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Efficient and Selective Synthesis of *E*-Vinylamines *via* Tungsten(0)-Catalyzed Hydroamination of Terminal Alkynes

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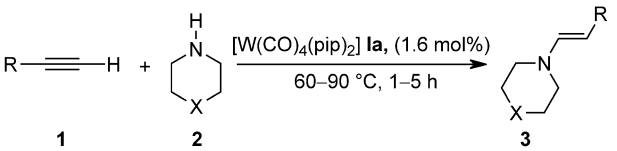
Abstract: The hydroamination of terminal alkynes (RC≡CH = phenylacetylene, 4-methylphenylacetylene, 4-fluorophenylacetylene, 1-hexyne, methyl 2-propynyl ether, prop-2-yn-1-ol) with secondary amines (piperidine, pyrrolidine, morpholine, piperazine, methylpiperazine, 4-methylpiperidine and 3-methylpiperidine) was achieved in high yield (up to 99%), regioselectivity (only *anti*-Markovnikov product) and stereoselectivity (only *E*-isomers) within a maximum of 5 h in reactions catalyzed by the tungsten tetracarbonyl complex *cis*-$[W(CO)_4(piperidine)_2]$ at 90 °C without any additional solvent.

Keywords: *E*-enamines; hydroamination reaction; secondary amines; terminal alkynes; tungsten catalyst

Alkynes are widely available reagents and the catalytic addition of the N–H bond of amines to the triple bond of alkynes, RC≡CH, is of great significance in the synthesis of enamines and the other nitrogen-containing compounds.[1] This atom-economical process is mostly catalyzed by complexes based on such metals as Rh, Ru, Pd, Au, Ag, lanthanides or actinides.[1d,f,2] The development of a catalyst for this synthetic process that will be efficient, regio- and stereoselective, but cheaper and easier available compared with noble metal catalysts, has attracted significant interest. Tungsten(0) and molybdenum(0) carbonyl complexes are very well-known catalysts for nucleophilic addition of O–H bond of alcohols to a triple bond of alkynes and the cyclization of alkynols.[1d,3] To date, however, no group 6 complexes have been reported as catalysts for the hydroamination of alkynes.

Here, we report on the application of a very well-known, easily available, simple and relatively cheap complex of tungsten(0), *cis*-$[W(CO)_4(pip)_2]$ **Ia** (pip = piperidine),[4] as an efficient regio- and stereo-selective catalyst in the synthesis of *E*-vinylamines under relatively mild conditions. Synthesis of the complex **Ia** can be achieved *via* photochemical or thermal substitution of two carbonyl groups by piperidine in the commercially available $W(CO)_6$.[4] The reactions of terminal alkynes **1** (phenylacetylene **1a**, 4-methylphenylacetylene **1b**, 4-fluorophenylacetylene **1c**, 1-hexyne **1d**, methyl-2-propynyl ether **1e**, prop-2-yn-1-ol **1f**, but-3-yn-2-ol **1g**, but-3-yn-1-ol **1h** or 2-methyl-but-3-yn-2-ol **1i**) with secondary amines **2** (piperidine **2a**, pyrrolidine **2b**, morpholine **2c**, methylpiperazine **2d**, piperazine **2e**, 4-methylpiperidine **2f** and 3-methylpiperidine **2g**) conducted in the presence of complex **Ia** (1.6 mol%), in the absence of a solvent and in the temperature range 60–90 °C, were completed in a maximum of 5 h and gave up to 99% yield of *E*-vinylamines **3** (Scheme 1). The hydroamination products **3** were extracted into *n*-hexane, from which clean *trans*-vinylamines were isolated after evaporation of the solvent and any remaining non-reacted substrates under vacuum, and characterized using ^1H and ^{13}C NMR spectroscopy and GC-MS analysis.

In our initial studies, the reaction of phenylacetylene **1a** with piperidine **2a**, was chosen as a model to optimize the hydroamination reaction conditions. The optimization included the selection of the most suitable solvent, amount of the catalyst, reaction time and reaction temperature (Table 1).

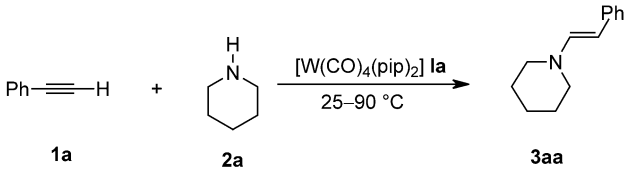


1 2 3

R = Ph **1a**, C_6H_4-4-Me **1b**, C_6H_4-4-F **1c**, *n*-C_4H_9 **1d**, CH_2OMe **1e**, CH_2OH **1f**, CH(OH)Me **1g**, CH_2CH_2OH **1h**, $C(OH)Me_2$ **1i**
X = CH_2 **2a**, - **2b**, O **2c**, NMe **2d**, NH **2e**, CHMe **2f**, CH_2-3-Me **2g**

Scheme 1. Hydroamination of terminal alkynes **1**, by secondary amines **2**, catalyzed by **Ia**.

Table 1. Optimization of the reaction conditions for the addition of phenylacetylene **1a** to piperidine **2a**, and the formation of 1-[(*E*)-(2-phenylethenyl)piperidine] **3aa**.[a]



Entry	Catalyst **Ia** [mol%]	Temperature [°C]	Time [h]	Conversion[b] [%]	Yield[c] [%]
1	1.6[d]	r.t.	24	19	~1
2	1.6[e]	r.t.	24	14	~0.1
3	1.6	r.t.	24	16	1.5
4	1.6	90	1	58	–[f]
5	1.6	90	2	66	–[f]
6	1.6	90	5	90	84
7	1.0	90	5	83	80
8	1.0	90	24	93	67
9	0.5	90	5	81	77
10	0.5	90	24	84	76

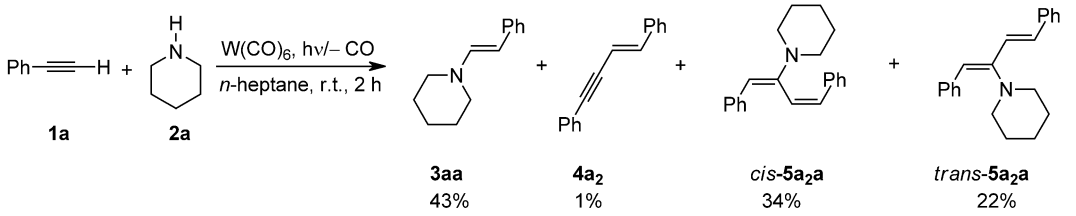
[a] *Reaction conditions*: Catalyst **Ia**, **1a** (0.33 g, 3.3 mmol), and **2a** (0.27 g, 3.3 mmol) under N_2.
[b] Conversion was determined by NMR on the basis of the consumption of phenylacetylene.
[c] NMR yield of **3aa** was based on the ^{1}H NMR analysis of the crude reaction mixture.
[d] In 30 mL of tetrahydrofuran.
[e] In 30 mL of diethyl ether.
[f] Not calculated.

The addition of the N–H bond of piperidine **2a**, across the triple bond of phenylacetylene **1a**, catalyzed by complex **Ia** was first observed in solution of diethyl ether and tetrahydrofuran at room temperature (r.t.). However, only a small amount of the enamine product was detected after 24 h reaction time; Table 1, entries 1 and 2. The reason was a very low solubility of complex **Ia** in the solvents. Dichloromethane is a better solvent for complex **Ia**; however, as has been recently observed, it reacts very easily with **2a** to give dipiperidylmethane.[5] Very good solubility of complex **Ia** was achieved in a 1:1 mixture of an alkyne and amine in the temperature range 60–90 °C. The results in Table 1 illustrate the excellent performance of the tungsten catalyst **Ia** in this hydroamination process. The 1:30 molar ratio of the catalyst **Ia** and the alkyne **1a** was sufficient to give the desired product **3aa**, in good yield.

The decrease of the catalyst loading from 1.6 to 1.0 and 0.5 mol% lowered the conversion of alkyne from 90 to 81% (entries 6, 7 and 9). The increase of the reaction time from 5 to 24 h only slightly improved the conversion of an alkyne but had a negative effect on the yield of an enamine (entries 8 and 10).

Attempts to replace complex **Ia** by $W(CO)_6$ **Ib** as the catalyst failed. In reactions of **1a** and **2a** in the presence of **Ib** in the molar ratio 30:30:1, respectively, carried out in *n*-heptane solution at 90 °C, only traces of **3aa** were detected after 5 h, similarly as in reaction carried out under the same conditions but without any solvent. However, in the latter reaction, also styrene, a product of hydrogenation of PhC≡CH, was identified by ^{1}H NMR. After a 5 h reaction time and *ca.* 1% conversion of the alkyne, the ratio of **3aa** to styrene reached 1.6:1.

Alternatively, the photochemical reactions were conducted at room temperature in an *n*-heptane solution containing **Ib**, **1a** and **2a** in the molar ratio 1:30:30 (Scheme 2). During photolysis of the reaction mixture at least two carbonyl groups in the coordina-



Scheme 2. Reaction of phenylacetylene **1a** and piperidine **2a** in the presence of photochemically activated $W(CO)_6$ **Ib**.

tion sphere of $W(CO)_6$ **Ib** are easily substituted by molecules of substrates. In this way the substrates are activated. After 2 h of photochemical reaction, the conversion of **1a** reached 100%. However, the yield of **3aa** was not high (43%). The major side product detected by GC-MS ($M_r = 289.4$) was the three-molecules coupling product (1-[1,4-diphenylbuta-1,3-dien-2-yl]piperidine **5a$_2$a**), involving two molecules of the alkyne **1a** and one molecule of the amine **2a**. Compound **5a$_2$a** was detected by NMR spectroscopy as a mixture of *cis* (34%) and *trans* (22%) isomers.

The dimerization of the alkyne **1a** and the formation of *trans*-enynes **4a$_2$** was also observed by GC-MS and NMR but in very low yield (*ca.* 1%).

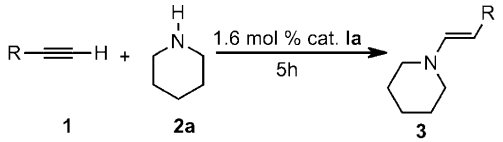
The above results show that using complex **Ia**, which contains two loosely coordinated amine ligands in the *cis* position, as catalyst has pronounced effects on the efficiency and selectivity of the hydroamination reaction.

Based on the promising catalytic activity displayed by **Ia** in the hydroamination reaction of **1a**, we next investigated the scope of this reaction with a variety of terminal alkynes (Table 2).

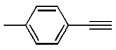
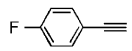
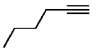
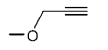
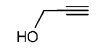
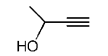
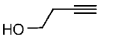
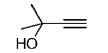
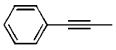
In general, we observed good conversion in 5 h when 1.6 mol% of **Ia** was used as catalyst (Table 2). Phenylacetylene is hydroaminated with high yield, 84% (entry 1); substituents on the phenyl ring of the arylacetylenes induced evident electronic effects (entries 1–3). The presence of an electron-withdrawing fluorine atom in the 4-position of arylacetylene **1c** decreased the reactivity of the alkyne and the yield of the enamine **3ca**, whereas an Me group in the 4-position of the arylacetylene **1b**, increased the yield of the enamine **3ba**. The electron-rich arylalkynes RC≡CH (R = Ph **1a**, C_6H_4-4-Me **1b**) react more smoothly than the electron-poor arylalkyne **1c**. The highest conversion was achieved for **1b** (100%) with a selectivity of 99% to the target product, *trans*-vinylamine **3ba** (Table 2, entry 2). The aliphatic alkyne 1-hexyne **1d** is also transformed to the corresponding product **3da**, but in low yield, 8% (entry 4). Under similar conditions, a methyl propargyl ether **1e** is converted to the *E*-enamine **3ea** with a much higher yield (entry 5). It is also worth noting that an alkyne with a free hydroxy group, prop-2-yn-1-ol **1f**, but-3-yn-2-ol **1g**, but-3-yn-1-ol **1h** or 2-methylbut-3-yn-2-ol **1i** reacted with piperidine **2a** to give the expected hydroamination products **3fa**, **3ga**, **3ha**, and **3ia**, but the yield of the enamine was very low (entries 6, 7, 8, and 9) compared with the yield of the three-molecules coupling product **5**, and the product formed in the nucleophilic addition of O–H bond to a C≡C triple bond of the alkyne.[6] The enamines **3fa**, **3ga**, **3ha** and **3ia** were identified by NMR spectroscopy but not isolated. It should, however, be pointed out that only terminal alkynes are reactive under these conditions. The attempted **Ia**-catalyzed addition of piperidine to internal alkyne 1-phenyl-1-propyne **1j** failed (Table 2, entry 10). Apparently, the catalytic activity of **Ia** is strongly affected by the presence of an alkyne C–H bond.

We later found that also other secondary amines, pyrrolidine **2b**, morpholine **2c**, methylpiperazine **2d**, piperazine **2e**, 4-methylpiperidine **2f** and 3-methylpiperidine **2g**, could be effectively reacted with phenylacetylene and the other terminal alkynes under the current reaction conditions (Table 3). Morpholine **2c**, methylpiperazine **2d** and piperazine **2e** with the electron-withdrawing oxygen or nitrogen atoms in the ring gave significantly higher yields of enamines than piperidine **2a** or pyrrolidine **2b** with electron-donating CH_2 groups (entries 3, 4 and 5). However, in the reac-

Table 2. Effect of alkynes **1** on the yield of *trans*-vinylpiperidines **3**.[a]

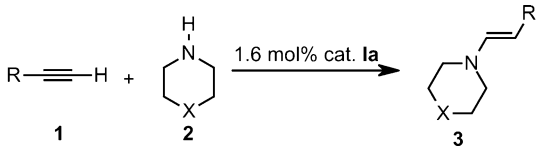


R = Ph **1a**, C_6H_4-4-Me **1b**, C_6H_4-4-F **1c**, *n*-C_4H_9 **1d**, CH_2OMe **1e**, CH_2OH **1f**, CH(OH)Me **1g**, CH_2CH_2OH **1h**, $C(OH)Me_2$ **1i**

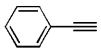
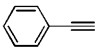
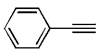
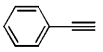
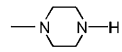
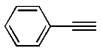
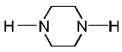
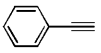
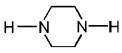
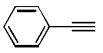
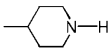
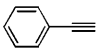
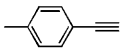
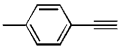
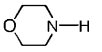
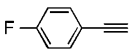
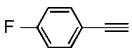
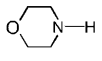
Entry	Alkyne		Temp [°C]	Conv[b] [%]	Isolated yield [%]
1		**1a**	90	90	84
2		**1b**	90	100	99
3		**1c**	90	54	51
4		**1d**	60	15	8[c]
5		**1e**	57	66	58[c]
6		**1f**	90	61	6[c]
7		**1g**	60	78	21[c]
8		**1h**	90	34	–[d]
9		**1i**	90	10	2[c]
10		**1j**	90	0	0

[a] *Reaction conditions*: **Ia** (0.05 g, 0.11 mmol), **1** (3.3 mmol), and **2a** (0.27 g, 3.3 mmol) without any solvent, under N_2.
[b] Conversion was determined by ^{1}H NMR on the basis of the consumption of the alkyne **1**.
[c] NMR yield of **3** was based on the ^{1}H NMR analysis of the crude reaction mixture.
[d] Only the three-molecules coupling product **5h$_2$a** was detected.

Table 3. Effect of amines **2** on the yield of *trans*-vinylamines **3**.[a]



R = Ph **1a**, C_6H_4-4-Me **1b**, C_6H_4-4-F **1c**
X = CH_2 **2a**, - **2b**, O **2c**, NMe **2d**, NH **2e**, CHMe **2f**, CH_2-3-Me **2g**

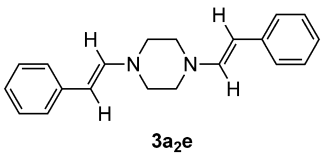
Entry	Alkyne		Amine		Temp[°C]	Time [h]	Conv[b] [%]	Isolated yield [%]
1		**1a**		**2a**	90	5	90	84
2		**1a**		**2b**	85	5	80	63
3		**1a**		**2c**	90	1	100	99
4		**1a**		**2d**	90	1	97	96
5		**1a**		**2e**	90	1.5	88	79[c][d]
6		**1a**		**2e**	90	0.5	100	90[c][e]
7		**1a**		**2f**	90	0.5	97	96
8		**1a**		**2g**	90	0.5	92	91
9		**1b**		**2a**	90	5	100	99
10		**1b**		**2c**	90	1	100	99
11		**1c**		**2a**	90	5	54	51
12		**1c**		**2c**	90	1	100	99

[a] *Reaction conditions*: **Ia** (0.05 g, 0.11 mmol), **1** (3.3 mmol), and **2a** (3.3 mmol) without any solvent.
[b] Conversion was determined by NMR on the basis of the consumption of the alkyne **1**.
[c] NMR yield of **3** was based on the ^{1}H NMR analysis of the crude reaction mixture.
[d] Two- and three-molecules coupling products **3ae** and **3a$_2$e** were formed in a 58:42 molar ratio, respectively.
[e] Reaction was carried out at the molar ratio of **1a**:**2e** = 2:1. The hydroamination products **3ae** and **3a$_2$e** were formed in a 17:83 molar ratio, respectively.

tion of piperazine **2e** and alkyne **1a**, the three-molecules coupling product **3a$_2$e** (Scheme 3), involving two molecules of the alkyne **1a** and one molecule of the amine **2e** was isolated as a major product in the reaction carried out at alkyne to piperazine molar ratio 2:1 (entry 6).

A methyl group in the 4-position or 3-position of the piperidine, **2f** and **2g**, increased the reactivity of amine and the yield of the enamine **3af** and **3ag** (entries 7 and 8) compared to that with piperidine **2a**.

The major side products, which were detected during prolonged reaction (90 °C, 5 h) of **1** and **2** in



3a$_2$e

Scheme 3. Three-molecules coupling product (1,4-bis[(*E*)-2-phenylethenyl]piperazine **3a$_2$e**) isolated in the reaction of phenylacetylene **1a** and piperazine **2e**.

the presence of **Ia** were identified by GC-MS as containing two molecules of the alkyne and one molecule of the amine. The NMR analysis of these products (**5a$_2$b**, **5b$_2$c**, **5h$_2$a** and **5i$_2$a**) revealed their existence as a mixture of *cis* and *trans* isomers (see Scheme 2).

The initial experiments carried out with primary amines (aniline and cyclohexylamine) revealed that, under comparable reaction conditions which were applied for secondary amines, the reactivity of primary amines was markedly lower. The yield of the major hydroamination product of phenylacetylene by aniline reached 7% and by cyclohexylamine 3%, after 5 h reaction at 90 °C in the presence of 1.6 mol% of **Ia**.

The reaction was not selective and gave isomers of two-molecules and three-molecules coupling products.

In conclusion, the regio- and stereoselective hydroamination of terminal alkynes with secondary amines can be achieved with good to excellent yields in reactions catalyzed by the relatively inexpensive, simple and readily available tungsten complex *cis*-[W(CO)$_4$(pip)$_2$] **Ia**. Corresponding additions of secondary amines to the terminal alkynes take place at 90 °C under solvent-free conditions at low catalyst loading (1.6 mol%). In all of the terminal alkynes and secondary amines tested, only *anti*-Markovnikov selectivity of hydroamination reactions was detected.

A small disadvantage of the catalyst **Ia** is constituted by the impurities of the hydroamination product with *E*-vinylpiperidines **3** formed in reaction of the alkyne **1** and piperidine **2a** derived from the catalyst. This problem can be omitted by the replace catalyst **Ia** with a tungsten complex containing the appropriate secondary amines **2b–g** in place of piperidine **2a** as ligands. The diamine complexes of the type [W(CO)$_4$(amine)$_2$] can be easily prepared in reaction of W(CO)$_6$ and amine.[4]

In summary, this work represents a major step forward in the development of regio- and stereoselective hydroamination catalysts. To the best of our knowledge, this is the first example of the hydroamination of alkynes with such a very well-known and simple tungsten complex as catalyst. It should be noted that the catalytic activity of **Ia** meets or exceeds the activity of other catalytic systems based on Rh and Ru.[2d,e,f,h] It is also worth mentioning that the hydroamination reaction can be realized in the presence of W(CO)$_6$ **Ib**, as the precursor of the catalyst **Ia**. However, with the catalyst **Ib**, the yield of the enamine is much lower than with **Ia** under comparable reaction conditions. The application of **Ib** under photochemical conditions was very promising. Unfortunately, undesirable reaction pathways became more favourable diminishing the yield of the desired product **3aa** to 43%.

The mechanism of the tungsten(0)-catalyzed addition of secondary amines to terminal alkynes is unclear at this stage. However, based on the *anti*-Markovnikov regioselectivity of the reaction and on the result that no hydroamination of internal alkynes was observed, the reaction may proceed *via* a vinylidene-tungsten intermediate. Nucleophilic attack of the amine at the α-carbon of the vinylidene ligand would lead to the formation of the *anti*-Markovnikov products observed here.[8] The formation of vinylidene ligands in reaction of terminal alkynes with tungsten(0) d^6 complexes is very well documented in literature.[9]

In conclusion, a facile, catalytic hydroamination reaction of terminal alkynes with secondary amines has been revealed yielding selectively *E*-enamines. The scope and mechanism of this reaction are currently under investigation.

Experimental Section

Synthesis of Complex [W(CO)$_4$(pip)$_2$] Ia

The piperidine (pip) complex [W(CO)$_4$(pip)$_2$] **Ia** was prepared in a photochemical reaction of W(CO)$_6$ (0.7 g, 2.0 mmol) and piperidine (0.6 mL, 6.1 mmol) in *n*-hexane (50 mL). During this reaction (*ca.* 8 h) the tungsten complex containing two piperidine ligands settled out as a light yellow powder, which was separated, washed several times with *n*-hexane and dried under vacuum to give *ca.* 0.6 g of analytically pure and sufficiently stable in the solid state complex **Ia**. Photochemical reactions were carried out under an atmosphere of nitrogen in a glass reactor with a quartz window. The photolysis source was an HBO 200 W medium-pressure Hg lamp.

General Procedure for Hydroamination of Terminal Alkynes

The reactions were carried out under a nitrogen atmosphere in Schlenk tubes equipped with a condenser and a magnetic stir bar. In a typical run, tungsten complex (**Ia**, 0.05 g, 0.11 mmol) was loaded into the tube. The tube was evacuated and filled with nitrogen. The corresponding liquid reagents: alkyne **1** (3.3 mmol) and the corresponding amine **2** (3.3 mmol) in a 1:1 molar ratio were then introduced to the tube *via* syringes and needles. The solid reagents were loaded into the tube together with the catalyst. Next the reaction mixture was stirred in a silicon oil bath at the suitable temperature (slightly lower than the boiling temperature of reagents but not exceeding 90 °C) for a maximum 5 h. The course of the reaction was monitored by regular sampling (0.1 mL every one hour) and analysis by ^{1}H NMR. The re-

sulting products were extracted into *n*-hexane, from which they were isolated as clean compounds after the evaporation of the solvent and any remaining non-reacted substrates under vacuum. Purity of the compounds has been checked by ^{1}H NMR spectroscopy and GC-MS analysis. Only the three-molecules coupling product **3a$_2$e** was isolated in the solid state and purified by crystallization in dichloromethane/*n*-hexane mixture. All products were characterized using ^{1}H and ^{13}C NMR spectroscopy and GC-MS analysis. The results of these analysis were compared to the available previously reported data.[2,7,9] The IR spectra were measured only for clean products.

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