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Iron Achieves Noble Metal Reactivity and Selectivity: Highly Reactive and Enantioselective Iron Complexes as Catalysts in the Hydrosilylation of Ketones

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Supporting Information

ABSTRACT: Chiral iron alkyl and iron alkoxide complexes bearing boxmi pincers as stereodirecting ligands have been employed as catalysts for enantioselective hydrosilylation reactions with unprecedented activity and selectivity (TOF = 240 h^{-1} at −40 °C, ee up to 99% for alkyl aryl ketones), which match the performance of previously established noble-metal-based catalysts. This shows the potential of earth-abundant metals such as iron for replacing platinum—metals without any drawbacks for the reaction design.

Enantioselective, transition-metal-catalyzed reductions of ketones are valuable tools for the synthesis of chiral alcohols. Typically, these reactions are catalyzed by platinum-group metals such as Ru, Rh, Ir, or Pt, which suffer from common drawbacks in that they are quite scarce and frequently toxic. Recently, more environmentally benign catalyst systems based on earth-abundant metals[1−7] such as Fe have been the focus of research studies.[8−18] In general, these iron-based molecular catalysts did not display the selectivity nor the reactivity of the systems they aim to replace, and the quest has thus been for catalysts which match—or even exceed—the performance of the latter.[19] The recent breakthrough in Fe-catalyzed asymmetric transfer hydrogenation has fueled the search for further molecular catalysts that are competitive with their noble metal analogues.[20−23]

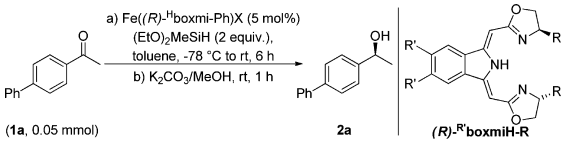
In the hydrosilylation of ketones, optimized rhodium catalysts may display high activities down to −60 °C and achieve greater than 90% ee for a wide range of substrates.[24−26] Fe complexes which have been studied as catalysts for this reaction usually require higher temperatures of up to 65 °C and longer reaction times to give a product with generally lower selectivity.[27−36] Only for sterically very demanding substrates, ee values for the resulting secondary alcohols of >95% were obtained.[28]

Chirik, Tilley, and Glorius have shown that the choice of catalyst precursor ([(N-donor-ligand)Fe($CH_2TMS)_2$], [Fe(N-$(TMS)_2)_2$], or [$(NHC)_2FeMe_2$]) has an enormous impact upon catalyst activity.[37−40] Here, we present the first iron-based precatalyst that achieves *both* activity *and* selectivity which are comparable to noble metals in catalytic hydrosilylation reactions.

Based on previous studies in our group[29] and Nishiyama's lab,[27,30] we explored the Fe-catalyzed enantioselective hydrosilylation of aryl alkyl ketones. We employed the bis(oxazolinylmethylidene)isoindoline (boxmi) ligand, a monoanionic NNN pincer that already showed excellent chiral induction in Nozaki−Hiyama−Kishi reactions as well as a wide range of reactions of electrophiles with β-ketoesters and oxindoles.[41−46]

The boxmi iron(II) acetato complexes (either prepared in situ or isolated beforehand) catalyzed hydrosilylation of the test substrate **1a** at 65 °C with full conversion and 83% ee (Table 1, entry 1). At 5 mol % catalyst loading, 72 h reaction time was necessary due to a long induction period to generate the active catalyst. To overcome this, suitable precatalysts were developed that gave rise to significantly greater overall reaction rates.

Table 1. Precursor Screening for the Hydrosilylation of 4-Phenylacetophenone

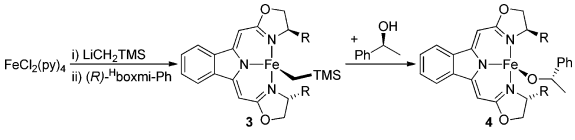


entry	X	conv (%)[a]	ee (%)[a]
1	OAc	>95[b]	83 (*S*)
2	CH_2TMS (**3**)	>95	94.5 (*S*)
3	(*S*)-$OCHPhCH_3$ (**4**)	>95	99.0 (*S*)
4	(*S*)-$OCHPhCH_3$ (**4**)	>95[c]	98.0 (*S*)
5	(*S*)-$OCHPhCH_3$ (**4**)	>95[d]	94.0 (*S*)

[a]Determined by HPLC analysis. [b]Reaction temperature = 65 °C for 72 h. [c]Silane added at −78 °C, cold bath removed immediately, quenched after 1 h. [d]Reaction carried out at room temperature and quenched after 2 h.

Using the iron(II) neosyl complexes **3**, which were readily available by reaction of [$FeCl_2(py)_4$] with $LiCH_2TMS$ and boxmiH (Scheme 1), instead of the actetate resulted in a dramatic increase in activity and allowed the reaction temperature to decrease. Under the conditions indicated in Table 1, a significantly increased 94.5% ee was observed for the reduction of

Scheme 1. Synthesis of Fe(boxmi) Neosyl and Alkoxido Complexes



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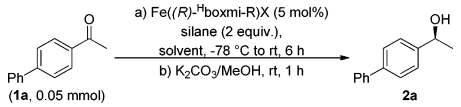
the test substrate **1a** (Table 1, entry 2). That the combination of the tridentate chiral boxmi ligand and an alkyl coligand system gave rise to a highly reactive *and* selective catalytic species contrasts with previous results for Fe(II) alkyl complexes bearing chiral box or pybox ligands, which only displayed modest selectivity.[38]

In a first reaction step of the highly reactive iron alkyl precatalyst, an alkoxido iron complex was formed. Since this was also potentially a key intermediate in the catalytic cycle of the hydrosilylation, it was thought to be an active catalyst in its own right. The excellent selectivity obtained with the alkyl precatalyst was superseded by using the (*S*)-1-phenyl-1-ethanolato complex **4**, which had been obtained by clean alcoholytic transformation of the alkyl complex **3** into the alkoxido derivative **4** (Table 1, entry 3, and Scheme 1). The observed 99% ee for **1a** matches the results of the most selective rhodium catalysts reported to date. Even at room temperature, the test substrate was reduced with 94% ee (Table 1, entry 5).

Variation of the substituent pattern on the boxmi ligand showed that alterations in the backbone (R′) did not significantly influence the selectivity of the reaction (Table 2, entry 1).

Table 2. Optimization of Reaction Conditions for the Hydrosilylation of Ketones



entry	[Fe]	R	silane	solvent	conv (%)[a]	ee (%)[a]
1	**3**	Ph[b]	$(EtO)_2MeSiH$	tol	>95	94.2 (*R*)
2	**3**	^{i}Pr[c]	$(EtO)_2MeSiH$	tol	>95	98.7 (*R*)
3	**3**	Bn[d]	$(EtO)_2MeSiH$	tol	>95	33 (*R*)
4	**4**	Ph	$(EtO)_2MeSiH$	tol	>95	99.0 (*S*)
5	**4**	Ph	PMHS[d]	tol	90	93.4
6	**4**	Ph	$^i Pr_3SiH$	tol	<5	nd[e]
7	**4**	Ph	$^n BuSiH_3$	tol	83	57
8	**4**	Ph	$(EtO)_2MeSiH$	THF	>95	92.3
9	**4**	Ph	$(EtO)_2MeSiH$	Et_2O	>95	99.2[f]
10	**4**	Ph	$(EtO)_2MeSiH$	CH_2Cl_2	>95	93.8

[a]Determined by HPLC analysis. [b](*S*)-^{Ph}boxmi-Ph employed. [c](*S*)-^{Ph}boxmi-^{i}Pr used. [c](*S*)-^{Me}boxmi-Bn employed. [d]PMHS = poly(methylhydrosiloxane). [e]Not determined. [f]Precipitation observed upon cooling to −78 °C.

Variation of the chiral substituent R on the oxazoline rings had a significant impact on the enantioselectivity. Whereas higher selectivity in the test reaction was observed for the isopropyl-substituted derivative, the enantioselectivity dropped dramatically upon use of the benzyl-substituted boxmi ligand, with no conversion with the *tert*-butyl-substituted derivatives (Table 2, entries 2 and 3, and Supporting Information, SI). In general, the phenyl-substituted ligand proved to be the most efficient for the substrates in this work (vide infra and SI).

Silane screening showed that, by replacing $(EtO)_2MeSiH$ with comparatively inexpensive PMHS, the selectivity and conversion were slightly lower (Table 2, entry 4), whereas the use of $^i Pr_3SiH$ yielded almost no conversion (Table 2, entry 5), which we attribute to the high steric demand of that reagent and its tendency to react via radical pathways. $^n BuSiH_3$ was able to reduce 4-phenylacetophenone with good conversions but only with a moderate ee (Table 2, entry 7). These findings suggest that the cleavage of the Si−H bond is a heterolytic rather than a homolytic step, and the silane is involved in the reaction step determining selectivity.

Varying the solvent, we observed that coordinating solvents such as tetrahydrofuran or MeCN resulted in lower selectivities (Table 2, entry 8, and SI). Although the reaction took place with high selectivity in Et_2O, this solvent was not further used due to poor solubility of the catalyst and the ketone at lower temperatures (Table 2, entry 9). The same could be observed using hexane or $(EtO)_2MeSiH$ as solvents (see SI). Finally, chlorinated solvents were also found to provide suitable reaction conditions (Table 2, entry 10).

Catalyst activity was further probed for the hydrosilylation of acetophenone with reduced catalyst loadings (0.1 mol %). Turnover numbers greater than 500 were achieved under these conditions. For the standard 5 mol % catalyst loading employed in this study, turnover frequencies of at least 240 h^{-1} were observed at −40 °C. The reaction protocol is directly applicable to conversions on a gram scale. Reducing 1.0 g of **1a** with the appropriate amount of $(EtO)_2MeSiH$ in the presence of 2.3 mol % of **4** yielded the corresponding alcohol in 94% isolated yield and 98.4% ee.

Although the complexes employed in the catalyst screening were prepared in situ, the Fe boxmi compounds in question were found to be readily isolable and were used in all further studies. The molecular structure of a pyridine adduct of [Fe((*R*)-^{H}boxmi-Ph)(CH_2TMS)] (**3**) was determined by X-ray diffraction and is shown in Figure 1. The isolated complex possesses a trigonal-bipyramidal coordination sphere with the pincer ligand coordinating in the classical meridional fashion to the iron atom.

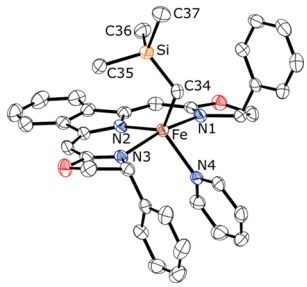


Figure 1. Molecular structure of **3(py)** at 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−C(34) 2.093(4); Fe−N(1) 2.208; Fe−N(2) 2.133(3); Fe−N(3) 2.205(3); Fe−N(4) 2.163(3); N(1)−Fe−N(3) 164.47(11); N(2)−Fe−C(34) 127.76(13); N(2)−Fe−N(4) 120.69(12); N(4)−Fe−C(34) 111.54(13).

As indicated above, the alkoxido complex [Fe((*R*)-^{H}boxmi-Ph)((*S*)-$OCHCH_3Ph$)] (**4**) could be prepared by reacting **3** with (*S*)-1-phenyl-1-ethanol at ambient temperature. Its pyridine adduct was characterized by single-crystal X-ray diffraction, and the molecular structure of **4(py)** is displayed in Figure 2. Both of the isolated pyridine adducts, **3(py)** and **4(py)**, were found to be catalytically active and displayed the same selectivity as the in situ generated catalysts **3** and **4**, respectively. All iron complexes employed in this study were determined to be in a high-spin state.

With the reaction conditions optimized, the substrate scope of this reaction was then investigated. Reduction of para-substituted acetophenone derivatives (**1a−f**) showed that para-substituents on the phenyl ring had almost no effect on the selectivity (Scheme 2, first and second row), and they were reduced with ee values usually greater than 98%. Cyclic derivatives such as α-

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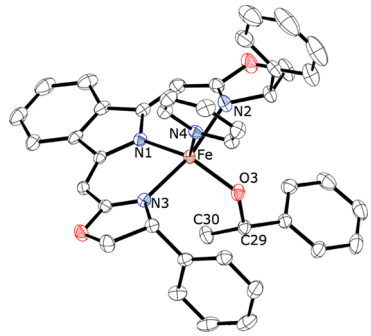
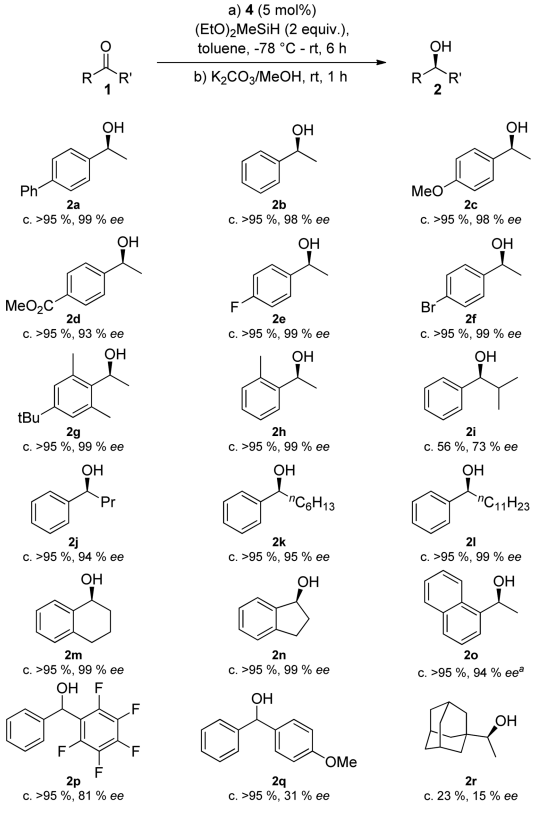


Figure 2. Molecular structure of **4(py)** at 50% probability ellipsoids; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe–O(3) 1.8925(17); Fe–N(4) 2.132(2); Fe–N(1) 2.107(2); Fe–N(2) 2.177(2); Fe–N(3) 2.1786(19); O(3)–Fe–N(4) 103.19(8); O(3)–Fe–N(1) 133.08(8); N(1)–Fe–N(4) 123.68(8); N(2)–Fe–N(3) 168.22(7).

Scheme 2. Substrate Scope of the Iron-Catalyzed Hydrosilylation of Ketones



[a]4 equiv of $(EtO)_2MeSiH$ was added.

tetralone (**1m**) were converted completely with an ee value of 99%.

We further investigated the reduction of aryl alkyl ketones (**1j–l**) with larger alkyl substituents (Scheme 2, third row). Whereas isobutyrophenone (**1i**) only partially reacted and the selectivity was also decreased considerably to 73% ee, *tert*-butylphenylketone did not react at all. The latter two substrates are too sterically encumbered to allow efficient reduction. Notably, the ee values for aryl alkyl ketones with long unbranched alkyl chains stayed at an excellent level of greater than 95%, and dodecanophenone (**1l**) is fully converted at 99% ee. Since 1-acetylnaphthone (**1o**) was only converted partially under standard conditions (see SI), but with a high ee value of 97%, prolonged reaction times or a larger excess of silane was necessary for sterically demanding substrates.

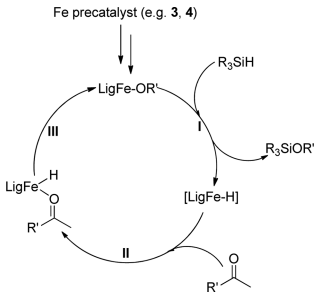
As observed previously for Fe-catalyzed hydrosilylations, the reduction of dialkyl ketones (**1r**) only occurs with low levels of ee.[11,27−29] Diaryl ketones could be reduced to the corresponding alcohol with significant selectivity. Phenyl-4′-methoxyphenyl ketone (**1q**) and phenyl-2′,3′,4′,5′,6′-pentafluorophenyl ketone (**1p**) were fully converted at 31 and 81% ee, respectively, demonstrating that stereodiscrimination is not exclusively based on the steric properties of the substituents on the carbonyl group but is directed by the electronic structure of the two aryl rings. This also explains the high selectivity for aryl alkyl ketones bearing α-unbranched alkyl moieties.

The drastic change in catalytic activity of the complexes employed in this work is likely due to precatalyst activation, which may be incomplete for the acetate complexes studied previously. In view of the results reported by Chirik et al. and Nishiyama et al.,[27,38] this seems to be a more general pattern in Fe-catalyzed hydrosilylation reactions.

Unlike noble metals, iron preferably undergoes one-electron transfers (or no changes in formal oxidation state) instead of two-electron processes such as oxidative addition or reductive elimination. Therefore, mechanisms such as the Ojima mechanism[47] for Rh catalysts are very unlikely for this catalyst system.[48] We probed the presence of radicals during the reaction by addition of 0.1 or 1 equiv (referring to the ketone at 5 mol % catalyst loading) of radical traps. Neither triphenylmethane nor 9,10-dihydroanthracene had a significant impact on the reactivity observed, which indicates that radical processes are unlikely. Treatment of **4** with 1 equiv of $(EtO)_2MeSiH$ yields the silylether of the alkoxide previously bound to Fe in compound **4**.

From our results and in analogy to the mechanism proposed for Cu(I)-catalyzed hydrosilylation,[49−52] we propose a mechanism for the Fe-catalyzed hydrosilylation shown in Scheme 3.

Scheme 3. Mechanistic Proposal for the Iron-Catalyzed Hydrosilylation of Ketones



After precatalyst activation, σ-bond metathesis takes place between the alkoxido complex and the silane, in which the silylether is formed (**I**). The remaining hydrido complex undergoes rapid coordination of the ketone (**II**) and subsequent insertion of the ketone into the Fe–H bond (**III**). This step determines the stereoselectivity of the reaction and re-forms the alkoxido complex. Numerous attempts to synthesize and isolate a hydrido complex remained unsuccessful. We attribute this to its high thermal instability, which is common for iron(II) high-spin hydrido complexes. This is illustrated by the fact that, to the best of our knowledge, only one such high-spin complex has been characterized by X-ray diffraction, whereas low-spin iron(II) hydride complexes are more common.[53,54]

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We have presented the first Fe-catalyzed hydrosilylation that gives rise to ee values greater than 95% for a broad range of aryl alkyl ketones bearing substituents of varying steric bulk. Substrates with long α-unbranched alkyl chains are reduced via hydrosilylation with a high enantioselectivity. Besides the high stereoselectivity, this catalyst system is the most active Fe-based hydrosilylation catalyst studied to date and allows catalytic transformations at low temperatures. This makes it a promising system for the further development of the field and, potentially, an important step toward applicability of iron complexes as catalysts in synthesis.[36] Further investigations concerning the mechanism of this reaction as well as the extension of the scope of iron boxmi complexes as catalysts are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Methods, additional data, and CIF files giving crystallographic data for compounds **3(py)** and **4(py)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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