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Z-selective Alkyne Semi-Hydrogenation Catalysed by Piano-Stool N-Heterocyclic Carbene Iron Complexes

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Chloe Johnson[a] and Martin Albrecht*[,a]

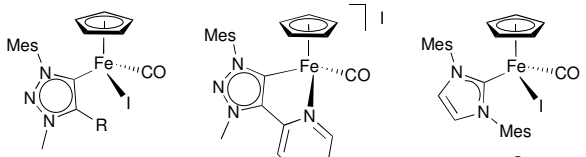
NHC iron(II) piano-stool complexes catalyse the selective semi-hydrogenation of alkynes to alkenes using silanes as reducing agents. Aromatic terminal alkynes are converted to styrenes without over-reduction to ethylbenzene derivatives. Furthermore, internal aryl alkynes afford *cis*-alkenes with excellent *Z*-selectivity.

The selective semi-hydrogenation of alkynes to alkenes is a valuable transformation in organic chemistry. The alkene products have utility in a wide range of industrially relevant processes, for example, polymerisation[1] and olefin metathesis[2] reactions. Semi-hydrogenation has been challenging since the alkene intermediate is generally a much better substrate for hydrogenation than the alkyne. This reactivity difference has long made it difficult to stop the reaction at the alkene stage, and instead exhaustive over-reduction to the alkane was observed with most catalysts. With the discovery of Lindlar's catalyst,[3] however, alkyne semi-hydrogenation became feasible. Ever since, a variety of homogeneous catalysts were developed based on precious metals such as Pd,[4] Ru,[5] Rh[6] and Ir.[7] More recently, semi-hydrogenation catalysts which exploit cheaper and more Earth-abundant base metals were introduced, and remarkable catalytic activity was accomplished with systems containing Co,[8] Ni,[9] and Cu[10]. However, efficient and selective semi-hydrogenation catalysts based on iron, arguably the most abundant, least toxic, and cheapest transition metal, have been elusive. Homo- and heterogeneous Fe(0) systems are potent alkyne reduction catalysts,[11] though they typically display low selectivity for semi-hydrogenation and generate fully saturated alkane products.

Since many of these catalysts operate under high H_2 pressures, a viable strategy to avoid over-reduction involves non-toxic and easy to handle hydrogen sources. While a hydrosilylation-desilylation approach satisfies these criteria, the *E*/*Z* selectivities observed by this method have so far been highly substrate and silane dependent, and are therefore not broadly applicable.[12] Using a similar approach, Beller and coworkers reported in 2012 a promising transfer hydrogenation protocol based on formic acid as a hydrogen source and an iron phopsphine catalyst, which was selective for terminal alkynes and resulted in the exclusive formation of alkene products.[13]

Recently we developed a series of triazolylidene iron(II) piano-stool complexes which efficiently catalyse the hydrosilylation of aldehydes and ketones.[14] Herein we show that in the presence of hydrosilanes, these complexes provide access to catalysts with excellent semi-hydrogenation selectivity with a variety of alkynes, both in terms of chemo- and stereoselectivity. The complexes produce exclusively the alkene product with excellent *Z*-selectivity when disubstituted alkynes were utilised as substrates.

Based on the established activity of carbene-containing piano-stool iron complexes,[15] the known[14,16] NHC iron complexes **1–3** (Figure 1) were evaluated for their activity in the semi-hydrogenation of terminal alkynes. We used phenylacetylene as model substrate and methyldiethoxysilane as hydrogen source. Excellent conversions were achieved for all catalysts after 24 h with a 7 mol% catalyst loading when the reaction was performed in 1,2-dichloroethane at 60 °C. Triazolylidene complexes **1a,b** containing diaryl wingtip groups performed almost identically (entries 1,2 Table 1), reaching appreciable conversions of 62% and 63% respectively after 4 h. While catalyst **1c** showed higher activity after 4 h (74%



1a (R = Mes)
1b (R = Ph)
1c (R = *n*-Bu)

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[a] *Department of Chemistry & Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland. Phone: +41 316314644; email: martin.albrecht@dcb.unibe.ch.*

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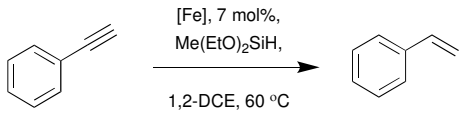
Figure 1 Triazolylidene and imidazolylidene iron(II) piano-stool semi-hydrogenation precatalysts.

Table 1 Catalytic semi-hydrogenation of phenylacetylene using catalysts **1**-**3**.[a]



entry	catalyst	conversion /%[b]		
		2 h	4 h	24 h
1	**1a**	42	62	100
2	**1b**	41	63	100
3	**1c**	38	74	93
4	**2**	27	36	84
5	**3**	27	64	100

[a] General conditions: Phenylacetylene (0.2 mmol), methyldiethoxysilane (0.4 mmol), [Fe] (14 µmol), C_6Me_6 (20 µmol; NMR internal standard) or hexadecane (0.2 mmol; GC standard), 1,2-dichloroethane (DCE, 1.25 mL), 60 °C. [b] Conversion determined spectroscopically by ^{1}H NMR or GC analysis.

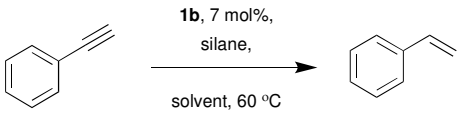
conversion, entry 3), full conversion was not achieved after 24h and the reaction stopped conversion, entry 3), full conversion was not achieved after 24 h and the reaction stopped at 93% completion. This reactivity suggests that the decreased steric demand of the n-butyl substituents is beneficial for the initial turnover rate, but results in a less robust catalyst that gradually decomposes before all substrate has been consumed. Introducing a chelating pyridine moiety (complex **2**) decreased the catalytic activity significantly, reaching only 36% conversion after 4 h (entry 4). The low activity is presumably due to the necessity for the pyridine to dissociate in order to allow for substrate binding. The imidazolylidene complex **3** (entry 5) displayed slower conversion after 2 h compared to the monodentate triazolylidene complexes, however, the performance is similar to that of **1a,b** at later stages of the reaction. All complexes **1–3** produced styrene as the only detectable product by ^{1}H NMR spectroscopy.[‡]

Overall, the activities within the mondentate series of catalysts vary only subtly. We observed previously[14] that the electronic properties (Tolman electronic parameters and oxidation potentials) of the monodentate triazolylidene and imidazolylidene complexes are very similar (ν(CO) = 1936±3 cm^{-1}; $E_{1/2}$ = 0.38±0.04 V), which provides a rationale for the essentially identical activity of complexes **1** and **3**.

In an effort to identify the oxidizing equivalent in this reduction reaction, crude reaction products were analysed by ^{29}Si NMR spectroscopy. A strong signal at −49.8 ppm was observed, consistent with the formation of $[Me(EtO)_2Si]_2O$ during the catalytic reaction.[17]

Further optimisation of the semi-hydrogenation and a preliminary substrate scope was performed with complex **1b** because the synthesis of this complex is easy and cost-effective. The catalytic reaction was monitored in a range of different solvents (see Table 2). Reactions carried out in THF (entry 1) and 1,2-dichloroethane (DCE, entry 4) resulted in very similar activities, with DCE slightly outperforming THF (95% vs. 89% conversion after 8 h). Other chlorinated solvents were less suitable and reactions proceeded slower in 1,2-dichlorobenzene (DCB, 66% conversion after 8 h, entry 2), while $CHCl_3$ severely inhibited the reaction (entry 3). In the latter case,

Table 2 Optimisation of phenylacetylene semi-hydrogenation catalysed by **1b**.[a]



entry	silane	solvent	conversion /%[b]		
			2 h	8 h	24 h
1[c]	$Me(EtO)_2SiH$	THF	33	89	100
2	$Me(EtO)_2SiH$	1,2-DCB	23	66	100
3	$Me(EtO)_2SiH$	$CHCl_3$	22	23	23
4	$Me(EtO)_2SiH$	1,2-DCE	41	95	100
5	PMHS	1,2-DCE	16	28	43
6	Et_3SiH	1,2-DCE	0	3	3
7	$PhSiH_3$	1,2-DCE	34	64	100

[a] General conditions: Phenylacetylene (0.2 mmol), hydrosilane (0.4 mmol), [Fe] (14 µmol), C_6Me_6 (20 µmol; NMR internal standard) or hexadecane (0.2 mmol; GC standard), solvent (1.25 mL), 60 °C; DCE = dichloroethane, DCB = dichlorobenzene. [b] Conversion and yield determined spectroscopically by ^{1}H NMR analysis. [c] Determined also by GC.

conversion reached only 23%, even after 24 h. The same conversion was already recorded after 2 h and was identical to reactions in DCB, suggesting that $CHCl_3$ is deactivating the catalyst at early stages, presumably due to the acidic character of chloroform, whereas DCB is not acidic and catalysis proceeds beyond the initial 2 h. Irrespective of the solvent, product selectivity towards styrene is exquisite and no over-reduction was observed in any of these catalytic runs.

Various silanes were evaluated (see Table 2) in order to further optimise catalytic activity and also to investigate the influence of the silane on the product selectivity. Methyldiethoxysilane afforded the highest activity (entry 4), while other monohydridosilanes gave significantly poorer conversion. For example, cheap and easy to handle polymethylhydrosiloxane (PMHS) decreased the activity by about a factor of three (entry 5), while Et_3SiH was essentially inactive (entry 6). The usually more active trihydrosilane $PhSiH_3$ is also a suitable hydrogen source for the semi-hydrogenation, though the activity is significantly lower when compared to methyldiethoxysilane (64% vs. 95% conversion after 8 h, entry 7). Since the choice of silane has a profound effect on the rate of substrate conversion, it is likely that the silane is involved in either a critical pre-equilibrium or in the rate-limiting step. We note that the type of silane did not have any effect on the product distribution. There was no evidence of alkyne hydrosilylation or carbon-silicon bond formation, and styrene was the only detectable product in the ^{1}H NMR spectrum.

A range of 4-substituted ethynylbenzenes were hydrogenated with **1b** as catalyst under the optimised reaction conditions. Both electron donating OMe, and Me groups and

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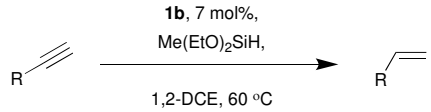
electron withdrawing substituents (Br, CF_3, CN) are compatible with the semi-hydrogenation protocol (Table 3), and neither dehalogenation nor nitrile reduction was observed. The electronic influence of the para-substituent does not have a profound effect on the reaction rate of alkyne reduction, (initial turnover frequency about 4 h^{-1}). After 8 h, the MeO-substituted ethynylbenzene (entry 3) reaches slightly lower conversion

Table 3 Semi-hydrogenation of terminal alkynes catalysed by **1b**.[a]



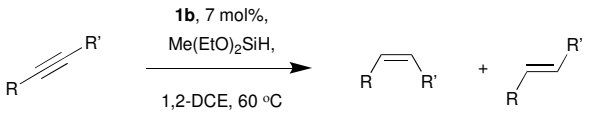
entry	R	conversion /%[b]		
		2 h	8 h	24 h
1	Ph	41	95	100
2	4-BrPh	39	91	100
3	4-MeOPh	39	83	93
4	4-CH_3Ph	42	94	99
5	4-CF_3Ph	39	98	100
6	4-NCPh	38	91	100[c]
7	*n*-Hex	25	57	76

[a] General conditions: Alkyne (0.2 mmol), methyldiethoxysilane (0.4 mmol), complex **1b** (14 µmol), C_6Me_6 (20 µmol; NMR internal standard) or hexadecane (0.2 mmol; GC standard), 1,2-DCE (1.25 mL), 60 °C. [b] Conversion determined spectroscopically by ^{1}H NMR or GC analysis. [c] Over-reduction to 4-ethylbenzonitrile after 24 h observed (28%).

(83%) than phenylacetylenes with other substituents (91–98%), and does not reach full conversion after 24 h. Slight deactivation has tentatively been attributed to ether coordination to the iron centre (*cf* lower conversion after 8 h in THF *vs* DCE). Again, the semi-hydrogenated functionalised styrene was the only detectable product for all phenylacetylene derivatives screened here. An exception is 4-ethynylbenzonitrile, which is partially over-reduced to 4-cyanoethylbenzene after prolonged reaction times.[6e,10c,18] After 24 h, the alkene/alkane distribution of products was about 3:1. If the catalytic reaction was stopped at 8 h (91% conversion), no alkane compound is present and 4-cyanostyrene was the exclusive product. Over-reduction may be promoted by the largely positive Hammett parameter of the 4-CN substituent (σ_p = +0.66),[19] which induces a higher polarisation of the vinyl moiety. The enhanced propensity for further reduction of the cyano-styrene product therefore points to a nucleophilic hydride attack as the initial step of hydrogenation. In comparison to phenylacetylenes, 1-octyne was reacted much slower and after 8 h, conversion was only 57% (Table 3, entry 7) and imcomplete even 24 h In addition, the aliphatic substrate was not converted selectivity to 1-octene. While the terminal olefin was the major product detected by GC analysis, a considerable number of unidentified side-products appeared at higher retention times. However, there was no evidence of over-reduction to octane.

The optimised conditions determined for terminal alkynes were applied for the catalytic semi-hydrogenation of internal alkynes using catalyst **1b** (Table 4). In general, the conversion of internal alkynes was notably slower than that of phenylacetylene. Diphenylacetylene was converted the fastest, reaching 88% conversion after 24 h (entry 1). Substituting one aromatic moiety for an *n*-butyl group resulted in comparable initial activity (14% vs. 19% after 2 h), but after longer reaction times the alkyl-substituted substrate was converted considerably less and reached only 63% after 24 h (entry 2). A similar reaction profile was noted when the substrate contained a trimethylsilyl rather than an n-butyl group (entry 3).

Table 4 Semi-hydrogenation of internal alkynes catalysed by **1b**.[a]



entry	R	R'	conversion /%[b]			
			2h	8h	24h	*Z*/*E* ratio
1	Ph	Ph	19	75	88	96:4
2	Ph	*n*-Bu	14	31	63	>99:1
3	Ph	$SiMe_3$	17	51	61	95:5
4	*n*-Bu	Me	21	38	65	n.d.
5	*n*-Bu	*n*-Bu	13	35	41	n.d.
6	CH_2OH	*n*-Pr	87	97	100	98:2[c]
7	$(CH_2)_2OH$	Et	77	89	89	>99:1[c,d]
8	CH_2OBn	*n*-Pr	26	59(88:12)	89	79:21
9	CH_2NHBn	Et	14	20	21[e]	n.d.
10	CH_2Br	Et	-	19	25[e]	n.d.

[a] General conditions: Alkyne (0.2 mmol), methyldiethoxysilane (0.4 mmol), complex **1b** (14 µmol), C_6Me_6 (20 µmol; NMR internal standard) or hexadecane (0.2 mmol; GC standard), 1,2-DCE (1.25 mL), 60 °C. [b] Conversion and *Z*/*E* ratio determined spectroscopically by GC (entries 1,5) or ^{1}H NMR spectroscopy (all other entries). [c] Product distribution determined after addition of Me_4NF. [e] Substantial amounts of side products formed.

Interestingly, the $-SiMe_3$ group is preserved during the reduction, a result that disfavours a mechanistic pathway involving first alkyne hydrosilylation and subsequent desilylation,. Likewise, the catalytic activity of **1b** towards dialkylated acetylenes is lower than phenylacetylene semi-hydrogenation. For example, 2-heptyne is reacting at similar rates to 1-phenyl-1-hexyne (entry 4) reaching 65% conversions after 24 h, while 5-decyne, was converted only to 41% after 24 h (entry 5). However, the catalytic activity during the first 8 h was essentially identical to that measured for phenyl-hexyne (*cf*. entry 2), suggesting some catalyst deactivation by the 5-decene product.

Catalytic semi-hydrogenation is accelerated by hydroxyl-functionalized substrates. For example, 2-hexyn-1-ol is semi-hydrogenated in 87% within 2 h (entry 6; *cf* ca 40% conversion of phenylacetylenes in the same time span, Table 3). Similarly, the regioisomer 3-hexyn-1-ol is converted to 77% (entry 7). Presumably the hydroxyl group coordinates to the iron centre, which facilitates Si–H bond cleaveage across the Fe–O bond. In agreement with such a model, the semi-hydrogenation product of hydroxyl-containing substrates features a silylated alcohol group, which was deprotected by treatment with Me_4NF in CH_3CN. When a benzyl group was installed as a

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protecting group onto 2-hexyn-1-ol, the rate of conversion of the resulting alkyne was significantly decreased compared to the deprotected alcohol (entry 8). Amine and halide groups are not compatible with the iron catalyst and lead to poor conversions after 24 h and no detectable quantities of olefin product (entries 9,10).

Z-selectivity of the iron NHC catalyst is very high for phenyl substituted internal acetylenes with >95% cis-olefin formation (entries 1-3), and exclusive formation of the *Z*-isomer in the reduction of 1-phenyl-1-hexyne. The selectivity is lower for the benzylether-containing substrate (entry 8) with a 4:1 bias towards the cis-olefin. The initial selectivity was higher (7:1 after 4 h and at 59% conversion), suggesting a gradual drift in catalyst conformation that may be product-induced, and concomitant loss of selectivity. In contrast, the same substrate with a free hydroxyl group affords the cis-product in excellent *Z*/*E* ratio (98:2, entry 6) and the isomeric 3-hexyn-1-ol is reduced exclusively to the *cis*-alkene.[20]

In summary, we have employed 1,2,3-triazolylidene and IMes iron piano-stool complexes for the catalytic semi-hydrogenation of alkynes using silanes as reducing agents. Monodentate complexes are more active than the NHC-pyridine chelate. In contrast to catalytic hydrogenation using platinum group transitions metals, the reduction is selective to alkynes, and alkenes are typically not converted, thus preventing any over-reduction to saturated alkanes. This distinct reactivity demonstrates the complementarity of iron as a catalyst compared to precious metals. The reduction of internal alkynes revealed excellent *Z*-selectivity using this protocol, offering an attractive and cheap methodology to access this synthetically valuable functional group. Further work is on-going to reduce the catalyst loading and to efficiently convert aliphatic alkynes by enhancing the reactivity of the iron centre through appropriate ligand tuning.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Upon extended reaction times (>10 h), the spectroscopic yields tend to decrease slowly, which has been attributed to the inherent instability of the styrene products towards polymerization in the absence of a stabilizer (see also ESI, Table S1).

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20 Due to overlap in the ^{1}H NMR spectrum, cis/trans ratios could not be unambiguously determined for 2-heptyne and 5-decyne semi-hydrogenation.

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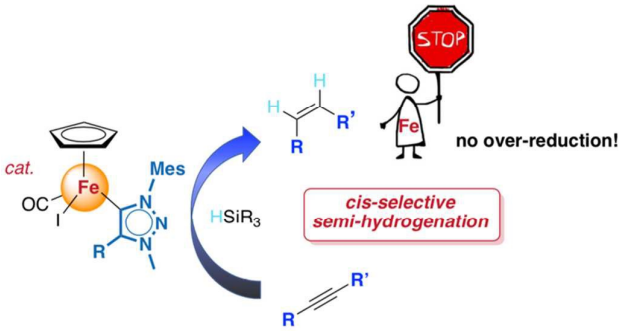

Piano-stool NHC iron complexes catalyze the selective semi-hydrogenation of alkynes without any over-reduction and with high selectivity towards *Z*-alkynes when starting from disubstituted alkynes.