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Neutral Ti Complexes as Catalysts for the Hydroamination of Alkynes and Alkenes: Do the Labile Ligands Change the Catalytic Activity?

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A detailed comparison between three four-coordinate Ti complexes featuring the general bidentate ligand [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu]$^{2-}$ and two ligands X (NMe_2, Me, Cl) as catalyst precursors (**I**–**III**) for the intermolecular hydroamination of alkynes and the intramolecular hydroamination of alkenes is presented. The results strongly suggest that the catalytically active species are only identical for reactions performed with the bis(dimethylamido) complex **I** or the dimethyl complex **II**. Under the reaction conditions, the labile ligands X are proteolytically removed by the reacting amine to form catalytically active imido or amido complexes, together with dimethylamine or methane. Although both catalyst precursors can be used successfully for many substrate combinations, the preparative and kinetic studies clearly indicate that dimethylamine, which is formed from the bis(dimethylamido) catalyst precursor **I** and the reacting amine, is able to convert the catalytically active imido or amido complexes back into the catalyst precursor and therefore inhibits the reactions. As a consequence, the bis(dimethylamido) catalyst precursor **I** shows a poorer catalytic performance than the corresponding dimethyl complex **II**. Additionally, it is shown that the dichloro complex **III** is only a suitable catalyst precursor for selected hydroamination reactions. Corresponding reactions that are more difficult to achieve – such as reactions of diarylalkynes or amino alkenes – do not work efficiently with this complex. A possible explanation for this observation is the finding that the dichloro catalyst precursor **III** is obviously converted into a different catalytically active species. This can happen if the [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu]-ligand system of the catalyst precursor is being destroyed and removed from the Ti center under the reaction conditions.

Introduction

The Ti-catalyzed hydroamination of alkynes[1] has attracted much attention during the past few years. Extensive mechanistic investigations are consistent with a catalytic cycle that involves three-coordinate Ti-imido complexes (e.g., **V**, Scheme 1) as catalytically active species.[2] Although some examples in which the corresponding Ti-imido complexes have been directly used as hydroamination catalysts are known,[3] most reports describe the use of four-coordinate Ti complexes bearing two labile ligands X (Me, NMe_2, or Cl) as catalyst precursors (e.g. **I**–**III**). For these catalytic systems, it is assumed that in the presence of a primary amine the labile ligands X are proteolytically removed to form the catalytically active imido complex **V**, together with two equivalents of HX (methane, dimethylamine, or HCl). In principle, variation of the labile ligands X should not alter the catalytically active species and therefore should not result in significant changes in the catalytic activity. On the other hand, one can argue that the generation of the imido complex also results in the formation of two equivalents of HX, which can interfere with the catalytic system and slow down the reaction. One possible scenario is that HX present in the reaction mixture converts the imido complex **V** back into the catalytically inactive amido complex **IV**–**X**, or even back into the catalyst precursor, and therefore inhibits the reaction. Consequently, the catalytic performance will be directly influenced by the ability of HX to undergo an addition reaction to the electrophilic imido complex **V**. In this context, it must be noted that Marks and co-workers have recently suggested that a Zr-chloride complex with a structure comparable to **IV**–**Cl** can mediate intramolecular hydroamination reactions of alkenes and alkynes through a σ-bond insertion reaction of the alkene or the alkyne into the Zr–N single bond.[4] Consequently, the Ti-amido complex **IV**–**X** can also be regarded as a possible catalytically active species of the hydroamination reactions. However, even in this case, the formation of **IV**–**X** from the catalyst precursor and the amine substrate generates one equivalent of HX, which can interfere with the catalytic system (e.g., the HX can inhibit the hydroamination by converting **IV**–**X** back into the catalyst precursor). Consequently, the ability of HX to react with amido complex **IV**–**X** can also directly influence the catalytic performance.

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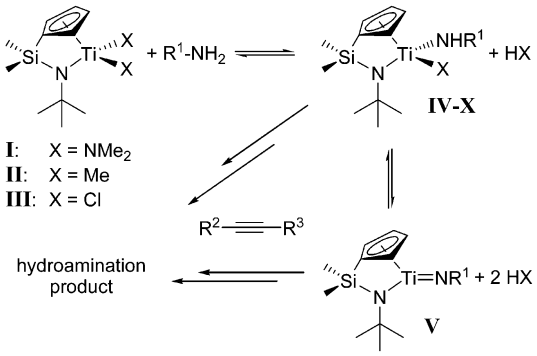


Scheme 1. Possible catalyst precursors **I**–**III** for the hydroamination of alkynes.

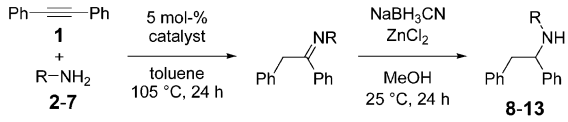
The suggested possibility of inhibition of the hydroamination through some reaction between HX and catalytically active Ti-imido or Ti-amido complexes leads to the assumption that the efficiency of the catalytic reaction should decrease with increasing ability of HX to react with the imido or amido complex. Of the three possibilities – methane, dimethylamine, and HCl – the last two are known to undergo facile addition reactions with Ti-imido complexes,[5] whereas the corresponding C–H activation of methane is far more difficult to achieve.[6] Since a corresponding reactivity trend would also be expected for Ti-amido complexes of type **IV**–**X**, our prediction was that the dimethyl complex **II** should show the best catalytic performance. In addition, HCl must be considered far more reactive towards imido or amido Ti complexes than dimethylamine, and so the dichloro complex **III** would be expected to be the worst hydroamination catalyst. Furthermore, and regardless of the mechanistic details, it is also possible that the HX formed from the catalyst precursor might react with other intermediates of the catalytic cycle and therefore influence the rate and the selectivity of the hydroamination. Additionally, the induction period needed for the conversion of the catalyst precursor into the imido complex **V** or the amido complex **IV**–**X** would be expected to be strongly influenced by the stabilities of the Ti–X bonds.[7]

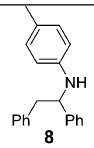
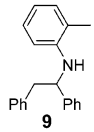
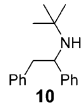
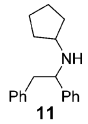
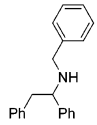
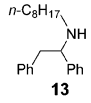
Interestingly, no corresponding study comparing the activities of catalyst precursors that differ only in the natures of the labile ligands X has yet been reported. In this publication we describe a detailed comparison of the three hydroamination catalysts **I**, **II**, and **III** (Scheme 1), featuring the common bidentate ligand $[\eta^5\text{-}(C_5H_4)\text{-}SiMe_2\text{-}N\textit{t}Bu]^{2-}$ together with labile dimethylamido, methyl, or chloro ligands,[8] respectively.

Results and Discussion

Initial hydroamination reactions were performed with diphenylacetylene (**1**) and *p*-toluidine (**2**), *o*-toluidine (**3**), *tert*-butylamine (**4**), cyclopentylamine (**5**), benzylamine (**6**), or oct-1-ylamine (**7**). All experiments were run at 105 °C for 24 h in the presence of 5 mol-% of one of the catalysts **I**, **II**, or **III**. After subsequent reduction of the initially formed imine with $NaBH_3CN$ and $ZnCl_2$ in methanol, the secondary amines **8**–**13** were isolated. As can be seen from Table 1, the dichloro complex **III** was only able to catalyze a single transformation of diphenylacetylene (**1**). However, the yield for the addition of oct-1-ylamine (**7**) to **1** is only 19% (Entry 18).

Table 1. Intermolecular hydroamination of diphenylacetylene (**1**) with various amines **2**–**7** in the presence of the catalysts **I**–**III**.



Entry	R (amine)	Product	Catalyst	Yield [%][a]	Recovered **1** [%]
1	*p*Tol (**2**)	 **8**	**I**	89	9
2			**II**	92	6
3			**III**	–	97
4	*o*Tol (**3**)	 **9**	**I**	89	9
5			**II**	94	5
6			**III**	–	97
7	*t*Bu (**4**)	 **10**	**I**	90	8
8			**II**	95	2
9			**III**	–	98
10	Cyclo-pentyl (**5**)	 **11**	**I**	92	6
11			**II**	94	2
12			**III**	–	98
13	Bn (**6**)	 **12**	**I**	11	88
14			**II**	95	4
15			**III**	–	97
16	$n\text{-}C_8H_{17}$ (**7**)	 **13**	**I**	64	34
17			**II**	58	40
18			**III**	19	79

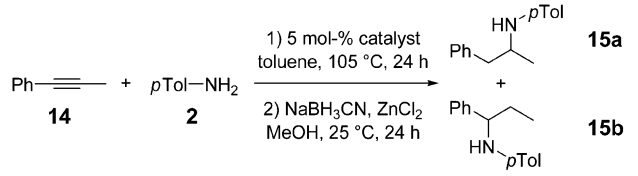
[a] Reaction conditions: 1) alkyne **1** (2.40 mmol), amine (2.64 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (1.0 mL), 105 °C, 24 h; 2) $NaBH_3CN$ (4.80 mmol), $ZnCl_2$ (2.40 mmol), MeOH (10 mL), 25 °C, 24 h. Yields refer to isolated pure compounds.

On the other hand, the reactions of the sterically demanding amines **2**–**5** in the presence of the bis(dimethylamido) complex **I** or the dimethyl complex **II** resulted in

the formation of the desired products **8**–**11** in very good to excellent yields. Although the yields obtained with these two catalysts do not differ dramatically, it is worth mentioning that a slightly better result is always obtained with the dimethyl complex **II**. A much stronger difference between **I** and **II** was observed when the sterically less hindered benzylamine (**6**) was employed (Entries 13, 14). In this case, the dimethyl complex **II** gave a much better yield of the product **12** (95%) than the bis(dimethylamido) complex **I** (11%). However, in this context it must be noted that sterically less demanding amines such as benzylamine (**6**) have often been recognized as poor substrates for Ti-catalyzed intermolecular hydroamination reactions of alkynes.[9] Obviously, the bis(dimethylamido) complex **I** is far more sensitive than the dimethyl complex **II** to the negative influence caused by this amine. Surprisingly, and in contrast with the results obtained with benzylamine (**6**), no big difference between **I** and **II** was observed when oct-1-ylamine (**7**) was used as the amine (Entries 16, 17). Furthermore, it must be noted that in this case a slightly improved yield is obtained with catalyst precursor **I**.

One possible explanation for the lack of activity of the dichloro catalyst precursor **III** in addition reactions of the amines **2**–**6** to diphenylacetylene (**1**) would be a lack of formation of the catalytically active species under the reaction conditions. Consequently, the catalytic hydroamination of the alkyne **1** would not be able to take place. In order to verify this assumption, we turned our attention towards the reaction between 1-phenylpropyne (**14**) and *p*-toluidine (**2**, Table 2). Surprisingly, we found that the dichloro complex **III** does catalyze the addition of *p*-toluidine (**2**) to 1-phenylpropyne (**14**) with high efficiency (Entry 7, 82% yield). First of all, this result clearly shows that the dichloro complex **III** is converted into a catalytically active species under these reaction conditions when *p*-toluidine (**2**) is used as the amine. However, the fact that the corresponding reaction with diphenylacetylene (**1**, Table 1, Entry 3) does not give the desired hydroamination product suggests that the generated catalytically active species does not undergo any further reaction with this alkyne while it does react with 1-phenylpropyne (**14**). This interpretation is in agreement with the well established fact that 1-phenylpropyne (**14**) is far more reactive than diphenylacetylene (**1**) in Ti-catalyzed intermolecular hydroaminations.[10] Consequently, one can assume that the dichloro complex **III** is only a suitable hydroamination catalyst for alkynes that are known to display improved reactivity in hydroamination reactions, such as 1-alkyl-2-arylalkynes and terminal alkynes (vide infra). The possibility that the reaction in the presence of the catalyst-precursor **III** might take place through a simple H^+-catalyzed addition[11] of *p*-toluidine (**7**) to 1-phenylpropyne (**12**) was ruled out at the start by a control experiment performed under identical conditions with 10 mol-% *p*-toluidine hydrochloride instead of 5 mol-% **III**. In this case, no hydroamination reaction was observed. Furthermore, an experiment performed with 5 mol-% **III** and 10 mol-% 1,8-bis(dimethylamino)naphthalene (proton sponge, Entry 8) gave the desired hydroamination product in an improved yield of 93%. These results clearly show that no H^+-catalyzed process is operative when the dichloro complex **III** is used as the catalyst precursor. This last result also suggests that the presence of a non-nucleophilic base slightly accelerates the catalytic reaction. Another interesting point is the fact that the hydroamination of **14** with **2** takes place with a surprisingly low regioselectivity of only 93:7 when the dichloro complex **III** is used [91:9 in the presence of 1,8-bis(dimethylamino)naphthalene]. In comparison, the anti-Markovnikov regioisomer is formed almost exclusively (99:1) in the presence of catalysts **I** and **II**. The best yield (96%, Entry 4) was again obtained with the dimethyl complex **II**.

Table 2. Intermolecular hydroamination of 1-phenylpropyne (**14**) with *p*-toluidine (**2**) in the presence of the catalysts **I**–**III**.



Entry	Catalyst	Yield (**15a**+**15b**) [%][a]	Ratio (**15a**/**15b**)[b]
1	**I**	91	99:1
2[c]	**I**	87	99:1
3[d]	**I**	66	99:1
4	**II**	96	99:1
5[c]	**II**	85	99:1
6[d]	**II**	59	98:2
7	**III**	82	93:7
8[e]	**III**	93	91:9

[a] Reaction conditions: 1) alkyne **14** (2.40 mmol), amine **2** (2.64 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (1.0 mL), 105 °C, 24 h; 2) $NaBH_3CN$ (4.80 mmol), $ZnCl_2$ (2.40 mmol), MeOH (10 mL), 25 °C, 24 h. Yields refer to isolated pure compounds. [b] Determined by GC prior to chromatography. [c] Reaction performed in the presence of 10 mol-% of pyrrolidine. [d] Reaction performed in the presence of 25 mol-% of pyrrolidine. [e] Reaction performed in the presence of 10 mol-% of 1,8-bis(dimethylamino)naphthalene.

Because our preparative studies did not so far clearly support the prediction that the catalytic efficiency should decrease from the dimethyl complex **II** through the bis(dimethylamido) complex **I** to the dichloro complex **III**, we performed additional kinetic investigations to compare the catalysts **I**, **II**, and **III** directly. For this purpose, we performed hydroamination reactions of 1-phenylpropyne (**14**) with *p*-toluidine (**2**) under identical reaction conditions with constant catalyst concentrations (5 mol-%). Monitoring of the alkyne concentration by ^1H NMR spectroscopy (Figure 1) revealed that the reaction catalyzed by **II** is indeed significantly faster than identical reactions catalyzed by **I** or **III**. Furthermore, a significant induction period was observed in the case of the dichloro complex **III**. As expected, analysis of the kinetic data showed that all reactions are first-order in the concentration of alkyne **14** (Figure 2). However, the calculated rate constants show that the di-

methyl complex **II** is approximately 1.5 times more active than the corresponding bis(dimethylamido) complex **I** and 7 times more active than the dichloro complex **III**.

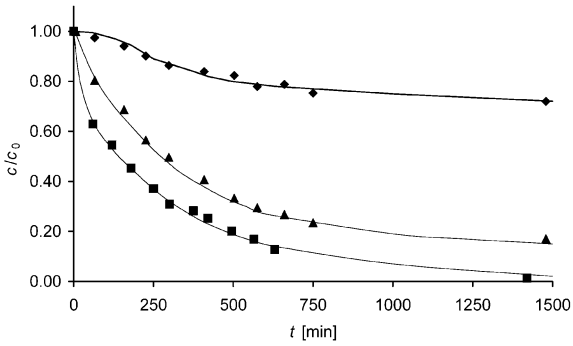


Figure 1. Plot of c(**14**)/c_0(**14**) vs. t for the catalysts **I** (▲), **II** (■), and **III** (♦).

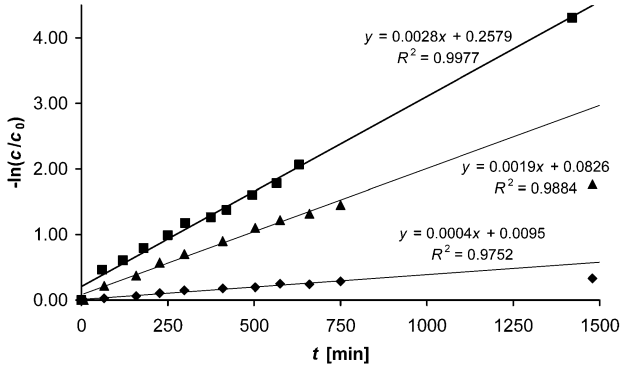


Figure 2. First-order plot {–ln [c(**14**)/c_0(**14**)] vs. t} for the catalysts **I** (▲), **II** (■), and **III** (♦).

However, more detailed in situ NMR studies revealed a number of additional pieces of mechanistic information. During a hydroamination of **14** with **2** performed in the presence of 22 mol-% of the dimethyl catalyst precursor **II** at 90 °C in C_6D_6, a single species was observed by in situ ^{29}Si NMR (65% conversion, 45 min reaction time) at δ = 17.4 ppm (relative to the signal of TMS at δ = 0.00 ppm). When the bis(dimethylamido) complex **I** (23 mol-%) was employed, the same signal at δ = 17.4 ppm was observed (70% conversion, 2 h reaction time) along with an additional signal at 5.9 ppm for the catalyst precursor **I**, a finding in agreement with corresponding in situ ^{1}H and ^{13}C NMR spectra. In addition, free dimethylamine was observed in the ^{1}H (δ =2.14 ppm) and ^{13}C NMR (δ =38.7 ppm) spectra. These observations strongly support the idea that the dimethylamine formed during the reaction converts the catalytically active imido or amido species back into the catalyst precursor **I** and therefore inhibits the catalytic reaction. Consequently, the reaction performed in the presence of **I** is slower than that in the presence of **II** (vide supra), in which no catalyst precursor could be observed by either ^{29}Si, ^{1}H, or ^{13}C NMR spectroscopy. This interpretation also explains the finding of Schafer et al.[12] that preformed Ti- and Zr-imido complexes show improved catalytic activities in relation to corresponding bis(dimethylamido) complexes. While the NMR studies suggest that for reactions performed in the presence of **I** or **II** the catalytically active species are identical, this seems not to be the case when the dichloro precursor **III** is employed. A different signal at δ = 20.8 ppm was observed by in situ ^{29}Si NMR (27% conversion, 3 h reaction time) when **III** was used as the catalyst precursor (23 mol-%), and corresponding differences were also observed by ^{1}H and ^{13}C NMR spectroscopy. A possible explanation could be that under these reaction conditions the [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu] ligand system is destroyed and removed from the Ti center. Consequently, at the moment, we are not sure whether the chloro ligands, or parts of the [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu] ligand system, or both represent the labile ligands that are exchanged by the reacting amine. This unexpected result makes it impossible to compare the catalytic performance of the dichloro catalyst precursor **III** directly with that of **I** or **II** because obviously different catalytically active species are involved. From a mechanistic point of view, it is also worth mentioning that no free [(C_5H_5)-$SiMe_2$-NH*t*Bu] ligand was observed during any of the NMR studies.

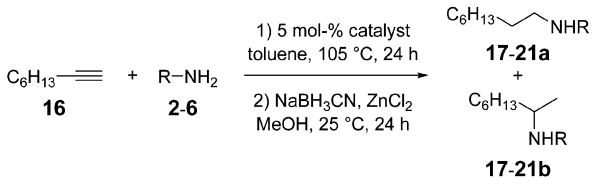
In order to verify the assumption that the dimethylamine formed from the catalyst precursor **I** and amine **2** under the reaction conditions is responsible for the decreased activity of catalyst precursor **I**, we performed additional hydroamination reactions of 1-phenylpropyne (**14**) with *p*-toluidine (**2**) in the presence of pyrrolidine. This amine, which was selected as an example of a more nucleophilic secondary amine, is believed to inhibit the hydroamination reaction because it can convert catalytically active imido or amido complexes into inactive bisamides of type **I**. First of all, it can be seen from Table 2 (Entries 4–6) that the presence of 10 or 25 mol-% pyrrolidine significantly inhibits the hydroamination reaction performed in the presence of the dimethyl catalyst precursor **II**. While the regioselectivity of the reaction is not significantly changed by the additive, the yield of the isolated product **15a** drops from 96% in the absence of pyrrolidine through 85% in the presence of 10 mol-% pyrrolidine to only 59% when 25 mol-% pyrrolidine is present. The fact that corresponding behavior is also observed for the bis(dimethylamido) complex **I** (Entries 1–3) strongly supports the idea that nucleophilic secondary amines such as pyrrolidine or dimethylamine can convert the catalytically active species into inactive Ti complexes when they are present in the reaction mixture. Consequently, their presence slows down the catalytic reaction. Since dimethylamine is always formed during reactions that employ the bis(dimethylamido) complex **I** as the catalyst precursor, the decreased efficiency of **I** relative to the dimethyl complex **II** can easily be understood.

The suggestion that the dichloro complex **III**, regardless of the structure of the catalytically active species, is only a suitable hydroamination catalyst for alkynes that are known

to possess improved reactivity in hydroamination reactions (vide supra) was verified in a number of transformations of the terminal alkyne oct-1-yne (**16**, Table 3). As predicted, all amines tested (**2**–**6**) underwent successful hydroaminations of **16** in the presence of 5 mol-% of the dichloro complex **III**. However, with two exceptions (Entries 9 and 15), better yields were usually obtained with the bis(dimethylamido) complex **I** or the dimethyl complex **II**. Of these two catalysts, the dimethyl complex **II** again turned out to be the more active one. Another interesting point is the fact that the use of complexes **I** and **II** led to identical regioselectivities (within experimental error) for reactions of amines **2**–**5**, behavior consistent with the idea that identical catalytically active species are present in reactions performed with **I** or **II**. Again, significant mechanistic changes obviously do not take place when the labile ligands are exchanged from methyl to dimethylamido groups (and vice versa). In contrast, hydroamination reactions with *p*-toluidine (**2**, Entries 1–3) or cyclopentylamine (**5**, Entries 10–12) performed in the presence of the dichloro complex **III** were found to take place with significantly changed regioselectivities. This observation, which had already been made in the case of reactions of 1-phenylpropyne (**14**, Table 2), strongly supports the results of the NMR studies, which suggest that the catalytically active species formed from **III** is different from the other two catalyst precursors. Interestingly, and in contrast with the reactions of 1-phenylpropyne (**14**, Table 2), in this case the reactions of oct-1-yne (**16**) take place with improved regioselectivity. In addition, identical (and excellent) regioselectivities were observed with all three catalysts in reactions employing *o*-toluidine (**3**, Entries 4–6) or *tert*-butylamine (**4**, Entries 7–9). In general, all these observations are in agreement with the well established fact that Ti-catalyzed hydroamination reactions of terminal alkyl alkynes with arylamines are Markovnikov-selective (Entries 1–6) and the corresponding reactions with alkylamines (Entries 7–12) are anti-Markovnikov-selective.[9c,13] In both cases, better regioselectivities are obtained with sterically more demanding amines.

Surprisingly, the results obtained with benzylamine (**6**, Entries 13–15) do not show the same trend. Although all yields are low and all regioselectivities are close to a ratio of 1:1, the bis(dimethylamido) complex **I** and the dimethyl complex **II** obviously do not give the same regioselectivity. However, this small difference in regioselectivity is in agreement with the difference in yield observed in hydroamination reactions of diphenylacetylene (**1**) with benzylamine (**6**, Table 1, Entries 13, 14). A possible explanation for both findings is that the dimethylamine generated from the bis(dimethylamido) complex **I** is able to interfere significantly with the catalytic system in reactions of benzylamine. This possibility can be understood in view of the fact that benzylamine (**6**) is known to be a poor substrate for Ti-catalyzed intermolecular hydroamination reactions of alkynes.[6] Consequently, one can imagine that at some stage of the catalytic cycle the dimethylamine is able to compete with benzylamine and therefore influences not only the efficiency, but also the selectivity, of the process.

Table 3. Intermolecular hydroamination reaction of oct-1-yne (**16**) with various amines (**2**–**6**) in the presence of the catalysts **I**–**III**.

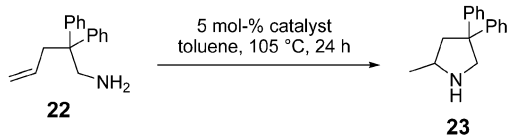


Entry	R (amine)	Catalyst	Product	Yield (**a**+**b**) [%][a]	Ratio (**a**/**b**)[b]
1	*p*Tol (**2**)	**I**	**17a/b**	92	17:83
2		**II**		95	17:83
3		**III**		45	3:97
4	*o*Tol (**3**)	**I**	**18a/b**	80	< 1:99
5		**II**		94	< 1:99
6		**III**		90	< 1:99
7	*t*Bu (**4**)	**I**	**19a/b**	65	> 99:1
8		**II**		81	> 99:1
9		**III**		91	> 99:1
10	cyclopentyl (**5**)	**I**	**20a/b**	79	65:35
11		**II**		99	66:34
12		**III**		51	82:18
13	Bn (**6**)	**I**	**21a/b**	31	57:43
14		**II**		42	43:57
15		**III**		49	48:52

[a] Reaction conditions: 1) alkyne **16** (2.40 mmol), amine (2.64 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (1.0 mL), 105 °C, 24 h; 2) $NaBH_3CN$ (4.80 mmol), $ZnCl_2$ (2.40 mmol), MeOH (10 mL), 25 °C, 24 h. Yields refer to isolated pure compounds. It was not possible to recover any unreacted alkyne. [b] Determined by GC prior to chromatography.

Finally, we turned our attention towards the intramolecular hydroamination of amino alkene **22** (Table 4). Since only a few neutral Ti catalysts for this difficult transformation have been identified,[14] it is not very surprising that in this case the dichloro complex **III** does not show any catalytic activity. On the other hand, the bis(dimethylamido) complex **I** and the dimethyl complex **II** both do catalyze the hydroamination/cyclization of **22**. Again, however, a better yield is obtained with the dimethyl complex **II**.

Table 4. Intramolecular hydroamination of 1-amino-2,2-diphenylpent-4-ene (**22**) in the presence of the catalysts **I**–**III**.



Entry	Catalyst	Yield (**23**) [%][a]	Recovered **22** [%]
1	**I**	26	72
2	**II**	74	16
3	**III**	–	100

[a] Reaction conditions: 1) amino alkene **22** (2.40 mmol), catalyst (0.12 mmol, 5 mol-%), toluene (1.0 mL), 105 °C, 24 h. Yields refer to isolated pure compounds.

Conclusions

In summary, we have presented a comparison of three four-coordinate Ti complexes featuring the common bidentate ligand [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu]$^{2-}$ together with two ligands X (NMe_2, Me, Cl) as catalyst precursors **I**–**III** for the intermolecular hydroamination of alkynes and the intramolecular hydroamination of alkenes. Our results strongly suggest that for reactions performed with the bis(dimethylamido) complex **I** or the dimethyl complex **II**, the catalytically active species are identical. Under the reaction conditions, the ligands X are proteolytically removed by the reacting amine to form catalytically active imido or amido complexes, together with dimethylamine or methane. Both catalyst precursors can be used successfully for many substrate combinations. However, the preparative and kinetic studies clearly indicate that the dimethylamine formed from the bis(dimethylamido) catalyst precursor **I** and the reacting amine is able to convert the catalytically active imido or amido complexes back into the catalyst precursor and therefore inhibits the reactions. As a consequence, the bis(dimethylamido) catalyst precursor **I** shows a worse catalytic performance than the corresponding dimethyl complex **II**. On the other hand, the dichloro complex **III** is only a suitable catalyst precursor for selected reactions that are known to proceed smoothly. Hydroamination reactions that are more difficult to achieve, such as reactions of diarylalkynes or amino alkenes, do not work efficiently with this complex. A possible explanation for this observation is the finding that the dichloro catalyst precursor **III** is converted into a different catalytically active species. This can happen if the [η^5-(C_5H_4)-$SiMe_2$-N*t*Bu] ligand system of the catalyst precursor is destroyed and removed from the Ti center under the reaction conditions.

Experimental Section

General Remarks: All reactions were performed under nitrogen in oven-dried Schlenk tubes (Duran glassware, 100 mL, Ø 30 mm) fitted with Teflon stopcocks and containing magnetic stirring bars (15 × 4.5 mm). The catalysts **I**–**III**[8] and 1-amino-2,2-diphenylpent-4-ene (**22**)[15] were synthesized by literature procedures. [D_6]Benzene was distilled from molten sodium. Toluene (toluene extra dry with molecular sieves), and methanol (methanol extra dry with molecular sieves) were purchased from Acros Organics. Prior to use, the volatile amines (**3**–**7**) and oct-1-yne (**14**) were purified and dried by distillation (20 cm Vigreux column) from CaH_2 on molecular sieves at ambient pressure under an inert atmosphere. Diphenylacetylene (**1**) and *p*-toluidine (**2**) were purified by kugelrohr distillation. All alkynes, amines, and catalysts were stored in a nitrogen-filled glovebox (M. Braun, Unilab). All other reagents were purchased from commercial sources and were used without further purification. Unless otherwise noted, yields refer to isolated yields of pure compounds as gauged by thin layer chromatography (TLC) and ^1H and ^{13}C NMR spectroscopy. All products were characterized by ^1H NMR, ^{13}C NMR and infrared (IR) spectroscopy and mass spectrometry (MS). Additional characterization data were obtained by CHN elemental analysis and/or high-resolution mass spectrometry (HRMS). NMR spectra were recorded on the following spectrometers: Bruker Avance DPX 300, Bruker Avance DRX 500. All ^1H NMR spectra are reported in δ units (ppm) relative to the signal of TMS at δ = 0.00 ppm. All ^{13}C NMR spectra are reported in δ units (ppm) relative to the central line of the triplet for $CDCl_3$ at δ = 77.0 ppm or C_6D_6 at δ = 128.0 ppm. NMR spectroscopic data recorded for kinetic studies are reported in δ units (ppm) relative to the signal of ferrocene (internal standard) at δ = 4.00 ppm. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer by an attenuated total reflection (ATR) method. Mass spectra were recorded on a Finnigan MAT 95 spectrometer (EI with an ionization potential of 70 eV or CI with isobutane as ionization gas). Elemental analyses were carried out on a Euro EA 3000 machine. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph fitted with a flame ionization detector. PE: light petroleum ether, b.p. 40–60 °C.

Intermolecular Hydroamination of Alkynes. General Procedure: A Schlenk tube fitted with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with the alkyne (2.40 mmol), the amine (2.64 mmol), the catalyst (0.12 mmol, 5 mol-%), and toluene (1.0 mL). The tube was then sealed, and the resulting mixture was heated to 105 °C for 24 h. After the mixture had been cooled to room temperature, $NaBH_3CN$ (302 mg, 4.80 mmol), $ZnCl_2$ (328 mg, 2.40 mmol), and MeOH (10 mL) were added. After this mixture had been stirred at 25 °C for 20 h, CH_2Cl_2 (50 mL) and saturated Na_2CO_3 solution (20 mL) were added. The resulting mixture was filtered, and the solid residue was washed with CH_2Cl_2 (50 mL). After extraction, the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (6 × 50 mL), and the combined organic layers were dried with $MgSO_4$. After concentration under vacuum, the crude product was purified by flash chromatography (SiO_2).

(1,2-Diphenylethyl)-*p*-tolylamine (8):[9c] The general procedure was used to synthesize **8** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and *p*-toluidine (**2**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 40:1), **8** (631 mg, 2.20 mmol, 92%, catalyst: **II**) was obtained as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.15 (s, 3 H), 3.00 (dd, *J* = 8.3, 14.0 Hz, 1 H), 3.12 (dd, *J* = 5.6, 14.0 Hz, 1 H), 4.02 (br. s, 1 H), 4.55 (dd, *J* = 5.7, 8.1 Hz, 1 H), 6.37 (d, *J* = 8.3 Hz, 2 H), 6.85 (d, *J* = 8.2 Hz, 2 H), 7.11 (d, *J* = 7.1 Hz, 2 H), 7.20–7.37 (m, 8 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 20.3 (CH_3), 45.2 (CH_2), 59.5 (CH), 113.8 (CH), 126.5 (CH), 126.7 (CH), 127.0 (CH), 128.5 (CH), 128.5 (CH), 129.2 (CH), 129.5 (CH), 137.8 (C), 143.6 (C), 145.0 (C) ppm.

(1,2-Diphenylethyl)-*o*-tolylamine (9): The general procedure was used to synthesize **9** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and *o*-toluidine (**3**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 20:1), **9** (646 mg, 2.25 mmol, 94%, catalyst: **II**) was obtained as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 3 H), 3.00 (dd, *J* = 8.8, 13.9 Hz, 1 H), 3.20 (dd, *J* = 5.2, 13.9 Hz, 1 H), 3.99 (br. s, 1 H), 4.58 (dd, *J* = 5.2, 8.7 Hz, 1 H), 6.28 (d, *J* = 8.0 Hz, 1 H), 6.56 (t, *J* = 7.3 Hz, 1 H), 6.89 (t, *J* = 7.4 Hz, 1 H), 6.97 (d, *J* = 7.3 Hz, 1 H), 7.16 (d, *J* = 7.0 Hz, 1 H), 7.21–7.37 (m, 9 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 17.4 (CH_3), 45.6 (CH_2), 59.3 (CH), 111.3 (CH), 117.0 (CH), 122.2 (C), 126.3 (CH), 126.8 (CH), 126.9 (CH), 127.0 (CH), 128.6 (CH), 128.6 (CH), 129.2 (CH), 129.8 (CH), 137.8 (C), 143.7 (C), 145.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 3413, 3022, 2915, 2839, 1607, 1588, 1510, 1453, 1322, 1266, 749, 698 cm^{-1}. MS (CI, 25 °C): *m*/*z* (%) = 288 (100) $[M + H]^+$, 196 (22) $[M - C_7H_7]^+$. HRMS (CI): calcd. ($C_{21}H_{22}N$) 288.1752; found: 288.1752. $C_{21}H_{21}N$ (287.4): calcd. C 87.76, H 7.36, N 4.87; found C 87.50, H 7.28, N 4.76.

***tert*-Butyl(1,2-diphenylethyl)amine (10):**[9c] The general procedure was used to synthesize **10** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and *tert*-butylamine (**4**, 193 mg, 2.64 mmol). After chromatography (PE/EtOAc, 20:1→5:1), **10** (576 mg, 2.28 mmol, 95%, catalyst: **II**) was obtained as a bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (s, 9 H), 1.33 (br. s, 1 H), 2.70 (dd, J = 9.0, 13.4 Hz, 1 H), 2.91 (dd, J = 5.5, 13.5 Hz, 1 H), 3.98 (dd, J = 5.6, 8.8 Hz, 1 H), 7.13 (d, J = 7.6 Hz, 2 H), 7.19 (d, J = 7.3 Hz, 2 H), 7.23–7.29 (m, 4 H), 7.38 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 29.9 (CH_3), 47.2 (CH_2), 51.1 (C), 59.2 (CH), 126.3 (CH), 126.4 (CH), 127.1 (CH), 128.1 (CH), 128.3 (CH), 129.3 (CH), 139.3 (C), 147.5 (C) ppm.

Cyclopentyl(1,2-diphenylethyl)amine (11):[9c] The general procedure was used to synthesize **11** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and cyclopentylamine (**5**, 225 mg, 2.64 mmol). After chromatography (PE/EtOAc, 20:1), **11** (596 mg, 2.25 mmol, 94%, catalyst: **II**) was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05–1.71 (m, 9 H), 2.75–2.95 (m, 3 H), 3.92 (t, J = 7.9 Hz, 1 H), 7.11 (d, J = 7.1 Hz, 2 H), 7.13–7.33 (m, 8 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 23.6 (CH_2), 32.3 (CH_2), 33.7 (CH_2), 45.4 (CH_2), 57.3 (CH), 63.2 (CH), 126.2 (CH), 126.9 (CH), 127.4 (CH), 128.2 (CH), 128.3 (CH), 129.2 (CH), 139.0 (C), 144.1 (C) ppm.

Benzyl(1,2-diphenylethyl)amine (12):[9c] The general procedure was used to synthesize **12** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and benzylamine (**6**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 5:1), **12** (654 mg, 2.28 mmol, 95%, catalyst: **II**) was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.68 (br. s, 1 H), 2.89 (dd, J = 8.6, 13.5 Hz, 1 H), 2.96 (dd, J = 5.5, 13.5 Hz, 1 H), 3.46 (d, J = 13.6 Hz, 1 H), 3.65 (d, J = 13.6 Hz, 1 H), 3.88 (dd, J = 5.6, 8.6 Hz, 1 H), 7.08–7.14 (m, 4 H), 7.15–7.29 (m, 7 H), 7.30–7.38 (m, 4 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 45.3 (CH_2), 51.4 (CH_2), 63.6 (CH), 126.3 (CH), 126.7 (CH), 127.1 (CH), 127.4 (CH), 127.9 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 129.3 (CH), 138.8 (C), 140.5 (C), 143.7 (C) ppm.

(1,2-Diphenylethyl)octylamine (13): The general procedure was used to synthesize **13** from diphenylacetylene (**1**, 428 mg, 2.40 mmol) and oct-1-ylamine (**7**, 341 mg, 2.64 mmol). After chromatography (PE/EtOAc, 40:1 to EtOAc), **13** (426 mg, 1.38 mmol, 58%, catalyst: **II**) was obtained as a bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.05–1.40 (m, 12 H), 1.81 (br. s, 1 H), 2.30–2.43 (m, 2 H), 2.84–2.96 (m, 2 H), 3.83 (dd, J = 6.0, 8.1 Hz, 1 H), 7.08–7.32 (m, 10 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 27.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.8 (CH_2), 31.7 (CH_2), 45.4 (CH_2), 47.6 (CH_2), 64.8 (CH), 126.2 (CH), 126.9 (CH), 127.2 (CH), 128.2 (CH), 128.3 (CH), 129.2 (CH), 138.9 (C), 143.8 (C) ppm. IR (neat): $\tilde{\nu}$ = 3027, 2924, 2853, 1602, 1494, 1454, 1115, 1070, 1029, 908, 757, 732, 698, 627 cm^{-1}. MS (EI, 25 °C): m/z (%) = 309 (1) $[M]^+$, 218 (100) $[M - C_7H_7]$, 181 (4) $[M - C_8H_{18}N]$.

(1-Methyl-2-phenylethyl)-*p*-tolylamine (15a):[9c] The general procedure was used to synthesize **15a** from 1-phenylpropyne (**14**, 279 mg, 2.40 mmol) and *p*-toluidine (**2**, 281 mg, 2.64 mmol). After chromatography (PE/EtOAc, 40:1), **15a** (490 mg, 2.18 mmol, 91%, catalyst: **II**) was obtained as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, J = 6.5 Hz, 3 H), 2.25 (s, 3 H), 2.69 (dd, J = 7.5, 13.5 Hz, 1 H), 2.94 (dd, J = 4.5, 13.0 Hz, 1 H), 3.45 (br. s, 1 H), 3.74 (sext, J = 6.5 Hz, 1 H), 6.57 (d, J = 8.5 Hz, 2 H), 7.01 (d, J = 8.5 Hz, 2 H), 7.17–7.24 (m, 3 H), 7.30 (t, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 20.2 (CH_3), 20.4 (CH_3), 42.3 (CH_2), 49.7 (CH), 113.7 (CH), 126.2 (C), 126.5 (C), 128.2 (CH), 129.5 (CH), 129.8 (CH), 138.7 (C), 144.9 (C) ppm.

Amines 17a/17b: The general procedure was used to synthesize amines **17a** and **17b** from oct-1-yne (**16**, 264 mg, 2.40 mmol) and *p*-toluidine (**2**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 20:1), a mixture of **17a** and **17b** (500 mg, 2.28 mmol, 95%, catalyst: **II**) was obtained as an orange oil. The **17a/17b** ratio was determined by GC as 17:83 (catalyst: **II**). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of **17a** and **17b**): δ = 0.88 (t, J = 6.5 Hz, 3 H), 0.88 (t, J = 7.1 Hz, 3 H), 1.15 (d, J = 6.3 Hz, 3 H), 1.20–1.70 (m), 2.22 (s, 3 H), 3.08 (t, J = 7.1 Hz, 2 H), 3.27 (br. s, 1 H), 3.43 (sext, J = 6.2 Hz, 1 H), 6.49–6.55 (m, 2 H), 6.94–7.00 (m 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, mixture of **17a** and **17b**): δ = 14.1 (CH_3), 20.3 (CH_3), 20.8 (CH_3), 22.6 (CH_2), 26.1 (CH_2), 27.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 37.2 (CH_2), 44.5 (CH_2), 48.9 (CH), 113.0 (CH), 113.5 (CH), 129.7 (CH), 129.7 (CH) ppm. IR (neat, mixture of **17a** and **17b**): $\tilde{\nu}$ = 3406, 2956, 2924, 2855, 1619, 1518, 1457, 1376, 1317, 1301, 1250, 1182, 805 cm^{-1}. MS (CI, 25 °C, mixture of **17a** and **17b**): m/z = 220 (100) $[M + H]^+$. HRMS (CI, mixture of **17a** and **17b**): calcd. ($C_{15}H_{26}N$) 220.2066; found 220.2065. $C_{15}H_{25}N$ (219.4, mixture of **17a** and **17b**): calcd. C 82.13, H 11.49, N 6.38; found C 82.53, H 11.89, N 6.83.

Amine 18b:[16] The general procedure was used to synthesize amine **18b** from oct-1-yne (**16**, 264 mg, 2.40 mmol) and *o*-toluidine (**3**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 40:1), **18b** (494 mg, 2.25 mmol, 94%, catalyst: **II**) was obtained as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.5 Hz, 3 H), 1.20 (d, J = 6.2 Hz, 3 H), 1.24–1.71 (m, 10 H), 2.11 (s, 3 H), 3.29 (br. s, 1 H), 3.50 (sext, J = 6.0 Hz, 1 H), 6.60 (t, J = 7.5 Hz, 2 H), 7.03 (d, J = 7.2 Hz, 1 H), 7.10 (t, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 14.1 (CH_3), 17.6 (CH_3), 21.0 (CH_3), 22.6 (CH_2), 26.2 (CH_2), 29.4 (CH_2), 31.9 (CH_2), 37.3 (CH_2), 48.3 (CH), 110.0 (CH), 116.2 (CH), 121.6 (C), 127.1 (CH), 130.2 (CH), 145.6 (C) ppm.

Amine 19a: The general procedure was used to synthesize amine **19a** from oct-1-yne (**16**, 264 mg, 2.40 mmol) and *tert*-butylamine (**4**, 193 mg, 2.64 mmol). After chromatography (EtOAc, + 5% 7 M NH_3 in MeOH), **19a** (361 mg, 1.95 mmol, 81%, catalyst: **II**) was obtained as a bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.7 Hz, 3 H), 1.09 (s, 9 H), 1.19–1.37 (m, 10 H), 1.38–1.50 (m, 2 H), 2.53 (t, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 14.1 (CH_3), 22.7 (CH_2), 27.6 (CH_2), 29.1 (CH_3), 29.3 (CH_2), 29.6 (CH_2), 31.1 (CH_2), 31.9 (CH_2), 42.6 (CH_2), 50.2 (C) ppm. IR (neat): $\tilde{\nu}$ = 2957, 2924, 2854, 1465, 1387, 1360, 1231, 1132, 1097, 1020, 692 cm^{-1}. MS (CI, 25 °C): m/z (%) = 186 (100) $[M + H]^+$. HRMS (CI): calcd. ($C_{12}H_{28}N$) 186.2222; found 186.2222. No correct CHN elemental analysis could be obtained because of the viscosity of the product.

Amines 20a/20b: The general procedure was used to synthesize the amines **20a** and **20b** from oct-1-yne (**16**, 264 mg, 2.40 mmol) and cyclopentylamine (**5**, 225 mg, 2.64 mmol). After chromatography (EtOAc, + 5% 7 M NH_3 in MeOH), a mixture of **20a** and **20b** (468 mg, 2.38 mmol, 99%, catalyst: **II**) was obtained as a yellow oil. The **20a/20b** ratio was determined by GC to be 66:34 (catalyst: **II**). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of **20a** and **20b**): δ = 0.88 (t, J = 6.7 Hz, 3 H), 0.88 (t, J = 6.7 Hz, 3 H), 1.02 (d, J = 6.3 Hz, 3 H), 1.18–1.95 (m), 2.56 (t, J = 7.3 Hz, 2 H), 2.65 (sext, J = 6.0 Hz, 1 H), 3.04 (quint, J = 6.9 Hz, 1 H), 3.15 (quint, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, mixture of **20a** and **20b**): δ = 14.1 (CH_3), 20.8 (CH_3), 22.7 (CH_2), 23.9 (CH_2), 24.1 (CH_2), 26.1 (CH_2), 27.5 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 30.5 (CH_2), 31.9 (CH_2), 31.9 (CH_2), 33.3 (CH_2), 33.4 (CH_2), 33.9 (CH_2), 37.6 (CH_2), 48.9 (CH_2), 51.4 (CH), 57.0 (CH), 60.0

(CH) ppm. IR (neat, mixture of **20a** and **20b**): $\tilde{\nu}$ = 2954, 2923, 2854, 1681, 1456, 1375, 1134, 722 cm^{-1}. MS (CI, 25 °C, mixture of **20a** and **20b**): *m*/*z* (%) = 198 (100) $[M + H]^+$. HRMS (CI, mixture of **20a** and **20b**): calcd. ($C_{13}H_{28}N$) 198.2222; found 198.2222. No correct CHN elemental analysis could be obtained, because of the viscosity of the product mixture.

Amines 21a/21b:[16,17] The general procedure was used to synthesize amines **21a** and **21b** from oct-1-yne (**16**, 264 mg, 2.40 mmol) and benzylamine (**6**, 282 mg, 2.64 mmol). After chromatography (PE/EtOAc, 2:1), a mixture of amines **21a** and **21b** (222 mg, 1.01 mmol, 42%, catalyst: **II**) was obtained as a colorless oil. The **21a**/**21b** ratio was determined by GC to be 43:57 (catalyst: **II**). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of **21a** and **21b**): δ = 0.88 (t, *J* = 5.5 Hz, 3 H), 0.88 (t, *J* = 5.5 Hz, 3 H), 1.08 (d, *J* = 6.2 Hz, 3 H), 1.18–1.55 (m), 2.62 (t, *J* = 7.2 Hz, 2 H), 2.67 (sext, *J* = 5.8 Hz, 1 H), 3.73 (d, *J* = 13.0 Hz, 1 H), 3.79 (s, 2 H), 3.83 (d, *J* = 12.9 Hz, 1 H), 7.20–7.35 (m) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$, mixture of **21a** and **21b**): δ = 14.1 (CH_3), 20.4 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 27.4 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.1 (CH_2), 31.8 (CH_2), 37.1 (CH_2), 49.6 (CH_2), 51.4 (CH_2), 52.5 (CH), 54.1 (CH_2), 126.8 (CH), 126.8 (CH), 128.1 (CH), 128.4 (CH), 140.6 (C), 141.0 (C) ppm.

2-Methyl-4,4-diphenylpyrrolidine (23):[12,14b–14d,14g–14k] A Schlenk tube fitted with a Teflon stopcock and containing a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with 1-amino-2,2-diphenylpent-4-ene (**22**, 570 mg, 2.40 mmol), the catalyst (0.12 mmol, 5 mol-%), and toluene (1.0 mL). The tube was then sealed, and the resulting mixture was heated to 105 °C for 24 h. After the mixture had been cooled to room temperature, the product was directly isolated by flash chromatography (SiO_2, PE/EtOAc, 1:2) to give **23** (422 mg, 1.78 mmol, 74%, catalyst: **II**) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.5 Hz, 3 H), 2.04 (dd, *J* = 9.1, 12.7 Hz, 2 H), 2.21 (br. s, 1 H), 2.74 (ddd, *J* = 0.8, 6.7, 12.7 Hz, 1 H), 3.32–3.43 (m, 1 H), 3.47 (d, *J* = 11.4 Hz, 1 H), 3.68 (d, *J* = 11.6 Hz, 1 H), 7.12–7.19 (m, 2 H), 7.20–7.33 (m, 8 H) ppm. ^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 22.3 (CH_3), 47.1 (CH_2), 53.1 (CH), 57.3 (C), 57.9 (CH_2), 126.0 (CH), 127.0 (CH), 127.0 (CH), 128.3 (CH), 128.3 (CH), 147.1 (C), 147.8 (C) ppm.

Kinetic Studies: In a nitrogen-filled glovebox, a stock solution was prepared by dissolution of *p*-toluidine (3.98 g, 37.3 mmol), 1-phenylpropyne (**14**, 465 mg, 4.0 mmol) and ferrocene (100 mg, internal standard) in toluene in a volumetric flask (20 mL). The solution was stored at 0 °C between uses. An oven-dried Schlenk tube (Duran glassware, 80 mL, Ø 26 mm) fitted with a Teflon stopcock and containing a magnetic stirring bar was charged with the catalyst (0.12 mmol) and the stock solution (10 mL). The Schlenk tube was then sealed and transferred into a pre-equilibrated heating unit at 105 °C (±0.2 °C). Every 60 min, the relative concentration of the alkyne **14** was determined by ^{1}H NMR spectroscopy. For this purpose, a sample (0.05 mL) of the reaction solution was transferred into an NMR tube and diluted with C_6D_6 by use of standard Schlenk line techniques. The following NMR signals were monitored: ^{1}H NMR (300 MHz, C_6D_6): δ = 3.96–4.04 (ferrocene, 10 H), 1.64–1.68 (**14**, –CH_3, 3 H) ppm.

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