New Titanium Complexes Containing a Cyclopentadienyl Ligand with a Pendant Aminoalkyl Substituent: Preparation, Behavior of the Amino Group, and Catalytic Hydroamination of Alkynes

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Complex Cp^NTiCl_3 (**1**) ($Cp^N = C_5H_4CH_2CH_2NMe_2$) reacts with 1.0, 2.0, and 3.0 equiv of MeMgCl to give $Cp^NTiMeCl_2$ (**2**), Cp^NTiMe_2Cl (**3**), and Cp^NTiMe_3 (**4**), respectively. In the solid state, the amino group of the pendant substituent of the cyclopentadienyl ligand is weakly coordinated to the metal center (d(Ti−N) = 2.445(2) Å in **2** and 2.433(4) Å in **3**), *transoid* disposed to a methyl ligand. In solution, the N-donor substituent is involved in a coordination−dissociation equilibrium ($\Delta H° = 2.4 \pm 0.3$ kcal·mol^{-1} and $\Delta S° = 6.5 \pm 0.9$ cal·mol^{-1}·K^{-1} for **2**, $\Delta H° = 3.8 \pm 0.4$ kcal·mol^{-1} and $\Delta S° = 12.3 \pm 1.0$ cal·mol^{-1}·K^{-1} for **3**, and $\Delta H° = 4.4 \pm 0.1$ kcal·mol^{-1} and $\Delta S° = 17.9 \pm 0.4$ cal·mol^{-1}·K^{-1} for **4**). In moist benzene, complex **3** affords the dinuclear species $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$ (**5**), containing a planar $Ti_2(\mu\text{-}O)_2$ core. In the solid state, the pendant amino groups of **5** are also coordinated to the metal centers (d(Ti−N) = 2.421(2) Å). Like in **2**, **3**, and **4**, the amino groups of **5** are involved in a coordination−dissociation equilibrium ($\Delta H° = 4.9 \pm 0.2$ kcal·(mol of Ti)$^{-1}$ and $\Delta S° = 20.7 \pm 0.6$ cal·K^{-1}·(mol of Ti)$^{-1}$). Complex **1** also reacts with LiNH(2,6-^{i}Pr$_2$C$_6$H$_3$). The reaction leads to the six-coordinate amido-imido derivative {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^NTi{N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**6**), which shows a strong coordination of the pendant amino group to the titanium atom (d(Ti−N$_{amino}$) = 2.227(2) Å). In solution the amino group remains coordinated. Complex **4** has been found to be an efficient catalyst precursor for the intermolecular regioselective anti-Markovnikov hydroamination of asymmetric alkynes. The reactions give enamine−imine mixtures, which are transformed into the corresponding secondary amines.

Introduction

For our objective of designing metallic homogeneous systems that are effective in the synthesis of functionalized organic molecules from basic hydrocarbon units,[1] the cyclopentadienyl group is of particular interest. This ligand occupies a face of the metal complex, while the other one remains free for the entry of the organic substrates.[2]

A modification is the use of a pendant donor substituent. Due to the reversible coordination of the pendant group,[3] cyclopentadienyl ligands with substituents of this type can stabilize highly reactive centers until the substrates coordinate and replace the pendant group.[4] The stabilizing effect has a strong influence on the catalytic properties of the active systems and facilitates the study of some processes.[5] As a consequence of this, complexes containing cyclopentadienyl ligands with a pendant donor substituent are attracting increased interest from those who study the chemistry of metals.[6] Our group also is actively interested in this type of compounds, and recently we have studied the chemical behavior of [2-(dimethylamino)ethyl]cyclopentadienyliridium[7] and [2-(diphenylphosphino)ethyl]cyclopentadienyl-,[8] (2-methoxyethyl)cyclopentadienyl-,[9] and [2-(dimethylamino)ethyl]cyclopentadienylosmium derivatives.[9,10] Now we report on [2-(dimethylamino)ethyl]-cyclopentadienyltitanium complexes.

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The chemistry of ring-substituted monocyclopentadienyl titanium(IV) compounds is an active field of group 4 metal research.[6f] Compared to the systems with constrained geometry, the monocyclopentadienyl titanium derivatives containing a dialkylamino side group[11] remain an underrepresented area within the group 4 metal complexes containing a cyclopentadienyl ligand with a pendant group.[6b−e] As far as we know, only trichloro derivatives have been reported.

Rausch and co-workers[12] have described the preparation of the half-sandwich complex Cp^NTiCl_3 (Cp^N = $C_5H_4CH_2CH_2NMe_2$), which is an active precursor in Ziegler−Natta polymerization catalysis.[13] The amino group affects significantly its catalytic reactivity as compared to that of the parent complex $CpTiCl_3$.[14] The system Cp^NTiCl_3-MAO (MAO = methylaluminoxane) shows a considerably lower activity toward styrene and an impressively increased activity toward ethylene and propylene. This has been attributed to the coordination behavior of the amino group, which influences the coordination of the incoming monomer.[13]

Although the influence of the pendant group on the catalytic activity of these systems is evident, studies on its behavior in the solid state and in solution are very scarce in the chemistry of group 4 metals.[15] In this paper we show the behavior of the pendant amine group of the [2-(dimethylamino)ethyl]cyclopentadienyl ligand in (i) the complexes resulting from the sequential methylation of Cp^NTiCl_3, (ii) the product from the hydrolysis of Cp^NTiMe_2Cl, and (iii) the amido-imido derivative $\{(2,6\text{-}^iPr_2C_6H_3)NH\}Cp^NTi\{N(2,6\text{-}^iPr_2C_6H_3)\}$. In addition, as a part of our effort to develop effective methods of C−N bond formation,[16] the catalytic activity of Cp^N-$TiMe_3$ in the hydroamination of alkynes is also reported.[17]

Results and Discussion

1. $Cp^NTiMe_xCl_{3-x}$ (x = 1−3) Complexes. The addition of 1.0 equiv of MeMgCl in tetrahydrofuran to a suspension of Cp^NTiCl_3 (**1**) in diethyl ether produces the selective substitution of one of the chloride ligands of **1** by a methyl group and the formation of the monomethyl derivative $Cp^NTiMeCl_2$ (**2**), which is isolated as a brown solid in 43% yield, according to Scheme 1.

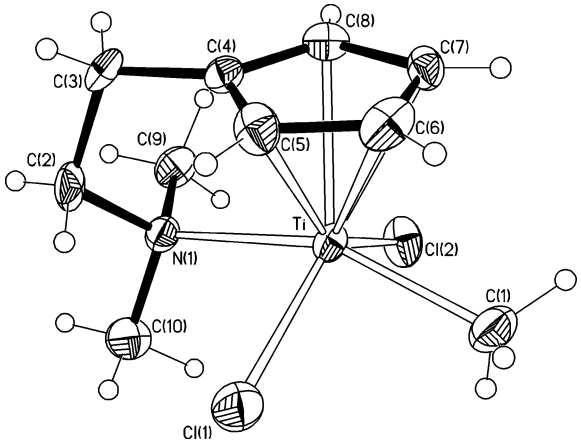
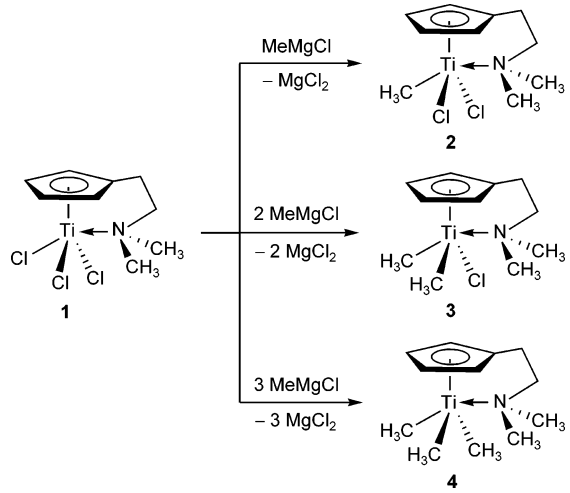


Figure 1. Molecular diagram of $Cp^NTiMeCl_2$ (**2**).

Scheme 1



In the solid state the dimethylamino group coordinates to the metal center of **2**. Figure 1 shows a view of the structure of this compound. Selected bond distances and angles are listed in Table 1.

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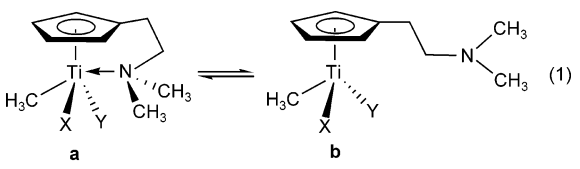
Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex $Cp^NTiMeCl_2$ (2)

Ti−Cl(1)	2.3004(8)	Ti−C(7)	2.355(2)
Ti−Cl(2)	2.3091(8)	Ti−C(8)	2.343(3)
Ti−C(1)	2.144(3)	N(1)−C(2)	1.489(3)
Ti−N(1)	2.445(2)	N(1)−C(9)	1.482(3)
Ti−C(4)	2.346(2)	N(1)−C(10)	1.480(3)
Ti−C(5)	2.342(3)	C(2)−C(3)	1.518(4)
Ti−C(6)	2.346(3)	C(3)−C(4)	1.502(4)
C(1)−Ti−Cl(1)	85.10(9)	N(1)−Ti−M[a]	102.0
C(1)−Ti−Cl(2)	83.61(9)	Ti−N(1)−C(2)	104.98(15)
C(1)−Ti−N(1)	151.34(11)	Ti−N(1)−C(9)	115.03(17)
C(1)−Ti−M[a]	106.6	Ti−N(1)−C(10)	113.85(16)
Cl(1)−Ti−Cl(2)	125.18(3)	C(2)−N(1)−C(9)	107.8(2)
Cl(1)−Ti−N(1)	83.42(6)	C(2)−N(1)−C(10)	108.5(2)
Cl(1)−Ti−M[a]	115.3	C(9)−N(1)−C(10)	106.5(2)
Cl(2)−Ti−N(1)	81.77(5)	N(1)−C(2)−C(3)	110.5(2)
Cl(2)−Ti−M[a]	119.3	C(2)−C(3)−C(4)	110.2(2)

[a] M represents the midpoint of the C(4)−C(8) Cp ligand.

The distribution of ligands around the titanium atom can be described as a four-legged piano stool geometry, with the cyclopentadienyl ring occupying the three-membered face, while the nitrogen atom of the pendant group lies in the four-membered face *transoid* disposed to the methyl ligand (C(1)−Ti−N(1) = 151.34(11)°). The Ti−N(1) and Ti−C(1) distances are 2.445(2) and 2.144(3) Å, respectively. In agreement with the sp^3 hybridization at N(1), the angles around this atom are between 104.98(15)° and 115.03(17)°.

In solution, the pendant N-donor substituent of the cyclopentadienyl ligand is involved in a coordination−dissociation process (eq 1). This is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra in toluene-d_8, which are temperature dependent. Figure 2 shows the ^1H NMR spectrum as a function of the temperature. At 363 K, the spectrum contains two cyclopentadienyl resonances at 6.40 and 5.99 ppm, a signal at 2.17 ppm for the pendant chain protons, and singlets at 2.09 (NMe_2) and 1.70 (TiMe) corresponding to the methyl groups of the molecule. Lowering the sample temperature produces an increase of the separation between the cyclopentadienyl resonances, which at 223 K appear at 6.34 and 5.68 ppm, whereas the signal due to the pendant chain protons is converted into two resonances, which are shifted toward higher field as the temperature decreases. Thus, at 223 K, they are observed at 1.76 (NCH_2) and 1.46 ($CpCH_2$) ppm. The NMe_2 resonance is also shifted to higher field. At 223 K, it appears at 1.95 ppm. On the other hand, the TiMe resonance is shifted toward lower field. At 223 K, it is observed at 1.83 ppm.



X = Y = Cl (**2**), CH_3 (**4**); X= CH_3, Y= Cl (**3**)

For the process shown in eq 1, the equilibrium constants between 363 and 223 K were determined by the procedure previously used by van der Zeijden and co-workers,[15a] according to eq 2.[18]

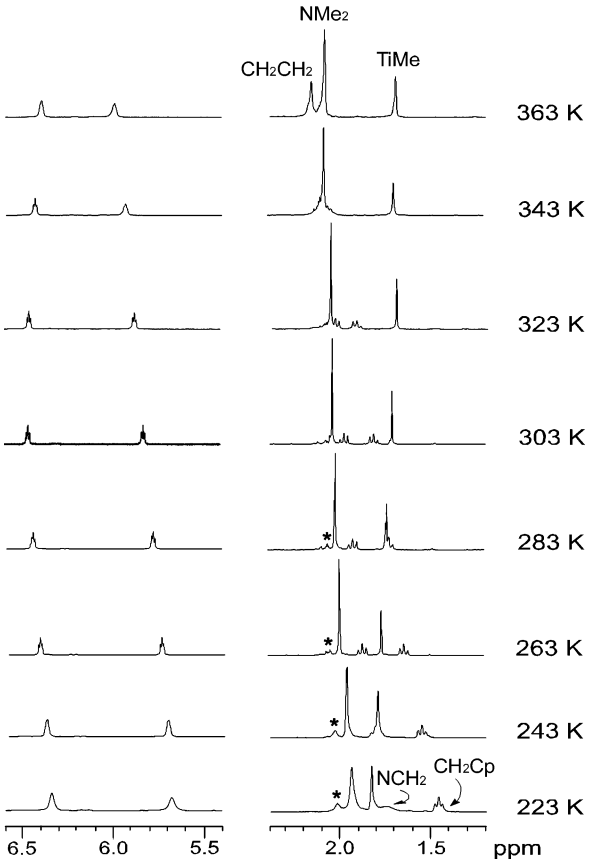


Figure 2. Variable-temperature ^1H NMR spectra for complex $Cp^NTiMeCl_2$ (**2**) (toluene-d_8). *Denotes residual solvent peak.

$$K = \frac{[\mathbf{b}]}{[\mathbf{a}]} = \frac{\delta_{min}(CpCH_2) - \delta(CpCH_2)}{\delta(CpCH_2) - \delta_{max}(CpCH_2)} = \frac{\delta_{min}(CH_2N) - \delta(CH_2N)}{\delta(CH_2N) - \delta_{max}(CH_2N)} \quad (2)$$

The temperature dependence of the equilibrium gives the values $\Delta H° = 2.4 \pm 0.3$ kcal·mol^{-1} and $\Delta S° = 6.5 \pm 0.9$ cal·mol^{-1}·K^{-1}. The positive value of $\Delta S°$ is in agreement with the free character of the dimethylamino pendant group in **2b**, whereas the low value of $\Delta H°$ indicates a weak Ti−N bond.

Treatment of **1** with 2.0 equiv of MeMgCl produces the substitution of two chloride ligands of the starting compound by methyl groups and the formation of the dimethyl derivative Cp^NTiMe_2Cl (**3**), which is isolated as a red solid in 50% yield (Scheme 1).

Like **2**, complex **3** was characterized by X-ray diffraction analysis. The structure proves that in the solid state the pendant dimethylamino group is also coordinated to the metal center of **3**. Figure 3 shows a view of the structure of this compound. Selected bond distances and angles are collected in Table 2.

The distribution of ligands around the titanium is like that of **2**, with the methyl groups mutually *cisoid* disposed (C(1)−Ti−C(2) = 81.7(2)°) and the pendant

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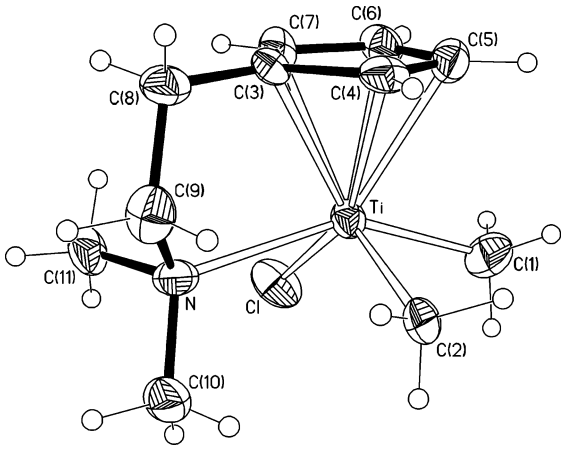


Figure 3. Molecular diagram of Cp^NTiMe_2Cl (**3**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex Cp^NTiMe_2Cl (3)

Ti−Cl	2.3253(19)	Ti−C(6)	2.376(5)
Ti−C(1)	2.150(5)	Ti−C(7)	2.355(5)
Ti−C(2)	2.130(5)	N−C(9)	1.500(6)
Ti−N	2.433(4)	N−C(10)	1.479(6)
Ti−C(3)	2.360(5)	N−C(11)	1.484(6)
Ti−C(4)	2.356(5)	C(3)−C(8)	1.473(6)
Ti−C(5)	2.376(5)	C(8)−C(9)	1.520(7)
C(1)−Ti−Cl	84.59(15)	N−Ti−M[a]	102.2
C(1)−Ti−C(2)	81.7(2)	Ti−N−C(9)	106.3(3)
C(1)−Ti−N	150.11(18)	Ti−N−C(10)	114.2(3)
C(1)−Ti−M[a]	107.4	Ti−N−C(11)	113.3(3)
Cl−Ti−C(2)	123.30(14)	C(9)−N−C(10)	107.5(4)
Cl−Ti−N	81.89(11)	C(9)−N−C(11)	107.5(4)
Cl−Ti−M[a]	125.4	C(10)−N−C(11)	107.7(4)
C(2)−Ti−N	83.69(17)	N−C(9)−C(8)	110.2(4)
C(2)−Ti−M[a]	111.2	C(9)−C(8)−C(3)	110.6(4)

[a] M represents the midpoint of the C(3)−C(7) Cp ligand.

dimethylamino group *transoid* disposed to C(1) (C(1)−Ti−N = 150.11(18)°). The Ti−N bond length of 2.433(4) Å is statistically identical with the related parameter in **2**, and both distances compare well with the Ti−N bond lengths found in complexes containing dative nitrogen−titanium bonds.[11b,c] The angles around the nitrogen atom are between 106.3(3)° and 114.2(3)°. The Ti−C(1) (2.150(5) Å) and Ti−C(2) (2.130(5) Å) distances are also statistically identical with the titanium−methyl separation in **2**. However, the Ti−Cl bond length (2.3253(19) Å) is slightly longer than the Ti−Cl distances in the monomethyl derivative (2.3004(8) and 2.3091(8) Å).

In solution, the pendant N-donor substituent of the cyclopentadienyl ligand of **3** is also involved in a coordination−dissociation process like that shown in eq 1. In agreement with this, the behavior of the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3** with the temperature is similar to that described for **2**. In this case, the temperature dependence of the equilibrium gives the values $\Delta H° = 3.8 \pm 0.4$ kcal·mol^{-1} and $\Delta S° = 12.3 \pm 1.0$ cal·mol^{-1}·K^{-1}, which are slightly higher than those obtained for **2**.

The addition of 3.0 equiv of MeMgCl to a diethyl ether suspension of **1** produces the substitution of the three chloride ligands of the starting complex by methyl groups. As a result, the trimethyl derivative Cp^NTiMe_3 (**4**) is formed, according to Scheme 1. Complex **4** is isolated as an orange oil in 55% yield.

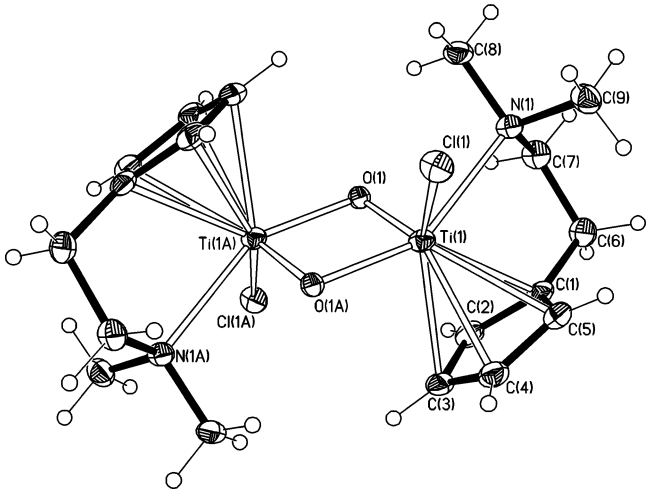
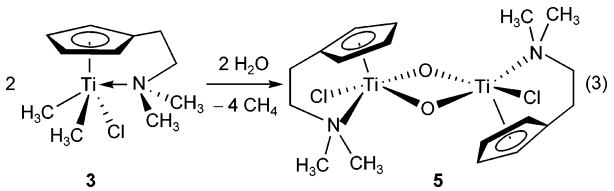


Figure 4. Molecular diagram of $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$ (**5**).

In solution, the behavior of the pendant amino group of **4** is like that of **2** and **3**. In accordance with this, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** are also temperature dependent and completely analogous to those of **2** and **3**. The values of parameters $\Delta H°$ and $\Delta S°$, obtained from the temperature dependence of the equilibrium, are 4.4 ± 0.1 kcal·mol^{-1} and 17.9 ± 0.4 cal·mol^{-1}·K^{-1}, respectively.

The values obtained for $\Delta H°$ and $\Delta S°$ in the sequence **2**−**3**−**4** show that both $\Delta H°$ and $\Delta S°$ increase as the chloride ligands at the titanium atom are replaced by methyl groups. Accordingly, the molar fraction of hexacoordinate form **b** at 20 °C increases in the sequence **2** (0.30) < **3** (0.35) < **4** (0.82). This appears to be a consequence of the steric hindrance experienced by the dimethylamino group and the methyl ligands, when they are mutually *cisoid* disposed.

2. $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$. The dimethyl complex **3** in moist benzene or toluene is transformed to the dimer derivative $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$ (**5**), as a result of the hydrolysis of the Ti−C bonds (eq 3). We note that the trimethyl complex $(\eta^5\text{-}C_5Me_5)TiMe_3$ undergoes hydrolysis to give first $[(\eta^5\text{-}C_5Me_5)TiMe_2]_2(\mu\text{-}O)$ and then $[(\eta^5\text{-}C_5Me_5)TiMe(\mu\text{-}O)]_3$, which has been characterized by X-ray diffraction analysis.[19]



A few crystals of **5** suitable for an X-ray diffraction study were obtained in an NMR tube, from a toluene-d_8 solution of this compound. Figure 4 shows a view of its structure. Selected bond distances and angles are collected in Table 3.

Complex **5** can be described as a dinuclear species containing a planar $Ti_2(\mu\text{-}O)_2$ core with Ti−O distances of 1.7980(17) (Ti(1)−O(1)) and 1.9271(16) (Ti(1)−O(1A)) Å and with angles of 82.29(7)° at the titanium atom and 97.71(7)° at the oxygen atom. These structural param-

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$ (5)

Ti(1)−Cl(1)	2.3579(8)	Ti(1)−C(4)	2.414(2)
Ti(1)−O(1)	1.7980(17)	Ti(1)−C(5)	2.424(2)
Ti(1)−O(1A)	1.9271(16)	N(1)−C(7)	1.480(3)
Ti(1)−N(1)	2.421(2)	N(1)−C(8)	1.476(3)
Ti(1)−C(1)	2.396(2)	N(1)−C(9)	1.483(3)
Ti(1)−C(2)	2.351(2)	C(1)−C(6)	1.503(3)
Ti(1)−C(3)	2.369(2)	C(6)−C(7)	1.532(3)
O(1)−Ti(1)−O(1A)	82.29(7)	Ti(1)−O(1)−Ti(1A)	97.71(7)
O(1)−Ti(1)−Cl(1)	120.11(5)	Ti(1)−N(1)−C(7)	105.03(14)
O(1)−Ti(1)−N(1)	80.48(7)	Ti(1)−N(1)−C(8)	109.28(14)
O(1)−Ti(1)−M[a]	119.7	Ti(1)−N(1)−C(9)	118.27(14)
O(1A)−Ti(1)−Cl(1)	87.39(5)	C(7)−N(1)−C(8)	108.01(18)
O(1A)−Ti(1)−N(1)	150.77(7)	C(8)−N(1)−C(9)	106.91(19)
Cl(1)−Ti(1)−N(1)	81.12(5)	C(7)−N(1)−C(9)	109.00(19)
Cl(1)−Ti(1)−M[a]	119.4	N(1)−C(7)−C(6)	110.81(19)
N(1)−Ti(1)−M[a]	99.7	C(7)−C(6)−C(1)	109.5(2)

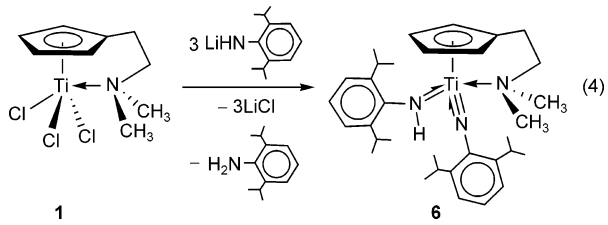
[a] M represents the midpoint of the C(1)−C(5) Cp ligand.

eters agree well with those recently reported for the complexes $Ti_2(O_2{}^{tBu}NN')_2(\mu\text{-}O)_2$ ($O_2{}^{tBu}NN'$ = (2-C_5H_4N)-CH_2N(2-O-3,5-$C_6H_2{}^tBu_2$)$_2$)[20a] and *trans*-[$Ti_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}O)_2\{Me_3SiNC(Ph)N(CH_2)_nNMe_2\}_2$] ($n$ = 2, 3).[20b] The separation between the titanium atoms of 2.8064(9) Å is comparable with those of other known examples with a planar $Ti_2(\mu\text{-}O)_2$, i.e., $[Ti(acac)_2(\mu\text{-}O)]_2$ (2.729(1) Å),[21] $K_4[Ti(O_2C_6H_4)_2(\mu\text{-}O)]_2\cdot 9H_2O$ (2.819(1) Å),[22] $[(\eta^5{:}\eta^1\text{-}C_5H_4CMe_2C_6H_4N)TiCl]_2(\mu\text{-}O)_2$ (2.801(1) Å),[23] $[\{\eta^5\text{-}C_5H_2(Me_3Si)_3\}TiCl]_2(\mu\text{-}O)_2$ (2.707(0) Å),[24] and $[(\eta^5\text{-}C_5Me_5)Ti(\mu\text{-}O)(CMePy_2)]_2$ (2.863(4) Å).[25]

Like in the mononuclear complexes **2** and **3**, the pendant dimethylamino groups are coordinated to the metal centers. Thus, the distribution of ligands around each titanium atom can be described as a four-legged piano stool geometry, with the nitrogen atom of the pendant group and the chloride ligand in the four-membered face, *transoid* disposed to the oxygen atoms of the $Ti_2(\mu\text{-}O)_2$ core (O(1A)−Ti(1)−N(1) = 150.77(7)° and O(1)−Ti−Cl(1) = 120.11(5)°). The Ti−N bond lengths of 2.421(2) Å are about 0.02 Å shorter than the Ti−N distance in **2** and about 0.01 Å shorter than that in **3**. However, the Ti−Cl bond lengths of 2.3579(8) Å are between 0.04 and 0.05 Å longer than the Ti−Cl distances in **2** and about 0.03 Å longer than that in **3**.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** in toluene-d_8 are similar to those of **2**−**4**. Their behavior with the temperature, like that of the mononuclear species, is consistent with a rapid coordination−dissociation equilibrium process of the nitrogen atom of the pendant substituent of the cyclopentadienyl ligand. Thus, at 333 K, the ^1H NMR spectrum shows two cyclopentadienyl resonances at 6.08 and 6.04 ppm, two CH_2 resonances at 2.60 and 2.44 ppm, and a methyl resonance at 2.13 ppm, while at 233 K, the resonances corresponding to the same protons appear at 6.08 and 5.89 (Cp), 2.40 (CH_2Cp), 2.05 (CH_2N), and 1.87 (CH_3) ppm. In this case, the values of parameters $\Delta H°$ and $\Delta S°$ for the coordination−dissociation equilibrium process are 4.9 ± 0.2 kcal·(mol of Ti)$^{-1}$ and 20.7 ± 0.6 cal·K^{-1}·(mol of Ti)$^{-1}$, respectively, whereas in toluene at 20 °C the molar fraction of six-coordinate titanium atoms is 0.88.

3. {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}Ti{N(2,6-^{i}Pr$_2$C$_6$H$_3$)}. The hydroamination of alkenes and alkynes constitutes an atom economical method for the synthesis of nitrogen-containing molecules from inexpensive starting materials.[17b,d,e,g;26] Among the catalysts used in these reactions, titanium metallocene derivatives occupy a prominent place.[27] Kinetic studies have revealed a cyclopentadienyl-amide ligand exchange reaction that transforms the titanium metallocene precursor into a monocyclopentadienyl-amido-imido derivative.[28] A species of this type containing the [2-(dimethylamino)ethyl]-cyclopentadienyl ligand can be easily prepared starting from **1**. Treatment of a diethyl ether suspension of the latter with 3.3 equiv of LiNH(2,6-^{i}Pr$_2$C$_6$H$_3$) affords the amido-imido complex {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}Ti{N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**6**), which is isolated as a yellow solid in 42% yield, according to eq 4.



A view of the molecular geometry of **6** is shown in Figure 5. Selected bond distances and angles are listed in Table 4. The geometry around the titanium center can be described as a very distorted octahedron, with the cyclopentadienyl group occupying a face. The distortion is revealed by the N(1)−Ti−N(2) (101.82(11)°), N(1)−Ti−N(3) (94.98(10)°), and N(2)−Ti−N(3) (109.20(10)°) angles, which strongly deviate from the ideal value of 90°, and it appears to be a consequence of both the constriction imposed by the CH_2-CH_2 string in the [2-(dimethylamino)ethyl]cyclopentadienyl ligand and the steric hindrance experienced by the isopropyl substituents of the phenyl groups of the mutually *cis*-disposed imido and amido ligands.

The N(2,6-^{i}Pr$_2$C$_6$H$_3$) group acts as a 4e$^-$ donor ligand. This is supported by the Ti−N(1) bond length of 1.742(2) Å, which compares well with those found in

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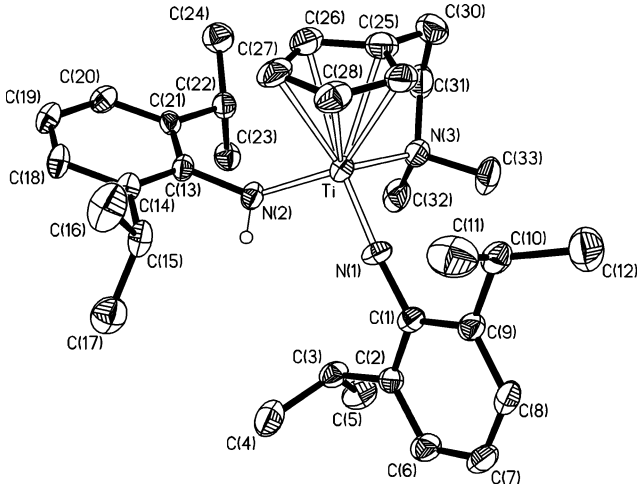


Figure 5. Molecular diagram of {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}-Ti{N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**6**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}Ti{N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (6)

Ti−N(1)	1.742(2)	N(1)−C(1)	1.383(3)
Ti−N(2)	1.939(2)	N(2)−C(13)	1.433(3)
Ti−N(3)	2.227(2)	N(3)−C(31)	1.486(3)
Ti−C(25)	2.395(3)	N(3)−C(32)	1.481(3)
Ti−C(26)	2.448(3)	N(3)−C(33)	1.485(3)
Ti−C(27)	2.418(3)	C(25)−C(30)	1.508(4)
Ti−C(28)	2.371(3)	C(30)−C(31)	1.530(4)
Ti−C(29)	2.365(3)		
N(1)−Ti−N(2)	101.82(11)	Ti−N(3)−C(31)	112.99(17)
N(1)−Ti−N(3)	94.98(10)	Ti−N(3)−C(32)	109.82(17)
N(1)−Ti−M[a]	131.0	Ti−N(3)−C(33)	109.01(17)
N(2)−Ti−N(3)	109.20(10)	C(31)−N(3)−C(32)	108.7(2)
N(2)−Ti−M[a]	113.5	C(31)−N(3)−C(33)	109.0(2)
N(3)−Ti−M[a]	103.6	C(32)−N(3)−C(33)	107.1(2)
Ti−N(1)−C(1)	174.7(2)	N(3)−C(31)−C(30)	110.6(3)
Ti−N(2)−C(13)	137.0(2)	C(25)−C(30)−C(31)	109.5(3)

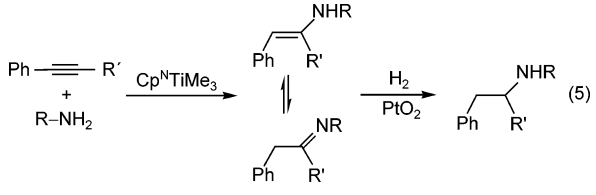
[a] M represents the midpoint of the C(25)−C(29) Cp ligand.

other titanium-imido complexes.[29] In agreement with an sp hybridization at N(1), the coordination of the imido is approximately linear with a Ti−N(1)−C(1) angle of 174.7(2)°. The Ti−N(2) distance of 1.939(2) Å is within the expected range for a titanium-amido compound,[30] and it is consistent with the planar geometry of the nitrogen atom. This indicates sp^2 hybridization at N(2) (Ti−N(2)−C(13) = 137.0(2)°) with the outplane lone pair giving a N(pπ)→M(dπ) interaction. Thus, the NH(2,6-^{i}Pr$_2$C$_6$H$_3$) group should be considered a 3e$^-$ donor ligand. Interestingly, the Ti−N(3) bond length of 2.227(2) Å is about 0.2 Å shorter than the Ti−amino separation in **2**, **3**, and **5**. This suggests that the coordination of the pendant amino group to the titanium center is much stronger in **6** than in **2**, **3**, and **5**, which could be related to the fact that **6** possesses one ligand less than **2**, **3**, and **5**.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** reveal that, in contrast to **2**−**5**, the pendant amino group of the [2-(dimethylamino)ethyl]cyclopentadienyl ligand does not dissociate in solution, in agreement with the expected high stability of the Ti−N(3) bond. Thus, both the ^{1}H and ^{13}C{^{1}H} NMR spectra are consistent with the structure shown in Figure 5. Due to the chirality of the titanium atom, the ^{1}H spectrum in toluene-d_8, which is temperature invariant between 333 and 213 K, shows an ABCD spin system for the methylene resonances. It appears between 2.50 and 1.97 ppm, whereas the resonances corresponding to the cyclopentadienyl protons, which also display an ABCD spin system, are observed between 6.38 and 5.48 ppm. The spectrum also contains two singlets at 2.26 and 2.25 ppm due to the dimethylamino group. In the ^{13}C{^{1}H} NMR spectrum the most noticeable resonances are those due to the cyclopentadienyl ring, which appear at 131.0, 115.4, 108.3, 106.6, and 106.0 ppm, and two singlets at 50.1 and 49.3 ppm corresponding to the dimethylamino group.

4. Hydroamination of Alkynes Catalyzed by Cp^{N}TiMe$_3$. Mechanistic studies suggest that the key step for the CpTi-catalyzed intermolecular hydroamination of alkynes is a reversible [2+2] cycloaddition between the alkyne and the imido group of the unsaturated amido-imido (RNH)CpTi(NR) catalyst.[28] Complex **6** is also an amido-imido species. However, it is saturated as a consequence of the coordination of the pendant amino group, and in agreement with the high stability of the titanium−amino bond, it is catalytically inactive for the hydroamination of phenylacetylene, 1-phenylpropyne, and diphenylacetylene with 2,6-diisopropylaniline.

In contrast to **6**, the trimethyl derivative **4** is a very efficient catalyst precursor for the regioselective anti-Markonikov hydroamination of phenylacetylene and 1-phenylpropyne, and the hydroamination of diphenylacetylene with amines such as cyclohexylamine, 2,6-dimethylaniline, *tert*-butylamine, and 2,6-diisopropylaniline. The reactions were performed in toluene at 100 °C using 5 mol % of complex **4**. Under these conditions the alkynes react with the amines to afford the corresponding enamine−imine mixtures, which were transformed in quantitative yield into the secondary amines, by reduction with molecular hydrogen in the presence of PtO_2 (eq 5).



R = Cy, 2,6-Me$_2$C$_6$H$_3$, *tert*-butyl, 2,6-^{i}Pr$_2$C$_6$H$_3$; R´ = H, Me, Ph

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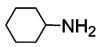
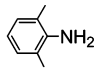
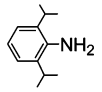
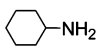
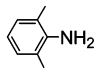
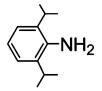
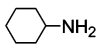
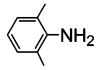
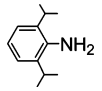
Table 5. Cp^NTiMe_3-Catalyzed Hydroamination of Alkynes[a]

Entry	Alkyne	Amine	*t* (h)	Conv. (%)[b]	Enamine : imine[c]
1	Ph—≡—H		8 24	35 78	50 : 50
2	Ph—≡—H		8 24	50 90	66 : 34
3	Ph—≡—H		1.25	100	40 : 60
4	Ph—≡—H		8 24	40 77	53 : 47
5	Ph—≡—Me		8 24	40 100	28 : 72
6	Ph—≡—Me		6	100	10 : 90
7	Ph—≡—Me		8 24	90 100	40 : 60
8	Ph—≡—Me		8 24	85 100	66 : 34
9	Ph—≡—Ph		8 24	75 100	56 : 44
10	Ph—≡—Ph		8 24	85 100	46 : 54
11	Ph—≡—Ph		8 24	40 85	100 : 0
12	Ph—≡—Ph		8 24	75 100	100 : 0

[a] Reaction conditions: alkyne (2.40 mmol), amine (2.64 mmol), octane (2.40 mmol), Cp^NTiMe_3 (0.12 mmol, 5 mol %), toluene (2.0 mL), 100 °C. [b] Determined by GC. [c] Determined by ^1H NMR spectroscopy at the end of the reaction.

The hydroamination products are obtained in high yield, with extremely high regioselectivity (Table 5). After 8 h the amount of alkyne transformed into hydroamination products mainly depends on the nature of the amine. For the three alkynes, the hydroamination with 2,6-dimethylaniline is favored with regard to that with 2,6-diisopropylaniline (entries 2 and 4, 6 and 8, and 10 and 12). However, for the cyclohexylamine−*tert*-butylamine pair, the steric requirement of the alkyl group appears to favor the N−H addition to the carbon−carbon triple bond of the alkyne. Thus, the hydroaminations of phenylacetylene and 1-phenylpropyne with *tert*-butylamine are easier than those with cyclohexylamine (entries 1 and 3, and 5 and 7). In contrast to the asymmetric alkynes, the reaction of diphenylacetylene with cyclohexylamine is favored with regard to the hydroamination of this alkyne with *tert*-butylamine (entries 9 and 11). Among the sterically less demanding amines cyclohexylamine and 2,6-dimethylaniline, the latter always gives better results than the first one (entries 1 and 2, 5 and 6, and 9 and 10). However, among the sterically more demanding amines *tert*-butylamine and 2,6-diisopropylaniline, the alkylamine gives better results than the arylamine for the hydroamination of phenylacetylene and 1-phenylpropyne (entries 3 and 4, and 7 and 8). In contrast to the asymmetric alkynes, the hydroamination of diphenylacetylene with 2,6-diisopropylaniline is faster than with *tert*-butylamine (entries 11 and 12).

The results shown in Table 5 also indicate that, in general, the hydroamination is favored with the increase of the bulkiness of the substituent R′ of the alkyne (H < Me < Ph), when the sterically less demanding amines cyclohexylamine and 2,6-dimethylaniline are used.

From the mechanistic point of view, it should be mentioned that in the absence of alkyne the catalyst precursor complex **4** reacts with 2,6-diisopropylaniline to give **6**. Because complex **6** is catalytically inactive, its formation under these conditions suggests that the alkyne plays a main role in the generation process of the catalytically active species. Furthermore, since the stability of the bond between the metal center and the pendant amino group is higher for six-coordinate derivatives than for seven-coordinate compounds, and the dissociation of the pendant amino group is necessary for the hydroamination reaction, it appears reasonable to think that the catalytically active species, in this type of system, is a six-coordinate complex containing a dissociated pendant amino group.

Concluding Remarks

As a result of the extension of our work on the chemistry of complexes containing cyclopentadienyl ligands with a pendant donor substituent on the group 4 metals, in addition to gaining new information about the behavior of the dimethylamino group of the [2-(dimethylamino)ethyl]cyclopentadienyl ligand, we have prepared new titanium complexes and have discovered a new catalytic system.

The reactions of complex Cp^NTiCl_3 with 1.0, 2.0, and 3.0 equiv of MeMgCl afford the mono-, di-, and trimethyl derivatives $Cp^NTiMeCl_2$, Cp^NTiMe_2Cl, and Cp^NTiMe_3, respectively. In the solid state, the aminoalkyl substituent of the cyclopentadienyl ligand of these compounds is weakly bonded to the metal center, *transoid* disposed to a methyl ligand. In solution, the amine dissociates and an equilibrium between seven-coordinate and six-coordinate species is reached. The molar fraction of dissociated amine increases as the number of methyl ligands at the titanium atom also increases. In moist benzene or toluene, the Ti−C bonds of Cp^NTiMe_2Cl undergo hydrolysis to give $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$, which can be described as a dinuclear species containing a planar $Ti(\mu\text{-}O)_2Ti$ core. The amino groups of this compound show a behavior similar to the mononuclear methyl complexes.

Complex Cp^NTiCl_3 also reacts with $LiNH(2,6\text{-}^iPr_2C_6H_3)$. The reaction affords the amido-imido derivative $\{(2,6\text{-}^iPr_2C_6H_3)NH\}Cp^NTi\{N(2,6\text{-}^iPr_2C_6H_3)\}$, which, in contrast to the previously mentioned compounds, contains a pendant dimethylamino group strongly coordinated to the metal center both in the solid state and in solution. Although unsaturated amido-imido-titanium species related to this compound have been proposed as active catalysts for the hydroamination of terminal alkynes,[17b,d,e,g] it is catalytically inactive. However, the trimethyl derivative Cp^NTiMe_3 has been found to be a very efficient catalyst precursor for the regioselective anti-Markovnikov hydroamination of phenylacetylene and 1-phenylpropyne, and the hydroamination of di-

phenylacetylene with cyclohexylamine, 2,6-dimethylaniline, *tert*-butylamine, and 2,6-diisopropylaniline. The reactions lead to the corresponding enamine−imine mixtures, which are transformed into the secondary amines by reduction with molecular hydrogen in the presence of PtO_2.

In conclusion, this paper shows the preparation and characterization of new seven- and six-coordinate titanium complexes containing the [2-(dimethylamino)ethyl]cyclopentadienyl ligand, analyzes the behavior of the pendant aminoalkyl group of these compounds in the solid state and in solution, and reveals the existence of a new titanium system to promote the intermolecular catalytic regioselective anti-Markovnikov hydroamination of asymmetric alkynes.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-line or drybox techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material Cp^NTiCl_3 (**1**) was prepared by the published method.[12] Diphenylacetylene was dissolved in CH_2Cl_2, dried with Na_2SO_4, and recovered by evaporation of the solvent. Phenylacetylene and 1-phenylpropyne were distilled and amines were distilled from CaH_2 and stored in the drybox. All other reagents were purchased from commercial sources and were used without further purification. The course of the catalytic reactions was followed using a Hewlett-Packard 5890 series gas chromatograph with a flame ionization detector, using a 100% cross-linked methyl silicone gum column (30 m × 0.25 mm, with 0.25 μm film thickness) and *n*-octane as the internal standard. The oven conditions used are as follows: 35 °C (hold 6 min) to 280 °C at 25 °C/min (hold 5 min). The reaction products were identified by GC-MS and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopies. GC-MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min to 280 °C at 25 °C/min for 5 min. The carrier gas was helium at a flow of 1 mL/min.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$). Coupling constants, *J*, are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $Cp^NTiMeCl_2$ (2). To an orange suspension of **1** (537 mg, 1.85 mmol) in 18 mL of diethyl ether at −40 °C was added dropwise 1.0 equiv of MgClMe 3 M in tetrahydrofuran (0.62 mL, 1.85 mmol). After addition, the mixture was warmed to room temperature and stirred for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (3 × 40 mL). The resultant brown solution was concentrated to ca. 3 mL, and a brown solid appeared, which was separated by decantation, washed with (2 × 3 mL) pentane, and dried in vacuo. Yield: 214 mg (43%). Anal. Calcd for $C_{10}H_{17}Cl_2NTi$: C, 44.46; H, 6.35; N, 5.19. Found: C, 44.57; H, 6.53; N, 5.23. ^1H NMR (300 MHz, C_7D_8, 363 K): δ 6.40, 5.99 (both m, each 2H, C_5H_4), 2.17 (m, 4H, CH_2CH_2), 2.09 (s, 6H, NMe_2), 1.70 (s, 3H, TiMe). ^1H NMR (300 MHz, C_7D_8, 223 K): δ 6.34, 5.68 (both m, each 2H, C_5H_4), 1.95 (br s, 6H, NMe_2), 1.83 (s, 3H, TiMe), 1.76 (m, 2H, CH_2N), 1.46 (br t, $^3J = 6.6$, 2H, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 135.5 (C_{ipso}-C_5H_4), 120.2, 119.1 (C_5H_4), 78.1 (TiMe), 62.0 (CH_2N), 48.3 (NMe_2), 25.2 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 233 K, plus APT): δ 135.3 (C_{ipso}-C_5H_4), 120.0, 118.9 (C_5H_4), 77.9 (TiMe), 61.8 (CH_2N), 48.3 (NMe_2), 24.4 ($C_5H_4CH_2$).

Preparation of Cp^NTiMe_2Cl (3). The same procedure described for **2** was followed, except that **1** (812 mg, 2.79 mmol) and 2 equiv of MgClMe 3 M in tetrahydrofuran (1.86 mL, 5.58 mmol) were used. The product was obtained as a red solid. Yield: 351 mg (50%). Anal. Calcd for $C_{11}H_{20}ClNTi$: C, 52.90; H, 8.09; N, 5.61. Found: C, 52.43; H, 8.47; N, 5.80. ^1H NMR (300 MHz, C_7D_8, 333 K): δ 6.16, 5.84 (both vt, $^{3+4}J = 6.0$, each 2H, C_5H_4), 2.14 (m, 4H, CH_2CH_2), 2.02 (s, 6H, NMe_2), 1.21 (s, 6H, $TiMe_2$). ^1H NMR (300 MHz, C_7D_8, 213 K): δ 6.21, 5.54 (both m, each 2H, C_5H_4), 1.82 (br s, 6H, NMe_2), 1.53 (m, 2H, $C_5H_4CH_2$), 1.40 (m, 2H, CH_2N), 1.20 (br s, 6H, $TiMe_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 133.0 (C_{ipso}-C_5H_4), 117.4, 114.5 (C_5H_4), 68.6 ($TiMe_2$), 62.1 (CH_2N), 47.7 (NMe_2), 25.9 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 233 K, plus APT and HETCOR): δ 132.7 (C_{ipso}-C_5H_4), 117.3, 114.0 (C_5H_4), 68.3 ($TiMe_2$), 62.2 (CH_2N), 48.0 (NMe_2), 25.0 ($C_5H_4CH_2$).

Preparation of Cp^NTiMe_3 (4). The same procedure described for **2** was followed, except that **1** (500 mg, 1.72 mmol) and 3 equiv of MgClMe 3 M in tetrahydrofuran (1.70 mL, 5.16 mmol) were used. The product was obtained as an orange oil. Yield: 217 mg (55%). Anal. Calcd for $C_{12}H_{23}NTi$: C, 62.90; H, 10.14; N, 6.11. Found: C, 62.43; H, 10.37; N, 6.15. ^1H NMR (300 MHz, C_7D_8, 303 K): δ 5.90, 5.81 (both vt, $^{3+4}J = 6.0$, each 2H, C_5H_4), 2.29 (m, 2H, $C_5H_4CH_2$), 2.25 (m, 2H, CH_2N), 2.03 (s, 6H, NMe_2), 1.13 (s, 9H, $TiMe_3$). ^1H NMR (300 MHz, C_7D_8, 183 K): δ 6.32, 5.49 (both m, each 2H, C_5H_4), 1.63 (br s, 6H, NMe_2), 1.57 (m, 2H, $C_5H_4CH_2$), 1.41 (m, 2H, CH_2N), 1.08 (s, 9H, $TiMe_3$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 293 K, plus APT and HETCOR): δ 131.1 (C_{ipso}-C_5H_4), 113.9, 112.5 (C_5H_4), 61.6 ($TiMe_3$), 61.2 (CH_2N), 45.9 (NMe_2), 28.3 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_7D_8, 203 K, plus APT): δ 130.3 (C_{ipso}-C_5H_4), 115.0, 111.3 (C_5H_4), 63.0 (CH_2N), 59.9 ($TiMe_3$), 47.8 (NMe_2), 24.8 ($C_5H_4CH_2$).

Preparation of $Cp^NTiCl(\mu\text{-}O)_2ClTiCp^N$ (5). In an NMR tube, complex Cp^NTiMe_2Cl (**3**) (20 mg, 0.08 mmol) was dissolved in wet C_6D_6 or C_7D_8. The tube was periodically checked by ^1H NMR spectroscopy. After 7 days, the transformation of **3** into **5** was complete. During that time, a few crystals of **5** suitable for the X-ray diffraction were obtained. Attempts to obtain this product by addition of a stoichiometric amount of water to toluene solutions of **3** led to decomposition. Anal. Calcd for $C_{18}H_{28}Cl_2N_2O_2Ti_2$: C, 45.87; H, 6.00; N, 5.95. Found: C, 45.66; H, 5.47; N, 6.19. ^1H NMR (300 MHz, C_7D_8, 333 K): δ 6.08, 6.04 (both m, each 2H, C_5H_4), 2.60 (m, 2H, $C_5H_4CH_2$), 2.44 (m, 2H, CH_2N), 2.13 (s, 6H, NMe_2). ^1H NMR (300 MHz, C_7D_8, 233 K): δ 6.08, 5.89 (both m, each 2H, C_5H_4), 2.40 (m, 2H, $C_5H_4CH_2$), 2.05 (m, 2H, CH_2N), 1.87 (br s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 129.9 (C_{ipso}-C_5H_4), 113.5, 113.4 (C_5H_4), 60.6 (CH_2N), 45.5 (NMe_2), 28.4 ($C_5H_4CH_2$).

Preparation of {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}Ti{N(2,6-^{i}Pr$_2$-C$_6$H$_3$)} (6). To an orange suspension of **1** (597 mg, 2.05 mmol) in 10 mL of diethyl ether at −40 °C was added a precooled (−40 °C) solution of LiNH(2,6-^{i}Pr$_2$C$_6$H$_3$) (1.25 g, 6.85 mmol) in 15 mL of diethyl ether. After addition, the mixture was warmed to room temperature and stirred for 18 h. The mixture was filtered and concentrated to ca. 5 mL. A yellow solid appeared, which was separated by decantation, washed with (2 × 3 mL) pentane, and dried in vacuo. Yield: 462 mg (42%). Anal. Calcd for $C_{33}H_{49}N_3Ti$: C, 73.98; H, 9.24; N, 7.84. Found: C, 73.55; H, 9.19; N, 7.66. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.81 (s, 1H, NH), 7.21−6.85 (m, 6H, C_6H_3), 6.38, 6.33, 5.83, 5.48 (all m, each 1H, C_5H_4), 4.25, 3.74 (both sept, $^3J = 6.9$, each 2H, $CH(CH_3)_2$), 2.50−2.41 (m, 1H, CHHN), 2.26, 2.25 (both s, each 3H, NMe_2), 2.16−1.97 (m, 3H, $C_5H_4CH_2$-CHHN), 1.30, 1.27, 1.26, 1.21 (all d, $^3J = 6.9$, each 6H, CH-

(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 155.9, 154.0 (C_{ipso}-N), 142.8, 138.8 (*o*-C_6H_3), 131.0 (C_{ipso}-C_5H_4), 122.5, 121.8, 120.4 (C_6H_3), 115.4, 108.3, 106.6, 106.0 (C_5H_4), 69.4 (CH_2N), 50.1, 49.3 (NMe_2), 28.2, 27.4 (*C*H-(CH_3)$_2$), 25.4 ($C_5H_4CH_2$), 24.5, 24.2, 23.7, 23.6 (CH(CH_3)$_2$).

Determination of Constants and Thermodynamic Parameters for the Equilibriums Shown in Eq 1. Variable-temperature ^1H NMR spectra of **2** (183−363 K), **3** (213−333 K), **4** (183−303 K), and **5** (233−333 K) were recorded in toluene-d_8. Equilibrium constants, *K*, were derived from the temperature-dependent $\delta(^1H)$ of the methylene signals CpCH_2 and NCH_2 using eq 2. Thermodynamic parameters were calculated from the equilibrium constants according to eq 6.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (6)$$

Reasonable values for δ_{min} and δ_{max} were obtained by computer-assisted iteration: δ_{min} and δ_{max} were optimized in such a way that plotting of ln *K* versus 1/*T* gives the straightest line possible.

General Procedure for Hydroamination. A Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was charged with the alkyne (2.40 mmol), the amine (2.64 mmol), complex **4** (27.5 mg, 0.12 mmol, 5.0% mol), toluene (2 mL), and *n*-octane (2.40 mmol). The Schlenk was removed from the glovebox and heated at 100 °C. The reaction was monitored by periodic GC analysis of samples removed with a syringe. Either when the reaction was complete or after 24 h, the volatiles were removed under reduced pressure and the residue was analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS.

General Procedure for Hydrogenation. In a Fischer-Porter bottle, PtO_2 (15 mg, 0.07 mmol) was stirred in THF (3.0 mL) at 25 °C under 1 atm of H_2 for 10 min. A solution of the crude hydroamination product in THF (3.0 mL) was then added. The resulting mixture was stirred under 3 atm of H_2 at 25 °C for 48 h. Filtration, concentration, and purification by flash chromatography on silica gel afforded the amines, whose purity was checked by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by GC-MS.

Hydroamination of Phenylacetylene with Cyclohexylamine. PhCH=CHNHCy: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.43−6.95 (m, 5H, Ph), 6.56 (dd, J = 8.7, J = 14.4, 1H, =CHN), 5.37 (d, J = 14.4, 1H, PhC*H*=), 3.00 (br t, J = 8.7, 1H, NH), 2.80−2.70 (m, 1H, CH, Cy), 1.79−0.80 (m, 10H, CH_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 137.5 (C_{ipso} Ph), 134.5 (=CHN), 128.3, 127.1, 123.5 (Ph), 98.7 (Ph*C*H=), 52.7 (CH, Cy), 33.3, 25.8, 24.8 (CH_2). **PhCH_2CH=NCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.90−7.87 (m, 1H, Ph), 7.43 (t, J = 5.1, 1H, CH=N), 7.43−6.95 (m, 4H, Ph), 3.39 (d, J = 5.1, 2H, PhCH_2), 2.80−2.70 (m, 1H, CH, Cy), 1.79−0.80 (m, 10H, CH_2, Cy). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 159.5 (CH=N), 140.6 (C_{ipso} Ph), 129.3, 128.8, 123.9 (Ph), 69.5 (CH, Cy), 42.7 (Ph*C*H$_2$), 33.9, 25.9, 24.8 (CH_2, Cy). MS: *m/z* 200 (M^+). **PhCH_2CH_2-NHCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.34−7.07 (m, 5H, Ph), 2.80−2.64 (m, 4H, CH_2CH_2), 2.32−2.25 (m, 1H, CH), 1.74−0.99 (m, 10H, CH_2, Cy). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 141.0 (C_{ipso} Ph), 129.1, 128.6, 126.2 (Ph), 56.6 (CH), 48.5 (CH_2), 37.2 (CH_2), 33.7, 26.4, 24.9 (*C*H$_2$, Cy).

Hydroamination of Phenylacetylene with 2,6-Dimethylaniline. PhCH=CHNH-2,6-$Me_2C_6H_3$: ^1H NMR: δ 7.19−6.90 (m, 8H, Ph), 6.56 (dd, J = 14.1, J = 6.9, 1H, =CHN), 5.22 (d, J = 14.1, 1H, PhC*H*=), 4.32 (br d, J = 6.9, 1H, NH), 2.08 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 132.9 (=CHN), 139.4, 136.4, 134.3 (C_{ipso} Ph), 129.5, 128.8, 128.6, 127.4, 125.6 (Ph), 101.5 (Ph*C*H=), 18.1 (CH_3). **PhCH_2CH=N-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.95−7.92 (m, 1H, Ph), 7.21 (t, J = 5.1, 1H, CH), 7.14−6.90 (m, 7H, Ph), 3.48 (d, J = 5.1, 2H, CH_2), 2.02 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 165.4 (CH), 138.9, 134.3 (C_{ipso} Ph), 129.3, 128.7, 128.5, 126.9 (Ph), 125.6 (C_{ipso} Ph), 124.3 (Ph), 43.5 (CH_2), 18.2 (CH_3). MS: *m/z* 223 (M^+), 208 ($M^+ - CH_3$), 193 ($M^+ - CH_3$). **PhCH_2CH_2NH-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.19−6.81 (m, 8H, Ph), 3.05 (t, J = 6.9, 2H, CH_2N), 2.59 (t, J = 6.9, 2H, PhCH_2), 2.02 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 146.5, 140.0, 129.5 (C_{ipso} Ph), 129.2, 129.1, 128.7, 126.5, 122.1 (Ph), 49.4 (CH_2N), 37.0 (Ph*C*H$_2$), 18.2 (CH_3).

Hydroamination of Phenylacetylene with *tert*-Butylamine. PhCH=CHNH^{t}Bu: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.23−6.96 (m, 5H, Ph), 6.71 (dd, J = 12.9, J = 13.5, 1H, =CH), 5.40 (d, J = 13.5, 1H, PhC*H*=), 3.16 (br d, J = 12.9, 1H, NH), 0.90 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 140.1 (C_{ipso}), 132.6 (=CH), 128.8, 124.1, 123.9 (Ph), 102.2 (Ph*C*H=), 50.3 (*C*(CH_3)$_3$), 29.7 (C(*C*H$_3$)$_3$). **PhCH_2CH=N^{t}Bu:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.47 (t, J = 5.1, 1H, CH), 7.23−6.96 (m, 5H, Ph), 3.44 (d, J = 5.1, 2H, CH_2), 1.10 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 155.9 (CH), 137.7 (C_{ipso} Ph), 129.3, 127.5, 126.7 (Ph), 56.6 (*C*(CH_3)$_3$), 43.3 (CH_2), 29.5 (C(*C*H$_3$)$_3$). MS: *m/z* 175 (M^+), 160 ($M^+ - CH_3$). **PhCH_2CH_2NH^{t}Bu:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.08 (m, 5H, Ph), 2.70−2.65 (m, 4H, CH_2CH_2), 0.96 (s, 9H, *t*Bu), 0.59 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 141.1 (C_{ipso} Ph), 129.1, 128.6, 126.2 (Ph), 49.8 (*C*(CH_3)$_3$), 44.1 (CH_2N), 37.8 (Ph*C*H$_2$), 28.9 (C(*C*H$_3$)$_3$). MS: *m/z* 177 (M^+), 162 ($M^+ - CH_3$).

Hydroamination of Phenylacetylene with 2,6-Diisopropylaniline. PhCH=CHNH-2,6-^{i}Pr$_2$C$_6$H$_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.15−6.97 (m, 8H, Ph), 6.65 (dd, J = 7.2, J = 14.4, 1H, =CHN), 5.19 (d, J = 14.4, 1H, PhC*H*=), 4.24 (br d, J = 7.2, 1H, NH), 3.19 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 1.18 (d, J = 6.9, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 146.5, 139.6, 135.8 (C_{ipso} Ph), 134.9 (=CHN), 129.3, 128.7, 128.5, 125.6, 124.0 (Ph), 101.3 (Ph*C*H=), 28.1 (*C*H(CH_3)$_2$), 23.9 (CH(*C*H$_3$)$_2$). **PhCH_2CH=N-2,6-^{i}Pr$_2$C$_6$H$_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.41 (t, J = 5.1, 1H, CH), 7.15−6.97 (m, 8H, Ph), 3.53 (d, J = 5.1, 2H, CH_2), 3.02 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 1.09 (d, J = 6.9, 12H, CH-(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 164.8 (CH), 149.6, 137.6, 136.3 (C_{ipso} Ph), 129.4, 128.9, 127.0, 124.4, 123.2 (Ph), 43.6 (CH_2), 27.8 (*C*H(CH_3)$_2$)), 23.3 (CH-(*C*H$_3$))$_2$. MS: *m/z* 279 (M^+), 188 ($M^+ - C_7H_7$). **PhCH_2-CH_2NH-2,6-^{i}Pr$_2$C$_6$H$_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.20−7.10 (m, 8H, Ph), 3.17 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 3.15 (t, J = 6.9, 2H, CH_2N), 2.81 (t, J = 6.9, 2H, PhCH_2), 1.21 (d, J = 6.9, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 143.7, 143.0, 140.2 (C_{ipso} Ph), 129.1, 128.7, 126.5, 124.4, 123.8 (Ph), 53.2 (CH_2N), 37.3 (Ph*C*H$_2$), 27.8 (*C*H(CH_3)$_2$), 24.4 (CH(*C*H$_3$)$_2$). MS: *m/z* 281 (M^+), 190 ($M^+ - C_7H_7$).

Hydroamination of 1-Phenylpropyne with Cyclohexylamine. PhCH=C(Me)NHCy: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.22−6.97 (m, 5H, Ph), 5.40 (s, 1H, CH=), 2.57 (br d, 1H, NH), 2.92−2.84 (m, 1H, CH, Cy), 1.73 (s, 3H, CH_3), 1.74−1.62 (m, 10H, CH_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 140.9, 137.8 (C_{ipso} + =C), 131.8, 128.5, 123.6 (Ph), 96.4 (CH=), 59.4 (CH, Cy), 34.9, 26.2, 25.0 (CH_2), 14.1 (CH_3). **PhCH_2C(Me)=NCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.22−6.97 (m, 5H, Ph), 3.45 (s, 2H, PhCH_2), 3.22−3.13 (m, 1H, CH), 1.74−1.62 (m, 10H, CH_2, Cy), 1.39 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 164.2 (C=N), 138.8 (C_{ipso} Ph), 129.3, 128.7, 126.6 (Ph), 59.2 (CH), 49.7 (Ph*C*H$_2$), 33.9, 26.0, 24.8 (*C*H$_2$, Cy), 15.3 (CH_3). MS: *m/z* 215 (M^+), 200 ($M^+ - CH_3$). **PhCH_2CH-(Me)NHCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.22−7.09 (m, 5H, Ph), 3.02 (sext, J = 6.3, 1H, CH), 2.68 (dd, J = 13.2, J = 6.3, 1H, PhCH_2), 2.49 (dd, J = 6.3, J = 13.2, 1H, PhCH_2), 2.49 (m, 1H, CH, Cy), 1.85−1.49 (m, 6H, CH_2, Cy), 1.27−0.81

(m, 4H, CH_2, Cy), 0.99 (d, J = 6.3, 3H, CH_3), 0.62 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, HETCOR and COSY): δ 140.4 (C_{ipso} Ph), 129.7, 128.5, 126.2 (Ph), 53.2 (*C*H, Cy), 50.9 (CH), 44.4 (Ph*C*H_2), 34.7, 33.7, 26.4, 25.2, 25.0 (CH_2, Cy), 21.1 (CH_3). MS: *m/z* 217 ([M^+), 126 (M^+ − C_7H_7).

Hydroamination of 1-Phenylpropyne with 2,6-Dimethylaniline. PhCH=C(Me)NH-2,6-$Me_2C_6H_3$: ^1H NMR: δ 7.23−6.96 (m, 8H, Ph), 5.12 (s, 1H, CH=), 4.05 (s, 1H, NH), 2.15 (s, 6H, CH_3), 1.82 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 140.1, 139.9, 136.7, 136.0 (C_{ipso} Ph + =C), 129.3, 128.5, 128.4, 126.7, 124.0 (Ph), 99.1 (CH=), 18.2 (CH_3), 17.9 (CH_3). **PhCH_2C(Me)=N-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.23−6.96 (m, 8H, Ph), 3.53 (s, 2H, CH_2), 1.97 (s, 6H, CH_3), 1.24 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 169.2 (C=N), 149.4, 137.8 (C_{ipso} Ph), 129.5, 128.8, 128.3, 126.9 (Ph), 125.8 (C_{ipso} Ph), 122.9 (Ph), 48.2 (CH_2), 18.3 (CH_3), 18.0 (CH_3). MS: *m/z* 237 (M^+), 146 (M^+ − C_7H_7). **PhCH_2CH(Me)NH-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.15−6.83 (m, 8H, Ph), 3.44−3.34 (m, 1H, CH), 2.80−2.74 (m, 2H, 1H, CH_2 + NH), 2.31 (dd, J = 8.4, J = 13.2, 1H, CH_2), 2.09 (s, 6H, CH_3), 0.87 (d, J = 6.3, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 145.3, 139.8 (C_{ipso} Ph), 129.7 (Ph), 129.6 (C_{ipso} Ph), 129.3, 128.5, 126.3, 121.9 (Ph), 54.2 (CH), 44.4 (CH_2), 20.5 (CH_3), 18.8 (CH_3). MS: *m/z* 239 (M^+), 148 (M^+ − C_7H_7).

Hydroamination of 1-Phenylpropyne with *tert*-Butylamine. PhCH=C(Me)NH^{t}Bu: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.21−6.96 (m, 5H, Ph), 5.58 (s, 1H, CH=), 2.60 (br s, 1H, NH), 1.70 (s, 3H, CH_3), 1.16 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 140.9, 139.1 (C_{ipso} Ph + =C), 128.9, 128.2, 123.8 (Ph), 99.7 (CH=), 54.6 (*C*(CH_3)$_3$)), 29.4 (C(*C*H_3)$_3$)), 19.4 (CH_3). **PhCH_2C(Me)=N^{t}Bu:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.21−6.96 (m, 5H, Ph), 3.40 (s, 2H, CH_2), 1.50 (s, 3H, CH_3), 1.25 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 164.2 (C=N), 140.1 (C_{ipso} Ph), 129.2, 128.7, 126.6 (Ph), 51.6 (CH_2), 50.9 (*C*(CH_3)$_3$), 30.4 (C(*C*H_3)$_3$), 19.9 (CH_3). MS: *m/z* 189 (M^+), 174 (M^+ − CH_3). **PhCH_2CH(Me)NH^{t}Bu:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.08 (m, 5H, Ph), 2.85 (sext, J = 6.3, 1H, CH), 2.59 (dd, J = 6.3, J = 13.2, 1H, CH_2), 2.46 (dd, J = 6.3, J = 13.2, 1H, CH_2), 0.97 (d, J = 6.3, 3H, CH_3), 0.92 (s, 9H, *t*Bu), 0.44 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 140.8 (C_{ipso} Ph), 129.8, 128.4, 126.2 (Ph), 50.5 (*C*(CH_3)$_3$), 49.2 (CH), 46.9 (CH_2), 29.9 (C(*C*H_3)$_3$), 24.2 (CH_3). MS: *m/z* 191 (M^+), 176 (M^+ − CH_3).

Hydroamination of 1-Phenylpropyne with 2,6-Diisopropylamine. PhCH=C(Me)NH-2,6-^{i}Pr$_2$C$_6$H$_3$. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.24−6.92 (m, 8H, Ph), 5.09 (s, 1H, CH=), 3.94 (s, 1H, NH), 3.24 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 1.81 (s, 3H, CH_3), 1.19 (d, J = 6.9, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 147.3, 142.1, 140.0, 135.7 (C_{ipso} Ph + =C), 129.3, 128.5, 128.2, 124.0, 123.9 (Ph), 99.9 (CH=), 28.3 (*C*H(CH$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 17.9 (CH_3). **PhCH_2C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.24−6.92 (m, 8H, Ph), 3.54 (s, 2H, CH_2), 2.84 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 1.33 (s, 3H, CH_3), 1.17, 1.06 (both d, J = 6.9, each 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 169.3 (C=N), 146.9, 137.8, 136.3 (C_{ipso} Ph), 129.5, 128.7, 126.9, 123.7, 123.2 (Ph), 48.4 (CH_2), 28.1 (*C*H(CH$_3$)$_2$), 23.2, 22.8 (CH(*C*H$_3$)$_2$), 18.9 (CH_3). MS: *m/z* 293 (M^+), 202 (M^+ - C_7H_7). **PhCH_2CH(Me)NH-2,6-^{i}Pr$_2$C$_6$H$_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.20−7.10 (m, 8H, Ph), 3.29 (m, 2H, 1H, C*H*(CH_3)$_2$, CH), 2.85 (m, 2H, 1H, CH_2 + NH), 2.44 (dd, J = 7.8, J = 12.8, 1H, CH_2), 1.22, 1.20 (both d, J = 6.6, 6H, CH(C*H*$_3$)$_2$), 1.00 (d, J = 6.3, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 143.0, 141.9, 139.9 (C_{ipso} Ph), 129.6, 128.5, 126.4, 124.1, 123.9 (Ph), 57.5 (CH), 44.3 (CH_2), 27.7 (*C*H(CH$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.0 (CH-(*C*H$_3$)$_2$), 20.1 (CH_3). MS: *m/z* 295 (M^+), 204 (M^+ − C_7H_7).

Hydroamination of Diphenylacetylene with Cyclohexylamine. PhCH=C(Ph)NHCy: A 1:1 mixture of *E* and Z isomers was obtained. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.63−7.60 (m, 2H, Ph), 7.45−7.39 (m, 2H, Ph), 7.27−6.99 (m, 16H, Ph), 5.69 (s, 1H, CH=), 5.61 (s, 1H, CH=), 4.11 (br s, 1H, NH), 4.08 (br s, 1H, NH), 3.27−3.14 (m, 1H, CH, Cy), 3.04 (m, 1H, CH, Cy), 1.95−0.83 (m, 20H, CH_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 147.2, 145.5, 140.7, 140.2, 139.9, 139.0 (C_{ipso} Ph + =C), 129.9, 129.4, 129.3, 128.9, 128.4, 128.3, 126.7, 126.5, 125.5, 123.7 (Ph), 106.8 (CH=), 98.3 (CH=), 53.1, 51.3 (CH, Cy), 34.3, 34.1, 34.0, 26.1, 25.9, 25.6, 24.5, 24.3 (CH_2). **PhCH_2C(Ph)=NCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.97 (m, 2H, Ph), 7.52−6.99 (m, 8H, Ph), 3.83 (s, 2H, PhCH_2), 3.63−3.54 (m, 1H, CH), 1.95−0.83 (m, 10H, CH_2, Cy). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 161.8 (C=N), 140.6, 137.8 (C_{ipso} Ph), 129.0, 128.5, 128.3, 128.1, 127.8 (Ph), 60.0 (CH), 34.6, 34.1 (CH_2, Cy), 32.9 (Ph*C*H_2), 26.0, 25.1, 24.8 (CH_2, Cy). MS: *m/z* 277 (M^+), 186 (M^+ − C_7H_7). **PhCH_2CH(Ph)NHCy:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.36−7.02 (m, 10H, Ph), 4.04 (dd, J = 5.7, J = 8.1, 1H, C*H*Ph), 2.86 (dd, J = 13.5, J = 5.7, 1H, PhCH_2), 2.76 (dd, J = 8.1, J = 13.5, 1H, PhCH_2), 2.28 (m, 1H, CH, Cy), 1.78 (br d, J = 12, 1H, NH), 1.44−0.70 (m, 10H, CH_2, Cy). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 145.6, 139.6 (C_{ipso} Ph), 129.6, 128.5, 127.6, 127.1, 126.5 (Ph), 61.4 (*C*HPh), 53.4 (CH, Cy), 46.3 (Ph*C*H_2), 34.9, 32.7, 26.2, 25.1, 24.6 (CH_2, Cy). MS: *m/z* 188 (M^+ − C_7H_7).

Hydroamination of Diphenylacetylene with 2,6-Dimethylaniline. PhCH=C(Ph)NH-2,6-$Me_2C_6H_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.51−7.48 (m, 2H, Ph), 7.12−6.76 (m, 11H, Ph), 5.31 (s, 1H, CH=), 4.23 (s, 1H, NH), 2.16 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 143.6, 139.1, 138.6, 137.8, 135.2 (C_{ipso} Ph + =C), 129.8, 128.9, 128.8, 128.5, 128.1, 125.9, 124.2 (Ph), 101.0 (CH=), 17.9 (CH_3). **PhCH_2C(Ph)=N-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.01−7.97 (m, 2H, Ph), 7.12−6.76 (m, 11H, Ph), 3.70 (s, 2H, CH_2), 1.96 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 166.2 (C=N), 149.2, 139.0, 136.7 (C_{ipso} Ph), 130.4, 129.1, 128.6, 128.5, 128.5, 128.3, 126.4 (Ph), 126.0 (C_{ipso} Ph), 123.3 (Ph), 36.7 (CH_2), 18.3 (CH_3). MS: *m/z* 299 (M^+), 208 (M^+ − C_7H_7). **PhCH_2CH(Ph)NH-2,6-$Me_2C_6H_3$:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.20−6.87 (m, 13H, Ph), 4.35 (t, J = 7.0, 1H, CH), 3.12 (dd, J = 13.2, J = 7.0, 1H, CH_2), 2.93 (dd, J = 13.2, J = 7.0, 1H, CH_2), 2.03 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 145.1, 144.0, 139.0 (C_{ipso} Ph), 129.8 (Ph), 129.7 (C_{ipso} Ph), 129.6, 129.3, 128.7, 127.2, 126.6, 126.4, 122.0 (Ph), 63.7 (CH), 43.5 (CH_2), 18.8 (CH_3).

Hydroamination of Diphenylacetylene with *tert*-Butylamine. PhCH=C(Ph)NH^{t}Bu: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.51−6.81 (m, 10H, Ph), 5.79 (s, 1H, CH=), 2.96 (br s, 1H, NH), 1.12 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 145.1, 140.9, 139.7 (C_{ipso} Ph + =C), 130.2, 128.6, 128.5, 128.1, 123.8 (Ph), 102.5 (CH=), 51.3 (*C*(CH_3)$_3$), 29.5 (C(*C*H_3)$_3$). MS: *m/z* 251 (M^+), 194 (M^+ − C_4H_9). **PhCH_2CH(Ph)NH^{t}Bu:** ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.42−6.98 (m, 10H, Ph), 3.94 (dd, J = 5.1, J = 9.3, 1H, CH), 2.84 (dd, J = 5.1, J = 13.5, 1H, CH_2), 2.59 (dd, J = 9.3, J = 13.5, 1H, CH_2), 1.09 (br s, 1H, NH), 0.81 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 148.5, 139.7 (C_{ipso} Ph), 129.6, 128.5, 127.4, 126.7, 126.5 (Ph), 59.3 (CH), 50.8 (*C*(CH_3)$_3$), 47.5 (CH_2), 29.8 (C(*C*H_3)$_3$). MS: *m/z* 253 (M^+), 181 (M^+ − $C_4H_{10}N$).

Hydroamination of Diphenylacetylene with 2,6-Diisopropylaniline. PhCH=C(Ph)NH-2,6-^{i}Pr$_2$C$_6$H$_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.55−7.52 (m, 2H, Ph), 7.19−6.75 (m, 11H, Ph), 5.30 (s, 1H, CH=), 4.38 (s, 1H, NH), 3.36 (sept, J = 6.9, 2H, C*H*(CH_3)$_2$), 1.20 (d, J = 6.9, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 146.7, 146.1, 139.3, 138.9, 135.6 (C_{ipso} Ph + =C), 129.6, 129.1, 128.9, 128.4, 128.1, 127.6, 124.2, 124.1 (Ph), 101.6 (CH=), 28.4 *C*H(CH$_3$)$_2$),

Table 6. Crystal Data and Data Collection and Refinement for 2, 3, 5, and 6

	2	**3**	**5**	**6**
		Crystal Data		
formula	$C_{10}H_{17}Cl_2NTi$	$C_{11}H_{20}ClNTi$	$C_{18}H_{28}Cl_2N_2O_2Ti_2$	$C_{33}H_{49}N_3Ti$
molecular wt	270.05	249.63	471.12	535.65
color and habit	red, irregular block	red, irregular block	yellow, irregular block	yellow, irregular block
size, mm	0.20,0.10,0.08	0.16,0.12,0.08	0.16,0.06,0.04	0.20,0.16,0.06
symmetry, space group	orthorhombic, $P2_12_12_1$	orthorhombic, $P2_12_12_1$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	8.8802(6)	8.9192(16)	8.4483(14)	17.038(2)
b, Å	9.1973(7)	9.1904(16)	7.8564(13)	11.1820(14)
c, Å	15.0299(11)	15.249(3)	14.967(3)	17.564(2)
β, deg	97.839(3)	112.791(2)		
V, Å ^{3}	1227.55(15)	1250.0(4)	984.1(0)	1819.0(7)
Z	4	4	2	4
D_{calc}, g cm^{-3}	1.461	1.326	1.590	1.153
		Data Collection and Refinement		
diffractometer		Bruker Smart APEX		
λ(Mo Kα), Å		0.71073		
monochromator		graphite oriented		
scan type		ω scans		
μ, mm^{-1}	1.095	0.863	1.098	0.302
2θ, range, deg	3, 57	3, 57	3, 57	3, 57
temp, K	100.0(2)	100.0(2)	100.0(2)	100.0(2)
no. of data collected	15 371	14 992	10 856	28 350
no. of unique data	3035 (R_{int} = 0.0528)	2961 (R_{int} = 0.0924)	2354 (R_{int} = 0.0438)	7500 (R_{int} = 0.0996)
no. of params/restraints	179/0	132/0	120/0	348/0
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0317	0.0610	0.0389	0.0539
wR_2[b] [all data]	0.0479	0.1095	0.0843	0.1041
S[c] [all data]	0.811	0.913	1.002	0.720

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof = $S = \{\sum[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

24.0 CH(CH_3)$_2$). MS: *m/z* 355 (M^+), 264 ($M^+ - C_7H_7$). **PhCH$_2$CH(Ph)NH-2,6-^{i}Pr$_2$C$_6$H$_3$:** ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.07 (m, 13H, Ph), 4.21 (t, J = 7.2, 1H, CH), 3.33 (dd, J = 7.2, J = 13.2, 1H, CH_2), 3.10 (sept, J = 6.9, 2H, CH(CH$_3$)$_2$), 3.08 (dd, J = 7.2, J = 13.2, 1H, CH_2), 1.26, 1.25 (d, J_{H-H} = 6.9, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 143.5, 143.4, 141.7, 139.7 (C_{ipso} Ph), 129.8, 128.4, 127.5, 127.3, 126.4, 124.4, 123.8, 123.7 (Ph), 67.6 (CH), 43.0 (CH_2), 27.6 (*C*H(CH$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$).

Structural Analysis of Complexes 2, 3, 5, and 6. X-ray data were collected for all complexes at 100.0(2) K on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 or 30 s covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[31] The structures for all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[32] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model, respectively. A summary of crystal data and data collection and refinement details is reported in Table 6.

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Supporting Information Available: Crystal structure determinations, including bond lengths and angles of compounds **2**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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