Synthesis, Structure, and Hydroamination Kinetics of (2,2′-Diaryldipyrrolylmethane)- and Bis(2-arylpyrrolyl)titanium Complexes

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The trifluoroacetic acid catalyzed reaction of acetone and 2-arylpyrroles results in the formation of 2,9-diaryl-5,5-dimethyldipyrrolylmethanes. Ligands bearing 3,5-$(CF_3)_2C_6H_3$ (H_2dmpm$^{3,5-CF_3}$) and mesityl (H_2dmpm^{mes}) arenes were prepared in 72% and 68% yields using this procedure. The new dipyrrolylmethanes react with $Ti(NMe_2)_4$ to form $Ti(NMe_2)_2$(dmpm$^{3,5-CF_3}$) and $Ti(NMe_2)_2$(dmpm^{mes}) in 92% and 30% yields, respectively. The solid-state structures of these complexes are quite similar to that of the sterically smaller 5,5-dimethyldipyrrolylmethane complex $Ti(NMe_2)_2$(dmpm) with one η^5- and one η^1-pyrrolyl; however, the substituted derivatives display much lower barriers to pyrrolyl conformational exchange, as judged by VT ^{1}H NMR spectroscopy. Also synthesized were bis(pyrrolyl) complexes without the methylene connector. Reactions of 2-arylpyrroles where the aryl group was 3,5-$(CF_3)_2C_6H_3$, mesityl, 4-$(CF_3)C_6H_4$, and *p*-tolyl generated $Ti(NMe_2)_2$(pyrr$^{3,5-CF_3}$)$_2$, $Ti(NMe_2)_2$(pyrr^{mes})$_2$, $Ti(NMe_2)_2$(pyrr$^{4-CF_3}$)$_2$, and $Ti(NMe_2)_2$(pyrr^{tol})$_2$ in 38%, 74%, 45%, and 37% purified yields, respectively. Hydroamination catalysis rates under pseudo-first-order conditions were tested using aniline and 1-phenylpropyne at 75 °C. On the dmpm framework, 2-substitution in $Ti(NMe_2)_2$(dmpm$^{3,5-CF_3}$) and $Ti(NMe_2)_2$(dmpm^{mes}) results in reduced pseudo-first-order rate constants of $(780 \pm 30) \times 10^{-7}$ and $(403 \pm 80) \times 10^{-7}$ s^{-1} relative to $Ti(NMe_2)_2$(dmpm) at $(1976 \pm 130) \times 10^{-7}$ s^{-1}, which is attributed to steric constraints near the substrate-binding pocket. Testing catalysis rates on the approximately isosteric complexes $Ti(NMe_2)_2$(pyrr$^{4-CF_3}$)$_2$ and $Ti(NMe_2)_2$(pyrr^{tol})$_2$ provided rate constants of $(1255 \pm 193) \times 10^{-7}$ and $(880 \pm 20) \times 10^{-7}$ s^{-1}, demonstrating that electron-withdrawing groups increase catalytic activity in these systems. $Ti(NMe_2)_2$(dmpm$^{3,5-CF_3}$), $Ti(NMe_2)_2$(dmpm^{mes}), $Ti(NMe_2)_2$(pyrr$^{3,5-CF_3}$)$_2$, and $Ti(NMe_2)_2$(pyrr^{mes})$_2$ were studied by single-crystal X-ray diffraction.

Introduction

Titanium-catalyzed C−N bond formation has recently seen an explosion of activity. A large portion of the new chemistry is based on pioneering studies by the groups of Bergman,[1] Rothwell,[2] and Livinghouse[3] in the reactivity of group 4 imido[4] complexes. Among the many functionalities available from the new intermolecular methodologies[5] are new routes to imines,[6] hydrazones,[7] indoles,[7] pyrroles,[8] α,β-unsaturated imines,[9] tautomers of 1,3-dimines,[10] and tautomers of 1,3-iminohydrazones.[11] In addition, a variety of nitrogenous heterocycles are available by intramolecular cyclization.[12]

The mechanism[13] for the reaction was elucidated by Bergman and co-workers using a zirconocene-based system.[1] The mechanism for the zirconium system involves terminal imido formation, [2 + 2] cycloaddition with alkyne, Zr−C bond protonolysis, and Zr−N protonolysis steps, as shown in Scheme 1. Evidence regarding the mechanism of the titanium-catalyzed reaction points to a route similar to that found for its heavier congener.[14]

One can easily draw analogies between the Bergman hydroamination mechanism[14a] and the Chauvin mechanism[15] for

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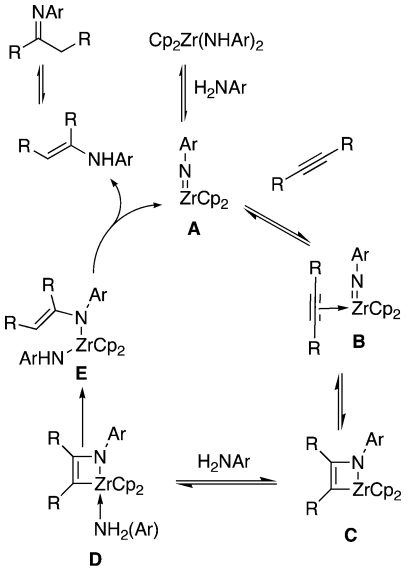
Scheme 1. Bergman Mechanism for Alkyne Hydroamination

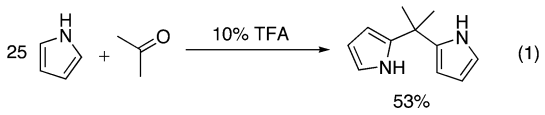


olefin metathesis. Both reactions are known to involve intermediates with metal−ligand multiple bonds (e.g., **A** in Scheme 1). In addition, a key step in both mechanisms is [2 + 2] cyclization between a C−C unsaturated bond and the metal−ligand multiple bond (compound **A** to **C**).[16] Increasing the Lewis acidity of the metal center in d^0 olefin metathesis catalysts, i.e., Schrock's catalyst, is well-known to increase catalysis rates,[17] which is likely due, at least in part, to stronger olefin−metal center interactions (**B** in Scheme 1) prior to cycloaddition. We anticipated that the increased Lewis acidity would be advantageous for titanium hydroamination for similar reasons.[18] In addition, the Bergman mechanism involves protolytic cleavage of an M−C bond by a coordinated amine (**D** to **E** in Scheme 1). Brønsted acidity of a coordinated amine (**D** in Scheme 1) increases on coordination to a metal center.[19] Consequently, increased Lewis acidity of the metal center may expedite the protonolysis event, which is believed to be the rate-limiting step.

Because so many of the applications listed above are based upon the hydroamination catalytic cycle, we often still use simple hydroamination of alkynes as a method for evaluating the efficacy of new catalyst designs, as will be done in this study.

Our group has been working to increase the activity of the complexes employed in titanium hydroamination through ancillary ligand studies. To do this, we have chosen as a basis a set of ligands using pyrrole as the unit interacting with titanium. The use of pyrrole in the ancillary ligands was driven by a couple of factors. The first was one of expediency; pyrroles are relatively easy to manipulate into multidentate ligands using a set of standard condensation reactions that take advantage of the nucleophilic nature of the ring. As a result, several classes of multidentate ligands can be synthesized in a small number of steps using methods such as the Mannich reaction. Second, pyrrole is a poor π-donor relative to commonplace amides and alkoxides when these bear typical organic substituents.[20] Considering the known improvement in catalytic activity of related d^0 Schrock carbenes on increased Lewis acidity and increased acidity of amines attached to more Lewis acidic metal centers (vide supra), we expected increased reactivity with decreased donor ability of the ancillary ligands.[5]

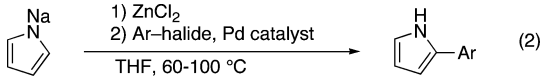
The most active precatalyst known thus far for simple alkyne hydroamination is the dipyrrolylmethane-ligated titanium complex $Ti(NMe_2)_2$(dmpm) (**1**),[21] where dmpm is 5,5-dimethyldipyrrolylmethane, and its derivatives. The ligand is readily prepared by the reaction (eq 1) of acetone and pyrrole catalyzed by trifluoroacetic acid (TFA) using the procedure of Lindsey and co-workers.[22]



In this study, we evaluated the effects on structure and catalysis of 2-aryl substitutions on the dmpm framework. In addition, we prepared related bis(pyrrolyl) complexes to evaluate the effect of the linker on the structure and catalysis.

Results and Discussion

Selective generation of 2-arylpyrrole complexes is greatly enabled by a recent methodological contribution by Sadighi and co-workers,[23] which involves coupling between chloro(pyrrolyl)-zinc and aryl halides catalyzed by palladium (eq 2). Using this



technique, a variety of 2-arylpyrroles can be synthesized selectively on multigram scales. For this study, we prepared

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(18) The added strength of dative interactions with the amines in solution could negate some of the effects of stronger alkyne/olefin binding. There could also be advantages to greater Lewis acidity in the [2 + 2] cycloaddition itself.

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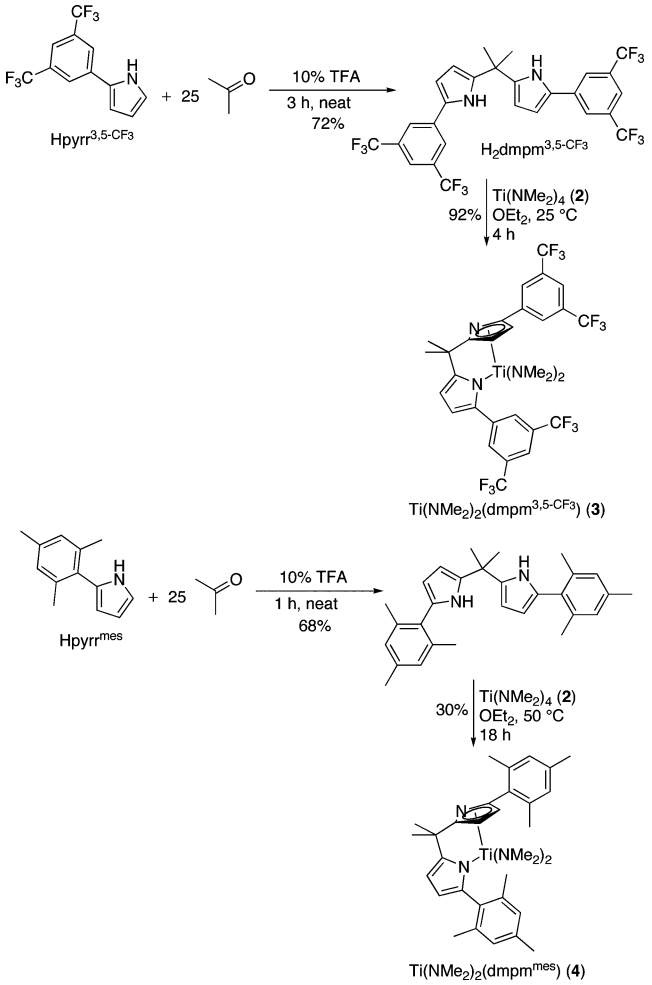
Scheme 2. Synthesis of $H_2dmpm^{3,5-CF_3}$ and H_2dmpm^{mes} and Reactions with $Ti(NMe_2)_4$ (2) To Form $Ti(NMe_2)_2(dmpm^{3,5-CF_3})$ (3) and $Ti(NMe_2)_2(dmpm^{mes})$ (4)



4-$(CF_3)C_6H_4$, 4-$(CH_3)C_6H_4$, 3,5-$(CF_3)_2C_6H_3$, and 2,4,6-$(CH_3)_3C_6H_2$ substituted pyrroles.

The usual procedure for the synthesis of dipyrrolylmethanes involves the use of a large excess of pyrrole (eq 1). We were quite relieved to find that the 2-arylpyrroles could be used as the limiting reagent in the synthesis of dipyrrolylmethane derivatives with acetone as the electrophile. The reactions are smoothly catalyzed by TFA to generate the ligands in good yield. We initially prepared two 5,5-dimethyldipyrrolylmethane derivatives for study, 2,9-[3,5-$(CF_3)_2C_6H_3$]-5,5-dimethyldipyrrolylmethane ($H_2dmpm^{3,5-CF_3}$) and 2,9-[2,4,6-$(CH_3)_3C_6H_2$]-5,5-dimethyldipyrrolylmethane (H_2dmpm^{mes}). These complexes react with $Ti(NMe_2)_4$ (**2**) to generate the new pyrrolyl complexes $Ti(NMe_2)_2(dmpm^{3,5-CF_3})$ (**3**) and $Ti(NMe_2)_2(dmpm^{mes})$ (**4**) (Scheme 2).

Parkin and Tanski[24] have shown that decreased sterics and decreased electron density at the metal favor the η^5 configuration in 2-arylpyrrolyl complexes. Our previous studies on $Ti(NMe_2)_2$-(dmpm) (**1**) showed the dipyrrolylmethane ligand was in the η^1:η^5 configuration in the solid state. In cold solutions on the NMR time scale, resonances consistent with the solid-state structure were observed. As the solution is warmed, resonances for the η^1-pyrrolyl and η^5-pyrrolyl groups coalesce. The fast exchange limit is reached well before room temperature, and a barrier for pyrrolyl ligand conformational exchange of 10 kcal/mol was measured.[21] It is assumed that the exchange occurs through an η^1:η^1 isomer, and this barrier is consistent in magnitude with other known pyrrole η^1 to η^5 isomerizations[25] in the literature[24] and even related phospholyl isomerizations.[26]

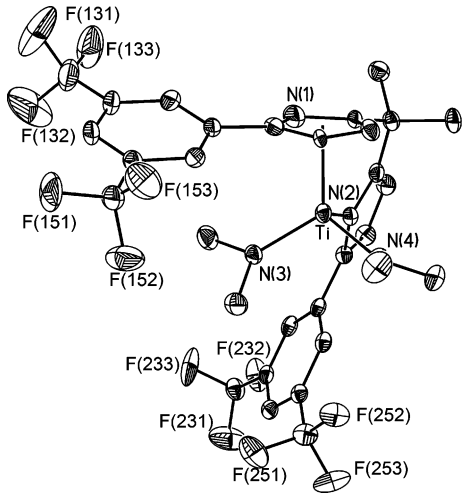


Figure 1. ORTEP structure from single-crystal X-ray diffraction on $Ti(NMe_2)_2(dmpm^{3,5-CF_3})$ (**3**). Selected bond distances (Å) and angles (deg): Ti−N(3) = 1.875(5), Ti−N(4) = 1.892(5), Ti−N(2) = 2.048(5), Ti−N(1) = 2.400(6); N(4)−Ti−N(3) = 107.1(2), N(4)−Ti−N(2) = 102.6(2), N(3)−Ti−N(2) = 104.8(2).

In the solid state the complexes with α-aryl substitution on the pyrrolyl rings show structures very similar to that of the unsubstituted derivative **1**. The metric parameters from **1** to the more sterically encumbered **3** and **4** do not change significantly. A structure for **3** is shown in Figure 1. For the structure of **4**, see the Supporting Information.

Consistent with Parkin's results, increased sterics lower the barrier for ring exchange in **3** and **4**. For example, the compounds are still at the fast exchange limit at −60 °C.

For comparison with the dmpm derivatives, we also prepared unlinked bis(pyrrolyl) derivatives with the same aryl group on the pyrrolyl rings. The two complexes $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (**5**) and $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**) were prepared by treatment of $Ti(NMe_2)_4$ with 2 equiv of the pyrrole (Scheme 3).

Interestingly, the solid-state structures of the bis(pyrrolyl) complexes **5** (Supporting Information) and **6** (Figure 2) bear pyrrolyl rings that are both in the η^1:η^1 configuration in the solid state. When solutions were cooled in the NMR probe, no new resonances could be seen in the baseline.

With these complexes in hand, we set out to answer several questions. First, how would sterics in the 2-position affect the catalysis rate? Second, how does the linker affect the catalysis rate? Third, can it be shown that electron-withdrawing groups definitively increase the rate, as argued in the Introduction?

To test the kinetic ability of the catalysts, we chose a standard set of conditions. The reactions are run pseudo first order in amine, which we chose as aniline. Aniline was chosen over other possible amines because it runs at a reasonable rate with a large variety of catalysts. For example, we hoped to compare the efficacy of the new catalysts with that of commercially available $Ti(NMe_2)_4$ (**2**), which is very effective with aniline but not with most alkylamines.[6l] The limiting reagent utilized was 1-phenylpropyne, which runs cleanly with good regioselectivity with most catalysts at a moderate rate. An internal alkyne was needed, due to the rapidity of hydroamination with catalysts such as

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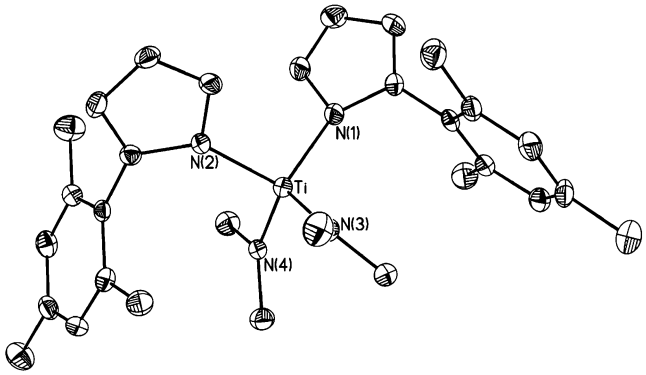
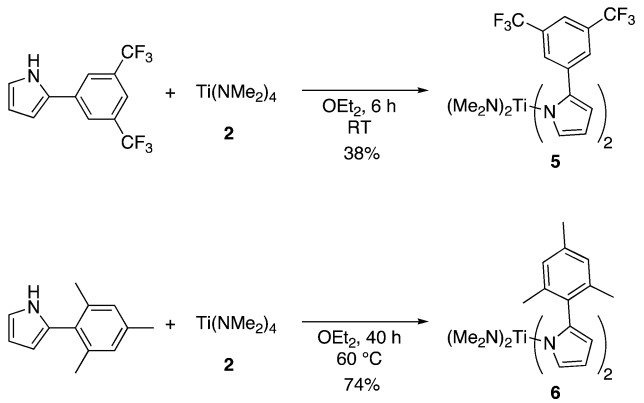
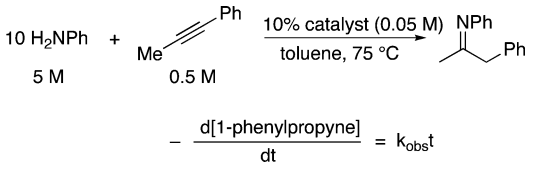


Figure 2. ORTEP structure from single-crystal X-ray diffraction on $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**). Selected bond distances (Å) and angles (deg): Ti−N(3) = 1.844(4), Ti−N(4) = 1.865(4), Ti−N(2) = 1.971(4), Ti−N(1) = 2.007(4); N(3)−Ti−N(4) = 109.3(2), N(3)−Ti−N(2) = 107.5(2), N(4)−Ti−N(2) = 108.4(2), N(3)−Ti−N(1) = 112.0(2), N(4)−Ti−N(1) = 114.1(2), N(2)−Ti−N(1) = 105.2(2).

Scheme 3. Synthesis of $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (5) and $Ti(NMe_2)_2(pyrr^{mes})_2$ (6)



Scheme 4. Conditions for the Kinetic Studies



$Ti(NMe_2)_2$(dmpm) (**1**) with terminal alkynes. For example, the reaction with 1-hexyne and aniline requires less than 5 min when started at room temperature using 5 mol % of **1**. Catalyst **1**, conveniently, requires less than 4 h at 75 °C to carry the reaction to completion with 1-phenylpropyne and excess aniline. The conditions for the catalyses are shown in Scheme 4. The reactions were run in d_8-toluene in the NMR probe.

Often, catalytic reactions show a first-order dependence on catalyst concentration. This was shown to be true with **1** under these conditions; changes in catalyst concentration track linearly with rate constant (Figure 3). With catalytic conditions that are at high concentrations of amine and with a linear dependence on catalyst concentration, the rate law for the reaction reduces to a pseudo-first-order expression in alkyne with standardized conditions for the catalyst. All the catalytic reactions studied fit well to the rate expression in Scheme 4.

A representative plot of ln[1-phenylpropyne] versus time under the conditions shown in Scheme 4 is provided as Figure 4 for complex **1**. The disappearance of the 1-phenylpropyne starting material versus time was used to fit the first-order

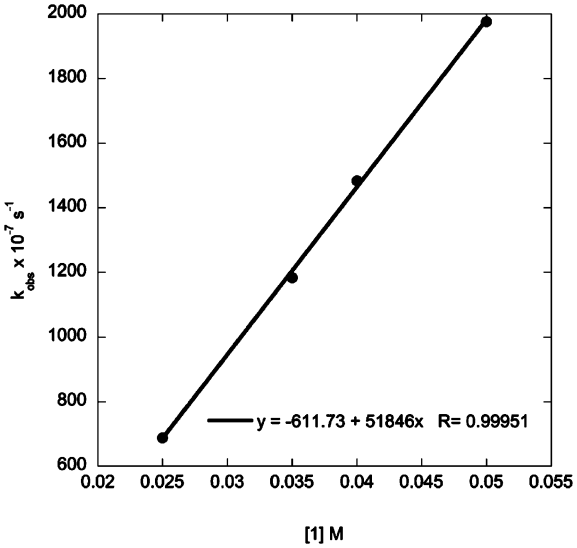


Figure 3. Plot of concentration of **1** versus pseudo-first-order rate constant for the hydroamination reaction.

equations. Even though most of the catalysts are quite regioselective for this reaction, the measurement of the disappearance of 1-phenylpropane was preferable to measuring the appearance of products to avoid missing potential rate contributions from the other regioisomer. Comparisons between catalysts use the magnitude of k_{obs} under these constant conditions as a measure of relative hydroamination reaction rate.

The results of the kinetic study on compounds **1** and **3**−**6** are shown in Table 1. The errors are based on repeated runs (at least three), are at the 99% confidence level, and varied with catalyst from as little as 4% to as high as 20%. The average error on the rate constants was about 10% at this confidence level.

It is obvious from comparison of the data in entries 1−3 of Table 1 that substitution on the 2-position of the pyrrole rings in the dmpm framework results in a reduction in rate constant by a factor of about 2.5−5 times relative to the parent framework. The increased sterics of the dipyrrolylmethane framework near the substrate binding sites results in slower kinetics.

Interestingly, the unlinked pyrrolyl catalysts were actually faster than the dmpm derivatives by a factor of 1.5−2 times (entries 4 and 5 versus entries 2 and 3). This increase in rate can again be explained by the steric congestion of the substituted dmpm derivatives. It is likely that the unlinked derivatives can rotate the bulky substituents away from the substrate-binding site, increasing the rate constant.

However, even the complexes bearing the unlinked pyrrolyl ligands were still slower than the parent complex Ti(dmpm)-$(NMe_2)_2$ (**1**) by a factor of ∼1.5 versus the fastest member, $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (**5**).

Comparison of the two catalysts $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (**5**) and $Ti(NMe_2)_2(pyrr^{mes})_2$(**6**) does not allow separation of steric and electronic factors. Consequently, we prepared two additional titanium compounds that differ only in the donor ability of a substituent in the 4-position of an aromatic group on the 2-position of a pyrrole. The pyrroles, synthesized using the Sadighi reaction, were 2-(4-(trifluoromethyl)phenyl)pyrrole ($Hpyrr^{4-CF_3}$) and 2-(4-tolyl)pyrrole ($Hpyrr^{tol}$). These were placed on titanium by transamination (Scheme 5) on $Ti(NMe_2)_4$ (**2**) to form $Ti(NMe_2)_2(pyrr^{4-CF_3})_2$ (**7**) and $Ti(NMe_2)_2(pyrr^{tol})_2$ (**8**).

Using the same experimental procedure as before (Scheme 4), the activities of **7** and **8** were also tested. As shown in Figure

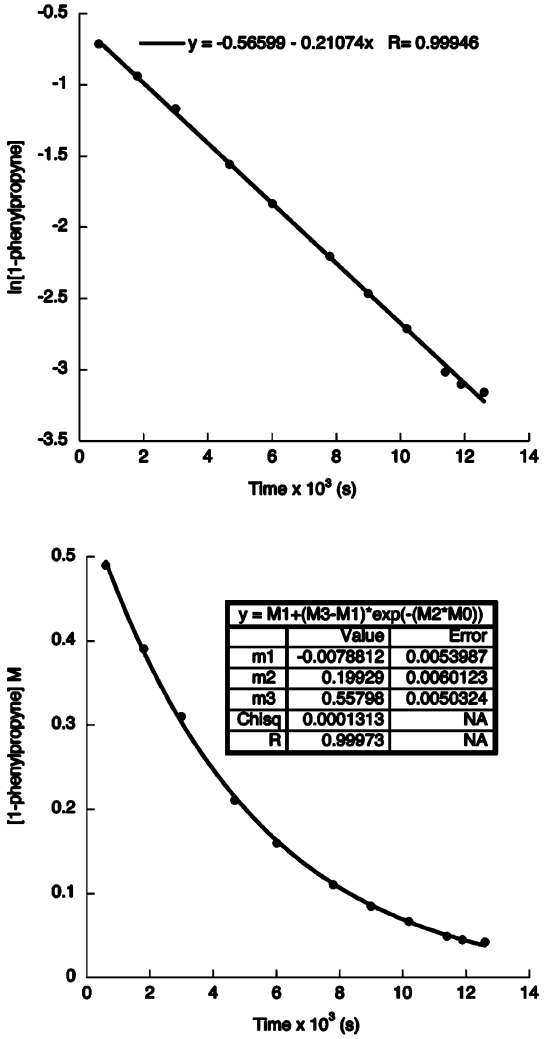


Figure 4. (top) Representative plot of ln[1-phenylpropyne] vs time with complex **1** as the hydroamination catalyst. (bottom) Representative plot of [1-phenylpropyne] vs time with fit curve. See the Experimental Section for a description of the equation used to fit the bottom plot.

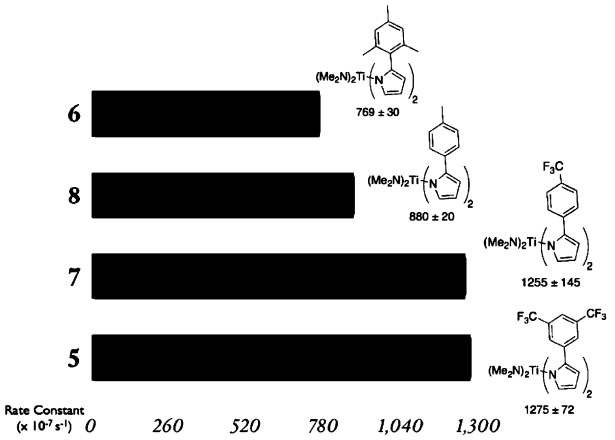
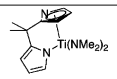
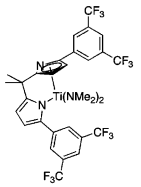
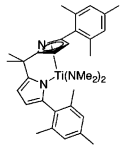
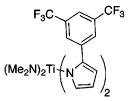
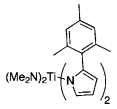


Figure 5. Comparison of rate constants for hydroamination of the bis(pyrrolyl) complexes. Errors are at the 99% confidence level, and rate constants are $\times 10^{-7}$ s^{-1}.

5, the compounds showed a dramatic difference with donor ability of the substituent in the *para* position of the arene ring. The *p*-CF_3 complex **7** has a rate constant of (1255 ± 145) × 10^{-7} s^{-1}, similar to that of the 3,5-$(CF_3)_2$ species **5** at (1275 ± 72) × 10^{-7} s^{-1}. The *p*-methyl complex **8** had a significantly smaller rate constant at (880 ± 20) × 10^{-7} s^{-1} relative to either CF_3 complex but slightly improved activity over the more sterically crowded mesityl-containing compound **6**.

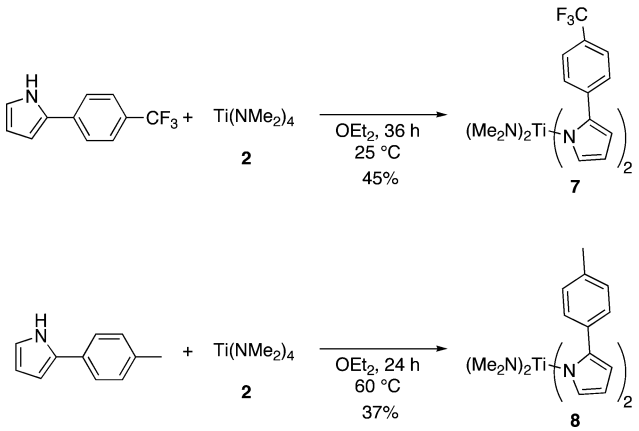
One possible complication with the bis(pyrrolyl) complexes is disproportionation reactions to generate a mixture containing mono(pyrrolyl) and tris(pyrrolyl) complexes.[27] Are the mono(pyrrolyl) or the bis(pyrrolyl) complexes actually the active catalysts? Thus far, we have only been able to isolate the mono(pyrrolyl) complexes as impure mixtures. Attempts to study kinetics using these impure complexes or mono(pyrrolyl) complexes generated in situ from $Ti(NMe_2)_4$ and Hpyrr deriva-

Table 1. Observed Rate Constants for Pyrrolyl Catalysts $Ti(NMe_2)_2(dmpm)$ (1), $Ti(NMe_2)_2(dmpm^{3,5-CF_3})$ (3), $Ti(NMe_2)_2(dmpm^{mes})$ (4), $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (5), and $Ti(NMe_2)_2(pyrr^{mes})_2$ (6)

Entry	Catalyst[a]	k_{obs} ($\times 10^{-7}$ s^{-1})[b]
1		1976 ± 130
2		780 ± 30
3		403 ± 80
4		1275 ± 72
5		769 ± 30

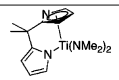
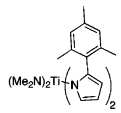
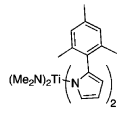
[a] Conditions are as shown in Scheme 4. [b] All errors are at the 99% confidence limit.

Scheme 5. Synthesis of $Ti(NMe_2)_2(pyrr^{4-CF_3})_2$ (7) and $Ti(NMe_2)_2(pyrr^{tol})_2$ (8)



(27) Crossover of pyrrolyl ligands is certainly possible in these complexes. Taking a C_6D_6 solution of $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (**5**) and $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**) in a 1:1 ratio leads to new resonances in the ^1H NMR spectra which are presumably due to pyrrolyl crossover. Further study is warranted on these issues.

Table 2. Comparison of Various Catalyst Architectures

Entry	Catalyst[a]	Temperature (°C)	k_{obs} (10^{-7} s^{-1})[b]
1		75 °C	1976 ± 130
2	$Ti(NMe_2)_4$	75 °C	866 ± 94
3		75 °C	769 ± 30
4		100 °C	3888 ± 764
5	$Ti(indenyl)_2Me_2$	100 °C	888 ± 61

[a] Conditions are the same as shown in Scheme 4, except in entries 4 and 5, where the temperature is 100 °C instead of 75 °C. [b] All errors are at the 99% confidence limit.

tives have given very large errors. While the average rate constants are generally smaller than those of their bis(pyrrolyl) counterparts, the errors do not allow a definitive answer to this question at this time.

It can be said definitively that the active species is not $Ti(NMe_2)_4$ (**2**), prepared by disproportionation of the bis(pyrrolyl) complexes. Since we do not observe Hpyrr during the reactions, the maximum amount of **2** that can be generated via diproportionation is half of the concentration generally employed in our kinetics runs (Scheme 4). Since the rates vary linearly with catalyst concentration (Figure 3), the rate constant for these reactions would have a maximum (full disproportionation to **2** and $(pyrr)_4Ti$) of $k_{obs} = (433 \pm 47) \times 10^{-7}$ s^{-1}. Since the rates for all of the bis(pyrrolyl) complexes are faster than this, **2** cannot be the active species in these reactions.

We can also use the same conditions to evaluate these pyrrolyl catalysts versus several commonly employed titanium complexes with various architectures. For this we wished to compare other catalyst types with the parent complex $Ti(NMe_2)_2$(dmpm) (**1**) and bis(pyrrolyl) species $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**). An important comparison is with $Ti(NMe_2)_4$ (**2**), which does not have as large a substrate scope as many of the other catalyst types;[6l] however, it is commercially available and is often the starting material for other titanium catalysts. We also compared with triple-recrystallized samples of $Ti(indenyl)_2Me_2$ (**9**), which has been shown by Doye and co-workers to be a fairly general catalyst for alkyne hydroamination.[6c]

We were able to run all the catalysts at 75 °C, with the exception of the indenyl complex **9**. While **9** was active at 75 °C, the results were inconsistent at this temperature, which was apparently due to a sensitive catalyst activation period.[28] Assuming that there was an activation problem, we incubated the catalyst with the aniline portion at 100 °C prior to alkyne addition. However, this still did not result in good reproducibility of the kinetics under these conditions. Consequently, we ran the reactions with **9** at 100 °C, which afforded plots that reliably fit well to first-order kinetics. For comparison, $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**), a very stable but relatively slow catalyst, was run at the higher temperature as well.[29]

The results in Table 2 suggest that the pyrrolyl framework is quite effective relative to other catalyst architectures currently in use. As in our previous report,[21] the results show that $Ti(NMe_2)_2$(dmpm) (**1**) is about a factor of 2 faster than $Ti(NMe_2)_4$ (**2**) (entries 1 and 2). The bis(pyrrolyl) species **6** provides activity comparable with that of **2**. The rate constant for **6** increased by ~5 times on raising the temperature from 75 to 100 °C. Comparison of $Ti(indenyl)_2(NMe_2)_2$ with **6** under identical conditions reveals that this pyrrolyl catalyst is about a factor of 4 times faster for these substrates.

Conclusions

Using readily available 2-substituted pyrroles, a route to 2,9-diaryldipyrrolylmethanes has been developed where the synthesized pyrroles can be used as the limiting reagent in condensation with acetone. Placing these new ligands on titanium is readily accomplished by reaction with $Ti(NMe_2)_4$ (**2**), and the resulting complexes show η^5:η^1 coordination of the dipyrrolylmethane in the solid state. However, the barrier for pyrrolyl exchange in these substituted dipyrrolylmethanes is quite low and is below what could be measured by variable-temperature ^{1}H NMR spectroscopy. Catalysis with these new dmpm complexes was slower than with unsubstituted **1**, which we currently assign to steric inhibition by the bulky groups near the substrate-binding site. Consistent with this, simple bis(pyrrolyl) complexes without the methylene linker and with the same substituents show faster catalysis rates, which is likely due to free rotation of the steric bulk away from the substrate binding site in the bis(pyrrolyl) derivatives. Using these bis(pyrrolyl) catalysts, we were able to show experimentally that hydroamination activity can be increased by adding electron-withdrawing groups to pyrrolyl substituents (Figure 5).

Comparison of various catalyst architectures shows that the pyrrolyl catalysts are quite rapid. It should be noted that this does not necessarily imply that these catalysts are superior for any particular application. The "best" catalyst for any particular application is a function of availability, selectivity, and activity with a particular set of substrates. For example, the fastest catalyst studied here, **1**, is a poor catalyst for some applications, e.g., hydrohydrazination,[30] and is the only catalyst studied that leads to any product for others, e.g., the synthesis of 1-phenyl-2,5-dibenzylpyrrolyl from 1,6-diphenyl-1,5-hexadiyne and aniline.[8] The aim is to optimize the activity of the most promising catalysts for these reactions, which our current results suggest are the dipyrrolylmethane complexes of titanium, especially $Ti(NMe_2)_2$(dmpm) (**1**). From these experiments, we are discovering what electronic features and steric profiles encourage these useful C−N bond forming reactions.

Good activity was obtained with simple bis(pyrrolyl) complexes such as $Ti(NMe_2)_2(pyrr^{3,5-CF_3})_2$ (**5**). Whether the somewhat faster rates with the dipyrrolylmethane **1** are due to electronic factors resulting from the different ligand architecture, smaller steric constraints in **1**, or a combination of the two effects is currently unknown, which is the subject of ongoing scrutiny.

Further optimization of the dmpm framework is currently under investigation. For previous studies, some data suggested that the active species for hydroamination is the η^1:η^1-dmpm isomer of **1**.[21] Consequently, moving the steric bulk from the 2- to the 3-position of the pyrrolyl ring may result in greater

(28) The only pyrrolyl catalyst for which an activation period was observed was for some of the less active bis(pyrrolyl) complexes such as $Ti(NMe_2)_2(pyrr^{mes})_2$ (**6**) and $Ti(NMe_2)_2(pyrr^{tol})_2$ (**8**). However, even with these, activation would occur at room temperature over a couple of hours if samples were allowed to rest before the kinetic run.

(29) A comparison with $Ti(NMe_2)_2$(dmpm) (**1**) would have been preferable. However, under these conditions at 100 °C the reaction was ~50% complete in <10 min, making its measurements unreliable.

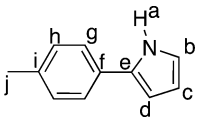
(30) Banerjee, S.; Odom, A. L. Unpublished results.

activity as the substituent is moved away from the active site. This assertion is currently being tested.

Experimental Section

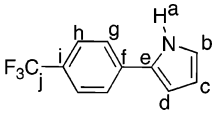
General Considerations. All manipulations of air-sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Anhydrous ether was purchased from Columbus Chemical Industries Inc., and pentane and toluene, purchased from Spectrum Chemical Mfg. Corp., were purified by sparging with dry N_2 and then removing the water by running the solvents through activated alumina systems purchased from Solv-Tek. Hexanes and ethyl acetate were purchased from Mallinckodt-Baker Inc., and reagent grade acetone was purchased from Fisher Scientific and distilled from $CaSO_4$ under N_2 and stored over 4Å molecular sieves. Trifluoracetic acid was purchased from Aldrich and used as received. Aniline was purchased from Matheson, Coleman and Bell Mfg. and was distilled two times from calcium hydride under vacuum. 1-Phenylpropyne was purchased from GFS Chemical, vacuum-distilled, and then passed over two columns of neutral alumina. $Ti(NMe_2)_4$ (**2**)[31] and $Ti(indenyl)_2(CH_3)_2$ (**9**)[32] were prepared using the literature procedures. 2-(2,4,6-Trimethylphenyl)-1*H*-pyrrole ($Hpyrr^{mes}$) and 2-[3,5-bis(trifluoromethyl)phenyl]-1*H*-pyrrole ($Hpyrr^{3,5-CF_3}$) were synthesized according to literature methods.[23] Deuterated solvents were dried over purple sodium benzophenone ketyl (C_6D_6) or phosphoric anhydride ($CDCl_3$) and distilled under a nitrogen atmosphere. Deuterated toluene was dried by passing through two columns of neutral alumina. ^1H and ^{13}C spectra were recorded on Inova-300 and VXR-500 spectrometers. All spectra were referenced internally to residual protio solvent (^1H) or solvent (^{13}C) resonances. ^1H and ^{13}C assignments were confirmed when necessary by using two-dimensional $^1H-^1H$ and $^1H-^{13}C$ correlation NMR experiments. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Typical coupling constants are not reported.

Synthesis of 2-(4-Methylphenyl)-1*H*-pyrrole ($Hpyrr^{tol}$).



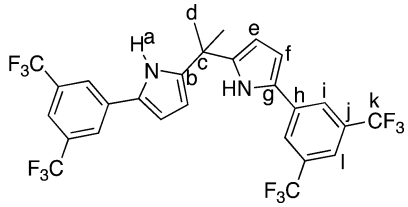
Under an atmosphere of dry nitrogen a threaded Schlenk tube was loaded with sodium pyrrole (4.69 g, 52.6 mmol), $ZnCl_2$ (7.17 g, 52.6 mmol), and a stirbar. To that same vessel was added 40 mL of THF slowly (*Caution!* exothermic). After 10 min, $Pd(OAc)_2$ (20 mg, 0.5 mol %) and 2-(di-*tert*-butylphosphino)biphenyl (26 mg, 0.5 mol %) were added to the Schlenk tube. The tube was then capped, taken from the dry box, and connected to a Schlenk line. Under a continuous flow of nitrogen the screw cap was removed, and 4-bromotoluene (3 g, 17.5 mmol) was quickly added. The screw cap was replaced after addition. The headspace in the Schlenk tube was evacuated, and the tube was then placed in a 100 °C oil bath for 24 h. After 24 h, the tube was removed from the oil bath and cooled to room temperature. The cap was removed, and the solution was transferred to a separatory funnel. The tube was rinsed with 30 mL of OEt_2 and 30 mL of H_2O, which were then added to the separatory funnel. The aqueous layer was extracted with OEt_2 (3 × 50 mL); the combined organic layers were collected and dried over $MgSO_4$. The solution was then filtered and concentrated in vacuo. Purification of the crude product was accomplished by column chromatography on silica gel using an eluting solution of hexanes: ethyl acetate (9:1). Removal of volatiles yielded the product as a white solid (1.44 g, 54%). Mp: 145 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.2 (br s, 1 H, H^a), 7.37 (d, $J_{HH} = 8.46$ Hz, 2 H, H^g or H^h), 7.18 (d, $J_{HH} = 8.07$ Hz, 2 H, H^g or H^h), 6.82 (m, 1 H, H^b or H^d), 6.50 (m, 1 H, H^b or H^d), 6.31 (q, $J_{HH} = 2.84$, 1 H, H^c), 2.39 (s, 3 H, H^j). ^{13}C NMR (500 MHz, $CDCl_3$) δ 135.85 (C^i or C^f), 132.19 (C^i or C^f), 129.97 (C^e), 129.50 (C^h or C^g), 123.77 (C^h or C^g), 118.42 (C^d or C^b), 109.90 (C^d or C^b), 105.31 (C^c), 21.38 (C^j). Anal. (Found) calcd: C, (84.10) 84.04; H, (7.02) 7.05; N, (8.66) 8.91.

Synthesis of 2-[4-(Trifluoromethyl)phenyl]-1*H*-pyrrole ($Hpyrr^{4-CF_3}$).



Under an atmosphere of dry nitrogen, a threaded Schlenk tube was loaded with sodium pyrrole (3.6 g, 40.4 mmol), $ZnCl_2$ (5.5 g, 40.4 mmol), and a stirbar. To that vessel was slowly added 32 mL of THF (*Caution!* exothermic). After 10 min, $Pd(OAc)_2$ (15 mg, 0.5 mol %) and 2-(dicyclohexylphosphino)biphenyl (24 mg, 0.5 mol %) were added to the Schlenk tube. The screw cap was replaced, and the tube was removed from the drybox and connected to a Schlenk line. Under a continuous flow of nitrogen the screw cap was removed and 4-bromobenzotrifluoride (3 g, 13 mmol) was quickly added. The screw cap was replaced, and the headspace in the tube was evacuated. The tube was then placed in a 80 °C oil bath, where the contents were allowed to react for 20 h. After the reaction was complete, the tube was removed from the oil bath and cooled to room temperature. The cap was removed, and the solution was transferred to a separatory funnel. The tube was rinsed with 30 mL of OEt_2 and 30 mL of H_2O, which were then added to the separatory funnel. The aqueous layer was extracted with OEt_2 (3 × 50 mL); the combined organic layers were collected and dried over $MgSO_4$. The solution was then filtered and concentrated in vacuo. Purification of the crude product was accomplished by column chromatography on silica gel using an eluting solution of hexanes: ethyl acetate (9:1). Removal of volatiles yielded the product as a white solid (2.53 g, 90%). Mp: 158 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.46 (br s, 1 H, H^a), 7.59 (d, $J_{HH} = 7.73$ Hz, 2 H, H^h), 7.53 (d, $J_{HH} = 7.73$ Hz, 2 H, H^g), 6.91 (m, $J = 1.70$ Hz, 1 H, H^d), 6.62 (m, $J_{HH} = 1.47$ Hz, 1 H, H^b), 6.33 (q, $J = 3.36$ Hz, 1 H, H^c). ^{13}C NMR (500 MHz, $CDCl_3$): δ 135.91 (C^f), 130.6 (C^e), 127.85 (q, $J_{CF} = 33$ Hz, C^i), 125.92 (q, $J_{CF} = 33$ Hz, C^h), 124.29 (q, $J_{CF} = 272$ Hz, C^j), 123.58 (C^g), 120.1 (C^d), 110.65 (C^c), 107.7 (C^b). Anal. (Found) calcd: C, (62.22) 62.56; H, (3.54) 3.82; N, (6.51) 6.67.

Synthesis of 2,9-Bis[3,5-bis(trifluoromethyl)phenyl]-5,5-dimethyldipyrrolylmethane ($H_2dmpm^{3,5-CF_3}$).

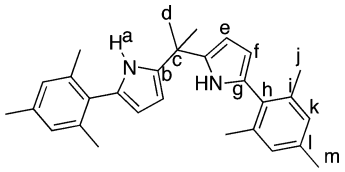


A single-necked 14/20 25 mL round-bottom flask was charged with 2-[3,5-bis(trifluoromethyl)phenyl]-1*H*-pyrrole (0.4 g, 1.4 mmol) and acetone (2.08 g, 36 mmol). The flask then was sealed with a septum. The solution was stirred at room temperature while it was degassed under a flow of argon. After 15 min, trifluoroacetic acid (0.4 g, 3.6 mmol) was added via syringe. The solution was stirred for 3 h under an argon atmosphere. The reaction mixture was quenched with ~15 mL of a 0.1 M NaOH solution. The resulting mixture was transferred to a separatory funnel, where the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers

(31) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3859.
(32) Balboni, D.; Camuratti, G. P.; Resconi, L. *Inorg. Chem.* **2001**, *40*, 6588.

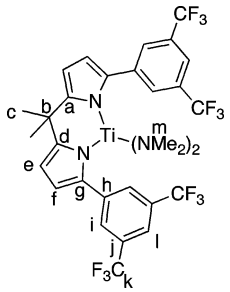
were dried over $MgSO_4$ and filtered. The solvent was removed in vacuo to give a purple oil. The oil was then tritrated with pentane to yield a pink solid (0.311 g, 72%). Mp: 130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (br s, 2 H, H^a), 7.73 (s, 4 H, H^i), 7.6 (s, 2 H, H^l), 6.6 (m, J_{HH} = 2.32 Hz, 2 H, H^e or H^f), 6.2 (m, J_{HH} = 3.23 Hz, 2H, H^e or H^f), 1.76 (s, 6 H, H^d). ^{13}C NMR (500 MHz, $CDCl_3$): δ 141.64 (C^h or C^g), 134.4 (C^h or C^g), 132.18 (q, J_{CF} = 31.94 Hz, C^j), 129.03 (C^b), 123.28 (q, J_{CF} = 272 Hz, C^k), 123.15 (q, J_{CF} = 2.54 Hz, C^i), 119.1 (q, J_{CF} = 3.91 Hz, C^l), 108.64 (C^e or C^f), 107.09 (C^e or C^f), 35.83 (C^c), 29.09 (C^d). Anal. (Found) calcd: C, (54.63) 54.19; H, (3.14) 3.03; N, (4.52) 4.68.

Synthesis of 2,9-Bis(2,4,6-trimethylphenyl)-5,5-dimethyldipyrrolylmethane (H_2dmpm^{mes}).



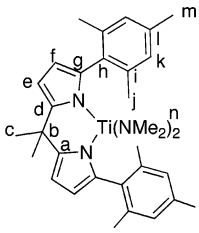
A single-necked 14/20 25 mL round-bottom flask was charged with 2-(2,4,6-trimethylphenyl)-1*H*-pyrrole (0.25 g, 1.3 mmol) and acetone (1.96 g, 33 mmol) and then sealed with a septum. The solution was stirred at room temperature while being degassed under a flow of argon. After 15 min, trifluoroacetic acid (0.384 g, 3.3 mmol) was added via syringe. The solution was stirred for 1 h. The reaction mixture was quenched with ~15 mL of a 0.1 M NaOH solution. The resulting mixture was transferred to a separatory funnel, where the aqueous layer was extracted with Et_2O (2 × 15 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed in vacuo to give an orange oil. The oil was then tritrated with pentane to yield an orange solid (0.187 g, 68%). Mp: 115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (br s, 2 H, H^a), 6.89 (s, 4 H, H^k), 5.88 (t, J_{HH} = 2.87 Hz, 2H, H^e or H^f), 5.8 (t, J_{HH} = 5.86 Hz, 2 H, H^e or H^f), 2.2 (s, 6 H, H^m), 2.0 (s, 12 H, H^j), 1.6 (s, 6 H, H^d). ^{13}C NMR (500 MHz, $CDCl_3$): δ 138.54 (C^l, C^i, or C^h), 138.31 (C^l, C^i, or C^h), 137.38 (C^l, C^i, or C^h), 130.83 (C^b or C^g), 128.76, 127.98 (C^k), 107.5 (C^e or C^f), 103.4(C^e or C^f), 35.30 (C^c), 28.95 (C^d), 20.99 (C^m), 20.52 (C^j). Anal. (Found) calcd for $C_{29}H_{34}N_2$: C, (84.85) 84.83; H, (8.37) 8.35; N, (6.78) 6.82.

Synthesis of Ti(NMe$_2$)$_2$(dmpm$^{3,5-CF_3}$) (3).



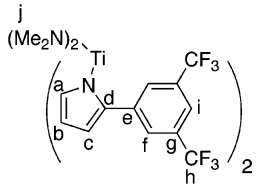
Under an atmosphere of dry nitrogen a vial was loaded with Ti(NMe$_2$)$_4$ (**2**; 0.131 g, 0.584 mmol) in ~3 mL of Et_2O. In a 20 mL scintillation vial was loaded 2,9-bis[3,5-bis(trifluoromethyl)phenyl]-5,5-dimethyldipyrrolylmethane (0.350 g, 0.584 mmol) in ~3 mL of OEt_2. The solutions were put into a cold well, where they sat until nearly frozen. To a thawing solution of H_2dmpm$^{3,5-CF_3}$ was added the cold solution of **2**. The solution was stirred at room temperature for 4 h. Volatiles were removed in vacuo to yield an orange solid (0.395 g, 92%). Mp: 150 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (s, 4 H, H^i), 7.63 (s, 2 H, H^l), 6.55 (d, J_{HH} = 3.19 Hz, 2 H), 6.44 (d, J_{HH} = 3.18 Hz, 2 H), 2.6 (s, 12 H, H^m), 1.8 (s, 6 H, H^c). ^{13}C NMR (500 MHz, $CDCl_3$): δ 162.84 (C^h), 138.18 (C^a or C^g), 138.04 (C^a or C^g), 131.17 (q, J_{CF} = 33.6 Hz, C^j), 126.26 (distorted q, C^i), 119.55 (q, J_{CF} = 3.7 Hz, C^l), 110.22 (C^e or C^f), 109.53 (C^e or C^f), 45.88 (C^m), 39.67 (C^b)29.33 (C^c). Anal. (Found) calcd: C, (50.45) 50.84; H, (3.75) 3.85; N, (7.48) 7.65.

Synthesis of Ti(NMe$_2$)$_2$(dmpm^{mes}) (4).



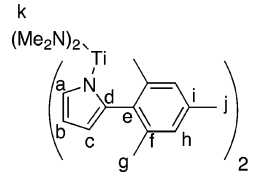
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with Ti(NMe$_2$)$_4$ (**2**; 0.316 g, 1.4 mmol), H_2dmpm^{mes} (0.578 g, 1.4 mmol), and ~8 mL of Et_2O. The pressure tube was sealed with a Teflon screw cap, taken out of the dry box, and put in a 50 °C oil bath, where it was left to react for 18 h. The pressure tube was then removed from the oil bath and taken back into an atmosphere of dry nitrogen, where the volatiles were removed in vacuo to yield an orange oily solid. Crystallization from pentane yielded an orange solid (0.225 g, 30%). Mp: 155 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.80 (s, 4 H, H^k), 6.37 (d, J_{HH} = 2.80 Hz, 2 H, H^f or H^e), 6.28 (d, J_{HH} = 2.77 Hz, 2H, H^f or H^e), 2.59 (s, 12 H, H^n), 2.23 (s, 6 H, H^m), 2.18 (s, 12 H, H^j), 1.94 (s, 6H, H^c). ^{13}C NMR (500 MHz, $CDCl_3$) 159.15 (C^h), 138.38 (C^i or C^l), 138.26 (C^i or C^l), 136.27 (C^d or C^g), 132.54 (C^g or C^d), 128.52 (C^k), 113.70 (C^e or C^f), 107.01 (C^e or C^f), 47.45 (C^n), 39.26 (C^b), 30.15 (C^m), 21.67 (C^j), 20.92 (C^c). After many attempts at elemental analysis, satisfactory results were not obtained. ^{1}H and ^{13}C NMR spectra are included in the Supporting Information to demonstrate purity.

Synthesis of Ti(NMe$_2$)$_2$(pyrr$^{3,5-CF_3}$)$_2$ (5).



Under an atmosphere of dry nitrogen, a 20 mL scintillation vial was loaded with Ti(NMe$_2$)$_4$ (**2**; 0.150 g, 0.669 mmol) in ~3 mL of OEt_2. A separate vial was loaded with Hpyrr$^{3,5-CF_3}$ (0.372 g, 1.33 mmol) in ~5 mL of OEt_2. The substituted arylpyrrole was then added to the vial containing **2** at room temperature. The solution was stirred at room temperature for 6 h. Volatiles were removed in vacuo to yield a red oil. Crystallization from pentane yielded the bis(pyrrolyl) species as an orange solid (0.175 g, 38%). Mp: 86 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 4 H, H^f), 7.61 (s, 2 H, H^i), 6.89 (m, 2 H, H^a, H^b, or H^c), 6.48 (m, 2 H, H^a, H^b, or H^c), 6.25 (m, 2 H, H^a, H^b, or H^c), 3.0 (s, 12 H, H^j). ^{13}C NMR (500 MHz, $CDCl_3$): δ 138.88 (C^e), 137.70 (C^d), 131.62 (q, J_{CF} = 33 Hz, C^g), 126.63 (C^a, C^b, or C^c), 125.96 (C^f), 123.35 (J_{CF} = 273 Hz, C^h), 119.1 (C^i), 111.86 (C^a, C^b, or C^c), 111.20 (C^a, C^b, or C^c), 44.53 (C^j). Anal. (Found) calcd for $C_{28}H_{24}F_{12}N_4Ti$: C, (48.48) 48.57; H, (3.53) 3.49; N, (7.78) 8.09.

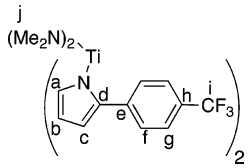
Synthesis of Ti(NMe$_2$)$_2$(pyrr^{mes})$_2$ (6).



Under an atmosphere of dry nitrogen a threaded pressure tube was loaded with Ti(NMe$_2$)$_4$ (0.075 g, 0.334 mmol), Hpyrr^{mes} (0.124 g,

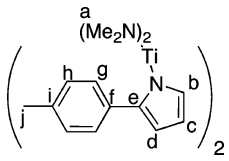
0.667 mmol), and ~5 mL of Et_2O. The pressure tube was then sealed with a Teflon screw cap and wrapped with Teflon tape. The pressure tube was then taken out of the drybox and put into a 60 °C oil bath for 40 h. The pressure tube was taken back into an atmosphere of dry nitrogen, and the volatiles were removed in vacuo to yield a yellow solid. The compound was purified by recrystallization from pentane (0.125 g, 74%). Mp: 160 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (s, 4 H, H^h), 6.81 (q, J_{HH} = 1.57 Hz, 2 H, H^b), 6.19 (t, J = 2.76, Hz, 2 H, H^a or H^c), 5.91 (t, J_{HH} = 1.61 Hz, 2 H, H^a or H^c), 2.77 (s, 12 H, H^k), 2.28 (s, 6H, H^j), 2.1 (s, 12 H, H^g). ^{13}C NMR (500 MHz, $CDCl_3$): δ 139.2 (C^f), 137.54 (C^i, C^e, or C^d), 136.85 (C^i, C^e, or C^d), 134.65 (C^i, C^e, or C^d), 127.6 (C^h), 123.09 (C^b), 108.6 (C^a or C^c), 108.3 (C^a or C^c), 44.14 (C^k), 21.04 (C^j), 20.36 (C^g). Anal. (Found) calcd: C, (70.98) 71.42; H, (8.01) 7.99; N, (10.97) 11.10.

Synthesis of Ti(NMe$_2$)$_2$(pyrr$^{4-CF_3}$)$_2$ (7).



Under an atmosphere of dry nitrogen, a 20 mL scintillation vial was loaded with Hpyrr$^{4-CF_3}$ (0.115 g, 0.544 mmol), Ti(NMe$_2$)$_4$ (**2**; 0.061 g, 0.272 mmol), OEt_2 (3 mL), and a stir bar. The vial was then capped and the mixture stirred for 36 h at room temperature. The volatiles were removed in vacuo to yield an orange oil. Crystallization from pentane yielded an orange solid (0.069 g, 45%). Mp: 72 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J_{HH} = 7.88 Hz, 4 H, H^g), 7.45 (d, J_{HH} = 7.89 Hz, 4 H, H^f), 7.00 (m, 2 H, H^c), 6.36 (m, 2 H, H^a or H^b), 6.27 (t, J_{HH} = 2.67 2 H, H^a or H^b), 3.16 (s, 12 H, H^j). ^{13}C NMR (500 MHz, $CDCl_3$): 140.43 (C^e), 139.50 (C^d), 127.64 (q, J_{CF} = 33 Hz, C^h), 126.56 (C^f), 126.51 (C^c), 125.12 (q, J_{CF} = 11.78 Hz, C^g), 124.31 (q, J_{CF} = 272 Hz, C^i), 111.07 (C^a or C^b), 109.86 (C^a or C^b), 44.68 (C^j). Anal. (Found) calcd: C, (55.83) 56.13; H, (5.11) 4.71; N, (10.29) 10.07.

Synthesis of Ti(NMe$_2$)$_2$(pyrr^{tol})$_2$ (8).



Under an atmosphere of dry nitrogen a threaded pressure tube was loaded with Hpyrr^{tol} (0.115 g, 0.732 mmol), Ti(NMe$_2$)$_4$ (**2**; 0.082 g, 0.366 mmol), OEt_2 (3 mL), and a stirbar. The pressure tube was then sealed with a Teflon screw cap and wrapped with Teflon tape. The tube was removed from the drybox and placed in a 60 °C oil bath, where the mixture was left to react for 24 h. After the reaction was complete, the tube was taken back into an atmosphere of dry nitrogen. The reaction mixture was transferred to a 20 mL scintillation vial, where the volatiles were concentrated in vacuo to yield an orange oil. Crystallization from pentane yielded an orange solid (0.060 g, 37%). Mp: 71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, J_{HH} = 7.68 Hz, 4 H, H^h or H^g), 7.04 (d, J_{HH} = 7.77, 4 H, H^h or H^g), 6.90 (m, 2 H, H^d), 6.27 (m, 2 H, (H^c or H^b), 6.18 (m, 2 H, H^c or H^b), 2.99 (s, 12 H, H^a), 2.29 (s, 6 H, H^j). ^{13}C NMR: δ 141.11 (C^i), 135.53 (C^f), 134.57 (C^e), 128.82 (C^h or C^g), 126.97 (C^h or C^g), 125.67 (C^d), 110.05 (C^b or C^c), 107.68 (C^b or C^c), 44.68 (C^a), 21.10 (C^j). Anal. (Found) calcd: C, (69.53) 69.94; H, (7.60) 7.19; N, (12.17) 12.49.

(33) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1995.

Table 3. Structural Parameters for Ti(NMe$_2$)$_2$(dmpm$^{3,5-CF_3}$) (3), Ti(NMe$_2$)$_2$(dmpm^{mes}) (4), Ti(NMe$_2$)$_2$(pyrr$^{3,5-CF_3}$)$_2$ (5), and Ti(NMe$_2$)$_2$(pyrr^{mes})$_2$ (6)

	3	**4**	**5**	**6**
formula	$C_{31}H_{28}F_{12}N_4Ti$	$C_{33}H_{44}N_4Ti$	$C_{28}H_{24}F_{12}N_4Ti$	$C_{30}H_{40}N_4Ti$
formula wt	732.47	544.62	692.41	504.56
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	12.60(1)	8.840(4)	19.534(3)	7.745(1)
b (Å)	12.63(1)	30.94(1)	8.104(1)	12.215(2)
c (Å)	12.79(1)	11.113(5)	19.178(3)	16.177(2)
α (deg)	78.12(1)			74.266(3)
β (deg)	64.44(1)	98.779(8)	105.277(3)	82.985(3)
γ (deg)	62.66(1)			72.952(3)
V (Å^3)	1631(2)	3004(2)	2928.5(7)	1406.8(3)
Z	2	4	4	2
μ (mm^{-1})	0.359	0.312	0.395	0.328
D_{calcd} (g cm^{-3})	1.491	1.204	1.570	1.291
total no. of rflns	10 574	25 589	24 219	12 039
no. of unique rflns (R_{int})	4699 (0.06)	4349 (0.31)	4215 (0.112)	4051 (0.0651)
extinction coeff	0.006(2)	0.029(4)	0.0025(6)	0.003(2)
$R(F_o)$ ($I > 2\sigma$)	0.0634	0.0809	0.0512	0.0632
$R_w(F_o^2)$ ($I > 2\sigma$)	0.1648	0.1948	0.1328	0.1690

General Considerations for X-ray Diffraction. Crystals grown from concentrated solutions at −35 °C were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced utilizing the program SAINTPLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques. Structural parameters for **3**−**6** are given in Table 3.

General Procedure for Kinetics. All manipulations were done in an inert atmosphere drybox. In a 2 mL volumetric flask was loaded the catalyst (10 mol %, 0.1 mmol), aniline (0.931 g, 911 μL, 10 mmol), 1-phenylpropyne (0.116 g, 125 μL, 1 mmol), and ferrocene (0.056 g, 0.3 mmol) as an internal standard. The solution was then diluted to 2 mL with deuterated toluene. An ample amount of solution (~0.75 mL) was put into a threaded J. Young tube that was sealed with a cap and then wrapped with Teflon tape. The tube was then removed from the drybox and heated at 75 or 100 °C in the NMR spectrometer. The relative 1-phenylpropyne versus ferrocene concentration was monitored as a function of time. The fits are to the exponential decay of the starting material using the scientific graphing programs Origin or KaleidaGraph. The exact expression used to fit the data was $Y_t = Y_\infty + (Y_0 - Y_\infty)\exp^{-k_{obs}t}$ where Y = [1-phenylpropyne] at time = t (Y_t), infinity (Y_∞), or initial (Y_0).[33] The variables Y_∞, Y_0, and k_{obs} were optimized in the fits. For a representative fit see Figure 4.

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Supporting Information Available: Tables and full labeling schemes for **3**−**6** from X-ray diffraction studies, CIF files giving X-ray data for **3**−**6**, and figures giving NMR spectra for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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