Iron Catalysis

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Iron Pincer Complex Catalyzed, Environmentally Benign, *E*-Selective Semi-Hydrogenation of Alkynes**

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Alkynes are useful building blocks in organic synthesis that allow for a plethora of transformations. Among them, the transition-metal catalyzed semi-hydrogenation of alkynes to alkenes is a very important reaction in organic chemistry.[1] It has been extensively used for the synthesis of biologically important molecules, such as natural products, pharmaceuticals, and fragrances, because many of these molecules have carbon–carbon double bonds with defined *Z* or *E* configurations.[2] Among the various catalytic (heterogeneous or homogenous) and non-catalytic methods[1,3], hydrogenation by using the Lindlar catalyst[4] is probably the most facile procedure for obtaining *Z*-alkenes. The *Z* selectivity arises from the addition of the two hydrogen atoms of H_2 suprafacially to the π system of the alkyne by a sequence of hydrometalation/reductive elimination steps. However, the analogous transformation of the alkyne functionality to the *E*-alkene remains a major challenge, particularly in late-stage synthesis. In fact, all commonly practiced methods for the direct conversion of alkynes into *E*-alkenes are stoichiometric in nature. The Birch-type reduction of alkynes by alkali metals (Li, Na) in liquid ammonia is the traditional and powerful method for the synthesis of *E*-alkenes,[5] but major limitations are the low functional-group tolerance as a result of the harsh reaction conditions, and the stoichiometric amounts of waste generated. Although the use of over-stoichiometric amounts of chromium reagents resulted in some improvement in the scope of the *E*-selective hydrogenation reaction,[6] the use of non-catalytic, toxic reagents, and the generation of copious toxic waste are major problems. In 1999, iridium-catalyzed selective hydrogenation of alkynes to *E*-alkenes using methanol as the hydrogen donor was described by Tani and co-workers.[7a] In 2002, Trost et al. reported an effective two-step method for the synthesis of *E*-alkenes, in which the alkyne is first subjected to a ruthenium-catalyzed *trans*-hydrosilylation[7b] followed by proto-desilylation of the resulting alkenylsilanes with stoichiometric amounts of a fluoride source. In 2005, Shirakawa et al. demonstrated reduction of alkynes with hexamethyldisilane and deuterium oxide to *E*-1,2-dideuterioalkenes.[7c] Cheng and co-workers[7d] described an efficient palladium-catalyzed reduction of alkynes by using $HSiEt_3$ and H_2O as the hydrogen donors, with *E*-selectivity resulting from isomerization of the nascent *Z*-alkene to the more stable *E*-alkene by using a catalytic amount of $CuSO_4$. Yin, Han et al.[7e] reported that in their palladium-catalyzed hydrogen-transfer reaction, changing the hydrogen donor from formic acid to 25% aqueous formic acid also led to the isomerization of *Z*- to *E*-alkenes. Bargon and co-workers reported an NMR study on ruthenium-catalyzed *E*-selective semi-hydrogenation that excluded the possibility of *Z*–*E* isomerism and confirmed direct *E*-hydrogenation, thus suggesting a bridged alkyne–dihydrogen dinuclear ruthenium complex.[7f] Very recently, Fürstner and co-workers disclosed a catalytic method for alkyne semi-hydrogenation using a mixture of [Cp*Ru(cod)Cl] (5.5 mol%) and AgOTf (5 mol%) with H_2 (10 bar) at ambient temperature, and this method produced excellent *E*-selectivity.[7g]

The replacement of expensive noble-metal catalysts by inexpensive and environmentally benign metals is a desirable goal in chemistry. Iron complexes in particular would provide an excellent alternative owing to the high natural abundance and low toxicity of iron.[8] Recently, we[9] and several other groups[10] have focused on developing homogeneous iron catalysts as precious-metal surrogates. We recently reported a highly efficient hydrogenation of ketones catalyzed by an iron pincer complex in the presence of catalytic amounts of base.[9a,c] A new mode of cooperation between the metal center and the pincer ligand, which has also been observed for the corresponding ruthenium complexes,[11] was suggested. In the context of the iron-catalyzed reduction of alkynes to alkenes, Plietker and Belger[12] presented a hydrosilylation–desilylation strategy involving the use of a [FeH(CO)(NO)-$(Ph_3P)_2$] catalyst to give alkenes with good stereo-selectivity, and Beller and co-workers[13] reported a method for the iron-catalyzed transfer hydrogenation of terminal alkynes to the corresponding alkenes using formic acid as a hydrogen donor. Of particular interest is the atom-economical semi-hydrogenation of alkynes with H_2 gas. Chirik and co-workers[14] reported the hydrogenation of diphenylacetylene catalyzed by a bis(imino)pyridine iron dinitrogen complex in a reaction that initially resulted in the selective formation of *Z*-stilbene followed by complete conversion into bibenzyl. An *E*-selective catalytic semi-hydrogenation of internal alkynes with an iron-catalyst is highly desirable, especially when compatible with a diverse range of functional groups. Herein, we present such a reaction, catalyzed by a novel acridine-based PNP iron complex.

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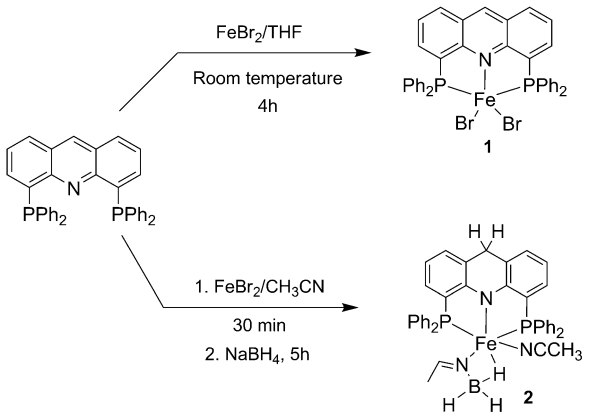
We prepared the new iron pincer complexes [(^{ACR}PNP)FeBr$_2$] (**1**) and [(^{HACR}PNP)Fe(CH$_3$CN)(η^2-CH$_3$CHCNBH$_3$)] (**2**) (^{ACR}PNP = 4,5-bis(diphenylphosphino)-acridine, ^{HACR}PNP = 4,5-bis(diphenylphosphino)-9H-acridine-10-ide). Reaction of 4,5-bis(diphenylphosphino)acridine[15] with FeBr$_2$ in THF gave the paramagnetic complex **1** (Scheme 1). The crystal structure of **1** reveals a distorted square-pyramidal Fe^{II} center formed by the pincer ligand and the two bromide ligands. The Fe1 center deviates from the P1, N1, P2 plane by 0.31 Å. (for the crystal structure see the Supporting Information). Interestingly, reaction of the 4,5-bis(diphenylphosphino)acridine ligand with FeBr$_2$ in an acetonitrile solution containing 2 equivalents of sodium borohydride gave the novel imino borohydride complex **2** (characterized by single-crystal X-ray diffraction; Figure 1). This reaction represents insertion of the nitrile CN group into an Fe–H bond and hydride attack at the electrophilic 9 position of acridine. Insertion of a nitrile into a low coordinate iron hydride complex was reported by Holland et al.[16] In the X-ray structure of complex **2,** the iron occupies the center of a distorted octahedron in which the nitrile and the imine nitrogen occupy the axial sites. One of the hydride ligands (H1C) bridges between iron and boron, resulting in the corresponding B–H bond being considerably longer (1.27 Å) than the other two B–H bonds (1.07 Å and 1.09 Å). Comparable bridging B–H bond lengths (1.25 Å and 1.28 Å) were reported for the complex [(*i*Pr-PNP)Fe(H)(η^2-BH$_4$)].[7c] The Fe1–B1 bond length (2.278 Å) in complex **2** is shorter than in the previously described iron hydrido borohydride complexes [(dmpe)$_2$FeH(η^1-BH$_4$)] (2.84 Å, dmpe = 1,2-bis(dimethylphosphino)ethane),[17] and [(*i*Pr-PNP)Fe(H)(CO)(η^1-BH$_4$)] (2.67 Å),[7c] but it is longer than in the complex [(*i*Pr-PNP)Fe(H)(η^2-BH$_4$)] (2.095 Å).[7c] The B1–N3 bond length (1.514 Å) is considerably shorter than the one calculated for CH$_3$CN–BH$_3$ (1.584 Å).[18] Furthermore, the C–N bond of the imine ligand (1.258 Å) is much longer than the C–N bond of CH$_3$CN–BH$_3$ (1.159 Å), a result that is in agreement with the double bond character of the coordinated C=N.[16] The bond angle N3-C40-C41 122.5(3)° is also in line with the double-bond character of the N3–C40 bond.

Complexes **1** and **2** were investigated as catalysts for the hydrogenation of alkynes. In preliminary experiments, hydrogenation of diphenylacetylene was attempted using 0.6 mol%



Scheme 1. Synthesis of acridine-based PNP iron complexes.

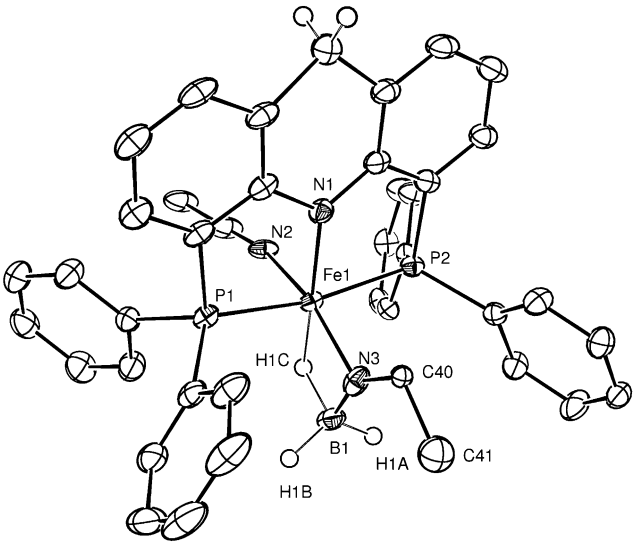
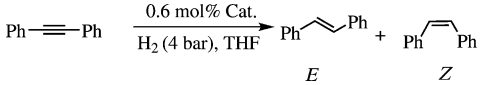


Figure 1. Molecular structure of complex **2** with thermal ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: Fe1–N3 1.9023(19), Fe1–N2 1.945(16), Fe1–N1 2.0167(19), Fe1–P2 2.2202(7), Fe1–P1 2.2224(8), Fe1–B1 2.278(3), Fe1–H1C 1.61(2), B1–N3 1.514(4), B1–H1C 1.27(2), B1–H1A 1.07(3), B1–H1B 1.09(3), N3–C40 1.258(3); N3-Fe1-N2 160.2(5), N3-Fe1-N1 108.48(8), N2-Fe1-N1 91.3(5), N3-Fe1-P2 92.59(7), N2-Fe1-P2 88.7(6), N1-Fe1-P2 84.32(6), N3-Fe1-P1 92.54(6), N2-Fe1-P1 90.0(6), N1-Fe1-P1 84.09(6), P2-Fe1-P1 168.31(3), N3-Fe1-B1 41.26(9), N3-Fe1-H1C 74.1(8), N3-C40-C41 122.5(3).

of complex **1** in THF solvent under 4 bar H$_2$ pressure at 90 °C. Disappointingly, no hydrogenation had taken place after 30 h and the starting material was recovered unchanged. (Table 1, entry 1). Adding 2 equiv KO*t*Bu (with respect to catalyst **1**) under similar conditions did not help (Table 1, entry 2). Next we studied the catalytic activity of complex **2**. To our delight, after 12 h under 4 bar H$_2$ at 90 °C in THF in the presence of 0.6 mol% catalyst **2**, diphenylacetylene was consumed completely to give 99% *E*-stilbene (Table 1, entry 3, corresponding to a turnover frequency (TOF) of 14 h^{-1}). Formation of *Z*-stilbene was not detected by GC or GC–MS. Filtration and evaporation of the solvent gave *E*-stilbene in 96% yield, as confirmed by NMR spectroscopy.

Table 1: Iron pincer complex catalyzed hydrogenation of diphenylacetylene.[a]



E *Z*

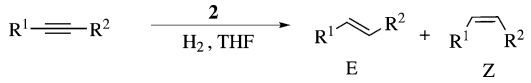
Entry	Solvent	Cat.	*t* [h]	*T* [°C]	Stilbene [%][b]	*E*:*Z*[b]
1	THF	**1**	30	90	–	–
2	THF	**1**[c]	15	90	–	–
3	THF	**2**	12	90	99	100:0
4	THF	**2**	17	50	61	66:34
5	THF	**2**	65	25[d]	29	45:55
6	EtOH	**2**	12	90	17	70:30
7	MeOH	**2**	12	90	19	37:63
8	Toluene	**2**	12	90	90	99:1

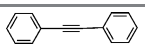
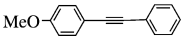
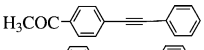
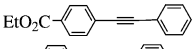
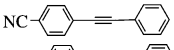
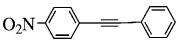
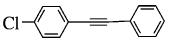
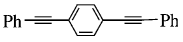
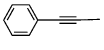
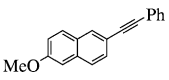
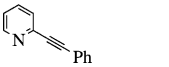
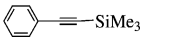
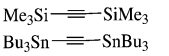
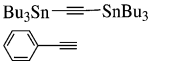
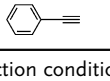
[a] Reaction conditions: Complex (0.006 mmol), diphenylacetylene (1 mmol), THF (1.5 mL), H$_2$ (4.0 bar), 90 °C. [b] Conversion was determined by GC analysis and distribution was determined by GC and NMR spectroscopy. [c] KO*t*Bu (0.012 mmol) was added. [d] 10 bar H$_2$ pressure.

When the reaction was performed at 50 °C for 17 h under the same hydrogen pressure, 61 % conversion of diphenylacetylene was observed, with a 40 % yield of *E*-stilbene and a 21 % yield of *Z*-stilbene (Table 1, entry 4). Performing the reaction at room temperature under 10 bar pressure resulted in only 29 % conversion to stilbene after 65 h with 45:55 *E*/*Z* ratio (Table 1, entry 5). These results prompted us to examine the origin of the *E*-selectivity. When *Z*-stilbene was stirred at 90 °C with 0.6 mol % catalyst **2** in the absence of H_2, it isomerized to *E*-stilbene. In situ fast isomerization of the alkene during the hydrogenation of the alkyne thus plays an important role in the *E*-selectivity. Various solvents were tested. Using EtOH or MeOH resulted in very poor activity; only 17 % and 19 % conversion to stilbene, respectively, were observed under 4 bar H_2 in THF at 90 °C in the presence of 0.6 mol % complex **2** (Table 1, entries 6 and 7). Using toluene as the solvent resulted in the formation of *E*-stilbene in 90 % yield, together with 1,2-diphenylethane in 10 % yield (Table 1, entry 8).

After initial optimization of the hydrogenation reactions, we investigated the substrate scope of this reaction. The hydrogenation of 1-methoxy-4-(phenylethynyl)benzene gave 99 % conversion (by GC) to the corresponding *E*-alkene after 36 h using 0.6 mol % complex **2** and 4 bar H_2 at 90 °C (Table 2, entry 2). Filtration and solvent evaporation gave pure *E*-1-methoxy-4-styrylbenzene in 97 % yield. To investigate the scope of this reaction with regard to other functional groups, 1-(4-(phenylethynyl)phenyl)ethanone was used as the substrate, and the result was complete conversion into an *E*/*Z* (64:36) mixture of 1-(4-styrylphenyl)ethanone (Table 2, entry 3). Notably, the hydrogenation is completely chemoselective towards the alkyne; the keto- group remained intact. Similarly, an ester functionality also remained intact; ethyl-4-(phenylethynyl)benzozte gave 89 % ethyl 4-styrylbenzoate (*E*:*Z* 99:1) and 11 % ethyl-4-phenethyl benzoate after 22 h stirring with 2.2 mol % cat **2** under 4 bar H_2 at 90 °C (Table 2, entry 4). When 4-(phenylethynyl)benzonitrile was stirred with 2.2 mol % complex **2** in 1 mL THF under 4 bar H_2 at 90 °C for 72 h, no catalytic reaction took place. However, upon increasing the hydrogen pressure to 10 bar and the catalyst loading to 4 mol %, hydrogenation took place, yielding 94 % of 4-styrylbenzonitrile with high selectivity (*E*/*Z* 99:1); significantly, the nitrile group remained intact (Table 2, entry 5). Unfortunately, 1-nitro-4-phenylethynyl)benzene failed to give any hydrogenation product even under 10 bar H_2 (Table 2, entry 6). Interestingly, no hydrogenolysis of the C–Cl bond took place during the hydrogenation of 1-chloro-(4-phenylethynyl)benzene. After 23 h at 10 bar H_2 in presence of 2.2 mol % cat **2**, 1-chloro-4-styrylbenzene was obtained in 87 % yield with excellent *E*/*Z* (99:1) selectivity. The product of alkene hydrogenation, 1-chloro-4-phenethylbenzene was observed in 13 % yield (Table 2, entry 7). Apparently, diarylacetylenes bearing electron-withdrawing substituents such as $COCH_3$, CO_2Et, or CN groups require higher catalyst loading and longer reaction times, or high pressure to reach full conversion to the alkene. This might be due to the lower tendency of the less donating alkyne to coordinate to the catalyst. The importance of the coordination ability of the alkyne is supported by the observed slow progress of the reaction of 1-methyl-2-(phenylethynyl)benzene; in this case, the *ortho* methyl groups sterically hamper coordination to the catalyst (Table 2, entry 8). Similarly, 1,4-bis(phenylethynyl)benzene gave a 90:10 mixture of 1,4-di((*E*)-styryl)benzene and 1-((*E*)-styryl)-4-((*Z*)-styryl)benzene under 10 bar H_2 (Table 2, entry 9). Notably, unlike in the reported palladium-catalyzed reduction of alkynes with formic acid,[7e] trimethylsilyl groups survive under the mild pH neutral conditions described herein. Phenyltrimethylsilyl acetylene thus gave 76 % *E*-trimethyl(styryl)silane and 24 % trimethyl(phenethyl)silane after 17 h with 1.7 mol % complex **2** under 4 bar H_2 (Table 2, entry 13). Similarly, bis(trimethyl-

Table 2: Iron pincer complex catalyzed hydrogenation of alkynes.[a]



Entry	Alkyne	Cat [mol %]	*t* [h]	Pressure [bar]	Stilbene [%][b]	*E*:*Z*[b]
1		0.6	12	4	99	100:0
2		0.6	36	4	99	99:1
3		2	65	4	99	64:36
4		2.2	22	4	89 (11)[c]	99:1
5		4	72	10	94	99:1
6		2	48	10	NR[d]	–
7		2.2	23	10	87 (13)	99:1
8		2.5	70	10	99	99:1
9		2.2	70	10	90	90:10
10		2	27	10	94 (6)	95:5
11		4	21	4	98 (2)	100:0
12		2	48	4	70 (30)	61:39
13		1.7	17	4	76(24)	99:1
14		1	30	4	85	100:0
15		2	40	4	Complicated mixture	–
16		0.6	11	4	99	–

[a] Reaction conditions: Complex **2**, alkyne (0.5 mmol), THF (1 mL), H_2, 90 °C. [b] Conversion was determined by GC analysis and selectivity was determined by GC and NMR spectroscopy. [c] Yield in parenthesis is the yield of the corresponding alkane. [d] No reaction.

silyl)acetylene gave 85% conversion to *E*-1,2-bis(trimethylsilyl)ethylene (Table 2, entry 14). Under similar reaction conditions, bis(tributylstannyl)acetylene gave a complicated mixture. We also explored the catalytic behavior of complex **2** with a terminal alkyne under similar reaction conditions. Hydrogenation of phenylacetylene using 0.6 mol% complex **2** under 4 bar H_2 gave quantitative conversion into styrene after 11 h (Table 2, entry 16).

In conclusion, iron-catalyzed semi-hydrogenation of alkynes to *E*-alkenes using H_2 has been achieved. The reaction is catalyzed by a novel acridine-based PNP iron complex, [(^{HACR}PNP)Fe(CH_3CN)(η^2-$CH_3CHCNBH_3$)] (**2**), under mild conditions with no added base.[19] Carbonyl, nitrile, and chloro substituents remain intact. The high *E*-selectivity is due to isomerization of the resultant *Z* alkene to the corresponding *E*-alkene. The mechanistic aspects of catalysis by the novel iron pincer complex, and in particular the role of the amidoborane ligand in the process, are currently under investigation.

Experimental Section

A 100 mL Fischer-Porter tube was charged under nitrogen with catalyst **2** (0.003 mmol, 0.6 mol%), alkyne (0.5 mmol), and THF (1 mL). The nitrogen present in the Fischer Porter tube was replaced by H_2 (twice with 3 bar) at room temperature, then it was filled with H_2 (4 bar). The solution was heated at 90°C (bath temperature) with stirring for the specified time. After cooling to room temperature, the H_2 was vented carefully and analysed by GC or GC–MS. The solution was also filtered through syringe filter and after evaporation of the solvent, the crude mixture was analysed by NMR spectroscopy.

CCDC 953370(1) and 953371(2) 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

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