Iron-catalyzed homogeneous hydrosilylation of ketones and aldehydes. Advances and mechanistic perspective

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ABSTRACT. This review is focused on iron-based homogeneous catalytic systems described so far for the reduction of carbonyl compounds (ketones and aldehydes) into alcohols via hydrosilylation. It begins explaining the basic concepts of the hydrosilylation reaction, addressing its main advantages and procedural differences with other common reduction methods, and highlighting its interest in organic chemistry. Then, the advances in the development of iron-based catalysts, as a more sustainable alternative to the traditional noble-metal catalysts, that have taken place to date are reviewed in depth. The revision of the different type of catalysts is followed by a profound discussion of the mechanistic proposals found in the literature for this type of catalysts.

KEYWORDS. hydrosilylation, reduction of carbonyls, homogeneous catalysis, iron, carbonyl compounds, mechanistic studies

1. INTRODUCTION

The use of iron as core metal in homogeneous catalysis has become a research topic of interest during the last years.¹ The reasons are clear: iron is the most abundant transition metal in Earth's crust, is widely distributed across the world and it has been extracted and processed since the dawn of civilization. All these features render iron as a non-contaminant, biocompatible, non-toxic and inexpensive metal, and therefore it constitutes the perfect candidate to replace noble metals (rhodium, palladium, platinum, iridium, etc.) that are being currently employed in homogeneous catalysis, and whose toxicity and increasing market price are a growing concern. Although heterogeneous catalysts are usually preferred for industrial bulky processes, the use of homogeneous catalysts that permit mild reaction conditions to achieve chemo-, regio-, and stereo-selectivity is favored in small and medium scale syntheses such as those employed in fine chemicals. In this context, the generation of alcohols via reduction of carbonyl functionalities (aldehydes and ketones) is a frequent transformation, and therefore the implementation of iron-based catalysts in reduction processes has already been reviewed.² Among the catalytic reduction methods currently available, hydrosilylation offers the advantage of combining safe and mild reaction conditions with a convenient reducing power. Thus, the iron-catalyzed hydrosilylation reduction of carbonyls into alcohols gathers all the desirable properties of a chemical process aimed to fulfill the needs of such a widespread transformation in organic chemistry. However, the first report on iron-catalyzed hydrosilylation of carbonyls is relatively recent³ and the most remarkable advances have only been achieved during the present decade. Hence, this is a process of ongoing development and there are some aspects that remain understudied such as the mechanism of the catalysis.

This review comprises more than a hundred publications covering the literature until summer 2018, and it is exclusively focused on iron complexes used as homogeneous catalysts for the reduction of ketone and aldehyde functionalities into alcohols (or silyl ethers) via hydrosilylation. The reaction conditions (temperature, catalyst loading, reaction time, hydrosilane reductant) employed so far to achieve efficient catalysis with iron complexes will be revised and possible correlations between those hydrosilylation conditions and the nature of the iron complex are suggested. The different catalytic systems reviewed will therefore be sorted regarding the nature of the ligands that take part in the iron coordination compounds. Those complexes that feature different types of ligands around the iron center, will be classified considering that (or those) ligand chosen by the authors as the most relevant to define the catalytic ability of the iron complex under study. In addition, a section dedicated to the mechanistic and kinetic studies reported to date is included, aiming to sum up the scarce knowledge within this regard.

2. HYDROSILYLATION REDUCTION

Reduction of functional groups containing double or triple bonds in organic molecules is one of the most employed transformations in organic chemistry at any scale. The particular case of the reduction of carbonyl groups into alcohols is of wide interest to agrochemical and pharmaceutical industries as well as for the synthesis of natural products. Hydrogenation is an atom-efficient method in which no reaction side-products are generated and is found very useful in the presence of an heterogeneous catalyst for large-scale synthesis or using more finely tuned homogeneous catalysts for selective and asymmetric synthesis. However, the high H_2 pressure needed for this process makes it difficult to scale it down to laboratory-sized settings, and the high flammability of hydrogen gas constitutes a real hazard to be regarded. On the other hand, metal hydride

compounds, such as LiAlH_4 , NaBH_4 or diisobutylaluminum hydride (DIBAL), employed in stoichiometric amounts are prevalent in medium- and small-scale synthesis, being their low selectivity and the generation of large amounts of waste their main disadvantages. Transfer hydrogenation has emerged as an interesting reduction methodology as it avoids the use of high pressure of H_2 gas and utilizes readily available hydrogen donors (frequently 2-propanol) instead, in the presence of a catalyst.⁴

As an alternative to the aforementioned methods, hydrosilylation operates under mild conditions and it does not require high hydrogen pressure nor stoichiometric amounts of moisture sensitive reactants as LiAlH_4 or borohydrides. Hydrosilylation consists on the addition of a primary, secondary or tertiary substituted silane across a double bond ($\text{C}=\text{X}$) in which new $\text{H}-\text{C}$ and $\text{X}-\text{Si}$ single bonds are formed. Hydrolysis of the silylated intermediate affords the final reduced product. A general reaction scheme for the particular case of carbonyl hydrosilylation is depicted in Scheme 1. As a further utility of this reaction, the silylether intermediate can also be used as a protecting group in synthesis.⁵

Scheme 1. General reaction scheme for the hydrosilylation of carbon-oxygen double bonds.

The difference in the electronegativity values of Si (1.9) and H (2.2) atoms makes the $\text{Si}-\text{H}$ bond slightly polarized in a way that it tends to produce hydrides. This feature, along with the strength of the $\text{Si}-\text{O}$ bond, renders the reduction of $\text{C}=\text{O}$ bonds via hydrosilylation a thermodynamically favored process. Nevertheless, the reaction needs of a promoter to proceed, which activates either

the carbonyl substrate (acid catalysts) or the silane (transition-metal catalysts or bases). As a consequence, catalytic hydrosilylation combines an exceptional reducing capability with a high selectivity that can be finely tuned by the hydrosilane choice and ligand design.

Silanes used in hydrosilylation processes are usually air-stable liquids and therefore easy to handle; likewise, the silicon byproducts can be readily removed from the reaction crude by means of common laboratory methods as vacuum pump, extraction with organic solvents or column chromatography. At the same time, the need for stoichiometric hydrosilanes as reductants and subsequent generation of organosilicon byproducts represents the main drawback of this reduction method, despite such waste are essentially not toxic nor hazardous. Many hydrosilanes are commercially available and their reactivity and price can vary substantially between them,⁶ which can considerably compromise the viability of a hydrosilylation process. Some hydrosiloxanes, as polymethylhydrosiloxane (PMHS) and 1,1,3,3-tetramethyldisiloxane (TMDS)⁷ (Figure 1), are produced as intermediates or byproducts in the silicone industry and are therefore inexpensive.

Figure 1. Molecular structure of common hydrosiloxanes.

Unfortunately, these di- or polysiloxanes usually show poor activity towards hydrosilylation when compared to other monomeric silanes as phenylsilanes ($\text{Ph}_n\text{SiH}_{(4-n)}$; $n = 1 - 3$), triethoxysilane $((\text{EtO})_3\text{SiH})$ or methyldiethoxysilane $((\text{EtO})_2\text{MeSiH})$. Among the most active hydrosilanes, phenylsilane (PhSiH_3), which actually contains 3 equivalents of hydride, is frequently employed for the reduction of carbonyls due to its high activity, but its market price prevents its implementation on large-scale synthesis. The electronic properties of alkoxysilanes are favorable

for some catalytic processes, and therefore are a common choice. However, $(\text{EtO})_3\text{SiH}$ has been reported to be potentially hazardous when used for gram-scale reactions, as it disproportionates in the presence of Lewis acids, producing mixtures of $(\text{EtO})_n\text{SiH}_{4-n}$ ($n = 0 - 4$) including silane (SiH_4), an extremely pyrophoric gas.⁸ While non-hazardous silanes of medium price, such as $(\text{EtO})_2\text{MeSiH}$ and Ph_2SiH_2 , are the best option for small and medium scale processes, only PMHS and TMDS are suitable for large-scale synthesis, due to their low cost and safety.

The first hydrosilylation of a double bond, in which HSiCl_3 was added to 1-octene, was reported in 1947 by Leo H. Sommer *et al.*⁹ This reaction was catalyzed by diacetyl peroxide and was proposed to follow a free-radical mechanism. The use of a peroxide (*tert*-butyl perbenzoate) as catalyst was also reported by Speier and coworkers in 1956,¹⁰ and it was Speier's team as well who first reported during following years the use of precious metal salts (RuCl_2 , IrCl_3 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, among others) as catalysts for the hydrosilylation of terminal¹¹ and internal¹² olefins.

It was in 1972 that Ojima published the first catalytic hydrosilylation of carbonyl compounds, using $\text{RhCl}(\text{PPh}_3)_3$ as catalyst (Wilkinson's catalyst) and Et_3SiH as hydride source.¹³ The hydrosilylation of cyclohexanone under such conditions proceeded quantitatively at room temperature in very short times, though the reaction of aromatic ketones needed to be heated at 60 °C. Shortly thereafter, the use of chiral ligands to induce asymmetry was implemented by the groups of Kumada,^{14,15} Kagan¹⁶ and Ojima.¹⁷ Since these early reports, an explosive development in transition-metal-catalyzed hydrosilylation took place. The advances reported during the first decades of intense research, until the late 2000s have been accounted in a number of books and reviews,^{18,19,20} among which are worth of special consideration those by Ojima¹⁹ and by Marciniak.¹⁸ In the last decades, however, there has been a growing interest in the replacement of second- and third-row transition metals (such as ruthenium, rhodium, palladium, iridium or

platinum), by more economically available first-row transition metals such as manganese, iron, cobalt, nickel or copper. Although the electronic properties of 2nd-/3rd-row transition metals have permitted the development of highly efficient homogeneous catalytic systems based on coordination compounds of such metals, their increasing market prices and concern about environmental impact have prompted many researchers to direct their efforts to the design of new catalytic systems based on cheap and environmentally-friendly first-row transition metals.

3. IRON-BASED CATALYSTS

The quest for the development of base-metal catalysts with an activity comparable to those of precious metals in different organic transformations has long been a research topic of great interest. The usual approach is to incorporate ancillary ligands around the metal center in order to alter its electronic properties and tune its reactivity and selectivity towards the desired process. Many first-row transition metals have been tested in catalytic hydrosilylation of carbonyl compounds,^{18,21} as they are usually more earth-abundant and environmentally-friendly as well as less toxic than their second- and third-row counterparts. On such traits, no other metal competes with iron, since it is the second most abundant metal on the Earth's crust (topped by aluminum, which in turn is more difficult to extract), it is widely integrated in biological systems and therefore its use in chemical processes does not constitute a relevant threat to the environment nor human health. Due to its abundance, many low-price iron salts are commercially available for their use at laboratory or industry scale. Consequently, the use of iron-based catalysts for organic reactions has received considerable attention during the last two decades, and several reviews have summarized the advances in this field.¹ Especially after the review by Bolm *et al.* in 2004,^{1a} some organic transformations have experimented a remarkable development, reductions among them,² as has

been highlighted in the extensive recent review by Bauer and Knölker.^{1b} In the particular case of ketone hydrosilylation, the first example of an homogeneous iron catalyst was reported by Brunner in 1991,³ but it was not until the mid 2000's decade when this kind of process became the focus of many research works.

3.1. Nitrogen-based ligands. The earliest example of efficient iron-catalyzed hydrosilylation of ketones was reported by Nishiyama and Furuta in 2007.²² They converted a wide range of ketones into alcohols using 5 mol% of iron(II) acetate, adding different nitrogen-based ligands (Figure 2) in refluxing THF.

Figure 2. Nitrogen-based ligands employed by Nishiyama *et al.*

Interestingly, the best catalytic performance was obtained using a 10 mol% of the structurally simple ligand *N,N,N',N'*-tetramethylethylenediamine (tmeda), and good conversions were also achieved with cost-effective PMHS (polymethylhydrosiloxane) as hydrosilane. By using chiral tridentate bisoxazoline ligands *pybox-bn*, *bopa-ip* and *bopa-tb* (Figure 2), several ketones were

asymmetrically reduced with moderate enantiomeric excesses (*ee*) ranging from 37 to 79%, depending on the substrate and on the *N*-based ligand of choice, and thus establishing the first methodology for the asymmetric hydrosilylation of carbonyls catalyzed by iron. The use of chiral NNN pincer ligands to form Fe(II) and Co(II) complexes active as homogeneous catalysts in enantioselective hydrosilylation and cyclopropanation was reported by the group of Gade by the same time.²³ For the asymmetric hydrosilylation of acetophenone, several iron complexes bearing bis(pyridylimino)isoindole-derived ligands were tested at 5 mol% ratio adding 2 equivalents of diethoxymethylsilane in THF, in a range of reaction times and temperatures. Optimum catalyst and conditions (Scheme 2) were then applied in order to study the scope of the reaction. Significantly, best enantioselectivities (80-93% *ee*) were obtained for aryl ketones reacting at 40 °C, while alkyl ketones afforded lower yields (50-51%) and enantioselectivities (56-59% *ee*) under the same reaction conditions.

Scheme 2. Asymmetric iron-catalyzed hydrosilylation where the ligand used is a chiral bis(pyridylimino)isoindole.

164 The group of Chirik reported in 2008 the first example of iron-catalyzed hydrosilylation of
 165 carbonyl compounds at room temperature with low catalyst loadings, using well-defined iron
 166 complexes bearing bis(imino)pyridine (PDI) ligands.²⁴ Complex (ⁱPrPDI)Fe(N₂)₂ (Figure 3) had
 167 already demonstrated to be active for alkene reduction²⁵ and thus the applicability in ketone and
 168 aldehyde hydrosilylation of this and similar iron complexes (Figure 3) was also studied. Several
 169 aromatic and aliphatic ketones as well as *p*-tolualdehyde were successfully reduced to their
 170 corresponding alcohols with 2 equivalents of Ph₂SiH₂ employing 1 mol% of
 171 (ⁱPrPDI)Fe(CH₂SiMe₃)₂ or 0.1 mol% of (^{Cy}APDI)Fe(CH₂SiMe₃)₂ at 23 °C within times ranging
 172 from 1 to 12 hours.

Figure 3. Bis(imino)pyridine, pyridine bis(oxazoline) and bis(oxazoline) iron complexes used by Chirik and co-workers.

This study was later continued by using chiral pyridine bis(oxazoline) "pybox" and bis(oxazoline) "box" ligands instead.²⁶ Prior to their application in the formation of iron complexes and their use as catalysts, pyridine bis(oxazoline) and bis(imino)pyridine ligands were compared in terms of redox potentials. The resulting dialkyl iron complexes (Figure 3) were used as catalysts for the asymmetric hydrosilylation of various aromatic and aliphatic ketones in the presence of 2 equivalents of PhSiH₃ at room temperature with 0.3 mol% [Fe] for Pybox complexes or 1 mol% for Box complexes. After one hour, for both groups of catalysts, most of the substrates were quantitatively converted to alcohols, except sterically hindered ketones 2,4,6-trimethylacetophenone and 2,6-dimethyl-4-*tert*-butylacetophenone, that showed very poor yields. Interestingly, it was found for (*S,S*)-(iPrPybox)Fe(CH₂SiMe₃)₂ that the formation of a bis(chelate) complex (*S,S*)-(iPrPybox)₂Fe within the reaction media is the main mechanism of catalyst inactivation. Enantiomeric excesses of the products were also found to be generally low (less than 50% *ee* using (*S,S*)-(RPybox)Fe(CH₂SiMe₃)₂ complexes, and less than 33% *ee* for (*S,S*)-(RBox)Fe(CH₂EMe₃)₂ complexes). Aiming to improve the catalytic performance of these iron complexes while taking advantage of their potential enantioselectivity, the reactions using (*S,S*)-(iPrPybox)Fe(CH₂SiMe₃)₂ and (*S,S*)-(iPrBox)Fe(CH₂SiMe₃)₂ catalysts were reproduced at the same conditions, but adding 0.95 equivalents (relative to Fe) of neutral borane B(C₆F₅)₃ as electrophilic activator.²⁷ However, conversions remained virtually unchanged while enantioselectivities were only slightly improved, staying generally under 50% *ee*, except for 2,4,6-trimethylacetophenone, that reached 93% *ee* using (*S,S*)-(iPrBox)Fe(CH₂SiMe₃)₂ (but only 16% yield). In sight of the results of catalytic hydrosilylation and the comparative study of the one-electron reduction potentials of

the free ligands, they concluded that the more electron-donating character of pyridine bis(oxazoline) ligands disfavors electron transfer with the metal center in comparison to bis(imino)pyridine ligands.

Continuing their work on hydrosilylation catalyzed by a combination of iron(II) acetate and polidentate nitrogen-based ligands,²² the group of Nishiyama focused on the use of chiral bis(oxazolinyphenyl)amine "Bopa" ligands (Scheme 3) with the ability to induce asymmetry in the reduced product.²⁸ In this case, the use of cobalt(II) acetate instead of the iron precursor was also explored. After optimization experiments on the hydrosilylation of methyl 4-phenylphenyl ketone, probing different Bopa ligands, the bis(benzyl)- and bis(phenyl)-substituted ligands were found to provide the best conversions and enantioselectivities for the iron- and the cobalt-catalyzed reactions, respectively. Using the optimized catalytic systems (Scheme 3), a wide range of methyl aryl ketones were conveniently reduced to their corresponding alcohols (with *R* absolute configuration in all cases), with excellent yields and moderate to good enantioselectivities, being notably higher for the cobalt-based catalytic mixture.

Scheme 3. Iron(II) and cobalt(II) catalyzed asymmetric hydrosilylation of methyl aryl ketones using chiral Bopa ligands.

Although iron and cobalt chlorides had previously demonstrated to be inefficient as the metal precursor for this kind of catalytic settings,^{22,28} the combination of the iron(III) chloride complex (Bopa-*dpm*)FeCl₂ (Scheme 4) with zinc powder allowed to convert a variety of ketones into alcohols with good conversions and enantioselectivities.²⁹ The most remarkable aspect of this new catalytic system is that, under similar reaction conditions (Scheme 4), the resulting alcohols show *S* absolute configuration, in contrast to the products of the previous method.^{28,29} It is worth noting that magnetic susceptibility measurements using the Evans method³⁰ of (Bopa-*dpm*)FeCl₂ in solution, suggested that the addition of zinc powder causes the reduction of the metal center from Fe(III) to Fe(II).

Scheme 4. Iron-catalyzed asymmetric hydrosilylation of alkyl aryl ketones using (Bopa-*dpm*)FeCl₂ with zinc powder.

An outstanding example of iron-catalyzed hydrosilylation of carbonyl compounds is that reported by Yang and Tilley in 2010.³¹ They directly employed an Fe(II) precursor commonly

used in specialized coordination chemistry laboratory such as iron bis(hexamethyldisilazide) ($\text{Fe}(\text{HMDS})_2$) as the catalyst of choice, without any other ligand or activator. The reduction of several aromatic and aliphatic ketones and aldehydes in the presence of Ph_2SiH_2 was achieved at room temperature with low catalyst loadings (0.01-2.7 mol%) in benzene solution. Most substrates were completely converted to their corresponding silylethers within one hour, albeit some of them needed up to 28 hours. The possibilities of performing these catalyses in the absence of a solvent, as well as generating the iron catalyst *in situ* from FeBr_2 and KHMDs were also tested with excellent results. While the main strength of this method relies on the simplicity and efficiency of the catalyst, the absence of any ancillary ligand prevents control of chemo- or stereoselectivities, limiting its applicability.

In 2015 the group of Gade presented a new iron alkoxide complex bearing a chiral bis(oxazolinylmethylidene)isoindoline (boxmi) ligand able to catalyze the hydrosilylation of a wide range of ketones with remarkable high enantiomeric excesses and excellent conversions.³² Reaction conditions were optimized for the use of a 5 mol% of iron catalyst and 2 equivalents of $(\text{EtO})_2\text{MeSiH}$ in toluene solution, adding the silane at $-78\text{ }^\circ\text{C}$ and then allowing the mixture to warm up to room temperature (Scheme 5). Most of the substrates were reduced above 95% conversion after 6 hours and the enantiomeric excesses surpassed 90% *ee* in most cases. Although relatively high catalyst loadings were utilized (5 mol%) for the process, this system proved to be active enough to work at very low temperatures, thus enabling to achieve the high enantioselectivities needed in many cases for the implementation of a catalyst in a synthetic process.

Scheme 5. Enantioselective hydrosilylation of ketones by an NNN pincer iron complex.

Good enantioselectivities at room temperature were obtained by the catalytic system reported by Zuo *et al.*, which featured a well-defined iron complex bearing a chiral iminopyridine-oxazoline (IPO) ligand.³³ Under optimized conditions, a variety of aryl ketones were reduced to alcohols via hydrosilylation catalyzed by a 1 mol% of [(*S*)-IPO]FeBr₂ at room temperature with excellent yields, albeit the presence a 2 mol% of NaBHET₃ was necessary to activate the iron pre-catalyst (Scheme 6). Good enantioselectivities (60-90% *ee*) were achieved for many of the aryl-substituted ketones, however only very poor enantiomeric excesses (1-9%) were reached from the reduction of dialkyl ketones.

Scheme 6. Iron-based catalytic IPO-system for the enantioselective hydrosilylation of aryl ketones at room temperature.

The group of Findlater reported in 2015 the use of an iron catalyst for the efficient reduction of ketones and aldehydes via hydrosilylation under solvent-free conditions.³⁴ A dichloride iron complex with a bis(arylimino)acenaphthene (BIAN) ligand was initially formed and then reduced with Na/Hg amalgam in the presence of toluene to afford an η^6 -arene type iron(0) complex BIAN-Fe(C₇H₈) (Scheme 7). This complex was employed at 1 mol% loading as catalyst for the hydrosilylation of aldehydes and ketones with Ph₂SiH₂ as reductant at 70 °C. Most of the aldehydes reached conversions of around 90% within 30 minutes, while most of the ketones needed 3 hours for obtaining similar yields.

Scheme 7. Solvent-free hydrosilylation of carbonyl compounds with a BIAN-based Fe(0) catalyst.

Yu *et al.* have also reported the use of a bis(arylimino)acenaphthene (BIAN) ligand to form an iron(II) complex active for catalytic hydrosilylation of aldehydes and ketones.³⁵ Under the optimized reaction conditions, complex [Mes-BIAN^{M_e}]₂FeCl₂ (Scheme 8) achieved very good conversions of aldehydes and ketones to alcohols at room temperature after 1 hour with 1 mol% of iron catalyst. Dihalide complex [Mes-BIAN^{M_e}]₂FeCl₂ needed to be treated with 2 equivalents of LiCH₂SiMe₃ prior to add the carbonyl substrate in order to replace the chloride ligands and furnish the catalytically active species.

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280 **Scheme 8.** Room-temperature hydrosilylation of carbonyl compounds catalyzed by a BIAN-Fe(II)
 281 complex.

282 In 2018, Lin *et al.* employed an NNN-pincer ligand with pyrazole groups for the synthesis of a
 283 low-coordinate iron(II) complex featuring a bis(trimethylsilyl)amide ligand.³⁶ Structural
 284 characterization of the complex revealed that the NNN-pincer ligand acted as a bidentate ligand,
 285 rather than a tridentate one, presumably due to the steric interactions with the bulky
 286 hexamethyldisilazide ligand. The iron complex was then probed for the catalytic hydrosilylation
 287 of several aromatic and aliphatic aldehydes and ketones (Scheme 9). The substrates were
 288 completely converted to silyl ethers (derived from PhSiH₃) within 24 hours at room temperature,
 289 using 1 mol% of iron pre-catalyst.

Scheme 9. Hydrosilylation of aldehydes and ketones catalyzed by a low-coordinate Fe complex.

In our group, we have recently reported the use of anthraquinone-derived tridentate NNO ligands for the synthesis of iron(II) complexes with high activity as hydrosilylation catalysts.^{37,38} Preliminary results on the hydrosilylation of acetophenone were obtained employing an iron-based pre-catalyst with a picolylamino-substituted anthraquinone ligand "AQPic" (Figure 4).³⁷ The amount of Fe(II) pre-catalyst Fe(AQPic)₂ was initially set to 0.25 mol%, obtaining a 52% conversion into 2-phenylethanol after 1 hour of reaction (or 80% after 24 hours) at room temperature using (EtO)₂MeSiH as reductant. The possibility of generating the catalyst *in situ* was also explored using a mixture of LiHMDS, Et₃N and FeCl₂ or Fe(OAc)₂. When FeCl₂ was employed as Fe(II) precursor, the same results as using isolated Fe(AQPic)₂ were obtained, but when Fe(OAc)₂ was used, a notable enhancement of the catalytic performance was observed (77% conversion after 1 hour).

Fe(AQPic)₂

Figure 4. Anthraquinoid Fe(II) pre-catalyst for efficient ketone hydrosilylation.

Continuing our work on Fe-catalyzed hydrosilylation, a new iron(II) complex was synthesized bearing an anthraquinone-derived ligand substituted with a 2-pyridylethylamino arm "AQ^{Et}Py" (Scheme 10), which showed excellent activity towards carbonyl hydrosilylation.³⁸ Employing Fe(AQ^{Et}Py)₂ as catalyst, aromatic aldehydes were reduced to primary alcohols using 0.25 mol% of catalyst at room temperature in very short times (Scheme 10). Substrates bearing an electron-donating substituent on the aromatic ring proceeded faster than those with electron-withdrawing groups, but in all cases the hydrosilylations were completed in less than 60 minutes. Ketone hydrosilylation required 0.5 mol% of the Fe(II) catalyst and slightly longer reaction times, but all substrates, aromatic and aliphatic, provided excellent or quantitative conversions in under 2 hours of reaction (Scheme 10). Only but-3-en-2-one reacted notably slower (31% conversion in 2 hours), although only [1,2]-hydrosilylation product was detected. Importantly, the catalyst loading could be lowered down to 0.05 mol%, yielding a 91% conversion of acetophenone after 14 hours of reaction.

Scheme 10. Fe-catalyzed hydrosilylation of aldehydes and ketones with an anthraquinone-based iron(II) complex.

The group of Nishiyama have also explored the field of well-defined iron complexes for their use in catalysis.^{39,40} A chiral bis(oxazolinyl)phenyl "phebox" ligand was initially used to form the iron bromide complex [phebox-*iPr*] $\text{Fe}(\text{CO})_2\text{Br}$ (Figure 5) which was employed to catalyze the asymmetric hydrosilylation of 4-phenylacetophenone.³⁹ Optimized reaction conditions were found to require 24 hours at 50 °C in hexane solution in the presence of 1.5 equivalents of $(\text{EtO})_2\text{MeSiH}$, with a 2 mol% loading of the iron pre-catalyst and equal amount of $\text{Na}(\text{acac})$. Under these reaction conditions, 99% yield and 66% *ee* of the (*R*) alcohol were obtained.

Later, in 2015, the study of similar complexes for asymmetric reduction of ketones was expanded by describing a series of iron-phebox complexes with stannyl, silyl and methyl ligands.⁴⁰ Several iron complexes with the general formula [phebox-*R*] $\text{Fe}(\text{CO})_2\text{X}$ (Figure 5) were prepared and tested as catalysts for the hydrosilylation of some methyl aryl ketones. The trimethylsilyl

substituted complexes ($[\text{phebox-}R]\text{Fe}(\text{CO})_2(\text{SiMe}_3)$) proved to be the most catalytically active species, as apparently the stannyl derivatives were too stable to react while the methylated complexes were too unstable within the reaction media. A yield of 99%, but only 34% *ee* (*R*), of 1-(4-phenyl-phenyl)ethanol was obtained using 2 mol% of $[\text{phebox-}i\text{Pr}]\text{Fe}(\text{CO})_2(\text{SiMe}_3)$ in toluene at 50 °C after 24 hours, with 1.5 equivalents of $(\text{EtO})_2\text{MeSiH}$ as reductant and no other additives in this case.

Figure 5. Iron dicarbonyl complexes with chiral bis(oxazolinyl)phenyl ligands.

3.2. Phosphorus-based ligands. Following an analogous methodology to that initially reported by Nishiyama *et al.*,²² Beller and co-workers aimed to improve catalytic performance and enantioselectivity of iron-catalyzed hydrosilylation of pro-chiral ketones, expanding the study to the use of electron-rich chiral phosphine ligands and different iron(II) and iron(III) salts.⁴¹ Among the large variety of phosphine ligands tested for the hydrosilylation of acetophenone, 1,2-bis((2*S*,5*S*)-2,5-diethyl-phospholano)benzene ((*S,S*)-Et-duphos) provided the best results, with quantitative conversion (> 99%) and 77% *ee*. However, (*S,S*)-Me-duphos (Scheme 11), which afforded the same yield and similar *ee* (75%), was chosen to conduct the rest of the optimization process for practical and economic reasons. Up to eleven iron salts or iron/silver salt combinations

were screened, proving $\text{Fe}(\text{OAc})_2$ to be the most convenient in terms of both conversion and enantioselectivity. Different hydrosilanes, solvents and temperatures were tested, finding that $(\text{EtO})_2\text{MeSiH}$ and PMHS gave similar results, and that different organic solvents (THF, diethylether, *n*-hexane, toluene, dichloromethane) had no relevant influence on the conversion nor the enantioselectivity of the reaction. When the temperature was dropped from 65 °C down to room temperature, an appreciable loss of yield was observed, without a significant influence on *ee* values. Once the reaction conditions were optimized (Scheme 11) the reaction scope was studied on aryl and alkyl ketones; good to excellent yields and selectivities were obtained for most of the substrates under study, with enantioselectivities of up to 99% *ee* for some sterically hindered aryl ketones.

Scheme 11. Optimized conditions for the asymmetric hydrosilylation of acetophenone catalyzed by $\text{Fe}(\text{OAc})_2$ and a phosphine ligand.

Plietker and his group reported the catalytic activity of a mixture based on iron complex $\text{Bu}_4\text{N}[\text{Fe}(\text{CO})_3(\text{NO})]$ for the hydrosilylation of ketones and aldehydes.⁴² This iron precursor was used in a 1 mol% concentration, in the presence of equimolar amount of tricyclohexylphosphine, at 30 °C within 1,4-dioxane solution. Employing 3 equivalents of PMHS as hydrogen source,

excellent yields were obtained after 14 hours, although the catalyst loading, and temperature needed to be raised to 2.5 mol% and 50 °C, respectively, for some substrates.

The group of Darcel and Sortais reported in 2011 and 2012 the utilization of several iron complexes with simple phosphine ligands as pre-catalyst for the hydrosilylation of aldehydes and ketones upon visible light activation.^{43,44}

Guan and co-workers described in 2011 the synthesis of several iron hydride complexes with phosphinite-based POCOP pincer ligands.⁴⁵ After the optimization of the hydrosilylation reaction, (POCOP)FeH(PMe₃)₂ (Figure 6) was employed for the reduction of a variety of aldehydes and ketones. Aromatic aldehydes gave very good yields (>80%) after 1-3 hours at 50-65 °C using 1 mol% of iron catalyst and 1 equivalent of (EtO)₃SiH in THF. Using the same catalyst loading and reducing agent, ketones afforded lower yields (40-88%) after longer reaction times (4.5-48 hours) and in some cases a higher temperature of 80 °C, and therefore the use of toluene as a solvent, was necessary.

Replacement of the hydride ligand, as well as one or both of the trimethylphosphines, by CO and CH₃CN was later reported by Guan's team in 2014.⁴⁶ This process renders cationic complexes with enhanced catalytic activity towards the hydrosilylation of benzaldehyde and acetophenone compared to their hydride counterparts. The most active among them (Figure 6) achieved complete conversion of benzaldehyde after 24 hours at 50 °C and 79% yield for acetophenone after 48 hours at 80 °C, with 1 mol% of iron pre-catalyst in both cases.

Figure 6. Iron hydride (left) and cationic (right) complexes with a phosphinite pincer used for the hydrosilylation of aldehydes and ketones by Guan and coworkers.

3.3. Mixed nitrogen/phosphorus-based ligands.

Turculet and her team presented in 2013 a ground-breaking advance towards the applicability of iron catalysts at room temperature and low catalyst loadings.⁴⁷ Inspired by the high activity of $\text{Fe}(\text{HMDS})_2$ as hydrosilylation catalyst,³¹ they aimed to improve the stability and performance of the iron complex by introduction of an ancillary ligand, while retaining the catalytic properties of a low-coordinate complex. A notably wide range of aromatic and aliphatic ketones and aldehydes were successfully reduced to alcohols at room temperature in toluene solution, in the presence of 1 equivalent of phenylsilane as hydrogen source and employing (*N*-phosphinoamidinate) $\text{Fe}(\text{HMDS})$ as catalyst (Scheme 12) at loadings between 0.01 and 1 mol%, depending on the carbonyl substrate. Noteworthy, this same iron pre-catalyst and reaction conditions were effective for the reduction of several esters to primary alcohols as well, although the minimum catalyst concentration needed for this process was 0.25 mol%. The outstanding catalytic ability of this iron complex was attributed mainly to the redox non-innocent properties of the *N*-phosphinoamidinate ligand.

Scheme 12. Optimized reaction conditions for the catalytic hydrosilylation of carbonyl compounds with a *N*-phosphinoamidinate iron complex.

Findlater and co-workers studied iron and cobalt complexes bearing neutral pincer PNP ligands and their reactivity under hydrosilylation conditions.⁴⁸ Up to four complexes (Figure 7) were synthesized, structurally characterized, and then probed as catalysts (1 mol% loading) for the reduction of ketones (aliphatic and aromatic) and aldehydes (aromatic) with 1 equivalent of (EtO)₃SiH without any solvent. After 24 hours at room temperature, all catalysts afforded moderate to good conversions for the substrates tested. Importantly, activation of the catalyst with NaBHET₃ (2 mol%) proved to be necessary.

Figure 7. (PONOP)MCl₂ and (PNP)MCl₂ iron and cobalt complexes.

3.4. N-Heterocyclic Carbene (NHC) ligands. The application of an iron complex bearing *N*-heterocyclic carbene (NHC) ligands on catalytic hydrosilylation of carbonyl compounds was reported for the first time by Royo and co-workers in 2010.⁴⁹ The reduction of various *para*-substituted benzaldehydes via hydrosilylation was achieved using a (Cp*-NHC)FeCl complex (Figure 8) as catalyst in 1 mol% concentration. The reaction in refluxing acetonitrile in the presence of (EtO)₂MeSiH yielded the corresponding benzyl alcohols in quantitative conversions within times ranging from 2 to 24 hours. The hydrosilylation of hexanal or 4-nitrophenyl methyl ketone gave no conversion under the same reaction conditions.

Another Fe-NHC pre-catalyst developed a few years later⁵⁰ achieved the hydrosilylation of similar aldehydes improving the reaction conditions in terms of temperature and reaction times. Using 1 mol% of Fe(IMes)(CO)₄ (Figure 8) as catalyst and 1.2 equivalents of PhSiH₃ as hydrogen source, quantitative conversions were obtained after 4 hours at room temperature.

Figure 8. Iron complexes bearing NHC ligand employed for catalytic hydrosilylation of aldehydes.

The group of Royo also presented in 2013 another Fe-NHC complex catalytically active for the hydrosilylation of ketones.⁵¹ The active species (Cp-NHC)Fe(CO)(OH) (Scheme 13) was generated *in situ* through basic treatment of its iodinated precursor (Cp-NHC)Fe(CO)I with

KO^tBu, in the presence of traces of water within the solvent. Employing 0.5 mol% of the iron(II) precursor and equal amount of KO^tBu, *para*-substituted acetophenones were completely converted into the hydrosilylated product in 1 hour at room temperature, using either PMHS or Ph₂SiH₂ as reductant (Scheme 13). The reduction of aliphatic ketones proceeded at comparable rate in the presence of Ph₂SiH₂, but notably slower when using PMHS, needing 24 - 48 hours to reach complete conversion of this kind of substrate.

Scheme 13. Hydrosilylation of ketones catalyzed by a Fe-NHC complex generated *in situ*.

Darcel and Sortais described throughout 2011 and 2012 the synthesis and characterization of several NHC-iron complexes and their use as catalysts in aldehyde and ketone hydrosilylation.^{52,53} Using 1 mol% of complex [Cp(IMes)Fe(CO)₂]I under visible light irradiation, or the isolated complex [Cp(IMes)Fe(CO)(I)] (Scheme 14), different aldehydes were quantitatively reduced in the presence of PhSiH₃. Heating of the reaction was needed: 70 °C for 1 hour in THF solution or 30 °C for 3 hours in toluene solution.⁵² This catalytic setting was also tested with no solvent providing excellent results, also for the reductions of ketones, although 2 mol% of iron catalyst and longer reaction times were required in the latter case.⁵³

Scheme 14. NHC-based iron complexes described by Darcel and co-workers and used for hydrosilylation.

A series of similar Fe-NHC complexes (Figure 9) have also been tested for the catalytic hydrosilylation of some substituted benzaldehydes and acetophenones.⁵⁴ Using 1 mol% of the iron complexes bearing the NHC ligand with 2,4,6-trimethylbenzyl and 3,5-dimethylbenzyl substituents (Figure 9) in the presence of 1 equivalent of PhSiH₃ at 100 °C, without solvent, the substrates screened were conveniently reduced in 5 to 60 minutes for aldehydes and 2 to 4 hours for ketones.

Figure 9. Cationic iron piano-stool cyclopentadienyl complexes bearing saturated NHC carbene ligands.

Under similar reaction condition as those employed using $[\text{Cp}(\text{IMes})\text{Fe}(\text{CO})_2]\text{I}$ as catalyst,^{52,53} complex $[\text{CpFe}(\text{CO})_2(\text{maloNHC})]$ at 1 mol% loading successfully catalyzed the transformation of aromatic aldehydes and ketones into the corresponding alcohols. In these studies, temperature, solvent, reaction time and hydrogen source were varied depending on the substrate nature (Scheme

15).⁵⁵ Aromatic imines were also reduced to secondary amines under these conditions. In all the cases assayed, activation of the iron catalyst by visible light irradiation was necessary.

Scheme 15. Hydrosilylation of ketones, aldehydes and imines light-catalyzed by a zwitterionic Fe-NHC complex.

Well-defined NHC-iron complexes have also been the focus of Frank Glorius and co-workers.^{56,57} After thorough characterization, the dimethyl iron complex *trans*-(IMes)₂Fe(CH₃)₂ (Figure 10) was used as catalyst for transfer hydrogenation and hydrosilylation of 2-naphtyl methyl ketone.⁵⁶ Transformation to the corresponding alcohol by hydrosilylation was achieved in quantitative conversion after 5 hours at room temperature, using only 1.2 mol% of *trans*-(IMes)₂Fe(CH₃)₂ and 1.1 equivalents of (EtO)₃SiH without any other additive. It is worth mentioning that the chloride analogous of this complex, (IMes)₂FeCl₂, showed no catalytic activity for hydrosilylation, even upon heating at 80 °C.

In a parallel work, chloride complex (B^{Me}IPyEN)FeCl₂, bearing a bis-NHC ligand (Figure 10) was studied, and tested as catalyst for the hydrosilylation of acetophenone.⁵⁷ In this case, 95%

yield was obtained after 16 hours at 60 °C, using Ph₂SiH₂ and 1 mol% of the iron catalyst. Notably, the use of 2 mol% of methyl lithium was also needed for the reaction to proceed conveniently, what suggests that it is the methylated analogous, (B^{Me}IPyEN)Fe(CH₃)₂, which is actually the catalytically active species.

Figure 10. Bi-coordinated Fe-NHC complexes active in hydrosilylation of aromatic ketones.

Buitrago and Adolffson developed in 2011 a methodology for the hydrosilylation of ketones by *in situ* generation of an iron catalyst from Fe(OAc)₂ and an NHC ligand.⁵⁸ Several NHC precursors were tested for the reduction of acetophenone, and was [IPr][HCl] the one selected for the rest of the optimization process and reaction scope (Scheme 16). The catalytic mixture consisted of 2.5 mol% of iron(II) acetate and a 3 mol% of both the imidazolium chloride salt of the NHC-derived ligand and *n*-BuLi. A variety of ketones were reduced in good yields after 16 to 18 hours in refluxing THF. Remarkably, inexpensive silane PMHS worked well in this system.

496

497 **Scheme 16.** General conditions for the hydrosilylation of ketones with an *in-situ* generated Fe-
 498 NHC catalyst.

499 In 2012, Buitrago *et al.* screened new NHC ligands⁵⁹ and accomplished an improvement of their
 500 previous results. Using [HEMIM][OTf] as NHC precursor under otherwise the same conditions,
 501 very good yields were obtained lowering the Fe(OAc)₂ loading down to 1 mol%, the same molar
 502 amount of the NHC ligand and 2.2 mol% of *n*-BuLi, after reaction times ranging from 10 minutes
 503 to 3 hours (Scheme 17). In this case, the catalytic system was also applied on aldehydes.

504

505 **Scheme 17.** Improved conditions for the hydrosilylation of aldehydes and ketones with an *in-situ*
 506 generated Fe-NHC catalyst.

Johnson and Albrecht described in 2017 a series of iron complexes with a triazolilydene ligand and their application as catalysts for carbonyl hydrosilylation processes.⁶⁰ The use of a monodentate 1,2,3-triazolylidene iron(II) piano-stool complex (Figure 11) as catalyst at 1 mol% loading afforded complete and rapid (reaction times from 9 minutes to 2.5 hours) reduction of a series of *para*-substituted benzaldehydes and acetophenones in the presence of 1 equivalent of PhSiH₃ at 60 °C. For this optimized reaction conditions, 1,2-dichloroethane was used as solvent.

Figure 11. Triazolilydene iron(II) complex used for catalytic hydrosilylation of aromatic aldehydes and ketones.

Also recently, Liang *et al.* have reported the synthesis⁶¹ and utilization in catalytic hydrosilylation⁶² of a new NHC-based complex bearing two *N*-picolyl-NHC ligands coordinated to an iron center. Complex [pic-NHC]₂Fe (Figure 12) was obtained via deprotonation of the CH₂ bridge between the pyridine and NHC moieties of the ligand, resulting in a dearomatized pyridine which favors a strong N-Fe bond. The hydrosilylation of several aromatic and aliphatic ketones was performed using loadings of 0.05-1 mol% of the iron catalyst in excess PMHS acting as both solvent and hydride source (THF or toluene was added as co-solvent for solid ketones) and excellent conversions were obtained after times ranging from 1.5 to 22 hours at room temperature, though heating at 50 °C was necessary for some substrates. These results establish this catalytic system as one of the most active reported to date, considering the low catalyst loading (0.05 mol%,

while most other catalytic systems require at least 1 mol%) needed to perform the reduction of the substrates at room temperature employing the poorly reactive hydrosilane PMHS.

[pic-NHC]₂Fe

Figure 12. *N*-picolyl-NHC iron(II) complex highly active for ketone hydrosilylation.

3.4.1. *N*-Heterocyclic Silylene (NHSi) ligands. Driess and Inoue described the synthesis of a set of novel iron(0) complexes bearing a *N*-heterocyclic silylene (NHSi) ligand which were fully characterized prior to testing their catalytic ability.⁶³ A silyl-hydride complex, featuring two diphosphine ligands attached to the iron center (Figure 13) was probed as catalyst for the hydrosilylation of several ketones in the presence of 1.5 equivalents of (EtO)₃SiH. Excellent conversions were obtained, but long reaction times (24 hours) at 70 °C and 5 mol% of iron catalyst were needed.

Figure 13. Fe-NHSi complex employed in catalytic hydrosilylation of ketones.

The efforts of Driess and co-workers were later directed towards the use of pincer-type bis(silylene)-pyridine ligands for the synthesis of Fe(0) complexes.⁶⁴ The catalytic activity of [SiNSi]Fe(PMe₃)₂ (Figure 14) for hydrosilylation was tested on acetophenone and some *para*-substituted derivatives applying the same reaction conditions as those previously reported for their NHSi-based system;⁶³ similar results were obtained, but only 2.5 mol% of iron pre-catalyst was needed.

[SiNSi]Fe(PMe₃)₂

Figure 14. Iron(0) bis(silylene)-pyridine complex tested in catalytic hydrosilylation.

3.5. Others. Xiaoyan Li and co-workers reported throughout the last few years the synthesis of a range of hydrido-iron complexes bearing phosphine ligands (Figure 15) and their use as catalysts for the reduction of aldehydes and ketones via hydrosilylation.⁶⁵ In all cases, (EtO)₃SiH was employed as reductant, and heating of the reaction at 40-60 °C in THF was necessary for the transformation to proceed conveniently. The most effective catalyst among them^{65b} (the synthesis of the Fe complex had previously been described)⁶⁶ needed only 0.3-0.6 mol% of the iron complex to afford good to excellent yields in times slightly below 12 hours for ketones or 4 hours for aldehydes.

Figure 15. Iron hydride complexes used by Li and co-workers as catalysts for hydrosilylation of carbonyls.

The group of Nagashima reported in 2013 an iron disilyl complex with an η^2 -(H-Si) coordinating 1,2-bis(dimethylsilyl)benzene (BDSB) ligand, which exhibited a high catalytic activity for the hydrogenation of alkenes and hydrosilylation of alkenes, amides, aldehydes, ketones and esters.⁶⁷ For the reduction of aldehydes and ketones, 1 mol% of the iron complex (Figure 16) was employed with TMDS (tetramethyldisiloxane) as reductant under solvent-free conditions at room

temperature, achieving above 90% yield after 3-6 hours. Lowering the iron loading to 0.2 mol% afforded similar results after 36 hours for aldehydes.

Figure 16. Disilyl-dicarbonyl iron complex with high catalytic activity for hydrogenation and hydrosilylation.

In 2016, Jung *et al.* reported the successful application of the readily available iron complex $[\text{CpFe}(\text{CO})_2]_2$ as catalyst for the hydrosilylation of aldehydes and ketones.⁶⁸ Optimized conditions required a 5 mol% loading of the iron precursor, in the presence of 2 equivalents of $(\text{EtO})_2\text{MeSiH}$, at 100 °C during 24 hours. Remarkably the reaction worked well under air and no solvent was needed either. Under these conditions, both aldehydes and ketones (most of them aromatic) afforded excellent or quantitative conversions.

Aiming to orient the reader into the advances made on the iron-catalyzed hydrosilylation of carbonyls in terms of applicability in laboratory settings, Table 1 summarize the iron-based catalysts revised on this work, gathering the experimental conditions for the utilization of the most relevant catalytic systems that appear in the literature. The included data correspond to the optimized or most representative conditions employed for the reduction of acetophenone or either benchmark ketone tested in each case. Therefore, aldehyde hydrosilylation is not represented in Table 1, as the reaction conditions needed for the reduction of these substrates are in all cases notably milder (in terms of reaction temperature, time, catalyst loading, etc.) than those required for ketones.

585 **Table 1.** Optimized reaction conditions for the most representative iron-based catalytic systems
 586 for ketone hydrosilylation.

Entry	Catalyst	Fe (mol%)	T (°C)	t (h) ^a	Silane	Ref.
1	Fe(OAc) ₂ + tmeda	5	65	24	(EtO) ₂ MeSi H	22
2	[Fe(tetraphenyl-carbpi)(OAc)]	5	65	16	(EtO) ₂ MeSi H	23
3	(^{Cy} APDI)Fe(CH ₂ SiMe ₃) ₂	0.1	r.t.	3	Ph ₂ SiH ₂	24
4	(Pybox)Fe(CH ₂ SiMe ₃) ₂	0.3	r.t.	1	PhSiH ₃	26
5	Fe(OAc) ₂ + bopa- <i>dpm</i>	2	65	24	(EtO) ₂ MeSi H	28
6	Fe(HMDS) ₂	0.31	r.t.	1	Ph ₂ SiH ₂	31
7	(boxmi)Fe(OCH(Ph)CH ₃)	5	-78	6	(EtO) ₂ MeSi H	32
8	[(<i>S</i>)-IPO]FeBr ₂ ^b	1	r.t.	3	Ph ₂ SiH ₂	33
9	BIAN-Fe(C ₇ H ₈)	1	70	3	Ph ₂ SiH ₂	34
10	[Mes-BIAN ^{Me}]FeCl ₂ ^c	1	r.t.	1	Ph ₂ SiH ₂	35
11	[(κ ² -CZ ^{<i>t</i>Bu} (PZ ^{<i>t</i>Bu}) ₂)Fe(MHDS)]	1	r.t.	24	PhSiH ₃	36
12	Fe(AQPic) ₂	0.5	r.t.	24	(EtO) ₂ MeSi H	37
13	Fe(AQ ^{Et} Py) ₂	0.5	r.t.	1	(EtO) ₂ MeSi H	38
14	[phebox- <i>iPr</i>]Fe(CO) ₂ Br ^d	2	50	24	(EtO) ₂ MeSi H	39
15	[phebox- <i>iPr</i>]Fe(CO) ₂ (SiMe ₃)	2	50	24	(EtO) ₂ MeSi H	40
16	Fe(OAc) ₂ + (<i>S,S</i>)-Me-duphos	5	65	16	(EtO) ₂ MeSi H	41
17	Bu ₄ N[Fe(CO) ₃ (NO)] ^e	1	30	14	PMHS	42

18	(POCOP)FeH(PMe ₃) ₂	1	65	6	(EtO) ₃ SiH	45
19	(<i>N</i> -phosphinoamidinate)Fe(HMDS)	0.015	r.t.	4	PhSiH ₃	47
20	(PNP)FeCl ₂ ^b	1	r.t.	24	(EtO) ₃ SiH	48
21	(Cp-NHC)Fe(CO)(OH)	0.5	r.t.	1.5	PMHS	51
22	[Cp(IMes)Fe(CO)(I)]	2	50	16	PhSiH ₃	53
23	[Cp(<i>NHC</i>)Fe(CO) ₂]I	1	100	4	PhSiH ₃	54
24	[CpFe(CO) ₂ (<i>malon</i> NHC)]	1	70	16	PhSiH ₃	55
25	<i>trans</i> -(IMes) ₂ Fe(CH ₃) ₂	1.2	r.t.	5	(EtO) ₃ SiH	56
26	(B ^{Me} IPyEN)FeCl ₂ ^f	1	60	16	Ph ₂ SiH ₂	57
27	Fe(OAc) ₂ + [IPr][HCl] ^g	2.5	65	16	PMHS	58
28	Fe(OAc) ₂ + [HEMIM][OTf] ^h	1	65	1	PMHS	59
29	[Cp(1,2,3-triazolylidene)(CO)I]	1	60	2	PhSiH ₃	60
30	[pic-NHC] ₂ Fe	0.05	r.t.	2	PMHS	62
31	(NHSi)Fe(dmpe) ₂	5	70	24	(EtO) ₃ SiH	63
32	[SiNSi]Fe(PMe ₃) ₂	2.5	70	22	(EtO) ₃ SiH	64
33	{[(4-MeO-Ph)(Ph)CNH]Fe(H)(PMe ₃) ₃ }	0.6	55	4	(EtO) ₃ SiH	65b
34	[(BDSB) ₂ Fe(CO) ₂]	1	r.t.	6	TMDS	67
35	[CpFe(CO) ₂] ₂	5	100	24	(EtO) ₂ MeSiH	68

^a Time required for a substrate to be converted above 90% under the conditions stated. ^b NaBHEt₃ (2 mol%) was added. ^c LiCH₂SiMe₃ (2 mol%) was added. ^d Na(acac) (2 mol%) was added. ^e Tricyclohexylphosphine (1 mol%) was added. ^f MeLi (2 mol%) was added. ^g *n*-BuLi (3 mol%) was added. ^h *n*-BuLi (2.2 mol%) was added.

4. MECHANISM OF IRON-BASED CATALYSTS

The field of iron-catalyzed carbonyl hydrosilylation is relatively recent, and therefore the understanding of the mechanistic details of such process has not reached great depth. Besides, there are certain aspects of iron-based catalyst that further hamper their study; while most noble metals prefer low spin states ($S = 0$),⁶⁹ iron complexes often have spin states with similar energies, resulting in a tendency to form high spin complexes and to undergo spin crossover processes.^{1d} Such high spin states give rise to paramagnetism, which prevents the practical use of nuclear magnetic resonance (NMR) spectroscopy, depriving the researchers of a powerful tool that provides structural as well as behavioral information of the compounds analyzed. Therefore, many of the mechanistic studies on iron complexes catalytically active for carbonyl hydrosilylation reported to date focus on low spin complexes with strong η -donor ligands, such as silylene, carbene or phosphine ligands.

The group of Guan reported in 2011 their studies on the reactivity of iron(II) hydride complex (POCOP)FeH(PMe₃)₂ (Figure 17) as catalyst for the hydrosilylation of aldehydes.⁴⁵ Stoichiometric experiments were performed and monitored via NMR in order to identify possible interactions between the iron complex and each of the hydrosilylation substrates. When a 1:1 mixture of (POCOP)FeH(PMe₃)₂ and benzaldehyde was heated at 50 °C (hydrosilylation reaction conditions) during 2 days, no changes were observed, evidencing that insertion of the carbonyl from the aldehyde into the Fe-H bond does not take place under such conditions. Another experiment was performed in which (POCOP)FeH(PMe₃)₂ and deuterated diphenylsilane (Ph₂SiD₂) were mixed in 1:1 ratio in order to detect an exchange equilibrium between the deuterium from the silane and the hydride from the Fe complex, but no evidence of such exchange was observed via NMR. Finally, all three components of the reaction ((POCOP)FeH(PMe₃)₂, benzaldehyde and Ph₂SiD₂) were

combined in 1:1:1 ratio, heated at 50 °C within THF-*d*₈ solution and monitored during 10 hours; deuterated silyl ether products were found, but the hydride of Fe-H remained intact.

(POCOP)FeH(PMe₃)₂

Figure 17. Iron hydride complex employed by Guan and coworkers to carry out mechanistic investigations on carbonyl hydrosilylation.

They concluded that the hydride in the iron complex was a mere spectator and does not take part actively on the catalytic process, and therefore the catalysis must proceed via a vacant coordination site at the Fe center left after dissociation of one of the two PMe₃ substituents. However, their investigations did not go any further and either possibility that it was the silane or the carbonyl that interacted with the iron's vacant site were left open.

In 2014, Wang *et al.* carried out theoretical DFT studies⁷⁰ on the possible catalytic pathways of two analogous metal hydride complexes with POCOP ligands: an Ir(III) cationic complex described by Brookhart^{71,72} and the Fe(II) complex studied by Guan in 2011 (Figure 17).⁴⁵ In the case of Brookhart's iridium-based catalyst, an ionic hydrosilylation mechanism was found to occur. However, the results obtained for the iron catalyst contradicted those initially reported by Guan's team. The DFT calculations showed that coordination of the carbonyl to the iron center followed by migratory insertion into the Fe-H bond was the most favored path. These results are therefore in contrast with the experimental work described by the group of Guan, that ruled out direct involvement of the hydride from (POCOP)FeH(PMe₃)₂ in the catalytic process.

Three years later, Driess and Oestreich performed an extensive mechanistic study, including experimental work and DFT calculations, on their catalytically active *N*-heterocyclic silylene (NHSi) iron(0) complex [SiNSi]Fe(PMe₃)₂ (Scheme 18).⁷³ They found that the active catalyst (Scheme 18) was formed after oxidative addition of one molecule of hydrosilane to the Fe(0) center of pre-catalyst [SiNSi]Fe(PMe₃)₂, resulting in the Fe(II) silyl hydride species *A*. Then, this silane moiety bond to the Fe(II) center would act as a Lewis acid, activating the carbonyl substrate (Scheme 18, *B*). Approach of another molecule of hydrosilane to the activated carbonyl would follow (Scheme 18, *C*), yielding the silyl ether product and recovering the silyl hydride Fe(II) catalyst *A*. This so-called *peripheral* mechanism, in which neither the iron center nor the hydride attached to the Fe are directly involved in the catalysis, was supported by not only experimental evidence but also by DFT calculations. Computational studies also found conventional outer and inner sphere mechanisms feasible, but the peripheral mechanism was the most favorable.

646

647 **Scheme 18.** Peripheral mechanism for the hydrosilylation of carbonyl compounds catalyzed by a
 648 NHSi-Fe complex.

649 The first exhaustive mechanistic study on a high spin iron(II) complex acting as catalyst for
 650 carbonyl hydrosilylation so far reported was carried out by Bleith and Gade in 2016.⁷⁴ Their study
 651 was focused in their iron(II) alkoxide complexes with a bis(oxazolinylmethylidene)isoindoline
 652 (boxmi) ligand that had demonstrated high activity and enantioselectivity for the catalysis of
 653 ketone hydrosilylation in the presence of (EtO)₂MeSiH.³² As part of the experimental work, kinetic

654 experiments allowed to determine the order of reaction of each component (first order for iron
 655 catalyst and for hydrosilane, zeroth order for ketone) and to describe a kinetic equation for the
 656 reaction. Also, the rate-determining step was found to be the σ -bond metathesis of the iron
 657 alkoxide complex with the Si-H of the hydrosilane (in red in Scheme 19). In addition,
 658 hydrosilylation tests using a ketone substrate with a radical clock (a cyclopropyl function)
 659 incorporated were performed in order to rule out single electron transfer reactions, thus proving
 660 that the oxidation state of the Fe(II) catalyst remains unchanged throughout the reaction. DFT-
 661 modeling of the proposed mechanistic cycle corroborated their experimental findings and rendered
 662 the insertion of the ketone into the Fe-H bond (see below and Scheme 19) as the stereodetermining
 663 step.

664

Scheme 19. Mechanism proposed by Bleith and Gade for the Fe(II)-catalyzed hydrosilylation of ketones.

The proposed mechanism starts with the activation of the iron(II) pre-catalyst (Scheme 19, **A**) by σ -bond metathesis of the alkoxide complex with the hydrosilane, resulting in an iron hydride **B**. This first step proceeds quickly when the pre-catalyst complex has an alkoxide ligand (-OR = 1-phenylethoxide), but if it bears a carboxylate ligand (-OR = acetate), an induction period of approximately 5 hours in which the carboxylate is reduced to an alkoxide is observed. The next step is the coordination of the ketone substrate to the iron hydride complex (Scheme 19, **C**), followed by rapid insertion into the Fe-H bond, thus regenerating an iron(II) alkoxide pre-catalyst. Consequently, the final silyl ether product from the reaction is released from the activation step of the pre-catalyst at the second (and subsequent) cycle of catalysis, when the hydrosilane regenerates the Fe-H (Scheme 19).

As part of our investigations on iron-catalyzed hydrosilylation, we were able to model a mechanism for the catalytic hydrosilylation of acetophenone via DFT computational calculations.³⁷ The mechanistic proposal (Scheme 20) was analogous to that reported by Bleith and Gade in 2016 (see above), and starts with an activation step that transform the iron(II) pre-catalyst into an iron(II)-hydride active species by decoordination of one ligand in Fe(AQPic)₂ and transfer of the hydride from the hydrosilane. Then, the ketone coordinates the Fe center (Scheme 20, **A**) and undergoes insertion into the Fe-H bond (Scheme 20, **B**), followed by coordination of another molecule of (EtO)₂MeSiH to the Fe center through an O atom (Scheme 20, **C**). Finally, an hydride from the coordinated (EtO)₂MeSiH is transferred to the Fe center and the silyl ether product is released via σ -bond metathesis as the iron hydride species is regenerated.

Scheme 20. Mechanism proposed by DFT calculations for the Fe(II)-catalyzed hydrosilylation of acetophenone promoted by Fe(AQPic)₂.

5. POTENTIAL PROSPECTS

Many active catalytic systems based on iron metal cores have been described so far for ketone and aldehyde hydrosilylation. Usually the substrates of choice have no special relevance in terms of direct application on industrial chemical synthesis and are normally used as benchmarks for catalytic performance evaluation. Here we would like to provide some insights into real

possibilities of practical applications that might open the door to many new ones or improve the existing ones.

5.1. Hydrosiloxane polymers as source of reduction. To make carbonyl hydrosilylation a realistic alternative to hydrogenation it would be convenient to develop new catalysts active enough to allow the use of polymethylhydrosiloxane (PMHS) as a reductant source. In fact, PMHS is an inexpensive and environmentally benign hydrosilane, generated as a waste product in the synthesis of silicones.⁷⁵ Alternatives based on continuous flow chemistry where the microfluidic channels could be functionalized with this type of polymers could be an enhancement for this process as a future line of research.

5.2. Structurally defined polysiloxanes. Polysiloxanes, and silicones in general, are currently being applied on a wide range of research areas due to their unique and valuable features.⁷⁶ The main properties of this type of structures such as resistance to heat and oxidation, gas permeability or electrical insulation are mainly controlled by siloxane units distribution, and its fine tuning still represents a major challenge in silicone chemistry. In this sense, hydrosilylation of tertiary silanes with acetone for instance could play a main role in the controlled synthesis of oligosiloxanes (Scheme 21) and for this specific process to become more suitable, active and environmental benign catalysts should be developed.

Scheme 21. Synthesis of silicone materials based on sequenced metal-catalyzed hydrosilylations.

5.3. Applications on molecules of industrial interest. Catalysts based on precious metals have already been evaluated on processes of industrial interest such as the synthesis of (-)-carbovir,⁷⁷ (-)-abacavir⁷⁷ and (+)-cassiol⁷⁸ (Scheme 22), where the pivotal step is an enantio- or regio-selective hydrosilylation reaction employing Et₃SiH as the reductant silane and a rhodium or platinum-based catalyst. These transformations are described as one-pot reactions requiring 1 mol% of catalyst and temperatures in the range of 50 to 70 °C. It is therefore necessary to invest on the development of new active iron catalysts able to achieve the performance of precious metals in the synthesis of molecules relevant to the industry.

Scheme 22. Synthesis of (+)-cassiol, (-)-carbovir and (-)-abacavir where at least one step is a precious-metal catalyzed hydrosilylation.

6. CONCLUDING REMARKS

In sight of the results published during the last decade, some trends on what an iron-based homogeneous system needs in order to behave as an effective catalyst for the hydrosilylation of ketones and aldehydes can be discerned. Dichloride and dibromide iron complexes show very poor activity or no activity at all. All the reported employments of such complexes require stoichiometric (relative to catalyst) amounts of an activating agent, namely a reductant, an hydride source or any compound that *in situ* replaces the halide for a different ligand. As far as the literature goes, the best results have been achieved with *N*-based pincer or monodentate ligands, (Table 1, entries 3, 4, 6, 7, 11, 12, 13, 19, 29) meanwhile phosphine or silylene ligands, despite being frequently employed, do not provide outstanding catalytic activity (Table 1, entries 16, 17, 18, 30, 31, 33). Nonetheless, asymmetric phosphine ligands have been proven useful to induce enantioselectivity in the reduced products.

Regarding the hydrosilanes employed, the activated rather hazardous (EtO)₃SiH₇ appears in the literature as the most frequently used in optimized reaction conditions so far (Table 1, entries 18, 20, 25, 31-33), followed by the expensive PhSiH₃ (Table 1, entries 4, 11, 19, 22-24, 29).⁶ Safe and relatively inexpensive (EtO)₂MeSiH and Ph₂SiH₂ are also widely employed (Table 1, entries 1-3, 5-10, 12-16, 26, 35), however the most desirable PMHS and TMDS^{7,6} remain under-used in reported iron-based catalytic systems (Table 1, entries 17, 21, 27, 28, 30, 34).

It is interesting to notice that the early attempts on iron-catalyzed hydrosilylation consisted of a catalytic mixture generated *in situ* by the addition of a ligand to an Fe(II) source (usually Fe(OAc)₂), while later a trend for the thorough study of the iron complexes' structure and properties prior to their use as catalysts was established. Though the first approach has the advantage of being more practical, the latter has led to a deeper understanding of the ways these

750 catalysts react, thus allowing the development of better catalytic systems via improving the designs
751 of both ligands and complexes.

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764 The manuscript was written through contributions of all authors. All authors have given approval

765 to the final version of the manuscript.

766 **Notes**

767 The authors declare no competing financial interest.

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REFERENCES

¹ For reviews on iron-catalyzed organic reactions: a) Bolm, C.; Legros, J.; Le Pailh, J.; Zani, L. Iron-Catalyzed Reactions in Organic Synthesis. *Chem. Rev.* **2004**, *104*, 6217-6254. b) Knölker, H. J.; Bauer, I. Iron catalysis in Organic Synthesis. *Chem. Rev.* **2015**, *115*, 3170-3387. c) Enthaler, S.; Junge, K.; Beller, M. Sustainable Metal Catalysis with Iron: From Rust to a Rising Star? *Angew. Chem. Int. Ed.* **2008**, *47*, 3317-3321. d) Nagashima, H. Catalyst Design of Iron Complexes. *Bull. Chem. Soc. Jpn.* **2017**, *90*, 761-775.

² For reviews on iron-catalyzed reductions: a) Morris, H. R. Asymmetric hydrogenation, transfer hydrogenation and hydrosilylation of ketones catalyzed by iron complexes. *Chem. Soc. Rev.* **2009**, *38*, 2282-2291. b) Chakraborty, S.; Guan, H. First-row transition metal catalyzed reduction of carbonyl functionalities: a mechanistic perspective. *Dalton Trans.* **2010**, *39*, 7427-7436. c) Zhang, M.; Zhang, A. Iron-catalyzed hydrosilylation reactions. *Appl. Organometal. Chem.* **2010**, *24*, 751-757. d) Junge, K.; Schröder, K.; Beller, M. Homogeneous catalysis using iron complexes: recent developments in selective reductions. *Chem. Commun.* **2011**, *47*, 4849-4859. e) Le Bailly, B. A. F.; Thomas, S. P. Iron-catalysed reduction of carbonyls and olefins. *RSC Adv.* **2011**, *1*, 1435-1445. f) Mérel, D. S.; Do, M. L. T.; Gaillard, S.; Dupau, P.; Renaud, J. L. Iron-catalyzed reduction of

carboxylic and carbonic acid derivatives. *Coord. Chem. Rev.* **2015**, 288, 50-68. g) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. Nickel and Iron Pincer Complexes as Catalysts for the Reduction of Carbonyl Compounds. *Acc. Chem. Res.* **2015**, 48, 1995-2003. h) Lopes, R.; Royo, B. Iron N-Heterocyclic Carbenes in Reduction Reactions. *Isr. J. Chem.* **2017**, 57, 1151-1159. i) Wei, D.; Darcel, C. Iron Catalysis in Reduction and Hydrometalation Reactions. *Chem. Rev.* **2019**, 119, 2550-2610.

³ Brunner, H.; Fisch, K. Synthesis of $(C_5H_5)Fe(CO)(SiHPh_2)_2H$, a catalytically active intermediate in the hydrosilylation of acetophenone by diphenylsilane. *J. Organomet. Chem.* **1991**, 412, C11-C13.

⁴ For recent comprehensive reviews on transfer hydrogenation, see: a) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, 115, 6621-6686. b) Filonenko, G. A.; Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (de)hydrogenation promoted by non-precious metals – Co, Fe and Mn: recent advances in an emerging field. *Chem. Soc. Rev.* **2018**, 47, 1459-1483.

⁵ Yahata, K.; Fujioka, H. *In Situ* Protection Methodology in Carbonyl Chemistry. *Chem. Pharm. Bull.* **2014**, 62, 1-11.

⁶ Addis, D.; Das, S.; Junge, K.; Beller, M. Selective Reduction of Carboxylic Acid Derivatives by Catalytic Hydrosilylation. *Angew. Chem. Int. Ed.* **2011**, 50, 6004-6011.

⁷ Pesti, J.; Larson, G. L. Tetramethyldisiloxane: A Practical Organosilane Reducing Agent. *Org. Process Res. Dev.* **2016**, 20, 1164-1181.

⁸ Well, A. S. On the Perils of Unexpected Silane Generation. *Org. Process Res. Dev.* **2010**, *14*, 484-484.

⁹ Sommer, L. H.; Pietrusza, E. W.; Whitmore, F. C. Peroxide-Catalyzed Addition of Trichlorosilane to 1-Octene. *J. Am. Chem. Soc.* **1947**, *69*, 188-188.

¹⁰ Speier, J. L.; Zimmerman, R.; Webster, J. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part I. The Use of Phenylsilane, Diphenylsilane, Phenylmethylsilane, Amylsilane and Tribromosilane. *J. Am. Chem. Soc.* **1956**, *78*, 2278-2281.

¹¹ Speier, J. L.; Webster, J. A.; Barnes, G. H. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. *J. Am. Chem. Soc.* **1957**, *79*, 974-979.

¹² Speier, J. L.; Saam, J. C. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part III. The Addition to Non-terminal Olefins in the Presence of Chloroplatinic Acid. *J. Am. Chem. Soc.* **1958**, *80*, 4104-4106.

¹³ Ojima, I.; Nihonyanagi, M.; Nagai, Y. Rhodium Complex Catalysed Hydrosilylation of Carbonyl Compounds. *J. Chem. Soc., Chem. Commun.* **1972**, 938a-938a.

¹⁴ Yamamoto, K.; Hayashi, T.; Kumada, M. Asymmetric hydrosilylation of ketones catalyzed by chiral phosphine-platinum(II) complexes. *J. Organomet. Chem.* **1972**, *46*, C65-C67.

¹⁵ Yamamoto, K.; Hayashi, T.; Kumada, M. Asymmetric hydrosilylation of ketones catalyzed by a chiral cationic rhodium complex. *J. Organomet. Chem.* **1973**, *54*, C45-C47.

¹⁶ Dumont, W.; Poulin, J. C.; Dang, T. P.; Kagan, H. B. Asymmetric Catalytic Reduction with Transition Metal Complexes. II. Asymmetric Catalysis by a Supported Chiral Rhodium Complex. *J. Am. Chem. Soc.* **1973**, *95*, 8295-8299.

¹⁷ Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. Reduction of Carbonyl Compounds via Hydrosilylation. II. Asymmetric Reduction of Ketones via Hydrosilylation Catalyzed by a Rhodium(I) Complex with Chiral Phosphine Ligands. *J. Organomet. Chem.* **1976**, *122*, 83-97.

¹⁸ a) Marciniak, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z. W. *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, U.K., 1992. b) Marciniak, B. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer: Dordrecht, The Netherlands, 2009.

¹⁹ a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, U.S.A., 1989; Vol. 1, Part 2, pp 1479-1526. b) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, U.S.A., 1998; Vol. 2, Part 2, pp 1687-1792.

²⁰ Roy, A. K. A Review of Recent Progress in Catalyzed Homogeneous Hydrosilation (Hydrosilylation). *Adv. Organomet. Chem.* **2007**, *55*, 1-59.

²¹ For some examples of non-iron first-row transition metals: a) Trovitch, R. J. Comparing Well-Defined Manganese, Iron, Cobalt, and Nickel Ketone Hydrosilylation Catalysts. *Synlett* **2014**, *25*, 1638-1642, and references cited therein. b) Chen, X.; Lu, Z. Iminophenyl Oxazolinyphenylamine for Enantioselective Cobalt-Catalyzed Hydrosilylation of Aryl Ketones. *Org. Lett.* **2016**, *18*, 4658-4661. c) Chakraborty, S.; Krause, J. A.; Guan, H. Hydrosilylation of Aldehydes and Ketones Catalyzed by Nickel PCP-Pincer Hydride Complexes. *Organometallics* **2009**, *28*, 582-586. d) Tran, B. L.; Pink, M.; Mindiola, D. J. Catalytic Hydrosilylation of the Carbonyl Functionality via

a Transient Nickel Hydride Complex. *Organometallics* **2009**, 28, 2234-2243, and references cited therein. e) César, V.; Barthes, C.; Farré, Y. C.; Cuisiat, S. V.; Vacher, B. Y.; Brousses, R.; Lugan, N.; Lavigne, G. Anionic and zwitterionic copper(I) complexes incorporating an anionic N-heterocyclic carbene decorated with a malonate backbone: synthesis, structure and catalytic applications. *Dalton Trans.* **2013**, 42, 7373-7385.

²² Nishiyama, H; Furuta, A. An iron-catalysed hydrosilylation of ketones. *Chem. Commun.* **2007**, 760-762.

²³ Langlotz, B. K.; Wade, H.; Gade, L. H. Chiral Bis(pyridylimino)isoindoles: A Highly Modular Class of Pincer Ligands for Enantioselective Catalysis. *Angew. Chem. Int. Ed.* **2008**, 47, 4670-4674.

²⁴ Tondreau, A. M.; Lobkovsky, E.; Chirik, P. J. Bis(imino)pyridine Iron Complexes for Aldehyde and Ketone Hydrosilylation. *Org. Lett.* **2008**, 10, 2789-2792.

²⁵ a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation. *J. Am. Chem. Soc.* **2004**, 126, 13794-13807. b) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. Functional Group Tolerance and Substrate Scope in Bis(imino)pyridine Iron Catalyzed Alkene Hydrogenation. *Organometallics* **2008**, 27, 1470-1478.

²⁶ Tondreau, A. M.; Darmon, J. M.; Wile, B. M.; Floyd, S. K.; Lobkovsky, E.; Chirik, P. J. Enantiopure Pyridine Bis(oxazoline) "Pybox" and Bis(oxazoline) "Box" Iron Dialkyl Complexes: Comparison to Bis(imino)pyridine Compounds and Application to Catalytic Hydrosilylation of Ketones. *Organometallics* **2009**, 28, 3928-3940.

²⁷ a) Bart, S. C.; Hawrelak, E. J.; Schmisser, A. K.; Lobkovsky, E.; Chirik, P. J. Synthesis, Reactivity, and Solid State Structures of Four-Coordinate Iron(II) and Manganese(II) Alkyl Complexes. *Organometallics* **2004**, *23*, 237-246. b) Chen, E. Y. X.; Marks, T. J. Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure – Activity Relationships. *Chem. Rev.* **2000**, *100*, 1391-1434. c) Volbeda, J.; Meetsma, A.; Bouwkamp, M. W. Electron-Deficient Iron Alkyl Complexes Supported by Diimine Ligand (Ph₂CN)₂C₂H₄: Evidence for Reversible Ethylene Binding. *Organometallics* **2009**, *28*, 209-215. d) Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. Bis(imino)pyridine Iron(II) Alkyl Cations for Olefin Polymerization. *J. Am. Chem. Soc.* **2005**, *127*, 9660-9661.

²⁸ Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. Iron- and Cobalt-Catalyzed Asymmetric Hydrosilylation of Ketones and Enones with Bis(oxazolinyphenyl)amine Ligands. *Chem. Eur. J.* **2010**, *16*, 3090-3096.

²⁹ Inagaki, T.; Ito, A.; Ito, J.; Nishiyama, H. Asymmetric Iron-Catalyzed Hydrosilane Reduction of Ketones: Effect of Zinc Metal upon the Absolute Configuration. *Angew. Chem. Int. Ed.* **2010**, *49*, 9384-9387.

³⁰ Evans, D. F. The determination of the paramagnetic susceptibility of substances in solution by nuclear magnetic resonance. *J. Chem. Soc.* **1959**, 2003-2005.

³¹ Yang, J.; Tilley, T. D. Efficient Hydrosilylation of Carbonyl Compounds with the Simple Amide Catalyst [Fe{N(SiMe₃)₂}₂]. *Angew. Chem. Int. Ed.* **2010**, *49*, 10186-10188.

³² Bleith, T.; Wadepohl, H.; Gade, L. H. Iron Achieves Noble Metal Reactivity and Selectivity: Highly Reactive and Enantioselective Iron Complexes as Catalysts in the Hydrosilylation of Ketones. *J. Am. Chem. Soc.* **2015**, *137*, 2456-2459.

-
- ³³ Zuo, Z.; Zhang, L.; Leng, X.; Huang, Z. Iron-catalyzed asymmetric hydrosilylation of ketones. *Chem. Commun.* **2015**, *51*, 5073-5076.
- ³⁴ Wekesa, F. S.; Arias-Ugarte, R.; Kong, L.; Sumner, Z.; McGovern, G. P.; Findlater, M. Iron-Catalyzed Hydrosilylation of Aldehydes and Ketones under Solvent-Free Conditions. *Organometallics* **2015**, *34*, 5051-5056.
- ³⁵ Yu, X.; Zhu, F.; Bu, D.; Lei, H. Ferrous complexes supported by sterically encumbered asymmetric bis(arylimino) acenaphthene (BIAN) ligands: synthesis, characterization and screening for catalytic hydrosilylation of carbonyl compounds. *RSC Adv.* **2017**, *7*, 15321-15329.
- ³⁶ Lin, H. J.; Lutz, S.; O'Kane, C.; Zeller, M.; Chen, C. H.; Assil, T. A.; Lee, W. T. Synthesis and characterization of an iron complex bearing a hemilabile NNN-pincer for catalytic hydrosilylation of organic carbonyl compounds. *Dalton Trans.* **2018**, *47*, 3243-3247.
- ³⁷ Raya-Barón, A.; Ortuño, M. A.; Oña-Burgos, P.; Rodríguez-Diéguez, A.; Langer, R.; Cramer, C. J.; Kuzu, I.; Fernández, I. Efficient Hydrosilylation of Acetophenone with a New Anthraquinonic Amide-Based Iron Precatalyst. *Organometallics* **2016**, *35*, 4083-4089.
- ³⁸ Raya-Barón, A.; Galdeano-Ruano, C. P.; Oña-Burgos, P.; Rodríguez-Diéguez, A.; Langer, R.; López-Ruiz, R.; Romero-González, R.; Kuzu, I.; Fernández, I. A new anthraquinoid ligand for the iron-catalyzed hydrosilylation of carbonyl compounds at room temperature: new insights and kinetics. *Dalton Trans.* **2018**, *47*, 7272-7281.
- ³⁹ Hosokawa, S.; Ito, J.; Nishiyama, H. A Chiral Iron Complex Containing a Bis(oxazolinyl)phenyl Ligand: Preparation and Asymmetric Hydrosilylation of Ketones. *Organometallics* **2010**, *29*, 5773-5775.

-
- ⁴⁰ Ito, J.; Hosokawa, S.; Khalid, H. B.; Nishiyama, H. Preparation, Characterization, and Catalytic Reactions of NCN Pincer Iron Complexes Containing Stannyl, Silyl, Methyl, and Phenyl Ligands. *Organometallics* **2015**, *34*, 1377-1383.
- ⁴¹ Shaikh, N. S.; Enthaler, S.; Junge, K.; Beller, M. Iron-Catalyzed Enantioselective Hydrosilylation of Ketones. *Angew. Chem. Int. Ed.* **2008**, *47*, 2497-2501.
- ⁴² Dieskau, A. P.; Begouin, J. M.; Plietker, B. Bu₄N[Fe(CO)₃(NO)]-Catalyzed Hydrosilylation of Aldehydes and Ketones. *Eur. J. Org. Chem.* **2011**, 5291-5296.
- ⁴³ Castro, L. C. M.; Bézier, D.; Sortais, J. B.; Darcel, C. Iron Dihydride Complex as the Pre-catalyst for Efficient Hydrosilylation of Aldehydes and Ketones Under Visible Light Activation. *Adv. Synth. Catal.* **2011**, *353*, 1279-1284.
- ⁴⁴ Zheng, J.; Castro, L. C. M.; Roisnel, T.; Darcel, C.; Sortais, J. B. Iron piano-stool phosphine complexes for catalytic hydrosilylation reaction. *Inorg. Chim. Acta* **2012**, *380*, 301-307.
- ⁴⁵ Bhattacharya, P.; Krause, J. A.; Guan, H. Iron Hydride Complexes Bearing Phosphinite-Based Pincer Ligands: Synthesis, Reactivity, and Catalytic Application in Hydrosilylation Reactions. *Organometallics* **2011**, *30*, 4720-4729.
- ⁴⁶ Bhattacharya, P.; Krause, J. A.; Guan, H. Activation of Dihydrogen and Silanes by Cationic Iron Bis(phosphinite) Pincer Complexes. *Organometallics* **2014**, *33*, 6113-6121.
- ⁴⁷ Ruddy, A. J.; Kelly, C. M.; Crawford, S. M.; Wheaton, C. A.; Sydora, O. L.; Small, B. L.; Stradiotto, M.; Turculet, L. (N-Phosphinoamidinate)Iron Pre-Catalysts for the Room Temperature Hydrosilylation of Carbonyl Compounds with Broad Substrate Scope at Low Loadings. *Organometallics* **2013**, *32*, 5581-5588.

-
- ⁴⁸ Smith, A. D.; Saini, A.; Singer, L. M.; Phadke, N.; Findlater, M. Synthesis, characterization and reactivity of iron- and cobalt- pincer complexes. *Polyhedron* **2016**, *114*, 286-291.
- ⁴⁹ Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B. Iron(II) Complexes Bearing Chelating Cyclopentadienyl-N-Heterocyclic Carbene Ligands as Catalysts for Hydrosilylation and Hydrogen Transfer Reactions. *Organometallics* **2010**, *29*, 2777-2782.
- ⁵⁰ Warratz, S.; Postigo, L.; Royo, B. Direct Synthesis of Iron(0) N-Heterocyclic Carbene Complexes by Using Fe₃(CO)₁₂ and Their Application in Reduction of Carbonyl Groups. *Organometallics* **2013**, *32*, 893-897.
- ⁵¹ Lopes, R.; Cardoso, J. M. S.; Postigo, L.; Royo, B. Reduction of Ketones with Silanes Catalysed by a Cyclopentadienyl-Functionalised N-Heterocyclic Iron Complex. *Catal. Lett.* **2013**, *143*, 1061-1066.
- ⁵² Jiang, F.; Bézier, D.; Sortais, J. B.; Darcel, C. N-Heterocyclic Carbene Piano-Stool Iron Complexes as Efficient Catalysts for Hydrosilylation of Carbonyl Derivatives. *Adv. Synth. Catal.* **2011**, *353*, 239-244.
- ⁵³ Bézier, D.; Jiang, F.; Roisnel, T.; Sortais, J. B.; Darcel, C. Cyclopentadienyl-NHC Iron Complexes for Solvent-Free Catalytic Hydrosilylation of Aldehydes and Ketones. *Eur. J. Inorg. Chem.* **2012**, 1333-1337.
- ⁵⁴ Demir, S.; Gökçe, Y.; Kaloğlu, N.; Sortais, J. B.; Darcel, C.; Özdemir, İ. Synthesis of new iron-NHC complexes as catalysts for hydrosilylation reactions. *Appl. Organometal. Chem.* **2013**, *27*, 459-464.

⁵⁵ César, V.; Castro, L. C. M.; Dombray, T.; Sortais, J. B.; Darcel, C.; Labat, S.; Miqueu, K.; Sotiropoulos, J. M.; Brousses, R.; Lugan, N.; Lavigne, G. (Cyclopentadienyl)iron(II) Complexes of N-Heterocyclic Carbenes Bearing a Malonate or Imidate Backbone: Synthesis, Structure, and Catalytic Potential in Hydrosilylation. *Organometallics* **2013**, *32*, 4643-4655.

⁵⁶ Hashimoto, T.; Urban, S.; Hoshino, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. Synthesis of Bis(N-heterocyclic carbene) Complexes of Iron(II) and Their Application in Hydrosilylation and Transfer Hydrogenation. *Organometallics* **2012**, *31*, 4474-4479.

⁵⁷ Grohmann, C.; Hashimoto, T.; Frölich, R.; Ohki, Y.; Tatsumi, K.; Glorius, F. An Iron(II) Complex of a Diamine-Bridged Bis-N-Heterocyclic Carbene. *Organometallics* **2012**, *31*, 8047-8050.

⁵⁸ Buitrago, E.; Zani, L.; Adolfsson, H. Selective hydrosilylation of ketones catalyzed by in situ-generated iron NHC complexes. *Appl. Organometal. Chem.* **2011**, *25*, 748-752.

⁵⁹ Buitrago, E.; Tinnis, F.; Adolfsson, H. Efficient and Selective Hydrosilylation of Carbonyl Compounds Catalyzed by Iron Acetate and N-Hydroxyethylimidazolium Salts. *Adv. Synth. Catal.* **2012**, *354*, 217-222.

⁶⁰ Johnson, C.; Albrecht, M. Triazolylidene Iron(II) Piano-Stool Complexes: Synthesis and Catalytic Hydrosilylation of Carbonyl Compounds. *Organometallics* **2017**, *36*, 2902-2913.

⁶¹ Liang, Q.; Janes, T.; Gjergji, X.; Song, D. Iron complexes of a bidentate picolyl-NHC ligand: synthesis, structure and reactivity. *Dalton Trans.* **2016**, *45*, 13872-13880.

⁶² Liang, Q.; Liu, N. J.; Song, D. Constructing reactive Fe and Co complexes from isolated picolyl-functionalized N-heterocyclic carbenes. *Dalton Trans.* **2018**, *47*, 9889-9896.

⁶³ Blom, B.; Enthaler, S.; Inoue, S.; Irran, E.; Driess, M. Electron-Rich N-Heterocyclic Silylene (NHSi)–Iron Complexes: Synthesis, Structures, and Catalytic Ability of an Isolable Hydridosilylene–Iron Complex. *J. Am. Chem. Soc.* **2013**, *135*, 6703-6713.

⁶⁴ Gallego, D.; Inoue, S.; Blom, B.; Driess, M. Highly Electron-Rich Pincer-Type Iron Complexes Bearing Innocent Bis(metallylene)pyridine Ligands: Syntheses, Structures, and Catalytic Activity. *Organometallics* **2014**, *33*, 6885-6897.

⁶⁵ a) Wu, S.; Li, X.; Xiong, Z.; Xu, W.; Lu, Y.; Sun, H. Synthesis and Reactivity of Silyl Iron, Cobalt, and Nickel Complexes Bearing a [PSiP]-Pincer Ligand via Si–H Bond Activation. *Organometallics* **2013**, *32*, 3227-3237. b) Zuo, Z.; Sun, H.; Wang, L.; Li, X. Hydrosilylation of aldehydes and ketones catalyzed by hydrido iron complexes bearing imine ligands. *Dalton Trans.* **2014**, *43*, 11716-11722. c) Zhao, H.; Sun, H.; Li, X. Synthesis and Catalytic Property of Iron Pincer Complexes Generated by C_{sp}³–H Activation. *Organometallics* **2014**, *33*, 3535-3539. d) Huang, S.; Zhao, H.; Li, X.; Wang, L.; Sun, H. Synthesis of [POCOP]-pincer iron and cobalt complexes via C_{sp}³–H activation and catalytic application of iron hydride in hydrosilylation reactions. *RSC Adv.* **2015**, *5*, 15660-15667. e) Wang, L.; Sun, H.; Li, X. Synthesis of Iron Hydrides by Selective C–F/C–H Bond Activation in Fluoroarylimines and Their Applications in Catalytic Reduction Reactions. *Eur. J. Inorg. Chem.* **2015**, 2732-2743. f) Zheng, T.; Li, J.; Zhang, S.; Xue, B.; Sun, H.; Li, X.; Fuhr, O.; Fenske, D. Selective C–F and C–H Activation of Fluoroarenes by Fe(PMe₃)₄ and Catalytic Performance of Iron Hydride in Hydrosilylation of Carbonyl Compounds. *Organometallics* **2016**, *35*, 3538-3545. g) Xue, B.; Sun, H.; Niu, Q.; Li, X.; Fuhr, O.; Fenske, D. Catalytic hydrosilylation of carbonyl compounds by hydrido thiophenolato iron(II) complexes. *Catal. Commun.* **2017**, *94*, 23-28. h) Ren, S.; Xie, S.; Zheng, T.; Wang, Y.; Xu, S.; Xue, B.; Li, X.; Sun, H.; Fuhr, O.; Fenske, D. Synthesis of silyl iron hydride *via* Si–H activation and its dual

catalytic application in the hydrosilylation of carbonyl compounds and dehydration of benzamides.

Dalton Trans. **2018**, 47, 4352-4359.

⁶⁶ Camadanli, S.; Beck, R.; Flörke, U.; Klein, H. F. C-H Activation of Imines by Trimethylphosphine-Supported Iron Complexes and Their Reactivities. *Organometallics* **2009**, 28, 2300-2310.

⁶⁷ Sunada, Y.; Tsutsumi, H.; Shigeta, K.; Yoshida, R.; Hashimoto, T.; Nagashima, H. Catalyst design for iron-promoted reductions: an iron disilyl-dicarbonyl complex bearing weakly coordinating η^2 -(H-Si) moieties. *Dalton Trans.* **2013**, 42, 16687-16692.

⁶⁸ Jung, T. C.; Argouarch, G.; van de Weghe, P. Cyclopentadienyliron dicarbonyl dimer: A simple tool for the hydrosilylation of aldehydes and ketones under air. *Catal. Commun.* **2016**, 78, 52-54.

⁶⁹ Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry*; Pearson Education: U.S.A., 2014.

⁷⁰ Wang, W.; Gu, P.; Wang, Y.; Wei, H. Theoretical Study of POCOP-Pincer Iridium(III)/Iron(II) Hydride Catalyzed Hydrosilylation of Carbonyl Compounds: Hydride Not Involved in the Iridium(III) System but Involved in the Iron(II) System. *Organometallics* **2014**, 33, 847-857.

⁷¹ Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. Structural and Spectroscopic Characterization of an Unprecedented Cationic Transition-Metal η^1 -Silane Complex. *Angew. Chem. Int. Ed.* **2008**, 47, 4141-4143.

⁷² Park, S.; Brookhart, M. Hydrosilylation of Carbonyl-Containing Substrates Catalyzed by an Electrophilic η^1 -Silane Iridium(III) Complex. *Organometallics* **2010**, *29*, 6057-6064.

⁷³ Metsänen, T. T.; Gallego, D.; Szilvási, T.; Driess, M.; Oestreich, M. Peripheral mechanism of a carbonyl hydrosilylation catalysed by an SiNSi iron pincer complex. *Chem. Sci.* **2015**, *6*, 7143-7149.

⁷⁴ Bleith, T.; Gade, L. H. Mechanism of the Iron(II)-Catalyzed Hydrosilylation of Ketones: Activation of Iron Carboxylate Precatalysts and Reaction Pathways of the Active Catalyst. *J. Am. Chem. Soc.* **2016**, *138*, 4972-4983.

⁷⁵ a) Díez-González, S.; Nolan, S. P. Transition metal-catalyzed hydrosilylation of carbonyl compounds and imines. A review. *Org. Prep. Proced. Int.* **2007**, *39*, 523-559; b) Liu, R. Y.; Zhou, Y.; Yang, Y.; Buchwald, S. L. Enantioselective Allylation Using Allene, a Petroleum Cracking Byproduct. *J. Am. Chem. Soc.* **2019**, *141*, 2251-2256.

⁷⁶ Matsumoto, K.; Oba, K.; Nakajima, Y.; Shimada, S.; Sato, K. One-Pot Sequence-Controlled Synthesis of Oligosiloxanes. *Angew. Chem. Int. Ed.* **2018**, *57*, 4637-4641.

⁷⁷ Freira, M.; Whitehead, A. J.; Motherwell, W. B. Formal Enantioselective Synthesis of (-)-Carbovir and (-)-Abacavir: An Application of the Rhodium(I)-Catalysed Tandem Hydrosilylation-Intramolecular Aldol Reaction. *Synthesis*, **2005**, 3079-3084.

⁷⁸ Trost, B. M.; Li, Y. A New Catalyst for a Pd Catalyzed Alder Ene Reaction. A Total Synthesis of (+)-Cassiol. *J. Am. Chem. Soc.* **1996**, *118*, 6625-6633.

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