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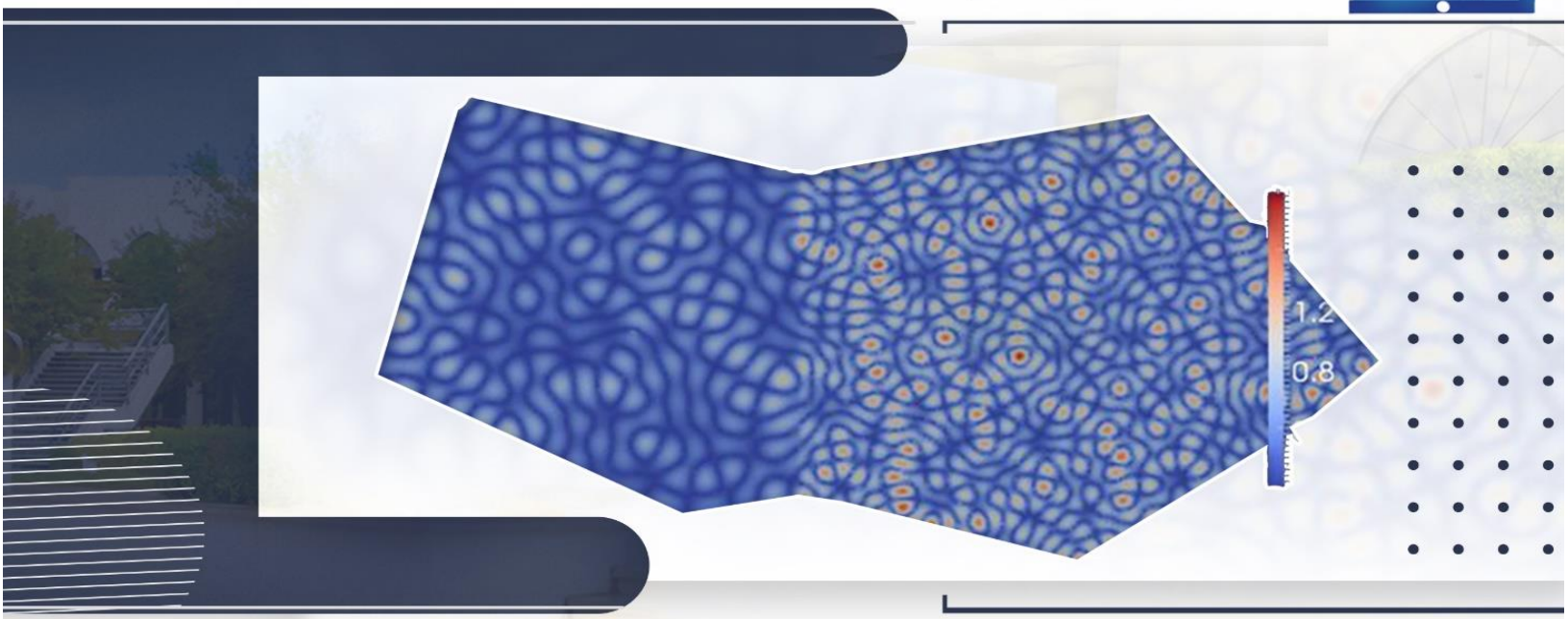

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Review Study of Chiral *N*-Heterocyclic Carbene (NHC) Ligands in Stereoselective Metal-Catalyzed Reduction Reactions

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A B S T R A C T

Stereoselective metal-catalyzed reactions using *N*-heterocyclic carbene (NHC) ligands have shown significant recent advances, due to the ability of NHC ligands as strong σ-donor species to coordinate with a wide variety of transition metals. Therefore, the design of new ligands and the subsequent strategies for their synthesis enables new applications of their metal complexes in catalysis to be investigated. This study focuses on the applications of different classes of Ir-, Pd-, Au- and Rh-NHC ligand complexes as promising catalysts in the asymmetric hydrogenation, hydrosilylation and transfer hydrogenation reactions.

1 Introduction

During the last two decades, *N*-heterocyclic carbenes (NHCs) as highly active and stable species have attracted considerable attention by chemists, due to their importance as versatile spectator ligands in the area of asymmetric metal-catalyzed reactions (César et al., 2004). Since the first reported stable NHC **1** by Arduengo (Figure 1) (Arduengo et al., 1991), tremendous advances on the design of NHCs and the application of their complexes in asymmetric catalysis have been achieved (Clavier et al., 2005). NHC ligands such as imidazolylidenes **2**, benzimidazolylidenes **3**, imidazolinylidenes **4** and triazolinylidines **5** are strong σ-donors and poor π-acceptors that form strong carbon-metal bonds. Therefore, catalysts derived from these ligands have better thermal and air stability than others containing phosphine ligands (Perry & Burgess, 2003). Many complexes derived from NHC ligands have been synthesized and applied in stereoselective catalysis, yielding high enantioselectivities. These include NHC-rhodium and -ruthenium complexes for asymmetric reduction of olefins and ketones.

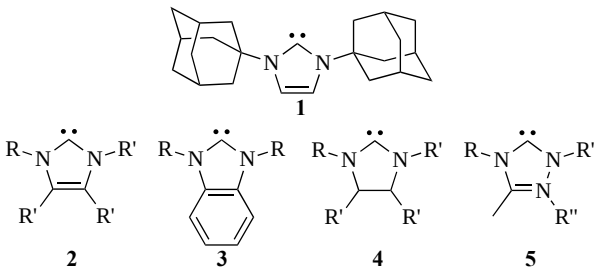

Figure 1. The first reported NHC ligand **1** and other NHC ligands **2**-**5**.

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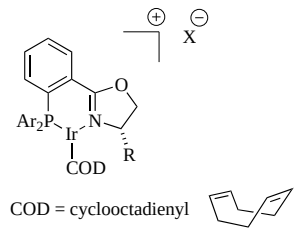
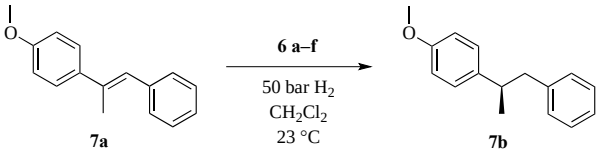
2 Stereoselective Hydrogenation

Stereoselective hydrogenation of alkenes is one of the earliest and important catalytic reactions, enabling the potential for the generation of stereogenic carbons. Ir-catalyzed hydrogenation of alkenes using phosphine-oxazoline ligands (Ir-PHOX complexes **6a-f**) was developed by Pfaltz and found to be one of the highly selective catalysts for wide variety of non-functionalized alkenes such as **7a**, affording the corresponding product **7b** in up to 98% ee and 99% yield (Scheme 1) (Lightfoot et al., 1998).



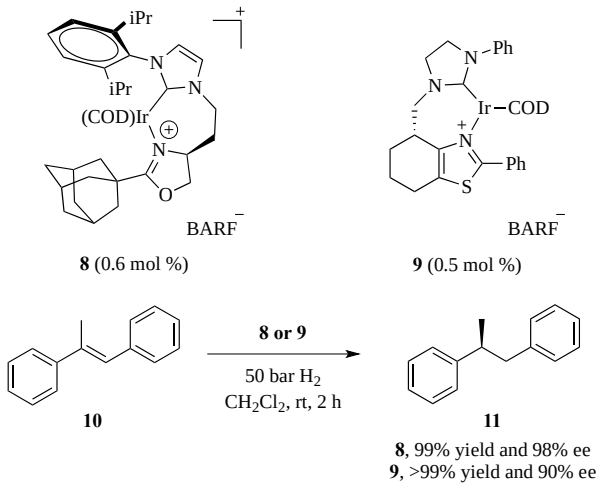
	Ar	R	X
6a	Ph	*i*Pr	PF_6
6b	Ph	*t*Bu	PF_6
6c	*o*-Tol	*i*Pr	PF_6
6d	*o*-Tol	*t*Bu	BARF
6e	Ph	*i*Pr	BARF
6f	*o*-Tol	*t*Bu	BARF



99% yield and up to 98% ee

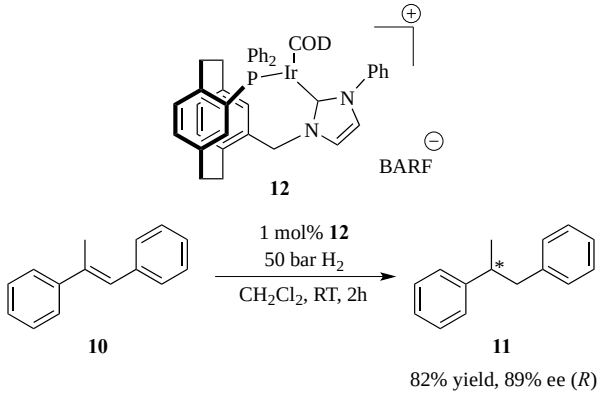
Scheme 1. Stereoselective hydrogenation of alkenes **7a** with Ir-PHOX complexes **6a-f**

Gade and Bellemin-Laponnaz (2007) reported the synthesis of a new type of NHC-Ir complex **8** containing NHC-oxazolines, and tested its catalytic activity in the stereoselective hydrogenation of non-functionalized alkenes, such as (*E*)-1,2-diphenyl propene (Gade & Bellemin-Laponnaz, 2007). This complex proved to be highly active and more selective than others from the same family, due to the electronic nature and the steric hindrance effects. The electronic effect forces the alkene towards the NHC to enable the steric effect to control the enantioface discrimination. The presence of the bulky adamantly group made the catalyst more efficient and highly selective, yielding **11** in excellent yield and enantioselectivity (99% yield, and 98% ee) (Scheme 2) (Gade & Bellemin-Laponnaz, 2007; Normand & Cavell, 2008). The Ir-NHC-thiozole complex **9** catalyzes the asymmetric hydrogenation of olefins with up to 90% ee and greater than 99% yield (Källström & Andersson, (2006).



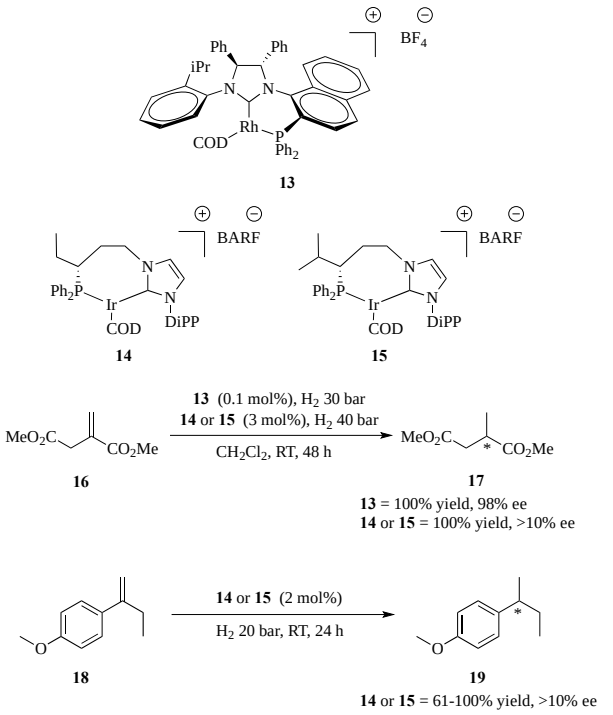
Scheme 2. Stereoselective hydrogenation of olefin **10** with chiral bidentate oxazoline- and thiazole-NHC-Ir complexes **8** and **9**.

Focken et al. (2004) reported the synthesis of iridium imidazolylidene complex **12** from a chiral phosphinoimidazolium salt (Focken et al. 2004). The asymmetric hydrogenation of simple and functionalized alkenes such as (*E*)-1,2-diphenyl-1-propene **10** gave the alkane **11** in high yield and enantioselectivity (up to 82% yield and up to 89% ee) using CH_2Cl_2 as a solvent at 25 °C (Scheme 3).



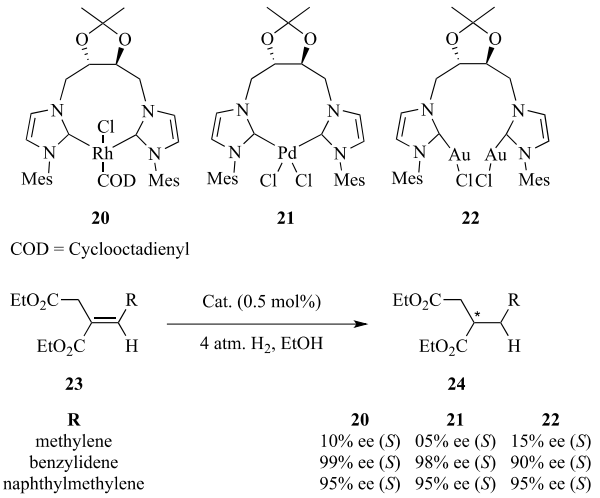
Scheme 3. The stereoselective hydrogenation of **10** catalyzed by complex **12**.

The *P*-functionalized Rh complex **13** hydrogenates dimethyl itaconate **16** with 98% ee. A wide variety of functionalized alkenes have been examined with complex **13**, giving the corresponding alcohols in up to 99% ee (Normand & Cavell, 2008). However, the Ir catalysts **14** and **15** displays poor catalytic activities towards the deactivated substrates **16** and **18**, giving the corresponding products **17** and **19** in lower enantioselectivities (> 10% ee) (Scheme 4) (Passays et al., 2011).



Scheme 4. The catalytic hydrogenation of the functionalized alkenes **16** and **18** with complexes **13**, **14** and **15**.

Arnanz et al. (2010) synthesized stable diimidazolidinylidene ligands linked by a *trans*-2,2-dimethyl-1,3-dioxolane and prepared chelated rhodium, palladium and gold complexes (*bis*-NHC-complexes) **20**, **21** and **22** (Arnanz et al. 2010). The efficiency of these catalysts was tested in the hydrogenation of (*E*)-diethyl-2-*R*-succinates **23** and showed high enantioselectivities, up to 99% (Scheme 5).



Scheme 5. The asymmetric hydrogenation of (*E*)-diethyl-2-(*R*)-succinates **23** with bis-NHC-complexes **20-22**.

3 Stereoselective Hydrosilylation

Stereoselective metal-catalyzed hydrosilylation of ketones using diphenylsilane is an important and efficient alternative process to the catalytic hydrogenation for the preparation of the corresponding chiral alcohols. This is advantageous as it uses mild conditions and avoids the over use of high pressure hydrogen (Kuang et al., 2009; Malkov et al., 2008).

Song et al. (2011) prepared three NHC-Rh complexes **25a-c** derived from dibenzimidazolium salts and tested their catalytic activities in the asymmetric hydrosilylation of acetophenone **27** under the reaction conditions given in table 1 (Song et al. 2011; Liu et al. 2009). The results show the importance of Rh-complexes as good catalysts for the catalytic hydrosilylation of acetophenones. Complex **25b** was found to be more selective than complex **25a** at 20 °C with 60% ee, due to the steric hindrance of the bulky substituents (entry 2), while 0% ee is observed with complex **25c** at the same temperature (entry 3), presumably because the bulky substituents are far from the metal center and are therefore outside the coordination sphere. By making the temperature lower with increasing the reaction time, the reduction product **28a** can be afforded in better enantioselectivities (54-70% ee) (entries 4-7) (Song et al. 2011).

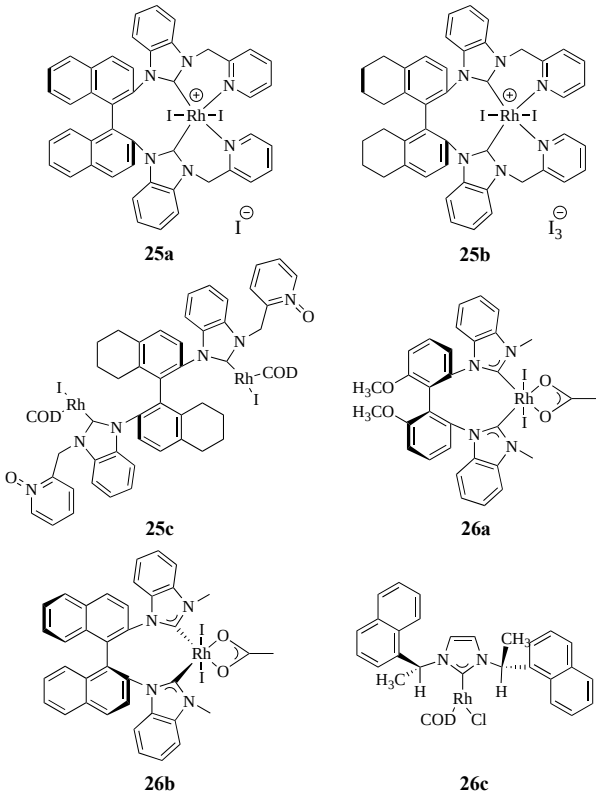
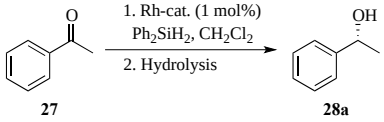


Figure 2. NHC-Rh complexes **25a-c** derived from dibenzimidazolium salts and bis NHC-Rh complexes **26a-c**

Shi and co-workers (2009) reported the use of *bis*-NHC-Rh complexes **26a-c** for the hydrosilylation of ketones (Normand & Cavell, 2008; Liu et al. 2009; Duan et al. 2003). It was found that using CH_2Cl_2 as the solvent, complex **26a** was ineffective (20% yield and 0% ee) (entry 8), while the reduction was proceeded with 55% ee and 70% yield using toluene. Furthermore, up to 98% and 32% enantioselectivities were afforded using complex **26b** and **26c** respectively (entries 10 and 11) (Liu et al. 2009).

Table 1. Stereoselective hydrosilylation of acetophenone **27** with Rh-catalysts **25a-c** and **26a-c**.

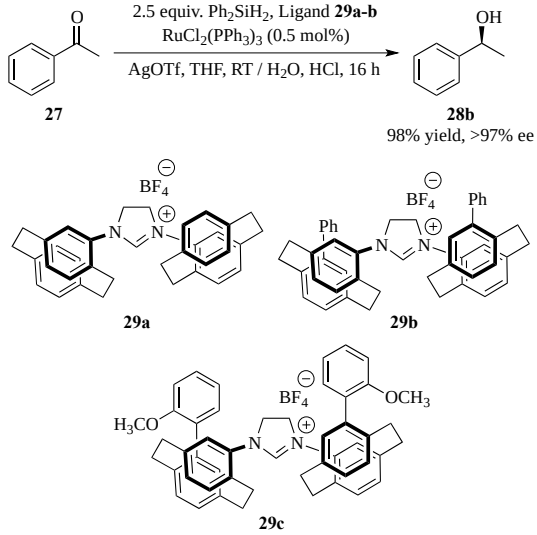


Entry	Complex	T °C	Time h	ee %	Yield %
1	**25a**	20	24	46	96
2	**25b**	20	24	60	90
3	**25c**	20	24	0	94
4	**25a**	0	36	54	82
5	**25b**	0	36	70	76
6	**25a**	– 20	72	56	54
7	**25b**	– 20	72	70	42
8	**26a**	25	48	0	20
9	**26a**[a]	25	48	55	70
10	**26b**	25	48	98	n.d.
11	**26c**	25	48	32	n.d.

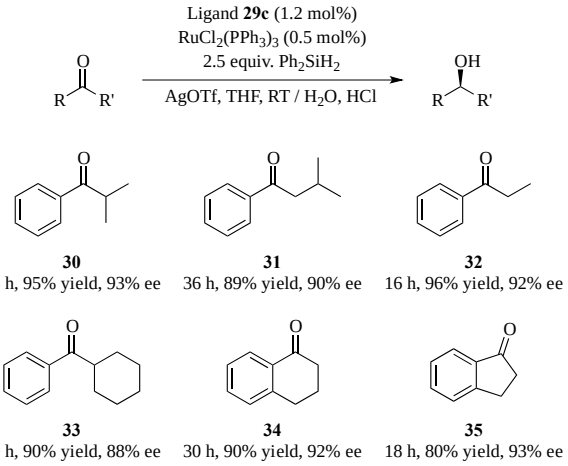
[a]Solvent = toluene

Bis-paracyclophane NHC-ligands **29a-b** have been synthesized from the known precursor (*Sp*-pseudo-orthobromoamino-[2.2]-paracyclophane). These ligands have been examined for Ru-catalysed asymmetric hydrosilylation of acetophenone **27** (under the conditions shown in scheme 6) to enantioenriched *S*-phenylethanol **28b** with 98% yield and 97% ee. Ligand **29c** was also used to optimize the reaction conditions. Different solvents were tested and THF proved to be the best for excellent enantioselectivities, where as using chloroform the selectivity reduced to 77%. Other solvents such as benzene, toluene and dioxane lowered the yield to 20%, 36% and 58% respectively, and poor selectivity was obtained using benzene and toluene. Further additives were also investigated such as using copper(II) triflate instead of silver(I) triflate, and this led to an increase in the reactivity with lowering the selectivity to 92% ee (Song et al. 2005).

The ligand **29c**-Ru combination has been also tested in asymmetric hydrosilylation of more hindered ketone substrates and gave high selectivities. For instance, isopropyl, sec-butyl and ethyl phenyl ketones **30-32** were afforded in excellent selectivities (up to 93% ee), as well as cyclohexylphenyl ketone **33**, benzocyclohexanone **34** and indanone **35** with enantiomeric excess of 88%, 92% and 93% respectively (Scheme 7).



Scheme 6. Hydrosilylation of acetophenone **27** with *bis*-paracyclophane NHC-ligands **29a-b**.

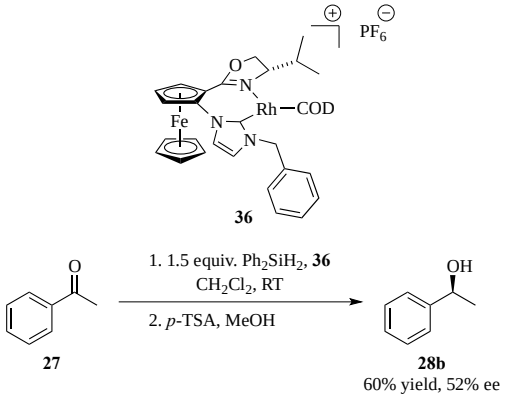


Scheme 7. Hydrosilylation of hindered ketone substrates with cyclophane ligand **29c**.

Kuang et al. (2009) reported the synthesis of NHC-oxazoline ligand **36** which has a rigid backbone consisting of an imidazole ring linked directly to ferrocene (Kuang et al., 2009). This new ligand was tested in the Ru-catalyzed asymmetric hydrosilylation of prochiral ketones, giving moderate enantioselectivity (52% ee) and reactivity (60% yield) (Scheme 8).

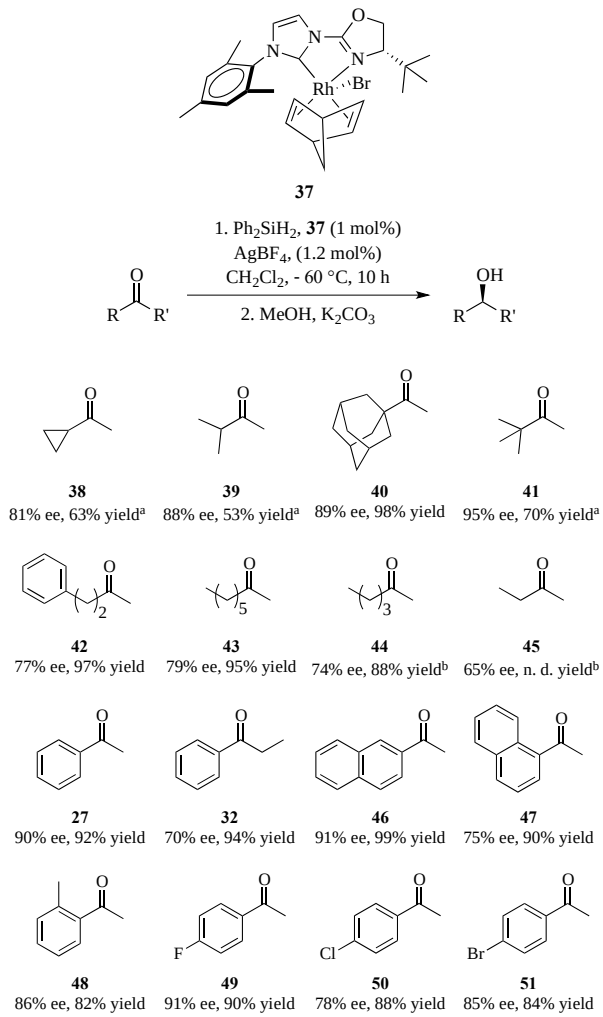
César et al. reported the synthesis of hydrosilylation catalysts derived from the condensation of both

oxazoline and imidazole rings (César et al., 2005). Among these catalysts, only **37** with the bulky ligand substituents such as mesitylene and *tert*-butyl gave the corresponding products in high yields and enantioselectivities. The catalyst **37** was exceptionally selected in the hydrosilylation of difficult unsymmetrical dialkyl and alkyl aryl ketone substrates. Dialkyl ketones have previously been reported to be difficult substrates to obtain high ee values in hydrosilylation reactions. The results shown in scheme 9 identified complex **37** as a highly selective catalyst for the nonaromatic ketones **38-45**. For example, cyclopropyl methyl ketone **38** gave the corresponding chiral alcohol with an ee value of 81% ee. The enantioselectivity can be superior using more highly steric alkyl groups such as *tert*-butyl methyl ketone **41**, reaching 95% ee. Furthermore, linear chain alkyl methyl ketone substrates **43-45** were obtained in moderate enantioselectivities (from 65% to 79%) (Scheme 9) (Gade & Bellemin-Laponnaz, 2007; César et al., 2005).



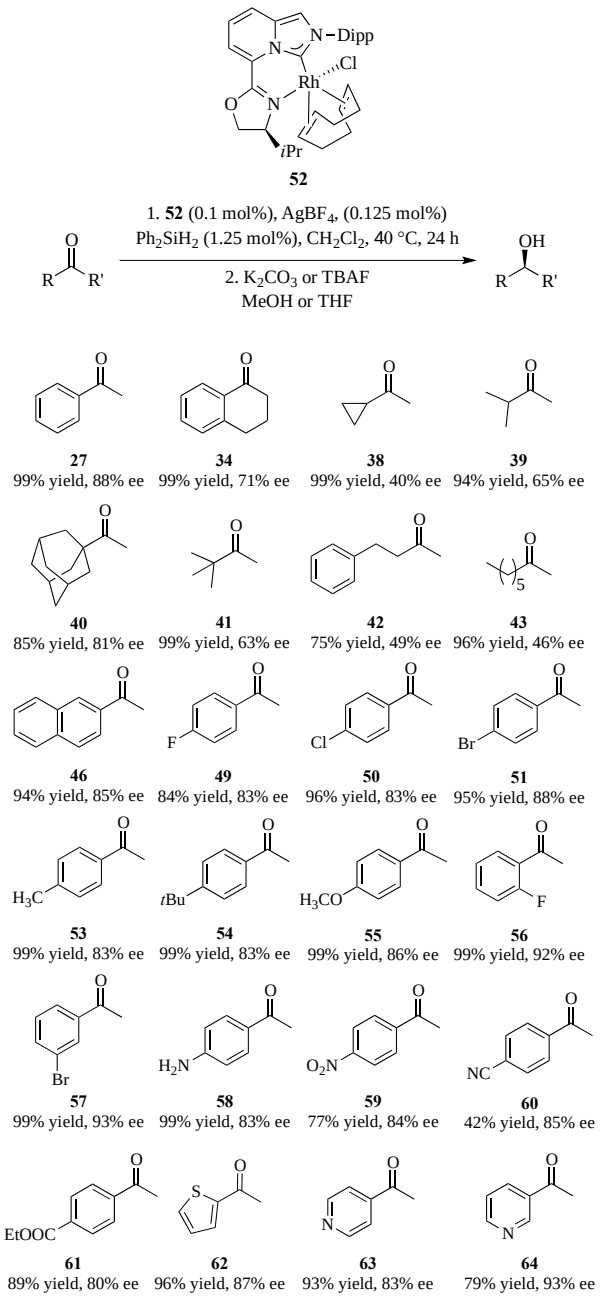
Scheme 8. Hydrosilylation of acetophenone **27** catalyzed by **36**.

In case of hydrosilylation of aryl ketones, complex **37** was similarly found to give high yields and enantioselectivities (César et al., 2005). For example, acetophenone **27** and 2-naphthyl methyl ketone **46** were produced in 90% and 91% ee (with 92% and 99% isolated yield) respectively. In addition, the effects of the reaction conditions such as solvent choice and temperature on the catalytic selectivity were also investigated with complex **37**. Solvent such as CH_2Cl_2 was found to be the best among different polar solvents that were tested, giving the best results. The effect of the temperature on the catalyst selectivity was also examined between –78 to 25 °C, and it was found that the highest enantioselectivity was obtained at –60 °C (up to 95% ee with different dialkyl and aryl alkyl ketones), while it drops with higher and lower temperatures (Gade & Bellemin-Laponnaz, 2007; César et al., 2005).



Scheme 9. Hydrosilylation of unsymmetrical dialkyl and alkyl aryl ketone substrates with catalyst **37** .[a]Moderate yield due to the volatility of the product. [b]Reaction carried out at –40 °C.

In a comparison with complex **37 (Scheme 9)**, Swamy et al. (2020), reported the synthesis of rhodium(I) complex **52**, with chiral bidentate NHC-oxazoline ligands (Swamy et al. 2020). This complex was found to be active for the asymmetric hydrosilylation of unsymmetrical dialkyl and alkyl-aryl ketone substrates. The corresponding alcohols were obtained in yields greater than 90% and up to 95% enantioselectivities (Scheme 10). It is worth noted that this catalyst was tested in different ketones bearing a wide range of functional groups as well as ketones bearing heterocyclic substituents such as **62-64**.

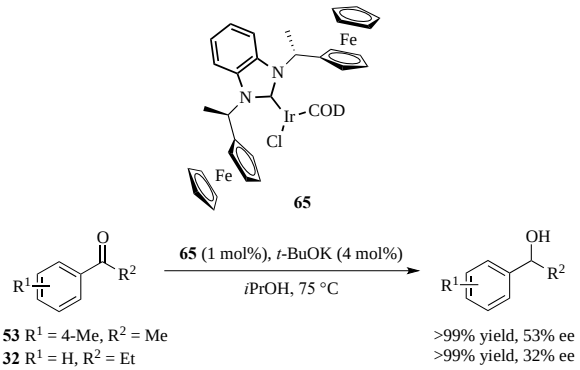


Scheme 10. Hydrosilylation of unsymmetrical dialkyl and alkyl aryl ketone substrates with catalyst **52**.

4 Stereoselective Transfer Hydrogenation

The catalytic asymmetric transfer hydrogenation of prochiral ketones is fundamentally an important synthetic reaction due to its simplistic operation with low cost reducing agents and the efficiency of this reaction as a synthetic route to optically active secondary alcohols (Jiang et al. 2009; Chiyojima et al. 2011). Although the asymmetric hydrogenation and hydrosilylation have shown a marked progress in the last two decades, only few studies were conducted on the asymmetric transfer hydrogenation using chiral NHCs.

Seo et al. (2003) reported the synthesis of the chiral ferrocenyl-NHC-Ir complex **65** for the asymmetric transfer hydrogenation of 4-methylacetophenone **53** and propiophenone **32**, giving the corresponding chiral alcohols with moderate enantioselectivities of 53% and 32% ee respectively. However, the selectivity was low or even racemic with other ketone substrates (Scheme 11) (Seo et al., 2003; Chiyojima et al. 2011).



Scheme 11. Stereoselective transfer hydrogenation of **32** and **53** with chiral ferrocenyl-NHC-Ir complex **65**.

Hodgson and Douthwaite (2005) synthesized a new class of chiral NHC-phosphine ligands **66a-e**, and investigated their applications in the asymmetric transfer hydrogenation of acetophenone (Figure 3). It was found that their complexes displayed poor selectivities with iridium(I) (11 - 37% ee) (Hodgson & Douthwaite, 2005).

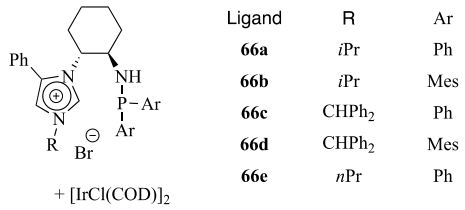
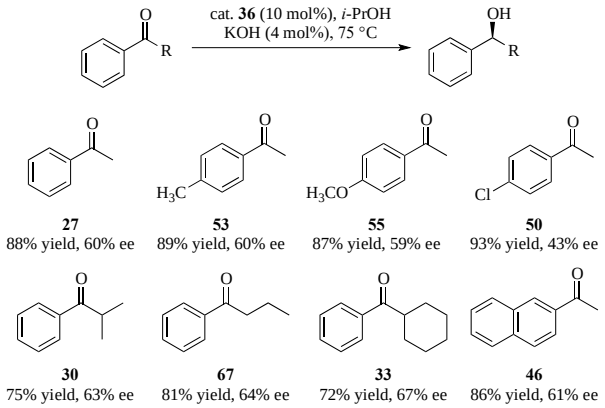


Figure 2. Chiral NHC-phosphine ligands **66a-e** and their application in asymmetric transfer hydrogenation.

The ferrocene based-NHC-Rh(I) complex **36** (previously shown in Scheme 8) was applied to the asymmetric transfer hydrogenation of aryl alkyl ketone substrates (Jiang et al. 2009). The catalytic activity of **36** was investigated under different reaction conditions and the highest selectivity was achieved by using KOH as a base at 75 °C. With these optimized conditions, various ketone substrates were examined (Scheme 12). The corresponding alcohols were afforded in slightly different yields and enantioselectivities, probably due to the effect of the electronic and steric properties of

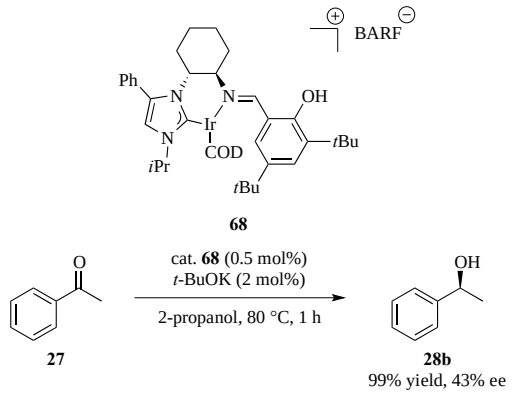
different aryl and alkyl ketones. The electron-donating substituents on the phenyl group of acetophenones such as methyl and methoxy (**53** and **55**) did not affect the yield or the selectivity of the corresponding product. On the other hand, the presence of an electron-withdrawing group such as chlorine (**50**) led to lower enantioselectivities and higher yields. Furthermore, the bulky R groups (*i*-propyl and *n*-propyl) on the ketone (**30** and **67**) can positively affect the selectivity with a negative effect on the reactivity. Finally, cyclohexyl phenyl ketone **33** gave the highest selectivity of 67% ee, while no considerable difference was shown on the reactivity and selectivity when the phenyl group replaced by naphthyl group **46** (Scheme 12).



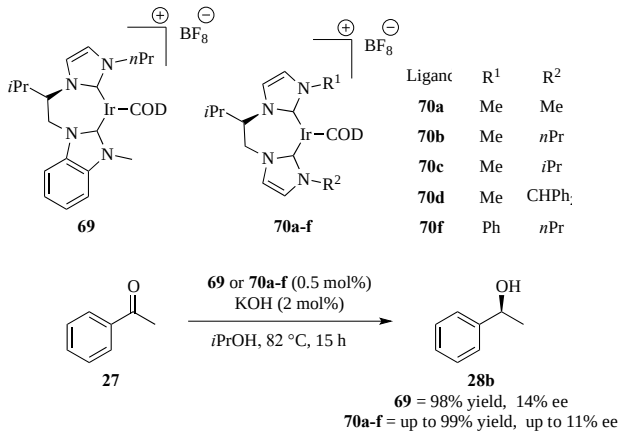
Scheme 12. The effects of the electronic and steric properties on the enantioselectivity of different aryl and alkyl ketones with NHC-Rh(I) **36**.

Dyson et al. (2009) reported the synthesis of iridium NHC–phenolimine complex **68** and tested its catalytic activities in the asymmetric transfer hydrogenation of acetophenone **27** (Scheme 13). The corresponding alcohol **28b** was obtained with moderate selectivity (43% ee) and high yield (99%). Complex **68** was also tested with other ketone substrates, in which lower enantioselectivities were obtained (Dyson et al., 2009).

Diez and Nagel (2010) reported the synthesis of novel chiral Ir(I)-*bis*(NHC) complexes **69** and **70a-f** and their applications in the catalytic transfer hydrogenation of acetophenone and its derivatives using isopropyl alcohol as a hydrogen donor. It was found that the corresponding alcohol products were obtained in high yields (up to 99%) with low enantioselectivity for acetophenone (11% ee), and higher enantioselectivities for more sterically hindered ketone substrates such as propiophenone, 2-methylpropiophenone, 2,2-dimethylpropiophenone, phenyl propyl ketone and mesityl methyl ketone (up to 68% ee) with all complexes shown in scheme 14 (Diez & Nagel, 2010).

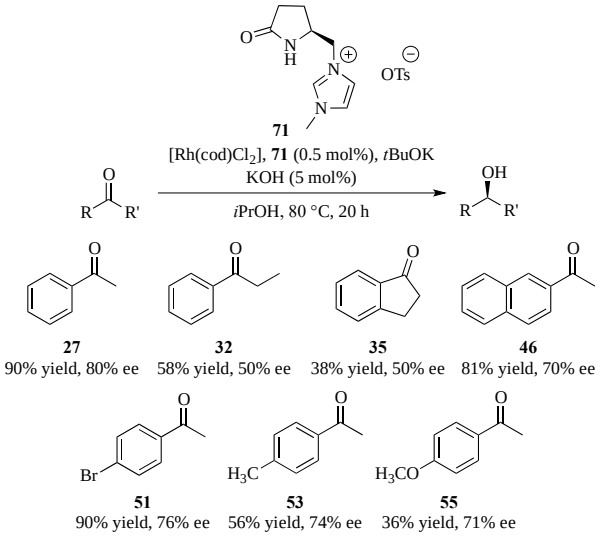


Scheme 13. Transfer hydrogenation of acetophenone **27** catalyzed by iridium NHC–phenolimine **68**.



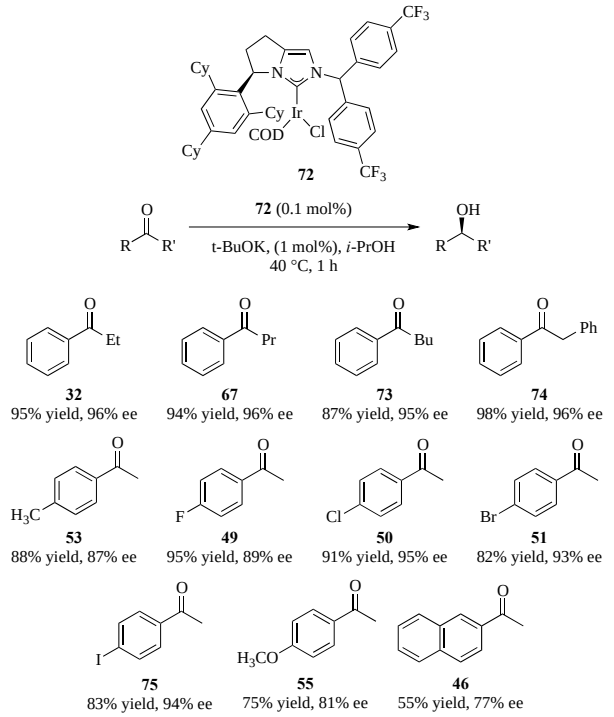
Scheme 14. The application of Ir(I)-*bis*(NHC) catalysts **69** and **70a-f** in asymmetric transfer hydrogenation of ketones.

The chiral NHC ligand **71**, prepared from (*S*)-pyroglutamic acid, was reported by Aupoix et al. (2011). This ligand was successfully applied in the rhodium-catalyzed asymmetric transfer hydrogenation of prochiral ketones using isopropanol as a hydrogen donor. High conversion and enantioselectivity were obtained for acetophenone (90% yield and 80% ee). Indeed, the results achieved using this ligand represented the highest enantioselectivities until the year 2011 for these types of reduction reactions. The imidazolium salt **71** was also tested in various ketone substrates giving the corresponding alcohols with good selectivities (up to 76% ee) (Scheme 15). Moreover, as previously mentioned, the electronic and steric properties of the ketone substituents can affect the yield and selectivity, such as electron-withdrawing groups, which led to lower enantiomeric excess and higher yields (Aupoix et al., 2011).



Scheme 15. Enantioselective transfer hydrogenation with NHC-Rh complex **71**.

Yoshida et al. (2015) have developed another successful example of NHC-Ir catalyst precursor **72** which was tested in the asymmetric transfer hydrogenation of acetophenone derivatives shown in scheme 16, giving the corresponding alcohols in excellent yields (up to 98%) and enantioselectivities (up to 96%) (Yoshida et al., 2015). The main reason of having such excellent results was using a bulky ligand substituent having an electron-withdrawing group.



Scheme 16. Enantioselective transfer hydrogenation of acetophenone derivatives with NHC-Ir complex **72**.

5 Conclusions

During the last two decades, different metal-NHC catalysts have been developed and applied in various types of asymmetric reactions. For example, Ir-NHC complexes, as well as other complexes have been used in the asymmetric hydrogenation of different functionalized and non-functionalized alkenes, affording the corresponding products in enantiomeric excess values ranged from 13-98% ee with up to 99% isolated yield. Rh-NHC catalysts proved to be highly active and selective in the stereoselective hydrosilylation of different ketone substrates, giving products with high enantioselectivities (up to 97% ee). Although the asymmetric hydrogenation and hydrosilylation reactions have shown considerable progress recently, only few studies have been conducted on the asymmetric transfer hydrogenation reactions using Ir-NHC catalysts, giving the corresponding products in moderate enantioselectivities (from 32-53% ee).

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