Enhanced Reactivity Results in Reduced Catalytic Performance: Unexpected Ligand Reactivity of a Bis(*N*-2,6-diisopropylphenylperflourophenyl-amidate)titanium-bis(diethylamido) Hydroamination Precatalyst

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A bis(amidate)titanium-bis(amido) complex incorporating electron withdrawing pentafluorophenyl substituents has been prepared to enhance reactivity in this class of hydroamination precatalyst. This bis(*N*-2,6-diisopropylphenylperflourophenylamidate)titanium-bis(diethylamido) titanium complex has been fully characterized, including its X-ray crystal structure. As a precatalyst, the title compound proved to be effective for intermolecular hydroamination of internal and terminal alkynes with primary amines with yields as high as 97% and modest intramolecular alkene hydroamination. However, the elevated reactivity of this complex also resulted in reduced Markovnikov/anti-Markovnikov selectivity with some terminal alkynes. Substrate scope limitations revealed that this complex is susceptible to decomposition as a direct consequence of nucleophilic addition of the amine substrate to the pentafluorophenyl substituent of the amidate ligand.

Introduction

Hydroamination, the addition of N−H across a carbon−carbon multiple bond, is a very useful and highly atom-economical transformation for the preparation of imines, enamines, and amines. Numerous metal-based catalytic systems have been developed over the past few years for the hydroamination of alkynes and alkenes.[1] In particular, there has been intense investigation into the development of flexible catalyst systems that take advantage of the low cost and high reactivity of group 4 metals while providing enhanced and selective reactivity.[2] There are a number of examples in which these types of catalytic systems have been successfully applied to the regioselective hydroamination of both internal and terminal alkynes,[2k,n,o,3] and more recent reports have demonstrated that group 4 complexes are indeed capable of affecting alkene hydroamination.[4−6]

The primary focus of our group has been the development of hydroamination precatalysts based on bis(amidate) complexes of Ti and Zr. Amidates are a group of monoanionic, N,O chelating ligands derived from amides that can be easily prepared from commercially available acid chlorides and primary amines. The modular nature of this synthetic route allows one to systematically vary the substituents in the R^1 and R^2 positions (eq 1). This in turn permits the study of how electronic and steric properties of the ligand affect the catalytic activity in the resulting precatalyst. Prior to our work with amidates, they had been rarely employed as auxiliary ligands in transition metal chemistry.[7] The bis(amidate) complexes are

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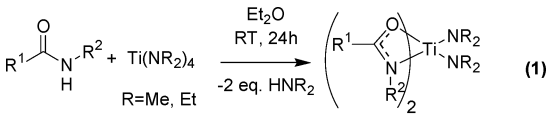
generated from commercially available $Ti(NR_2)_4$ or $Zr(NR_2)_4$ and two equivalents of the amide proligand via protonolysis as illustrated in eq 1.

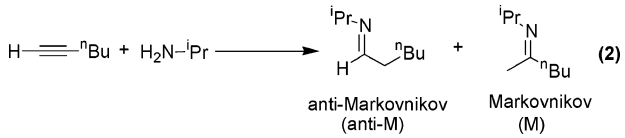


(1)

1: R^1= C_6F_5, R^2= *t*butyl
2: R^1= Ph, R^2= 2,6-diisopropylphenyl
3: R^1= C_6F_5, R^2= 2,6-diisopropylphenyl

Previously we reported that varying the electronic properties of the amidate ligand while maintaining consistent steric properties could dramatically modify reactivity.[2i] More specifically, we showed that by replacing a phenyl group in the R^1 position with a perflourophenyl group (complex **1**), the relative rate of intramolecular alkyne hydroamination could be increased by approximately 14 times. The electron withdrawing perflourophenyl group in this position creates a more electrophilic metal center, resulting in enhanced reactivity.

In a subsequent report,[3d] we probed the effect of the steric environment about the reactive metal center by changing the substituent in the R^2 position from a *t*-butyl group to a more bulky 2,6-diisopropylphenyl group (complex **2**) while leaving the phenyl group in the R^1 position unchanged. We demonstrated that increasing the steric bulk of the ligand enhances the anti-Markovnikov regioselectivity for the reaction of 1-hexyne with iso-propylamine (eq 2).



(2)

In addition to the enhanced regioselectivity, we also observed an increase in the relative rate of reaction when complex **2** was employed as the precatalyst. To explain the latter observation, we propose a mechanism based upon the catalytic cycles investigated by Bergman[2u,8] and Doye[2q] for cyclopentadienyl titanium imido catalyzed intermolecular hydroamination of alkynes (Scheme 1). Thus, the increased rate of catalysis in the presence of complex **2** can be attributed to the added steric bulk of the *N*-2,6-diisopropylphenyl substituents inhibiting the formation of the inactive dimeric species **B**.

Due to the fact that both electron withdrawing substituents (e.g., complex **1**) and enhanced steric bulk (e.g., complex **2**) both contribute to enhanced selectivity, as well as increased catalytic activity, we propose an improved catalyst design, complex **3**, having a perfluorophenyl group in the R^1 position and a 2,6-diisopropylphenyl group in the R^2 position, that should be an even more active precatalyst, capable of effecting the hydroamination of a wide range of alkyne and alkene substrates with optimized reactivity and selectivity. This paper presents the synthesis and structural characterization of complex **3**, as well as the results of experiments assessing its performance as a hydroamination precatalyst. In addition, the unexpected susceptibility to decomposition of this complex, under hydroamination reaction conditions, is also discussed.

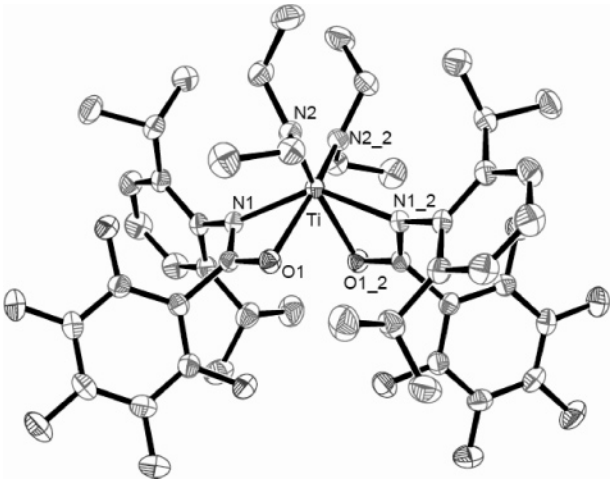
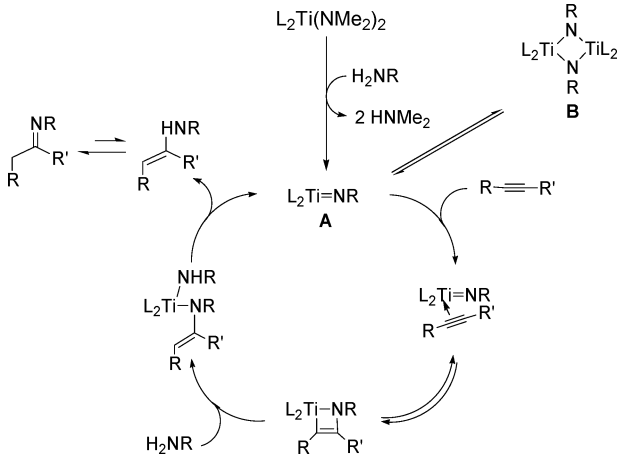


Figure 1. ORTEP diagram of bis(amidate)titanium-bis(amido) complex **3** with thermal ellipsoids set at the 50% probability level.

Scheme 1. Simplified Proposed Catalytic Cycle for the Group 4 Catalyzed Hydroamination of Alkynes



Results and Discussion

Metal Complexes. Complex **3** was prepared by the reaction of 2 equiv of *N*-2,6-diisopropylphenylperflourophenylamide with 1 equiv of $Ti(NEt_2)_4$ in anhydrous ether, followed by filtration through Celite and removal of all volatiles to give a red microcrystalline solid. Crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from benzene, and the solid-state molecular structure is shown in Figure 1. (Selected bond lengths and angles are given in Table 1.) It should be noted that either the crude microcrystalline or the recrystallized product could be used for subsequent hydroamination experiments without any notable difference in activity.

As previously reported for complex **2**,[3d,9] the bis(amido) titanium complex **3** is rigorously C_2-symmetric, with N atoms of the amidate ligand being trans to each other, whereas the

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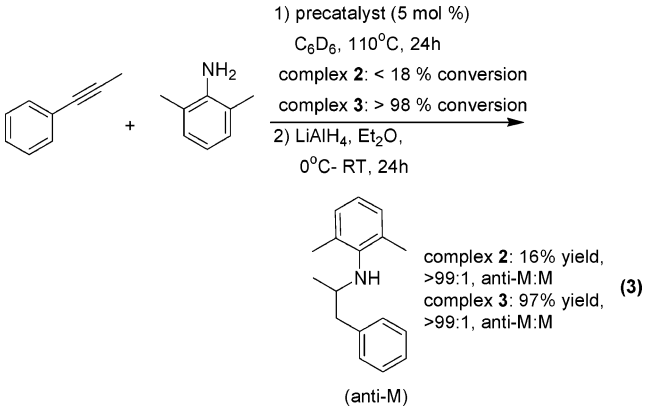
Table 1. Selected Bond Distances (Å) and Angles (deg) for Bis(*N*-2,6-diisopropylphenyl-perflourophenylamidate) titanium-bis(diethylamide) Complex 3

Ti−N(2)	1.903(1)
Ti−O(1)	2.170(1)
Ti−N(1)	2.201(1)
C(1)−O(1)	1.281(2)
C(1)−N(1)	1.315(2)
O(1)−C(1)−N(1)	117.4(1)
C(21)−N(2)−C(23)	113.5(2)
O(1)−Ti−O(1_2)	80.53(5)
N(1)−Ti−N(1_2)	139.06(6)
N(1)−Ti−N(2)	104.82(4)
N(1)−Ti−N(2_2)	100.16(4)
O(1)−Ti−N(1_2)	87.22(4)
O(1)−Ti−N(2_2)	159.23(4)
O(1)−Ti−N(1)	60.98(4)

amido ligands are in a cis orientation. This N-trans geometry is favored for steric reasons due to the bulky 2,6-diisopropylphenyl substituents. Another notable feature of **3** is that, like complex **2**, the binding of the oxygen and nitrogen donors of the amidate ligand to the metal center is nearly symmetric, with the Ti−O bond being the shorter (Ti−N(1) = 2.201(1) Å and Ti−O(1) = 2.170(1) Å for complex **3** and Ti−N(1) = 2.156(1) Å and Ti−O(1) = 2.146(1) Å for complex **2**). In addition, one will notice that the Ti−N and Ti−O bond lengths found in complex **3** are both longer than the analogous bonds found in complex **2**. This is suggestive of an enhanced ionic ligand−metal interaction in complex **3** versus complex **2**. The nearly symmetric Ti−N and Ti−O bonding found in complexes **2** and **3** is in contrast to complex **1**, which was reported to have substantially different Ti−O and Ti−N bond lengths (Ti−N = 2.356(7) Å vs Ti−O = 2.044(6) Å)[2i] and is best characterized as an alkoxide, neutral imine donor. Also, as with all of our previously reported bis(amidate) titanium-bis(amido) complexes, the sum of the bond angles about the amido N atoms in **3** indicates sp^2 hybridization and formal donation of 4 electrons to the metal center, resulting in a 16 electron complex.

Reactivity. To probe the scope, activity, and regioselectivity of complex **3** in terms of the intermolecular hydroamination of alkynes, a selection of alkynes and primary amines with differing steric bulk and electronic properties were screened. The most notable results clearly demonstrate the much higher reactivity of complex **3** over complex **2** in terms of alkyne hydroamination. These results were obtained with the internal alkyne phenyl-1-propyne and 2,6-dimethylaniline as substrates, as depicted in eq 3.



In this case, an elevated reaction temperature of 110 °C was required for the reaction to proceed to completion within 24 h. The imine product was subsequently reduced to the corresponding amine. Using complex **3**, this reaction is nearly quantitative and exhibits extremely high regioselectivity, with the anti-Markovnikov product being formed exclusively. Complex **2** also affords the anti-Markovnikov compound with high selectivity, but with a substantially lower isolated yield. The symmetrically substituted internal alkynes 3-hexyne and diphenylacetylene were also screened on an NMR tube scale under the same hydroamination reaction conditions and were found to be modestly reactive in the presence of complex **3** and completely unreactive in the presence of complex **2**. With complex **3**, conversions of up to 12 and 16% were observed for these two substrates, respectively, following 24 h at 110 °C, whereas no reaction was observed at all in the presence of complex **2** under the same conditions. Interestingly, this limited catalytic activity toward symmetrically substituted internal alkynes is in contrast to a number of other group 4 based systems, including $Ti(NR_2)_4$, that have been found to be effective precatalysts for these transformations.[2e]

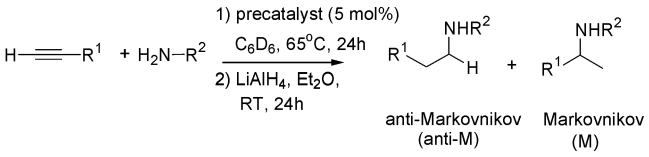
As substrates, we also screened a number of terminal alkynes such as phenylacetylene, 4-methoxy-phenylacetylene, and 1-hexyne with the primary amines 2,6-dimethylaniline, *t*-butylamine, and benzylamine. In an earlier report,[3d] it was demonstrated that for some of these substrates, under the same reaction conditions employed here, these transformations proceed with excellent yield and selectivity with complex **2**. Results for both complex **2** and complex **3** are listed in Table 3, thereby permitting a direct comparison of activity and regioselectivity.

These reactions were carried out on small scale with benzene as a solvent. The resulting imine mixture was diluted with ether and reduced with $LiAlH_4$ to give the corresponding amine products. It should be emphasized that the times and temperatures employed do not reflect optimized reaction conditions and were chosen for consistency. While monitoring by ^1H NMR spectroscopy, it was found that in the case of entries 3 and 4, when using complex **3**, the reactions had both gone to completion within 4 h at 65 °C, again consistent with the enhanced activity of this precatalyst.

Table 2. Crystallographic Parameters

	3
formula	$C_{58}H_{66}F_{10}N_4O_2Ti$
formula wt	1245.26
cryst dimens, mm	0.40 × 0.40 × 0.20
temp, K	293(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	29.207(3)
b, Å	10.8442(9)
c, Å	22.707(2)
α, deg	90
β, deg	115.209(4)
γ, deg	90
V, Å^3	6507.0(10)
Z	4
D_c, Mg/m^3	1.271
abs coeff, mm^{-1}	0.207
F(000)	2616
θ range, deg	1.54−28.02
index ranges	$-38 \le h \le 38$ $-13 \le k \le 14$ $-29 \le l \le 29$
no. of rflns	72029
no. of indep rflns	7703
no. of data/restraints/params	19.6
goodness of fit on F^2	1.027
final *R* indices ($I > 2\sigma(I)$)	0.0390, 0.0980
R indices (all data)	0.0586, 0.1069

Table 3. Hydroamination Reactions with Terminal Alkynes and Primary Amines



entry	R^1	R^2	complex **2** yield[a] (anti-M:M)[b]	complex **3** yield[a] (anti-M:M)[b]
1	Ph	2,6-dimethylphenyl	62%(>49:1)	69%(3:1)
2	*p*-MeOPh	2,6-dimethylphenyl	57%(>49:1)	65%(1.2:1)
3	*n*Bu	2,6-dimethylphenyl	72%(<1:49)	84%(<1:49)
4	*n*Bu	*t*-butyl	82%(>49:1)[3a]	>90%(>49:1)[c]
5	*n*Bu	benzyl	88%(>49:1)[3a]	45%(2:1)

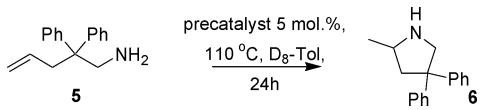
[a] Isolated yields unless otherwise stated. [b] Ratio determined by NMR. [c] Yield and ratio of the imine hydroamination product determined by NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

In general, with respect to entries 1 through 4, the yields obtained using complex **3** are comparable to, if not marginally better than, those obtained using complex **2** as the precatalyst. However, the regioselectivity observed when using precatalyst **3** was found in some cases to be lower than when **2** was used as the precatalyst. It should be noted that the comparable regioselectivities observed for entry 4 can be attributed to the significant steric bulk of the reactive *t*-butyl substituted titanium-imido intermediate (**A**, of Scheme 1), which has been previously reported to favor the formation of the anti-Markovnikov product.[2n] The enhanced steric accessibility to the reactive metal center in complex **3**, due to the increased ionic character of the metal−ligand bonding interaction, may promote the observed enhanced rates of reaction and the reduced regioselectivity with less bulky substrate combinations.

Although entries 1 through 4 suggest that the reactivity of **3** toward alkynes is similar to the analogous nonfluorinated complex **2**, an important difference can be observed when **3** is used for the hydroamination of 1-hexyne with benzylamine (entry 5). Not only is the regioselectivity diminished using **3** (only the anti-Markovnikov product is detected when **2** is used as the precatalyst), but the yield obtained using this precatalyst (45%) is substantially lower than when **2** is used (88%).[3d] Interestingly, it has been previously shown that commercially available $Ti(NR_2)_4$ shows the reverse regioselectivity, with the Markvonikov product formation being favored over the anti-Markovnikov product.[2r] Thus, in the cases where bulkier amines are used as substrates, the yields obtained using complex **3** are slightly better than those obtained using complex **2** as the precatalyst. However, the dramatic change in reactivity when benzylamine is used as the substrate can be attributed to undesirable side reactions between benzylamine and the pentafluorophenyl bearing ligand (*vide infra*). Furthermore, the significant differences in observed reactivity and regioselectivity between the bis(amidate) bis(amido) titanium complexes **1**, **2**, and **3** and $Ti(NR_2)_4$ (which could be formed in situ if conproportionation is occurring) suggest that the modified reactivity reported here can be attributed to the unique reaction environment afforded by the N,O chelating ligands.

As a further challenge to the competency of precatalysts **1**, **2**, and **3**, they were also tested for intramolecular alkene hydroamination activity using 2,2-diphenylpentenylamine (**5**) as a substrate (Table 4). Alkene hydroamination reactivity remains a significant challenge and provides a useful example

Table 4. Comparing Intramolecular Aminoalkene Hydroamination Using Precatalysts 1, 2, and 3



precatalyst	yield[a]
1	4%[b]
2	90%
3	30%

[a] Isolated yields. [b] Yield determined by NMR spectroscopy using 1,3,5-trimethoxy benzene as an internal standard.

for contrasting catalytic activity. This particular substrate, geminally disubstituted in the 2 position, was chosen to take advantage of the *gem*-disubstituent effect, which has been observed to have a significant effect on the rate of reaction using these and similar precatalysts.[6,10]

A temperature of 110 °C was required for this transformation to occur in the presence of complex **2**, and for consistency, the reactions where complexes **1** and **3** were used as precatalysts were also carried out at 110 °C. Where isolated yields are given, the reaction mixtures were quenched by the addition of CH_2Cl_2, and all volatiles were removed in vacuo to give an oily brown solid that could then be purified by column chromatography to yield the pyrrolidine product.

Unfortunately, the results listed in Table 4 show that precatalysts **1** and **3** are substantially less effective than complex **2** in effecting this transformation. In fact, only complex **2** exhibited reactivity similar to that of the precursor to these complexes, $Ti(NEt_2)_4$, which has been previously reported[6e] to catalyze this reaction with an isolated yield of 92% using the same reaction conditions. This indicates that the perfluorophenyl group has a significant detrimental effect on the application of these complexes for intramolecular alkene hydroamination.

In the reactions in which complexes **1** and **3** were used as precatalysts, extended reaction times at 110 °C did not significantly improve conversion. However, when the same reaction using complex **3** as the precatalyst was carried out with a higher catalyst loading (20 mol %) and at a lower reaction temperature (65 °C) over a longer period of time (168 h), a higher conversion (56%) was observed. Complex **2** does not promote intramolecular alkene hydroamination at this temperature. The improved low-temperature reactivity of **3** suggests that, at elevated temperatures, this complex decomposes or converts to some catalytically inactive species. Again, the substantial difference in catalytic activity between the fluorinated and nonfluorinated precatalysts can be attributed to undesirable side reactions of the pentaflourophenyl bearing ligand.

Reactivity of the *N*-2,6-Diisopropylphenylperflourophenylamidate Ligand. To investigate catalyst decomposition/inactivation as a possible explanation for the differences in reactivity between the fluorinated and nonflourinated precatalysts, the reaction conditions employed in the hydroamination experiments with complex **3** were used for reaction with substrate **8**, 2,2-diphenylpentylamine. This modified substrate does not contain an alkene, thereby eliminating hydroamination as a possible reaction pathway. The mixture of products obtained from this initial experiment resulted from nucleophilic displacement of fluorine on the perfluorinated aromatic ring of the ligand

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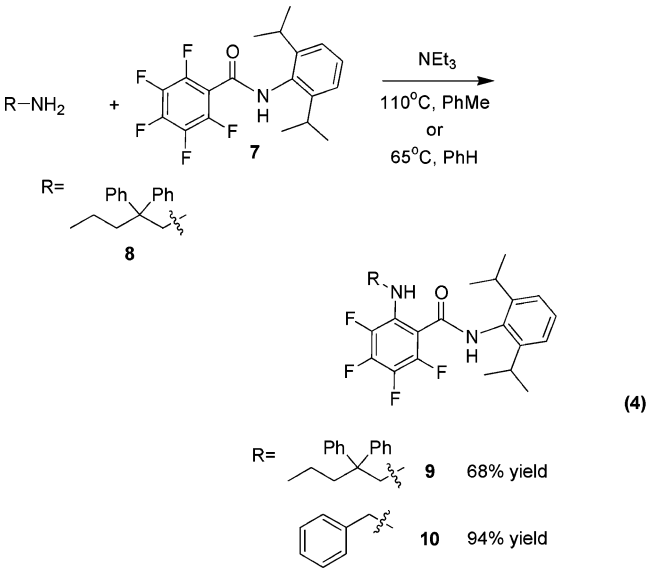
by 2,2-diphenylpentylamine to give product **9** and also by the diethylamido ligand of the precatalyst.[11c] We also found that simply heating complex **3** to 110 °C in toluene for several days resulted in significant complex decomposition caused by the addition of the amido ligand to the amidate ligand. In addition to these findings, while studying the hydroamination of 1-hexyne with benzylamine using complex **3** as the precatalyst, we were able to isolate a byproduct (**10**) that is consistent with the addition of benzylamine to the amidate ligand via nucleophilic aromatic substitution. The characterization of the decomposition products **9** and **10** were confirmed by their independent syntheses in the absence of metal, as shown in eq 4.



All of these observations are consistent with the fact that perfluorinated aromatic compounds can undergo nucleophilic aromatic substitution reactions due to their highly electron deficient ring systems and availability of leaving groups (F^-).[11] In the aforementioned decomposition reactions, the concomitant formation of HF would cause immediate catalyst decomposition via the formation of unidentified Ti−F species. This unexpected catalyst decomposition is consistent with the poor yields observed when less bulky amine substrates are used for hydroamination.

Summary and Conclusions

In summary, we have prepared and characterized a new bis(amidate)titanium-bis(amido) complex and screened it as a hydroamination precatalyst. Complex **3** proved to be more reactive than its nonfluorinated analogue, complex **2**, which was indicated by higher reactivity toward internal alkynes and reduced regioselectivity in the hydroamination of terminal alkynes. It has been determined that the side reactivity of the perfluorophenyl-bearing ligand and resulting complex decomposition explains the lower relative yields obtained when using complex **3** in combination with sterically unencumbered amine substrates. These investigations point to the importance of judicious selection of electron-withdrawing substituents for enhancing reactivity and suggest that incorporation of perfluoroaromatic groups should be avoided in hydroamination catalyst design.

Experimental Procedures

General. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker 300 MHz or 400 MHz Avance spectrometer at ambient temperature and chemical shifts are given relative to residual solvent. GCMS spectra were recorded on an Agilent series 6890 GC system with a 5973 Mass Selective Detector. Single-crystal X-ray structure determinations, MS (ESI) and elemental analyses determinations were performed at the Department of Chemistry, University of British Columbia. All reactions were carried out using standard Schlenk line and glovebox techniques under an atmosphere of nitrogen, unless described otherwise. $Ti(NEt_2)_4$ was purchased from Strem and used as received. d_6-Benzene and d_8-toluene were degassed and dried over molecular sieves. Acid chlorides were purchased from Aldrich and used as received. Amines were distilled from CaH_2 under nitrogen. Alkynes were purchased from Aldrich and purified by distillation prior to use. 2,2-Diphenyl-4-pentenylamine was prepared as described in the literature[12] with some modification from commercially available starting materials purchased from Aldrich. The amide proligands were prepared from the appropriate amines and acid chlorides according to literature procedures.[2i,3d,13] Complexes **1** and **2** were prepared as previously reported in the literature.[2i,3d]

***N*-2,6-Diisopropyl(phenyl)perflourophenylamide (Proligand for Complex 3).** Prepared using modified literature procedures.[13] The signals in the ^{13}C NMR spectrum for the carbons of the aromatic ring bearing the fluorine atoms were obscured due to extensive coupling to fluorine. Yield: 51%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.22 (12H, d, J = 6.9 Hz, CH−(CH_3)$_2$, 3.12−3.21 (2H, septet, J = 6.9 Hz, C*H*−(CH_3)$_2$), 7.06−7.40 (3H, m, Ar-*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.5, 28.8, 123.6, 129.2, 129.3, 146.2, 157.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −63.6 (2F), −73.9 (1F), −83.0 (2F); MS (EI): *m*/*z* 371 (M^+), 356 (M^+-CH_3), 328 ($M^+-CH(CH_3)_2$), 195 ($M^+-NHC_6H_3(CH(CH_3)_2)_2$); Anal. Calcd for $C_{19}H_{18}F_5NO$: C, 61.45; H, 4.89; N, 3.77. Found: C, 61.71; H, 4.50; N, 3.78.

Bis(*N*-2,6-diisopropyl(phenyl)perflourophenylamidate)titanium-bis(diethylamido) (3). Prepared using modified literature procedures.[3d,14] Yield: 65%. The NMR specta of this compound are very complicated and not helpful for characterization due to the presence of multiple isomers in solution. Suitable crystals for X-ray crystallography were grown from benzene at ambient temperature; MS (EI): *m*/*z* 860 (M−NEt_2), 788 (M−NEt_2 X 2); Anal. Calcd for $C_{46}H_{56}F_{10}N_4O_2Ti$: C, 59.10; H, 6.04; N, 5.99. Found: C, 59.15; H, 5.99; N, 6.20.

General Procedure for Intermolecular Alkyne Hydroamination. All hydroamination reactions were prepared in an N_2-filled glovebox. A small Schlenk tube equipped with a magnetic stir bar was charged with a solution of the precatalyst (0.05 mmol, 0.05 equiv), the alkyne (1.0 mmol, 1.0 equiv), and the primary amine (1.2 mmol, 1.2 equiv) dissolved in benzene (∼2 mL) or toluene (∼2 mL). The Schlenk tube was then sealed and heated to either 65 or 110 °C for 24 h. The reaction mixture was then allowed to cool to room temperature and transferred to a small round-bottom flask containing a stirring slurry of $LiAlH_4$ (1.5 mmol, 1.5 equiv) in diethylether (5−10 mL). This mixture was stirred at room temperature overnight under N_2(g). The reaction would then be quenched by the slow addition of water (0.06 mL), then 1 M NaOH

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(14) Full crystallographic data is available in the included cif.

(0.06 mL), and a further aliquot of water (0.18 mL). Following suction filtration and removal of the solvents under reduced pressure, column chromatography (hexane: ether, SiO_2) afforded the purified amine products either as single compounds or as a mixture of regioisomers. *N*-(2,6-Dimethylphenyl)-2-phenylethylamine,[15] *N*-(2,6-dimethylphenyl)phenylethylamine,[16] *N*-(2,6-dimethylphenyl)-1-(4-methoxyphenyl)ethylamine,[16] *N*-(2,6-dimethylphenyl)-1,2-methylphenylethylamine,[15] *N*-benzylhexylamine,[3d] and *N*-benzyl-1-methylpentylamine[17] are known compounds. Full characterization data for *N*-(2,6-dimethylphenyl)-2-(4-methoxyphenyl)-ethylamine and *N*-(2,6-dimethylphenyl)-1-methylpentylamine is provided below.

***N*-(2,6-Dimethylphenyl)-2-(4-methoxyphenyl)ethylamine.** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.25 (6H, s, Ar−CH_3), 2.92 (2H, t, J = 6.9 Hz, pMeOPh−CH_2), 3.16 (1H, br s, CH_2−NH−Ar), 3.33 (2H, J = 6.9 Hz, ArNH−CH_2), 3.88 (3H, s, Ar−O−CH_3), 6.88−7.26 (7H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.7, 36.3, 49.8, 55.5, 56.4, 114.2, 121.9, 129.0, 129.3, 130.0, 131.7, 132.8, 146.2, 158.5; HRMS Calcd for $C_{17}H_{21}NO$ [M+]: 255.16231; Found: 255.16226.

***N*-(2,6-Dimethylphenyl)-1-methylpentylamine.** ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.91 (3H, t, J = 6.9 Hz, CH_2−CH_2−CH_3), 1.05 (3H, d, J = 6.3 Hz, ArNH−CH−CH_3), 1.29−1.57 (6H, m, ArNH−CH−(CH_2)$_3$−CH_3), 2.26 (6H, s, Ar−CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.5, 20.5, 22.8, 24.3, 30.1, 39.6, 53.9, 122.5, 130.2, 130.3, 146.7; HRMS Calcd for $C_{14}H_{23}N$ [M+]: 205.18305; Found: 205.18315.

General Procedure for the NMR-Tube Scale Intermolecular Alkyne Hydroamination Reactions. All NMR-tube scale reactions were prepared in an N_2-filled glove box. A J. Young NMR tube was charged with the internal standard (1,3,5-trimethoxybenzene) (0.17 mmol, 0.33 equiv), the precatalyst (0.025 mmol, 0.05 equiv), the alkyne (0.5 mmol, 1.0 equiv), and the primary amine (0.6 mmol, 1.2 equiv) and dissolved in either d_6-benzene (∼1 mL) or d_8-toluene (∼1 mL). The tube was sealed, heated to, and maintained at 65 or 110 °C for the stated duration of time. The conversion and yield were determined by comparing the integration of the internal standard with a well-resolved signal for the imine product.

Procedure for the NMR-Tube Scale Intramolecular Hydroamination of 2,2-Diphenyl-4-pentenylamine. All NMR-tube scale reactions were prepared in an N_2-filled glove box. A J. Young NMR tube was charged with the precatalyst (0.025 mmol) and 2,2-diphenyl-4-pentenylamine (0.5 mmol) dissolved in d_8-toluene (∼1 mL). Where yields were determined, 1,3,5-trimethoxybenzene (0.5 mmol) was also added as an internal standard. The tube was then sealed, heated to, and maintained at the appropriate temperature for the stated duration of time. Yields were determined by comparing the integration of the internal standard with a well-resolved signal for the heterocyclic product. Conversions were determined by comparing well-resolved signals for the substrate and product.

Procedure for the Intramolecular Hydroamination of 2,2-Diphenyl-4-pentenylamine and Isolation of 2-Methyl-4,4-diphenylpyrrolidine. All reactions were prepared in an N_2-filled glovebox. A small Schlenk tube equipped with a magnetic stir bar was charged with the catalyst (0.025 mmol) and 2,2-diphenyl-4-pentenylamine (0.5 mmol) dissolved in toluene (∼ 1 mL). The Schlenk tube was then sealed, heated to the appropriate temperature, and stirred for the stated duration of time. After cooling to room temperature, "wet" CH_2Cl_2 (∼1 mL) was added, and the solution was stirred for ∼10 min. Then, following concentration under reduced pressure, the crude product was directly subjected to flash column chromatography (ether, SiO_2) to afford 2-methyl-4,4-diphenylpyrrolidine[6d] as a colorless oil.

2,2-Diphenylpentylamine (8). Prepared using modified literature procedures,[12] with full characterization data presented here. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85−0.90 (5H, m, CH_2−CH_3, CH_2−NH_2), 1.02−1.04 (2H, m, CH_2−CH_2−CH_3), 2.05−2.10 (2H, m, Ph_2C−CH_2−CH_2), 3.32 (2H, s, Ph_2C−CH_2−NH_2), 7.15−7.30 (10H, m, Ar−H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.75, 17.39, 38.94, 49.11, 51.89, 125.85, 127.94, 128.24, 146.71; MS (EI): m/z 209 (M^+-CH_2NH_2); Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85. Found: C, 85.08; H, 8.93; N, 6.05.

***N*-(2,6-Diisopropylphenyl)-2-(*N*-2,2-diphenylpentylamino)-3,4,5,6-tetrafluorobenzamide (9).** To a round-bottom flask equipped with a magnetic stir bar was added toluene (∼10 mL), 2,2-diphenylpentylamine (0.125 g, 0.52 mmol, 1.0 equiv), *N*-2,6-diisopropyl(phenyl)perflourophenylamide (0.187 g, 0.50 mmol, 1.0 equiv), and triethylamine (0.22 mL, 1.6 mmol, 3.0 equiv). The reaction mixture was heated to reflux for 16 h and then allowed to cool to room temperature. The crude reaction mixture was diluted with ether (250 mL), washed with 1 M NaOH, water, and brine. Following drying of the organic phase over Na_2SO_4 and removal of solvents under reduced pressure, the crude material was subjected to column chromatography (36:1 hexanes: ether, SiO_2) to provide **9** as a colorless foam. The signals in the ^{13}C NMR spectrum for the carbons of the aromatic ring bearing the fluorine atoms were obscured due to extensive coupling to fluorine. Yield: 68%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.87 (3H, t, J = 7.2 Hz, CH_3−CH_2), 1.01−1.09 (2H, m, CH_3−CH_2−CH_2), 1.24 (12H, d, J = 6.8 Hz, CH−(CH_3)$_2$), 2.18−2.23 (2H, m, Ph_2C−CH_2−CH_2), 3.08−3.15 (2H, m, CH−(CH_3)$_2$), 4.23 (2H, d, J = 2.8 Hz, Ph_2C−CH_2−NH), 7.13−7.60 (13H, m, Ar−H), 7.75 (1H, br s, NH); ^{13}C NMR ($CDCl_3$, 75 MHz): d 14.57, 17.33, 23.62, 28.79, 38.77, 50.51, 50.53, 52.33, 52.46, 101.49, 123.48, 126.06, 127.90, 127.95, 128.65, 130.43, 137.67, 146.09, 146.197, 163.60; ^{19}F NMR ($CDCl_3$, 400 MHz): δ −140.8 (1F), −152.3 (1F), −155.3 (1F), −175.0 (1F); MS (ESI): m/z 589 (M^-−H); Anal. Calcd for. $C_{36}H_{38}F_4N_2O$: C, 73.20; H, 6.48; N, 4.74. Found: C, 73.40; H, 6.38; N, 4.70.

***N*-(2,6-Diisopropylphenyl)-2-(*N*-benzylamino)-3,4,5,6-tetrafluorobenzamide (10).** To a round bottomed flask equipped with a magnetic stir bar was added toluene (∼10 mL), benzylamine (0.070 mL, 0.64 mmol, 1.2 equiv), *N*-2,6-diisopropyl(phenyl)perflourophenylamide (0.200 g, 0.50mmol, 1.0 equiv), and triethylamine (0.30 mL, 2.2 mmol, 4.0 equiv). The reaction mixture was heated to reflux for 24 h and then allowed to cool to room temperature. The crude reaction mixture was diluted with CH_2Cl_2 (150 mL), washed with 1 M NaOH, water, and brine. Following drying of the organic phase over Na_2SO_4 and removal of solvents under reduced pressure, the crude material was subjected to column chromatography (16:1 hexanes/ether, SiO_2) to provide **10** as a white amorphous solid. The signals in the ^{13}C NMR spectrum for the carbons of the aromatic ring bearing the fluorine atoms were obscured due to extensive coupling to fluorine. Yield: 94%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ1.25 (12H, d, J = 6.9 Hz, CH−(CH_3)$_2$), 3.10−3.17 (2H, septet, J = 6.9 Hz CH−(CH_3)$_2$), 4.58 (2H, d, J = 3.6 Hz, Ph−CH_2−NH), 7.25−7.37 (8H, m, Ar−H), 7.6 (2H, br s, ArNHC=O, ArNHCH_2Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): d 23.75, 29.09, 49.97, 50.13, 123.89, 127.58, 127.67, 128.79, 129.20, 130.24, 139.30, 146.35, 164.12; ^{19}F NMR ($CDCl_3$, 282 MHz): δ −140.8 (1F), −151.8 (1F), −155.7 (1F), −173.1 (1F); MS (EI): m/z 458 (M^-−H); Anal. Calcd for. $C_{26}H_{26}F_4N_2O$: C, 68.11; H, 5.72; N, 6.11. Found: C, 67.95; H, 5.92; N, 6.21.

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Supporting Information Available: NMR spectra of the new hydroamination products as well as a CIF file giving X-ray crystallographic data for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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