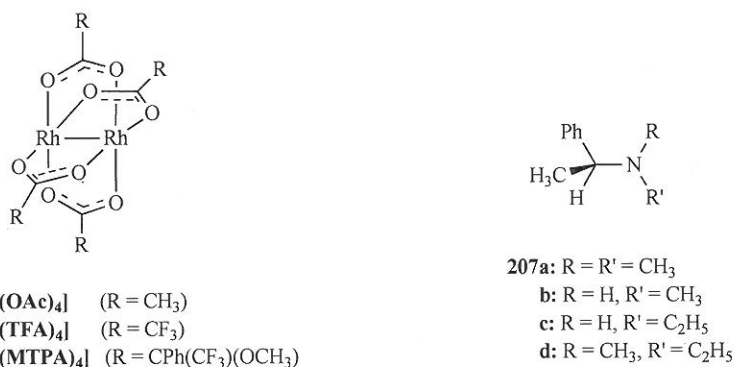Głaszczka *et al.* [104] have also studied the complexation effects of different rhodium(II) dimeric tetraacylates (i.e., tetraacetate [Rh$_2$(OAc)$_4$], tetratrifluoroacetate [Rh$_2$(TFA)$_4$], and (S)-Mosher's acid salt [Rh$_2$(MTPA)$_4$] **67**) with both enantiomerically pure and racemic methionine and its derivatives **203-206** (i.e. hydrochloric salt of methionine, hydrochloric salt of methionine methyl ester, N-formyl methionine, N-phthaloyl methionine, N-phthaloyl methyl ester of methionine, and methyl ester of N,N-dimethylmethionine) (Fig. **29**) which was investigated by means of ^{1}H and ^{13}C NMR and absorption electronic spectroscopy in the visible range. All ligands have been investigated form 1:1 and 1:2 adducts in solution, depending on the rhodium salt to ligand molar ratios. The complexation site in the ligands (S atom) was deduced on the basis of the NMR parameter adduct formation shift ($\Delta\delta = \delta_{adduct} - \delta_{ligand}$) and calculated chemical shifts (DFT, NMR GIAO). In the cases of the [Rh$_2$(TFA)$_4$] and [Rh$_2$(MTPA)$_4$] adducts, decreasing the temperature within the range 220-254 K slowed down the ligand exchange

and allowed the researchers to observe the signals of all diastereoisomers in the ^{1}H and ^{13}C NMR spectra.

The configuration of nitrogenous stereogenic centres in adducts of rhodium(II) tetraacylates with chiral amines **207**, as shown in Fig. (**30**), was studied by Jaźwiński and Sadlej [105] through ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra of enantiomerically pure amines as (S)-N,N-dimethyl-1-phenylethylamine, (S)-N-methyl-1-phenylethylamine, (S)-N-ethyl-1-phenylethylamine and (S)-N-ethyl-N-methyl-1-phenylethylamine in the presence of a twofold molar excess of dirhodium(II) tetratrifluoroacetate and Mosher's acid derivatives [(4S) and (4R)] were measured in CDCl$_3$ as a solvent. The amines having various substituents at the nitrogen atom (H, CH$_3$ and CH$_2$CH$_3$) are formed in such conditions as an equilibrium mixture of C$_S$N$_R$ and C$_S$N$_S$ 1:1 adducts**. The signals of both diastereoisomers were observed in NMR spectra at either room temperature (303K) or moderately decreased temperatures (263-273K). The rates of mutual diastereoisomer conversion were estimated by selective inversion recovery experiments and varied from less than 0.1 to ca. 10s^{-1}, depending on the nature of the ligand and temperature. The analysis of ^{13}C NMR and NOE experimental

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*Larger δ v restrict the conformational mobility of ligands within the molecule.

**C$_S$N$_R$ and C$_S$N$_S$ means the mutual exchange of two non-equivalent N(CH$_3$)$_2$ groups led to the presence of two side for attack (pro-R to pro-S and vice versa) of the rhodium salt to the nitrogen atom in the adduct and structure inversion (SN^2-like mechanism) or via adduct dissociation, ligand inversion and adduct recombination.
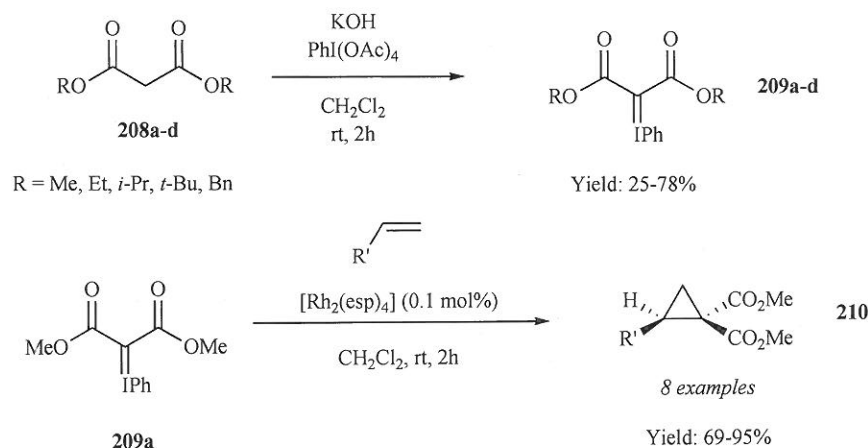
Fig. (31). Intermolecular cyclopropanation reaction.

data resulted in an unambiguous determination of the configuration at the nitrogen atom with respect to the carbon stereogenic center. Modeling of adduct structures and calculations of molecular energy and NMR parameters (GIAO) using Density Functional Theory (DFT) were performed in order to support the experimental findings. The calculations have been carried out using 3-21G//B3LYP (structure optimizing) and 311G(2d,p)/LanL2DZ//B3LYP theory levels (molecular energy and NMR shielding). The catalytic activity of these complexes have not yet been studied.

Recently, Szilvagyi *et al.* [106] reported the vibrational circular dichroism (VCD) and electronic circular dichroism (ECD) spectroscopic studies for the chiral Rh₂(O-Phe-Cbz).(OAc)₃ and Rh₂(O-Phe-Ac).(OAc)₃ complexes and supported their studies by theoretical calculations. The ECD spectra of complexes, depending on temperature, indicated that there was a conformational mobility of the chiral ligands and, also, calculations of the VCD spectra of the conformers were in an excellent agreement with the experimintal VCD spectra. As a result, the combination of VCD and ECD spectroscopic methods led to the structure characterization of the complexes.

3. APPLICATIONS

The decomposition of diazoketones and diazoesters in the presence of chiral transition metal catalysts has a remarkable potential for asymmetric catalysis [13,107]. Phenyliodonium ylids are potential substitutes for diazo compounds in metal-carbenoid reactions [108-110]. They are readily accessible by reaction of C-H acidic compounds with iodobenzene diacetate, (**80**; PhI(OAc)₂) giving rise to the product as an amorphous solids or oils. Often, their decomposition occurs at temperatures well below those required for diazo decomposition. The main potential for phenyliodonium ylids is not only for their photochemical, [111,112] thermal [113], and transition metal-catalysed decompositions [113,114] and higher reactivity versus diazo compounds, but also because of the possibility to carry out carbene transfer in a one-pot procedure in which the phenyliodonium ylide is generated. Also, the decomposition *in situ* in the presence of a transition metal catalyst and accordingly, carbene or carbenoid intermediates are usually assumed to be involved in these reactions [51,109,115-119]. Recently, the employment of iodonium ylides in this chemistry has shown appealing complementary reactivity to that of diazo compounds [51,109,115-128]. Thus, we report here the recent applications that show the utility of phenyliodonium ylides as a carbenoid precursor for chiral dirhodium catalyzed reactions.

Catalytic intramolecular C-H insertion reaction of metal-carbenoids is a powerful tool for the formation of five-membered rings and, occasionally, other ring sizes [10,16]. In 2008, Zalatan and Du Bois [60] described a novel method for the enantioselective synthesis of cyclic sulfamate esters using an asymmetric C-H amination reaction from the prochiral sulfamate ester [61], catalyzed by [Rh₂(S-nap)₄] as previsouly shown in scheme 7. A chiral valerolactam-derived, dirhodium(II) complex affords some of the highest levels of asymmetric control in cyclization reactions. Interestingly, the chemoselective allylic C-H insertion has shown to be dependent on the olefin geometry.

In 2009, Charette *et al.* [129] reported the general method to access phenyliodonium ylides **209** from malonate esters **208**. These ylides provide an easy access to a variety of useful 1,1-cyclopropane diesters **210** using dirhodium catalysts [Rh₂(esp)₄] (Fig. **31**).

Hashimoto and coworkers [50], in 2008 disclosed the first example for the enantioselective amination for an allylic C-H bond of silyl enol ethers **212** derived from cyclic ketones **211** or enones of six-membered-rings by using [(2-nitrophenylsulfonyl)imino]phenyliodinane (**213**; NsN=IPh) as a nitrogen precursor catalyzed by dirhodium(II) tetrakis[N-tetrachlorophthaloyl-(S)-*tert*-leucinate] complex **33e** [144, 145], [Rh₂(S-TCPTTL)₄] which has provided, after desilylation, N-pNs-protected (S)-β-aminocyclohexanone **215** as a sole product in up to 72% *ee* (Fig. **32**).

Hashimoto *et al.* have also developed a new, concise, and catalytic asymmetric route to the 5,11-methanomorphanthridine Amaryllidaceae (-)-pancracine **219** [130,131] from 2-cyclohexen-1-one of which a key feature of this synthetic strategy is the use of a one-pot **33e**-catalyzed sequential 1,4-hydrosilylation/enantioselective C-H amination of 2-cyclohexen-1-one **209**, followed by N-alkylation of the NpNs-protected β-amino silyl enol ether **215** (Fig. **33**).

Ghanem *et al.* [42] in 2010 reported the one-pot procedure for carbene transfer reaction by using CH acidic reagents such as **49** (as shown in Fig. **11**) or **208a** (Fig. **34**) in the presence of appropriate catalysts **47** and **48** which allows the generation and enantioselective transfer of metallocarbenes without any need for preparing undesirable diazo precursors or isolating the often unstable phenyliodonium ylide intermediates. Ghanem *et al.* also reported that the cyclopropanes were afforded in up to 92% yield with 98% *ee*. *tert*-Leucinate protected with 4-Br substituted 1,8-naphthalic anhydride are found to afford an exceptionally selective ligand. In contrast, unsatisfactory results were obtained with the 1,8-naphthoyl-protected phenylalaninate-based system. The presence of halogen in
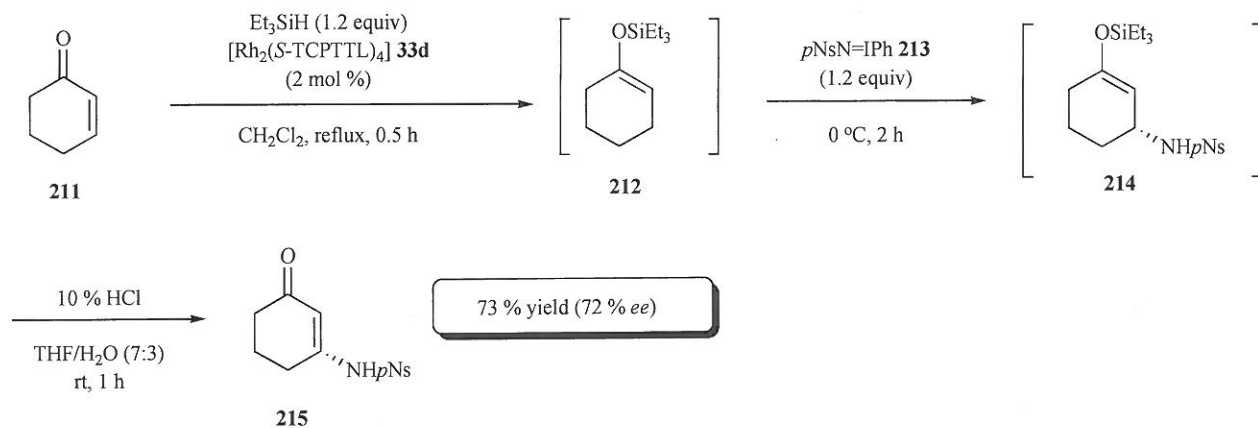
Fig. (32). One pot sequential 1,4-hydrosilylation/enantioselective C-H amination.
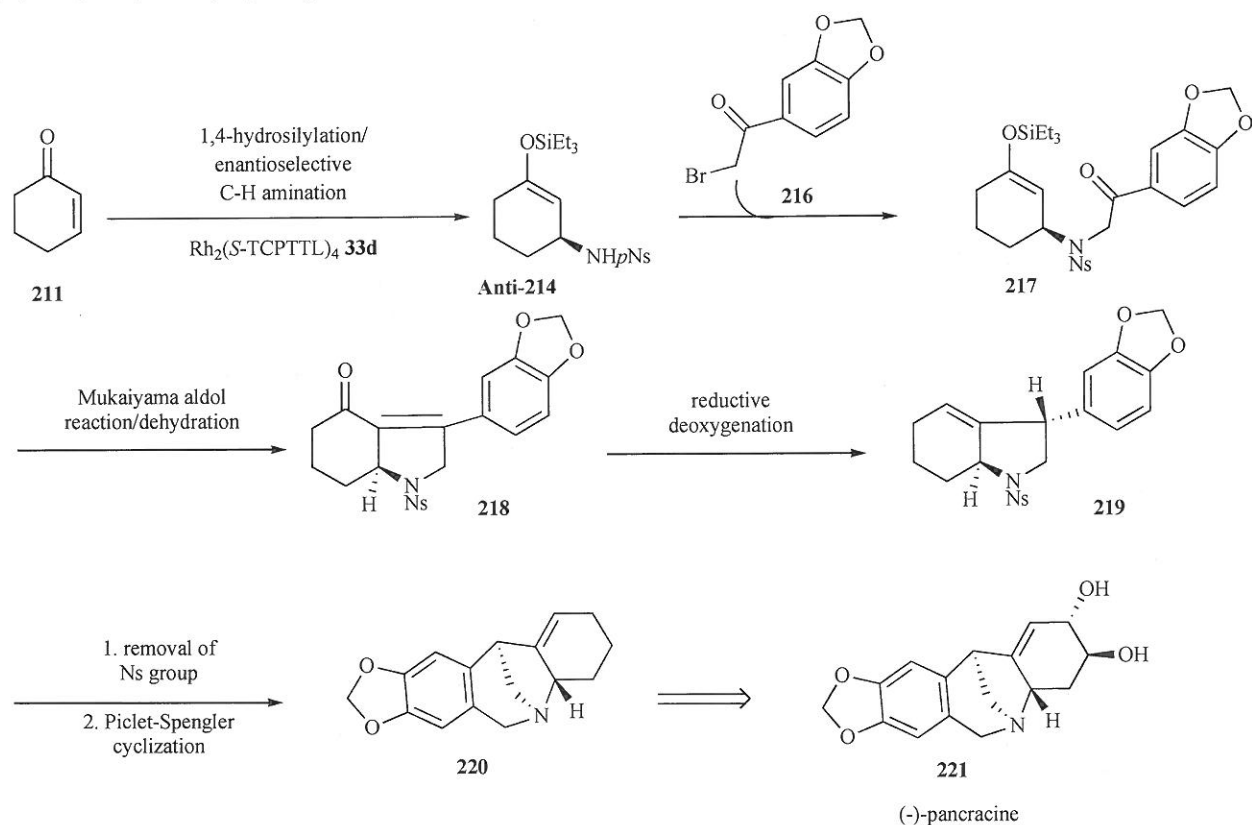
Fig. (33). Synthetic strategy for (-) Pancracine.
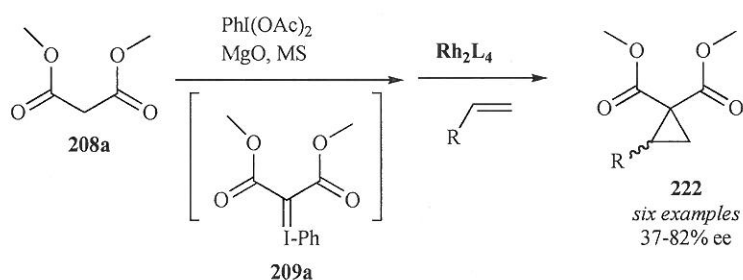
Fig. (34). Intermolecular cyclopropanation reaction.

the ring have greatly improved enantioselectivity through the cavity rim steric impedance due to the greater rigidity of the cavity corners in accounting for enhanced catalytic selectivity.

Kang and Lee [132] developed a highly efficient, enantioselective sequence for the synthesis of the antidepressant (*S*)- and (*R*)-dapoxetine **228** through the intermediacy pathways of the 6-

(a)

(b)
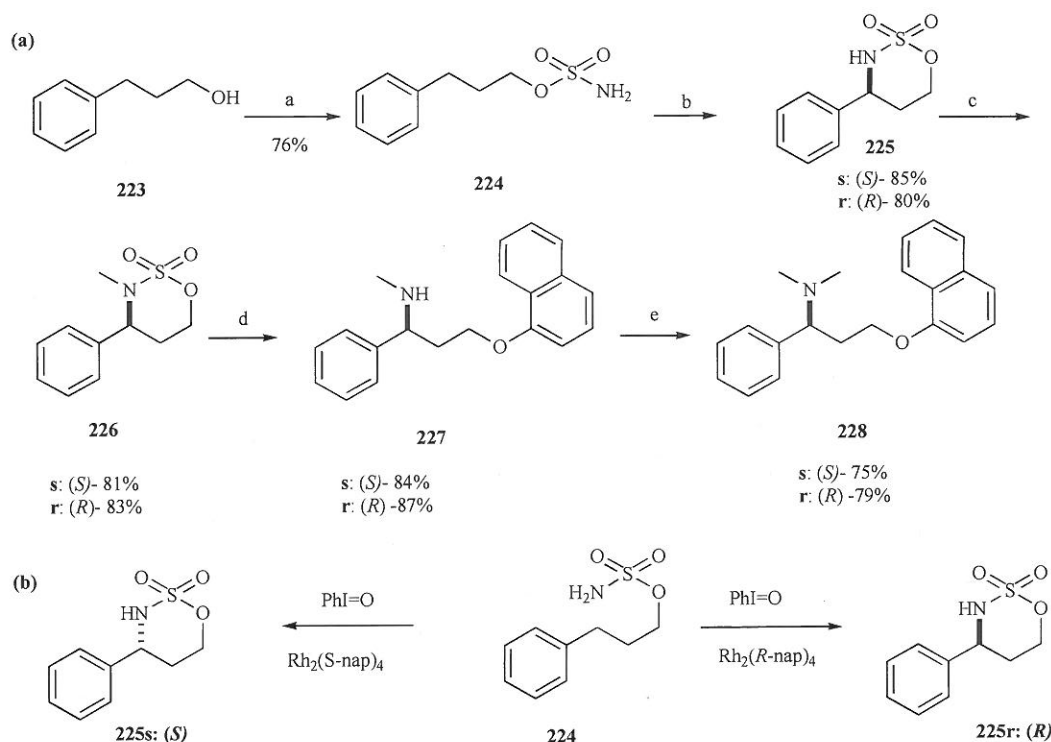
Reagent and conditions: (a) ClSO$_2$NH$_2$, DMA, 0 °C to rt; (b) 2 mol% Rh$_2$(S-nap)$_4$, PhI=O, 4 Å MS, CH$_2$Cl$_2$, rt; (c) CH$_3$I, K$_2$CO$_3$, cat. T BAI, DMF, 0 °C to rt; (d) NaH, 1-naphthol, DMF then 5 M HCl, rt; (e) HCO$_2$H, HCOH, reflux.

Fig. (35). (a) Synthetic process to Dapoxetine **228** from 3-phenyl-1-propanol **223**; (b) Du Bois asymmetric C-H amination reaction of **226** with respective Rh$_2$(S-nap)$_4$ and Rh$_2$(R-nap)$_4$ catalysts.

membered-ring sulfamate esters **225**, which have been generated by Du Bois' asymmetric C-H amination reactions of the prochiral sulfamate **224** [60], catalyzed by the chiral dirhodium(II) complexes [Rh$_2$(S-nap)$_4$] and [Rh$_2$(R-nap)$_4$], (Fig. **35**).

The absolute configuration of the enantiomer of 4-phenyl[1,2,3]oxathiazinane 2,2-dioxide (**225r**), prepared by the Du Bois asymmetric C-H amination reaction of **224** and the Rh$_2$(S-nap)$_4$ catalyst, has been found to be *R* not *S* (confirmed by X-ray crystal structure analysis), as reported before [60].

Since 2011, Collet and co-worker [133] studied the catalytic stereoselective intermolecular C-H amination of dirhodium complex [134-139] [Rh$_2$(S-NTA)$_4$] **229** on different substrate categories (i.e., benzylic C-H amination cyclic substrates, benzylic C-H amination of linear substrates, and alyllic C-H amination of terpens) (Table **3**). They have found that the complex is site selective giving very good yields up to 91% with exceptional levels of regio-, chemo- and stereoselectivity (up to 99%). The researchers have also stated their attempt to propose the nitrine C-H insertion mechanism by physical organic experiments. However, these have turned out to be poorly informative since they do not allow the researchers to discriminate between a concerted and a stepwise pathway for the nitrene C-H insertion.

Recently, Du Bois highlighted the remarkable versatility of dirhodium based catalysts for promoting oxidation of aliphatic C-H centers in both intra- and intermolecular reaction processses [140].

In 2011, Goto and coworkers, after previously demonstrated the first examples of highly enantio-, diastereo- and chemoselective intramolecular C-H insertion reactions of α-alkyl-α-diazo-esters by using dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-tert-leucinate] (Rh$_2$(S-pttl)$_4$) in which high levels of asymmetric induction (up to 95% *ee*)

Table 3. C-H Amination of Differennt Substrate Categories

Rh$_2$(*S*-NTA)$_4$　　**229**

Benzylic C-H amination of cyclic substrates		
230	1.2 equiv S$^{(S)}$NH$_2$ **231** 3 mol% Rh$_2$(S-NTA)$_4$ **229** 1.4 eqiv Ph(O$_2$C^{t}Bu)$_2$	**232**
Benzylic C-H amination of linear substrates		
233	1.2 equiv S$^{(S)}$NH$_2$* **231** 3 mol% Rh$_2$(S-NTA)$_4$ **229** 1.4 eqiv Ph(O$_2$C^{t}Bu)$_2$	**234**
Allylic C-H amination of terpenes		
235	1.2 equiv S$^{(S)}$NH$_2$ **231** 3 mol% Rh$_2$(S-NTA)$_4$ **229** 1.4 eqiv Ph(O$_2$C^{t}Bu)$_2$	**236**

*　S$^{(S)}$NH$_2$: *S*-Sulfonimidamide

Scheme 8.

R = H, Me, Et, *i*Pr, Ph
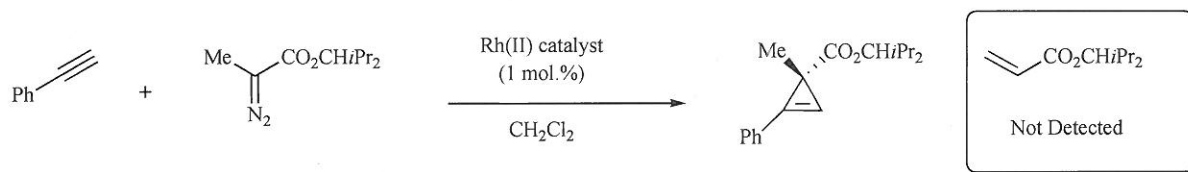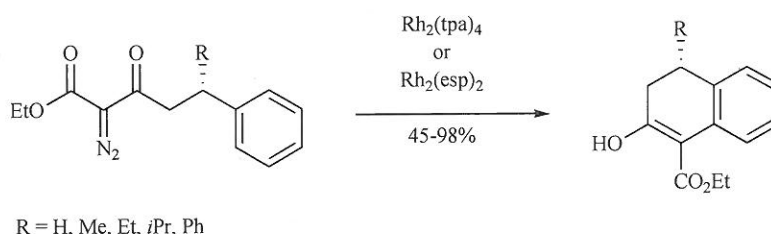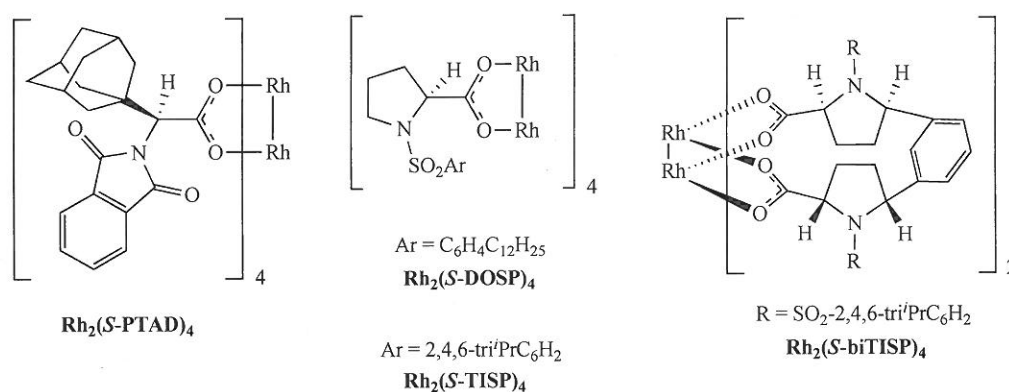
Scheme 9.

Fig. (36). Chiral dirhodium catalysts.
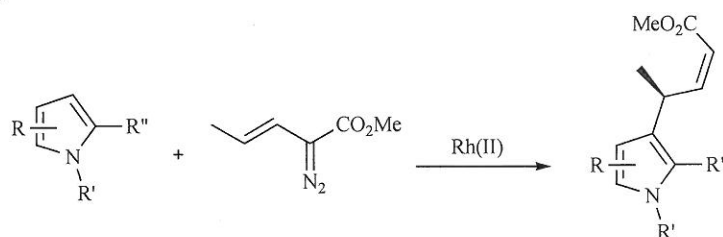
Scheme 10.

were achieved [94,141-143]. They reported that [Rh$_2$(*S*-topttl)$_4$], a new dirhodium(II) carboxylate complex that incorporates *N*-tetrabromophthaloyl-(*S*)-tert-leucinate as chiral bridging ligands, catalyzes the cyclopropanation reaction of terminal alkynes with 2,4-dimethyl-3-pentyl-α-alkyl-α-diazoacetates to give 1,2-disubstituted 2-cyclo-propenecarboxylates in good to high yields and with up to 99% *ee* [144] (Scheme **8**).

Recently, Cárdenas *et al.* [145] decided to investigate the Rh(II) carbenoid aromatic C-H insertion of α-diazo-β-ketoesters. They have shown a valuable chemoselective Rh(II) catalyzed C-H aromatic insertion reaction. The reaction involved the insertion of a carbenoid moiety into C-H aromatic bond, delivering a tetralin possessing a benzylic stereogenic center. Both Rh$_2$(tpa)$_4$ and Rh$_2$(esp)$_2$ were shown to be superior to a Rh$_2$(OAc)$_4$ catalyst for his chemoselective reaction (Scheme **9**), in addition to, good to excellent yields of the aromatic C-H insertion products were observed.

This is an alternative strategy to prepare tetralines carrying a methyl group on the benzylic position, a structural motif found in several types of natural products.

Yajing and Davies [146] described an approach for asymmetric functionalization of indoles and pyroles by exploring the vinylogous electrophilic character of vinyl carbenoids (Scheme **10**) in the presence of catalytic amounts of Rh$_2$(*S*-PTAD)$_4$, Rh$_2$(*S*-DOSP)$_4$, Rh$_2$(*S*-TISP)$_4$ and Rh$_2$(*S*-biTISP)$_4$ (Fig. **36**). They found that Rh$_2$(*S*-biTISP)$_4$ bridged dirhodium catalyst, not only, selectively enforces the reaction to occur at the vinylogous position of the carbenoid, but also, affords high levels of asymmetric induction.

Żukrzewska [147] has established the intramolecular C-H insertion of diazoacetamide using CO$_2$ as a solvent. This process afforded the expected lactams in yields over 97%. The asymmetric intramolecular C-H insertion was also achieved, and β-lactam was obtained in >97% yield and 65% *ee* using the chiral dirhodium(II) catalyst Rh$_2$(*S*-PTTL)$_4$. Finally, the dirhodium(II) complex Rh$_2$(OAc)$_2$ was used in two consecutive cycles in which a complete conversion to the lactam product was obtained (Scheme **11**). This recycling experiment demonstrated that CO$_2$ can be used as an efficient solvent for C-H insertions based on diazo-compounds/dirhodium(II) complexes and that the extraction with
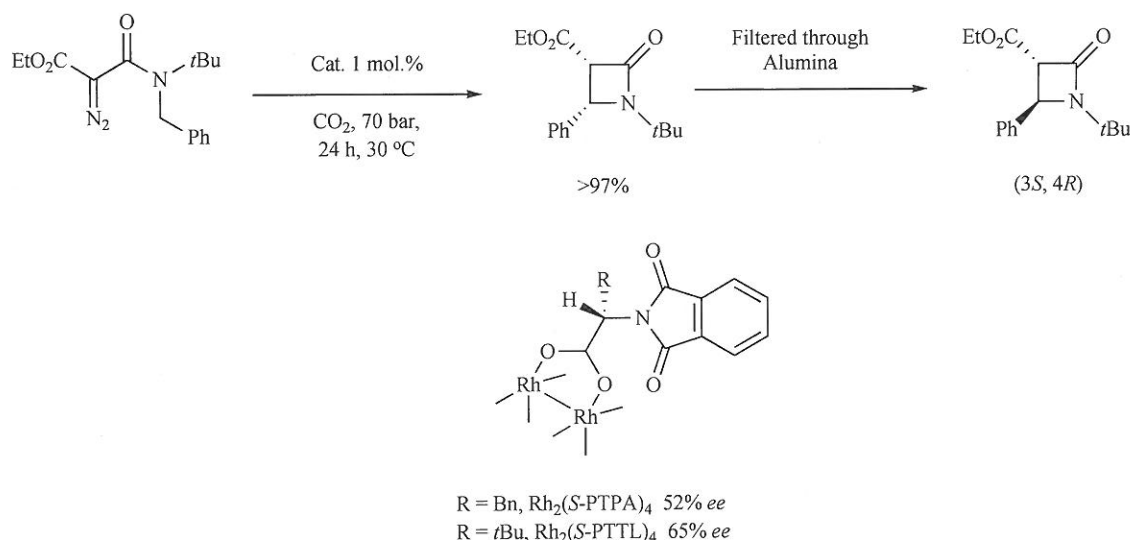
Scheme 11.

$scCO_2$ may indeed allow the catalyst reutilization and at the same time reduces the use of organic solvents in the isolation process.

4. CONCLUSION

Several classes of chiral dirhodium(II) complexes have been developed as catalysts in asymmetric catalysis. The review presented above covered the general preparation methods for most homogeneous chiral dirhodium(II) complexes that have appeared to date and their recent applications with a carbenoid precursors (i.e., iodonium ylides) in asymmetric catalysis. High symmetry chiral complexes can be readily prepared by coordination of several identical lower symmetry ligands onto the dirhodium centre. The development of dirhodium paddlewheel catalysts is highly dependent on the electronic and/or steric properties of the ligands and any modification in these properties will affect their reactivity. Indeed, the last 4 years have witnessed significant development in rationalizing the enantioinduction of chiral dirhodium catalysts in the point of view of advanced spectroscopic analysis and X-ray crystal structure.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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