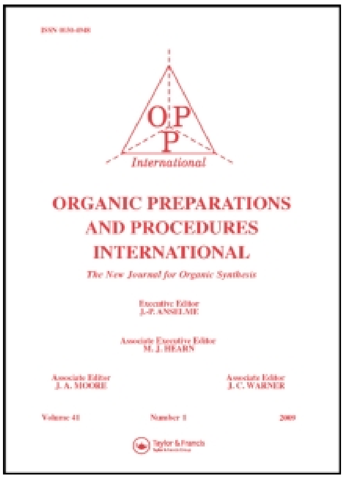

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INTRODUCTION

Reduction of carbonyl and pseudo-carbonyl functions represents a ubiquitous protocol in organic synthesis. Transition-metal catalysis has been successfully applied to the reduction of olefins, alkynes and many carbonyl compounds *via* hydrogenation or hydrosilylation.[1] Hydrogenation reactions often proceed in good yields but only under high pressure or elevated temperature. In contrast, since the first report of metal-catalyzed hydrosilylation of ketones in the presence of Wilkinson's catalyst,[2] smooth reaction conditions have been devised and in consequence over-reduced products are rarely detected. Furthermore, the development of chiral ligands has also allowed for the production of optically active products under mild and simple conditions.

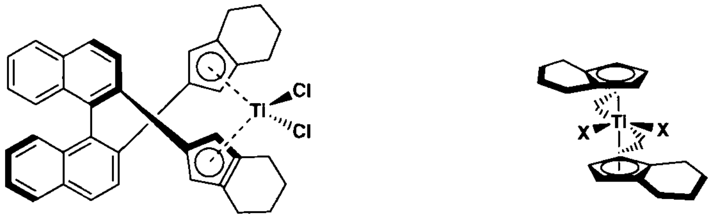
On the other hand, since a large number of multiple bonds may be involved, the hydrosilylation reaction can be regarded as a useful method for the synthesis of a whole family of silicon-containing organic molecules and/or a convenient way of reducing organic compounds. A sequence hydrosilylation/hydrolysis leads to the formation of alcohols and amines, but the silyl group may also be retained as a protecting group, a process that can be of great interest in organic synthesis. Moreover, the great majority of the hydrosilanes employed in this reaction are easy to handle and economical. PMHS (polymethylhydrosiloxane) deserves to be specifically mentioned as a very convenient and totally inexpensive reagent.

This review will give a general overview of the possible applications of metal-catalyzed hydrosilylation of carbonyl compounds. Although the article will focus on recent reports (1999–2006), a comprehensive historical development will also be presented.

I. GROUP 4 METAL CATALYSTS (Ti, Zr)

Metallocene derivatives of Group 4 are known mainly as catalysts for the dehydrogenative coupling of organosilanes,[3] *O*-silation of alcohols and aldehydes[4] and hydrosilylation of alkenes.[5] The first report of a titanium complex, Cp_2TiPh_2 for the hydrosilylation of ketones[6] and subsequent work on the chiral catalysts for this reaction represented a major breakthrough in the asymmetric reduction of ketones.

The activity of titanocene complexes bearing different chiral backbones was reported independently by Halterman,[7] Buchwald[8] and Harrod[9] (*Fig. 1*). The main drawbacks of these systems are the low enantioselectivities and the need of prior activation by treatment with an organolithium reagent (0.1 equiv for the first example, 2 equiv for the others) before the addition of the hydrosilane and the substrate.



Halterman, 1994

X = Cl or F Harrods, 1995
X = 1,1'-binaphth-2,2'-diolate Buchwald, 1994

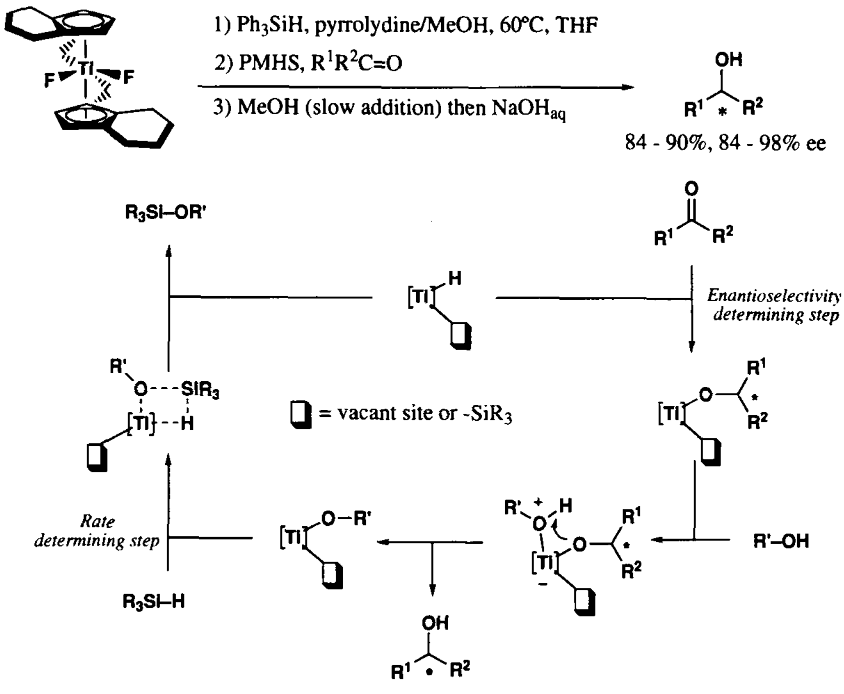
Titanium-based Pre-catalysts for the Hydrosilylation of Ketones

Fig.1

Since these initials reports, new catalytic systems based on chiral titanocenes, such as BINOL-derivatives or bisoxazolines have been published.[10] Notably, in 1999 Yun *et al.* reported the efficient hydrosilylation of conjugated ketones using PMHS as a stoichiometric reducing agent.[11] In this case, generation of a well-defined titanium(III) hydride from a difluorotitanocene and phenylsilane obviated the need of alkyllithium reagents for catalyst activation; and higher turnover numbers and enantioselectivities were achieved by slow addition of methanol to the catalyst. It has been postulated that the alcohol enhances the rate of σ-bond metathesis, the rate-determining step of the mechanism, because –OR' is smaller than $-O(CHR^1R^2)$ (*Scheme 1*). Minimization of non-selective reductive pathways with this system could explain the uniformly high ee's.

The reduction of esters to alcohols has been achieved in high yields under mild conditions with titanocene[12] or titanium alkoxide-based catalysts.[13] The latter systems have the advantage of being inexpensive, air-stable and is tolerated by a number of functional groups. These protocols can be extended efficiently to the reduction of lactones[14] or carboxylic acids, provided a large excess of silane is used.[15]

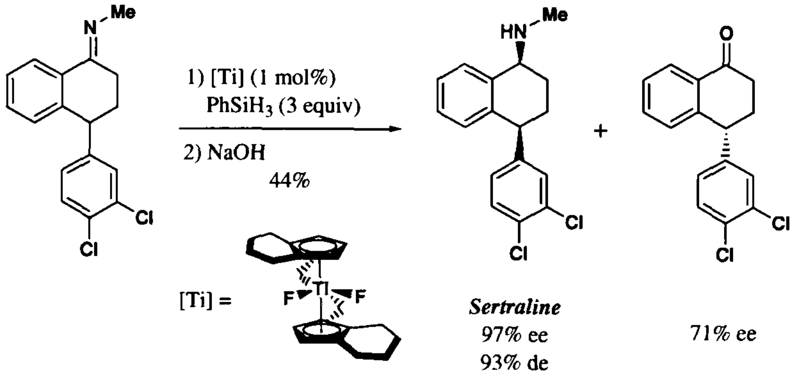
Concomitant with the development of catalyst for the hydrosilylation of ketones, Buchwald *et al.* also studied the reduction of imines. Similar systems allowed the preparation of amines under mild conditions and remarkable turnover number (TON) and ee's.[16] This technique has been successfully applied to the kinetic resolution of racemic acyclic *N*-methylimines



Enantioselective Hydrosilylation of Ketones and Postulated Mechanism

Scheme 1

of 3-substituted indanones and 4-substituted tetralones[17] to yield enantiomerically enriched ketones and amines. The synthesis of *sertraline*, a commercially available antidepressant, is a representative example for this methodology (*Scheme 2*).



Ti-Catalyzed kinetic resolution of imine

Scheme 2

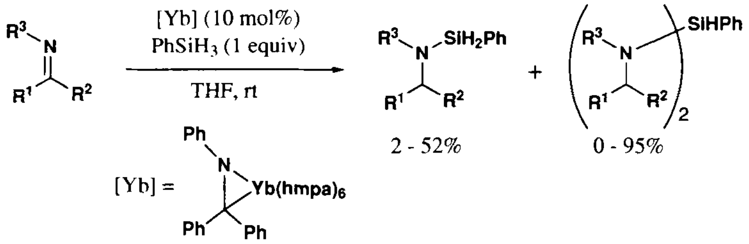
This reaction is extremely sensitive to the steric bulk on the nitrogen substituent due to the low rate of Ti–N cleavage in the titanium-imido intermediate with moderate to large nitrogen substituents. As it is well known,[18] the use of a nucleophilic additive renders the imido species more reactive, greatly expanding the scope of this system.[19] Among the tested nucleophiles, slow addition of primary amines such as isobutylamine provided the best results. Hydrosilylation of *N*-aryl imines of aromatic and non-aromatic ketones, regardless of the *E*:*Z* ratio of the starting material, was achieved in good yields.[20] Nevertheless, in the case of arylimines, a great disparity in the enantioselectivity of the reaction was observed.

Finally, the hydrosilylation of ketones by phenylsilane has also been achieved with dimethylzirconocene as catalyst.[21] Fair yields were obtained from simple aliphatic ketones but more sterically demanding ketones led to significant amounts of by-products.

II. LANTHANIDE-BASED CATALYST (Yb)

Most of the reported systems for the hydrosilylation of carbonyl compounds are based on late transition metal complexes. Apart from titanium, only scattered attention has been paid to early transition metal complexes.

The hydrosilylation of imines catalyzed by an ytterbium-imine complex was first reported by Takai *et al.*[22] With phenylsilane as the hydride source, a mixture of mono- and diaminosilanes was generally formed but more encumbered silanes were not efficient in this reaction (*Scheme 3*).



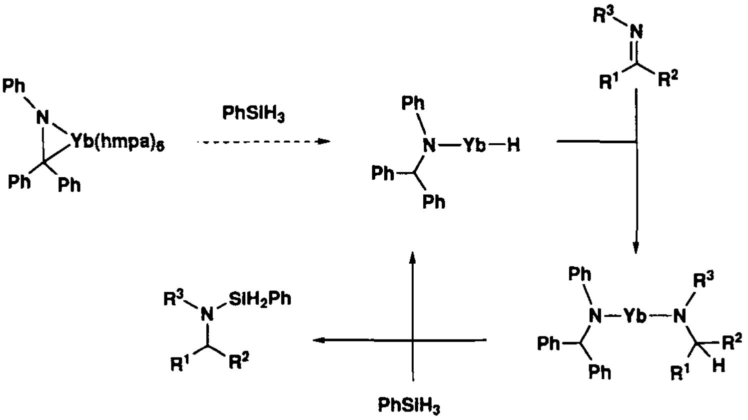
Yb-Catalyzed Hydrosilylation of Imines

Scheme 3

As in hydrosilylation of olefins with organolanthanides,[23] it has been suggested that the imine hydrosilylation involves an insertion of imine into the Yb–H bond, followed by silanolysis of the resulting Ln–N bond (*Scheme 4*). This second step is very rare as the opposite process had been envoked for the rationalization of the accelerator role of phenylsilane in lanthanocene-catalyzed imine hydrogenation.[24]

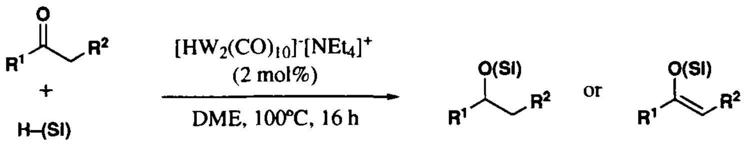
III. GROUP 6 METAL CATALYSTS (Cr, Mo, W)

The use of group VI metal complexes has been studied mainly in the reduction of Michael acceptors where the addition of the hydrosilane occurs mainly in a 1,4-mode.[25] Anionic dimeric hydride complexes $[(CO)_5M(\mu\text{-}H)M(CO)_5]^-[NEt_4]^+$ (M = Cr, Mo, W) catalyze the hydrosilylation of aldehydes and ketones using a monohydrosilane,[26] while silyl enol ethers are obtained selectively from dihydrosilanes (*Scheme 5*).



Proposed Mechanism for the Yb-catalyzed Hydrosilylation of Imines

Scheme 4

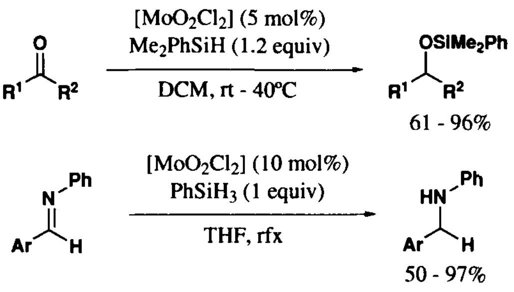


(Si) = SiEt3	66 - 97%	----
(Si) = SiPh2H	----	81 - 90%

Hydrosilylation/Silyl Enol Ether Formation with Group 6 Hydrides

Scheme 5

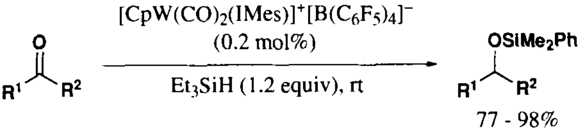
Milder conditions have been utilized with *bis*(benzene)chromium as a pre-catalyst in the hydrosilylation of unsaturated ketones and aldehydes with Ph_2SiH_2 (6 mol% [Cr], benzene, 70°C, air)[27] or with a high valent molybdenum-dioxo complex.[28] Metal-oxo complexes are usually known to catalyze oxidation and oxygen-transfer reactions.[29] However, following the innovative work by Toste and co-workers on hydrosilylation of carbonyl compounds by rhenium-oxo species (*vide infra*), the authors showed the effectiveness of $[MoO_2Cl_2]$ in this reaction, even at room temperature (*Scheme 6*). Under slightly different conditions, aromatic imines could also be hydrosilylated.[30]



Mo-Catalyzed Hydrosilylation of Aldehydes, Ketones and Imines

Scheme 6

A tungsten-based catalyst, $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^-$, has recently been reported to catalyze the solvent-free hydrosilylation of ketones and an ester (*Scheme 7*).[31] A particular feature of this system is that it remains active until all the liquid substrate is converted to liquid products, which can be separated by decantation as the catalyst precipitates from the products.

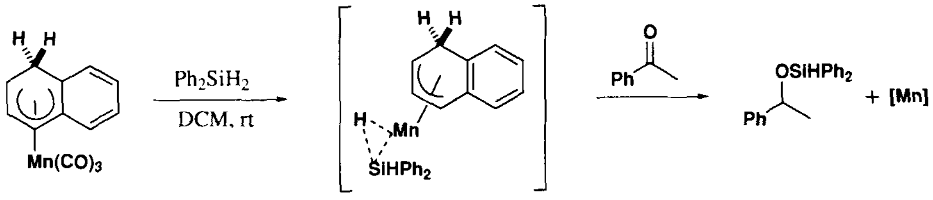


W-Catalyzed Hydrosilylation of Carbonyl Compounds

Scheme 7

IV. GROUP 7 METAL CATALYSTS (Mn, Re)

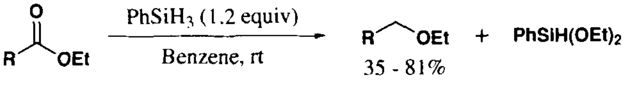
Manganese complexes $(naphthalene)Mn(CO)_3$[32] and $[(naphthalene)Mn(CO)_3]^+BF_4^-$ [33] have been shown to be effective catalysts for the hydrosilylation of ketones at room temperature. In the presence of these complexes, alkyl ketones are quantitatively reduced, whereas the yields for aromatic ketones depend on the substitution pattern. Notably, strong electron-withdrawing substituents can totally inhibit the reaction. It is believed that the pre-catalyst has to be transformed to a coordinatively unsaturated species, but in these complexes, it is the facile ring-slippage η^5/η^3 in the hydronaphthalene ring that creates the unsaturation (*Scheme 8*).



Proposed Mechanism for the (naphthalene)Mn-catalyzed Hydrosilylation of Ketones

Scheme 8

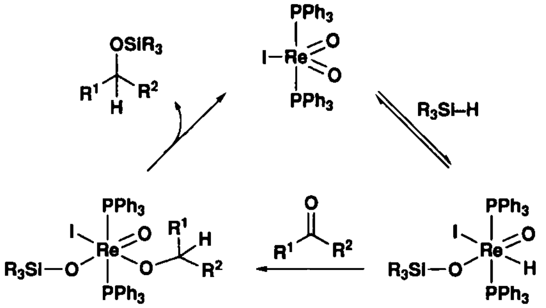
Manganese carbonyl acetyl complexes are well known catalysts for the hydrosilylation of non-labile iron acyls[34] or SiH/SiD isotope exchange,[35] for example. They have also been shown to be efficient and chemoselective catalysts for the hydrosilylation of ketones[36] and, more interestingly, esters and lactones[37] which are often considered as inert substrates. This smooth reaction produces silyl acetals rapidly as isolable intermediates, then ethers in fair yields (*Scheme 9*).



Mn-Catalyzed Hydrosilylation of Esters

Scheme 9

In 2003, Toste and co-workers described the $(PPh_3)_2Re(O)_2I$-catalyzed hydrosilylation of aldehydes and ketones (2-5 mol% [Re], benzene, rt –75°C, air).[38] This work represents not only the first rhenium-catalyzed hydrosilylation but also the first example for a hydrosilylation catalyst with a metal center in the oxidation state +5. The first proposed mechanism for this system involves a formal [2 + 2]-addition of a hydrosilane to the Re=O bond to produce a metal hydride (*Scheme 10*). Addition of the rhenium hydride to the carbonyl group followed by a transfer of the silyl group to the alkoxy ligand would produce the expected product and regenerate the catalyst.

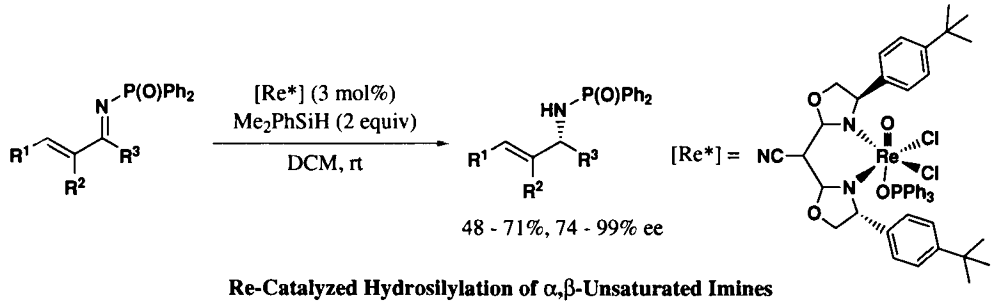


Proposed Mechanism for the Rhenium-dioxo-catalyzed Hydrosilylation

Scheme 10

However, it has been questioned that the postulated rhenium-hydride would be active enough to reduce organic carbonyl groups and further studies showed that the addition of Si–H to a Re=O bond is an unlikely pathway.[39] According to Abu-Omar's work,[40] as with Bullock's ionic hydrogenation mechanism,[41] the most viable reaction pathway would involve the activation of the hydrosilane and subsequent formation of a metal adduct without prior coordination of the carbonyl compound, or formation of a rhenium hydride.

Rhenium(V)-oxo complexes with a monoanionic bidentate ligand are efficient catalysts for the enantioselective reduction of imines.[42] Under optimized conditions (3 mol% [Re], DCM, rt, air), the expected phosphinyl amines were obtained in good yields and excellent ee's. Of note is the chemoselective hydrosilylation of α,β-unsaturated imines to allylic amines, an extremely rare transformation,[17] with this catalytic system (*Scheme 11*).

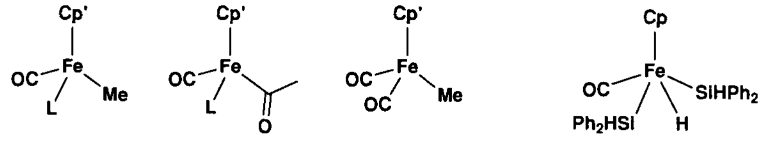


Re-Catalyzed Hydrosilylation of α,β-Unsaturated Imines

Scheme 11

V. GROUP 8 METAL CATALYSTS (Fe, Ru, Os)

While ferrocene ligands are commonly used in a number of transformations, little attention has been paid to the iron-catalyzed hydrosilylation reaction. A single report in 1990 showed the effectiveness of carbonyl-iron complexes in the hydrosilylation of acetophenone by diphenylsilane (*Fig. 2*).[43] Remarkably, the authors succeeded in isolating a Fe-silane complex that was a catalytically active intermediate in the reaction.[44]



Cp' = Cp or indenyl
L = (*S*)-(+)-$Ph_2PN(Me)CH(Me)Ph$

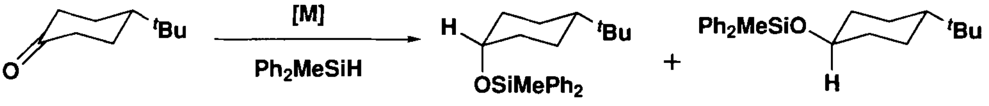
Isolated intermediate

Fe-based Catalysts for the Hydrosilylation of Acetophenone

Fig. 2

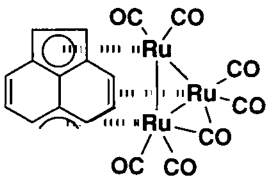
The hydrosilylation of ketones and aldehydes catalyzed by achiral ruthenium complexes has been known for a long time.[45] In recent years, a triruthenium carbonyl cluster has been reported to catalyze the hydrosilylation of ketones and aldehydes at room temperature to yield the corresponding silyl ethers in good yields.[46] Not only were the reaction rates higher with this cluster than with $RuCl_2(PPh_3)_3$ or even $RhCl(PPh_3)_3$,[47] but also regio- and stereoselectivities were observed as illustrated in *Table 1*.

Table 1. Ru-Catalyzed Hydrosilylation of 4-*tert*-Butylcyclohexanone



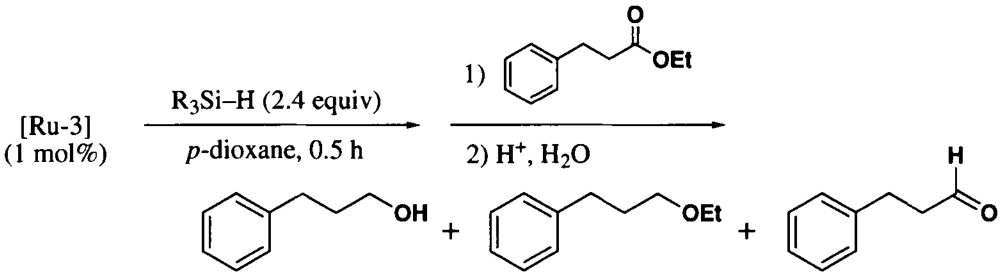
[M]	T (°C)	time (h)	*cis*	*trans*	yield (%)
[Ru-3]	50	3	72	28	100
$RhCl(PPh_3)_3$	80	12	29	71	
$RuCl_2(PPh_3)_3$	80	10	12	88	

[Ru-3] =



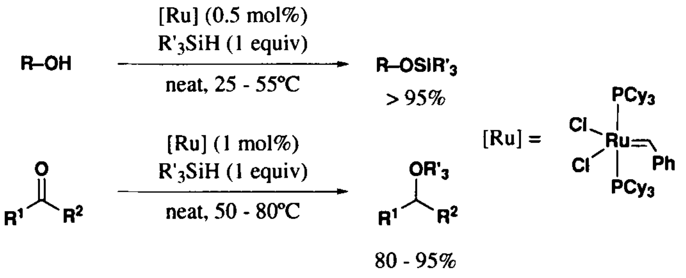
Whereas no active catalytic intermediate could be isolated in this case, NMR studies showed that the oxidative addition of the Si–H bond to the catalyst occurs without cluster fragmentation. The remarkable activity of this cluster has allowed the catalytic reduction of amides, carboxylic acids and esters.[48] The reactions proceeded smoothly at room temperature and, interestingly, the usually problematic product ratio in the hydrosilylation of esters could be controlled as a function of the silane (*Table 2*). Similarly, other ruthenium-carbonyl complexes such as $Ru_3(CO)_{12}$ or $[RuCl_2(CO)_3]_2$, catalyze the transformations of esters to aldehydes *via* the corresponding alkyl silyl acetals.[49] This method has the advantage of not requiring any special care to avoid air or moisture.

Table 2. Ru-Catalyzed Hydrosilylation of an Ester under Various Conditions



R_3Si–H				conv (%)
Ph_2MeSi–H	84	16	0	74
Et_2MeSi–H	24	76	0	100
Et_3Si–H	0	0	100	7

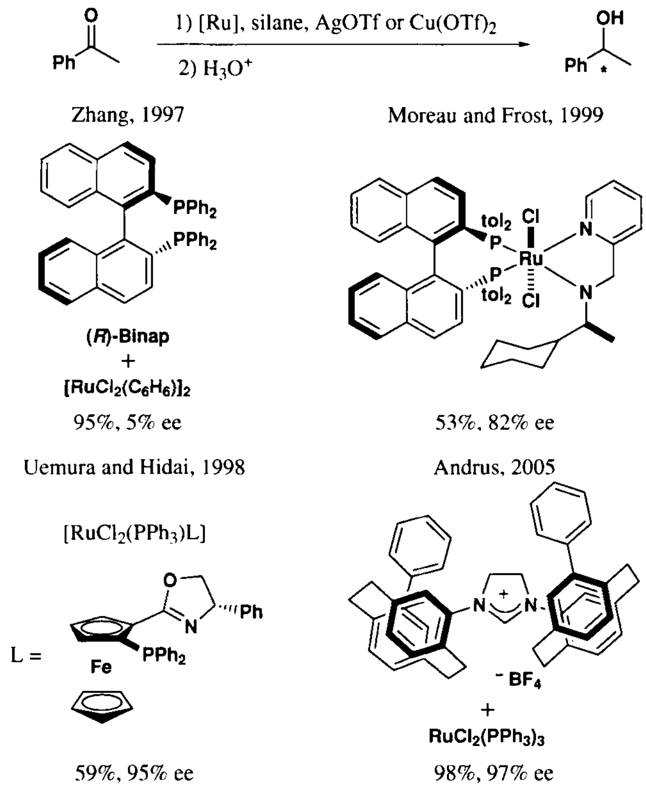
Ruthenium-carbene complexes have led for an explosion in olefin metathesis chemistry. Apart from its remarkable efficiency in promoting ring-opening, ring-closing or cross-metathesis reactions,[50] this family of complexes catalyzes, among others, the Kharasch addition of chloroform to alkenes,[51] the removal of allyl groups from amines[52] and to promote the atom transfer radical polymerization.[53] These complexes can also activate a variety of silanes affording silyl ethers from dehydrogenative condensation with alcohols or from hydrosilylation of carbonyl (*Scheme 12*).[54]



Activation of Hydrosilanes by a Ruthenium-carbene Complex

Scheme 12

Based on previous work on rhodium and iridium complexes, asymmetric catalysts have also been developed. Ruthenium-based catalysts are highly desirable because this metal is more readily available and less expensive than either rhodium and iridium. Nevertheless, the initial studies with well known mixed ligands such as BINAP were either inactive or non-selective in the hydrosilylation of acetophenone.[55] Slightly better results were obtained from the association of (*S*)-TolBINAP and a chiral non C_2-symmetric diamine.[56] Enhanced enantioselectivity was eventually achieved with a heterobidentate oxazolinyl-ferrocenyl-phosphine[57] or a *bis*-paracyclophane N-heterocyclic carbene ligand.[58] In all these examples, the use of AgOTf, or even better $Cu(OTf)_2$, dramatically improved the enantioselectivity of the reaction (*Scheme 13*).



Asymmetric Ru-catalyzed Hydrosilylation of Acetophenone

Scheme 13

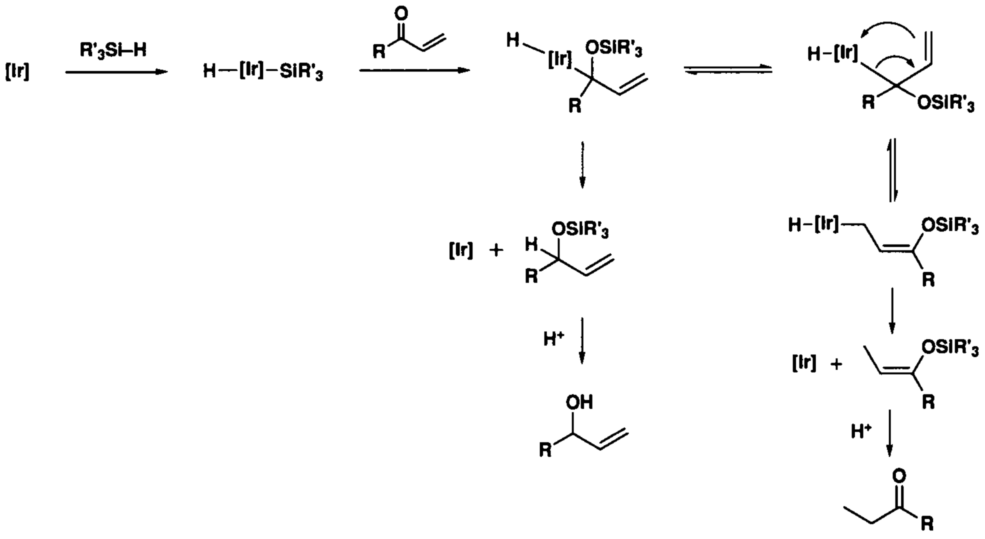
Uemura's catalyst (*Scheme 13*) also showed promising activity in the hydrosilylation of imines and ketoximes[59] to yield the corresponding secondary and primary amines after hydrolysis.[60] Remarkably, high enantioselectivities (up to 88% ee) were obtained from a number of aryl and alkyl ketoximes, improving the scope and effectiveness of the process when compared with the classic rhodium-DIOP system. Nevertheless, unidentified by-products represent from 50% to 95% of the converted substrates.

Finally, hydrosilylation of amides has also been studied in the presence of Group 8 metals.[61] Ruthenium- as well as osmium-containing complexes were shown to yield the corresponding amines in good yields after hydrolysis when co-catalysts (iodoethane and diethylamine) were used.

VI. GROUP 9 METAL CATALYSTS OTHER THAN RHODIUM (Co, Ir)

Hydrosilylated products have generally been considered as undesirable secondary products in the cobalt-catalyzed reactions of carbonyl compounds with hydrosilanes.[62] To date, only the cobalt-catalyzed hydrosilylation of aromatic nitriles[63] or carbon monoxide[64] are known. Compared to rhodium, very little attention has been paid to iridium-based systems as hydrosilylation catalysts. This might be explained by the high instability of ligand-free iridium complexes.[65] Moreover, iridium complexes bearing tertiary phosphines can undergo oxidative addition with silanes to form catalytically inactive adducts.[66]

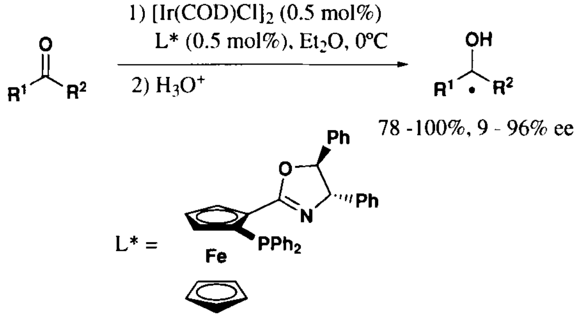
$[IrCl(diene)]_2$-type complexes were the first ones to be evaluated in the hydrosilylation of ketones by Nile *et al.*[67] Fair yields were obtained for the hydrosilylation of cyclohexanone by triethylsilane using 1 equivalent of PPh_3. The system was no longer operative with a Ir:P ratio of 1:2, due to the formation of a catalytically inert adduct. In the case of α,β-unsaturated ketones, both 1,2- and 1,4-additions occurred concurrently and the final allylic alcohol/saturated ketone ratio was dependent on the steric bulk of the silane. These results were rationalized in term of a mechanism involving the isomerization of an α-siloxyalkenylmetal hydride to a γ-isomer (*Scheme 14*). It is to be noted that more recently reported systems with iminophosphines[68] or metalloporphyrin-phosphine ligands[69] did not lead to better yields of reduced products. Only Ph-pybox/Ir system was shown to catalyze the hydrosilylation of acetophenone in high yield,[70] however only that ketone was tested.



Plausible Mechanism for the Ir-catalyzed Hydrosilylation of Conjugated Enones

Scheme 14

When chiral monodentate phosphines were used instead of PPh_3, extremely low ee's were obtained. Poor asymmetric inductions were also observed with bidentates *N,N* and *N,S* ligands,[71] tridentates *N,P,S* ligands[72] or chiral diaminoferrocenyl-chalcogenides.[73] Developed primarily for the rhodium-catalyzed hydrosilylation of ketones,[74] chiral oxazolinylferrocene-phosphine hybrid ligands allowed the hydrosilylation of aromatic and α,β-unsaturated ketones to proceed for the first time in both high yields and ee's.[75] However, only poor induction was achieved with aliphatic ketones (*Scheme 15*). Remarkably, in this example as well as the previous ones, the alcohols formed had an opposite configuration to that observed with the parent rhodium-based systems. This might imply a different pathway for the reaction or a significant change in the geometry of the intermediates.



Ir-Catalyzed Asymmetric Hydrosilylation of Ketones

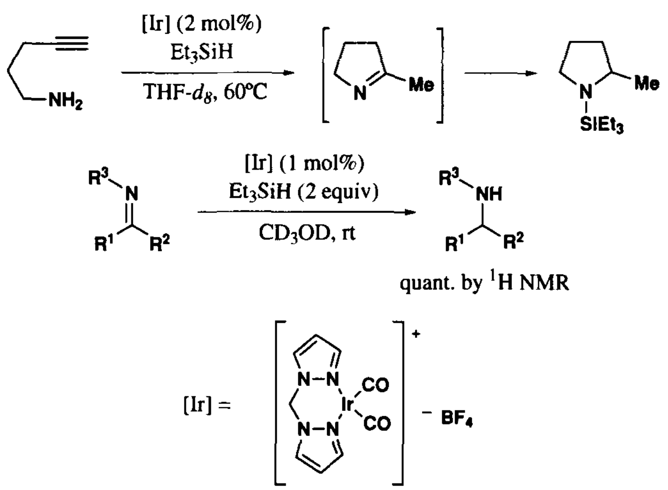
Scheme 15

Similar chiral oxazolinyl-phosphine ligands have been used for the asymmetric hydrosilylation of imines.[76] Of note, equivalent rhodium-based systems were less active than the iridium-based ones. In this case, the amines formed had the same configuration regardless of the catalyst, indicating that the mechanism of the hydrosilylation is most probably different for imines and ketones.

Recently, a cationic iridium complex has been reported to catalyze a tandem hydroamination-hydrosilylation to form, in one pot, a cyclic silyl amine from an aliphatic pentynylamine (*Scheme 16*).[77] The same group later reported that the same complex catalyzes the hydrosilylation of a range of imines, including *N*-alkyl and *N*-aryl imines and both aldimines and ketimines.[78] Remarkably, when the reaction was carried out in methanol, *in situ* protodesilylation of the corresponding *N*-silylamine was observed and desilylated amines were formed in high yields after only minutes of reaction at room temperature (*Scheme 16*).

VII. RHODIUM-BASED CATALYSTS

Rhodium-catalyzed hydrosilylation of carbonyl compounds has been extensively studied after the appearance of Wilkinson's catalyst, $(Ph_3P)_3RhCl$.[79] Since the pioneering work by Kagan with a Rh(I)/DIOP catalyst for the asymmetric hydrosilylation of ketones and imines,[80] considerable efforts have been focused on discovering new and efficient systems. Phosphorus-[81]

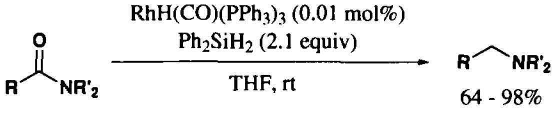


Ir-Catalyzed Tandem Reactions

Scheme 16

or nitrogen-based[82] ligands and mixed *P,N*[83] ligands have been developed. This subject has been reviewed,[84] and only the most recent advances will be discussed here.

Even if most of the attention has been focused on asymmetric hydrosilylation reactions, some original achiral systems are also worth describing. Ito and co-workers reported a useful chemoselective reduction of amides to amines *via* rhodium-catalyzed hydrosilylation.[85] Halogens, esters or epoxy groups, but not C–C double and triple bonds, were well tolerated by this system (*Scheme 17*).



Rh-Catalyzed Reduction of Amides with a Hydrosilane

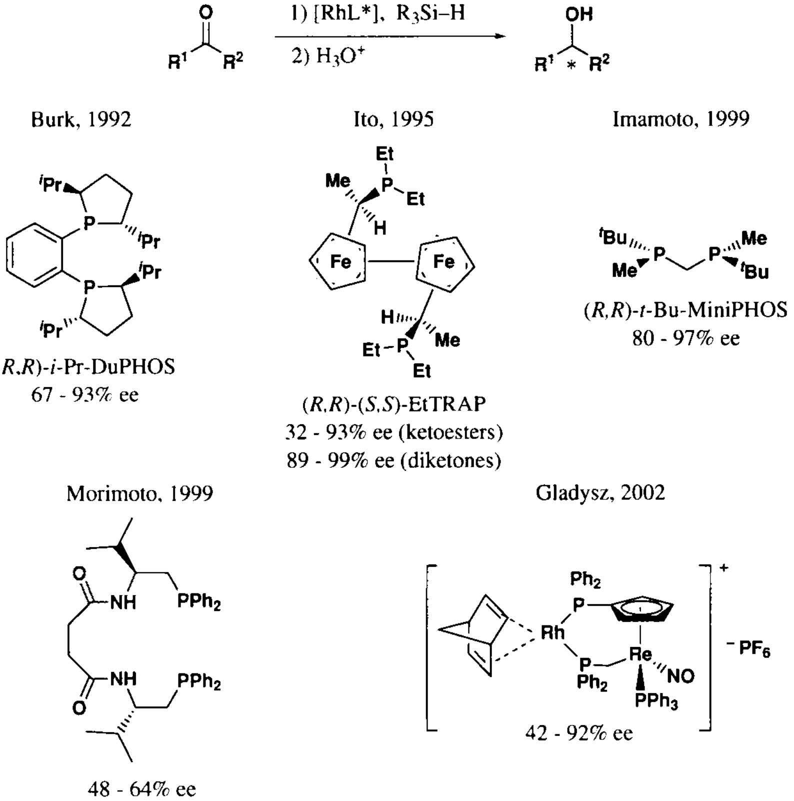
Scheme 17

Two different approaches to easily recyclable rhodium-based catalysts have been published up to now. Synthesis of a supported organorhodium catalyst and its application to the hydrosilylation of acetophenone has recently been reported.[86] The authors used 500 μm diameter beads[87] that behaved as single reactors, and thus, this approach might be an alternative to the standard Schlenck tubes.[88]

On the other hand, fluorous biphase chemistry[89] has also been successfully employed in the hydrosilylation of carbonyl compounds.[90] Aliphatic fluorous phosphine analogs of Wilkinson's catalyst in $CF_3C_6F_{11}$ solutions were treated with organic solutions of a hydrosilane and a ketone or an enone. Depending on the temperature, the reaction could proceed in monophasic ($CF_3C_6F_{11}$/hexanes, 28°C) or biphasic conditions ($CF_3C_6F_{11}$/toluene, 45°C). Simple extraction is sufficient to separate the reduced product from the catalyst, which could be reused with no significant loss of activity.

1. Phosphorus-based Ligands

Although some reports referring to monodentate phosphines or phosphites are known,[91] historically *cis*-chelating bisphosphines such as DIOP or BINAP have drawn most of the attention. Asymmetric induction remained modest until the introduction of the DuPHOS[92] ligand and of the C_2-symmetric bidentate ferrocenyl-phosphines TRAP (*Scheme 18*).[93] Highly enantioselective reactions have been described with methylene-bridged chiral diphosphine[94] but, on the other hand, diphosphine ligands derived from valine[95] or containing a rhenium stereocenter in the backbone[96] did not represent any significant improvement when compared to previously known systems (*Scheme 18*).

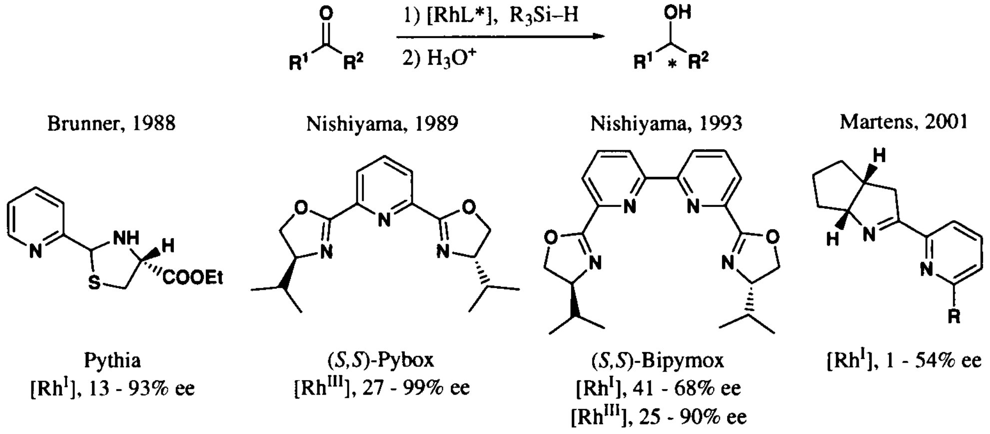


Phosphorus-based Ligands for Rh-catalyzed Hydrosilylation of Ketones

Scheme 18

2. Nitrogen-based Ligands

Similarly to phosphorus-based ligands, major improvements in the hydrosilylation of ketones were made in the late 80's and early 90's with nitrogen-based ligands. Pyridine-thiazolidine (Pythia),[97] pyridine-oxazolines (Pybox)[98] and bipyridine-oxazoline (Bypymox)[99] ligands were the first ligands that allowed the hydrosilylation of ketones to proceed under mild conditions with high enantioselectivities (*Scheme 19*). More recently reported ligands, such as cyclic ketimines[100] or differently substituted bipyridines[101] have only led to modest asymmetric induction (< 55% ee).

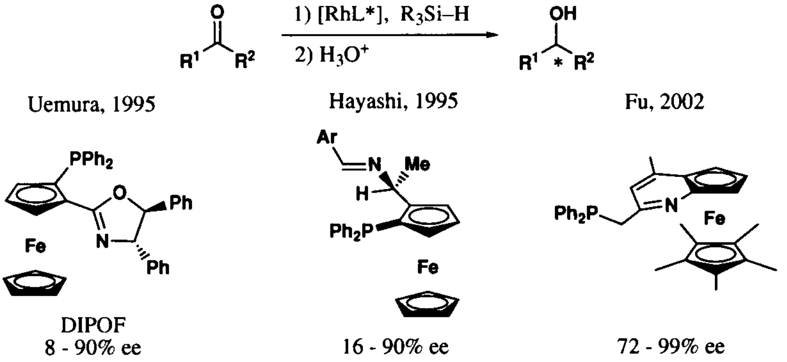


Nitrogen-based Ligands for Rh-catalyzed Hydrosilylation of Ketones

Scheme 19

3. *Mixed P,N- and P,S-based ligands*

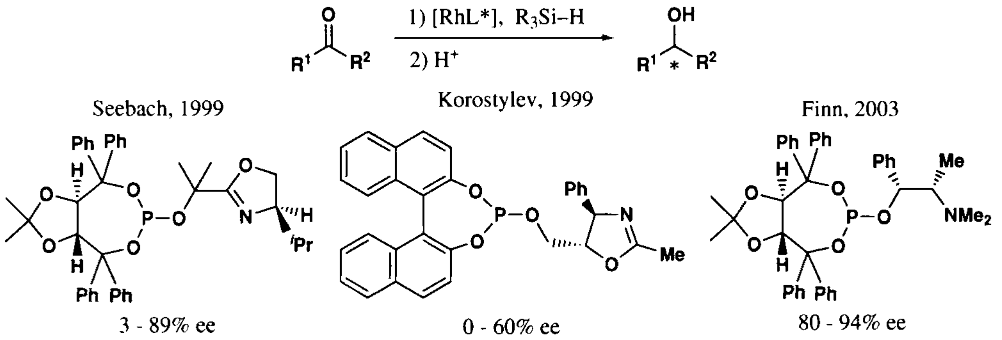
In 1995, Uemura and Hayashi independently reported the first application in hydrosilylation of ketones of mixed ligands containing both phosphorus and nitrogen. Ferrocenylphosphines bearing an oxazoline[102] or an imine[103] were shown to be effective, leading to enantioselectivities up to 80% ee (*Scheme 20*). A related planar-chiral ligand reported by Fu *et al.* in 2002,[104] showed an excellent asymmetric induction in the hydrosilylation of aromatic ketones at room temperature and more interestingly, dialkyl ketones at 0°C.



Rh-Catalyzed Asymmetric Hydrosilylation of Ketones using Ferrocenyl-containing Ligands

Scheme 20

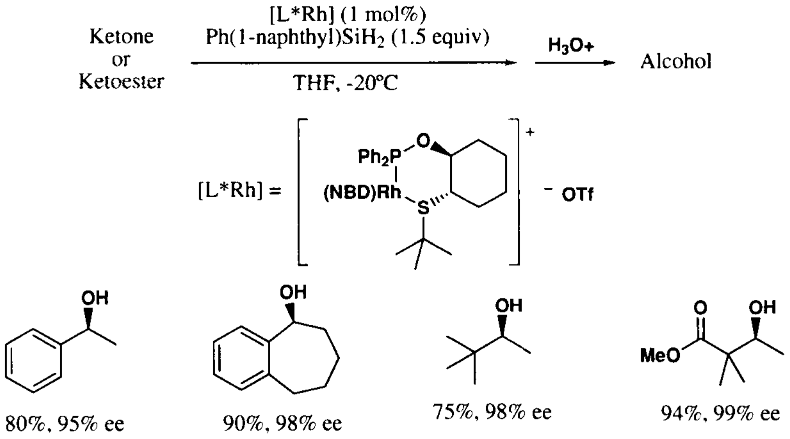
The activities of cyclic monodentate phosphinites and phosphites derived from TADDOL have also been reported. Easily prepared by phosphorylation of chiral amino or imino alcohols, they can induce up to 94% ee in the hydrosilylation of aromatic ketones (*Scheme 21*).



Rh-Catalyzed Asymmetric Hydrosilylation of Ketones using TADDOL Derivatives as Ligands

Scheme 21

Originally developed for the palladium-catalyzed allylic alkylation and amidation reactions,[105] the use of chiral mixed phosphorous and sulfur ligands has been extended to rhodium-catalyzed hydrosilylation of ketones by Evans.[106] Aryl alkyl or dialkyl ketones, even cyclic ketoesters were efficiently hydrosilylated under smooth conditions and with very high ee's (*Scheme 22*). The reaction temperature had to be lowered to –20°C to avoid uncontrollable reaction exotherms, probably silane polymerization, accompanied by hydrogen evolution.



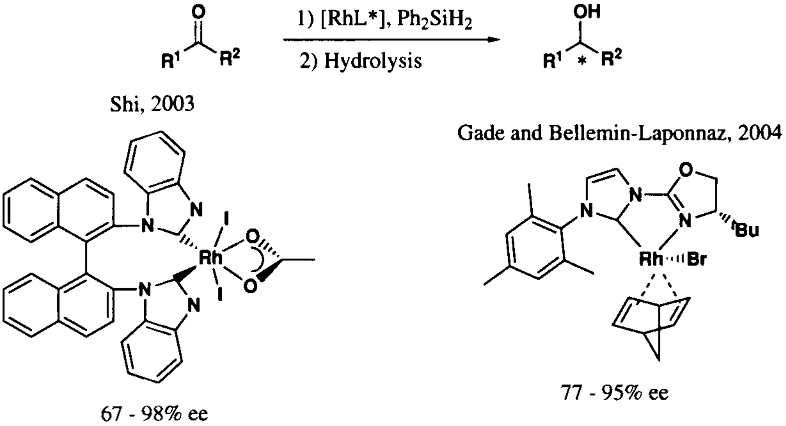
Rh-Catalyzed Asymmetric Hydrosilylation of Ketones using P,S Mixed Ligands

Scheme 22

4. N-Heterocyclic Carbene-containing Ligands

Hydrosilylation of ketones, alkenes and alkynes using achiral (NHC)–Rh complexes was first reported by Nile[107] and Lappert[108] in the 70s and 80s. Still, few systems based on this family of ligands have been reported to date.[109] Chiral carbene complexes have also been studied. Low to modest enantioselectivities were obtained with ferrocene-NHC[110] or triazolinylidene ligands.[111]

Axially chiral bis-carbenic ligands,[112] but not mono-carbenic ones,[113] led for the first time to the hydrosilylation of aryl alkyl and dialkyl ketones in good to excellent enantioselectivities (*Scheme 23*). Similar results were also obtained in the presence of chiral oxazolinylcarbene-rhodium complexes at room temperature.[114]

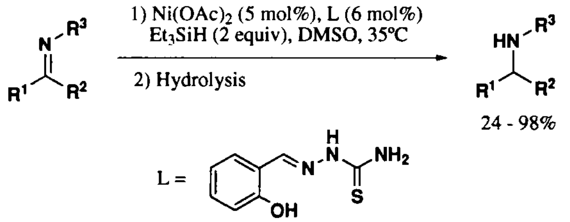


(NHC)–Rh-Catalyzed Asymmetric Hydrosilylation of Ketones

Scheme 23

VIII. GROUP 10 METAL CATALYSTS (Ni, Pd, Pt)

Hydrosilylation of carbonyl groups catalyzed by nickel[115] or palladium is generally of minor importance in the reaction of ketones or aldehydes with hydrosilanes. Conjugate reduction[116] or enoxysilanes and disiloxanes formation are normally observed.[117] Nevertheless, the combination of nickel(II) acetate with thiosemicarbazones of salicylaldehydes in DMSO efficiently catalyzes the hydrosilylation of imines (*Scheme 24*).[118] Remarkably, under similar conditions, the reaction failed to occur in the presence of manganese(II), cobalt(II), iron(II), copper(II), zinc(II) or chromium(II).

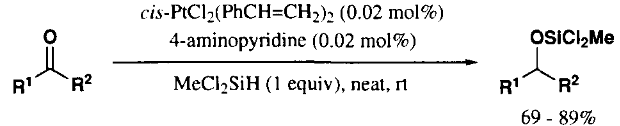


Ni-Catalyzed Hydrosilylation of Imines

Scheme 24

Similarly, little attention has been paid to platinum based-catalysts. Early studies by Kumada and co-workers showed that a number of platinum(II) complexes containing a chiral phosphine could convert alkyl phenyl ketones into their corresponding alcohols after hydrolysis in good yields.[119] However, extremely poor asymmetric inductions were obtained (from 2% to 19% ee). Similar observations were made using aminoferrocene derivatives as ligands.[120]

Achiral complexes of platinum(II) such as *cis*-$[Pt(Et_2SO)_2Cl_2]$[121] and $[Pt(MeCOD)Cl_2]$[122] have been reported to efficiently catalyze the hydrosilylation of variously substituted acetophenones. To date, only one report refers to the hydrosilylation of aromatic and non-aromatic ketones.[123] The combination of *cis*-$PtCl_2(PhCH{=}CH_2)_2$ with a co-catalyst (typically a pyridine or an aniline derivative) led to the formation of the corresponding silyl ether in good yields (*Scheme 25*).



Pt-Catalyzed Hydrosilylation of Ketones

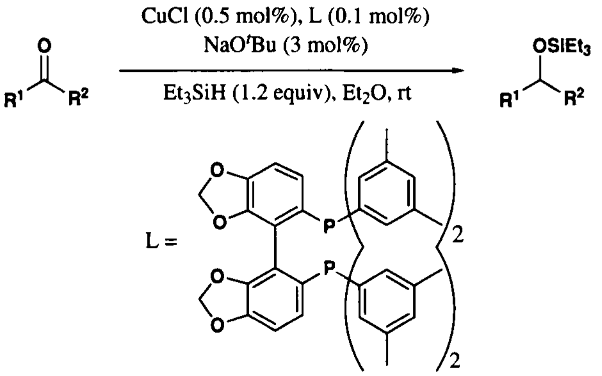
Scheme 25

IX. GROUP 11 METAL CATALYST (Cu, Au)

The "Cu–H" is among the earliest metal hydrides reported in the literature[124] but for a long time it was considered too unstable to have any potential as a reagent in organic chemistry. A stabilized form of copper hydride, the hexameric $[(Ph_3P)CuH]_6$, first reported by Osborn[125] was shown by Stryker *et al.* to be useful in conjugate reductions of a number of carbonyl derivatives with high regioselectivity[126]. The main drawback of this complex is that it is most effective as a stoichiometric reducing agent. Catalytic reactions under hydrogen atmosphere have been reported but very careful monitoring is required in order to avoid major formation of over-reduced products.[127] Combination of Stryker's catalyst with a hydrosilane as a hydride source allowed the regioselective conjugate reduction of carbonyl compounds under mild conditions.[128] Hydrosilylation can be performed asymmetrically in the presence of a non-racemic ligand.[129] Alternatively to the use of Stryker's catalyst, the active species can be simply *in situ* generated from a cuprous salt, the ligand of choice and a base.[130]

Interestingly, the conjugate reduction of ketones can be catalyzed by simple copper(I) salts when DMI (1,3-dimethylimidazolidinone) is used as solvent.[131] This system was also the first one to be utilized for the hydrosilylation of simple ketones although the process required a stoichiometric quantity of copper salt.[132]

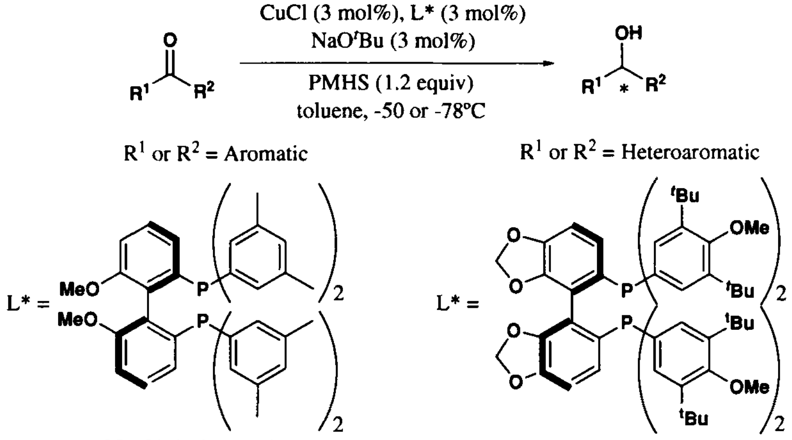
Lipshutz *et al.* achieved the catalytic hydrosilylation of ketones and aldehydes with Stryker's catalyst and different hydrosilanes.[133] Further studies, notably regarding the stoichiometry of the reagents and the influence of the ancillary ligand,[134] led to highly effective formation of silyl ethers in high yields at room temperature (*Scheme 26*). At the same time, asymmetric



Copper-catalyzed Hydrosilylation of Ketones

Scheme 26

versions of this reaction were reported. Aromatic ketones could be reduced by PMHS in excellent yields and optical purities using a chiral Roche ligand (*Scheme 27*).[135] However, a different



85 - 99%, 67 - 95% ee

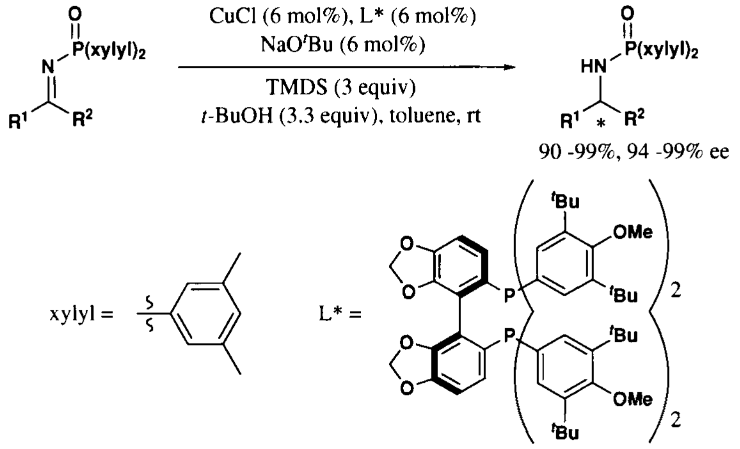
68 - 98%, 51 - 99% ee

Asymmetric Copper-catalyzed Hydrosilylation of Aromatic and Heteroaromatic Ketones

Scheme 27

ligand had to be used in the hydrosilylation of heteroaromatic ketones in order to ensure good asymmetric inductions.[136]

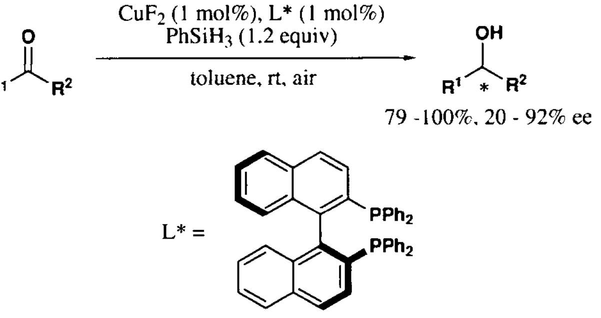
The catalytic system developed for the asymmetric hydrosilylation of heteroaromatic ketones was later reported to be also effective for aryl ketimines.[137] In this study, a diphenylphosphinyl moiety was introduced in the starting material to weaken the otherwise strong copper–nitrogen bond in the plausible reaction intermediate. Excellent yields and enantioselectivities were obtained at room temperature (*Scheme 28*) and after the reduction step the phosphinyl group can be readily hydrolyzed.[138]



Cu-Catalyzed Asymmetric Hydrosilylation of Imines

Scheme 28

The use of Cu–F systems was first studied for the conjugate reduction of α,β-unsaturated ketones in stoichiometric conditions.[139] Concomitant to Lipshutz's work,[133] Riant *et al.*[140] reported that the combination of copper(II) fluoride with a chiral phosphine catalyzed the hydrosilylation of ketones with moderate to excellent enantioselectivities (*Scheme 29*). Low catalyst loadings and compatibility with the presence of water are important features of this catalytic system, but above all, an interesting accelerating effect of oxygen allowed the reactions to proceed under aerobic conditions. Similar results using a dipyridylphosphine were later reported by Wu and co-workers.[141]

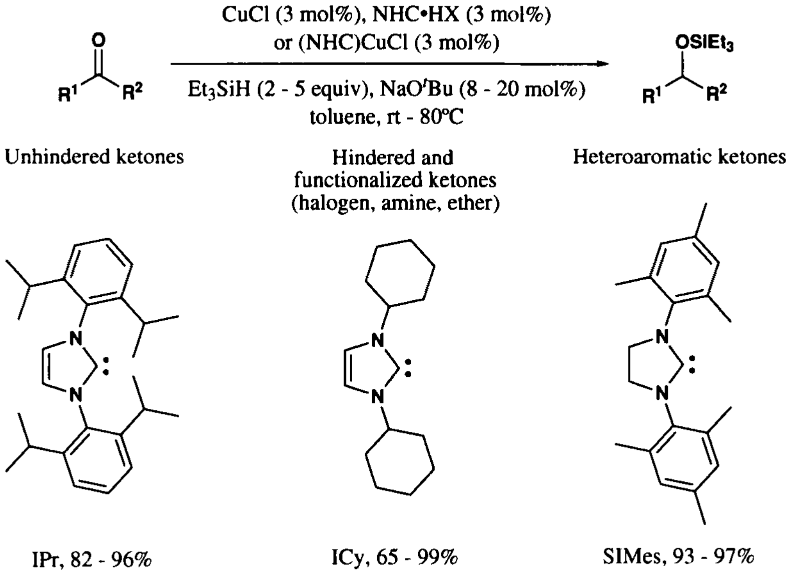


(*S*)-BINAP

Cu-Catalyzed Asymmetric Hydrosilylation of Ketones under Aerobic Conditions

Scheme 29

Although no asymmetric versions have been reported yet, NHCs have been shown to be interesting alternatives to phosphines for the copper-catalyzed hydrosilylation of carbonyl groups. While (IPr)CuCl was an efficient catalyst for the hydrosilylation of unhindered ketones[142] as well as for the conjugate reduction of tri- and tetra-substituted α,β-unsaturated ketones and esters,[143] more challenging ketones could be hydrosilylated in the presence of (ICy)CuCl or (SIMes)CuCl (*Scheme 30*).[144] The simplicity of the *in situ* generated systems and the higher effectiveness of well-defined complexes were highlighted in this work.

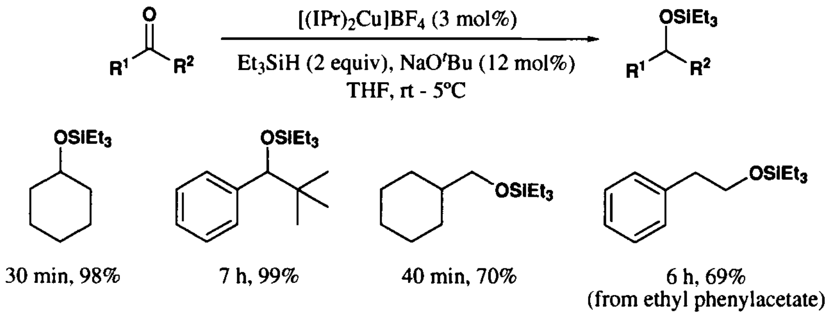


(NHC)–Copper-catalyzed Hydrosilylation of Ketones

Scheme 30

Interestingly, the authors also observed that copper(II) salts could be used in this reaction. Concomitantly, Yun *et al.* reported that copper(II) salts in combination with a NHC[145] or a chiral phosphine[146] catalyzed the hydrosilylation of ketones. To date, no insights have been provided to determine if the active species is a copper(I) or a copper(II) hydride.

Another family of complexes with NHCs, cationic bis-carbenic complexes, has recently shown remarkable activity as pre-catalyst in the hydrosilylation of ketones (hindered or not), aldehydes (even enolizable ones) and an ester (*Scheme 31*).[147] Smoother reaction conditions and

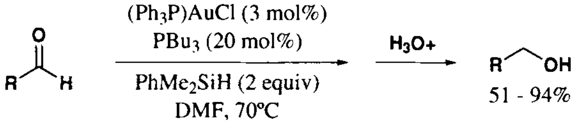


Hydrosilylation of Carbonyl Compounds in the Presence of a Cationic Bis-carbenic Complex

Scheme 31

smaller excess of hydrosilane are the main advantages of these complexes when compared to (NHC)CuCl complexes. Although the reaction pathway remains unclear for the moment, monocarbenic intermediates have been proposed to be the active species.

The first and to date only, gold-catalyzed hydrosilylation of carbonyl compounds was reported in 2000.[148] A soluble gold(I) complex in combination with an excess of phosphine led after hydrolysis to the formation of primary alcohols from the corresponding aldehydes (*Scheme 32*). α,β-Unsaturated aldehydes only reacted in a 1,2-manner with this system, and ketones were completely inert.



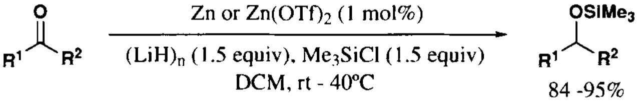
Gold-catalyzed Hydrosilylation of Aldehydes

Scheme 32

The reduction of an aldimine was also achieved after four days of reaction at room temperature. In all cases, a large excess of the phosphine ligand was required in order to have good catalytic activity. Its role would be to stabilize the active gold species, preventing the deactivation of the catalyst *via* formation of gold clusters and metallic gold.

X. GROUP 12 METAL CATALYSTS (Zn)

The first hydrosilylation of carbonyl compounds promoted by a zinc salt was reported by Caubère *et al.*[149] The initial system (NaH/*tert*-pentanol/$ZnCl_2$) was later revisited by Noyori,[150] who showed that a number of zinc salts and even metallic zinc could activate LiH, an otherwise inert hydride, towards the hydrosilylation of ketones and aldehydes (*Scheme 33*). Most of the reaction pathway for this system remains unclear, but it is believed that zinc acts as a Lewis acid. However, other Lewis acids such as $AlEt_3$ or BF_3•Et_2O did not activate LiH.

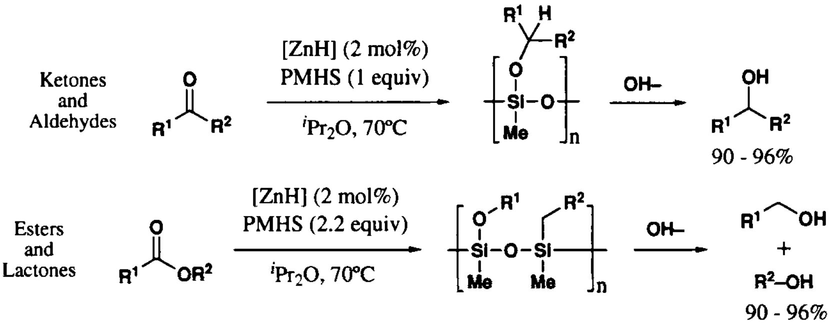


Zn-Catalyzed Hydrosilylation of Carbonyl Compounds

Scheme 33

In 1999, Mimoun showed that, after activation of a number of metals by sodium borohydride to generate the corresponding metal hydrides, the hydrosilylation of carbonyl compounds with PMHS could be easily performed.[151] This method proved to be general and ketones, aldehydes, esters and lactones could be successfully hydrosilylated (*Scheme 34*).

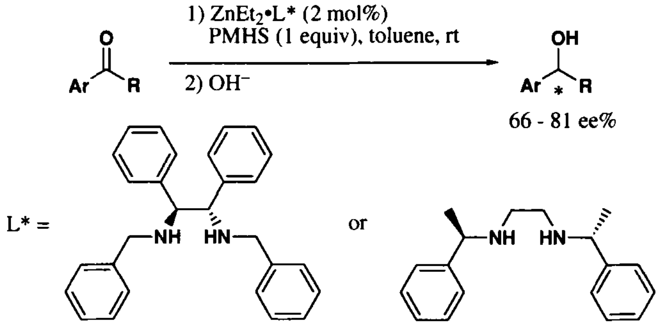
Highly encumbered substrates led to sluggish reactions with PMHS but they could be readily reduced using trimethoxysilane instead. Furthermore, Co, Mn, Sn, Fe, Cd, Zr, Ru, Ni, Pd and Cu salts were also tested in this study. Interestingly, complementary regioselectivities were observed in the reactions carried out with cyclohexenone. While Ni, Pd and Cu performed conjugate reductions principally, Zn, Co, Mn, Sn or Fe led largely to the formation of 1,2-addition products.



Zn-Catalyzed Hydrosilylation of Carbonyl Compounds

Scheme 34

An enantioselective process was later developed by the same authors.[152] Zinc catalysts activated by chiral diamines or diimines and in the presence of PMHS in toluene allowed the hydrosilylation of aromatic ketones in high yields and acceptable ee's (*Scheme 35*). Remarkably, this procedure could be scaled up to a kilogram scale with no loss of activity.



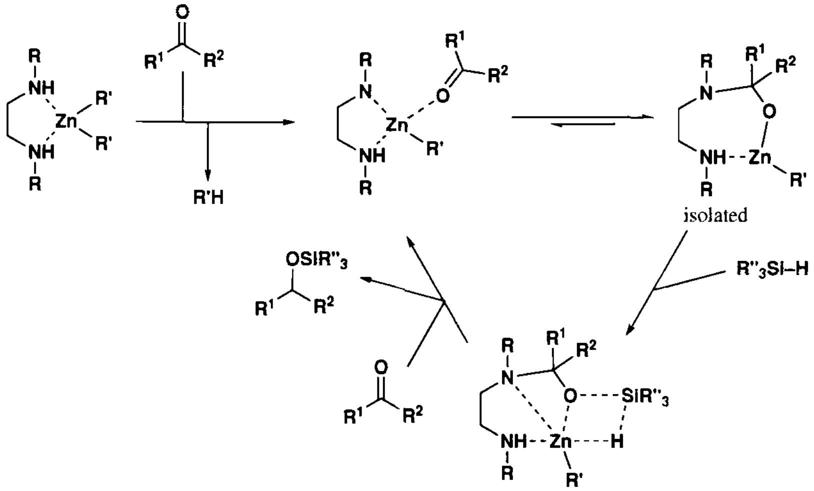
(*R,R*)-*N*-Bn-Dpen (*R,R*)-ebpe

Zn-diamine-catalyzed Asymmetric Hydrosilylation of Ketones

Scheme 35

Different mechanisms can be envisioned to explain the enantioselectivity of this reaction. In any case, the isolation and characterization of a seven-membered dimeric zinc complex in which the ketone is inserted into a Zn–N bond strongly suggest that the diamine is not a mere ancillary ligand, but plays an active role in the process (*Scheme 36*).

In this and related[153] systems, protic solvents cannot be used because they can undergo dehydrogenative silylation in the presence of PMHS. Therefore the formed silyl ether has to be



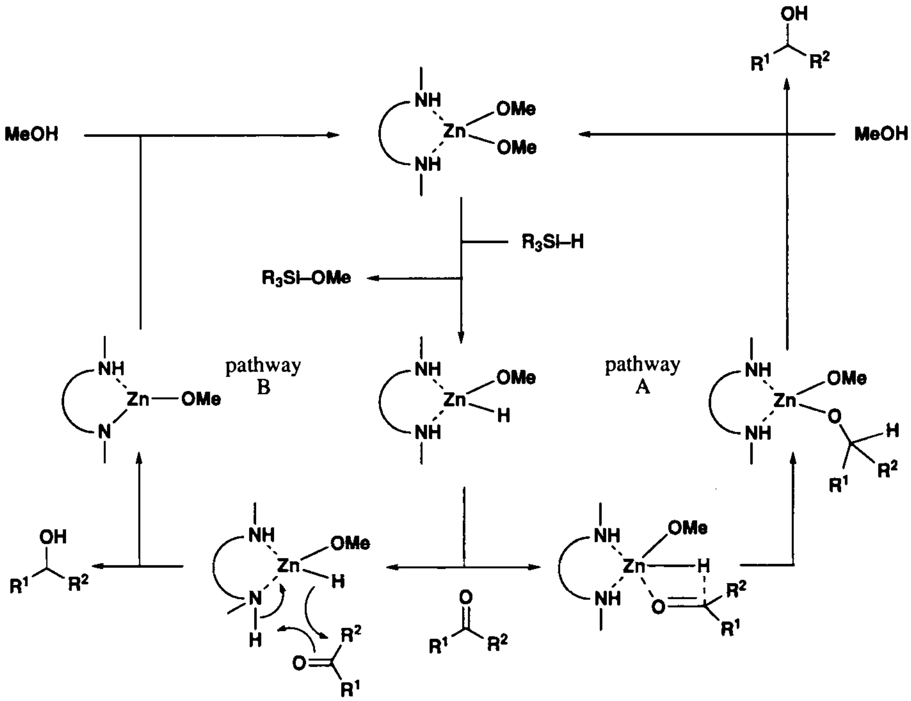
Proposed Mechanism for the ZnEt2•ebpe-catalyzed Hydrosilylation of Ketones

Scheme 36

hydrolyzed, a process that can be delicate. The use of *dbea* as ligand overcomes this limitation[154] and a number of ketones could be reduced in methanol at room temperature. Furthermore, this system can also perform the hydrosilylation of imines under mild conditions. Zn-catalyzed hydrosilylation of imines can also take place by simply using $ZnCl_2$ in ether solvents.[155] For the moment, efforts aimed at developing efficient Zn-catalyzed asymmetric hydrosilylation of carbonyl compounds in protic media have led to moderate to good induction (14–78% ee for aryl alkyl ketones and 12–47% ee for α and β-keto esters or amides).[156] However, it seems clear that the reaction takes a different pathway when compared with the systems in toluene (see *Scheme 36*). The catalytic activity cannot be ascribed to methanolysis rates as the observed rates from isolated silyl ethers under the reaction conditions were very slow. Two different mechanisms were postulated. In both, the role of PMHS would be to generate a [(diamine)Zn(H)(OR)] species (*Scheme 37*). According to the mechanism proposed by Buchwald[11] for the titanium-catalyzed hydrosilylation reaction (*vide supra*), this hydride could form a four-membered ring intermediate that would lead to the formation of the expected alcohol after methanolysis (pathway A). Alternatively, a concerted hydride transfer to the carbonyl to form directly the alcohol could also be considered (patway B). Methanolysis of the [(amine-amine)-Zn(OMe)] species would close the catalytic cycle.

XI. CONCLUSIONS AND PERSPECTIVES

We have shown that the hydrosilylation of carbonyl compounds and imines provides a plethora of possibilities to the organic chemist. A number of simple and versatile catalytic systems have been reported with various metals, even for asymmetric catalysis. However, there is still room for improvement, especially for the least reactive compounds such as imines, esters and lactones.



Proposed Mechanism for the Hydrosilylation of Ketones in Methanol

Scheme 37

ABBREVIATIONS

BINAM = 1,1'-diamino-2,2'-binaphthyl

BINAP = 2,2-bis(diphenylphosphino)-1,1'-binaphthalene

BINOL = 1,1'-bi(2-naphthol)

COD = cycloocta-1,5-diene

COE = cyclooctene

Cp = cyclopentadienyl

dbea = *N,N'*-dibenzylethylenediamine

DIOP = 2,3-*O,O'*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane

DIPOF = [2-(4,5-diphenyloxazolin-2-yl)ferrocenyl]diphenylphosphine

DME = 1,2-dimethoxyethane

DMI = 1,3-dimethylimidazolidinone

Dpen = 1,2-diphenyl-1,2-ethylenediamine

ebpe = *N,N'*-ethylenebis(1-phenylethylamine)

ee = enantiomeric excess

hmpa = hexamethyl phosphoramide

IMes = *N,N'*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene

IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
NBD = norbornadiene
NHC = N-heterocyclic carbene
PMHS = polymethylhydrosiloxane
SIMes = *N,N'*-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
TADDOL = α,α,α',α'-tetraaryl-1,2-dioxolane-4,5-dimethanol
TMDS = tetramethyldisiloxane
TON = turnover number

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