DOI: 10.1002/ejoc.201000648

Formamidines – Versatile Ligands for Zinc-Catalyzed Hydrosilylation and Iron-Catalyzed Epoxidation Reactions

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Keywords: Homogeneous catalysis / Zinc / Iron / Amidine ligands / Hydrosilylation / Epoxidation

In the present study the abilities of catalysts modified by formamidine ligands have been examined in the zinc-catalyzed hydrosilylation of ketones and the iron-catalyzed epoxidation of stilbene. In case of hydrosilylation diethylzinc combined with easily accessible formamidine ligands allow for the efficient reduction of various aryl and alkyl ketones. By using a convenient in situ catalyst system high turnover frequencies up to more than 1.000 h^{-1} and a broad functional group tolerance were achieved. Moreover, the formamidine ligands were successfully applied in the iron-catalyzed epoxidation of stilbene with hydrogen peroxide in good yield and chemoselectivity.

Introduction

The quest for sustainable and more efficient synthetic methods continues to be a primary research target in modern chemistry. In this regard, catalysis is a key technology, since high atom efficiency, reduced amounts of waste as well as energy, and in consequence advantageous economics are feasible.[1] Especially, the use of organometallic compounds as catalysts has become a well-established tool for both academia and industry.[2] The reactivity and selectivity of the reaction are significantly influenced by the selection of the central metal and by the abilities of surrounded ligands. Hence, a vast number of ligands were developed during the last decades. In recent times a special focus for new ligand approaches is devoted to the design of artificial catalysts/ligands inspired by active sites of "natural" biocatalysts.[3] Moreover, a second aspect, the substitution of expensive metals (e.g., Rh, Ru, Pd) by low-toxic and cheap biorelevant metals, e.g., iron or zinc, is currently highly requested, since the advantages are obvious.[4]

Recently, some of us became interested in this field of chemistry and showed the successful application of imidazole ligands in iron-catalyzed oxidation reactions.[5] This ligand concept is based on the occurrence of histidine, which participates in manifold biological processes.[6] In general, in metalloproteins the imine nitrogen of histidine coordinates to the corresponding metal. Hence, imidazole-based complexes should allow for similar catalytic applications (Figure 1).[5] However, applying imidazole ligands variations can be only done directly at α-position to the nitrogen atoms due to the fixed position of the heterocyclic ring carbons. By removal of the C_2-bridge a higher degree of structural variations is possible. The resulting formamidine structure allows for an easy variation of substituents on the imine nitrogen and an additional group bonded to the amine part. In consequence a convenient tuning is possible compared to imidazole ligands.[7]

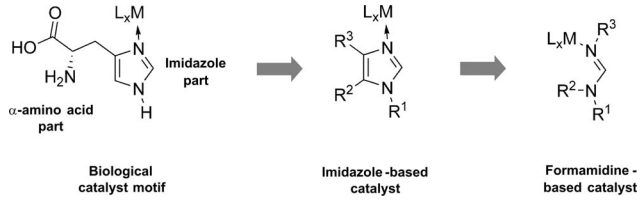

Figure 1. Bio-inspired catalysts related to histidine.

Herein, we report on our initial studies on the application of formamidine ligands in the zinc-catalyzed hydrosilylation of carbonyl compounds and the iron-catalyzed epoxidation of olefins.

Results and Discussion

Formamidines were synthesized following reported procedures. Thus, equimolar amounts of dimethylformamide were treated with phosphorus oxychloride in diethyl ether under inert conditions to form the corresponding Vilsmeier reagent. Then, the reagent was quenched with primary amines to obtain formamidines **2** after basification (Table 1).[8] The crude products were purified by vacuum distillation. Moderate yields were achieved for arylated amidines, while alkyl derivatives containing cyclohexyl, *tert*-butyl and adamantyl groups are derived only in low yields.

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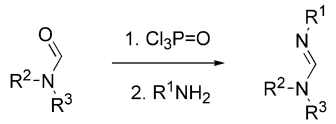
The formamidines based on methylphenylformamide and diphenylformamide were not accessible under these standard conditions. However, refluxing formamide and phosphorus oxychloride in toluene and subsequently heating to reflux after amine addition gave moderate yields of formamidines **3** and **4**. Noteworthy, in all cases we observed the selective formation of the *E*-isomer, which is in agreement with the literature.[9]

Table 1. Synthesis of a formamidine library.



1 **2-4**

Ligand	R^1	R^2	R^3	Yield [%]
2a	C_6H_5	CH_3	CH_3	57
2b	4-MeC_6H_4	CH_3	CH_3	35
2c	4-*t*BuC_6H_4	CH_3	CH_3	50
2d	4-$MeOC_6H_4$	CH_3	CH_3	37
2e	4-$CF_3C_6H_4$	CH_3	CH_3	54
2f	3,5-$F_2C_6H_3$	CH_3	CH_3	62
2g	3,4,5-$F_3C_6H_2$	CH_3	CH_3	49
2h	2,4,6-$Me_3C_6H_2$	CH_3	CH_3	69
2i	2,6-*i*$Pr_2C_6H_3$	CH_3	CH_3	45
3	2,4,6-$Me_3C_6H_2$	CH_3	C_6H_5	28
4	C_6H_5	C_6H_5	C_6H_5	44

In addition, we studied the influence of the various substituents in comparison to parent structure **2a**. In Table 2 typical analytical parameters are given. First, the formamidine proton was applied as sensor to detect geometrical and electronic changes. By measuring the ^{1}H chemical shift no significant influence was found when alkyl groups, electron-withdrawing groups as well as electron-donating groups are placed in the *para*-position, while increasing the bulkiness in the 2,6-position by methyl or isopropyl a high field shift was observed. Substitution of the Me_2N moiety by MePhN or Ph_2N led to a dramatic downfield shift. In general, only a small influence was seen by using the formamidine C-atom as sensor, since all values are in the range of 150–154 ppm.

In order to get insights into the geometrical structures of the formamidines, DFT-calculations at the RB3LYP/6-31G(d) level were performed.[9] In agreement with experimental observations (vide supra) the *E*-configuration corresponds to the thermodynamically most stable motif (Table 2). The *E*-isomer is favoured by approximately 30 kJ/mol. An exception is observed for compound **3** with a difference of only 10 kJ/mol. The calculated geometries for **2g** and **3** are in agreement with those recorded by X-ray crystallography (Figure 2). In all cases the *E*-isomer was found. In addition, we compared the obtained structures with structural information available for imidazoles, e.g., *N*-2,4,6-trimethylphenylimidazole.[10] Due to the aromatic character of imidazole the bond lengths of the embedded carbon to the "imine" and "amine" nitrogen are 132.6 pm vs. 136.8 pm, whereas in case of formamidine **2g** shorter

Table 2. Characterization of the formamidines.

L	^{1}H NMR δ [ppm][a]	^{13}C NMR δ [ppm][b]	IR [cm^{-1}][c]	λ [cm^{-1}][e]	ΔE[d] [kJ/mol]
2a	7.52	153.2	1634	269.4	–30.6
2b	7.51	153.1	1635	270.5	–30.8
2c	7.53	153.2	1639	273.0	–29.3
2d	7.40	153.0	1638	274.1	–22.0
2e	7.54	153.8	1603	275.5	–29.6
2f	7.47	153.7	1696	269.3	–30.0
2g	7.46	153.8	1647	269.0	–31.5
2h	7.18	153.2	1644	263.8	–30.8
2i	7.15	152.5	1644	270.7	–21.2
3	7.82	151.0	1634	264.8	–10.7
4	8.18	150.6	–	276.5	–25.3

[a] The chemical shift (^{1}H-NMR) of the formamidine proton was measured in [D_1]chloroform at 25 °C. [b] The chemical shift (^{13}C-NMR) of R–N=*C*(H)NR_2 was measured in [D_1]chloroform at 25 °C. [c] KBr. [d] ΔE = (Energy *E*-isomer)-(Energy *Z*-isomer), energies obtained by calculations: B3LYP/6-31G(d). [e] All measurements were carried out in EtOH at 25 °C.

distances were measured (129.0 vs. 133.4 pm), which is in agreement with literature values.[11] In case of **3** the amine bond is similar to the imidazole bond (136.2 pm), while the imine bond is shorter (126.8 pm). The open structure in formamidines results in an elongation of the angle N1–C1–N2 124.1° (**2g**), 123.5° (**3**) compared to 111.8° in *N*-2,4,6-trimethylphenylimidazole.

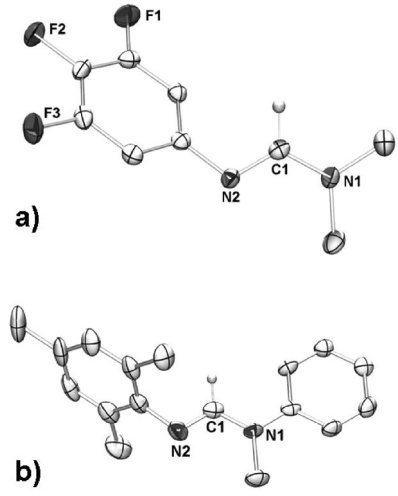


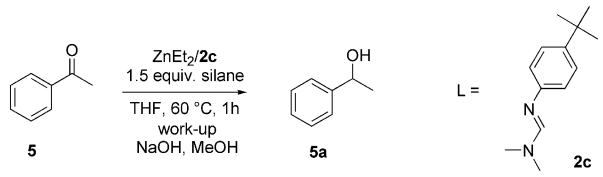
Figure 2. Molecular structure of **2g** (a), and **3** (b). Hydrogen atoms have been omitted for clarity except the formamidine protons. Selected bond lengths [pm] and angles [°]: **2g**: N1–C1 133.4(2), N2–C1 129.0(2), N1–C1–N2 124.1(16); **3**: N1–C1 136.3(3), N2–C1 126.8(3), N1–C1–N2 123.5(3).

After preparation and characterization of a small library of formamidine ligands, we were interested in the catalytic performance of this ligand class in homogeneous catalysis. First we focused on the catalytic hydrosilylation of carbonyl compounds. Up to now manifold catalysts for the hydrosilylation of ketones rely on precious metals such as rhodium, ruthenium, and iridium.[12] Due to the high price and sometimes toxicity less expensive "biological" metal-based catalysts are highly requested.[4] At this point the use of iron and zinc complexes is probably of most interest.[13] Several

research groups have demonstrated the abilities of zinc catalysts in hydrosilylation reactions.[14] For example, it was shown by Mimoun that unmodified $ZnEt_2$ is not able to catalyze the hydrosilylation of carbonyl compounds, but the addition of ligands can improve the outcome of the reaction significantly.[14] Most ligands applied for this reaction are based on chelating diamines containing NH-functionalities to create a covalent N–Zn bond. We asked ourselves if it is possible to obtain active catalysts containing monodentate nitrogen ligands without NH group, since a plethora of simple amines is available. Based on this idea initial studies on the influence of the reaction conditions were carried out with acetophenone **5** as benchmark substrate by using 1 mol-% of an in-situ-generated zinc catalyst composed of diethylzinc and formamidine **2c** in a ratio of 1:1 (Table 3). The generated silyl ether was hydrolyzed under basic conditions to obtain the corresponding alcohol **5a**. First, the abilities of some hydride sources were studied at 60 °C for one hour. High conversion (98%) was found in case of triethoxysilane as hydrogen source (Table 1, entry 1). Good yields of 1-phenylethanol **5a** were obtained with diphenylsilane and phenylsilane (Table 3, entries 4 and 5), while poly(methylhydrosiloxane) (PMHS) furnished only moderate amounts of 1-phenylethanol. In contrast, with triphenylsilane, dimethylphenylsilane, and triethylsilane no hydride transfer was detected. Replacement of one ethoxy by a methyl group led to a dramatic decrease of product formation. For further understanding of the abilities of applied hydride sources, the hydridic character of the Si–H bond was determined by NMR spectroscopy. Unfortunately, no correlation was observed.

To clarify the influence of the ligand unmodified diethylzinc was also applied as catalyst (Table 4, entry 1). Here, lower conversion was observed, while in the absence of any catalyst no reaction took place. Apparently, the addition of the formamidine ligand is of importance for acceleration of the reaction. Next, the zinc to ligand ratio was examined in the range of 1:1 to 1:5 (Table 4, entries 4–7). No significant effects were observed. In addition, the influence of the reaction temperature was investigated. At ambient condition a turnover number of 58 h^{-1} was obtained. At 90 °C full con-

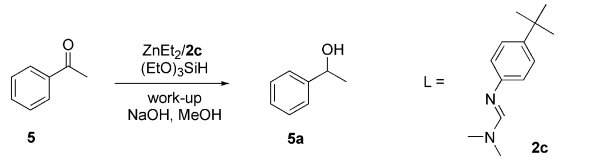
Table 3. Influence of the hydride source on the hydrosilylation of acetophenone **5**.



Entry[a]	H source	δ [ppm] ^{1}H-NMR[c]	δ [ppm] ^{29}Si-NMR[d]	Yield [%]
1	$(EtO)_3SiH$	4.22	–58.2	**98**
2	$Me(EtO)_2SiH$	4.66	–34.4	17
3	Ph_3SiH	5.49	–17.8	<1
4	Ph_2SiH_2	5.02	–33.1	95
5	$PhSiH_3$	4.29	–58.7	92
6	Me_2PhSiH	4.61	–16.7	<1
7	Et_3SiH	3.66	–0.5	<1
8	PMHS[b]	4.74	–34.4[e]	53

[a] Reactions were carried out with 0.024 mmol $ZnEt_2$ (1.0 M in *n*-hexane), 0.024 mmol **2c**, 2.4 mmol acetophenone, 3.6 mmol silane, 1.0 mL of THF for 1 h at 60 °C, The conversion was determined by GC (30 m Rxi-5ms column, 40–300 °C; 1-phenylethanol: 6.20 min, acetophenone: 6.28 min) with dodecane: 7.84 min as the internal standard. [b] PMHS = poly(methylhydrosiloxane). [c] Chemical shift for the hydride. [d] With TMS (tetramethylsilane) as internal standard. [e] Besides the major signal at –34.4 ppm [according to literature assigned as $(RO)_2MeSi$–H subunit] the following signals were observed: –35.4, –34.9, –34.5, 10.3 ppm.

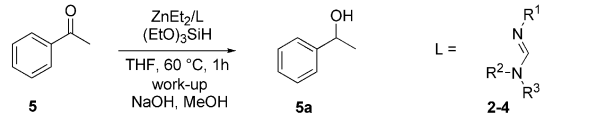
Table 4. Catalytic hydrosilylation of acetophenone **5**: influence of various reaction parameters.



Entry[a]	Cat. loading [mol-%]	M/L	T [°C]	Yield [%]
1[b]	1.0	1:0	60	40
2[c]	0	0:0	60	< 1
3[d]	0	0:1	60	< 1
4	1.0	1:1	25	51
5	1.0	1:2	25	46
6	1.0	1:3	25	48
7	1.0	1:5	25	48
8	1.0	1:1	90	> 99
9	0.1	1:1	60	> 99

[a] Reactions were carried out with 0.024 mmol $ZnEt_2$ and 0.024 mmol **2c**, 2.4 mmol acetophenone, 3.6 mmol triethoxysilane, 1.0 mL of THF for 1 h, The conversion was determined by GC (30 m Rxi-5ms column, 40–300 °C; 1-phenylethanol: 6.20 min, acetophenone: 6.28 min) with dodecane: 7.84 min as the internal standard. [b] 0.024 mmol diethylzinc (1.0 M in *n*-hexane) without addition of ligand were applied as catalyst precursor. [c] Without catalyst, 96% of acetophenone was recovered. [d] Addition of 1.0 mol-% ligand, without diethylzinc.

Table 5. Catalytic hydrosilylation of acetophenone **5**: variation of ligands.



Entry[a]	Ligand	$R^1/R^2/R^3$	Yield [%]
1	**2a**	$C_6H_5/CH_3/CH_3$	37
2	**2b**	4-$MeC_6H_4/CH_3/CH_3$	38
3	**2c**	4-$tBuC_6H_4/CH_3/CH_3$	51
4	**2d**	4-$MeOC_6H_4/CH_3/CH_3$	39
5	**2e**	4-$CF_3C_6H_4/CH_3/CH_3$	37
6	**2f**	3,5-$F_2C_6H_3/CH_3/CH_3$	82
7	**2g**	3,4,5-$F_3C_6H_2/CH_3/CH_3$	33
8	**2h**	2,4,6-$Me_3C_6H_2/CH_3/CH_3$	87
9	**2i**	2,6-$iPr_2C_6H_3/CH_3/CH_3$	18
10	**3**	2,4,6-$Me_3C_6H_2/CH_3/C_6H_5$	53
11	**4**	$C_6H_5/C_6H_5/C_6H_5$	33

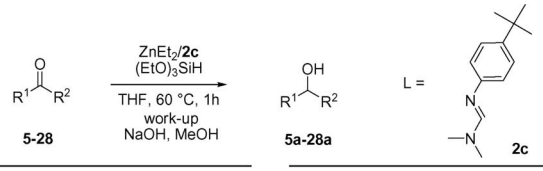
[a] Reactions were carried out with 0.024 mmol $ZnEt_2$ (1.0 M in *n*-hexane), 0.024 mmol ligand, 2.4 mmol acetophenone, 3.6 mmol triethoxysilane, 1.0 mL of THF for 1 h at 25 °C. The conversion was determined by GC (30 m Rxi-5ms column, 40–300 °C; 1-phenylethanol: 6.20 min, acetophenone: 6.28 min) with dodecane: 7.84 min as the internal standard.

version was reached within one hour, even if a black precipitate was formed after several minutes. Reducing the catalyst loading to 0.1 mol-% demonstrated excellent activity at 60 °C with a catalyst turnover frequency of at least 999 h^{-1}.

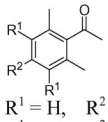
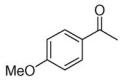
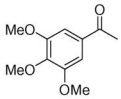
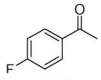
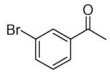
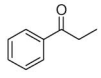
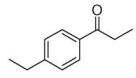
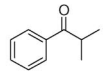
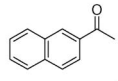
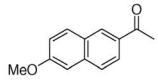
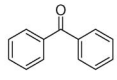
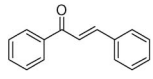
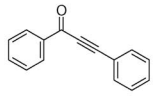
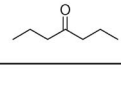
The influence of the ligand structure was explored by combination of various formamidines with diethylzinc (Table 5). Those in-situ-generated pre-catalyst were subjected to the hydrosilylation of acetophenone at room temperature. The parent ligand **2a** gave a conversion of 37% and substitution in 4-position showed no significant difference. Only with ligand **2c** slightly higher conversion was observed. However, fluoro-substitution in 3,5-position provided high conversion (82%), whereas an additional fluoro-substituent diminished the yield again (Table 5, entries 6 and 7). Best performance was demonstrated with the in-situ-catalyst containing ligand **2h**.

After establishing suitable reaction conditions (1.0 mol-% catalyst, 60 °C, 1 h) for the hydrosilylation of the benchmark substrate, the scope and limitations of the catalyst composed of diethylzinc and formamidine **2c** in a ratio of 1:1 were studied. The obtained silyl ethers were hydrolyzed under basic conditions to yield the corresponding alcohols. As shown in Table 6 an influence of substitution on the phenyl-moiety of acetophenone was observed. Excellent yields were attained with electron-withdrawing as well as with electron-donating substituents (Table 6, entries 2, 4–9). However, *ortho*-substituted substrates showed no conversion at all under these conditions (Table 6, entry 3). In contrast to this, an increase of bulkiness on the alkyl chain

Table 6. Scope and limitations of the in situ system composed of $ZnEt_2$ and ligand **2c**.



5-28 5a-28a 2c

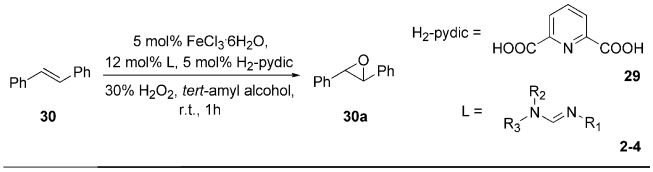
Entry[a]	Substrate	Conv. [%][b]
1	 **5**	> 99 (90)
2	 **6**	> 99 (87)
3	 **7**: R^1 = H, R^2 = Me **8**: R^1 = H, R^2 = *t*Bu **9**: R^1 = Me, R^2 = Me	< 1 < 1 < 1
4	 **10**	> 99 (97)
5	 **11**	> 99 (89)
6	 **12**	> 99 (91)
7	 **13**	> 99 (94)
8	 **14**	> 99 (91)
9	 **15**	> 99 (83)
10	 **16**	> 99 (96)
11	 **17**	> 99 (81)
12	 **18**	> 99 (79)
13	 **19**	> 99 (83)
14	 **20**	> 99 (87)
15	 **21**	> 99 (85)
16	 **22**	> 99 (91)
17	 **23**	> 99[c]
18	 **24**	> 99 (98)
19	 **25**	> 99 (76)
20	 **26**	> 99 (97)
21	 **27**	96 (79)
22	 **28**	> 99 (82)

[a] Reactions were carried out with 0.024 mmol $ZnEt_2$ and 0.024 mmol **2c**, 2.4 mmol ketone, 3.6 mmol triethoxysilane, 1.0 mL of THF for 1 h at 60 °C; the conversion was determined by GC (30 m Rxi-5ms column, 40–300 °C) and the yield by ^{1}H NMR after isolation. [b] In brackets the isolated yield is stated. [c] Mixture of products: 4-phenylbut-3-en-2-ol (78%), 4-phenylbutan-2-one (22%).

showed no influence on the conversion (Table 6, entries 10–13). Hydrosilylation of ketones in the presence of an alkynyl group gave selectively the corresponding alcohol, whereas **23** yielded a mixture of the allylic alcohol and the saturated ketone (Table 6, entries 17 and 18). In addition, several dialkyl ketones were reduced with excellent conversions by the zinc catalyst (Table 6, entries 19–23).

In addition to the zinc-catalyzed hydrosilylation, the general catalytic potential of the formamidine ligands was demonstrated by applying them also in iron-catalyzed epoxidations of C–C double bonds. In general, oxiranes provided by catalytic epoxidation are of fundamental importance in various fields of chemistry ranging from pharmaceutical intermediates to monomers for bulk polymers. Hence, there is an ongoing interest in active, simple and selective catalyst systems. Environmentally benign epoxidation catalysts should work with inexpensive ligands without tedious complex preparation and with sustainable terminal oxidants. For our purposes hydrogen peroxide is regarded as oxidant of choice due to ecological and economic considerations with only water as by-product.[15] Based on the earlier developed approaches of iron-catalyzed epoxidation reactions with pyridine-2,6-dicarboxylic acid **29** and nitrogen ligands like pyrrolidine or benzylamines[16] as well as with imidazole ligands,[5] we adopted these biomimetic methods on the formamidine ligands. Fortunately, starting with the benchmark substrate *trans*-stilbene (**30**) we obtained good yields up to 78% in the presence of ligand **2i** (Table 7). Generally, all formamidine ligands with two methyl groups attached to the amine nitrogen (**2a**–**2i**) exhibited moderate to good reactivity and high selectivity. Notably, ligands **2e**, **2h** and **2i** gave the highest yields (>75%). However, ligands with electron donating- or electron withdrawing-substituents at the aromatic ring which are owing to inductive effects (-alkyl, -CF_3) displayed significantly higher yields than those which showed a complete or partly donation or withdrawal by conjugation effects (-OMe, -F). Besides, ligands **4**, **2g** and **2f** demonstrate an interesting behaviour. After the first hour of hydrogen peroxide addition the ligands showed only low conversions. However, the product yield increased to 22% for **4**, to 54% for **2g**, and to 56% for **2f** after stirring for 24h. These results guided us to explore the stability of the ligands under slightly acidic, airy and hydrous conditions. When applying our reaction conditions to a mixture of $FeCl_3 \cdot 6H_2O$, pyridine-2,6-dicarboxylic acid, *tert*-amyl alcohol and ligand **2a** no change in structure was observed by GC-MS. Besides also the use of hydrogen peroxide (30%) and *trans*-stilbene gave no decomposition of the ligand.

Table 7. Epoxidation of *trans*-stilbene.



Entry[a]	Ligand	$R^1/R^2/R^3$	Conv. [%][b]	Yield [%][b]	Sel. [%][c]
1	**2a**	$C_6H_5/CH_3/CH_3$	77	69	90
2	**2b**	4-$MeC_6H_4/CH_3/CH_3$	77	69	90
3	**2c**	4-*t*$BuC_6H_4/CH_3/CH_3$	80	63	79
4	**2d**	4-$MeOC_6H_4/CH_3/CH_3$	24	22	98
5	**2e**	4-$CF_3C_6H_4/CH_3/CH_3$	87	76	87
6	**2f**	3,5-$F_2C_6H_3/CH_3/CH_3$	36	30	85
7	**2g**	3,4,5-$F_3C_6H_2/CH_3/CH_3$	21	17	83
8	**2h**	$Mes/CH_3/CH_3$	77	77	99
9	**2i**	2,6-*i*$Pr_2C_6H_3/CH_3/CH_3$	79	78	99
10	**3**	$Mes/CH_3/C_6H_5$	61	56	92
11	**4**	$C_6H_5/C_6H_5/C_6H_5$	6	6	97

[a] Reaction conditions: 0.5 mmol *trans*-stilbene, 5 mol-% $FeCl_3 \cdot 6H_2O$ and 12 mol-% formamidine ligand, 5 mol-% H_2-pydic, *tert*-amyl alcohol, 0.44 mmol dodecane, (100 μL, internal standard) were added in sequence at room temp. in air. To this mixture, a solution of 30% H_2O_2 (170 μL, 1.5 mmol) in *tert*-amyl alcohol (830 μL) was added over a period of 1h at room temp. by a syringe pump. [b] Conversion and yield were determined by GC analysis, for reproducibility the reactions were at least repeated twice. [c] Selectivity refers to the chemoselectivity of epoxide from olefin.

Apart from *trans*-stilbene this protocol was also applied to *cis*-stilbene, styrene, and cyclooctene. For cyclooctene and *cis*-stilbene the reactivity was diminished compared to the benchmark reaction. Nevertheless, cyclooctene oxide was obtained in 20% yield with iron trichloride hexahydrate modified by ligands **2a** and **2b**. To our delight styrene was oxidized in excellent yield, e.g., ligand **2h** gave up to 99% conversion with a yield of 92%, whereas ligand **2a** and **2b** gave good yields towards the corresponding oxiranes.[17]

Conclusions

In the present study we demonstrated the catalytic potential of formamidine ligands both in zinc-catalyzed hydrosilylations as well as iron-catalyzed epoxidations. In case of hydrosilylation diethylzinc combined with easily accessible formamidine ligands allowed the efficient reduction of acetophenone with high catalyst turnover frequencies up to 1.000 h^{-1}. Furthermore, the hydrosilylation of various aryl and alkyl ketones can be performed with broad functional group tolerance. Moreover, the combination of formamidine ligands with iron(III) chloride and pyridine-2,6-dicarboxylic acid yielded a practical in situ catalyst for the epoxidation of C–C double bonds. Using hydrogen peroxide as terminal oxidant the stilbene epoxide was formed in selectivities up to 99% at mild reaction conditions. Further work in the direction of enantioselective hydrosilylation and epoxidation, based on Zn and Fe catalysts modified by chiral formamidines, are under way in our laboratories.

Experimental Section

General: All manipulations with oxygen- and moisture-sensitive compounds were performed under dinitrogen using standard Schlenk techniques. THF was distilled from sodium/benzophenone ketyl under dinitrogen. Diethylzinc solution (1.0 M in *n*-hexane purchased from Aldrich) was used without further manipulations. ^1H and ^{13}C NMR spectra were recorded on a Bruker AFM 200 spec-

trometer (^{1}H: 200.13 MHz; ^{13}C: 75.5 MHz) using the proton signals of the deuterated solvents as reference. Single-crystal X-ray diffraction measurements were recorded on an Oxford Diffraction Xcalibur S Saphire spectrometer. IR spectra were recorded either on a Nicolet Series II Magna-IR-System 750 FTR-IR or on a Perkin–Elmer Spectrum 100 FT-IR. Electron-impact mass spectra (EI-MS) were recorded on a Finnigan MAT95S. Melting points (m.p.) were determined on a BSGT Apotec II capillary-tube apparatus and are uncorrected. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 20 spectrometer. GC–MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer.

Safety Consideration: During our studies we used triethoxysilane as reducing reagent without incident. However, Buchwald et al. reported on difficulties when working with triethoxysilane.[18]

Synthesis of *N*,*N*-Dimethylformamidine (2): Dimethylformamide (25.3 mmol) was dissolved in dry diethyl ether (50 mL) and cooled to 10 °C. Under an atmosphere of nitrogen phosphorus oxychloride (25.3 mmol) was added carefully maintaining the reaction temperature, while a white precipitate was formed. The mixture was stirred for two hours at room temperature yielding an insoluble (in diethyl ether) oily residue. A white precipitate was obtained after cooling to 10 °C and slow addition of the corresponding primary amine (25.3 mmol). The stirring was continued for 12 h at room temperature. The mixture was transferred to a separation funnel and carefully treated with water (50 mL) and aqueous sodium hydroxide solution until pH > 8 for the aqueous layer. The aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL). Drying with Na_2SO_4 and removal of the solvent yield the crude product, this was purified by distillation.

***N*,*N*-Dimethyl-*N*′-phenylformamidine (2a):** Yield 57%; colourless liquid; b.p. 84–85 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.02 (s, 6 H, CH_3), 6.92–7.06 (m, 3 H, C_6H_5), 7.20–7.32 (m, 3H C_6H_5), 7.52 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 34.3 (NCH_3), 39.8 (NCH_3), 120.9 (C_6H_5), 122.1 (C_6H_5), 128.6 (C_6H_5), 151.9 (C_q), 153.1 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 3440 (m), 3055 (m), 3027 (m), 2987 (m), 2922 (s), 2853 (m), 2801 (m), 2588 (w), 2470 (w), 2004 (w), 1933 (m), 1634 (s), 1589 (s), 1482 (m), 1384 (s), 1258 (m), 1214 (m), 1170 (m), 1099 (s), 970 (m), 834 (m), 761 (m), 696 (m), 637 (m), 549 (m), 503 (m) cm^{-1}. MS (ESI): *m*/*z* (%) = 149 (100) [M$^+$], 104 (21). HRMS calcd. for $C_9H_{12}N_2$+H: 149.10732; found 149.10721. UV/Vis: (EtOH, 25 °C): λ = 269.4 nm.

***N*,*N*-Dimethyl-*N*′-(4-methylphenyl)formamidine (2b):** Yield 35%; colourless liquid; b.p. 95 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, $C_6H_4CH_3$), 3.00 [s, 6 H, $N(CH_3)_2$], 6.84–6.93 (m, 2 H, C_6H_4), 7.04–7.14 (m, 2 H, C_6H_4), 7.51 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6 ($C_6H_4CH_3$), 34.6 (NCH_3), 39.7 (NCH_3), 120.8 (CH), 129.4 (CH), 131.5 (C_q), 149.4 (C_q), 153.1 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 3441 (s), 2921 (m), 1635 (m), 1509 (w), 1384 (m), 1258 (w), 1173 (w), 1100 (m), 1064 (w), 970 (w), 816 (w), 588 (w), 502 (w) cm^{-1}. MS (ESI): *m*/*z* (%) = 163 (100) [M$^+$], 118 (27). HRMS calcd. for $C_{10}H_{14}N_2$+H: 163.12298; found 163.12286. UV/Vis: (EtOH, 25 °C): λ = 270.5 nm.

***N*,*N*-Dimethyl-*N*′-(4-*tert*-butylphenyl)formamidine (2c):** Yield 50%; b.p. 120 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.32 [s, 9 H, $C(CH_3)_3$], 3.01 [s, 6 H, $N(CH_3)_2$], 6.86–6.95 (m, 2 H, C_6H_4), 7.24–7.33 (m, 2 H, C_6H_4), 7.53 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 31.4, 34.0, 120.5 (CH), 125.7 (CH), 145.0 (C_q), 149.3 (C_q), 153.2 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 2958 (m), 1639 (s), 1600 (m), 1515 (m), 1416 (m), 1364 (m), 1258 (m), 1182 (m), 1098 (m), 974 (w), 834 (m), 569 (w), 519 (w) cm^{-1}. MS (ESI): *m*/*z* (%) = 205 (18) [M$^+$], 190 (56), 160 (100). HRMS calcd. for $C_{13}H_{20}N_2$+H: 205.16993; found 205.16930. UV/Vis: (EtOH, 25 °C): λ = 273.0 nm.

***N*,*N*-Dimethyl-*N*′-(4-methoxyphenyl)formamidine (2d):** Yield 37%; colourless liquid; b.p. 108–110 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.913 (s, 3 H,CH_3), 2.914 (s, 3 H,CH_3), 3.69 (s, 3 H, OCH_3), 6.70–6.86 (m, 4 H, C_6H_4), 7.40 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 34.1 (NCH_3), 39.6 (NCH_3), 55.2 (OCH_3), 114.3 (CH), 121.5 (CH), 145.3 (C_q), 152.8 (C_q), 155.2 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 1638 (s), 1509 (s), 1368 (m), 1239 (s), 1179 (m), 1103 (m), 1036 (m), 831 (m), 765 (m), 591 (w), 552 (w) cm^{-1}. MS (ESI): *m*/*z* (%) = 179 (61) [M$^+$], 134 (100). HRMS calcd. for $C_{10}H_{14}ON_2$+H: 179.11789; found 179.11797. UV/Vis: (EtOH, 25 °C): λ = 274.1 nm.

***N*,*N*-Dimethyl-*N*′-(4-trifluoromethylphenyl)formamidine (2e):** Yield 54%; white solid crystallized from ethanol; m.p. 47–49 °C; b.p. 92–94 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.06 [s, 6 H, $N(CH_3)_2$]; 6.99–7.03 (m, 2 H, C_2H_4); 7.48–7.51 (m, 2 H, C_2H_4); 7.54 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 34.4 (NCH_3), 40.1 (NCH_3), 114.0 (CH), 121.1 (CH), 126.1 (CH), 127.4 (C_q), 153.7 [N=C(H)N], 155.2 (C_q) ppm. IR (KBr): $\tilde{\nu}$ = 2926 (m), 1915 (w), 1603 (s), 1516 (m), 1443 (m), 1373 (m), 1331 (s), 1263 (m), 1161 (m), 1107 (s), 1066 (s), 975 (m), 846 (m), 663 (m), 599 (m), 516 (w), 484 (w) cm^{-1}. MS (ESI): *m*/*z* (%) = 217 (100) [M$^+$], 172 (46). HRMS calcd. for $C_{10}H_{11}F_3N_2$+H: 217.09471; found 217.09473. UV/Vis: (EtOH, 25 °C): λ = 275.5 nm.

***N*,*N*-Dimethyl-*N*′-(3,5-difluorophenyl)formamidine (2f):** Yield 62%; colourless solid (–25 °C), colourless liquid (room temp.); b.p. 92–93 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.98 [s, 6 H, $N(CH_3)_2$], 6.31–6.51 (m, 3 H, C_6H_4), 7.47 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 34.3 (s, NCH_3), 40.0 (s, NCH_3), 97.1 (t, J = 26.07 Hz, C_6H_3), 103.8 (dd, ^1J = 9.34, ^2J = 15.69 Hz, CH), 153.7 [N=C(H)N], 154.9 (t, J = 11.67 Hz, C_q), 160.9 (d, J = 15.38 Hz, CF), 165.7 (d, J = 15.36 Hz, CF) ppm. IR (KBr): $\tilde{\nu}$ = 3431 (m), 2921 (m), 1696 (m), 1617 (m), 1384 (s), 1310 (w), 1257 (w), 1102 (m), 987 (m), 840 (w), 680 (w), 509 (w) cm^{-1}. MS (ESI): *m*/*z* = 185.1. HRMS calcd. for $C_9H_{10}F_2N_2$+H: 185.08848; found 185.08835. UV/Vis: (EtOH, 25 °C): λ = 269.3 nm.

***N*,*N*-Dimethyl-*N*′-(3,4,5-trifluorophenyl)formamidine (2g):** Yield 49%; white solid; m.p. 38 °C; b.p. 84–85 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.03 [s, 6 H, $N(CH_3)_2$], 6.46–6.64 (m, 2 H, C_6H_2), 7.46 (s, 1 H), 7.54 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 34.3 (s, NCH_3), 40.1 (s, NCH_3), 98.4 (d, J = 23.25 Hz, C_6H_2), 104.6 (td, ^1J = 7.68, ^2J = 6.65, ^3J = 1.03 Hz, C_6H_2), 133.2 (t, J = 15.8 Hz, C_q), 138.0 (t, J = 15.86 Hz, C_q), 148.1 (qd, ^1J = 13.35, ^2J = 9.83, ^3J = 9.48, ^4J = 3.35 Hz, C_q), 148.7 (dd, ^1J = 10.35, ^2J = 5.72 Hz, C_q), 153.5 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 3491 (w), 2928 (m), 2808 (w), 1647 (s), 1622 (s), 1522 (s), 1430 (m), 1381 (m), 1332 (m), 1229 (m), 1099 (m), 1038 (m), 856 (m), 788 (m), 681 (m), 640 (m), 532 (m) cm^{-1}. MS (ESI): *m*/*z* (%) = 203 (74) [M$^+$], 158 (100). HRMS calcd. for $C_9H_9F_3N_2$+H: 203.07906; found 203.07922. UV/Vis: (EtOH, 25 °C): λ = 269.0 nm.

***N*,*N*-Dimethyl-*N*′-(2,4,6-trimethylphenyl)formamidine (2h):** Yield 69%; colourless liquid; b.p. 100–102 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.13 (s, 6 H), 2.26 (s, 3 H, *p*-Me), 3.01 (s, 6 H), 6.84 (m, 2 H, Ar-H), 7.18 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 18.4 [$C_6H_2(CH_3)_2$], 20.5 ($C_6H_2CH_3$), 37.0 (NCH_3), 128.3 (C_6H_2), 129.2 (C_q), 130.7 (C_q),

147.4 (C_q), 153.2 [N=C(*H*)N] ppm. IR (KBr): $\tilde{\nu}$ = 3435 (m), 3282 (m), 2921 (s), 2854 (m), 2805 (m), 2729 (m), 1950 (w), 1644 (s), 1607 (m), 1479 (m), 1436 (m), 1384 (s), 1260 (m), 1213 (m), 1094 (m), 852 (m), 744 (m), 588 (m) cm^{-1}. MS (ESI): *m*/*z* (%) = 191 (100) [M^+], 146 (65). HRMS calcd. for $C_{12}H_{18}N_2$+H: 191.15428; found 191.15437. UV/Vis: (EtOH, 25 °C): λ = 263.8 nm.

***N*,*N*-Dimethyl-*N*′-(2,6-diisopropylphenyl)formamidine (2i):** Yield 45%; colourless solid (–25 °C), colourless liquid (room temp.); b.p. 90–93 °C (1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.18 [d, *J* = 6.90 Hz, 12 H, $CH(CH_3)_2$], 2.82 [s, 6 H, $N(CH_3)_2$], 3.15 [sept, *J* = 6.90 Hz, 2 H, $CH(CH_3)_2$], 6.98–7.12 (m, 3 H, Ar), 7.15 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 22.4 [$CH(CH_3)_2$], 23.7 [$CH(CH_3)_2$], 27.6 (NCH_3), 27.8 (NCH_3), 118.4 (CH), 122.6 (CH), 132.3 (C_q), 140.3 (C_q), 147.8 (C_q), 152.5 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 3408 (m), 3061 (w), 2959 (s), 2926 (m), 2869 (m), 1647 (s), 1588 (m), 1459 (m), 1441 (m), 1363 (m), 1322 (w), 1262 (m), 1089 (s), 934 (w), 833 (w), 800 (w), 757 (m) cm^{-1}. MS (ESI): *m*/*z* (%) = 203 (74) [M^+], 158 (100). HRMS calcd. for $C_{17}H_{20}N_2$+H: 233.20123; found 253.16904. UV/Vis: (EtOH, 25 °C): λ = 270.7 nm.

***N*-Methyl-*N*-phenyl-*N*′-(2,4,6-trimethylphenyl)formamidine (3):** The corresponding formamide (25.3 mmol) was dissolved in dry toluene (50 mL) and cooled to 10 °C. Under an atmosphere of nitrogen phosphorus oxychloride (25.3 mmol) was added carefully while maintaining the reaction temperature. The mixture was refluxed for three hours. After cooling to 10 °C the corresponding aniline (25.3 mmol) was added carefully. The stirring was continued for 12 h at room temperature. The mixture was refluxed for three hours and afterwards transferred to a separation funnel and carefully treated with water (50 mL) and an aqueous sodium hydroxide solution until the aqueous layer was alkaline (pH > 8). The aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL). Drying with Na_2SO_4 and removal of the solvent yields the crude product. yield 28%; colourless crystals (crystallized from ethanol/*n*-hexane 90:10); m.p. 81 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.18 [s, 6 H, $C_6H_2(CH_3)_2$], 2.27 (s, 3 H, $C_6H_2CH_3$), 3.58 (s, 3 H, NCH_3), 6.87 (s, 2 H, C_6H_2), 7.18–7.05 (m, 3 H, C_6H_5), 7.42–7.30 (m, 2 H, C_6H_5), 7.28 [s, 1 H, N=C(H)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 18.6 (CH_3), 20.6 (CH_3), 33.4 (NCH_3), 116.1 (CH), 123.4 (CH), 128.5 (CH), 128.9 (C_q), 129.3 (CH), 131.6 (C_q), 145.0 (C_q), 146.8 (C_q), 151.0 [N=C(H)N] ppm. IR (KBr): $\tilde{\nu}$ = 2915 (m), 1634 (s), 1595 (m), 1501 (m), 1483 (m), 1374 (w), 1346 (m), 1264 (m), 1210 (m), 1148 (m), 1126 (m), 1035 (w), 974 (w), 856 (w), 762 (m), 693 (m), 520 (w) cm^{-1}. MS (ESI): *m*/*z* (%) = 253 (43) [M^+], 146 (55), 131 (24), 120 (26), 108 (100), 93 (26). HRMS calcd. for $C_{17}H_{20}N_2$+H: 253.16993; found 253.16904. UV/Vis: (EtOH, 25 °C): λ = 264.8 nm.

***N*,*N*,*N*′-Triphenylformamidine (4):** Diphenylformamide (25.3 mmol) was dissolved in dry toluene (50 mL) and cooled to 10 °C. Under an atmosphere of nitrogen phosphorus oxychloride (25.3 mmol) was added carefully while maintaining the reaction temperature. The clear mixture was refluxed for three hours. A white precipitate was obtained after cooling to 10 °C and slow addition of aniline (25.3 mmol). The stirring was continued for 12 h at room temperature. The mixture was refluxed for three hours. After cooling to room temperature the solid was filtered off and washed with diethyl ether. The solid was transferred to a separation funnel and treated with water (50 mL) and diethyl ether (50 mL). A solution of sodium hydroxide was carefully added until pH > 8. The aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL). Drying with Na_2SO_4 and removal of the solvent yields a yellow powder; yield 44%; yellow solid; m.p. 85 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.01–7.46 [m, 1 H, $(C_6H_5)_2N$, C_6H_5N=], 8.18 [s, 1 H, N=C(*H*)N] ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 25 °C): δ = 121.2 (CH), 123.5 (CH), 124.9 (CH), 125.5 (CH), 128.9 (CH), 129.2 (CH), 143.3 (C_q), 150.6 [N=C(H)-N], 151.1 (C_q) ppm. IR (KBr): $\tilde{\nu}$ = 3053 (m), 2923 (m), 1686 (w), 1633 (s), 1586 (s), 1494 (s), 1449 (m), 1348 (s), 1284 (m), 1207 (s), 1138 (m), 966 (m), 759 (s), 693 (s), 555 (m) cm^{-1}. MS (ESI): *m*/*z* (%) = 273 (47) [M^+], 170 (100). HRMS calcd. for $C_{19}H_{16}N_2$+H: 273.13863; found 273.13889. UV/Vis: (EtOH, 25 °C): λ = 276.5 nm.

General Procedure for the Hydrosilylation Reaction: A pressure tube was charged with an appropriate amount of the corresponding formamidine (0.024 mmol, 1.0 mol-%) and purged with nitrogen (nitrogen/vacuum, three cycles). The formamidine was dissolved in anhydrous tetrahydrofuran (760 μL). Diethylzinc [240 μL (0.024 mmol) of a stock solution (1.0 mL of diethylzinc, 1.0 M in *n*-hexane, diluted with 9.0 mL of THF)] was added and the mixture was stirred for 10 min at room temperature. To the clear solution acetophenone (2.4 mmol) and triethoxysilane (3.6 mmol, 1.5 equiv.) were added via syringe. The reaction mixture was stirred in a preheated oil bath at 60 °C for 60 min. The mixture was cooled on an ice bath and was treated with dodecane (10 μL) as GC standard (for GC analysis), methanol (1.0 mL), and aqueous sodium hydroxide solution (1.0 mL) with vigorous stirring (***Caution***: The reaction mixture bubbled vigorously upon addition of the base). The reaction mixture was stirred for 60 min at 0 °C and was then extracted with diethyl ether (2 × 10.0 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered, and an aliquot was removed for GC-analysis. The yield was monitored by GC (30 m Rxi-5ms column, 40–300 °C; 1-phenylethanol: 6.20 min, acetophenone: 6.28 min). The analytical properties of the corresponding alcohols are in agreement with literature.

General Procedure for the Epoxidation of Olefins: In a test tube, $FeCl_3 \cdot 6H_2O$ (0.025 mmol), *tert*-amyl alcohol (9 mL), formamidine ligand (0.060 mmol), pyridine-2,6-dicarboxylic acid (0.025 mmol), olefin (0.50 mmol) and dodecane (GC internal standard, 100 μL) were added in sequence at room temperature in air. To this mixture a solution of 30% hydrogen peroxide (aqueous, 170 μL, 1.5 mmol) in *tert*-amyl alcohol (830 μL) was added over a period of 1 h at room temperature by a syringe pump. Conversion and yield were determined by GC analysis without further manipulations. Reactions were carried out twice due to reproducibility.

Single-Crystal X-ray Structure Determination: Crystals were each mounted on a glass capillary in perfluorinated oil and measured under a flow of nitrogen. The data of **2g**, and **3** were collected on an Oxford Diffraction Xcalibur S Sapphire at 123 K (Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[19] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

2g: Monoclinic, space group $P2_1/n$; *a* = 7.3941(3), *b* = 16.0027(6), *c* = 7.7584(3) Å; *b* = 100.526(4)°; *V* = 902.57(6) $Å^3$; *Z* = 4; ρ_{calc} = 1.488 mg m^{-3}; μ(Mo-K_α) = 0.092 mm^{-1}; 4462 collected reflections; 1585 crystallographically independent reflections (R_{int} = 0.0259); 1585 reflections with $I > 2\sigma(I)$; θ_{max} = 25.00°; $R(F_o)$ = 0.0380 [$I > 2\sigma(I)$]; w$R(F^2_o)$ = 0.0903 (all data); 129 refined parameters.

3: Monoclinic, space group $P2_1/n$; *a* = 6.8218(5), *b* = 7.0009(4), *c* = 15.1640(10) Å; *b* = 93.431(6)°; *V* = 722.92(8) $Å^3$; *Z* = 2; ρ_{calc} = 1.159 mg m^{-3}; μ(Mo-K_α) = 0.092 mm^{-1}; 3155 collected reflections; 2136 crystallographically independent reflections (R_{int} = 0.0251);

2136 reflections with $I > 2\sigma(I)$; θ_{max} = 25.00°; $R(F_o)$ = 0.0476 [$I > 2\sigma(I)$]; w$R(F^2_o)$ = 0.0858 (all data); 176 refined parameters.

CCDC-765371 (for **2g**) and -765372 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Cluster of Excellence "Unifying Concepts in Catalysis", sponsored by the Deutsche Forschungsgemeinschaft (DFG), and administered by the Technische Universität Berlin. K. S. appreciates financial support provided by the Graduiertenkolleg 1213 ("Neue Methoden für Nachhaltigkeit in Katalyse und Technik") and the Max-Buchner-Forschungsstiftung (DECHEMA). We thank Katja Pavel for excellent technical assistance.

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Received: May 7, 2010
Published Online: July 16, 2010

