# Intermolecular Hydroamination of Methylenecyclopropane Catalyzed by Group IV Metal Complexes

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The intermolecular hydroamination of methylenecyclopropane (MCP) and phenylmethylenecyclopropane (PhMCP) promoted by group IV metal complexes is presented. The reactivity and chemoselectivity of two titanium complexes having two different ancillary ligands, $Ti(Ph_2PNpy)_2(NEt_2)_2$ and $Ti(NMe_2)_4$, are presented and compared to those of the zirconium complexes $Zr(Ph_2PNpy)_3NEt_2$ and $Zr(NMe_2)_4$. For the titanium complexes, the linear imine product **A** is always the predominant species, having *E* stereochemistry. For the zirconium complexes, the branched imine product **B** is obtained preferentially. Comparison of the activity of the complex $Ti(Ph_2PNpy)_2(NEt_2)_2$ with that of $Ti(NMe_2)_4$ reveals a strong relationship between the ancillary ligand at the catalytic complex and the suitability of the amine for the MCPs hydroamination reaction. A complex with a bulky ancillary ligand is suitable for the hydroamination of aliphatic amines and small aromatic amines, whereas a complex with a small ancillary ligand (steric hindrance) will allow the hydroamination of MCPs with bulky aromatic amines. Kinetic studies show that the hydroamination promoted by the homoleptic titanium complex exhibit a first-order dependence in complex and olefin and an inverse order dependence in amine. A plausible mechanism is presented on the basis of the obtained products, kinetic measurements, and syntheses of key intermediates.

## Introduction

The hydroamination reaction, an addition of an N−H bond to an unsaturated hydrocarbon, is an especially attractive transformation for industrial, environmental, and basic synthetic purposes. This reaction offers an atom-economical transformation that produces desired products in a high yield with no side products. The hydroamination reaction catalyzed by early-transition-metal organometallic complexes[1−55] manages to combine interesting and unique benefits. Among these benefits are the high general reactivity of the metals and their ubiquitous availability as compared to toxic metals (Hg,[56,57] Tl,[58] U, and Th[59−62]) or the more expensive lanthanides and late-transition-

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metal complexes (Ru,[63−72] Rh,[73−77] Ir,[74,78−80] Pd,[54,63,81−109] Ni,[110] Pt,[63,86,111−116] Cu,[63,117−119] Ag,[120−123] and Au[124−133]). This "win−win" combination has motivated widespread interest over the past decade and has made the hydroamination reaction catalyzed, especially by early-transition-metal complexes, a highly advantageous transformation. The hydroamination reaction allows the formation, upon concomitant reactions, of substituted amines,[19,28,36,39,45,134,135] α,β-unsaturated imines,[14,25,29,39] ketones,[14,28] hydrazines,[23,30] pyrroles,[5,27,35] indoles,[5,17,26,35,48] and other cyclic amines.[14] However, to date, this field has remained limited mainly to alkyne and allene substrates.[136] The main challenge of this topic is to expand the reaction scope to include the discovery of new group IV organometallic complexes that

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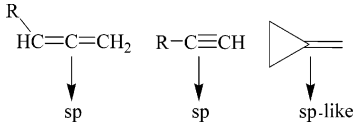
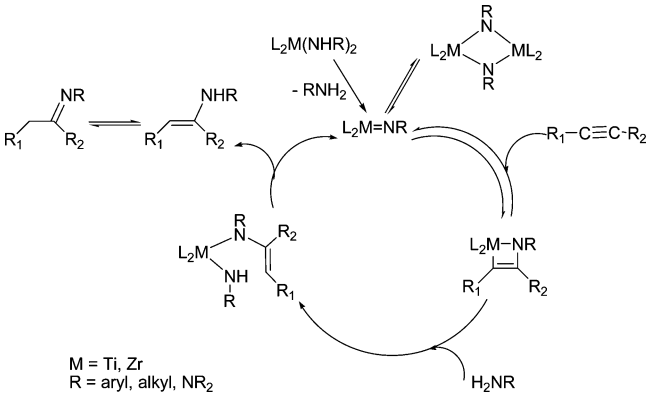
will catalyze intermolecular hydroamination reactions for simple inactivated alkenes.[137−145] A comparison of the already known substrates suitable for the hydroamination reactions shows that both allenes and alkynes contain a carbon with an sp orbital. Looking for additional compounds containing an orbital with a sp charater led to the assumption that methylenecyclopropanes (MCPs) can also be an appropriate substrate for these reactions.



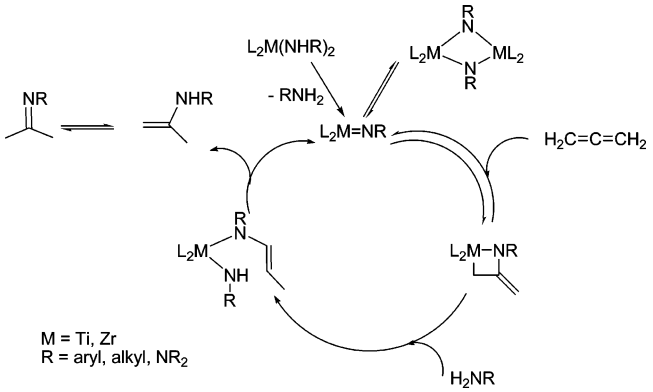

Although MCPs are highly strained compounds, they are remarkably stable and have been tested in hydroamination reactions promoted by late transition metals[94,103,146,147] and lanthanides,[148] producing allylamines and imines, correspondingly. We have recently found that MCP hydroamination can also be performed using the well-designed octahedral titanium catalyst $Ti(Ph_2PNpy)_2(NEt_2)_2$.[149]

However, two main basic questions concerning the MCP's hydroamination reaction remain unanswered. Both of them pertain to the main structural motifs that an organometallic complex should contain in order to function as a catalyst in this process and the possibility of fine-tuning the hydroamination.

**Scheme 1. Simplified Mechanistic Scheme for the Hydroamination of Alkynes**




**Scheme 2. Simplified Mechanistic Scheme for an Allene Hydroamination**




The first question involves the ligands surrounding the metal center. For most alkyne and allene inter- and intramolecular hydroamination reactions promoted by Cp-free catalysts, our catalyst was designed to contain two alkylamido groups and at least one additional ancillary ligand. The roles of the alkylamido groups are involved in the formation of a presumably imido titanium species, as can be seen from both the alkyne and allene hydroamination reaction mechanisms (Schemes 1 and 2).[2] With regard to the generality of the reaction, the first basic question refers to the role of the ancillary ligand in the regio- and chemoselectivity of the reaction. This issue has been recently elegantly investigated by Beller and coworkers, showing the different role of aryloxo and alkoxo ancillary ligands in the titanium-catalyzed intermolecular hydroamination of alkynes.[14] Hence, in order to answer this question regarding the MCP's hydroamination reaction, we present here a thorough study which compares the reactivity and selectivity of a titanium complex having two ancillary ligands, $Ti(Ph_2PNpy)_2(NEt_2)_2$, with that of the homoleptic $Ti(NMe_2)_4$.

The second basic question to be addressed in this study concerns the metal center. We were interested in finding out the impact of switching of the metal center from titanium to zirconium on the reactivity and selectivity of the catalysts in the MCP's hydroamination reaction. To illuminate the question, we present a comparative study between titanium- and zirconium-catalyzed intermolecular hydroamination reactions of MCP's.

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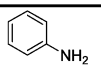
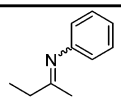
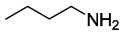
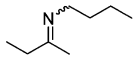
(144) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 9546−9547.
(145) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20*, 1960−1964.
(146) Nakamura, I.; Itagaki, H.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 6458−6459.
(147) Nakamura, I.; Itagaki, H.; Yamamoto, Y. *Chem. Heterocycl. Compd.* **2001**, *37*, 1532−1540.
(148) Ryu, J. S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584−12605.
(149) Smolensky, E.; Kapon, M.; Eisen, M. S. *Organometallics* **2005**, *24*, 5495−5498.

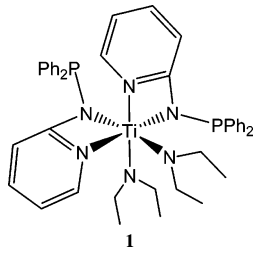
**Table 1. Symmetrical MCP Hydroamination Results with Complex 1 as Precatalyst**

| Entry | Amine | Products (%E : %Z) | Time (h) | Conversion[b] (%) | Isolated Yield[c] (%) | $N_t$[d] ($h^{-1}$) |
|---|---|---|---|---|---|---|
| 1 |  |  **I** (81 : 19) | 36 | 78 | | 1.08 |
| | | | 45 | 95 | 90 | 1.05 |
| 2 |  |  **II** (82 : 18) | 36 | 93 | 90 | 1.29 |
| 3 |  |  **III** (80 : 20) | 36 | 60 | 56 | 0.83 |
| 4 |  |  **IV** (81 : 19) | 36 | 81 | 76 | 1.12 |

[a] All of the hydroamination reactions were performed with 2 mol % catalyst in toluene as the solvent at 110 °C; with low-boiling-point amines, the reactions were performed in heavy-duty glass Schlenk vessels. [b] Determined by following the reaction using $^1$H NMR spectroscopy in toluene-$d_8$. [c] Percent yield of the isolated product. [d] Turnover frequencies ($n_{product}/(n_{cat}$ h)) measured in toluene-$d_8$.

## Results and Discussion

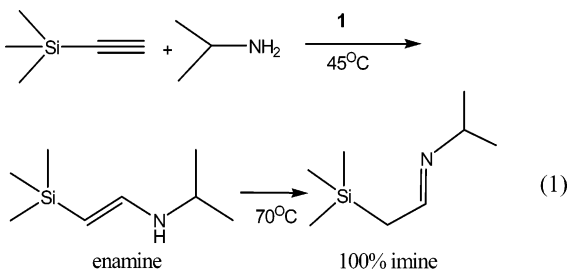
**Ti(Ph$_2$PNpy)$_2$(NEt$_2$)$_2$ (1) as a Catalyst in the Hydroamination Reaction.** The octahedral titanium complex Ti(Ph$_2$PNpy)$_2$(NEt$_2$)$_2$ (**1**; py = pyridine) is a well-characterized compound that was initially designed to contain two non-Cp (Cp = cyclopentadianyl) ancillary ligands and two labile amido groups. The idea was to design a catalyst that, upon activation



**1**

with MAO (methylalumoxane), will have a dynamic behavior toward the formation of elastomeric polypropylene.[150−152] Back in 2002, Bergman,[42,49] Odom,[37,48,51] and Schafer[36] reported on titanium complexes containing two dialkylamido groups and at least one additional ancillary ligand, which were found to be a new generation of catalysts for the hydroamination reaction, all of them performing with high activities and regioselectivities. These researches motivated us to study complex **1** as a suitable active catalyst in the hydroamination reaction.

In order to test complex **1** as a catalyst in the intermolecular hydroamination reaction, 2 mol % of complex **1** was added to an equimolar mixture of (TMS)C≡CH and *i*PrNH$_2$ (eq 1). The

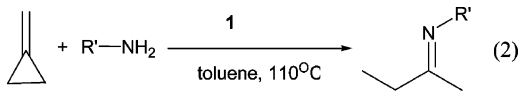


enamine 100% imine (1)

reaction mixture was slowly heated and monitored by NMR spectroscopy, to detect possible intermediates. After the mixture was heated to 45 °C, the enamine intermediate was clearly detected by NMR as the sole product. Heating the reaction mixture up to 70 °C resulted in the formation of the expected imine. The product was obtained in high yield (95%) and excellent selectivity (>99%). NOE-NMR analysis confirmed that the product obtained exhibited *E* stereochemistry.

Catalyst **1** showed high activity and regioselectivity similar to those of the known "*new generation hydroamination catalysts*" toward alkyne hydroamination. Encouraged by the performance of the complex in the hydroamination of alkynes, we decided to expand the substrate scope to MCP's.

Catalyst **1** was found to be an efficient catalyst in MCP hydroamination with either aliphatic amines or small aromatic amines. Table 1 summarizes the results obtained in the hydroamination of a symmetrical MCP with various amines, toward the formation of N-substituted imine products (**I**−**IV**) (eq 2).



(2)

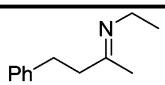
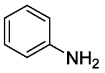
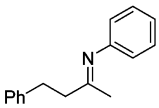
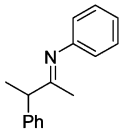
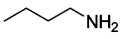
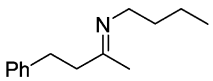
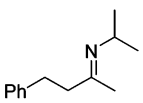
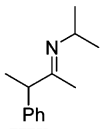
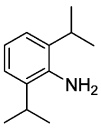
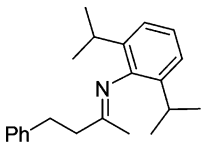
The imines **I**−**IV** were obtained as the single products, with no side reactions. The conversion and the yield in these reactions were found to vary from moderate to high values, and in all cases the isomer with *E* stereochemistry was obtained as the main product. The ratio between the *E* and *Z* forms (80:20) is the same for all the substrates, indicating that the equilibrium among the two stereochemistries is governed by the reaction temperature.

(150) Smolensky, E.; Kapon, M.; Woollins, J. D.; Eisen, M. S. *Organometallics* **2005**, *24*, 3255−3265.

(151) Volkis, V.; Smolensky, E.; Lisovskii, A.; Eisen, M. S. *J. Polym. Sci., A: Polym. Chem.* **2005**, *43*, 4505−4516.

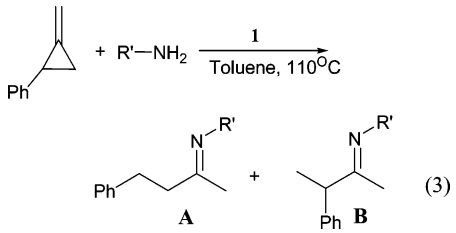
(152) Xavier, K. O.; Smolensky, E.; Kapon, M.; Aucott, S. M.; Woollins, J. D.; Eisen, M. S. *Eur. J. Inorg. Chem.* **2004**, 4795−4802.

**Table 2. Unsymmetrical PhMCP Hydroamination Results with 1 as Precatalyst**

| Entry | Amine | Products (Products distribution) | Time (h) | Conversion[b] (%) | Isolated Yield[c] A (B) (%) | Nt[d] (h-1) |
|---|---|---|---|---|---|---|
| 1 |  |  **V** (100%) | 4 | 38.5 | | 1.93 |
| 2 | | | 40 | 100 | 95 | 0.50 |
| 3 |  |  **VIa** (87%)  **VIb** (13%) | 4 | 73 | | 3.65 |
| 4 | | | 17 | 100 | 83 (10) | 1.15 |
| 5 |  |  **VIIa** (100%) | 20 | 94 | 90 | 6.25 |
| 6 |  |  **IIXa** (84%)  **IIXb** (16%) | 96 | 80 | 62 (8) | 0.41 |
| 7 |  |  **IXa** (100%) | 120 | 24 | | 0.04 |
| 8 | | | 2.5e | 100 | 97 | 0.01 |

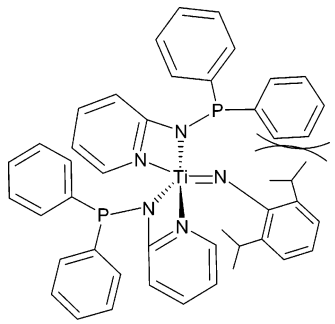
[a] All of the hydroamination reactions were performed with 5 mol % catalyst in toluene as the solvent at 110 °C; with low-boiling-point amines the reactions were performed in heavy-duty glass Schlenk vessels. [b] Determined by following the reaction by $^1$H NMR in toluene-$d_8$. [c] Percent yield of the isolated products. [d] Turnover frequencies ($n_{product}/(n_{cat}$ h)) measured in toluene-$d_8$. [e] Reaction time in months.

For the hydroamination reaction of unsymmetrical MCP's two products were obtained: the linear imine **A** and the branched imine **B** (eq 3).



(3)

The scope and chemo- and regioselectivity of the intermolecular hydroamination of phenylmethylenecyclopropane (Ph-MCP) promoted by complex **1** is summarized in Table 2. As can be seen from Table 2, in all cases, the linear imine product **A** was always obtained as the only or main product. In the intermolecular hydroamination of unsymmetrical MCPs with aliphatic amines, a slightly decreased trend in turnover frequencies ($N_t$) is observed as compared to values for the aromatic amine (entries 2, 4, 6, in addition to entry 5). This result may reflect the increased nucleophilicity of the aliphatic amines, promoting the formation of the bis(amido) species (vide infra). Interestingly, in comparison to organolanthanide complexes, the opposite effect was observed for similar substrates.[148] It is noteworthy that the hydroamination of an ortho-disubstituted amine (entries 7 and 8) is extremely slow, presumably due to the steric hindrance between the ortho substituent of the amine and the diphenylphosphino motif of the ligands, inhibiting the insertion of the olefin into the titanium−imido complex **3** since the ortho substitutes at the amine ring will be disposed preferentially on the plane of the imido moiety.

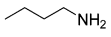
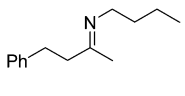
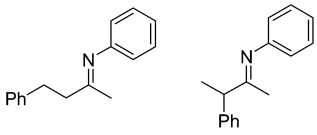
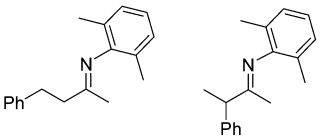
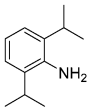
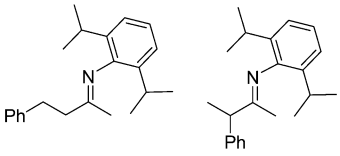
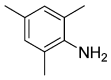
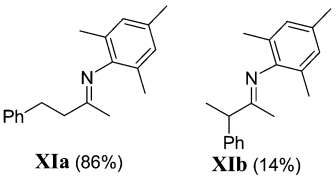


**3** (R = 2,6-disopropylbenzene)

With regard to the stereoselectivity of the reaction, unlike the case for the symmetrical MCP, in every hydroamination reaction of the unsymmetrical MCP, the *E* stereoisomer was the only product obtained.

**Hydroamination of MCP's Promoted by Ti(NMe$_2$)$_4$.** As shown above, catalyst **1** has shown good activity toward the hydroamination of MCP and PhMCP substrates with small aliphatic and aromatic amines, whereas a slower catalytic

**Table 3. PhMCP Hydroamination Results with $Ti(NMe_2)_4$ as Precatalyst**

| Entry | Amine | Products (Products distribution) | Time (h) | Conversion [b] | $N_t$ [c] ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 |  | No reaction | | | |
| 2 |  | No reaction | | | |
| 3 |  |  **VIIa** (90%) **VIIb** (10%) | 100<br>258<br>1100 | 19%<br>25%<br>48% | 0.05 |
| 4 |  |  **VIa** (83%) **VIb** (17%) | 24 | 100% | 5.0 |
| 5 |  |  **Xa** (84%) **Xb** (16%) | 23 | 100% | 6.9 |
| 6 |  |  **IXa** (80%) **IXb** (20%) | 22 | 100% | 7.8 |
| 7 |  |  **XIa** (86%) **XIb** (14%) | 96 | 100% | 3.9 |

[a] All of the hydroamination reactions were performed with 2 mol % catalyst in toluene as the solvent at 110 °C. [b] Determined by following the reaction by $^1H$ NMR in toluene-$d_8$. [c] Turnover frequencies determined at 25% conversion ($n_{product}/(n_{cat}$ h)), measured in toluene-$d_8$.

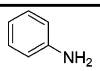
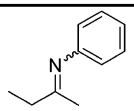
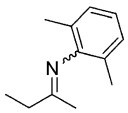
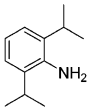
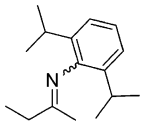
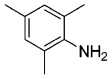
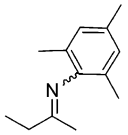
activity was achieved with bulky aromatic amines, due to expected steric hindrance. Therefore, we anticipated that the homoleptic tetrakis(dimethylamido)titanium compound, which probably will not induce such a large steric hindrance of the ancillary ligands, will show a better catalytic efficacy toward the hydroamination of MCPs with bulky aromatic amines. Tables 3 and 4 summarize the results obtained for $Ti(NMe_2)_4$ as a catalyst in the hydroamination reactions of PhMCP and MCP, correspondingly. As can be seen from entries 1−3 in Table 4, $Ti(NMe_2)_4$ showed only slight or no catalytic activity toward the hydroamination of PhMCP with aliphatic amines, as expected, due to the greater nucleophilicity of the aliphatic imines impeding the formation of the metal−imido motif. The reaction of the homoleptic complex with small aliphatic amines rapidly produces an oligomeric solid precipitate that was found to be totally insoluble. However, the reaction of the oligomeric solid with acids produces $TiO_2$. For the bulkier butylamine, while a precipitate was also formed, a slow reaction was also observed. However, as expected, the homoleptic $Ti(NMe_2)_4$ complex was found to be an efficient catalyst for the hydroamination of PhMCP with bulky aromatic amines (entries 4−6, Table 4). Interestingly, for the bulkier ortho-disubstituted aniline similar turnover frequencies for the hydroamination reaction were observed (entries 4−6, Table 4). A comparison of entry 7 with entries 4−6 in Table 4 shows that a para substituent on the aniline ring dramatically decreases the reaction rate, due to the enhanced nucleophilicity of the amine increasing the imido character of the Ti═N bond. Similar observations were recorded in the hydroamination of the symmetric MCP with aromatic amines (Table 3).

Hydroamination of MCP with bulky aromatic amines catalyzed by $Ti(NMe_2)_4$ has allowed us to synthesize new highly steric hindered aromatic imine products (**XII**−**XIV**). It is important to point out that the imine **XII** was reported already as an extremely difficult compound to make.[153] Hence, the catalytic hydroamination of MCP offers an efficient synthetic route to produce bulky imines from simple and commercially available reactants.

Importantly, for both titanium catalysts the main product obtained in all PhMCP hydroamination reaction was the linear product (**A**). A comparison of the results observed in Tables 1 and 2 with those in Tables 3 and 4 demonstrates a strong relationship between the ancillary ligand of the catalytic complex and the suitability of the amine for the hydroamination reaction.

(153) Lai, J. T. *Tetrahedron Lett.* **2002**, *43*, 1965−1967.

**Table 4. MCP Hydroamination Results with $Ti(NMe_2)_4$ as Precatalyst**

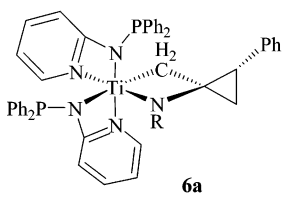
| Entry | Amine | Products (E : Z) | Time [h] | Conversion [b] | $N_t$ [c] [$h^{-1}$] |
|---|---|---|---|---|---|
| 1 |  |  **I** (80 : 20) | 100 | 100% | 2.5 |
| 2 |  |  **XII** (85 :15) | 47 | 100% | 10.4 |
| 3 |  |  **XIII** (87 : 13) | 72 | 100% | 8.3 |
| 4 |  |  **XIV** (85 : 15) | 140 | 100% | 1.14 |

[a] All of the hydroamination reactions were performed with 2 mol % catalyst in toluene as the solvent at 110 °C. [b] Determined by following the reaction by $^1$H NMR in toluene-$d_8$. [c] Turnover frequencies determined at 25% conversion ($n_{product}/(n_{cat}$ h)), measured in toluene-$d_8$.

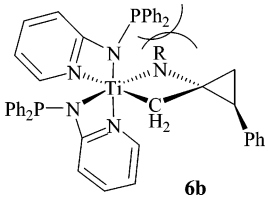
A complex with bulky ancillary ligands is suitable for the hydroamination reaction with aliphatic and small aromatic amines, whereas a complex with small ancillary ligands will allow the hydroamination preferentially of bulky aromatic amines. A similar trend has been previously observed for intermolecular hydroamination of alkynes.[134]

**Plausible Mechanism for MCP Hydroamination Promoted by Titanium Organometallic Complexes.** On the basis of the well-studied mechanisms for the hydroamination of alkynes and allenes promoted by group IV metal complexes,[52,154,155] a plausible mechanism for the intermolecular hydroamination of MCPs, which might explain the obtained products and their distribution, is presented for titanium organometallic complexes (Scheme 3).

The first step of the mechanism is the transformation of complex **1** to complex **2**; this is a fast step, as shown by the immediate changes in color after the addition of the amine to complex **1**. In addition, the evolution of diethylamine is also instantaneously observed, when the reaction is followed by NMR spectroscopy. The concomitant amine elimination from complex **2** produces the active imido complex **3** when the reaction mixture is heated. This complex was found to produce the dimeric complexes **4** and **5** in the absence of MCP. When MCP is present, the concerted 1,2-insertion of the MCP double bond into the Ti═N imido bond results in the formation of the azatitanacyclobutane complex **6** as the rate-determining step.[24,156] Complex **6** may undergo two different ring-opening transformations to form more stable five-membered-ring complexes (**7A** and **7B**). The cleavage of the C2−C3 bond (pathway *a*) will result in the formation of **7A**, whereas the cleavage of the C2−C4 bond (pathway *b*) will induce the formation of complex **7B**. Complex **7A** is more stable than **7B**, since the metal in the former complex is bonded to a benzylic carbon, whereas at the latter complex the metal is bonded to a primary carbon. Therefore, pathway *a* is expected to be the preferential route, as observed from the product distribution in Table 1. Rapid protonolysis of complexes **7A** and **7B** will form the corresponding bis(amido) complexes (**8A** and **8B**). As in the hydroamination of alkynes, we suggest that the associated elimination of the enamines will regenerate the imido complex **3**. Products **A** and **B** will most likely be obtained by the tautomerization of **9A** and **9B**, correspondingly. With regard to regioselectivity, one or two regioisomers are observed (**A** and **B**, eq 3). It is most likely that both isomers are produced via 1,2-addition of the Ti═N into the MCP exo methylene. For the metallacyclic complex **6**, two regioisomers can be expected (**6a** and **6b**).[24] Complex **6a** will be the preferred isomer, due to the lack



**6a**



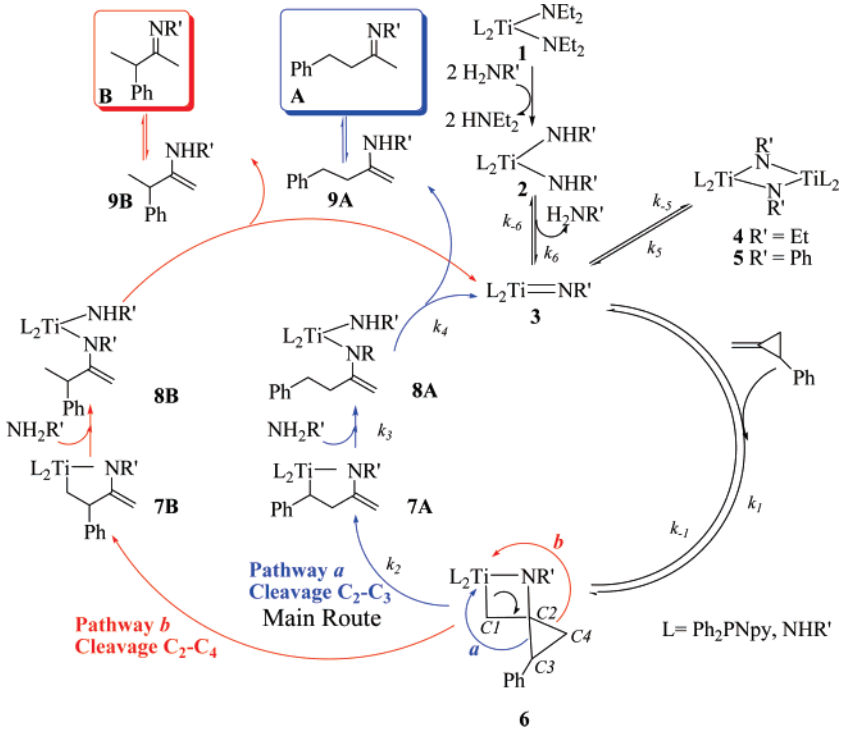
**6b**

of steric hindrance between the amine substituent (R′) and the diphenylphosphine moiety.

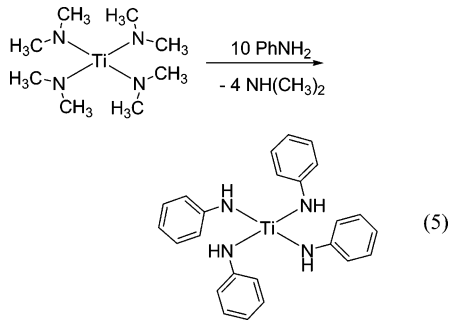
Kinetic calculations for the proposed catalytic cycle shown in Scheme 3 were derived[157] by assuming steady-state conditions for the species **3** and **6**−**8**, since none of them were observed when all the reactions were followed via $^1$H NMR spectrometry at all reaction times. The insertion of the methylene group into the Ti═N bond was assumed to be the slower reaction step. The rate law obtained for this mechanism is presented in eq 4.

$$\frac{d[\text{enamine}]}{dt} = \frac{k_1 k_2 (k_6[2] + k_5[4]^{1/2})[\text{PhMCP}]}{(k_{-1} + k_2)(k_{-6}[\text{amine}] + k_{-5})} \quad (4)$$

**Scheme 3. Proposed Mechanism for the PhMCP Hydroamination Reaction Promoted by Titanium Organometallic Complexes**



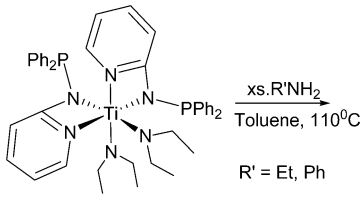

**Trapping Key Intermediates.** To shed some light on the fate of the $Ti(NMe_2)_4$ complex in the first steps of the hydroamination process, its reactivity with various primary amines in a catalyst to amine ratio of 1:10 was studied using NMR spectroscopy. When the amines were added to the $Ti(NMe_2)_4$ solution in toluene-$d_8$, the reaction mixture color changed immediately. Heating the reaction mixture to 110 °C resulted in the formation of a precipitate residue. Monitoring the reaction solution of $Ti(NMe_2)_4$ with $PhNH_2$ by $^1H$ NMR revealed that the singlet signal at $\delta$ 3.1 ppm, corresponding to the four dimethylamido groups, disappears and is replaced with one set of signals for the four exchanged aromatic primary amines (eq 5). FTIR spectroscopy of the precipitate residue

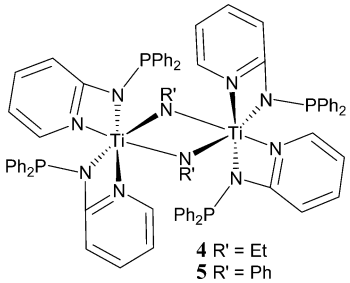



(5)

indicates that the residue contains an N−H bond (band at 3450−3370 $cm^{-1}$ for amine stretching and additional bands at 1460−1619 $cm^{-1}$ for N−H bending). In the formation of the homoleptic complex, the reaction is presumably in equilibrium, since when a lower catalyst to amine ratio, 1:4, was applied, a myriad of complexes were obtained. It was also interesting for us to characterize the same type of reactions with complex **1**.

To shed some light on the fate of the precatalyst **1** in the first steps of the hydroamination process, the reactivity of complex **1** with various primary amines was also studied. The reaction of complex **1** with an excess of ethylamine or aniline produces rapidly the dimeric titanium complexes $Ti_2(Ph_2PNpy)_2(\mu\text{-}NEt)_2$ (**4**)[150] and $Ti_2(Ph_2PNpy)_2(\mu\text{-}NPh)_2$ (**5**),[149] respectively (eq 6).




(6)

The ORTEP plot of complex **5** is shown in Figure 1. In complex **5,** both titanium atoms exhibit an octahedral environment, with N1 and N4 disposed in apical positions. The four-membered ring Ti−N(3)−Ti−N(3)* is totally planar (sum of internal angles 360.0°), although both bridging nitrogen atoms are placed asymmetrically (Ti(1)−N(3) = 2.0117(14) Å; Ti(1)−N(3)# = 1.8794(14) Å). Complex **4** was found to be isostructural with complex **5**.

(154) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719.

(155) Swartz, D. L.; Odom, A. L. *Organometallics* **2006**.

(156) NMR studies of the reaction of 1 equiv of complex **1** with 2 equiv of aniline and 1 equiv of PhMCP show, after a short time of heating (110 °C), the disappearance of the signal (5.50 ppm, doublet of quartets) associated with the exocyclic methylene group of the PhMCP and the appearance of new signals (5.446, 5.455 ppm, two doublets with $^2J_{HH}$ = 4.5 Hz) associated with the $-CH_2-$ group of the azatitanacyclobutane **6**.

(157) The full mathematical derivation of eq 4 can be found in the Supporting Information.

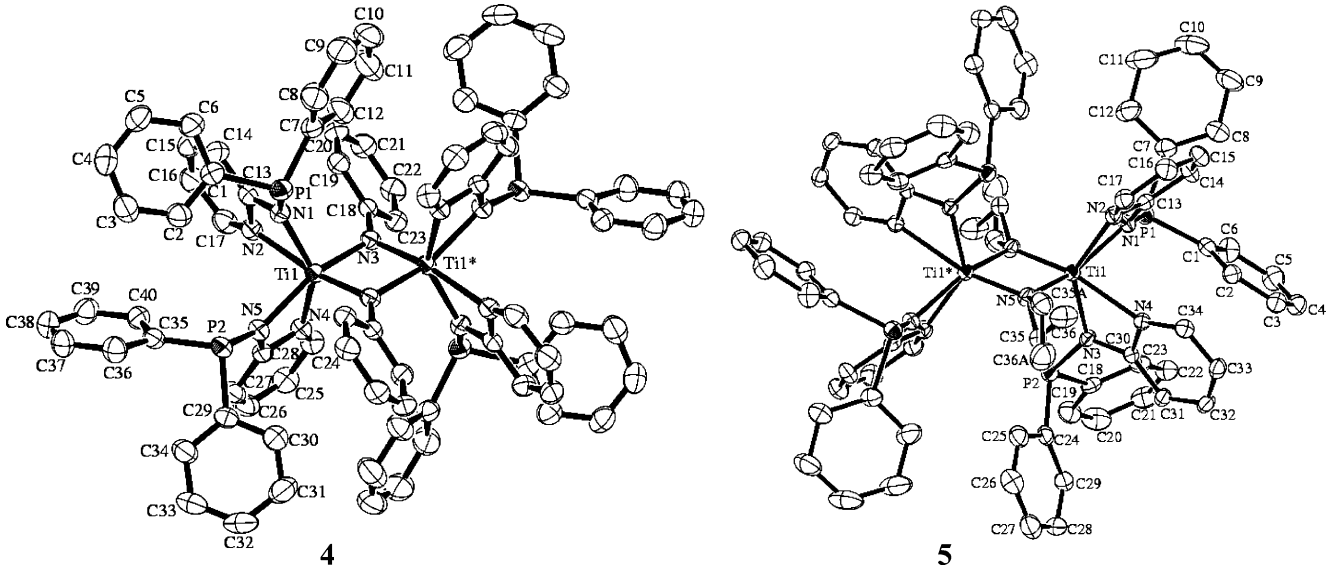



**Figure 1.** ORTEP plot of the structures of the complexes $Ti_2(Ph_2PNpy)_2(\mu\text{-}NEt)_2$ (**4**) and $Ti_2(Ph_2PNpy)_2(\mu\text{-}NPh)_2$ (**5**). Thermal ellipsoids are given at the 50% probability level.

The dimeric complexes **4** and **5** showed only negligible solubility in toluene, even with large solvent volumes and high temperatures. Therefore, we can assume that the transformation of the bis(amido) complex **2** to the corresponding imido complex **3** occurs much more quickly than the cleavage of dimeric complexes **4** and **5** to the corresponding complexes **3** (R′ = Ph, Et). Hence, we can assume that $k_6[\mathbf{2}] \gg k_5[\mathbf{4}]^{1/2}$. Combining this assumption along with eq 4 allows us to obtain a simplified rate law, as presented in eq 7. This rate law suggests a general

$$\frac{\mathrm{d[enamine]}}{dt} = \frac{k_1 k_2 k_6[\mathbf{2}][\mathrm{PhMCP}]}{k_{-5}(k_{-1} + k_2)(k_{-6}[\mathrm{amine}] + k_{-5})} \qquad (7)$$

reaction having first-order dependence in PhMCP, first order in the titanium imido catalyst, and probably an inverse order in the amine.

**Kinetic Studies on the Hydroamination of PhMCP with Aniline Catalyzed by $Ti(NMe_2)_4$.** To test the proposed mechanism, and to learn about the MCP, amine, catalyst, and temperature influences on the reaction rate, kinetic experiments were conducted. Kinetic studies of the $Ti(NMe_2)_4$-catalyzed hydroamination of PhMCP with aniline in toluene-$d_8$ were carried out, followed by in situ $^1$H NMR spectroscopy, using 1,3,5-trimethylbenzene as an internal standard.

To check the influence of the catalyst concentration on the reaction rate, different concentrations of the catalyst $Ti(NMe_2)_4$, within a 10-fold range, were used, while PhMCP and amine concentrations were kept constant. The kinetics of the reaction was monitored using the intensity changes in the substrate resonance (on NMR spectroscopy) over 3 or more half-lives. The rate constant $k_{obs}$ (M $s^{-1}$) was calculated from the pseudolinear part of the plot, showing the product concentration vs time. Figure 2 shows a linear increase of the product formation with an increase of the catalyst concentration until a catalyst to PhMCP ratio of 1:20. For higher catalyst concentrations, a red precipitate of complex **4** was observed in the reaction mixture. This precipitation process limits the catalyst concentration and therefore limits the reaction rate. Thus, the rate of product formation as a function of the catalyst concentration follows a first-order behavior only until its solubility limit.

To check the influence of the PhMCP concentration on the reaction rate, the concentration of PhMCP was varied, over a 10-fold range, while the catalyst and amine concentrations were kept constant. The kinetics of the reaction was monitored using the intensity changes in the substrate PhMCP. The rate constant, $k_{obs}$, was calculated from the pseudolinear part of the plot showing the product concentration vs time (Figure 3). As can be seen from Figure 3, the higher the PhMCP concentration, the faster the hydroamination reaction proceeds in a good linear fitting (Figure 4). Consequently, the kinetic rate law shows a first-order dependence on the PhMCP concentration. This result corroborates the suggested catalytic cycle.

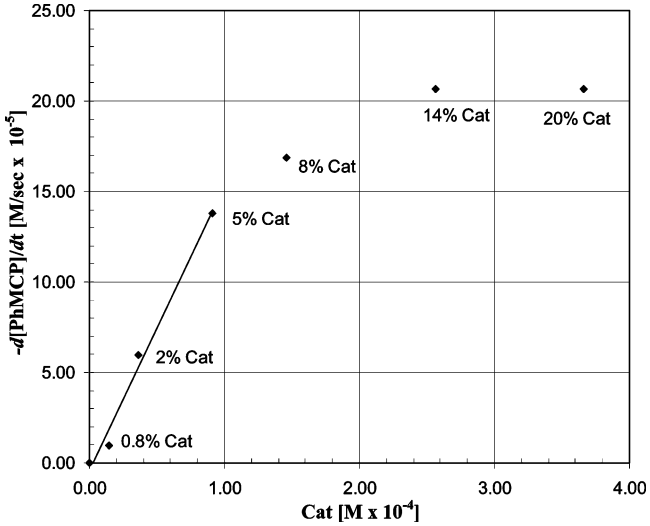



**Figure 2.** Plot of initial concentrations of the catalyst $Ti(NMe_2)_4$ versus pseudo-first-order rate constants for the hydroamination reaction.

The influence of the amine concentration on the reaction rate was studied at different concentrations of amine, within a 10-fold range, while PhMCP and catalyst concentrations were kept constant. For low concentrations of amine (below $10^{-2}$ M), no reaction was observed. In this case, $k_{-5}$ becomes larger than $k_{-6}$[amine] (see eq 7) and, as shown above, the reaction follows the formation of the dimeric complexes (such as complexes **4** and **5**), which are inactive in the hydroamination reaction. For higher amine concentrations, a nonlinear relationship between the rate (d[amine]/d$t$) and amine concentration was observed.

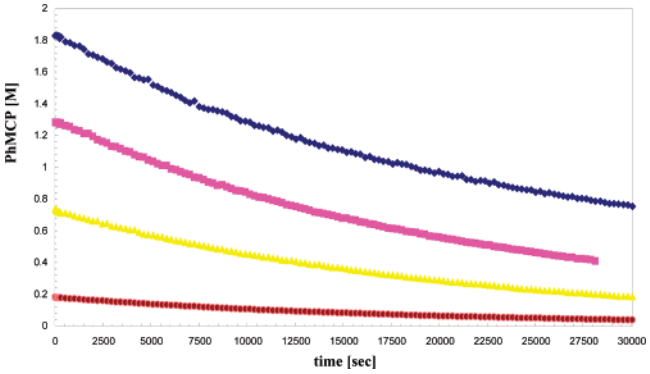



**Figure 3.** Plot of PhMCP concentration as function of time for various initial concentrations of PhMCP measured in toluene-$d_8$ at 110 °C.

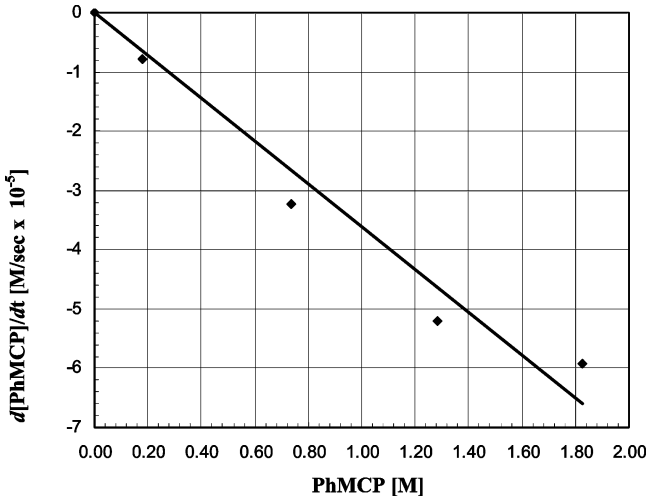



**Figure 4.** Plot of the PhMCP concentrations versus pseudo-first-order rate constants, for the PhMCP hydroamination reaction. The line represents the least-squares fit to the data points.

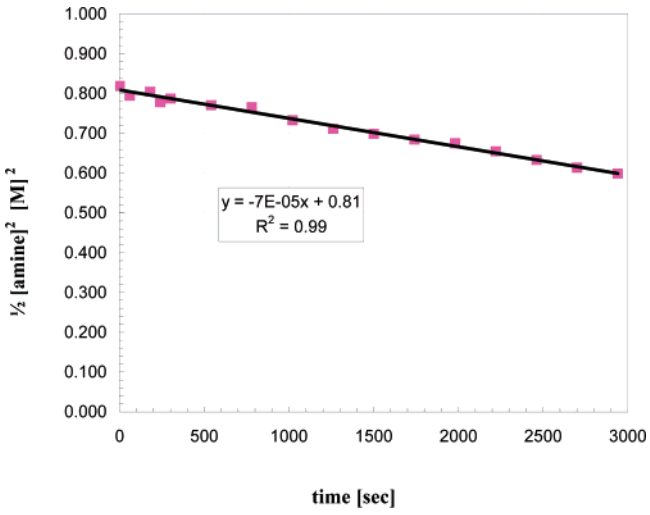



**Figure 5.** Plot of concentration of $^1/_2$[amine]$^2$ versus reaction time for the hydroamination reaction of PMCP promoted by the complex Ti(NMe$_2$)$_4$. The line represents the least-squares fit to the data points.

However, as can be seen from Figure 5, plotting $^1/_2$[amine]$^2$ versus reaction time did show good linear fitting. This is consistent with an inverse order dependence on the amine concentration as presented in eq 8 and its integrated form (eq 9).

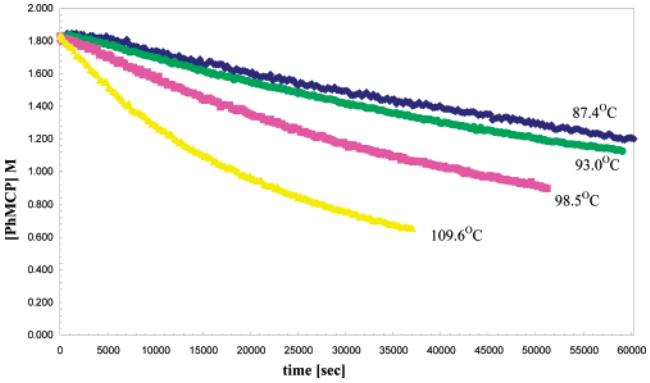



**Figure 6.** Plot of PhMCP concentration as function of time at different temperatures measured for the hydroamination of PhMCP with aniline catalyzed by Ti(NMe$_2$)$_4$ in toluene-$d_8$.

$$-\frac{\mathrm{d[amine]}}{dt} = k_{\mathrm{obs}}\frac{1}{\mathrm{[amine]}} \tag{8}$$

$$^1/_2[\mathrm{[amine]}^2 - \mathrm{[amine]}_0{}^2] = k_{\mathrm{obs}}t \tag{9}$$

The kinetic studies of the hydroamination reaction of PhMCP with aniline catalyzed by Ti(NMe$_2$)$_4$ showed that the reaction is first order in PhMCP, first order in the titanium catalyst, and inverse order in the amine (beyond a minimum concentration). These findings can be summarized as a general rate law, as presented in eq 10. The experimental rate law in eq

$$\mathrm{rate} = k_{\mathrm{obs}}\frac{\mathrm{[cat][PhMCP]}}{\mathrm{[amine]}} \tag{10}$$

10 corroborates with the proposed mechanism shown in Scheme 3 and the theoretical calculated rate law presented in eq 7.

The temperature influence on the reaction rate was also investigated by repeating the same experiment at different temperatures, keeping the concentrations of the catalyst, PhMCP, and amine constant (Figure 6). The rate constant, $k_{\mathrm{obs}}$, was calculated at each temperature from the pseudolinear part of the plot showing the PhMCP concentration as a function of time. From the plot of ln $k_{\mathrm{obs}}$ versus $1/T$ the energy of activation for the rate-determining step was calculated to be $E_a = 19.5 \pm 0.3$ kcal/mol.

The enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) for the rate-determining step was derived from the Eyring equation. $\Delta H^{\ddagger}$ was calculated from the slope of the Eyring plot graph (Figure 7) to be $18.8 \pm 0.4$ kcal/mol, whereas from the intersection the value of $\Delta S^{\ddagger} = -29.2 \pm 0.2$ eu was obtained. This highly negative value of $\Delta S^{\ddagger}$ indicates a highly organized transition state. Thus, the value obtained is consistent with a four-centered transition intermediate, as is encountered in the insertion of the PhMCP's double bond into the titanium−imido bond, corroborating it as the rate-determining step.

**Hydroamination of MCPs Promoted by Zr(NMe$_2$)$_4$.** In order to study the role of the metal center in the MCP hydroamination reactions, we were interested in testing how the replacement of the titanium metal center with zirconium may affect the activity and regioselectivity of the catalysts. It is worth noting that the homoleptic Zr(NMe$_2$)$_4$ was reported previously as an active catalyst for the intramolecular hydroamination of allenes[42] and alkenes.[7] Table 5 summarizes the results

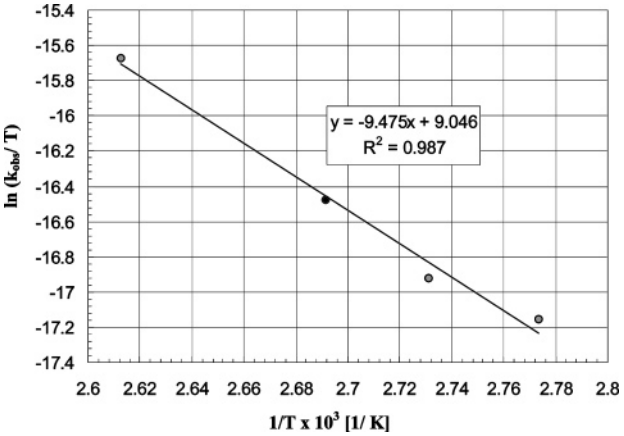
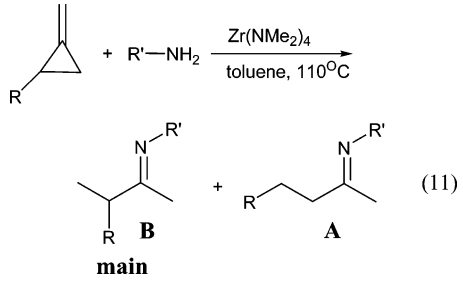



**Figure 7.** Eyring plot for the hydroamination of PhMCP with aniline catalyzed by $Ti(NMe_2)_4$ in toluene-$d_8$. The line represents the least-squares fit to the data points.

obtained for the hydroamination of symmetric MCP with various amines catalyzed by the homoleptic $Zr(NMe_2)_4$. Comparison of the results obtained for $Ti(NMe_2)_4$ (Table 4) with those obtained with $Zr(NMe_2)_4$ (Table 5) indicates that similar tendencies are observed when both isolobal complexes are compared. Both catalysts showed no activity toward aliphatic amines; however, both of them showed high activities for ortho-substituted aromatic amines and a reduced activity for para-substituted amines. Interestingly, the activity of the zirconium complex was found to be much lower (by an order of magnitude) than that of the corresponding titanium, similar to cases reported previously.[42] The results for the hydroamination of PhMCP promoted by the homoleptic $Zr(NMe_2)_4$ are presented in Table 6 (eq 11). For aliphatic amines, similarly to the titanium

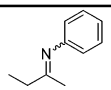
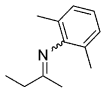
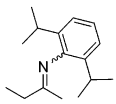
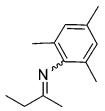



(11)

complex, an oligomeric complex precipitate is formed, and no hydroamination is observed. For the aromatic amines, the reaction proceeds much more slowly than that for the corresponding titanium complex. The most important finding is that the main products obtained with the zirconium complex for those reactions are the branched imines, in contrast to the results obtained when the titanium analogue was utilized (Table 3, eq 11).

Interestingly, we observe that the selectivity in the hydroamination of PhMCP depends on the nature of the metal center. A similar observation has been made by Bergman and co-workers in the intramolecular hydroamination of allenes using bis(sulfonamide) complexes. Hence, a titanium bis(sulfonamide) complex has converted an aminoallene to the six-membered imine product, while the corresponding zirconium complex yielded the corresponding five-membered product.[42] In view of the fact that we are observing different selectivities in the hydroamination of PhMCP for comparable titanium and zirconium complexes, we propose different mechanistic pathways for titanium and zirconium complexes. Since complex **7A** (Scheme 3), which is responsible for the formation of the linear product **A**, is more stable than complex **7B**, we can assume

**Table 5. Data for the MCP Hydroamination Reaction Promoted by $Zr(NMe_2)_4$ as a Precatalyst**

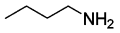
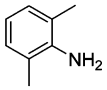
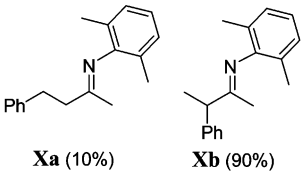
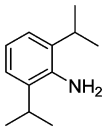
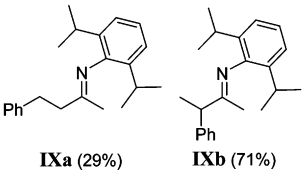
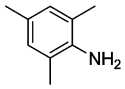
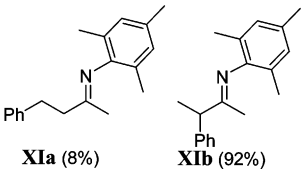
| Entry | Amine | Products (E : Z) | Time (h) | Conversion [b] | $N_t$ [c] ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 |  |  **I** (93 : 7) | 528 | 8.5% | |
| 2 |  |  **XII** (84 :16) | 143 | 91.5% | 0.74 |
| 3 |  |  **XIII** (88 : 12) | 92 | 92% | 4.17 |
| 4 |  |  **XIV** (84 : 16) | 192 | 89% | 0.32 |

[a] All the hydroamination reactions were preformed with 2 mol % catalyst in toluene as the solvent at 110 °C. [b] Determined by following the reaction by $^1H$ NMR in toluene-$d_8$. [c] Turnover frequencies determined at 25% conversion ($n_{product}/(n_{cat}$ h)), measured in toluene-$d_8$.

that the formation of the branched product **B**, as the main product, will not proceed through the cleavage of complex **6** to **7**. As an alternative pathway, we propose that **11**, the zirconium analogue of complex **6**, will first undergo a protonolysis by an additional amine to form the putative complex **12**. Rearrangement of complex **12** will result in the formation of the imido zirconium complex and the corresponding enamines, which will rapidly tautomerize to the imine products (Scheme 4). In this proposed mechanism, both isomers can be obtained. However, pathway b is now preferred, since the amine will react with the cyclopropyl ring mainly via the opposite side of the phenyl ring; therefore, the branched products are obtained as the main products. As compared to Scheme 3, the protonolysis is expected to occur preferentially at the zirconium center rather than at the titanium center, due to the larger ionic radii of the former as compared to that of the latter. Of course, it is possible that both schemes are operative simultaneously, each one producing the preferred product.

**Synthesis and Characterization of the Complex $Zr(Ph_2PNpy)_3NEt_2$ (13).** In order to synthesize the zirconium analogue of complex **1**, 2 equiv of the neutral ligand $Ph_2PNHpy$ (L-H) was reacted with 1 equiv of the homoleptic complex $Zr(NEt_2)_4$. Recrystallization of the resulting complex showed that, instead of the desired $L_2Zr(NEt_2)_2$ complex, we have obtained a zirconium complex containing three ancillary ligands L and only one amido group. The single-crystal X-ray diffraction studies of the obtained complex **13** show that the metal is disposed in a distorted-pentahedral-bipyramidal environment. Seven nitrogen atoms are bonded to the zirconium metal center. The diethylamido nitrogens N(7) and N(6) are located at the axial positions (N(6)−Zr(1)−N(7) = 146.52(19)°), and the ligand nitrogens N(1), N(2), N(3), N(4), and N(5) are located at the equatorial positions (the total sum of the angles is equal to 363.1°). There are three different Zr−N bond lengths. The Zr−N(diethylamido) bond (Zr(1)−N(7) = 2.018(4) Å) is shorter than any of the Zr−N(phosphinoamido) bond lengths (Zr(1)−N(5) = 2.324 Å, Zr-

**Table 6. Data for the PhMCP Hydroamination Reaction Promoted by $Zr(NMe_2)_4$ as a Precatalyst**

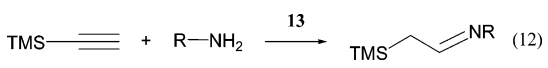
| Entry | Amine | Products (Products distribution) | Time (h) | Conversion [b] | $N_t$ [c] ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 |  | No reaction | | | |
| 2 |  | No reaction | | | |
| 3 |  | No reaction | | | |
| 4 |  | No reaction | | | |
| 5 |  |  **Xa** (10%) **Xb** (90%) | 145 | 92% | 0.48 |
| 6 |  |  **IXa** (29%) **IXb** (71%) | 215 | 100% | 0.42 |
| 7 |  |  **XIa** (8%) **XIb** (92%) | 380 | 89% | 0.30 |

[a] All of the hydroamination reactions were performed with 2 mol % catalyst in toluene as the solvent at 110 °C; with low-boiling-point amines the reactions were performed in heavy-duty glass Schlenk vessels. [b] Determined by following the reaction by $^1$H NMR in toluene-$d_8$. [c] Turnover frequencies determined at 25% conversion ($n_{product}/(n_{cat}$ h)), measured in toluene-$d_8$.

(1)−N(1) = 2.342 Å, Zr(1)−N(3) = 2.345 Å) or the Zr−N(pyridine) bond lengths (Zr(1)−N(2) = 2.240 Å, Zr(1)−N(4) = 2.247 Å, Zr(1)−N(6) = 2.253 Å) (Figure 8).

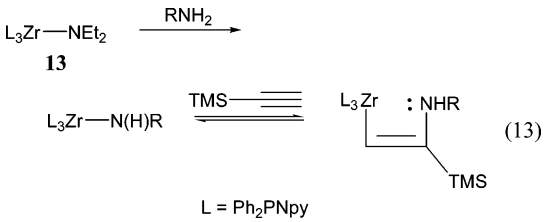
All attempts to synthesize the desired $L_2Zr(NEt_2)_2$ structure were unsuccessful. This result indicates that the replacement of the third diethylamido group at the larger zirconium atom occurs too fast to be controlled. This result suggests that the equilibrium replacement of the third ligand lies strongly toward the formation of complex **13**.

**Hydroamination Reaction Catalyzed by the Complex Zr-($Ph_2PNpy)_3NEt_2$ (13).** As can be seen from the unsuccessful attempts to synthesize the bis(amido) zirconium complex $L_2$-$Zr(NEt_2)_2$, complex **13** cannot be directly transformed into the bis(amido) complex, even in the presence of excess amine. Therefore, we assume that if complex **13** were to be active in the hydroamination reaction, since the imido zirconium complex Zr═NR would not be generated from **13**, a mechanism similar to that encountered for a cationic uranium complex or recently for constrained-geometry organoactinides would be operative.[59,158,159] Complex **13** was found to be an active catalyst in the intermolecular hydroamination of alkynes (eq 12). The results for the hydroamination reaction of (trimethylsilyl)-acetylene are summarized in Table 7. However, as can be seen from Table 7, catalyst **13** showed a very low catalytic activity as compared to complex **1**. In order to obtain higher conversions (>99%), a larger amount of the catalyst and longer reaction times were required, as presented in entries 2 and 3 in Table 7.



(12)

In a previous report, we showed that the cationic uranium complex $[(Et_2N)_3U][BPh_4]$ mediates the addition of secondary amine to alkynes.[59] This transformation can be obtained only through an insertion of an unsaturated carbon−carbon bond into a U−NHR bond. Since the Zr═NR complex was not generated by the reaction of complex **13** with an excess of primary amine, we expected that if the hydroamination of an alkyne catalyzed by complex **13** were to proceed, it would be operative via a $\sigma$-bonded Zr−N(H)R species (eq 13).

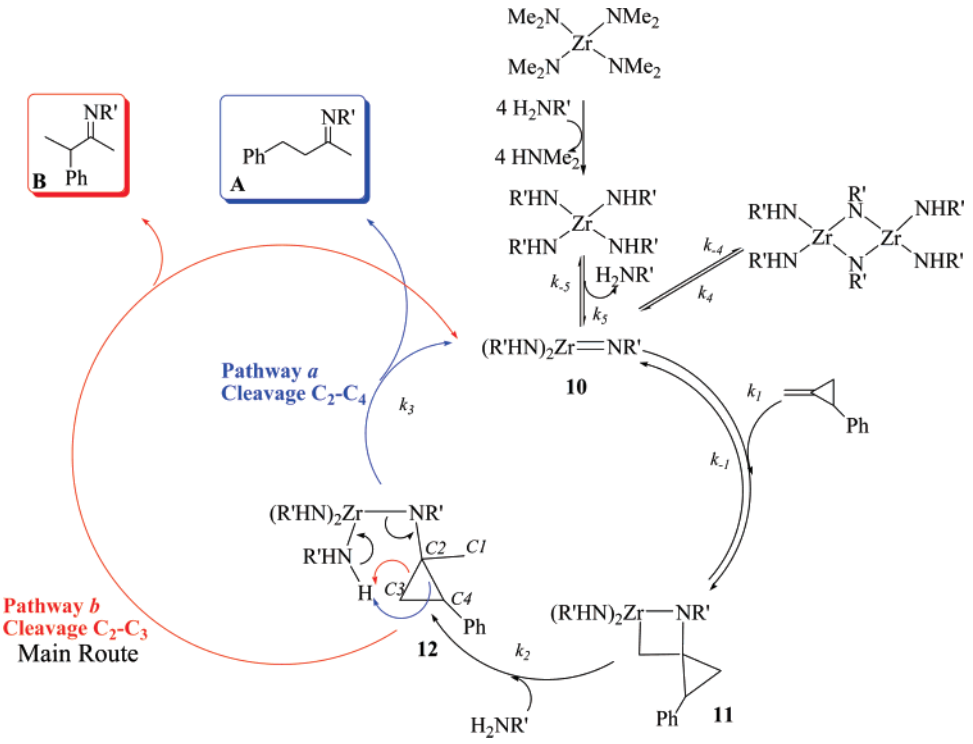


(13)

The slow catalytic activity of complex **13** in the hydroamination of an alkyne and the failure of complex **13** to carry out the hydroamination of secondary amines indicate that presum-

(158) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149.
(159) Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 4253−4271.

**Scheme 4. Proposed Mechanism for the Hydroamination of PhMCP Promoted by $Zr(NMe_2)_4$**




ably a very small catalytic amount of the bis(amido) species is formed in the presence of the alkyne, which must be responsible for the catalysis. Complex **13** was also found to be inactive for the hydroamination of MCP. Presumably, in the hydroamination of MCP a more coordinative unsaturated complex is required to allow a stronger coordination to the double bond as compared to that of the terminal alkynes. We believe that different ligand environments should allow tailoring the catalytic activity of these complexes to induce the hydroamination reaction with secondary amines.

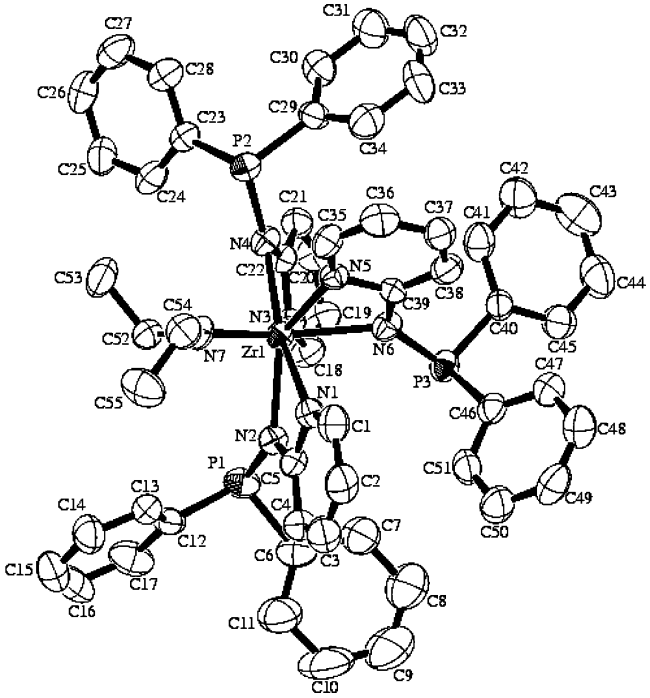



**Figure 8.** ORTEP plot of the structure of the complex $Zr(Ph_2PNpy)_3NEt_2$ (**13**). Thermal ellipsoids are given at the 50% probability level.

**Table 7. Catalytic Hydroamination of (TMS)C≡CH and $RNH_2$ Promoted by Complex 13**

| entry no. | amt of **13** (mol %) | R on $RNH_2$ | reacn time (days) | $N_t$ $(h^{-1})^a$ | conversion (%)$^b$ |
|---|---|---|---|---|---|
| 1 | 2 | Ph | 9 | 0.018 | 8 |
| 2 | 2 | Et | no reacn | | |
| 3 | 10 | Et | 20 | 0.020 | >99 |

$^a$ Turnover frequencies ($n_{product}/(n_{cat}$ h)). $^b$ Determined by following the reaction by $^1$H NMR in toluene-$d_8$ at 110 °C.

## Conclusions

In this research the hydroamination of symmetrical and unsymmetrical MCPs promoted by group IV catalysts was studied. The goals of this research were to answer two main questions: (i) the effect of the ligands surrounding the metal centerr and (ii) the influence of the metal center. With regard to the first question, a strong relationship was found between the ancillary ligand at the catalytic complex and the suitability of the amine for the MCP hydroamination reaction. A complex with a bulky ancillary ligand is suitable for the hydroamination of aliphatic amines and small aromatic amines, whereas a complex with a small ancillary ligand (steric hindrance) will allow the hydroamination of MCPs with bulky aromatic amines.

The second basic question that was addressed in this study was the metal center. We have found that titanium catalysts will promote the formation of linear imines **A**, while the main products obtained for those reactions catalyzed by the analogous zirconium complex are the branched imines **B**. The mechanism of the MCP hydroamination reaction was studied using kinetic measurements and synthesis of intermediates.

## Experimental Section

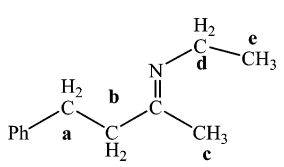
**General Remarks.** All manipulations of air-sensitive materials were carried out with the vigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line or interfaced to a high-vacuum ($10^{-6}$ Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity

recirculator (1−2 ppm of $O_2$). Argon and nitrogen were purified by passage through an MnO oxygen removal column and a Davison 4 Å molecular sieve column. Toluene-$d_8$ and $Et_2O$ were freshly distilled under argon from Na−K alloy. The reagent 2-phenylmethylenecyclopropane was purchased from Merck and was vacuum-distilled from $CaH_2$. Methylenecyclopropane (Aldrich) was dried over Na−K and freshly distilled. Aniline, isopropylamine, butylamine, and 2,6-diisopropylaniline (Aldrich) were distilled from barium oxide and stored over activated molecular sieves (4 Å). Ethylamine (Aldrich) was degassed and freshly vacuum-distilled. 2,6-Dimethylaniline and 2,4,6-trimethylaniline (Aldrich) were vacuum-distilled from KOH. Tetrakis(dimethylamido)titanium and tetrakis(dimethylamido)zirconium (Aldrich) were stored in a glovebox and used as received. Complex **1** was prepared by following procedures given in the literature.[150] NMR spectra were recorded on Avance-300 and Avance-500 spectrometers. Chemical shifts for $^1$H NMR and $^{13}$C NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. The NMR experiments were conducted with sealed-tube Schlenk vessels (J. Young stopcock). GCMS spectra were recorded on a Finigan MAT TSQ 700 instrument equipped with a DB5 MS column (length 30 m, internal diameter 0.25 mm, phase thickness 0.25 $\mu$m). IR spectra were recorded on a Bruker Vector 22 instrument. Samples for IR measurement were prepared with KBr inside the glovebox.

**Hydroamination of TMSC≡CH with i-PrNH$_2$ by Ti(Ph$_2$PNpy)$_2$(NEt$_2$)$_2$ (1).** In a glovebox, 0.1 g (0.134 mmol) of the precatalyst **1** was loaded into a heavy-duty glass Schlenk tube containing 5 mL of toluene and 0.96 mL (6.7 mmol) of TMSC≡CH. Approximately 1 mL (6.7 mmol) of iPrNH$_2$ was vacuum-transferred into the tube. The tube was heated by means of a thermostated oil bath (±0.1 °C) to 45 °C for 3 days and for 70 °C for another week to obtain 95% conversion and 100% of the product. The product was characterized by comparison of $^1$H and $^{13}$C NMR spectra to published data.[62]

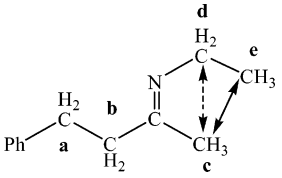
**General Procedure for the Intermolecular MCP Hydroamination Reaction.** In a typical procedure, the specific amount of MCP and an equimolar amount of the respective amine were loaded into a Schlenk vessel containing a solution of the catalyst in 3 mL of toluene-$d_8$. Low-boiling-point amines (ethylamine and isopropylamine) were loaded into a heavy-duty glass Schlenk vessel by vacuum transfer. The Schlenk vessel was heated by means of a thermostated oil bath to 110 ± 0.1 °C, over a particular amount of time. The reaction was monitored by $^1$H NMR. The products were isolated and then identified by $^1$H, $^{13}$C, and 2D (COSY, HMBC, HMQC) NMR spectroscopy. The stereochemistry around the nitrogen atom was determined by $^1$H-NOE NMR experiments. Conversion was determined by $^1$H NMR analysis; product distribution was determined by GC analysis. The product structures were confirmed by GCMS analyses. The *E* and *Z* stereochemistry was determined by $^1$H NOE experiments.

**Characterization of *N*-(4-Phenylbutane-2-ylidene)ethanamine (Va).** The product **Va** (CAS registry no. 35021-89-7) was reported previously,[160] but to our knowledge, NMR and MS data have not been reported, and therefore, we present the data here.



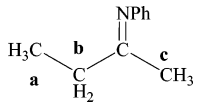

$^1$H NMR (300 MHz, toluene-$d_8$): $\delta$ 1.23 (t, 3H, $^3J_{HH}$ = 7.2 Hz, *H*(e)), 1.38 (s, 3H, *H*(c)), 2.33 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(b)), 2.87 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(a)), 3.40 (q, 2H, $^3J_{HH}$ = 7.2 Hz, *H*(d)), 6.85−7.14 (Ph). $^{13}$C NMR (125 MHz, toluene-$d_8$): $\delta$ 15.7 (*C*(c)), 16.7 (*C*(e)), 32.5 (*C*(a)), 43.8 (*C*(b)), 45.6 (*C*(d)), 126−132 (Ph).

The stereochemistry was confirmed by a $^1$H NOE experiment. H(e) shows a NOE correlation with H(c), at $\delta$ 1.23 ppm. H(c) at $\delta$ 1.38 ppm exhibited a strong NOE correlation with H(e) at $\delta$ 1.23 ppm, and a weak NOE correlation with H(d) at $\delta$ 3.40 ppm. No NOE correlation was found between H(a) at $\delta$ 2.87 ppm and H(e) at $\delta$ 1.23 ppm or H(d) at $\delta$ 3.40 ppm, which confirmed the *E* isomer:




GC/MS (EI): *m*/*z* 175 ($M^+$), 160 ($M^+ - CH_3$), 146 ($M^+ - CH_2CH_3$), 132 ($M^+ - C_3H_8$), 105 ($M^+ - C(CH_3)$═NEt), 91 ($CH_2Ph$), 84 ($M^+ - CH_2C(CH_3)$═NEt), 77 (Ph), 70 ($M^+ - N$═$CCH_2CH_2Ph$).

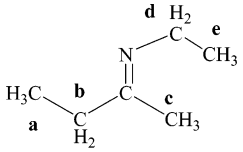
**Characterization of *N*-(Butan-2-ylidene)benzenamine (I).** The product **I** (CAS registry no. 40296-03-5) was reported previously,[16,161−165] but to our knowledge, NMR and MS data have not been reported, and therefore we present the data here.




*E* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 1.12 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 1.43 (s, 3H, *H*(c)), 2.12 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 6.3−7.2 (Ph); $^{13}$C NMR (125 MHz, toluene-$d_8$) $\delta$ 10.1 (*C*(a)), 18.7 (*C*(c)), 34.2 (*C*(b)); GC/MS (CI): *m*/*z* 147 ($M^+$), 132 ($M^+ - CH_3$), 118 ($M^+ - CH_2CH_3$).

Z stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 0.74 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.86 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 1.92 (s, 3H, H(c)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 11.3 (C(a)), 24.8 (C(c)), 26.9 (C(b)).

**Characterization of *N*-(Butan-2-ylidene)ethanamine (II).** The product **II** (CAS registry no. 55007-49-3) was reported previously,[166] but to our knowledge, NMR data have not been reported, and therefore we present the data here.

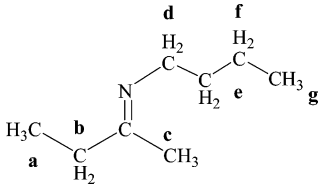



*E* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 1.06 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 1.24 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(e)), 1.42 (s, 3H, *H*(c)), 2.07 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 3.14 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(d)); $^{13}$*C*{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 10.5 (*C*(a)), 16.2 (*C*(a)), 16.3 (*C*(c)), 35.2 (*C*(b)), 45.5 (*C*(d)).

(160) Warren, R. G.; Chow, Y.; Ferguson, L. N. *J. Chem. Soc. D: Chem. Commun.* **1971**, 1521−1522.
(161) Martorell, A.; Claver, C.; Fernandez, E. *Inorg. Chem. Commun.* **2000**, *3*, 132−135.
(162) Brunel, J. M.; Buono, G. *Synlett* **1996**, 177−8.
(163) Cho, B. T.; Chun, Y. S. *Tetrahedron: Asymmetry* **1992**, *3*, 1583−90.
(164) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G. J.; Rettig, S. J. *Inorg. Chem.* **1991**, *30*, 5002−5008.
(165) Cho, B. T.; Chun, Y. S. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3200−3201.
(166) Roubineau, A.; Pommier, J. C. *Sci. Chim.* **1974**, *279*, 953−956.

Z stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 0.79 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 0.91 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(e)), 1.84 (s, 3H, H(c)), 1.86 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 2.51 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(d)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 10.7 (C(a)), 19.2 (C(e)), 24.2 (C(b)), 26.0 (C(c)), 37.0 (C(d)).

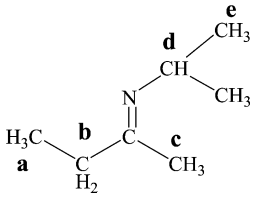
**Characterization of *N*-(Butan-2-ylidene)butanamine (III).** The product **III** (CAS registry no. 20764-17-4) was reported previously,[167−172] but to our knowledge, NMR and MS data have not been reported, and therefore we present the data here.



*E* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 0.94 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(g)), 1.06 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.44 (sextet, 2H, $^3J_{HH}$ = 7.5 Hz, H(f)), 1.46 (s, 3H, H(c)), 1.66 (quint, 2H, $^3J_{HH}$ = 7.5 Hz, H(e)), 2.09 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 3.13 (t, 2H, $^3J_{HH}$ = 7.5 Hz, H(d)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 9.5 (C(a)), 13.0 (C(g)), 13.1 (C(c)), 19.2 (C(f)), 33.0 (C(e)), 41.3 (C(b)), 50.1 (C(d)); GC/MS (CI) m/z 127 ($M^+$), 112 ($M^+ - CH_3$), 98 ($M^+ - CH_2CH_3$), 84 ($M^+ - CH_2CH_2CH_3$), 70 ($M^+ - C_4H_9$).

*Z* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 0.82 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 0.99 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(g)), 1.44 (sextet, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(f)), 1.66 (quint, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(e)),1.85 (s, 3H, *H*(c)), 1.92 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 3.17 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(d)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 9.7 (*C*(a)), 15.5 (*C*(g)), 23.7 (*C*(b)), 25.1 (*C*(c)), 34.3 (*C*(e)), 49.4 (*C*(d)).

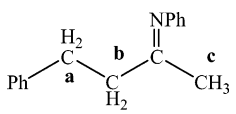
**Characterization of *N*-(Butan-2-ylidene)isopropylamine (IV).** The product **IV** (CAS registry no. 33836-39-4) was reported previously,[161,173] but to our knowledge, NMR data have not been reported, and therefore we present the data here.



*E* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 1.04 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 1.06 (d, 6H, $^3J_{HH}$ = 6 Hz, *H*(e)), 1.45 (s, 3H, *H*(c)), 2.05 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 3.48 (sept, 1H, $^3J_{HH}$ = 6 Hz, *H*(d)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 9.6 (*C*(a)), 15.0 (*C*(c)), 22.9 (*C*(e)), 34.3 (*C*(b)), 49.5 (*C*(d)).

*Z* stereoisomer: $^1$H NMR (500 MHz, toluene-$d_8$) $\delta$ 0.8 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 1.06 (d, 6H, $^3J_{HH}$ = 6 Hz, *H*(e)), 1.81 (s, 3H, *H*(c)), 1.91 (q, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 3.07 (sept, 1H, $^3J_{HH}$ = 6 Hz, *H*(d)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$) $\delta$ 10.6 (*C*(a)), 23.0 (*C*(e)), 23.4 (*C*(b)), 25.3 (*C*(c)), 49.0 (*C*(d)).

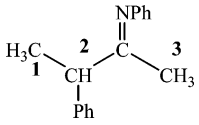
**Characterization of *N*-(4-Phenylbutan-2-ylidene)benzenamine (VIa).** The products **VIa** (CAS registry no. 334709-21-6) was reported previously,[12] but to our knowledge, NMR and MS data have not been reported, and therefore we present the data here.



**15a**

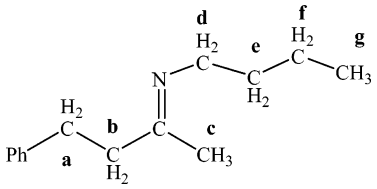
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.41 (s, 3H, *H*(c)), 2.41 (dd, 2H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 7.7 Hz, *H*(b)), 2.94 (dd, 2H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 7.7 Hz, *H*(a)), 6.3−7.3 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 19.6 (*C*(c)), 32.3 (*C*(a)), 42.7 (*C*(b)), 115−132 (Ph). GC/MS (CI): *m*/*z* 147 ($MH^+ - Ph$), 131 ($MH^+ - CH_2Ph$), 118 ($MH^+ - CH_2CH_2Ph$), 105 ($MH^+ - C(CH_3)$(=NPh)), 91 ($M^+ - CH_2C(CH_3)$(=NPh)), 77 ($M^+ - (CH_2)_2C(CH_3)$(=NPh)).

**Characterization of *N*-(3-Phenylbutan-2-ylidene)benzenamine (VIb).** The product **VIb** (CAS registry no. 94660-15-8) was reported previously,[174] but to our knowledge, NMR and MS data have not been reported, and therefore we present the data here.



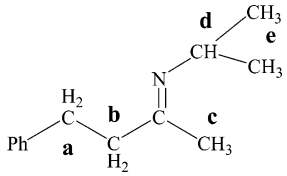
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.39 (s, 3H, *H*(3)), 1.52 (d, 3H, $^3J_{HH}$ = 4.2 Hz,-*H*(1)), 3.45 (q, 1H, $^3J_{HH}$ = 4.2 Hz, *H*(2)), 6.3−7.3 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 18.4 (*C*(1)), 19.3 (*C*(3)), 50.8 (*C*(2)), 115−132 (Ph). GC/MS (CI): *m*/*z* 224 ($MH^+$), 223 ($MH^+ - H$) 146 ($MH^+ - Ph$), 131 ($MH^+ - CHPh$), 118 ($MH^+ - CH(CH_3)Ph$), 104 ($MH^+ - C(CH_3)$=NPh), 91 ($CH_2$-Ph), 77 (Ph).

**Characterization of *N*-(4-Phenylbutan-2-ylidene)butanamine (VIIa).**



$^1$H NMR (300 MHz, toluene-$d_8$): $\delta$ 0.94 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(g)), 1.39 (sext, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(f)), 1.41 (s, 3H, *H*(c)), 1.63 (quint, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(e)), 2.37 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(b)), 2.86 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(a)), 3.12 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(d)), 7.02−7.14 (Ph). $^{13}$C-{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 14.3 (*C*(g)), 17.2 (*C*(c)), 20.3 (*C*(f)), 32.5 (*C*(a)), 33.8 (*C*(e)), 43.9 (*C*(b)), 51.1 (*C*(d)), 126−132 (−Ph). GC/MS (CI): *m*/*z* 203 ($M^+$), 188 ($M^+ - CH_3$), 174 ($M^+ - CH_2CH_3$), 160 ($M^+ - CH_2\ CH_2CH_3$), 146 ($M^+ - C_4H_9$), 132 ($M^+ - C_4H_9N$), 126 ($M^+ - Ph$), 112 ($M^+ - CH_2Ph$), 105 ($CH_2CH_2Ph$), 98 ($M^+ - CH_2CH_2Ph$), 91 ($CH_2Ph$), 77 (Ph), 70 ($C_4H_9N$).

**Characterization of *N*-(4-Phenylbutan-2-ylidene)isopropylamine (VIIIa).**



$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.06 (d, 6H, $^3J_{HH}$ = 6 Hz, *H*(e)), 1.42 (s, 3H, *H*(c)), 2.31 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(b)), 2.85 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.0 Hz, *H*(a)), 3.49 (sept, 1H, $^3J_{HH}$ = 6 Hz, *H*(d)), 6.95−7.18 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 16.7 (*C*(c)), 23.9 (*C*(e), 32.5 (*C*(a)), 43.8 (*C*(b)), 124−142 (Ph), 163.5 (*C*(d)). GC/MS (CI): *m*/*z* 189 ($M^+$), 174 ($M^+ - CH_3$), 146 ($M^+ - NC_2H_6$), 132 ($M^+ - NC_3H_7$), 126 ($M^+ - Ph$), 98 ($M^+ - CH_2Ph$), 91 ($CH_2Ph$), 77 (Ph).

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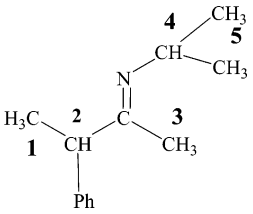
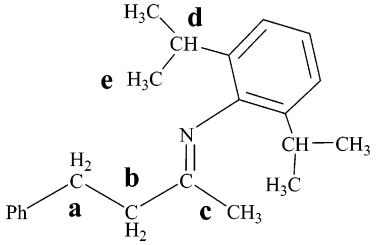
**Characterization of *N*-(3-Phenylbutan-2-ylidene)isopropylamine (VIIIb).**



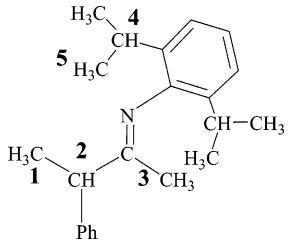
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.01 (d, 6H, $^3J_{HH}$ = 5.5 Hz, *H*(5)), 1.38 (s, 3H, *H*(3)), 1.66 (d, 3H, $^3J_{HH}$ = 5 Hz, *H*(1)),3.35 (q, 1H, $^3J_{HH}$ = 5 Hz, *H*(2)), 3.51 (sept, 1H, $^3J_{HH}$ = 5.5 Hz, *H*(4)), 6.95−7.18 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 15.6 (*C*(3)), 15.7 (*C*(5)), 19.3 (*C*(1)), 50.5 (*C*(2)), 124−142 (Ph). GC/MS (CI): *m*/*z* 189 ($M^+$), 174 ($M^+ - CH_3$), 131 ($M^+ - NC_3H_6$).

**Characterization of *N*-(4-Phenylbutan-2-ylidene)-2,6-diisopropylbenzenamine (IXa).**



$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.43 (d, 12H, $^3J_{HH}$ = 7 Hz, *H*(e)), 1.37 (s, 3H, *H*(c)), 2.48 (sept, 2H, $^3J_{HH}$ = 7 Hz, *H*(d)), 2.53 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 2.97 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 6.8−7.14 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 20.2 (*C*(c)), 22.6 (*C*(e), 32.1 (*C*(a)), 41.7 (*C*(b)), 119−132 (Ph), 164.5 (*C*(d)). GC/MS (CI): *m*/*z* 307 ($M^+$), 292 ($M^+ - CH_3$), 264 ($M-CH(CH_3)_2$), 202 ($M^+ - CH_2CH_2Ph$), 91 ($CH_2Ph$), 77 (Ph).

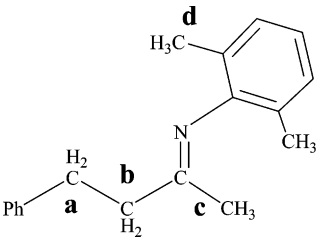
**Characterization of *N*-(4-Phenylbutan-2-ylidene)-2,6-diisopropylbenzenamine (IXb).**



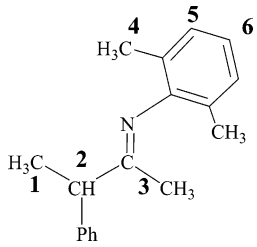
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.01 (d, 3H, $^3J_{HH}$ = 7 Hz, *H*(5)), 1.15 (d, 3H, $^3J_{HH}$ = 7 Hz, *H*(5′)), 1.34 (s, 3H, *H*(3)), 1.56 (d, 3H, $^3J_{HH}$ = 7 Hz, *H*(1)), 2.76 (sept, 1H, $^3J_{HH}$ = 7 Hz, *H*(4)), 2.86 (sept, 1H, $^3J_{HH}$ = 7 Hz, *H*(4′)), 3.52 (q, 1H, $^3J_{HH}$ = 7 Hz, *H*(2)), 7.02−7.16 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 17.8 (*C*(1)), 18.0 (*C*(3)), 21.5 (*C*(5)), 22.7 (*C*(5′)), 27.1 (*C*(4)), 27.5 (*C*(4′)), 49.7 (*C*(2)), 122−128 (Ph). HRMS (EI): *m*/*z* found 307.2292, calculated 307.2300.

**Characterization of *N*-(4-Phenylbutan-2-ylidene)-2,6-dimethylbenzenamine (Xa).**

$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.29 (s, 3H, *H*(c)), 1.88 (s, 6H, *H*(d)), 2.50 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 2.95 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 6.95 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, *H*(e)), 6.92−7.17 (Ph + *H*(f)). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 17.2 (*C*(d)), 18.7 (*C*(c), 31.4 (*C*(a)), 40.8 (*C*(b)), 121.7 (*C*(e)), 125.3 (*C*(f)), 127.1−127.9 (Ph). HRMS (EI): *m*/*z* found 251.1674, calculated 251.1674.

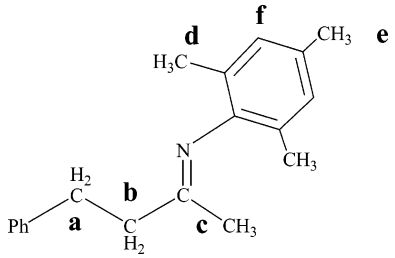


**Characterization of *N*-(3-Phenylbutan-2-ylidene)-2,6-dimethylbenzenamine (Xb).**



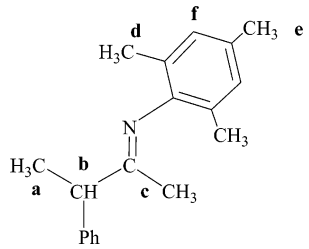
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.24 (s, 3H, *H*(3)), 1.54 (d, 3H, $^3J_{HH}$ = 7 Hz, *H*(1)), 1.94 (s, 3H, *H*(4)), 1.98 (s, 3H, *H*(4′)), 3.50 (q, 2H, $^3J_{HH}$ = 7 Hz, *H*(2)), 6.85 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, *H*(5)), 6.92−7.17 (Ph), 7.25 (d, $^3J_{HH}$ = 7.5 Hz, 1H, *H*(6)). $^{13}$C-{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 17.1 (*C*(4)), 17.2 (*C*(4′)), 17.4 (*C*(3)), 18.1 (*C*(1)), 49.6 (*C*(2)), 121.7 (*C*(5)), 121.8 (*C*(5′)), 125.2−128.2 (Ph, *C*(6)). HRMS (EI): *m*/*z* found 251.1679, calculated 251.1674.

**Characterization of *N*-(4-Phenylbutan-2-ylidene)-2,4,6-trimethylbenzenamine (XIa).**



$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.32 (s, 3H, *H*(c)), 1.88 (s, 6H, *H*(d)), 2.19 (s, 3H, *H*(e)), 2.50 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(b)), 2.96 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *H*(a)), 6.74 (s, 2H, *H*(f)), 6.97−7.18 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 17.0 (*C*(d)), 18.7 (*C*(c)), 19.9 (*C*(f)), 31.4 (*C*(a)), 40.9 (*C*(b)), 127.1−128.2 (Ph, *C*(e)). HRMS (EI): *m*/*z* found 265.1839, calculated 265.1830.

**Characterization of *N*-(3-Phenylbutan-2-ylidene)-2,4,6-trimethylbenzenamine (XIb).**



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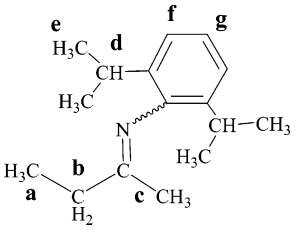
$^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 1.27 (s, 3H, *H*(c)), 1.55 (d, 1H, $^3J_{HH}$ = 7 Hz, *H*(a)), 1.94 (s, 3H, *H*(d)), 1.98 (s, 3H, *H*(d′)), 2.18 (s, 3H, *H*(e)), 3.52 (q, 2H, $^3J_{HH}$ = 7 Hz, *H*(b)), 6.73 (s, 1H, *H*(f)), 6.78 (s, 1H, *H*(f′)), 7.04−7.28 (Ph). $^{13}$C{$^1$H} NMR (125 MHz, toluene-$d_8$): $\delta$ 17.0 (*C*(d)), 17.1 (*C*(c)), 17.4 (*C*(a)), 19.9 (*C*(e)), 49.7 (*C*(b)), 127.1−128.2 (Ph, *C*(e)). HRMS (EI): *m*/*z* found 265.1823, calculated 265.1830.

**Characterization of *N*-(Butan-2-ylidene)-2,6-dimethylbenzenamine (XII).** The product **21** (CAS registry no. 444200-40-2; *E* stereoisomer CAS registry no. 446030-33-7) was reported previously.[46,154] NMR data are comparable to published data. HRMS (EI): *m*/*z* found 175.1357, calculated: 175.1361.

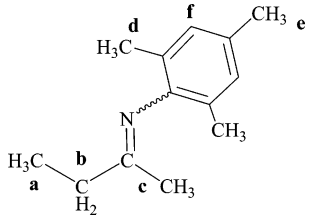
**Characterization of *N*-(Butan-2-ylidene)-2,6-diisopropylbenzenamine (XIII).**




*E* stereoisomer: $^1$H NMR (500 MHz, toluene-d$_8$) $\delta$ 1.12 (d, 12H, $^3J_{HH}$ = 7 Hz, H(e)), 1.15 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.38 (s, 3H, H(c)), 2.18 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 2.76 (sept, 2H, $^3J_{HH}$ = 7 Hz, H(d)), 6.73 (s, 4H, H(e)), 7.015 (d, 1H, $^3J_{HH}$ = 8 Hz, H(g)), 7.05 (dd, 2H, $^3J_{HH}$ = 8 Hz, H(f)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-d$_8$) $\delta$ 9.6 (C(a)), 18.9 (C(c)), 22.3 (C(e)), 27.4 (C(d)), 32.8 (C(b)), 121.8 (C(g)), 122.1 (C(f)); HRMS (EI) m/z found 231.1988, calculated 231.1987.

*Z* stereoisomer: $^1$H NMR (500 MHz, toluene-d$_8$): $\delta$ 0.72 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.15 (s, 6H, H(e)), 1.76 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 1.96 (s, 3H, H(c)), 2.65 (sept, 2H, $^3J_{HH}$ = 7.5 Hz, H(d)).

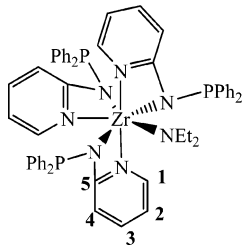
**Characterization of *N*-(Butan-2-ylidene)-2,4,6-trimethylbenzenamine (XIV).**




*E* stereoisomer: $^1$H NMR (500 MHz, toluene-d$_8$) $\delta$ 1.14 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.32 (s, 3H, H(c)), 1.93 (s, 6H, H(d)), 2.17 (s, 3H, H(e)), 2.18 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 6.73 (s, 4H, H(f)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-d$_8$) $\delta$ 9.7 (C(a)), 16.8 (C(d)), 18.1 (C(c)), 19.8 (C(e)), 32.8 (C(b)), 127.8 (C(f)); HRMS (EI) m/z found 189.1507, calculated 189.1517.

*Z* stereoisomer: $^1$H NMR (500 MHz, toluene-d$_8$) $\delta$ 0.686 (t, 3H, $^3J_{HH}$ = 7.5 Hz, H(a)), 1.68 (q, 2H, $^3J_{HH}$ = 7.5 Hz, H(b)), 1.93 (s, 6H, H(d)), 1.96 (s, 3H, H(c)), 2.17 (s, 3H, H(e)), 6.73 (s, 4H, H(f)); $^{13}$C{$^1$H} NMR (125 MHz, toluene-d$_8$) $\delta$ 9.5 (C(a)), 17.1 (C(d)), 20.2 (C(e)), 23.1 (C(c)), 26.4 (C(b)), 127.9 (C(f)).

**Synthesis of Zr(Ph$_2$PNpy)$_3$NEt$_2$ (13).** To a stirred solution of 2.11 g (7.58 mmols) of the ligand Ph$_2$PNHPy in 10 mL of toluene, we added 1.4 mL (3.78 mmols) of Zr(NEt$_2$)$_4$ dropwise at 0 °C under a nitrogen atmosphere. The mixture was slowly warmed to room temperature and stirred for 48 h. The toluene and diethylamine were evacuated from the reaction flask overnight on a high-vacuum line. Traces of the ligand and Zr(NEt$_2$)$_4$ were removed from the complex by washing with hexane (3 × 50 mL). Yellow crystals of the complex were obtained by recrystallization from toluene at room temperature.




$^1$H NMR (300 MHz, $C_6D_6$, 295 K): $\delta$ 0.97 (t, 6H, $^3J_{HH}$ = 7.2 Hz, −C*H*$_3$), 2.49 (q, 2H, $^3J_{HH}$ = 7.2 Hz, −C*H*$_2$−), 6.00 (t, 3H, $^3J_{HH}$ = 6 Hz, *H*(2)), 6.08 (d, 3H, $^3J_{HH}$ = 9 Hz, *H*(4)), 6.61 (t, 3H, $^3J_{HH}$ = 7.5 Hz, *H*(3)), 6.68−7.8 (30H, Ph), 7.83 (br, 3H, *H*(1)). $^{13}$C NMR (125 MHz, toluene-$d_8$, 295 K): $\delta$ 21.1 (−*C*H$_3$), 38.1 (−*C*H$_2$−), 42.4 (−*C*H$_2$′−), 109.7 (*C*(2)), 111.5 (*C*(4)), 136.5 (*C*(3)), 125−130 (Ph).

**Hydroamination of TMSC≡CH with PhNH$_2$ by 13.** In a glovebox, 0.005 g (0.005 mmol) of the precatalyst **10**, 0.5 mL of toluene-$d_8$, and 23 $\mu$L (0.25 mmol) of PhNH$_2$ were loaded into a NMR tube. Then 36 $\mu$L (0.25 mmol) of TMSC≡CH was vacuum-transferred into the tube. The tube was heated by means of a thermostated oil bath (±0.1) to 110 °C for 9 days to obtain 8% conversion and more than 95% of the product (TMS)CH$_2$CH═NPh. $^1$H NMR (300 MHz, toluene-$d_8$): $\delta$ −0.09 (s, 9H, −SiMe$_3$), 1.76 (d, 2H, $^3J_{HH}$ = 6.0 Hz, −C*H*$_2$−), 6.86−6.93 (m, 5H, Ph), 7.51 (t, 1H, $^3J_{HH}$ = 6.0 Hz, ═C*H*−). $^{13}$C NMR (125 MHz, toluene-$d_8$): $\delta$ −2.4 (−SiMe$_3$), 19.3 (−*C*H$_2$−), 162.1 (−*C*H═N), 114−128 (Ph). GC/MS (EI): Rt = 13:59 min; *m*/*z* 191 (M), 190 (M − H), 176 (M − CH$_3$), 77 (−Ph), 73 (−SiMe$_3$).

**Hydroamination of TMSC≡CH with EtNH$_2$ by 13.** In a glovebox, 0.038 g (0.038 mmol) of the precatalyst **14** was dissolved in 0.5 mL of toluene-$d_8$ in a heavy-duty glass Schlenk vessel. Then 25 $\mu$L (0.38 mmol) of EtNH$_2$ and 54 $\mu$L (0.38 mmol) of (TMS)C≡CH were vacuum-transferred into the tube. The tube was heated by means of a thermostated oil bath (±0.1) to 110 °C for 20 days to obtain 99% conversion containing more than 95% of the product (TMS)CH$_2$CH═NCH$_2$CH$_3$. $^1$H NMR (300 MHz, toluene-$d_8$): $\delta$ −0.01 (s, 9H, −SiMe$_3$), 1.11 (t, 3H, $^3J_{HH}$ = 7.5 Hz, −C*H*$_3$), 1.64 (d, 2H, $^3J_{HH}$ = 6.0 Hz, −C*H*$_2$(TMS)), 3.26 (q, 2H, $^3J_{HH}$ = 7.5 Hz, −C*H*$_2$N), 7.47 (t, 1H, $^3J_{HH}$ = 6.0 Hz, ═C*H*−). $^{13}$C NMR (125 MHz, toluene-$d_8$): $\delta$ −2.3 (−SiMe$_3$), 16.0 (−*C*H$_3$), 26.4 (−*C*H$_2$(TMS)), 55.1 (−*C*H$_2$N), 158.6 (−*C*H═N).

**Reaction of Ti(NMe$_2$)$_4$ with Aniline.** In a glovebox, 7 $\mu$L of Ti(NMe$_2$)$_4$, 13.5 $\mu$L of aniline, and 600 $\mu$L of toluene-$d_8$ were charged into a J. Young NMR tube. Immediately, with the addition of the amine, a color change from bright yellow to dark brown was observed. The tube was heated by means of a thermostated oil bath to 110 ± 0.1 °C for 30 min. The tube was connected to a vacuum line and evacuated overnight to remove all the amine, and the NMR tube was recharged with toluene-$d_8$ by vacuum transfer. The obtained solution was characterized by NMR spectroscopy. $^1$H NMR (500 MHz, toluene-$d_8$): $\delta$ 2.77 (br, 1H, −N*H*Ph), 6.28 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *o*-Ph), 6.67 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.00 (dd, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, *m*-Ph). $^{13}$C NMR (125 MHz, toluene-$d_8$): $\delta$ 124.4 (*o*-Ph), 127.2 (*p*-Ph), 128.3 (*m*-Ph).

**Kinetic Studies of Hydroamination Reactions.** In a typical experiment, the sample was prepared in a glovebox. After the addition of the catalysts, the sample was taken out immediately, from the glovebox, and frozen using liquid nitrogen. The sample was thawed, placed directly into an Avance 300 MHz NMR spectrometer, and heated to the desired reaction temperature (calibrated with an ethylene glycol standard). Substrate and product concentration were determined relative to the intensity of

1,3,5-trimethylbenzene, which was added as internal standard, over 3 half-lives or more.

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**Supporting Information Available:** Text giving the mathematical derivation of eq 4 and a CIF file giving the crystallographic data for the structure of complex **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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