Preparation of Half-Sandwich Alkyl−Titanium(IV) Complexes Stabilized by a Cyclopentadienyl Ligand with a Pendant Phosphine Tether and Their Use in the Catalytic Hydroamination of Aliphatic and Aromatic Alkynes

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Complex Cp^PTiCl_3 (**1**; $Cp^P = C_5H_4CH_2CH_2PPh_2$) reacts with 3.0, 2.0, and 1.0 equiv of MeMgCl to give Cp^PTiMe_3 (**2**), Cp^PTiMe_2Cl (**3**), and $Cp^PTiMeCl_2$ (**4**). In solution the P-donor substituent of the cyclopentadienyl ligand is involved in a coordination−dissociation equilibrium ($\Delta H° = 7.7 \pm 0.1$ kcal·mol^{-1} and $\Delta S° = 36.9 \pm 0.4$ cal·mol^{-1}·K^{-1} for **2**, $\Delta H° = 6.0 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 22.3 \pm 0.6$ cal·mol^{-1}·K^{-1} for **3**, and $\Delta H° = 6.1 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 24.4 \pm 1$ cal·mol^{-1}·K^{-1} for **4**). The reaction of **1** with 3.0 equiv of $PhCH_2MgCl$ affords $Cp^PTi(CH_2Ph)_3$ (**5**), containing a free phosphine pendant group between −90 and 20 °C. In contrast to **5**, the PPh_2 group of {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^PTi-{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**7**), which is formed from the reaction of **2** with 2,6-diisopropylaniline, remains coordinated to the titanium atom between 60 and −60 °C. Complex **2** is an efficient catalyst precursor for the regioselective hydroamination of aliphatic (1-octyne and cyclohexylacetylene) and aromatic (phenylacetylene and 1-phenylpropyne) alkynes with aromatic (2,6-dimethylaniline and 2,6-diisopropylaniline) and aliphatic (*tert*-butylamine, dodecylamine, and cyclohexylamine) amines. The reactions give imines or imine−enamine mixtures, which are reduced to the corresponding secondary amines. The Markovnikov or anti-Markovnikov nature of the obtained products depends on the aliphatic or aromatic character of both the alkyne and the amine. Markovnikov products with regioselectivities of 100% are formed from the reactions between aliphatic alkynes and aromatic amines, while anti-Markovnikov derivatives with regioselectivies of 100% are obtained from the reactions of aromatic alkynes with all the studied amines and from the reactions of the aliphatic alkynes with *tert*-butylamine and dodecylamine. The reaction of 1-octyne and cyclohexylacetylene with cyclohexylamine gives mixtures of both types of products. Some considerations about the mechanism of the catalysis are also presented.

Introduction

The search for the highest selectivity in the organic transformations mediated by transition metal complexes is one of the driving forces of modern organometallic chemistry.

Half-sandwich titanium complexes with constrained geometry, including phosphido derivatives,[1] have received great attention as a consequence of their catalytic properties, in particular for olefin polymerization.[2] In contrast, complexes containing a cyclopentadienyl ligand with a two-electron-donor pendant group have been scarcely studied.[3] Those with a PR_2 function are particularly rare.[4] As far as we know, the unique half-sandwich titanium examples previously reported are the trichloro derivatives Cp^PTiCl_3 ($Cp^P = C_5H_4CH_2CH_2PPh_2$)[5] and ($C_5H_4CMe_2PH^tBu$)$TiCl_3$[6] and the trialkoxide $Cp^PTi(OBu)_3$.[7]

Transition metal complexes with cyclopentadienyl ligands bearing two-electron-donor substituents are an option with a promising future for some reactions. Their potential stems from the reversible coordination of the pendant function, which stabilizes highly reactive electrophilic metal centers until the substrate coordination.[8]

As a part of our work on transition metal complexes containing a cyclopentadienyl ligand with a pendant donor group,[9] we have recently reported that complexes Cp^NTiCl_3[10] ($Cp^N =$

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$C_5H_4CH_2CH_2NMe_2$) and Cp^OTiCl_3[11] ($Cp^O = C_5H_4CH_2CH_2OMe$) react with 1.0, 2.0, and 3.0 equiv of MeMgCl to afford the mono-, di-, and trimethyl derivatives $Cp^NTiMeCl_2$ and $Cp^OTiMeCl_2$, Cp^NTiMe_2Cl and Cp^OTiMe_2Cl, and Cp^NTiMe_3 and Cp^OTiMe_3, respectively. The trimethyl compounds are efficient catalyst precursors for the regioselective anti-Markovnikov hydroamination of nonsymmetrically substituted aromatic alkynes with aliphatic and aromatic amines. The pendant group of the precursors affects significantly their catalytic properties as compared to those of the parent compound $CpTiMe_3$, which contains an unsubstituted cyclopentadienyl ligand. Thus, while the amine derivative is less efficient than $CpTiMe_3$ in all cases,[10] the presence of the ether substituent in the cyclopentadienyl ligand increases the activity of the system for the hydroamination reactions with cyclohexylamine and 2,6-dimethylaniline.[11]

Within the transition-metal-catalyzed hydroaminations,[12] important progress in the intermolecular hydroamination of alkynes with titanium complexes has been reported by the groups of Beller,[13] Bergman,[14] Doye,[15] Odom,[16] and others.[17] Beller and co-workers have found that, among others, titanocene−π-alkyne complexes of the type $Cp_2Ti(\eta^2\text{-}Me_3SiC_2R)$ catalyze the anti-Markovnikov hydroamination of aliphatic alkynes and phenylacetylene.[13] Bergman's group has developed Cp(ArNH)Ti=NAr for the reaction of diphenylacetylene and 2,6-dimethylaniline.[14] Doye and co-workers have described the hydroamination of various internal alkynes by using Cp_2TiMe_2 and Ind_2TiMe_2.[15] Odom and co-workers have demonstrated that titanium amido complexes, such as $Ti(NMe_2)_4$ and $Ti(NMe_2)$(dpma) (dpma = di(pyrrolyl-α-methyl)methylamine), are effective precatalysts for the hydroamination of terminal alkynes to form Markovnikov imines.[16]

As a part of our effort to develop effective methods of C−N bond formation,[10,11,18] we have recently studied the catalytic activity of the novel (2-diphenylphosphinoethyl)cyclopentadienyltitanium complex Cp^PTiMe_3 in the intermolecular hydroamination of alkynes. This paper reports (i) the sequential methylation of Cp^PTiCl_3 until Cp^PTiMe_3, the thermodynamic parameters for the intramolecular dissociation−coordination equilibria of the pendant phosphine group of the resulting methyl derivatives, and their comparison with those of the $Cp^NTiMe_xCl_{3-x}$ and $Cp^OTiMe_xCl_{3-x}$ ($x = 1-3$) counterparts; (ii) the hydroamination of unsymmetrical aliphatic alkynes in the presence of Cp^PTiMe_3 and its comparison with the hydroamination catalyzed by $CpTiMe_3$; (iii) the hydroamination of unsymmetrical aromatic alkynes in the presence of Cp^PTiMe_3 and its comparison with the hydroaminations catalyzed by Cp^OTiMe_3 and $CpTiMe_3$; and (iv) some considerations about the mechanism of the hydroamination of alkynes catalyzed by half-sandwich titanium complexes, containing cyclopentadienyl ligands with a two-electron-donor ligand, which relate the coordination ability of the pendant donor group and the activity of the systems.

Results and Discussion

1. Methylation of Cp^PTiCl_3: Formation and Characterization of Cp^PTiMe_3 and Related Compounds. Treatment at −40 °C of a diethyl ether solution of Cp^PTiCl_3 (**1**) with 3.0 equiv of MeMgCl in tetrahydrofuran gives rise to the trimethyl derivative Cp^PTiMe_3 (**2**), as a result of the replacement of the three chloride ligands of the starting compound by methyl

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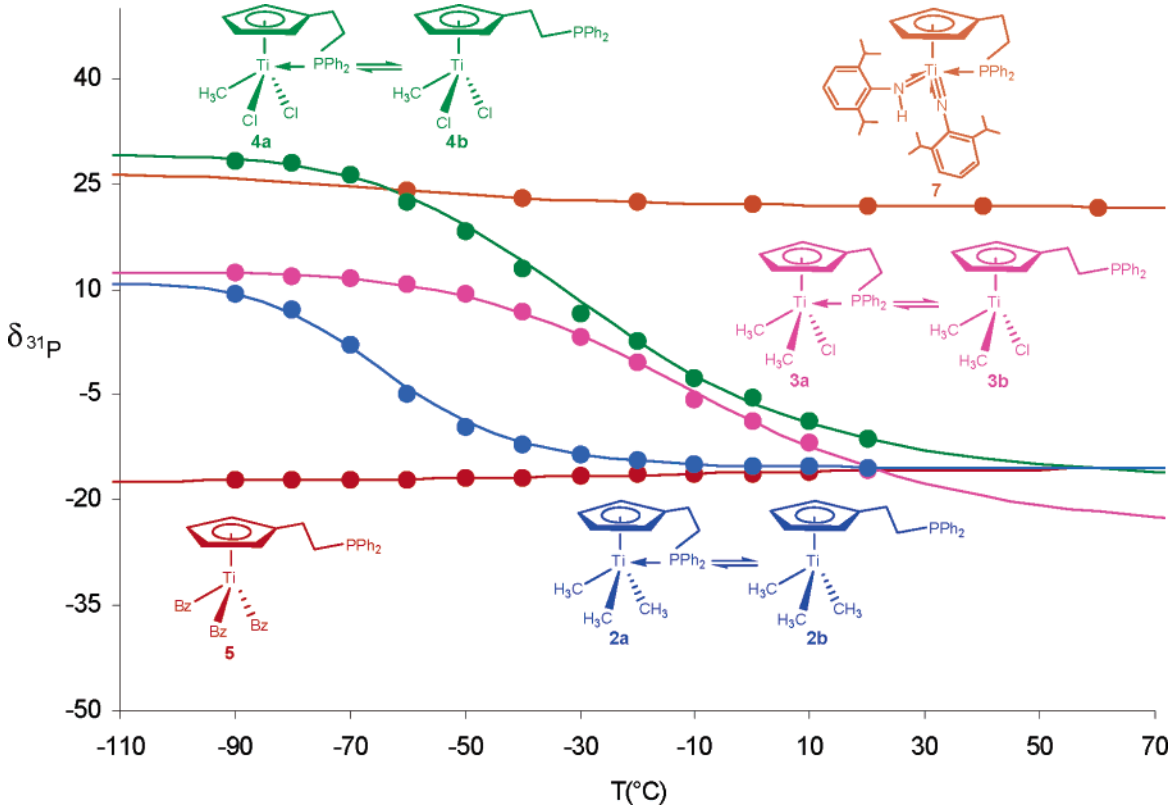

Figure 1. Temperature-dependent ^{31}P NMR of complexes **2**, **3**, **4**, **5**, and **7** in C_7D_8. (●) Denotes the measured chemical shifts.

groups. Complex **2** is isolated as an analytically pure orange oil in 48% yield. Under the same conditions, the addition of 2.0 equiv of MeMgCl to **1** produces the selective substitution of two chloride ligands, to form the dimethyl derivative Cp^P-$TiMe_2Cl$ (**3**), which is isolated as an analytically pure red oil in 44% yield. Treatment of **1** with 1.0 equiv of MeMgCl yields the monomethyl species $Cp^PTiMeCl_2$ (**4**), as a consequence of the selective substitution of one of the chloride ligands of **1** by a methyl group. Complex **4** is isolated as an orange solid in 31% yield. These methyl compounds are notable because they are the first half-sandwich alkyltitanium complexes stabilized by a cyclopentadienyl ligand containing a phosphine pendant group.

In solution the pendant P-donor substituent of the cyclopentadienyl ligand of **2**−**4** is involved in a coordination−dissociation process. This is strongly supported by the phosphine chemical shifts in the $^{31}P\{^1H\}$ NMR spectra, which are temperature dependent (Figure 1). In toluene-d_8, the chemical shift of the singlet due to the phosphine group of **2** changes from −15.4 ppm at 20 °C to 9.2 ppm at −90 °C ($\Delta\delta(^{31}P)$ = 24.6). In the same temperature range, the values of $\Delta\delta(^{31}P)$ for **3** and **4** are 27.9 and 42.8 ppm, respectively.

For the coordination−dissociation processes shown in Figure 1, the equilibrium constants between 20 and −90 °C were determined according to eq 1.[19]

$$K = \frac{[\mathbf{b}]}{[\mathbf{a}]} = \frac{\delta_{max} - \delta_T}{\delta_T - \delta_{min}} \qquad (1)$$

The temperature dependence of the equilibrium gives the values $\Delta H° = 7.7 \pm 0.1$ kcal·mol^{-1} and $\Delta S° = 36.9 \pm 0.4$ cal·mol^{-1}·K^{-1} for **2**, $\Delta H° = 6.0 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 22.3 \pm 0.6$ cal·mol^{-1}·K^{-1} for **3**, and $\Delta H° = 6.1 \pm 0.2$ kcal·mol^{-1} and $\Delta S° = 24.4 \pm 1$ cal·mol^{-1}·K^{-1} for **4**. The positive values of $\Delta S°$ are in agreement with the free character of the pendant group in the six-coordinate isomers **b**, whereas the low values of $\Delta H°$ indicate weak Ti−P bonds in the seven-coordinate isomers **a**.

According to the values of $\Delta H°$ and $\Delta S°$ calculated for **2**−**4**, the molar fractions of hexacoordinate form **b** at 20 °C in toluene-d_8 are about 1.0 (**2**) and between 0.7 and 0.9 (**3** and **4**). These values are similar to those of $Cp^OTiMe_xCl_{3-x}$ (x = 1−3) and significantly higher than those found for $Cp^NTiMe_xCl_{3-x}$ (about 0.8 and between 0.3 and 0.4). Their comparison reveals that the affinity of the amine group of the ligand (2-dimethylaminoethyl)cyclopentadienyl toward titanium(IV) is notably higher than those of the pendant groups of the ligands (2-methoxyethyl)cyclopentadienyl and (2-diphenylphosphinoethyl)cyclopentadienyl.

For the three cyclopentadienyl ligands the molar fraction of hexacoordinate form **b** increases as the chlorine atoms at the metal center are replaced by methyl groups. Although electronic factors are certainly determinant, this suggests that the steric hindrance experienced by the pendant group and the monodentate ligands at the metal also has a significant contribution to the destabilization of the bond between the titanium atom and the pendant donor group. In fact, the treatment of **1** in diethyl ether with 3.0 equiv of $PhCH_2MgCl$ (bulkier than CH_3) affords the six-coordinate complex $Cp^PTi(CH_2Ph)_3$ (**5**), containing a free phosphine pendant group between −90 and 20 °C. This complex is isolated as an analytically pure red oil in 62% yield.

The free character of the phosphine substituent of the cyclopentadienyl ligand is strongly supported by the chemical shift of the singlet observed in the $^{31}P\{^1H\}$ NMR spectrum of **5** in toluene-d_8 at −90 °C (δ, −17.2), which is similar to that previously reported for (2-diphenylphosphinoethyl)(trimethylsilyl)-cyclopentadiene (δ, −14.2)[8a] and not very sensitive to the temperature (Figure 1).

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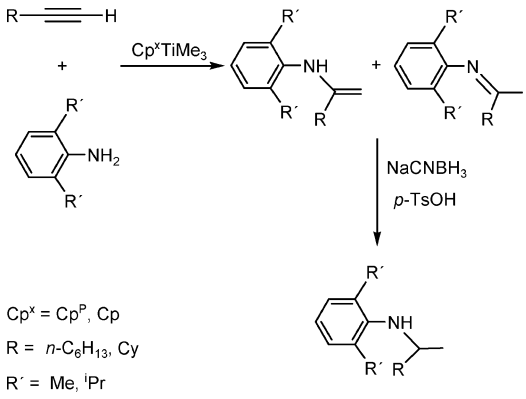
Scheme 1



2. Hydroamination of Terminal Aliphatic Alkynes. Complex **2** and the parent compound $CpTiMe_3$ (**6**), which contains an unsubstituted cyclopentadienyl ligand, are very efficient catalyst precursors for the addition of one of the N−H bonds of aromatic and aliphatic primary amines to the carbon−carbon triple bond of alkynes such as 1-octyne and cyclohexylacetylene. The reactions were performed in toluene at 100 °C, using 5 mol % of catalyst precursor and stoichiometric amounts of alkyne and amine. In contrast to metallocene precursors,[13f,15k] under the used conditions, the loss of alkyne as a consequence of dimerization or polymerization side-reactions does not take place.

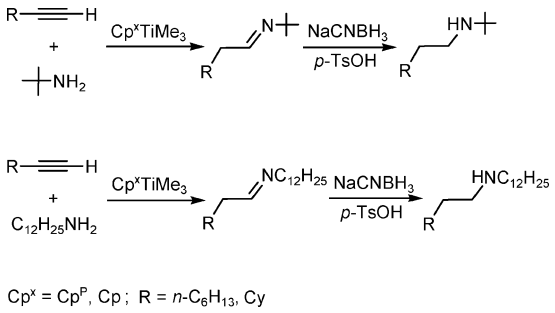
As can be seen in Table 1, both alkynes react with aromatic amines, such as 2,6-dimethylaniline and 2,6-diisopropylaniline, to give enamine−imine mixtures resulting from regioselective Markovnikov couplings. The mixtures were transformed in quantitative yield into the corresponding secondary amines, by reduction with $NaCNBH_3$/*p*-TsOH in tetrahydrofuran at room temperature (Scheme 1).

For the reactions shown in Scheme 1, the presence of a 2-diphenylphosphinoethyl substituent at the cyclopentadienyl ligand certainly increases the efficiency of the half-sandwich titanium precursor. This is clearly evident when the results of the hydroamination in the presence of **2** are compared with those in the presence of **6** (Table 1). With the first precursor (entries 1, 3, 5, and 7) the quantitative conversion of the alkynes into the hydroamination products occurs within a short time (0.75−1.5 h), while with **6** as a catalyst precursor (entries 2, 4, 6, and 8) high conversions are achieved only after longer times (6−24 h). From the regioselectivity point of view, the quantitative transformation of the alkynes into Markovnikov products is also remarkable. In this context, it should be mentioned that for the reaction of 1-octyne and 2,6-dimethylaniline both catalyst precursors are even more regioselective than the metallocenes $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ and $Cp^{Et}_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$.[13f]

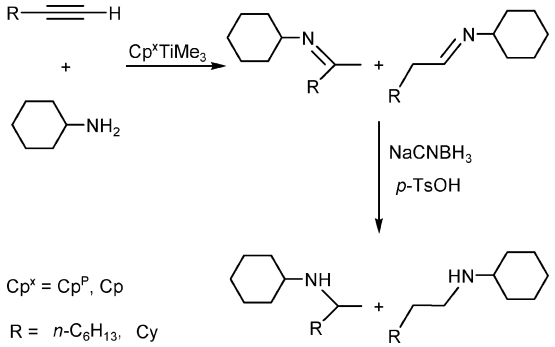
In contrast to the anilines, *tert*-butylamine and dodecylamine selectively give the imines resulting from regioselective anti-Markovnikov couplings (Scheme 2). This surprising change of regioselectivity by changing the nature of the substituent of the amine has been also observed by Beller using $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$[13f] and Doye using Ind_2TiMe_2.[15k] However, it should be noted that in our case the regioselectivity is 100%. Like the enamine−imine mixtures shown in Scheme 1, the imines resulting from aliphatic amines were transformed in quantitative yield into the corresponding secondary amines, by treatment with $NaCNBH_3$/*p*-TsOH in tetrahydrofuran at room temperature.

Also in contrast to the reactions with anilines, for the reactions shown in Scheme 2, the 2-diphenylphosphinoethyl substituent does not appear to exercise a significant influence on the activity

Scheme 2



Scheme 3



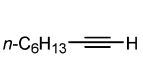
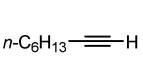
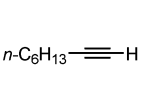
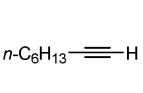
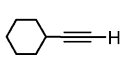
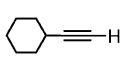
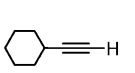
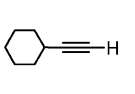
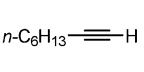
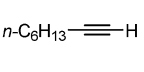
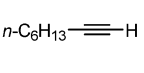
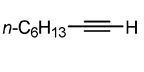
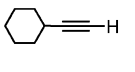
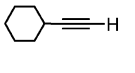
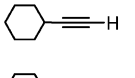
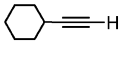
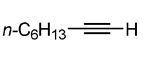
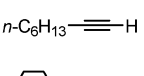
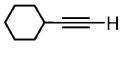
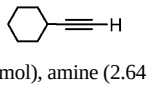
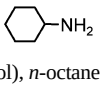
of the half-sandwich precursor. Both compounds **2** and **6** are much more efficient for the reactions with *tert*-butylamine than for those with dodecylamine. Thus, while with the first of them (entries 9, 10, 13, and 14) the quantitative transformation of the alkynes into the corresponding imines occurs within short times (0.25−0.5 h), with the latter (entries 11, 12, 15, and 16) conversions lower than 50% are achieved in all the cases after 24 h.

Cyclohexylamine also reacts with 1-octyne (entries 17 and 18) and cyclohexylacetylene (entries 19 and 20) to give selectively imines. However, in this case, although the formation of the anti-Markovnikov products is favored, the regioselectivity of the addition is much lower than in the previous cases, and mixtures of the Markovnikov and anti-Markovnikov products are formed, which were also transformed into the corresponding secondary amines by reduction with $NaCNBH_3$/*p*-TsOH (Scheme 3). For these reactions, the 2-diphenylphosphinoethyl susbtituent does not exercise a significant influence either on the activity of the precursor or on the regioselectivity of the hydroamination.

3. Hydroamination of Aromatic Alkynes. The trimethyl complex **2** is also an efficient catalyst precursor for the addition of one of the N−H bonds of 2,6-dimethylaniline, 2,6-diisopropylaniline, *tert*-butylamine, cyclohexylamine, and dodecylamine to the carbon−carbon triple bond of alkynes such as phenylacetylene and 1-phenylpropyne (Table 2). In all the cases, the reactions lead to enamine−imine mixtures resulting from the regioselective anti-Markovnikov couplings. The mixtures were transformed in quantitative yield into the corresponding secondary amines, by reduction with molecular hydrogen in the presence of PtO_2 (Scheme 4).

It should be noted that, unlike 1-octyne and cyclohexylacetylene, the products resulting from phenylacetylene and 1-phenylpropyne are always anti-Markovnikov. In addition, it should also be pointed out that the regioselectivity of the addition is 100% for all studied reactions. This is in contrast to that observed by Doye and co-workers, using the bis(indenyl) derivative Ind_2TiMe_2 as catalyst precursor. They have found that the regioselectivity of the reactions is influenced by the nature of the substituent of the aromatic alkyne and the bulkiness of the primary amine.[15k]

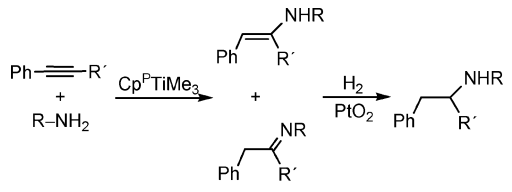
Table 1. Hydroamination of Terminal Aliphatic Alkynes[a]

Entry	Catalyst	Alkyne	Amine	*t* (h)	Conv.[b] (%)	Markovnikov[c] 		Anti-Markovnikov[c] 
1	**2**			0.75	100	40	60	0
2	**6**			6	100	0	100	0
3	**2**			1.5	100	75	25	0
4	**6**			8 24	54 75	55	45	0
5	**2**			1	100	0	100	0
6	**6**			8 24	95 100	0	100	0
7	**2**			1	100	100	0	0
8	**6**			8 24	80 100	76	24	0
9	**2**			0.5	100	0	0	100
10	**6**			0.25	100	0	0	100
11	**2**		$CH_3(CH_2)_{11}NH_2$	8 24	10 20	0	0	100
12	**6**		$CH_3(CH_2)_{11}NH_2$	8 24	19 24	0	0	100
13	**2**			0.5	100	0	0	100
14	**6**			0.25	100	0	0	100
15	**2**		$CH_3(CH_2)_{11}NH_2$	8 24	12 23	0	0	100
16	**6**		$CH_3(CH_2)_{11}NH_2$	8 24	28 50	0	0	100
17	**2**			8 24	75 100	0	16	84
18	**6**			8 24	56 100	0	14	86
19	**2**			8 24	47 68	0	25	75
20	**6**			8 24	35 55	0	5	95

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

In terms of efficiency, complex **2** is comparable with the (2-methoxyethyl)cyclopentadienyl derivative Cp^OTiMe_3, within the half-sandwich titanium family, the most efficient of the previously reported catalyst precursors. For some reactions, it has even been shown to be more efficient than Ind_2TiMe_2, which has been regarded as a "general catalyst".[11]

Scheme 4



R = 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, *tert*-butyl, Dodecyl, Cy

R´ = H, Me

Table 2. Hydroamination of Aromatic Alkynes[a]

Entry	Alkyne	Amine	*t* (h)	Conv. (%)[b]	Enamine : imine[c]
1	Ph—≡—H		1	100	68 : 32
2	Ph—≡—H		2	100	82 : 18
3	Ph—≡—H		0.5	100	56 : 44
4	Ph—≡—H	$CH_3(CH_2)_{11}NH_2$	8 24	14 25	43 : 57
5	Ph—≡—H		8 24	38 83	37 : 63
6	Ph—≡—Me		2	100	84 : 16
7	Ph—≡—Me		4	100	18 : 82
8	Ph—≡—Me		0.5	100	14 : 86
9	Ph—≡—Me	$CH_3(CH_2)_{11}NH_2$	8 24	0 8	
10	Ph—≡—Me		8 24	75 100	24 : 76

[a] Reaction conditions: alkyne (2.40 mmol), amine (2.64 mmol), *n*-octane (2.40 mmol), Cp^PTiMe_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 results shown in Table 2 indicate that the yield of the reactions is influenced mainly by the nature of the amine. Within the reactions with aromatic amines, it is observed that the quantitative transformation of the alkynes occurs with 2,6-dimethylaniline faster than with 2,6-diisopropylaniline; that is, for aromatic amines, the bulkiness of their substituents hinders the reaction. In the opposite direction, the bulkier aliphatic amines give rise to higher conversions. Thus, for both alkynes, the conversions decrease in the sequence *tert*-butylamine > cyclohexylamine > dodecylamine.

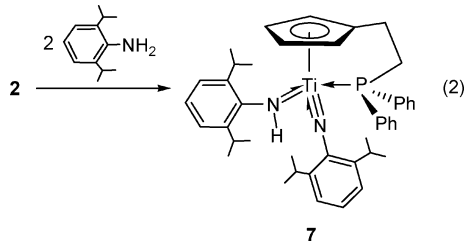
4. Comments about the Role of the Pendant Substituent during the Catalysis. The first clear fact from our previous results and those reported here is that the X group has a marked influence on the efficiency of the Cp^XTiMe_3 (X = CH_2CH_2-NMe_2, H, CH_2CH_2OMe, $CH_2CH_2PPh_2$) catalyst precursors for the hydroamination reactions of terminal alkynes. The efficiency increases as the affinity of the donor group of the cyclopentadienyl pendant substituent toward the titanium atom decreases, i.e., in the sequence NMe_2 < OMe ≈ PPh_2. Thus, while complex Cp^NTiMe_3 is less efficient than **6**, Cp^OTiMe_3 and **2** are more efficient than **6**.

It is generally assumed that under the catalytic conditions the metallocene precursors afford the half-sandwich catalytically active amido−imido species (R′NH)(η^5-C_5R_5)Ti(=NR′), which add the alkyne to give azametallacyclobutene intermediates by reversible [2 + 2] cycloaddition between the C−C triple and Ti−N double bonds. The protonation of the heterometallacycle by action of the amine, followed by an α-elimination reaction in the resulting intermediates, leads to the hydroamination products.[12a,d,13f,15d,h,i,k,l,20]

We have recently reported the preparation, spectroscopic characterization between 60 and −60 °C, and the X-ray structure of the amido−imido complex {(2,6-$^iPr_2C_6H_3$)NH}Cp^NTi{=N(2,6-$^iPr_2C_6H_3$)}, containing a coordinated pendant dimethylamino group, which in solution remains coordinated. In contrast with the assumed catalytic cycle, this compound is completely inactive for the hydroamination reactions with 2,6-diisopropylaniline, despite that the related trimethyl derivative Cp^NTiMe_3 is an efficient catalyst precursor and that its reaction with 2,6-diisopropylaniline also affords the amido−imido complex. To rationalize these results, we suggested that the alkyne plays a main role in the generation process of the catalytically active species in the reactions initiated by Cp^NTiMe_3.[10]

According to the assumed mechanism, for the activation of {(2,6-$^iPr_2C_6H_3$)NH}Cp^NTi{=N(2,6-$^iPr_2C_6H_3$)} the dissociation of the pendant amino group is necessary, and since the affinity of the 2-diphenylphosphino unit toward the titanium atom is lower than that of the 2-dimethylamino group, we decided to prepare {(2,6-$^iPr_2C_6H_3$)NH}Cp^PTi{=N(2,6-$^iPr_2C_6H_3$)} (**7**) and investigate its role in the hydroamination reactions initiated by the trimethyl Cp^PTiMe_3 precursor, with the intention of finding some explanation to our results, from the point of view of the assumed mechanism. The presence of a phosphine group in the system certainly should facilitate the study.

The addition of 2.0 equiv of 2,6-diisopropylaniline to an NMR tube containing a toluene-d_8 solution of **2** gives rise to the quantitative formation of **7**, acoording to eq 2.

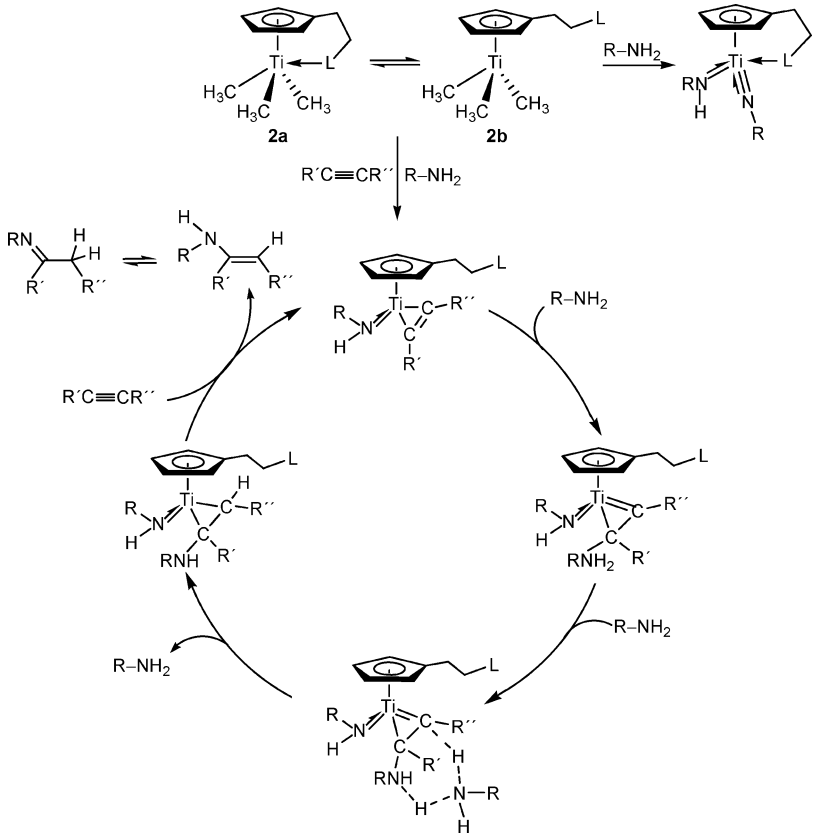


(2)

7

In agreement with the presence of an amido ligand in **7**, its ^1H NMR spectrum contains a NH resonance at 9.34 ppm. The isopropyl substituents of the aromatic rings of the amido and imido ligands display multiplets at 4.14 and 3.71 ppm and four doublets (J_{H-H} = 6.9 Hz) between 1.20 and 1.09 ppm for the eight diasterotopic methyl group. This spectrum, as well as the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, which are temperature invariant between 60 and −60 °C, reveals that the pendant phosphine group of the (2-diphenylphosphinoethyl)cyclopentadienyl ligand does not dissociate in solution, in agreement with that observed for the related (2-dimethylaminoethyl)-cyclopentadienyl derivative {(2,6-$^iPr_2C_6H_3$)NH}Cp^NTi{=N(2,6-$^iPr_2C_6H_3$)}. Thus, due to the chirality of the titanium atom, the ^1H NMR spectrum also shows an ABCD spin system for the methylene resonances. It appears between 2.60 and 2.44 ppm, whereas the resonances corresponding to the cyclopentadienyl protons, which also display an ABCD spin system, are observed between 6.39 and 5.42 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable fact is that the values of the P−C_{ipso} coupling

Scheme 5



constants, 28 (δ, 131.2) and 30 (δ, 131.1) Hz, exceed those of the P−C_{ortho} coupling constants, 13 (δ, 133.6 and 133.5) Hz, in the phosphino−phenyl resonances, while for compounds possessing a noncoordinated $Ph_2PCH_2CH_2$ moiety an inverse relationship is observed.[8a,b] The coordinated character of the phosphine substituent of the cyclopentadienyl ligand is also strongly supported by the chemical shift of the singlet observed in the $^{31}P\{^1H\}$ NMR spectrum, 21.9 ppm. Moreover, it is not very sensitive to the temperature (Figure 1).

The behavior of **7** is in total agreement with that of the related amino derivative {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{N}Ti{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)}. Complex **7** does not react with 2,6-diisopropylaniline or 1-octyne. Furthermore, it is completely inactive for the hydroamination reactions with 2,6-diisopropylaniline. Again, the facts indicate that amido−imido species of the type (RNH)Cp^{X}Ti(=NR) do not play any active role in the intermolecular hydroamination of alkynes initiated by Cp^{X}TiMe$_3$ (X = $CH_2CH_2NMe_2$, CH_2CH_2OMe, $CH_2CH_2PPh_2$) precursors.

The systematic study of the Cp^{X}TiL$_n$ systems in the solid state and in solution proves that the stability of the bond between the titanium atom and the pendant donor group is higher for six-coordinate derivatives than for seven-coordinate compounds. So, since the pendant group seems to be dissociated during the hydroamination reactions, it appears reasonable to think that the catalytically active species are six-coordinate complexes containing a free pendant donor group. Thus, one should expect that under the catalytic conditions the inactive six-coordinate amido−imido species (RNH)Cp^{X}Ti(=NR), with the X group coordinated to the metal center, coexist with active six-coordinate intermediates containing a dissociated pendant donor group. The concentration of the latter should increase as the affinity of the pendant donor group toward the titanium atom decreases, in agreement with the increase of the efficiency of the precursor as the affinity of its pendant donor group decreases.

To corroborate the reasoning, we carried out in a NMR tube the hydroamination of 1-octyne with 2,6-diisopropylaniline using **2** as a catalyst precursor. As expected, the $^{31}P\{^1H\}$ NMR spectrum of the mixture shows two singlets in a 1:2 molar ratio. That of intensity 1 appears at 22.1 ppm, the chemical shift found for **7**, while the other one, of intensity 2, is observed at −16.4 ppm, a chemical shift typical for a free 2-diphenylphosphinoethyl pendant substituent (see Figure 1).

In addition to a [2 + 2] cycloaddition between the C−C triple bond of the alkyne and the Ti−N double bond of an imido intermediate,[21] two approaches can be used to effect the hydroamination: (i) insertion of the C−C triple bond of the alkyne into Ti−H or Ti−NHR bonds,[12a,d,20,22] and (ii) nucleophilic attack of the amine to a coordinate η^2-alkyne.[12a,d,20] The insertion of a coordinated alkyne into a Ti−H or Ti−NHR bond should produce the diminution of the coordination number around the titanium atom in one unit, which should favor the coordination of the pendant donor group, resulting in the deactivation of the system. So, the nucleophilic addition of the amine to a coordinate η^2-alkyne seems to be the most reasonable proposal.

Scheme 5 shows a catalytic cycle for the intermolecular hydroamination of alkynes, which is consistent with our experimental observations and takes into account the previous considerations. The nucleophilic attack of the amine to a coordinated η^2-alkyne of a half-sandwich six-coordinate species containing a free pendant donor substituent at the cyclopentadienyl ring and both substrates, the amine as amido and the alkyne forming a metallacyclopropene, should lead to azonium−metallacyclopropene intermediates. The 1,3-hydrogen shift from the nitrogen

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atom to the C(sp^2) of the metallacycle, promoted by free amine, should afford coordinated enamines. In this context, it should be mentioned that the addition of electrophiles to the C_α carbon atom of early transition metal alkylidene complexes is a well-known process.[23] The enamine could be replaced by an alkyne molecule to regenerate the active species.

Metallacyclopropene complexes with a metal−carbon double bond, as those shown in Scheme 5, are considered important intermediates in several catalytic reactions including alkyne oligomerization,[24] alkyne cyclization,[25] and hydrodesulfurization.[26] They have been isolated mainly with early transition metals[27] and a few with 8 group elements.[28] With some exception, their formation generally involves the external nucleophilic attack on coordinated alkyne ligands.[29] Theoretical calculations show that their structure is stabilized by the presence of an aromatic substituent at the C(sp^2) atom. The stabilization already operative for alkyl substitution through hyperconjugation of the alkyl group is magnified for a phenyl group, where conjugation with a true π-system is possible.[28b] The participation of this type of intermediates in the intermolecular hydroamination of C−C triple bonds is certainly consistent with the fact that aromatic alkynes always selectively give anti-Markovnikov products.

Concluding Remarks

This study shows the preparation and spectroscopic characterization of the first half-sandwich alkyl−titanium complexes stabilized by a cyclopentadienyl ligand bearing a phosphine pendant group, as well as the catalytic properties of the Cp^PTi ($Cp^P = C_5H_4CH_2CH_2PPh_2$) moiety in the hydroamination of aliphatic and aromatic alkynes with aromatic and aliphatic amines.

The previously reported complex Cp^PTiCl_3 reacts with 1.0, 2.0, and 3.0 equiv of MeMgCl to afford the mono-, di-, and trimethyl derivatives $Cp^PTiMeCl_2$, Cp^PTiMe_2Cl, and Cp^PTiMe_3, respectively. In solution, the pendant P-donor substituent of the cyclopentadienyl ligand is involved in a coordination−dissociation process, and equilibria between six- and seven-coordinate compounds are reached. The comparison of the thermodynamic parameters of these equilibria with those of the systems Cp^N-$TiMe_xCl_{3-x}$ and $Cp^OTiMe_xCl_{3-x}$ ($Cp^N = C_5H_4CH_2CH_2NMe_2$, $Cp^O = C_5H_4CH_2CH_2OMe$, $x = 1-3$) reveals that the affinity of the donor group of the cyclopentadienyl substituent toward the titanium atom decreases in the sequence $NMe_2 > OMe \geq PPh_2$. In contrast to these alkyl compounds, the pendant donor group of the amido−imido complex {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^P-Ti{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)}, which is formed by reaction of Cp^P-$TiMe_3$ with 2,6-diisopropylaniline, remains coordinated in solution between 60 and −60 °C.

The trimethyl derivative Cp^PTiMe_3 is an efficient catalyst precursor for the regioselective hydroamination of aliphatic (1-octyne and cyclohexylacetylene) and aromatic (phenylacetylene and 1-phenylpropyne) alkynes with aromatic (2,6-dimethylaniline and 2,6-diisopropylaniline) and aliphatic (*tert*-butylamine, dodecylamine, and cyclohexylamine) amines. The Markovnikov or anti-Markovnikov nature of the obtained products depends on the aliphatic or aromatic character of both the alkyne and the amine. Markovnikov products with regioselectivities of 100% are formed from the reactions between aliphatic alkynes and aromatic amines, while anti-Markovnikov derivatives with regioselectivities of 100% are obtained from the reactions of aromatic alkynes with all the studied amines and from the reactions of the aliphatic alkynes with *tert*-butylamine and dodecylamine. The reaction of 1-octyne and cyclohexylacetylene with cyclohexylamine gives mixtures of both types of products.

The comparison of these results with those previously reported for Cp^NTiMe_3 and Cp^OTiMe_3 shows that the efficiency of this type of precursors increases as the affinity of the donor pendant group of the cyclopentadienyl ligand toward the titanium atom decreases, i.e., in the sequence $NMe_2 < OMe \approx PPh_2$. Since the imido-amido complexes {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^X-Ti{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)} ($Cp^X = Cp^N$, Cp^P) are completely inactive for the hydroamination reactions with 2,6-diisopropylaniline, this sequence suggests that during the catalysis the pendant donor group is not coordinated to the titanium atom.

In conclusion, complex Cp^PTiMe_3 is an efficient catalyst precursor for the hydroamination of aliphatic and aromatic alkynes with aromatic and aliphatic amines. Markovnikov or anti-Markovnikov products are obtained regioselectively depending upon the nature of the substituents of the alkynes and amines. According to the results of the systematic study of the behavior of the pendant substituent of the cyclopentadienyl ligand of complexes Cp^XTiL_n ($X = CH_2CH_2NMe_2$, CH_2CH_2-OMe, $CH_2CH_2PPh_2$), the PPh_2 group is not coordinated to the titanium atom during the catalysis.

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^PTiCl_3 (**1**) was prepared by the published method.[5] Alkynes 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 ^{1}H and ^{13}C-

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{^{1}H} 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.

^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian UNITY 300, a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 300 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P{^{1}H}). Coupling constants, *J*, are given in hertz. C and H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of Cp^{P}TiMe$_3$ (2). To a dark red suspension of **1** (610 mg, 1.41 mmol) in 20 mL of diethyl ether at −40 °C was added dropwise 3.0 equiv of MeMgCl (1.40 mL, 4.24 mmol, 3 M in tetrahydrofuran). After addition, the mixture was warmed slowly to 20 °C and stirred for 4 h. The volatiles were removed under reduced pressure, and the residue was extracted with pentane (3 × 50 mL). The solvent was removed from the resultant orange solution under vacuum, affording an orange oil. Yield: 252 mg (48%). Anal. Calcd for $C_{22}H_{27}PTi$: C, 71.36; H, 7.36. Found: C, 71.85; H, 7.56. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.39−6.98 (m, 10H, Ph), 5.81, 5.72 (both m, each 2H, C_5H_4), 2.46−2.38 (m, 2H, CH_2), 2.21−2.15 (m, 2H, CH_2), 1.11 (s, 9H, $TiMe_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): −15.4 (br s). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 183 K): 9.2 (br s).^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 253 K): δ 137.8 (d, $^3J_{CP}$ = 9, C_{ipso} C_5H_4), 133.1 (d, $^2J_{CP}$ = 18, *o*-Ph), 132.5 (d, $^1J_{CP}$ = 14, C_{ipso} Ph), 128.8 (d, $^3J_{CP}$ = 7, *m*-Ph), 128.7 (*p*-Ph), 113.4, 112.0 (C_5H_4), 62.0 ($TiMe_3$), 30.0 (d, $^1J_{CP}$ = 10, CH_2P), 26.6 (d, $^2J_{CP}$ = 20, $C_5H_4CH_2$).

Preparation of Cp^{P}TiMe$_2$Cl (3). The same procedure described for **2** was followed, except that **1** (566 mg, 1.31 mmol) and 2.0 equiv of MeMgCl (0.87 mL, 2.62 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as a red oil. Yield: 226 mg (44%). Anal. Calcd for $C_{21}H_{24}ClPTi$: C, 64.53; H, 6.20. Found: C, 65.11; H, 5.65. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.39−6.97 (m, 10H, Ph), 5.95, 5.78 (both m, each 2H, C_5H_4), 2.48−2.30 (m, 4H, CH_2CH_2), 1.25 (s, 6H, $TiMe_2$). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): −15.6 (br s). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 183 K): 12.3 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 253 K, plus APT): δ 135.9 (d, $^3J_{CP}$ = 8, C_{ipso} C_5H_4), 134.9 (d, $^1J_{CP}$ = 9, C_{ipso} Ph), 133.3 (d, $^2J_{CP}$ = 13, *o*-Ph), 129.6 (*p*-Ph), 128.8 (d, $^3J_{CP}$ = 6, *m*-Ph), 116.3, 114.3 (C_5H_4), 68.5 ($TiMe_2$), 30.0 (br, CH_2P), 24.9 (d, $^2J_{CP}$ = 20, $C_5H_4CH_2$).

Preparation of Cp^{P}TiMeCl$_2$ (4). The same procedure described for **2** was followed, except that **1** (526 mg, 1.22 mmol) and 1.0 equiv of MeMgCl (0.40 mL, 1.22 mmol, 3 M in tetrahydrofuran) were used. The product was obtained as an orange solid. Yield: 155 mg (31%). Anal. Calcd for $C_{20}H_{21}Cl_2PTi$: C, 58.40; H, 5.16. Found: C, 58.79; H, 5.07. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.45−6.97 (m, 10H, Ph), 6.06, 5.85 (both m, each 2H, C_5H_4), 2.50−2.35 (m, 4H, CH_2CH_2), 1.68 (s, 3H, TiMe). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): −14.5 (br s). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 183 K): 28.3 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 253 K, plus APT): δ 138.2 (d, $^3J_{CP}$ = 8, C_{ipso} C_5H_4), 134.9 (d, $^1J_{CP}$ = 9, C_{ipso} Ph), 133.9 (d, $^2J_{CP}$ = 12, *o*-Ph), 129.7 (*p*-Ph), 128.8 (br, *m*-Ph), 119.2, 118.1 (C_5H_4), 78.5 (TiMe), 31.2 (br, CH_2P), 26.6 (d, $^2J_{CP}$ = 20, $C_5H_4CH_2$).

Preparation of Cp^{P}Ti(CH$_2$Ph)$_3$ (5). The same procedure described for **2** was followed, except that **1** (616 mg, 1.43 mmol) and 3.0 equiv of $PhCH_2MgCl$ (2.1 mL, 4.28 mmol, 2 M in tetrahydrofuran) were used. The product was obtained as a red oil. Yield: 526 mg (62%). Anal. Calcd for $C_{40}H_{39}PTi$: C, 80.24; H, 6.58. Found: C, 79.70; H, 7.15. ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 7.32−6.70 (m, 25H, Ph), 5.54, 5.48 (both m, each 2H, C_5H_4), 2.90 (s, 6H, CH_2Ph), 2.11−1.99 (m, 4H, CH_2CH_2). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): −15.8 (br s). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 183 K): −17.2 (br s). ^{13}C{^{1}H} NMR (75.42 MHz, C_7D_8, 293 K, plus APT): δ 148.6 (C_{ipso} Ph), 139.1 (d, $^3J_{CP}$ = 14, C_{ipso} C_5H_4), 136.4 (d, $^1J_{CP}$ = 15, C_{ipso} Ph), 133.2 (d, $^2J_{CP}$ = 19, *o*-Ph), 129.5 (*p*-Ph), 128.5 (Ph), 128.7 (d, $^3J_{CP}$ = 7, *m*-Ph), 126.7, 122.9 (Ph), 117.9, 116.1 (C_5H_4), 92.3 (CH_2Ph), 29.9 (d, $^1J_{CP}$ = 15, CH_2P), 26.5 (d, $^2J_{CP}$ = 17, $C_5H_4CH_2$).

Preparation of {(2,6-^{i}Pr$_2$C$_6$H$_3$)NH}Cp^{P}Ti{=N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (7). An orange solution of **2** (200 mg, 0.54 mmol) in 10 mL of toluene was treated with 2.0 equiv of 2,6-diisopropylaniline (210 μL, 1.08 mmol) at 0 °C. Immediately gas evolution was observed. The mixture was heated to 100 °C and stirred for 4 h. Then the solvent was removed under vacuum and the product was washed with pentane (4 × 3 mL) and dried in vacuo. The product was obtained as a red oil. In our hands it was not possible to completely remove free 2,6-diisopropylaniline, and attempts to obtain satisfactory combustion analysis were unsuccessful. Yield: 274 mg (75%). ^{1}H NMR (300 MHz, C_7D_8, 293 K): δ 9.34 (s, 1H, NH), 7.74−7.39 (m, 10H, Ph), 7.14−6.80 (m, 6H, C_6H_3), 6.39, 6.06, 5.91, 5.42 (all m, each 1H, C_5H_4), 4.14, 3.71 (both m, each 2H, $CH(CH_3)_2$), 2.60−2.44 (m, 4H, CH_2CH_2), 1.20, 1.19, 1.12, 1.09 (all d, $^3J_{HH}$ = 6.9, each 6H, $CH(CH_3)_2$). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 293 K): 21.9 (s). ^{31}P{^{1}H} NMR (121.42 MHz, C_7D_8, 213 K): 24.1 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 156.3 (d, $^3J_{CP}$ = 1, C_{ipso} N), 153.7 (C_{ipso} N), 143.1, 143.0 (*o*-C_6H_3), 133.6 (d, $^2J_{CP}$ = 13, *o*-Ph), 133.6 (d, $^3J_{CP}$ = 7, C_{ipso} C_5H_4), 133.5 (d, $^2J_{CP}$ = 13, *o*-Ph), 133.3, 133.0 (both d, $^2J_{CP}$ = 2, *p*-Ph), 131.2 (d, $^1J_{CP}$ = 28, C_{ipso} Ph), 131.1 (d, $^1J_{CP}$ = 30, C_{ipso} Ph), 130.7 (d, $^3J_{CP}$ = 15, *m*-Ph), 130.6 (d, $^3J_{CP}$ = 15, *m*-Ph), 122.3, 122.0, 120.6 (C_6H_3), 114.3, 107.6, 106.6, 105.4 (C_5H_4), 36.3 (d, $^1J_{CP}$ = 23, CH_2P), 28.7, 27.9 ($CH(CH_3)_2$), 24.7, 24.2, 24.1 ($CH(CH_3)_2$), 24.1 ($C_5H_4CH_2$), 23.9 ($CH(CH_3)_2$).

Reaction of Cp^{P}TiMe$_3$ (2) with 1-Octyne and 2,6-Diisopropylaniline. In an NMR tube, complex Cp^PTiMe_3 (**2**) (15 mg, 0.04 mmol) was dissolved in C_7D_8. 1-Octyne (113 μL, 0.74 mmol) and 2,6-diisopropylaniline (157 μL, 0.81 mmol) were added. The mixture was warmed at 100 °C. The tube was checked by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After 30 min, the ^{1}H NMR spectrum showed the formation of enamine $CH_3(CH_2)_5C(=CH_2)NH$-2,6-^{i}Pr$_2$-C_6H_3, and the ^{31}P{^{1}H} NMR spectrum showed two singlets at 22.1 and −16.4 ppm in a 1:2 molar ratio.

Determination of Constants and Thermodynamic Parameters for the Equilibriums Shown in Figure 1. Variable-temperature ^{31}P{^{1}H} NMR spectra of **2** (−90 to 20 °C), **3** (−90 to 20 °C), and **4** (−90 to 20 °C) were recorded in toluene-d_8. Equilibrium constants, *K*, were derived from the temperature-dependent δ(^{31}P{^{1}H}) using eq 1. Thermodynamic parameters were calculated from the equilibrium constants according to eq 3.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (3)$$

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 **2** or complex **6** (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 on completion of the reaction or after 24 h, the volatiles were removed under reduced pressure and the residue was analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and by GC-MS.

General Procedure for Hydrogenation. Enamines and imines resulting from hydroamination of aromatic alkynes were hydroge-

nated as described elsewhere.[10,11] Enamines and imines resulting from hydroamination of aliphatic alkynes were hydrogenated as follows: The crude hydroamination product was dissolved in THF (2.0 mL). $NaCNBH_3$ (302 mg, 4.8 mmol) and *p*-toluenesulfonic acid monohydrate (46 mg, 0.24 mmol) were added, and the mixture was stirred at room temperature. After 4 h, diethyl ether (4.0 mL) and 2 N HCl (4.0 mL) were added. The mixture was stirred for 1 h at room temperature. The organic layer was separated, and saturated $NaHCO_3$ solution was added to the water layer until pH = 7 was reached. The water layer was extracted with diethyl ether (2 × 4 mL). The combined organic layers were dried with $MgSO_4$, and 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.

Characterization Data of New Compounds. Hydroamination of 1-Octyne with 2,6-Dimethylaniline. $CH_3(CH_2)_5C(=CH_2)NH$-2,6-$Me_2C_6H_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.02 (m, 3H, Ph), 4.03 (br s, 1H, NH), 3.74, 3.45 (both s, each 1H, $=CH_2$), 2.25 (s, 6H, CH_3), 2.06−2.01, 1.81−1.76, 1.56−1.49 (all m, 6H, CH_2), 1.38−1.28 (m, 4H, CH_2), 0.91 (t, J = 7.2, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 148.0 (C=), 143.3, 139.5 (C_{ipso} Ph), 129.3, 128.5 (Ph), 80.5 ($=CH_2$), 36.1, 34.4, 31.5, 29.3, 28.5 (CH_2), 18.1 (CH_3), 14.1 (CH_3CH_2). **$CH_3(CH_2)_5C(CH_3)$=N-2,6-$Me_2C_6H_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.04−6.89 (m, 3H, Ph), 2.21 (t, J = 7.3, 2H, $CH_2C=$), 2.00 (s, 6H, CH_3), 1.68−1.63 (m, 2H, CH_2), 1.37−1.24 (m, 6H, CH_2), 1.28 (s, 3H, CH_3), 0.91 (t, J = 7.3, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 170.2 (C=), 149.9 (C_{ipso} Ph), 128.6 (Ph), 125.6 (C_{ipso} Ph), 122.6 (Ph), 40.6, 31.9, 29.3, 26.3, 22.8 (CH_2), 19.3 ($=CCH_3$), 17.9 (CH_3), 14.1 (CH_3CH_2). MS: *m*/*z* 231 (M^+), 146 ($M^+ - (CH_3(CH_2)_5)$). **$CH_3(CH_2)_5CH(CH_3)$NH-2,6-$Me_2C_6H_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 6.85−6.66 (m, 3H, Ph), 3.04−2.97 (m, 1H, CH), 2.12 (s, 6H, CH_3), 1.73−1.07 (m, 10H, CH_2), 1.00 (d, J = 6.6, 3H, $CHCH_3$), 0.92 (t, J = 7.2, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 132.3, 130.7 (C_{ipso} Ph), 129.8, 128.9 (Ph), 61.3 (CH), 32.8, 31.6, 28.7, 25.6, 22.6 (CH_2), 18.1 (CH_3), 15.9 ($CHCH_3$), 14.0 (CH_3CH_2). MS: *m*/*z* 233 (M^+), 148 ($M^+ - (CH_3(CH_2)_5)$).

Hydroamination of 1-Octyne with 2,6-Diisopropylaniline. $CH_3(CH_2)_5C(=CH_2)NH$-2,6-$^iPr_2C_6H_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−6.82 (m, 3H, Ph), 4.00 (br s, 1H, NH), 3.70, 3.42 (both s, each 1H, $=CH_2$), 3.29 (sept, J = 6.9, 2H, $CH(CH_3)_2$), 2.03 (t, J = 7.6, 2H, $CH_2C=$), 1.45−1.38 (m, 2H, CH_2), 1.24−1.07 (m, 6H, CH_2), 1.14 (d, J = 6.9, 12H, $CH(CH_3)_2$), 0.91−0.87 (m, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 150.4 (C=), 147.1, 136.5 (C_{ipso} Ph), 125.6, 123.8 (Ph), 81.0 ($=CH_2$), 36.1, 32.0, 29.2, 28.3 (CH_2), 28.2 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 22.9 (CH_2), 14.1 (CH_3). **$CH_3(CH_2)_5C(CH_3)$=N-2,6-$^iPr_2C_6H_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.02 (m, 3H, Ph), 2.89 (sept, J = 6.9, 2H, $CH(CH_3)_2$), 2.25 (t, J = 7.5, 2H, $CH_2C=$), 1.75−1.63 (m, 2H, CH_2), 1.40 (s, 3H, CH_3), 1.35−1.23 (m, 6H, CH_2), 1.20, 1.17 (both d, J = 6.9, each 6H, $CH(CH_3)_2$), 0.91−0.87 (m, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 170.2 (C=), 137.8 136.2 (C_{ipso}−Ph), 123.5, 123.3 (Ph), 40.7, 31.9, 29.3 (CH_2), 28.2 ($CH(CH_3)_2$), 26.2 (CH_2), 23.2 ($CH(CH_3)_2$), 22.9 (CH_2), 22.8 ($CH(CH_3)_2$), 20.0 (CCH_3), 14.0 (CH_3CH_2). MS: *m*/*z* 287 (M^+), 202 ($M^+ - (CH_3(CH_2)_5)$). **$CH_3(CH_2)_5CH(CH_3)$NH-2,6-$^iPr_2C_6H_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.11−6.97 (m, 3H, Ph), 3.76 (sept, J = 6.9, 2H, $CH(CH_3)_2$), 3.23−3.18 (m, 1H, CH), 2.09−2.04 (m, 2H, CH_2), 1.51 (d, J = 4.5, 3H, $CHCH_3$), 1.26−1.00 (m, 8H, CH_2), 1.25 (d, J = 6.9, 12H, $CH(CH_3)_2$), 0.82 (t, J = 5.5, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 129.3, 128.9 (C_{ipso} Ph), 128.5, 127.7 (Ph), 62.6 (CH), 32.6, 31.9, 28.9, (CH_2), 28.8 ($CH(CH_3)_2$), 26.4 (CH_2), 24.0 ($CH(CH_3)_2$), 22.8 (CH_2), 16.2 ($CHCH_3$), 14.2 (CH_3CH_2). MS: *m*/*z* 289 (M^+), 204 ($M^+ - (CH_3(CH_2)_5)$).

Hydroamination of 1-Octyne with *tert*-Butylamine. $CH_3(CH_2)_5CH_2CH$=N^{t}Bu: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.46 (t, J = 4.5, 1H, CH), 2.20−2.14 (m, 2H, CH_2CH), 1.47−1.17 (m, 10H, $(CH_2)_5CH_2$), 1.15 (s, 9H, $C(CH_3)_3$), 0.86 (t, J = 5.4, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 157.1 (CH), 56.3 ($C(CH_3)_3$), 36.4, 31.9 (CH_2), 29.7 ($C(CH_3)_3$), 29.4, 29.3, 26.1, 22.8 (CH_2), 14.0 (CH_3). MS: *m*/*z* 183 (M^+), 168 ($M^+ - CH_3$). **$CH_3(CH_2)_6CH_2NH^tBu$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 9.01 (br s, 1H, NH), 2.62, 1.98 (both m, each 2H, CH_2), 1.49−1.20 (m, 10H, CH_2), 1.29 (s, 9H, $C(CH_3)_3$), 0.95 (t, J = 6.3, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 56.8 ($C(CH_3)_3$), 41.9, 32.0, 29.5, 29.4, 27.2, 26.7 (CH_2), 25.5 ($C(CH_3)_3$), 22.9 (CH_2), 14.2 (CH_3). MS: *m*/*z* 185 (M^+), 170 ($M^+ - CH_3$).

Hydroamination of 1-Octyne with Dodecylamine. $CH_3(CH_2)_5CH_2CH=NCH_2(CH_2)_{10}CH_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.47 (t, J = 4.5, 1H, CH=), 3.36 (t, J = 5.1, 2H, CH_2), 2.18−2.10 (m, 2H, CH_2CH), 1.90−1.40 (m, 10H, CH_2), 1.27−1.21 (m, 20H, CH_2), 0.91−0.84 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 163.1 (CH=), 61.8, 35.8, 32.2, 32.0, 31.3, 29.9, 29.8, 29.4, 27.6, 26.1, 22.9 (CH_2), 14.1, 14.0 (CH_3). MS: *m*/*z* 295 (M^+), 210 ($M^+ - CH_3(CH_2)_5$). **$CH_3(CH_2)_6CH_2NHCH_2(CH_2)_{10}CH_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 2.75−2.55 (m, 4H, CH_2), 1.85−1.50 (m, 10H, CH_2), 1.40−1.20 (m, 22H, CH_2), 0.93−0.90 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 53.4, 48.1, 32.4, 32.1, 30.3−29.4, 28.7, 27.0, 26.5, 26.2, 25.9 (CH_2), 14.1, 14.0 (CH_3). MS: *m*/*z* 297 (M^+), 212 ($M^+ - CH_3(CH_2)_5$).

Hydroamination of 1-Octyne with Cyclohexylamine. $CH_3(CH_2)_5CH_2CH=NCy$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.45 (t, J = 4.5, 1H, CH=), 2.89−2.80 (m, 1H, CH Cy), 2.14−2.07 (m, 2H, CH_2CH), 1.74−1.09 (m, 20H, CH_2), 0.84 (t, J = 7.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 160.9 (CH=), 69.9 (CH Cy), 35.9, 34.8, 31.9, 29.3, 26.1, 25.9, 24.8, 22.8 (CH_2), 14.1 (CH_3). **$CH_3(CH_2)_5C(CH_3)$=NCy**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 3.27−3.18 (m, 1H, CH Cy), 1.74−1.09 (m, 20H, CH_2), 1.47 (s, 3H, CH_3), 0.84 (t, J = 7.0, 3H, CH_3CH_2). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 164.2 (C=), 59.0 (CH Cy), 42.4, 34.0, 32.1, 29.5, 26.4, 26.3, 24.9, 22.9 (CH_2), 16.1 (CH_3), 14.1 (CH_3CH_2). MS: *m*/*z* 209 (M^+), 166 ($M^+-(CH_3(CH_2)_2)$). **$CH_3(CH_2)_6CH_2NHCy$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 2.56 (t, J = 6.3, 2H, CH_2N), 2.39−2.31 (m, 1H, CH Cy), 1.80−1.05 (m, 22H, CH_2), 0.87 (t, J = 7.2, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 56.9 (CH Cy), 47.2, 33.9, 32.1, 31.0, 29.8, 26.5, 25.6, 25.0, 22.9 (CH_2), 14.1 (CH_3). **$CH_3(CH_2)_5CH(CH_3)NHCy$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 2.74−2.68 (m, 1H, CH), 2.56−2.46 (m, 1H, CH Cy), 1.80−1.05 (m, 20H, CH_2), 0.99 (d, J = 6.0, 3H, $CHCH_3$), 0.87 (t, J = 7.2, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 53.4 (CH Cy), 49.4 (CH), 34.9, 33.9, 32.0, 31.0, 29.6, 27.7, 25.6, 22.9 (CH_2), 21.3 ($CHCH_3$), 14.1 (CH_3). MS: *m*/*z* 211 (M^+), 168 ($M^+ - (CH_3(CH_2)_2)$).

Hydroamination of Cyclohexylacetylene with 2,6-Dimethylaniline. $CyC(CH_3)$=N-2,6-$Me_2C_6H_3$: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.18−7.02 (m, 3H, Ph), 2.10−2.03 (m, 1H, CH), 1.98 (s, 6H, CH_3), 1.83−1.15 (m, 10H, CH_2), 1.28 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): δ 173.6 (C=), 149.8 (C_{ipso} Ph), 128.5 (Ph), 125.4 (C_{ipso} Ph), 122.5 (Ph), 48.6 (CH), 30.5, 26.3 (CH_2), 17.8 (CH_3), 17.3 (CCH_3). MS: *m*/*z* 229 (M^+), 146 ($M^+ - Cy$). **$CyCH(CH_3)$NH-2,6-$Me_2C_6H_3$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.04−6.90 (m, 3H, Ph), 3.03−2.90 (m, 1H, CH), 2.02 (s, 6H, CH_3), 1.93−0.87 (m, 11H, Cy), 1.00 (d, J = 4.8, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): δ 132.8, 132.0

(C_{ipso} Ph), 130.7, 125.9 (Ph), 65.7 (CH), 39.6 (CH Cy), 28.8, 25.9 (CH_2), 20.7 (CH_3), 20.2 (CH*C*H_3). MS: *m*/*z* 231 (M^+), 148 (M^+ − Cy).

Hydroamination of Cyclohexylacetylene with 2,6-Diisopropylaniline. CyC(═CH$_2$)NH-2,6-^{i}Pr$_2$C$_6$H$_3$: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.18−6.95 (m, 3H, Ph), 4.05 (br s, 1H, NH), 3.69, 3.35 (both s, each 1H, ═CH_2), 3.28 (sept, *J* = 6.9, 2H, C*H*(CH_3)$_2$), 1.92−1.28 (m, 11H, Cy), 1.21 (d, *J* = 6.9, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 155.7 (C═), 147.1, 136.4 (C_{ipso} Ph), 127.3, 123.8 (Ph), 79.0 (═CH_2), 44.7 (CH Cy), 32.4 (CH_2 Cy), 28.2 (*C*H(CH$_3$)$_2$), 26.8 (CH_2 Cy), 24.1 (CH(*C*H$_3$)$_2$). **CyC(CH$_3$)═N-2,6-^{i}Pr$_2$C$_6$H$_3$**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.18−6.95 (m, 3H, Ph), 2.88 (sept, *J* = 6.9, 2H, C*H*(CH_3)$_2$), 2.17−2.08 (m, 1H, CH), 1.95−1.41 (m, 10H, CH_2), 1.39 (s, 3H, CH_3), 1.20, 1.18 (d, *J* = 6.9, each 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 167.1 (C═), 147.1, 135.9 (C_{ipso} Ph), 123.3, 123.2 (Ph), 48.7 (CH), 30.5 (CH_2), 28.2 (*C*H(CH$_3$)$_2$), 26.3 (CH_2), 23.1, 22.7 (CH(*C*H$_3$)$_2$). MS: *m*/*z* 285 (M^+), 202 (M^+ − Cy). **CyCH(CH$_3$)-NH-2,6-^{i}Pr$_2$C$_6$H$_3$**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.10−6.80 (m, 3H, Ph), 3.60 (sept, *J* = 6.9, 2H, C*H*(CH_3)$_2$), 3.10−2.97 (m, 1H, CH), 2.00−1.34 (m, 11H, Cy), 1.20 (d, *J* = 6.9, 12H, CHC*H*$_3$), 0.98 (d, *J* = 4.5, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): *δ* 136.4, 136.2 (C_{ipso} Ph), 129.5, 128.1 (Ph), 67.7 (CH), 39.4 (*C*HCy), 34.8 (CH_2), 28.2 (*C*H(CH$_3$)$_2$), 25.7 (CH_2), 23.9 (CH(*C*H$_3$)$_2$), 12.3 (CH*C*H$_3$). MS: *m*/*z* 287 (M^+), 204 (M^+ − Cy).

Hydroamination of Cyclohexylacetylene with *tert*-Butylamine. CyCH$_2$CH═N^{t}Bu: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.49 (t, *J* = 4.8, 1H, CH═), 2.13−2.09 (m, 2H, C*H*$_2$CH), 1.61−0.82 (m, 11H, Cy), 1.16 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): *δ* 156.5 (CH═), 56.4 (*C*(CH$_3$)$_3$), 44.1 (*C*H$_2$-CH), 35.7 (CH Cy), 33.3 (CH_2 Cy), 29.6 (C(*C*H$_3$)$_3$), 26.5, 26.4 (CH_2 Cy). MS: *m*/*z* 181 (M^+), 166 (M^+ − CH_3). **CyCH$_2$CH$_2$-NH^{t}Bu**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 8.80 (br s, 1H, NH), 2.68, 1.82 (both m, each 2H, CH_2), 1.67−0.84 (m, 11H, Cy), 1.28 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): *δ* 59.6 (*C*(CH$_3$)$_3$), 39.9 (CH_2), 35.5 (CH Cy), 33.7 (CH_2), 33.0, 26.5, 25.8 (CH_2 Cy), 25.4 (C(*C*H$_3$)$_3$). MS: *m*/*z* 183 (M^+), 168 (M^+ − CH_3).

Hydroamination of Cyclohexylacetylene with Dodecylamine. CyCH$_2$CH═NCH$_2$(CH$_2$)$_{10}$CH$_3$: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.45 (t, *J* = 4.8, 1H, CH═), 3.31 (t, *J* = 6.7, 2H, NCH_2), 2.05−2.00 (m, 2H, C*H*$_2$CH), 1.53−1.01 (m, 31H, Cy + CH_2), 0.86 (t, *J* = 6.9, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): *δ* 162.3 (CH═), 61.9 (NCH_2), 43.6 (*C*H$_2$CH), 35.7 (CH Cy), 33.3, 32.2, 31.3, 30.0, 29.9, 29.7, 29.6, 27.6, 26.5, 26.4 (CH_2), 14.1 (CH_3). MS: *m*/*z* 293 (M^+), 278 (M^+ − CH_3). **CyCH$_2$-CH$_2$NHCH$_2$(CH$_2$)$_{10}$CH$_3$**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 9.0 (br s, 1H, NH), 2.80−2.68 (m, 4H, CH_2), 2.65−2.58 (m, 2H, CH_2), 2.07−1.03 (m, 31H, Cy + CH_2), 0.93−0.89 (m, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): *δ* 47.8, 47.4, 45.6 (CH_2), 39.7 (CH Cy), 33.2, 32.4, 32.3, 30.2, 29.6, 28.7, 27.6, 27.1, 26.7, 26.4, (CH_2), 14.4 (CH_3). MS: *m*/*z* 295 (M^+), 280 (M^+ − CH_3).

Hydroamination of Cyclohexylacetylene with Cyclohexylamine. CyCH$_2$CH═NCy: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.47 (t, *J* = 6.0, 1H, CH═), 2.91−2.83 (m, 1H, CH Cy), 2.09−2.05 (m, 2H, C*H*$_2$CH), 1.81−0.85 (m, 21H, Cy). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 160.2 (CH═), 70.0 (CH Cy), 43.5 (*C*H$_2$CH), 35.6 (CH Cy), 34.8, 33.3, 26.4, 24.8 (CH_2 Cy). MS: *m*/*z* 207 (M^+), 124 (M^+ − Cy). **CyC-(CH$_3$)═NCy**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 3.28−3.21 (m, 1H, CH Cy), 1.81−0.85 (m, 21H, Cy), 1.49 (s, 3H, CH_3). ^{13}C-{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 168.4 (═C), 58.6, 35.6 (CH Cy), 34.2, 30.6, 26.7, 26.1, (CH_2), 14.4 (CH_3). MS: *m*/*z* 207 (M^+), 192 (M^+−CH_3). **CyCH$_2$CH$_2$-NHCy**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 2.89−2.83 (m, 1H, CH Cy), 2.80−2.63 (m, 4H, CH_2), 2.10−0.82 (m, 21H, Cy). ^{13}C-{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): *δ* 62.0 (CH Cy), 49.2, 43.0 (CH_2), 35.7 (CH Cy), 33.8, 28.7, 25.6, 22.6 (CH_2). MS: *m*/*z* 209 (M^+), 126 (M^+ − Cy). **CyCH-(CH$_3$)NHCy**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 2.89−2.83 (m, 1H, CH Cy), 2.80−2.70 (m, 1H, C*H*CH$_3$), 2.10−0.82 (m, 21H, Cy), 1.20 (d, *J* = 5.1, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT, COSY, and HETCOR): *δ* 57.2 (CH), 56.2, 36.0 (CH Cy), 33.2, 28.7, 25.6, 24.6 (CH_2), 13.0 (CH_3). MS: *m*/*z* 209 (M^+), 194 (M^+ − CH_3).

Hydroamination of Phenylacetylene with Dodecylamine. PhCH═CHNHCH$_2$(CH$_2$)$_{10}$CH$_3$: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.32−7.01 (m, 5H, Ph), 6.73 (dd, *J* = 6.9, *J* = 14.4, 1H, ═CHN), 5.43 (d, *J* = 14.4, 1H, PhC*H*═), 3.40 (m, 2H, CH_2), 2.85−2.78 (m, 1H, NH), 1.50−1.20 (m, 20H, CH_2), 0.96 (t, *J* = 6.9, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 137.5 (C_{ipso} Ph), 135.6 (═CHN), 128.3, 127.0, 123.6 (Ph), 98.3 (Ph*C*H═), 52.2, 44.3, 32.2, 31.5, 31.2, 28.0, 27.8, 22.9 (CH_2), 14.2 (CH_3). **PhCH$_2$CH═NCH$_2$(CH$_2$)$_{10}$CH$_3$**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.97−7.93 (m, 1H, Ph), 7.52 (t, *J* = 5.1, 1H, CH═N), 7.32−7.01 (m, 4H, Ph), 3.48 (d, *J* = 5.1, 2H, PhC*H*$_2$), 3.35 (m, 2H, CH_2), 1.50−1.20 (m, 20H, CH_2), 0.96 (t, *J* = 6.9, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT and HETCOR): *δ* 161.6 (CH═N), 140.6 (C_{ipso} Ph), 129.3, 128.8, 123.9 (Ph), 61.5, 42.3 (CH_2), 42.5 (Ph*C*H$_2$), 32.1, 29.9, 29.6, 27.3, 27.2, 22.9 (CH_2), 14.2 (CH_3). MS: *m*/*z* 287 (M^+), 272 (M^+ - CH_3). **PhCH$_2$CH$_2$NHCH$_2$(CH$_2$)$_{10}$CH$_3$**: ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.24−7.03 (m, 5H, Ph), 3.26−3.21 (m, 2H, CH_2), 3.00−2.90 (m, 2H, CH_2), 2.73−2.64 (m, 2H, CH_2), 1.40−1.13 (m, 20H, CH_2), 0.93 (t, *J* = 7.0, 3H, CH_3). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): *δ* 141.0 (C_{ipso} Ph), 129.1, 128.6, 126.2 (Ph), 49.3, 48.1, 40.6, 32.4, 30.3−24.3, 27.1, 23.1 (CH_2), 14.3 (CH_3). MS: *m*/*z* 289 (M^+), 274 (M^+ - CH_3).

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