Imido-Alkyne Coupling in Titanium Complexes: New Insights into the Alkyne Hydroamination Reaction

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Titanium imido complexes [Ti(NR)($N_2^{Ar}N_{py}$)(L)] ($N_2^{Ar}N_{py}$ = MeC(2-C_5H_4N)(CH_2NAr)$_2$, Ar = 4-C_6H_4-Me or 3,5-$C_6H_3Me_2$) have been prepared from the corresponding bis(amide) complexes [Ti($N_2^{Ar}N_{py}$)-(NMe_2)$_2$]. The reaction chemistry of the imido ligand has been investigated with aryl acetylenes, affording the {2 + 2} cycloaddition products [Ti($N_2^{Ar}N_{py}$){κ^2-N(^{t}Bu)CH=CAr′}] (Ar′ = Ph and 4-C_6H_4Me) which represent a catalytic intermediate in the anti-Markovnikov hydroamination of terminal alkynes. Reaction of these azatitanacyclobutene complexes with *tert*-butylamine completes the catalytic cycle, affording *trans*-cinnamyl(*tert*-butyl)amine; conversely, reaction with a second equivalent of alkyne afforded a second insertion product, an azatitanacyclohexadiene [Ti($N_2^{Ar}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ar′)C(Ar′) = CH}], two examples of which have been characterized by X-ray crystallography. Studies into the catalytic hydroamination of phenyl acetylene with *tert*-butylamine have been performed and indicate that the formation of an azatitanacyclohexadiene complex represents a deactivation pathway in this catalytic reaction.

Introduction

The catalytic hydroamination of carbon−carbon multiple bonds has emerged as a powerful synthetic strategy in the preparation of a wide variety of building blocks in synthetic organic chemistry, both in an academic and industrial context.[1−9] The anti-Markovnikov hydroamination of terminal alkynes in particular is deemed to be useful, since this is used to form aldimines, which find application as intermediates for further chemical transformations. Despite considerable research efforts in this field[10−37] and a number of successful systems being reported, a generally applicable catalytic system has thus far remained elusive. Pioneering work by Bergman[22,38] and Livinghouse[39] established the propensity of zirconocene complexes

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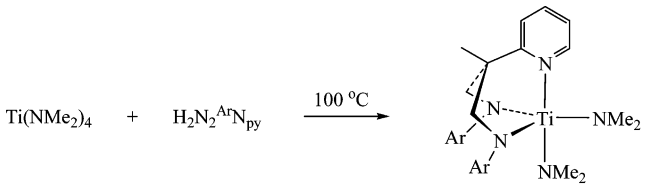
to act as hydroamination catalysts, and subsequent work naturally turned to titanium-based systems which has led to the development of a number of promising systems in recent years.[2,3,6]

However there remain unanswered questions regarding the mechanism of hydroamination catalysis as well as the catalyst degradation pathways.[40−43] Such understanding is necessary for the development of catalytic systems with greater scope and substrate tolerance. It is in this context that we turned our attention to the preparation and characterization of catalytic intermediates for the hydroamination of aryl alkynes with *tert*-butylamine. We recently reported the preparation and crystallographic characterization of an azatitanacyclobutene complex[44] supported by the diamido-pyridine ligand MeC(2-C_5H_4N)$(CH_2NSiMe_3)_2^{2-}$ ($N_2^{TMS}N_{py}$).[45] This complex represents a proposed intermediate in the catalytic anti-Markovnikov hydroamination of terminal alkynes. In addition, the titanacyclobutene was shown to undergo several catalytic cycles when reacted with 5 molar equiv of *tert*-butylamine and phenylacetylene. However, the complex was observed to undergo significant degradation, mainly via desilylation of the diamido-pyridine ligand. In general, the structural platform based on the diamidopyridyl ligand has been found to be particularly apt for the stabilization (and isolation) of reaction intermediates in a range of complex Ti-based transformations.[44] We have therefore embarked on studies using the more robust arylated ligands MeC(2-C_5H_4N)$(CH_2NAr)_2^{2-}$ (Ar = 4-C_6H_4Me, $N_2^{Tol}N_{py}$ or 3,5-$C_6H_3Me_2$, $N_2^{Xyl}N_{py}$) with the aim of improving the stability of the system under catalytic conditions while retaining its features in regard to the isolation of intermediates or catalyst degradation products.

Results and Discussion

Synthesis and Structural Characterization of the [Ti($N_2^{Ar}N_{py}$)(NMe_2)$_2$] Precursors. Arylated diamido-pyridine protio ligand precursors $H_2N_2^{Ar}N_{py}$ were prepared from the diamine MeC(2-C_5H_4N)$(CH_2NH_2)_2$ and the appropriate aryl bromide in a palladium-catalyzed Buchwald−Hartwig coupling reaction. The *p*-tolyl[46] and mesityl[47] derivatives have been previously reported by us and by Schrock et al., respectively. Since these two aryl groups represent two extremes in terms of steric demand, and since we found that the mesityl ligand was too bulky for titanium (vide infra), we prepared the 3,5-dimethylphenyl derivative MeC(2-C_5H_4N){CH_2NH(3,5-$C_6H_3Me_2$)}$_2$ ($H_2N_2^{Xyl}N_{py}$, **1**), the methyl groups in the meta position generating a substituent "bulkiness" which is intermediate between the steric demand of tolyl and mesityl groups. The synthesis was achieved using an analogous method to that reported for the aforementioned derivatives and **1** was employed in parallel to the tolyl ligand in the subsequent titanium chemistry.

Scheme 1. Synthesis of [Ti($N_2^{Ar}N_{py}$)(NMe_2)$_2$] 2a and 2b



Ar = Tol (**2a**) or Xyl (**2b**)

Titanium imido complexes of the form [Ti(NR)($N_2^{TMS}N_{py}$)(py)] (as well as related N-silylated derivatives) are readily synthesized by the reaction of the easily prepared imido precursor [Ti(NR)Cl_2(py)$_3$] with the lithium amide $Li_2N_2^{TMS}N_{py}$.[48] However, in the case of the arylated ligand congeners, we were unable to prepare the corresponding lithium amides. Indeed, in reports involving arylated polyamide ligands, the lithium amides are conspicuous by their absence, the chemistry normally being accessed *via* the protonolysis of a metal-alkyl or -amide precursor.[46,47,49] Studies carried out in one of our laboratories have indicated that this is due to complex undesired side reactions involving metalation of the aryl groups and rearrangement of the ligand backbone, thus rendering the lithium amides inaccessible.[50]

In light of the inaccessibility of the lithium amides $Li_2N_2^{Ar}N_{py}$, we chose an alternative route into the coordination chemistry with titanium via the protonolysis of Ti(NMe_2)$_4$ with the protio ligands $H_2N_2^{Ar}N_{py}$. Forcing conditions were required to effect a successful conversion, the reaction occurring only when carried out in a melt, rather than in solution. This method afforded the corresponding titanium complexes [Ti($N_2^{Ar}N_{py}$)(NMe_2)$_2$] (Ar = Tol **2a** or Xyl **2b**) in good yield (Scheme 1). No reaction was observed between Ti(NMe_2)$_4$ and the mesityl ligand $H_2N_2^{Mes}N_{py}$, presumably owing to the excessive steric demands imposed by the ortho methyl groups on the aromatic rings.

The NMR data for complexes **2a** and **2b** indicate molecular C_s symmetry, consistent with the structure provided in Scheme 1. The presence of two independent NMe_2 resonances is likewise fully in accordance with this coordination geometry. Moreover, the details of the molecular structures were confirmed by means of X-ray diffraction studies. The molecular structure of **2b** is depicted in Figure 1, and a comparative listing of selected bond lengths and angles for **2a** and **2b** is provided in Table 1.

The molecular structures of both **2a** and **2b** exhibit distorted trigonal bipyramidal geometries at titanium. The sum of angles subtended at the metal in the equatorial plane is 356.9(9)° and

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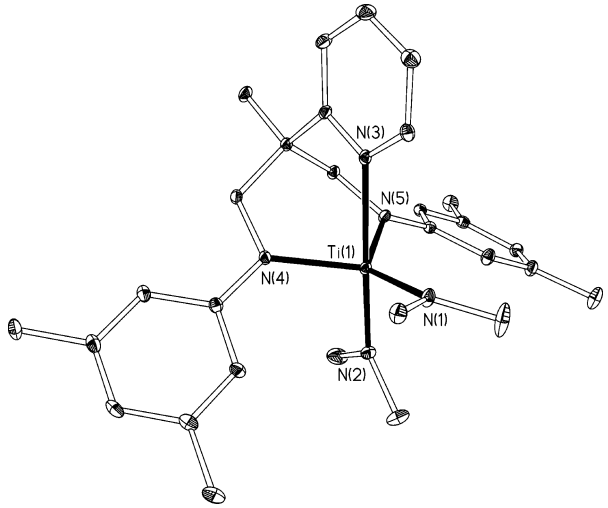
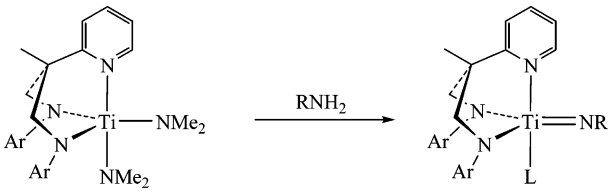


Figure 1. Molecular structure of $[Ti(N_2^{Xyl}N_{py})(NMe_2)_2]$ **2b**. Ellipsoids are drawn at 25% probability, and H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Ti(N_2^{Ar}N_{py})(NMe_2)_2]$ (Ar = Tol 2a and Xyl 2b)

	2a	2b		2a	2b
Ti−N(1)	1.9916(6)	1.932(2)	N(4)-Ti−N(5)	102.1(2)	103.63(7)
Ti−N(2)	1.919(6)	1.928(2)	N(1)-Ti−N(2)	94.8(3)	94.20(8)
Ti−N(3)	2.296(5)	2.301(2)	N(2)-Ti−N(4)	96.9(2)	99.89(8)
Ti−N(4)	1.975(5)	1.989(2)	N(2)-Ti−N(5)	95.9(3)	95.42(8)
Ti−N(5)	1.982(6)	1.968(2)	N(1)-Ti−N(3)	86.4(2)	88.25(8)
N(1)-Ti−N(4)	127.9(3)	122.80(7)	N(3)-Ti−N(4)	82.4(2)	81.81(7)
N(1)-Ti−N(5)	126.9(3)	129.91(7)	N(3)-Ti−N(5)	83.4(2)	80.18(7)

Scheme 2. Synthesis of the Imido Complexes 3a − 3e



L = py, R = ^{t}Bu, Ar = Tol (**3a**) or Xyl (**3c**); R = Tol, Ar = Tol (**3e**);
L = ^{t}BuNH$_2$, R = ^{t}Bu, Ar = Tol (**3b**) or Xyl (**3d**)

356.3(2)° for **2a** and **2b**, respectively, indicating a modest deviation from an ideal planar arrangement. The N_{amide} atoms all show an approximate trigonal planar arrangement, showing that they can, in principle, act as π-donors to the metal center. The Ti−N_{amide} bond lengths are in the expected range for titanium-amide bond lengths, although it is noteworthy that the Ti−N_{amide} distances of the N_2N_{py} ligand (1.966−1.987 Å) are significantly longer than those of the NMe_2 ligands (1.916 − 1.930 Å).

Synthesis and Structural Characterization of the [Ti(NR)-($N_2^{Ar}N_{py}$) (py)] Complexes. The diamide complexes **2a** and **2b** were subsequently converted to the corresponding imido complexes by reaction with *tert*-butylamine or *para*-toluidine, with the concomitant elimination of dimethylamine as represented in Scheme 2. Incomplete reactions were observed when carried out in hydrocarbon or halogenated solvents. However when the reaction was carried out using *tert*-butylamine as the solvent in the presence of pyridine, complete conversion was observed after heating to 55 °C for 2 days, affording the imido complexes $[Ti(N^tBu)(N_2^{Ar}N_{py})(py)]$ (Ar = Tol **3a** or Xyl **3c**). Interestingly, when the reaction was carried out in the absence of pyridine, the *tert*-butylamine-stabilized complexes were obtained, $[Ti(N^tBu)(N_2^{Ar}N_{py})(NH_2^tBu)]$ (Ar = Tol **3b** or Xyl **3d**).

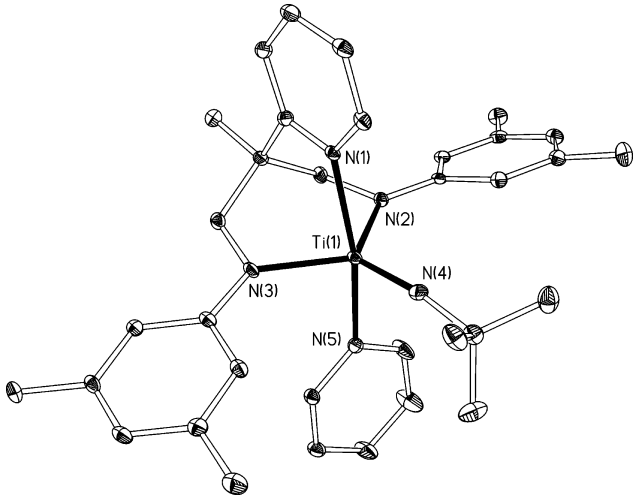


Figure 2. Molecular structure of $[Ti(N^tBu)(N_2^{Xyl}N_{py})(py)]$ **3c**. Ellipsoids are drawn at the 25% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti(1)−N(1) 2.202(2), Ti(1)−N(2) 1.985(2), Ti(1)−N(3) 2.018(2), Ti(1)−N(4) 1.706(3), Ti(1)−N(5) 2.241(2), N(1)−Ti(1)−N(2) 80.37(9), N(1)−Ti(1)−N(3) 81.83(10), N(2)−Ti(1)−N(3) 116.64-(10), N(1)−Ti(1)−N(4) 102.82(10), N(2)−Ti(1)−N(4) 119.85(11), N(3)−Ti(1)−N(4) 123.31(11), N(1)−Ti(1)−N(5) 163.22(9), N(2)−Ti(1)−N(5) 89.94(10), N(3)−Ti(1)−N(5) 90.48(10), N(4)−Ti(1)−N(5) 93.87(10), Ti(1)−N(4)−C(26) 170.5(2).

The identity of **3b** and **3d** as imido-amine complexes, rather than the isomeric bis(amide) complexes $[Ti(N_2^{Ar}N_{py})(NH^tBu)_2]$ was confirmed by analysis of the *tert*-butyl quarternary carbon resonances in the $^{13}C\{^1H\}$ NMR spectra. The imido resonances were observed at δ 68.9 and 69.1 for **3b** and **3d**, respectively, whereas the coordinated amine quarternary resonances were observed at 50.4 ppm for both. The significant downfield shift of the *tert*-butyl quarternary resonance is characteristic of imido complexes.[48a−c] The synthesis of the aryl imido complex [Ti-(N-4-C_6H_4Me)($N_2^{Ar}N_{py}$)(py)] (Ar = Tol **3e**) was found to proceed only in a concentrated pyridine solution, when heated to 80 °C for 1 h. Prolonged reaction times gave rise to an increased amount of protio ligand in the reaction mixture. Equally, reaction of the *tert*-butyl imido complexes **3a** or **3c** with *p*-toluidine, with the aim of an imide exchange,[48a] afforded only decomposition into the protio-ligand, presumably owing to a competition between proton transfer to the imido nitrogen and the amido nitrogen atoms, which have a greater propensity to act as a proton acceptor site because of the π-loaded nature of the system (vide infra).[48b]

The structure of the imido complex **3c** was confirmed by X-ray diffraction. The molecular structure of **3c** is shown in Figure 2 along with principal bond lengths and angles. Complex **3c** exhibits a distorted trigonal bipyramidal coordination geometry, with the imido group occupying an equatorial position. This geometry persists in solution, as inferred from a ^1H NOESY NMR spectrum. The bond lengths are almost identical to within experimental error to those of the silylated congener [Ti-(N^tBu)($N_2^{TMS}N_{py}$)(py)].[48b] Interestingly, the plane of the amido nitrogen atoms of the $N_2^{Ar}N_{py}$ moiety was found to have somewhat different orientation in the case of **3c** compared to **2a** and **2b**. In **3c**, the plane spanned by the substituents of the N_{amide} is rotated by 11.7° with respect to the equatorial plane (the plane spanned by the titanium atom, N_{imide}, and N_{amide}),

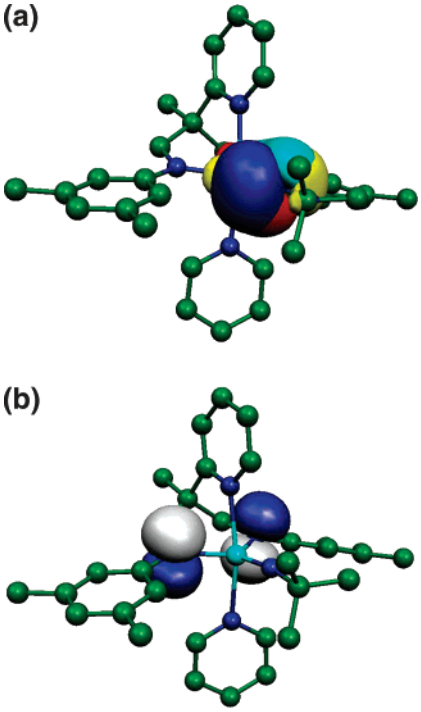


Figure 3. ONIOM calculated structure for [Ti(N^{t}Bu)(N$_2^{Xyl}$N$_{py}$)(py)] **3c**, showing the two orthogonal π-bonding orbitals of the linear imido ligands (a) and the highest occupied molecular orbitals (in a NBO analysis) which are dominated by the contributions of the nonbonding p-orbitals at the amido-N atom (b).

while the equivalent planes in **2a** and **2b** are rotated by 44.3° and 36.8°, respectively.

The near linear angle subtended at the imido nitrogen atom of 170.5(2)° indicates that the imido ligand acts as a four-electron donor to the metal center. The sum of the angles subtended at the N_{amide} atoms is 360° to within experimental error, showing that the amido nitrogens can, in principle, donate three electrons to the titanium. It is usually assumed that the presence of four π donors affords a π-loaded system, in which only three of the four π donor orbitals can donate into an appropriate metal-based π acceptor orbital.[48]

To further elucidate the electronic structure of the imido complexes, the structure of complex **3c** was computed using ONIOM (B3PW91:UFF) calculations. The metric parameters of the calculated structure were comparable to those obtained in the X-ray structure analysis, thus allowing further calculations to be regarded with greater certainty (vide infra). An analysis of the molecular frontier orbitals indicates that the imido ligand binds to the metal with two orthogonal π bonds, as suggested by the X-ray structure (Figure 3a). However, the amido-nitrogens show only partial bonding character. A natural bond order (NBO) analysis of the optimized structure shows that the two highest occupied molecular orbitals are dominated by the contributions of nonbonding p orbitals based solely on the N_{amide} atoms. Figure 3b shows the two NBO orbitals superimposed, in which it can be seen that there are two possible combinations: the in-phase and the out-of-phase. In principle the out-of-phase combination can interact with the $3d_\pi$ atomic orbitals, whereas the in-phase combination cannot. It is inferred from this that the N_{amide}-centered lone pairs can only partially donate into a metal π-acceptor orbital, as described above. The π-loaded nature of these imido complexes explains the residual basicity of the metal-bonded amido-N atoms and thus the observation that the reaction of [Ti(N^{t}Bu)(N$_2^{Ar}$N$_{py}$)(py)] with anilines resulted in protonation of the amido groups, rather than undergoing imido ligand metathesis to afford the aryl imido complexes [Ti(NAr)(N$_2^{Ar}$N$_{py}$)(py)].[48d,e]

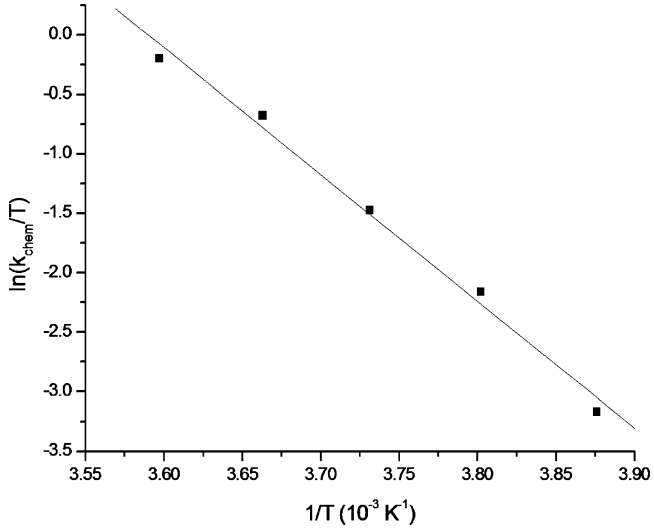


Figure 4. Eyring plot for the exchange of [Ti(N^{t}Bu)(N$_2^{Xyl}$N$_{py}$)(py)] **3c** with one molar equivalent of pyridine.

In all reactions of the imido complexes with organic substrates, a pre-equilibrium involving the dissociation of the axially bonded pyridine ligand is assumed. To investigate this pre-dissociation of the pyridine in [Ti(N^{t}Bu)(N$_2^{Xyl}$N$_{py}$)(py)] **3c**, a molar equivalent of pyridine was added to a solution of **3c** in toluene-d_8, and the exchange was monitored by variable temperature ^{1}H NMR spectroscopy. At ambient temperature only a single pyridine resonance was observed, indicating a fast exchange on the NMR time scale between the coordinated and free pyridine. On cooling to −25 °C however, decoalescence was observed, giving rise to two sets of resonances for the coordinated and free pyridine. The activation barrier to this exchange process was determined by line shape analysis and exchange modeling of the ortho pyridine resonance between −15 and 5 °C, at intervals of 5 °C. For each temperature, the rate of exchange was determined, and was used to construct an Eyring plot, from which the enthalpy and entropy of activation were obtained as 21.2 kcal mol^{-1} and 81 cal mol^{-1} K^{-1}, respectively (Figure 4).

The large positive entropy of activation suggests—as expected—a strongly dissociative mechanism, and the extrapolated rate constant of k(293 K) = 90 s^{-1} indicates that pre-dissociation occurs rapidly in relation to subsequent transformations (vide infra).

Coupling Reactions of the Ti imido Complexes with Aryl Acetylenes: The Formation of Four-Membered Titanacycles. The imido complexes [Ti(N^{t}Bu)(N$_2^{Ar}$N$_{py}$)(py)] (Ar = Tol **3a** and Xyl **3c**) react with phenyl or tolyl acetylene, affording the azatitanacyclobutene complexes [Ti(N$_2^{Ar}$N$_{py}$){κ^2-N(t-Bu)CH=CAr′}] (Ar = Tol, Ar′ = Ph **4a** or Tol **4b**; Ar = Xyl, Ar′ = Ph **4c** or Tol **4d**), where the imido ligands undergo a formal {2 + 2} cycloaddition (Scheme 3). The formation of such a metallacyclic species has been suggested as being a key reaction step in the catalytic hydroamination of alkynes.[40−42] Examples of imido-alkyne coupling products have been isolated and crystallographically characterized for both internal and terminal alkynes.[22,44] As in our earlier report, the azatitanacyclobutene complexes form exclusively as the anti-Markovnikov isomers which has been attributed to the steric bulk of the *tert*-butyl N-subsituent.[3,44] While the reaction with aryl acetylenes gave the respective cycloaddition products in good yield, the corresponding reaction with either terminal or internal alkyl

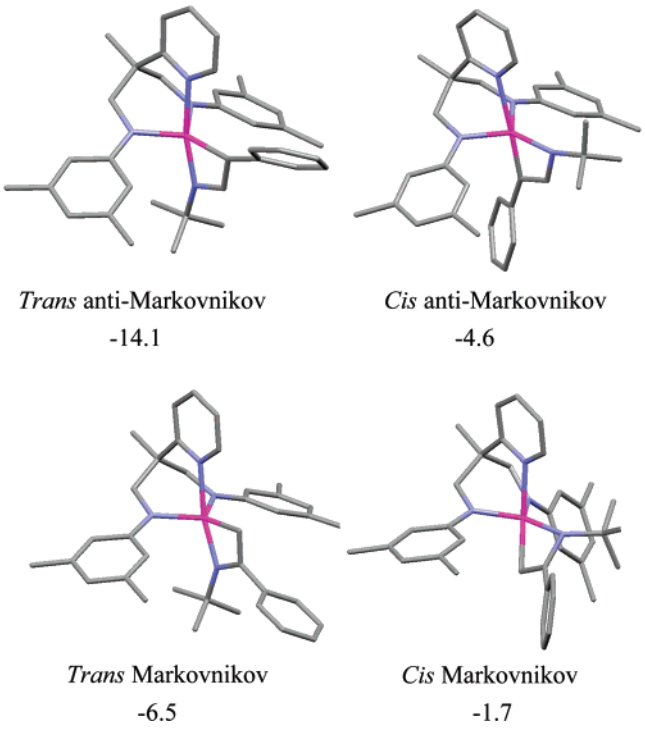
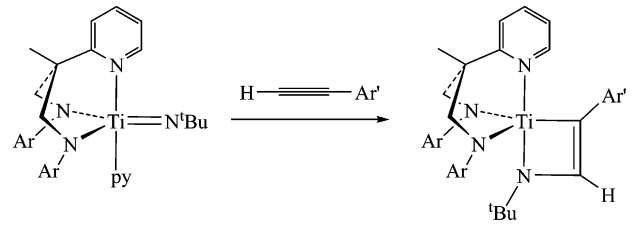


Figure 5. ONIOM calculated structures for the isomeric forms of [Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CHC(Ph)} **4c**. Energies are provided in kcal mol^{-1}.

Scheme 3. Synthesis of the {2 + 2} Cycloaddition Products 4a − 4d



Ar = Tol, Ar' = Ph (**4a**) or Tol (**4b**);
Ar = Xyl, Ar' = Ph (**4c**) or Tol (**4d**)

acetylenes were either incomplete or did not occur at all under these conditions. Subsequent tests with these substrates under catalytic conditions (vide infra) proved to be equally unsuccessful.

The NMR data of **4a**−**d** were found to be consistent with NMR data of the crystallographically characterized silyl derivative reported previously, with the metallacycle CH proton resonance being observed as a singlet at around 10 ppm. Moreover, ^{1}H NOESY NMR spectra of **4a**−**d** allowed us to place the *tert*-butyl group trans to the pyridyl moiety, as drawn in Scheme 3.

The relative stability of the four possible isomeric forms of [Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH═CPh}] (**4c**) was computed using ONIOM calculations. The relative electronic energies of the four isomers are displayed in Figure 5, and are computed in relation to the parent imido complex, the unreacted phenyl acetylene, and the released pyridine. Although all four isomers represent local energy minima, it can be clearly seen that the experimentally observed isomer is the most stable, with a cycloaddition enthalpy of 14.1 kcal mol^{-1}. The entropic contribution to the energies can be approximately ignored in this case, since the entropy change due to the association of the alkyne is

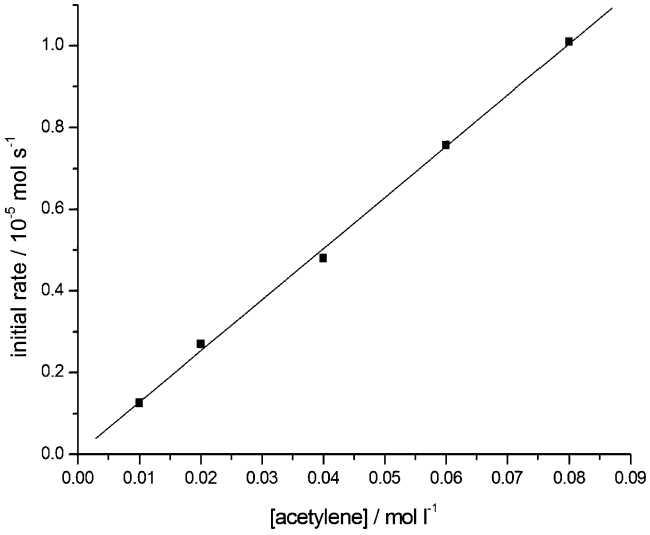


Figure 6. Plot of the initial rate versus concentration of alkyne for the reaction of 10 μmol of [Ti(N^tBu)($N_2^{Xyl}N_{py}$)(py)] **3c** with varying amounts of phenyl acetylene.

counterbalanced by the release of pyridine. The entropic contribution to the transition state is however not expected to be negligible, although in this study no transition state structures were located. The remaining isomers exhibit energies between −1.7 and −6.5 kcal mol^{-1}, and are thus less stable than the experimentally observed isomer, although the computed values should only be treated as semiquantitative estimates. Since there is no indication of a reversibility of the {2 + 2} cycloaddition, the four-membered metallacycles being stable even at high temperatures (100−110 °C) and not showing any cycloreversion, their formation is assumed to be kinetically controlled. As the computational study shows, the kinetically preferred product also happens to be also thermodynamically most stable. A further analysis of the structures suggests that the anti-Markovnikov isomer is preferred since this alleviates steric strain between the phenyl ring and the *tert*-butyl group.

The four-membered titanacycle may adopt two orientations in relation to the diamidopyridyl spectator ligand, and previous studies on such five-coordinate complexes have shown them to undergo exchange between the two remaining coordination sites. The observation of the *tert*-butyl group trans to the pyridyl ring in the pentacoordinate products **4a**−**d** is likely to avoid steric interaction with the pyridyl moiety, since there is more open space between the aryl substituents of the diamido-pyridine ligand.

Given the py-dissociation pre-equilibrium, the overall reaction of the imido complexes with phenyl acetylene is expected to be as follows:

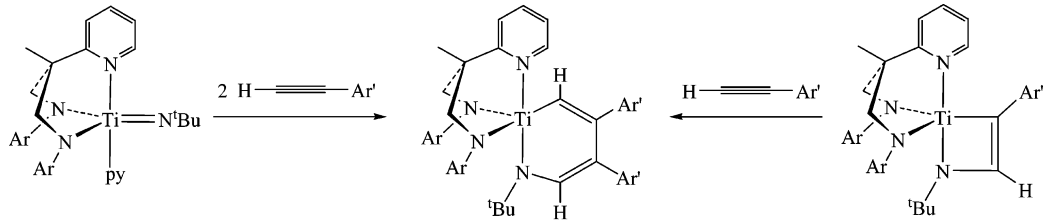
$$[(N_2^{Ar}N_{py})Ti(NR)(py)] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(N_2^{Ar}N_{py})Ti(NR)] + py$$

$$[(Ni_2^{Ar}N_{py})Ti(NR)] + R'CCH \xrightarrow{k_2} [(N_2^{Ar}N_{py})Ti(NRHCCR')]$$

$$\text{rate} = \frac{k_1k_2[(N_2^{Ar}N_{py})Ti(NR)(py)][R'CCH]}{k_{-1}[py] + k_2[R'CCH]}$$

Since $k_2 \ll k_{-1}$ the rate law simplifies to k_1k_2[($N_2^{Ar}N_{py}$)Ti(NR)(py)][R′CCH]/k_{-1}[py] in the absence of a large excess of the alkyne. To determine the reaction order with respect to the alkyne under these conditions, 10 μmol of [Ti(N^tBu)($N_2^{Xyl}N_{py}$)(py)] **3c** was reacted with varying amounts of phenyl acetylene,

Scheme 4. Synthesis of the Azatitanacyclohexadiene Complexes 5a − 5d



Ar = Tol, Ar' = Ph (**5a**) or Tol (**5b**);
Ar = Xyl, Ar' = Ph (**5c**) or Tol (**5d**)

from 0.5 to 4 molar equiv. The reaction was then monitored by ^{1}H NMR spectroscopy. The initial rate (i.e., at time = 0) was determined from the conversion curves; a plot of the initial rate versus concentration of alkyne is displayed in Figure 6, and the linear nature of the plot clearly denotes a first-order reaction in alkyne concentration.

Furthermore, the linear dependence of the initial reaction rates on 1/[py] upon varying the concentration of pyridine (at constant concentrations of the complex and a tenfold excess of the alkyne) is also consistent with the rate law proposed above. The rate coefficient $k_{obs} = k_1k_2/k_{-1}$[py] was determined by carrying out the reaction with varying concentrations of **3c**, in each case with a 20-fold excess of alkyne, that is, under pseudo-first-order conditions. The initial rates were plotted against the concentration of **3c**, which showed a linear relationship, thus allowing k_{obs} to be determined from the slope of the plot as 1.9×10^{-3} mol^{-1} s^{-1}.

The Insertion of a Second Alkyne Molecule into the Azatitanacyclobutenes Giving Six-Membered Azatitanacyclohexadienes. The preparation of the azatitanacyclobutene complexes was carried out with a slight excess of alkynes to obtain optimal yields of the {2 + 2} coupling product. It was noticed, however, that the crude material often contained a minor as yet unknown component. This component was successfully identified by reacting the imido complexes **3a** and **3c** with 2 equiv of aryl acetylene. After heating to 100 °C for 1 h, complete conversion was observed to this second component, identified as the azatitanacyclohexadiene complex [Ti($N_2^{Ar}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ar′)C(Ar′) = CH}] (Ar = Tol, Ar′ = Ph **5a** or Tol **5b**; Ar = Xyl, Ar′ = Ph **5c** or Tol **5d**), the product of a second alkyne insertion into the Ti−C bond (Scheme 4).

The structural details of complexes **5b** and **5d** were established by X-ray diffraction. Their molecular structures are displayed in Figures 7 and 8, respectively, with a comparison of selected bond lengths and angles being provided in Table 2. The C−C bond lengths of the metallacyclic moiety clearly indicate that the two double bonds are placed between the CH and the CTol carbons; the longer TolC-CTol bond lengths are typical of sp^2−sp^2 carbon−carbon single bonds.[51] The bonds to titanium are unremarkable compared with previously reported examples. To the best of our knowledge, there has been only one crystallographically characterized structural motif of this kind, in which Odom *et al.* reported the reaction of group 6 imido complexes with the sterically highly strained cyclooctyne.[52]

There are two possible isomers for the second insertion of alkyne into the azatitanacyclobutene complexes, corresponding to the two orientations of the second alkyne molecule (Scheme 5). Although only a single isomer is observed experimentally, an ONIOM study indicated that there is *no* significant thermodynamic preference for one of the two isomers, the difference in energy being only 1.9 kcal mol^{-1}, which is considered to be less than (or about equal to) the precision associated with the method. It is therefore evident that the preference for the observed isomer is due to kinetic control as was discussed above for the formation of the four-membered titanacycles in **4a**−**d**.

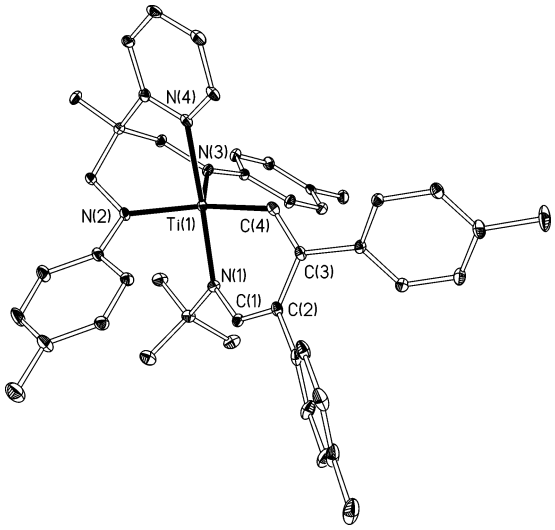


Figure 7. Molecular structure of [Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol) = CH}] **5b**. Ellipsoids are drawn at the 25% probability level, and H atoms are omitted for clarity.

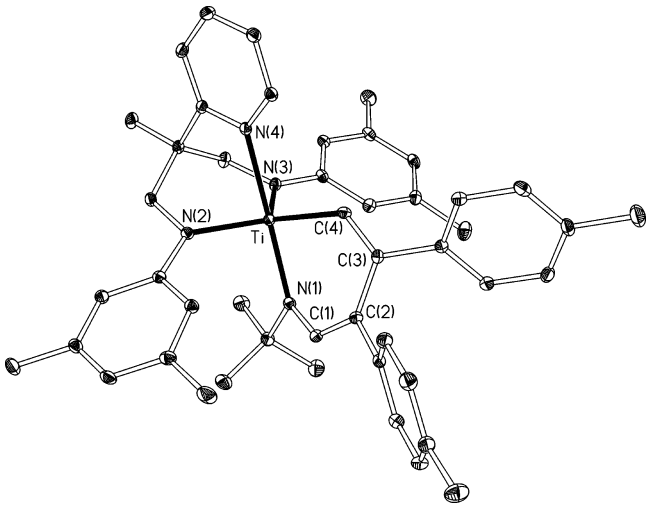


Figure 8. Molecular structure of [Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol) = CH}] **5d**. Ellipsoids are drawn at the 25% probability level, and H atoms are omitted for clarity.

(51) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 1, 31. Fletcher, D. A.; McMeeking, R. F.; Parkin, D. J. *Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

(52) Lokare, K. S.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2004**, *23*, 5386.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ti($N_2^{Ar}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol) = CH}] (Ar = Tol 5b and Xyl 5d)

	5b	5d		5b	5d
Ti−N(1)	2.036(3)	2.031(2)	C(4)−Ti−N(2)	132.1(2)	133.37(8)
Ti−N(2)	1.944(3)	1.958(2)	C(4)−Ti−N(3)	116.0(2)	113.60(8)
Ti−N(3)	1.934(3)	1.922(2)	N(2)−Ti−N(3)	109.04(14)	109.77(7)
Ti−N(4)	2.257(3)	2.260(2)	N(1)−Ti−C(4)	85.8(2)	86.24(8)
Ti−C(4)	2.046(4)	2.056(2)	N(1)−Ti−N(2)	93.89(14)	95.29(7)
N(1)−C(1)	1.363(5)	1.371(3)	N(1)−Ti−N(3)	109.65(14)	109.15(8)
C(1)−C(2)	1.374(5)	1.370(3)	N(4)−Ti−C(4)	87.8(2)	87.67(7)
C(2)−C(3)	1.443(5)	1.449(3)	N(4)−Ti−N(2)	81.03(13)	81.55(7)
C(3)−C(4)	1.365(6)	1.356(3)	N(4)−Ti−N(3)	84.66(14)	82.64(7)

Unfortunately, a transition-state structure for the reaction could not be found using ONIOM and DFT studies. The modeling of transition states of bimolecular reactions between molecules of the complexity as those involved in the process at hand is generally associated with difficulties arising from the multitude of orientational intra- and intermolecular degrees of freedom. However, a visual inspection of the in-plane approach of the second alkyne may give some insight into the observed structural preference. If it is assumed that the experimentally observed isomers of **4a** and **4b** are the only isomers present, as inferred from the results discussed above, the second alkyne must presumably approach from the upper side, nearest to the pyridyl group. For insertion into the Ti−C bond, the alkyne triple bond must lie parallel to the Ti−C bond in the transition state. As illustrated in Scheme 5, the two possible transition states differ only in a 180° rotation of the alkyne. Transition state **A** (leading to the experimentally observed isomer) possesses an alkyne−aryl group directed away from the diamido-pyridine ligand; conversely transition state **B** possesses the same group pointing toward it, causing significant steric repulsion. Should the pyridyl group dissociate from the metal center, there would still be significant steric repulsion for transition state **B**, although it should be noted that dissociation of the pyridyl moiety is likely to raise the transition-state energy significantly.

Reaction of complexes **4a** and **4b** with the appropriate aryl acetylene likewise gave quantitative conversion to the corresponding azatitanacyclohexadiene complex, suggesting that the conversion from **3a** or **3c** to **5a**−**d** proceeds in a stepwise manner. Interestingly, although the second alkyne insertion proceeds only slowly at ambient temperature, the reaction is deemed to be a deactivation pathway in the hydroamination of alkynes. The second insertion (as the first) is *irreversible* and the azatitanacyclohexadiene complexes are *stable toward aminolysis*,that is, **5a**−**d** do not react with *tert*-butylamine to reform the imido complexes **3a**−**d**, the final step in the catalytic hydroamination cycle. Consequently, the six-membered species represents a mechanistic "cul de sac" and, as will be shown below, compounds of type **5a**−**d** do indeed represent dead ends in the catalytic hydroamination with the Ti complexes reported in this work.

The Imidotitanium Complexes 3a and 3c as Model Catalysts for the Hydroamination of Aryl Acetylenes. Given their reactivity toward alkynes, the imido complexes [Ti(N^{t}Bu)($N_2^{Ar}N_{py}$)(py)] (Ar = Tol **3a** or Xyl **3c**) were investigated as potential catalysts for the hydroamination of phenyl acetylene with *tert*-butylamine, producing *trans*-cinnamyl(*tert*-butyl)amine. The reaction proceeded significantly faster than for the corresponding silylated derivative [Ti(N^{t}Bu)($N_2^{TMS}N_{py}$)(py)],[44] but was still slower at ambient temperature than the most active Ti-based catalysts reported in the literature.[1−6] The conversion curves for this reaction are presented in Figure 9.

Using 10 mol % catalyst (imido complex) loading, the reaction proceeded to ca. 70−80% conversion after 24 h at 293 K (80−90% after 48 h), after which no further reaction was observed. Under these conditions there was no significant difference between **3a** and **3c**. Since the reaction did not go to completion, the evolution of the catalyst was monitored by NMR spectroscopy during the catalytic reaction.

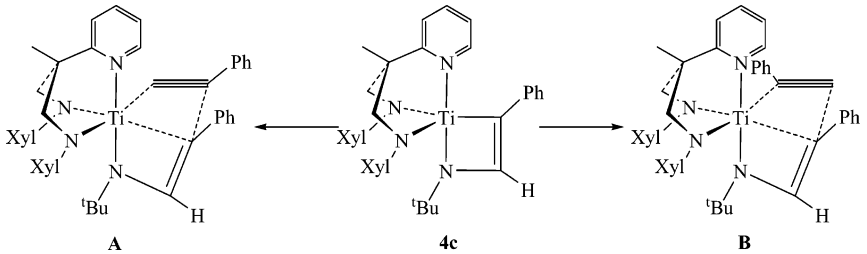
A mixture of compounds derived from the catalyst precursor was observed, including the respective imido complexes [Ti(N^{t}Bu)($N_2^{Ar}N_{py}$)(L)] (L = py or ^{t}BuNH$_2$, which are indistinguishable under the catalytic conditions, presumably owing to the fluxional nature of the system) used as catalyst (precursor) and the azatitanacyclobutene complexes [Ti($N_2^{Ar}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ph)}] (which were found to be catalytically active species themselves in a separate such experiment with compounds **4a** and **4b**). Futhermore, the azatitanacyclohexadiene complexes [Ti($N_2^{Ar}N_{py}$){N(^{t}Bu)CH=C(Ph)C(Ph) = CH}] and the protio ligand $H_2N_2^{Ar}N_{py}$ were observed. Both of the latter components are the result of catalyst deactivation (the azatitanacyclohexadiene being *inert* to aminolysis and the concomitant re-formation of the imido complex) and decomposition, respectively, and were observed to increase in intensity over time.

The protio ligand was formed under the conditions of catalysis by reaction of the imido intermediates with the primary amine as a competitive reaction with the cycloaddition with alkyne and ultimately the formation of the desired hydroamination product. This observation was independently verified in the absence of alkyne by reaction of with *tert*-butylamine with the imido complex **3c** (which afforded free protio ligand) and **4c** (which afforded no protio ligand).

To further investigate the amount of catalyst present, the quantity of the two catalytically active species (the respective imido complex and the four-membered metallacyclic intermediates) was measured by integration of the ^{1}H NMR signals corresponding to the H^6 proton of the coordinated $N_2^{Ar}N_{py}$ ligand, as a proportion of the total number of $N_2^{Ar}N_{py}$ ligand environments (as well an internal standard, 1,4-dimethoxybenzene).

A steady decrease in the catalyst concentrations over time was observed, with almost total catalyst deactivation after ca. 24 h (Figure 10), corresponding to the cessation of the catalytic

Scheme 5. Transition States for the Formation of 5c from 4c



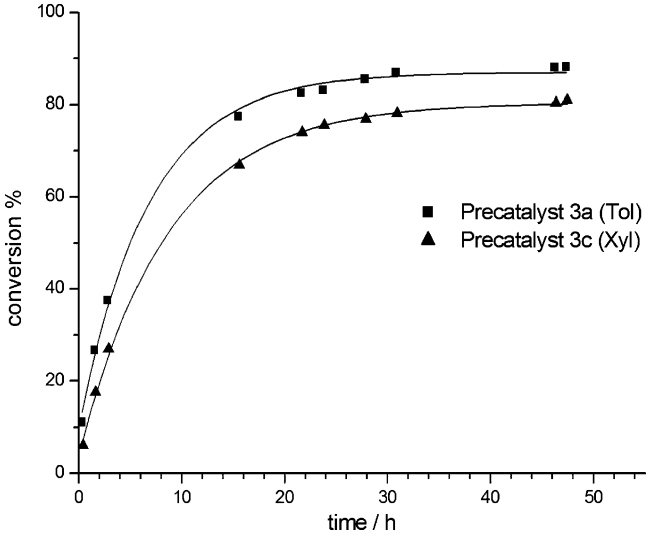


Figure 9. Conversion for the reaction of phenyl acetylene with *tert*-butylamine by **3a** and **3c** at 293 K using 10 mol % catalyst loading (internal reference for the NMR integration, 1,4-dimethoxybenzene).

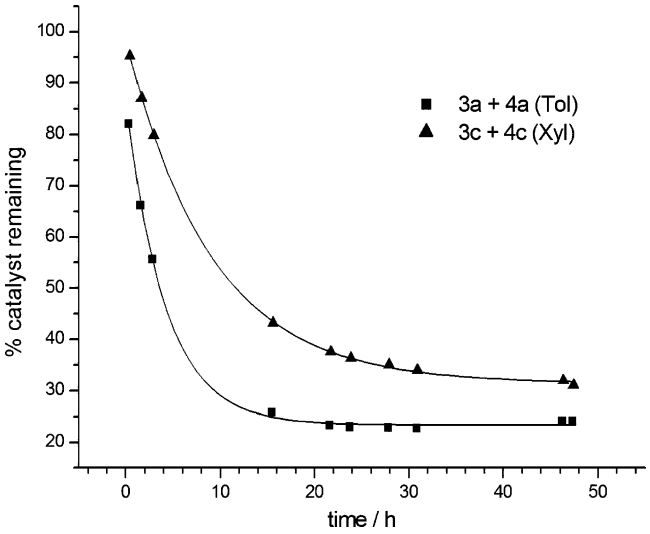


Figure 10. Catalyst decomposition for the reaction of phenyl acetylene with *tert*-butylamine, catalyzed by **3a** and **3c** (+**4a** and **4c**, respectively) at 293 K using 10 mol % catalyst loading (internal reference for the NMR integration, 1,4-dimethoxybenzene).

reaction. Since the formation of the azatitanacyclohexadiene complexes **5a**−**d** is significantly faster at elevated temperatures, the catalysis was repeated at 50 °C and monitored as above. Under these conditions the conversion was indeed much more rapid, with 60% conversion in 5 h but so was the deactivation which took place concomitantly.

The aminolysis reaction which completes the catalytic cycle was studied using the azatitanacyclobutene **4c** and *tert*-butylamine. This step was likewise found to be first order in amine concentration, and the second-order rate constant for this step, k_{aminol}, was found to be 1.1×10^{-3} s^{-1} mol^{-1}. The relative values of k_{obs} for the {2 + 2} cycloaddition of the alkyne and the imido complex (taking the predissociation of the donor in the imido complex into account) as well as the second-order rate constant for the subsequent aminolysis step (k_{aminol}) of approximately $k_{obs}/k_{aminol} \approx 2$ correspond well to the empirical observations made in NMR tube scale experiments, in which {2 + 2} cycloaddition of alkyne with the imido complexes was observed to be faster than the aminolysis of the azatitanacyclobutene. Overall, a rate law which is first order with respect to the complex and both substrates was deduced under the conditions of the catalytic reaction, which is consistent with the established mechanism.

Conclusion

We have demonstrated that the arylated diamido-pyridine ligands $N_2^{Ar}N_{py}$ are remarkably efficient at stabilizing catalytic intermediates in the hydroamination of aryl acetylenes. In addition, greater insight has been obtained into the catalyst decomposition pathways, in particular the previously unobserved double insertion of the alkyne which leads to an extremely stable six-membered azatitanacycle. The latter aspect will have to be considered in further research aimed at developing more efficient catalytic systems for this class of reactions.

Experimental

General Experimental. All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using standard Schlenk techniques or by working in a glovebox. Solvents were dried over sodium (toluene), potassium (hexanes), or sodium/potassium alloy (pentane, diethyl ether), distilled, and degassed prior to use. Deuterated solvents were dried over potassium (C_6D_6, toluene-d_8), vacuum distilled, and stored in Teflon valve ampoules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. ^1H, $^{13}C\{^1H\}$ and $^{15}N\{^1H\}$ NMR spectra were recorded on Bruker Avance 200, 400, and 600 NMR spectrometers and were referenced internally using the residual protio solvent (^1H) of solvent (^{13}C) resonances or externally vs. NH_3. Where necessary, NMR assignments were confirmed by the use of two-dimensional ^1H-^1H or ^1H-^{13}C NMR correlation experiments or by ^{13}C DEPT experiments. Elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department. Mass spectra were recorded on a Jeol JMS 700 mass spectrometer by the mass spectrometry service of the Heidelberg Chemistry Department. The diamido-pyridine protio-ligand $H_2N_2^{Tol}N_{py}$ was prepared according to published procedures.[46] All other reagents were obtained from commercial sources and used as received unless explicitly stated.

Preparation of the Compounds. $H_2N_2^{Xyl}N_{py}$ (1). A Schlenk flask was charged with $MeC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (2.15 g, 13.0 mmol),[45] 5-bromo-*m*-xylene (4.81 g, 26.0 mmol), [$Pd_2(dba)_3$] (0.18 g, 0.33 mmol, dba = dibenzylideneacetone), *rac*-BINAP (0.31 g, 0.50 mmol), and NaO^{t}Bu (5.00 g, 52.0 mmol) which were suspended in toluene (100 mL). After the reaction mixture was stirred at 110 °C for 3 days, the volatiles were removed under reduced pressure and the brown residue was redissolved in Et_2O (75 mL). The resulting solution was washed with H_2O (3 × 30 mL) and then with a saturated aqueous solution of NaCl (3 × 30 mL). The combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography (SiO_2, gradient pentane/ether started from 90/10 to 70/30; detection was made by TLC pentane/ether 70/30 $R_f = 0.4$) to give the desired product as a pale yellow oil (3.47 g, 72%). ^1H NMR ($CDCl_3$, 199.9 MHz, 296 K): δ 1.51 (3 H, s, Me of N_2N_{py}), 2.21 (12 H, s, $C_6H_3\mathit{Me}_2$), 3.46 (2 H, d, C*H*H, $^3J = 12.2$ Hz), 3.58 (2 H, d, CH*H*, $^3J = 12.2$ Hz), 4.15 (2 H, s, NH), 6.25 (4 H, s, *o*-$C_6H_3Me_2$), 6.34 (2 H, s, *p*-$C_6H_3Me_2$), 7.17 (1 H, m, H^5), 7.38 (1 H, d, H^3, $^3J = 8.0$ Hz), 7.66 (1 H, app td, H^4, $^3J(H^3H^4H^5) = 7.3$ Hz, $^4J(H^4H^6) = 1.9$ Hz), 8.62 (1 H, dd, H^6, $^3J(H^5H^6) = 4.8$ Hz, $^4J(H^4H^6) = 1.2$ Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 296 K): δ 21.4 ($C_6H_3\mathit{Me}_2$), 23.0 (Me of N_2N_{py}), 45.4 [$C(CH_2NXyl)_2$], 52.3 [($CH_2NXyl)_2$], 111.0 (*o*-$C_6H_3Me_2$), 119.3 (*p*-$C_6H_3Me_2$), 121.3 (C^3), 121.6 (C^5), 136.7 (C^4), 138.8 (overlapping *m*-$C_6H_3Me_2$ and *ipso*-$C_6H_3Me_2$) 148.8 (C^6),

164.2 (C^2) ppm. MS (EI): *m*/*z* (%) = 373.2 $[M]^+$ (8), 239.1 $[M(CH_2{-}NH\text{-}xyl)]^+$ (25), 134.1 $[M{-}((CH_2{-}NH\text{-}Xyl) - (Xyl))]^+$ (31), 121.0 $[M{-}\{MeC(2\text{-}C_5H_4N)(CH_2NXyl)(CH_2)\}]^+$ (100). HRMS (FAB) : *m*/*z* (%) = 374.264 (100) $[M + H]^+$. Anal. Found (calcd for $C_{25}H_{31}N_3$): C, 80.3 (80.4); H, 8.3 (8.4); N, 10.8 (11.3).

[Ti($N_2^{Tol}N_{py}$)(NMe_2)$_2$] (2a). A Schlenk tube was charged with $H_2N_2^{Tol}N_{py}$ (2.77 mg, 8.02 mmol) and 1.2 equiv of $Ti(NMe_2)_4$ (2.27 mL, 9.62 mmol), and placed under partial vacuum. The reaction mixture was stirred overnight at 100 °C, affording a red-orange solid, which was washed with pentane. After the residue was dried in vacuo, an orange powder was obtained. Yield 3.34 g (87%). Single crystals for X-ray diffraction study were grown from a saturated pentane solution at 5 °C (200 mg in 4 mL of pentane). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.28 (3 H, s, Me of N_2N_{py}), 2.31 (6 H, s, C_6H_4*Me*), 3.26 (6 H, s, N*Me*$_2$), 3.32 (2 H, d, C*H*H, ^3J = 12.2 Hz), 3.37 (6 H, s, N*Me*$_2$), 3.68 (2 H, d, CH*H*, ^3J = 12.2 Hz), 6.48 (1 H, app t, H^5, ^3J = 6.4 Hz), 6.90 (4 H, d, *o*-C_6H_4Me, ^3J = 8.6 Hz), 6.95 (1 H, d, H^3, ^3J = 8.3 Hz), 7.01 (1 H, app td, H^4, $^3J(H^3H^4H^5)$ = 7.8 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 7.14 (4 H, d, *m*-C_6H_4Me, ^3J = 8.7 Hz), 7.77 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^4H^6)$ = 1.5 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.7 (C_6H_4*Me*), 24.8 (Me of N_2N_{py}), 42.0 (N*Me*$_2$), 48.1 (N*Me*$_2$), 52.9 [*C*(CH_2NTol)$_2$], 63.7 [(*C*H_2NTol)$_2$], 114.4 (*o*-C_6H_4Me), 119.4 (*ipso*-C_6H_4Me), 121.9 (C^5), 126.1 (*p*-C_6H_4Me), 128.9 (*m*-C_6H_4Me), 129.9 (C^3), 138.2 (C^4), 147.4 (C^6), 163.2 (C^2) ppm. Anal. Found (calcd for $C_{27}H_{37}N_5Ti$): C, 68.1 (67.6); H, 7.7 (7.8); N, 14.0 (14.6).

[Ti($N_2^{Xyl}N_{py}$)(NMe_2)$_2$] (2b). A Schlenk tube was charged with $H_2N_2^{Xyl}N_{py}$ (3.28 g, 8.78 mmol) and 1.2 equiv of $Ti(NMe_2)_2$ (2.27 mL, 10.54 mmol) and placed under partial vacuum. The reaction mixture was stirred overnight at 100 °C, affording an orange solid, which was washed with pentane. After the residue was dried in vacuo an orange powder was obtained. Yield 3.52 g (79%). Diffraction-quality single crystals were grown from a saturated pentane solution at 5 °C (200 mg in 4 mL of pentane). ^{1}H NMR (C_6D_6, 600.1 MHz, 296 K): δ 1.27 (3 H, s, Me of N_2N_{py}), 2.37 (12 H, s, C_6H_3*Me*$_2$), 3.11 (6 H, s, N*Me*$_{2,ax}$), 3.37 (2 H, d, C*H*H, ^3J = 12.3 Hz), 3.40 (6 H, s, N*Me*$_{2,eq}$), 3.73 (2 H, d, CH*H*, ^3J = 12.2 Hz), 6.51 (1 H, app td, H^5, $^3J(H^4H^5H^6)$ = 5.8 Hz, $^4J(H^3H^5)$ = 1.1 Hz), 6.90 (2 H, s, *p*-$C_6H_3Me_2$), 6.67 (4 H, s, *o*-$C_6H_3Me_2$), 6.83 (1 H, d, H^3, ^3J = 7.9 Hz), 7.01 (1 H, app td, H^4, $^3J(H^3H^4H^5)$ = 7.7 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 7.79 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^4H^6)$ = 1.0 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 21.8 (C_6H_3*Me*$_2$), 24.6 (Me of N_2N_{py}), 41.7 (N*Me*$_2$), 44.1 [*C*(CH_2NXyl)$_2$], 47.9 (N*Me*$_2$), 63.2 [(*C*H_2NXyl)$_2$], 110.0 (*ipso*-C_6H_3-Me_2), 112.5 (*o*-$C_6H_3Me_2$), 119.1 (C^3), 119.2 (*p*-$C_6H_3Me_2$), 121.6 (C^5), 136.7 (*m*-$C_6H_3Me_2$), 137.9 (C^4), 147.1 (C^6), 154.4 (C^2) ppm. ^{15}N{^{1}H} NMR (C_6D_6, 60.8 MHz, 296 K): δ 215.8 (*N*$_2$N$_{py}$), 228.4 (*N*Me$_{2,ax}$), 256.1 (*N*Me$_{2,eq}$), 290.1 (N$_2$*N*$_{py}$) ppm. Anal. Found (calcd for $C_{29}H_{41}N_5Ti$): C, 68.5 (68.6); H, 8.1 (8.1); N, 13.5 (13.8).

[Ti(N^{t}Bu)($N_2^{Tol}N_{py}$)(py)] (3a). A Schlenk tube was charged with [Ti($N_2^{Tol}N_{py}$)(NMe_2)$_2$] (203 mg, 0.40 mmol), a large excess of *tert*-butylamine (10 mL), and pyridine (0.10 mL) and placed under partial vacuum. The reaction mixture was stirred for 2 days at 55 °C. The volatiles were removed under reduced pressure and the residue was washed with hexane. After the residue was dried in vacuo an orange-yellow powder was obtained. Yield 131 mg (57%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.22 (3 H, s, Me of N_2N_{py}), 1.63 (9 H, s, CMe_3), 2.28 (6 H, s, C_6H_4*Me*), 3.18 (2 H, d, C*H*H, ^3J = 12.3 Hz), 3.28 (2 H, d, CH*H*, ^3J = 12.3 Hz), 6.43 (2 H, br. s, *m*-C_5H_5N), 6.51 (2 H, app t, H^5, ^3J = 7.0 Hz), 6.67 (1 H, br. s, *p*-C_5H_5N), 6.72 (1 H, d, H^3, ^3J = 7.9 Hz), 6.91 (1 H, app td, H^4, $^3J(H^3H^4H^5)$ = 7.7 Hz, $^4J(H^4H^6)$ = 1.2 Hz), 7.11 (4 H, d, *m*-C_6H_4-Me, ^3J = 8.2 Hz), 7.39 (4 H, d, *o*-C_6H_4Me, ^3J = 8.4 Hz), 8.78 (2 H, br. s, *o*-C_5H_5N), 9.62 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^4H^6)$ = 1.0 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.4 (C_6H_4*Me*), 25.3 (Me of N_2N_{py}), 33.5 (C*Me*$_3$), 41.8 [*C*(CH_2NTol)$_2$], 62.5 [(*C*H_2NTol)$_2$], 69.1 (*C*Me_3), 114.8 (*ipso*-C_6H_4Me), 119.5 (C^3), 121.2 (C^5), 123.3 (*m*-C_5H_5N), 124.5 (*o*-C_6H_4Me), 129.4 (*m*-C_6H_4-Me), 129.7 and 137.7 (C^4 and *p*-C_5H_5N), 149.8 (*o*-C_5H_5N), 150.4 (C^6), 152.3 (*p*-C_6H_4Me) 159.8 (C^2) ppm. Anal. Found (calcd for $C_{32}H_{39}N_5Ti$): C, 70.4 (71.0); H, 7.6 (7.3); N, 12.7 (12.9).

[Ti(N^{t}Bu)($N_2^{Tol}N_{py}$)(NH_2^tBu)] (3b). A Schlenk tube was charged with [Ti($N_2^{Tol}N_{py}$)(NMe_2)$_2$] (209 mg, 0.43 mmol) and a large excess of *tert*-butylamine (20 mL) and placed under partial vacuum. The reaction mixture was stirred for 5 days at 55 °C. The volatiles were removed under reduced pressure, and the residue was washed with hexane. After the residue was dried in vacuo an orange-yellow powder was obtained. Yield 171 mg (73%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 0.75 (9 H, s, NH_2C*Me*$_3$), 1.20 (3 H, s, Me of N_2N_{py}), 1.59 (9 H, s, CMe_3), 2.26 (6 H, s, C_6H_4*Me*), 3.06 (2 H, d, C*H*H, ^3J = 12.4 Hz), 3.33−3.43 (2 H, br. s, N*H*$_2$CMe_3), 3.38 (2 H, d, CH*H*, ^3J = 12.3 Hz), 6.51 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.6 Hz, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^3H^5)$ = 1.2 Hz), 6.71 (1 H, dt, H^3, $^3J(H^3H^4)$ = 8.0 Hz, $^4J(H^3H^4H^5)$ = 1.0 Hz), 6.90 (1 H, td, H^4, $^3J(H^3H^4H^5)$ = 7.8 Hz, $^4J(H^4H^6)$ = 1.8 Hz), 7.13 (4 H, d, *m*-C_6H_4Me, ^3J = 8.6 Hz), 7.30 (4 H, d, *o*-C_6H_4Me, ^3J = 8.4 Hz), 9.60 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^4H^6)$ = 1.8 Hz, $^5J(H^3H^6)$ = 0.8 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.7 (C_6H_4*Me*), 25.4 (Me of N_2N_{py}), 31.2 (NH_2C*Me*$_3$), 33.6 (C*Me*$_3$), 42.4 [*C*(CH_2NTol)$_2$], 50.4 ($NH_2C$$Me_3$), 62.6 [(*C*$H_2$NTol)$_2$], 68.9 (*C*$Me_3$), 114.7 (*ipso*-$C_6H_4$Me), 119.5 ($C^3$), 121.5 ($C^5$), 125.0 (*o*-$C_6H_4$Me), 129.9 (*m*-$C_6H_4$Me), 137.8 ($C^4$), 151.4 ($C^6$), 152.8 (*p*-$C_6H_4$Me), 160.0 ($C^2$) ppm. Anal. Found (calcd for $C_{31}H_{45}N_5Ti$): C, 69.1 (69.5); H, 8.4 (8.5); N, 12.7 (13.1).

[Ti(N^{t}Bu)($N_2^{Xyl}N_{py}$)(py)] (3c). A Schlenk tube was charged with [Ti($N_2^{Xyl}N_{py}$)(NMe_2)$_2$] (618 mg, 1.22 mmol), a large excess of *tert*-butylamine (20 mL), and pyridine (0.20 mL) and placed under partial vacuum. The reaction mixture was stirred for 2 days at 55 °C. The volatiles were removed under reduced pressure and the residue was washed with diethyl ether. After the residue was dried in vacuo a yellow powder was obtained. Yield 487 mg (70%). Single crystals for X-ray diffraction were grown from a saturated diethyl ether solution at 5 °C (300 mg in 4 mL of diethyl ether). ^{1}H NMR (C_6D_6, 600.1 MHz, 296 K): δ 1.17 (3 H, s, Me of N_2N_{py}), 1.65 (9 H, s, CMe_3), 2.35 (12 H, s, C_6H_3*Me*$_2$), 3.25 (2 H, d, C*H*H, ^3J = 12.2 Hz), 3.33 (2 H, d, CH*H*, ^3J = 12.2 Hz), 6.37 (2 H, app t, *m*-C_5H_5N, ^3J = 7.7 Hz), 6.46 (2 H, br. s, *p*-$C_6H_3Me_2$), 6.55 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.6 Hz, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^3H^5)$ = 1.2 Hz), 6.58 (1 H, t, *p*-C_5H_5N, ^3J = 7.7 Hz), 6.73 (1 H, d, H^3, ^3J = 8.3 Hz), 6.93 (1 H, app td, H^4, $^3J(H^3H^4H^5)$ = 7.8 Hz, $^4J(H^4H^6)$ = 1.8 Hz), 7.22 (4 H, br. s, *o*-C_6H_3*Me*$_2$), 8.96 (2 H, d, *o*-C_5H_5N, ^3J = 4.7 Hz), 9.68 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.2 Hz, $^4J(H^4H^6)$ = 1.0 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz, 296 K): δ 21.9 (C_6H_3*Me*$_2$), 25.7 (Me of N_2N_{py}), 33.7 (C*Me*$_3$), 42.1 [*C*(CH_2NXyl)$_2$], 62.8 [(*C*H_2NXyl)$_2$], 69.6 (*C*Me_3), 113.4 (*o*-$C_6H_3Me_2$), 118.9 (*p*-$C_6H_3Me_2$), 119.8 (C^3), 121.5 (C^5), 123.7 (*m*-C_5H_5N), 137.2 (*p*-C_5H_5N), 137.7 (C^4), 137.9 (*ipso*-$C_6H_3Me_2$), 150.0 (*o*-C_5H_5N), 150.8 (C^6), 154.8 (*m*-$C_6H_3Me_2$), 160.2 (C^2) ppm. ^{15}N{^{1}H} NMR (C_6D_6, 60.8 MHz, 296 K): δ 193.4 (*N*$_2$N$_{py}$), 284.4 (*N*C_5H_5), 292.1 (N$_2$*N*$_{py}$), 442.9 (*N*^{t}Bu) ppm. Anal. Found (calcd for $C_{34}H_{43}N_5Ti$): C, 71.8 (71.7); H, 7.6 (7.6); N, 12.3 (12.3).

[Ti(N^{t}Bu)($N_2^{Xyl}N_{py}$)(NH_2^tBu)] (3d). A Schlenk tube was charged with [Ti($N_2^{Xyl}N_{py}$)(NMe_2)$_2$] (565 mg, 1.11 mmol) and a large excess of *tert*-butylamine (40 mL) and placed under partial vacuum. The reaction mixture was stirred for 5 days at 55 °C. The volatiles were removed under reduced pressure, and the residue was washed with ether. After the residue was dried in vacuo an orange-yellow powder was obtained. Yield 454 mg (83%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 0.84 (9 H, s, NH_2C*Me*$_3$), 1.28 (3 H, s, Me of N_2N_{py}), 1.69 (9 H, s, CMe_3), 2.43 (12 H, s, C_6H_3*Me*$_2$), 3.18 (2 H, d, C*H*H, ^3J = 12.4 Hz), 3.48 (2 H, d, CH*H*, ^3J = 12.3 Hz), 3.53−3.63 (2 H, br. s, N*H*$_2$CMe_3), 6.53 (2 H, br. s, *p*-$C_6H_3Me_2$), 6.62 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.6 Hz, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^3H^5)$ = 1.2 Hz), 6.80 (1 H, d, H^3, ^3J = 8.3 Hz), 7.01 (1 H, app td, H^4, $^3J(H^3H^4H^5)$

= 7.8 Hz, $^4J(H^4H^6)$ = 1.8 Hz), 7.22 (4 H, br. s, *o*-$C_6H_3Me_2$), 9.69 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.2 Hz, $^4J(H^4H^6)$ = 1.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100.5 MHz, 296 K): δ 22.0 ($C_6H_3Me_2$), 25.5 (Me of N_2N_{py}), 31.3 (NH_2CMe_3), 33.7 (CMe_3), 42.5 [$C(CH_2NXyl)_2$], 50.4 (NH_2CMe_3), 62.5 [$(CH_2NXyl)_2$], 69.1 (CMe_3), 112.9 (*o*-$C_6H_3Me_2$), 119.0 (*p*-$C_6H_3Me_2$), 119.6 (C^3), 121.6 (C^5), 138.0 (C^4), 138.2 (*ipso*-$C_6H_3Me_2$), 151.6 (C^6), 155.0 (*m*-$C_6H_3Me_2$), 160.2 (C^2) ppm. Anal. Found (calcd for $C_{33}H_{49}N_5Ti$): C, 69.2 (70.6); H, 8.3 (8.4); N, 11.6 (12.5). Despite repeated attempts, we were unable to obtain a more accurate elemental analysis. We attribute this inter alia to the relatively weak coordination of ^{t}BuNH$_2$ which leads to a slight variation of the composition of the product.

[Ti(N-4-C_6H_4Me)($N_2^{Tol}N_{py}$)(py)] (3e). To a solution of [Ti($N_2^{Tol}N_{py}$)(NMe_2)$_2$] (384 mg, 0.80 mmol) in pyridine (10 mL) was added 1 equiv of *p*-toluidine (86 mg, 0.80 mmol), and the mixture was placed under partial vacuum. The reaction mixture was stirred for 1 h at 80 °C. The volatiles were removed under reduced pressure, and the residue was washed with hexane. After the residue was dried in vacuo an orange-red powder was obtained. Yield 370 mg (81%). ^1H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.30 (3 H, s, Me of N_2N_{py}), 2.13 (6 H, s, C_6H_4Me), 2,31 (3 H, s, N-4-C_6H_4Me), 3.30 (2 H, d, C*H*H, ^3J = 12.4 Hz), 3.59 (2 H, d, CH*H*, ^3J = 12.4 Hz), 6.30 (2 H, br. s, *m*-C_5H_5N), 6.35 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.6 Hz, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^3H^5)$ = 1.2 Hz), 6.66 (1 H, br. s, *p*-C_5H_5N), 6.75 (1 H, d, H^3, ^3J = 8.0 Hz), 6.91 (1 H, app td, H^4, $^3J(H^3H^4H^5)$ = 7.8 Hz, $^4J(H^4H^6)$ = 1.8 Hz), 6.99 (4 H, d, *m*-C_6H_4-Me, ^3J = 8.2 Hz), 7.20 (2 H, d, *m*-N-4-C_6H_4Me, ^3J = 8.2 Hz), 7.32 (4 H, d, *o*-C_6H_4Me, ^3J = 8.4 Hz), 7.47 (2 H, d, *o*-N-4-C_6H_4-Me, ^3J = 8.4 Hz), 8.53 (2 H, br. s, *o*-C_5H_5N), 9.46 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.3 Hz, $^4J(H^4H^6)$ = 1.0 Hz) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.7 (C_6H_4Me), 21.2 (N-4-C_6H_4Me), 25.3 (Me of N_2N_{py}), 42.9 [$C(CH_2NTol)_2$], 63.3 [$(CH_2NTol)_2$], 114.5 (*ipso*-C_6H_4Me), 119.6 (C^3), 122.2 (C^5), 123.5 (*p*-C_5H_5N), 124.0 (*o*-N-4-C_6H_4Me), 126.0 (*ipso*-N-4-C_6H_4Me), 128.3 (*m*-C_5H_5N), 129.6 (*m*-C_6H_4Me), 129.9 (*m*-N-4-C_6H_4Me), 135.2 (*o*-C_6H_4Me), 138.4 (C^4), 150.4 (*o*-C_5H_5N), 151.0 (C^6), 151.8 (*p*-C_6H_4Me), 160.1 (*p*-N-4-C_6H_4Me), 160.2 (C^2) ppm. Anal. Found (calcd for $C_{34}H_{43}N_5$-Ti): C, 72.0 (71.7); H, 6.5 (7.6); N, 12.3 (12.3).

[Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=CPh}] (4a). To a solution of [Ti(N^tBu)($N_2^{Tol}N_{py}$)(py)] **3a** (12 mg, 22.2 mmol) in C_6D_6 (0.5 mL) was added phenyl acetylene (2.7 μL, 24.4 mmol, 1.1 equiv). Analysis by NMR spectroscopy indicated that the formation of **4a**, along with a small quantity of [Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ph)C-(Ph) = CH}] (**5a**) which could not be completely removed by repeated recrystallization. ^1H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.20 (9 H, s, CMe_3), 1.23 (3 H, s, Me of N_2N_{py}), 2.15 (6 H, s, C_6H_4Me), 3.22 (2 H, d, C*H*H, ^3J = 11.9 Hz), 4.02 (2 H, d, CH*H*, ^3J = 11.9 Hz), 6.31 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.2 Hz, $^3J(H^6H^5)$ = 5.3 Hz, $^4J(H^3H^5)$ = 1.4 Hz), 6.69 (4 H, d, *o*-C_6H_4Me, ^3J = 8.4 Hz), 6.81 (1 H, d, H^3, ^3J = 7.9 Hz), 6.85−6.92 (1 H, m, H^4), 6.46 (4 H, d, *m*-C_6H_4Me, ^3J = 8.2 Hz), 7.10−7.16 (1 H, m obscured by solvent, *p*-C_6H_5), 7.35−7.44 (4 H, m, *m*-C_6H_5 and *o*-C_6H_5), 9.17 (1 H, d, H^6, $^3J(H^5H^6)$ = 5.3 Hz), 10.00 (1 H, s, C=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 296 K): δ 20.7 (C_6H_4Me), 24.3 (Me of N_2N_{py}), 30.7 (CMe_3), 44.1 [$C(CH_2NXyl)_2$], 59.7 (CMe_3), 64.0 [$(CH_2NXyl)_2$], 115.1 (*o*-C_6H_4Me), 120.3 (C^3), 121.8 (C^5), 123.5 (*p*-C_6H_5), 126.3 (*o*-C_6H_5), 128.8 (*m*-C_6H_5), 129.4 (*m*-C_6H_4Me), 135.2 (*p*-C_6H_4Me), 138.4 (C^4), 147.7 (C^6), 150.2 (*ipso*-C_6H_5), 150.8 (C=*C*H), 152.2 (*ipso*-C_6H_4Me), 160.7 (C^2), 196.3 (*C*=CH) ppm.

[Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=CTol}] (4b). To a solution of [Ti(N^tBu)($N_2^{Tol}N_{py}$)(py)] **3a** (12 mg, 22.2 mmol) in C_6D_6 (0.5 mL) was added tolyl acetylene (3.1 μL, 24.4 mmol, 1.1 equiv). Analysis by NMR spectroscopy indicated the formation of **4a**, along with a small quantity of [Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol) = CH}] (**5b**) which could not be completely removed by repeated recrystallization. ^1H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.20 (9 H, s, CMe_3), 1.23 (3 H, s, Me of N_2N_{py}), 2.25 (6 H, s, C_6H_4Me), 2.31 (3 H, s, 4-C_6H_4Me), 3.22 (2 H, d, C*H*H, ^3J = 11.9 Hz), 4.02 (2 H, d, CH*H*, ^3J = 11.9 Hz), 6.34 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.1 Hz, $^3J(H^6H^5)$ = 5.4 Hz, $^4J(H^3H^5)$ = 1.3 Hz), 6.70 (4 H, d, *o*-C_6H_4-Me, ^3J = 8.4 Hz), 6.82 (1 H, d, H^3, ^3J = 7.9 Hz), 6.88 (1 H, td, H^4, $^3J(H^3H^4H^5)$ = 7.9 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 7.00 (4 H, d, *m*-C_6H_4Me, ^3J = 8.3 Hz), 7.20 (2 H, d, *m*-4-C_6H_4Me, ^3J = 7.8 Hz), 7.40 (2 H, d, *o*-4-C_6H_4Me, ^3J = 8.2 Hz), 9.22 (1 H, d, H^6, $^3J(H^5H^6)$ = 5.3 Hz), 10.03 (1 H, s, C=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 296 K): δ 20.8 (C_6H_4Me), 21.2 (4-C_6H_4Me), 24.3 (Me of N_2N_{py}), 30.8 (CMe_3), 44.1 [$C(CH_2NXyl)_2$], 59.8 (CMe_3), 64.0 [$(CH_2NXyl)_2$], 115.1 (*o*-C_6H_4Me), 120.4 (C^3), 121.9 (C^5), 123.5 (*p*-C_6H_5), 126.3 (*o*-4-C_6H_4Me), 129.0 (*m*-4-C_6H_4Me), 129.4 (*m*-C_6H_4Me), 135.4 (*p*-C_6H_4Me), 138.4 (C^4), 147.8 (C^6), 150.7 (*ipso*-4-C_6H_4Me), 150.9 (C=*C*H), 152.3 (*ipso*-C_6H_4Me), 160.9 (C^2), 197.4 (*C*=CH) ppm.

[Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH=CPh}] (4c). To a solution of [Ti(N^tBu)($N_2^{Xyl}N_{py}$)(py)] (954 mg, 0.17 mmol) in toluene (50 mL) was added an equimolar amount of phenylacetylene (22 μL, 1.67 mmol) via syringe. The resulting brown solution was stirred over night. Removing the volatiles under reduced pressure produced a brown waxy solid, which was redissolved into pentane (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Yield 553 mg (56%). ^1H NMR (C_6D_6, 600.1 MHz, 296 K): δ 1.19 (9 H, s, CMe_3), 1.22 (3 H, s, Me of N_2N_{py}), 2.25 (12 H, s, $C_6H_3Me_2$), 3.26 (2 H, d, C*H*H, ^3J = 12.0 Hz), 4.06 (2 H, d, CH*H*, ^3J = 12.0 Hz), 6.31 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.2 Hz, $^3J(H^6H^5)$ = 5.4 Hz, $^4J(H^3H^5)$ = 1.4 Hz), 6.45 (2 H, s, *p*-$C_6H_3Me_2$), 6.46 (4 H, s, *o*-$C_6H_3Me_2$), 6.81 (1 H, d, H^3, ^3J = 7.6 Hz), 6.86 (1 H, td, H^4, $^3J(H^3H^4H^5)$ = 7.9 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 7.13 (1 H, m obscured by solvent, *p*-C_6H_5), 7.38 (2 H, app. t, *m*-C_6H_5, J = 7.5 Hz), 7.46 (2 H, dd, *o*-C_6H_5, ^3J = 8.2 Hz, ^4J = 1.3 Hz), 9.19 (1 H, ddd, H^6, $^3J(H^5H^6)$ = 5.4 Hz, $^4J(H^4H^6)$ = 1.7 Hz, $^5J(H^3H^6)$ = 0.8 Hz), 9.99 (1 H, s, C=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 296 K): δ 21.8 ($C_6H_3Me_2$), 24.3 (Me of N_2N_{py}), 30.6 (CMe_3), 44.1 [$C(CH_2NXyl)_2$], 59.8 (CMe_3), 63.8 [$(CH_2NXyl)_2$], 112.9 (*o*-C_6H_3-Me_2), 120.4 (C^3), 121.4 (*p*-$C_6H_3Me_2$), 121.9 (C^5), 123.8 (*p*-C_6H_5), 126.4 (*o*-C_6H_5), 128.8 (*m*-C_6H_5), 137.7 (*m*-$C_6H_3Me_2$), 138.4 (C^4), 147.7 (C^6), 150.0 (*ipso*-C_6H_5), 150.8 (C=*C*H), 152.8 (*ipso*-C_6H_3-Me_2), 160.9 (C^2), 196.6 (*C*=CH) ppm. $^{15}N\{^1H\}$ NMR (C_6D_6, 60.8 MHz, 296 K): δ 240.9 (N_2N_{py}), 274.6 (N^tBu), 286.6 (N_2N_{py}) ppm. Anal. Found (calcd for $C_{37}H_{44}N_4Ti$): C, 74.9 (75.0); H, 7.4 (7.5); N, 8.9 (9.5).

[Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH=CTol}] (4d). To a solution of [Ti(N^tBu)($N_2^{Xyl}N_{py}$)(py)] (611 mg, 1.07 mmol) in toluene (50 mL) was added an equimolar amount of tolylacetylene (150 μL, 1.18 mmol) via syringe. The resulting brown solution was stirred over night. Removing the volatiles under reduced pressure produced a brown, waxy solid, which was redissolved into pentane (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Yield 337 mg (52%). ^1H NMR (C_6D_6, 600.1 MHz, 296 K): δ 1.21 (9 H, s, CMe_3), 1.24 (3 H, s, Me of N_2N_{py}), 2.26 (12 H, s, $C_6H_3Me_2$), 2.31 (3 H, s, 4-C_6H_4Me), 3.28 (2 H, d, C*H*H, ^3J = 12.0 Hz), 4.06 (2 H, d, CH*H*, ^3J = 12.0 Hz), 6.36 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.2 Hz, $^3J(H^6H^5)$ = 5.4 Hz, $^4J(H^3H^5)$ = 1.2 Hz), 6.46 (2 H, s, *p*-$C_6H_3Me_2$), 6.48 (4 H, s, *o*-$C_6H_3Me_2$), 6.83 (1 H, d, H^3, ^3J = 7.9 Hz), 6.88 (1 H, td, H^4, $^3J(H^3H^4H^5)$ = 7.9 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 7.21 (2 H, d, *m*-4-C_6H_4Me, ^3J = 8.0 Hz), 7.40 (2 H, d, *o*-4-C_6H_4Me, ^3J = 7.7 Hz), 9.26 (1 H, dd, H^6, $^3J(H^5H^6)$ = 5.4 Hz, $^4J(H^4H^6)$ = 1.7 Hz), 10.03 (1 H, s, C=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150.9 MHz, 296 K): δ 21.2 (4-C_6H_4Me), 21.9 ($C_6H_3Me_2$), 24.4 (Me of N_2N_{py}), 30.6 (CMe_3), 44.1 [$C(CH_2NXyl)_2$], 59.8 (CMe_3), 63.8 [$(CH_2NXyl)_2$], 112.9 (*o*-$C_6H_3Me_2$), 120.4 (C^3), 121.3 (*p*-$C_6H_3Me_2$), 121.9 (C^5), 126.4 (*o*-4-C_6H_4Me), 128.3 (*m*-4-C_6H_4-Me), 129.5 (*m*-$C_6H_3Me_2$), 132.8 (*p*-4-C_6H_4Me), 137.7 (*ipso*-4-C_6H_4-Me) 138.4 (C^4), 147.8 (C^6), 150.5 (C=*C*H), 152.9 (*ipso*-$C_6H_3Me_2$), 161.0 (C^2), 197.7 (*C*=CH) ppm. $^{15}N\{^1H\}$ NMR (C_6D_6, 60.8 MHz,

296 K): δ 265.8 (N_2N_{py}), 302.4 (N^tBu), 314.5 (N_2N_{py}) ppm. Anal. Found (calcd for $C_{38}H_{46}N_4Ti$): C, 75.2 (75.2); H, 7.7 (7.6); N, 8.9 (9.2).

[Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ph)C(Ph)=CH}] (5a). To a solution of [Ti(N^{t}Bu)($N_2^{Tol}N_{py}$)(py)] (758 mg, 1.40 mmol) in toluene (50 mL) was added 3 equiv of phenylacetylene (460 μL, 1.40 mmol) via syringe. The resulting brown solution was stirred for 60 min at 100 °C. Removing the volatiles under reduced pressure produced a brown waxy solid, which was redissolved into diethyl ether (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Yield 345 mg (37%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.14 (9 H, s, CMe_3), 1.18 (3 H, s, Me of N_2N_{py}), 2.03 (6 H, s, C_6H_3*Me*), 3.27 (2 H, d, C*H*HN, ^3J = 12.5 Hz), 3.69 (2 H, d, CH*H*N, ^3J = 12.5 Hz), 6.39 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.3 Hz, $^3J(H^6H^5)$ = 5.4 Hz, $^4J(H^3H^5)$ = 1.1 Hz), 6.74 (1 H, d, H^3, ^3J = 7.9 Hz), 6.87−7.03 (11 H, overlapping m, H^4, *p*-C_6H_5, *o*-C_6H_4-Me and *m*-C_6H_4Me), 7.12−7.21 (4 H, m obscured by the solvent, *o*-C_6H_5), 7.60 (4 H, t, *m*-C_6H_5, ^3J = 8.2 Hz), 8.08 (1 H, s, H_a), 9.29 (1 H, d, H^6, ^3J (H^5H^6) = 5.9 Hz), 10.38 (1 H, s, H_b) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.7 (C_6H_4*Me*), 25.3 (Me of N_2N_{py}), 31.7 (C*Me*$_3$), 42.9 [*C*(CH_2NTol)$_2$], 62.5 (*C*Me$_3$), 63.5 [(*C*H_2NTol)$_2$], 115.9 (*o*-C_6H_4Me), 120.0 (C^3), 121.8 (*C*=CH_a), 122.6 (C^5), 124.4 (*p*-C_6H_5), 126.2 (*p*-C_6H_5), 128.0 (*o*-C_6H_5), 128.4 (*o*-C_6H_5), 129.4 (*p*-C_6H_4Me), 129.5 (*m*-C_6H_4Me), 130.1 (*m*-C_6H_5), 130.4 (*m*-C_6H_5), 138.4 (C^4), 145.7 (*ipso*-C_6H_5), 145.9 (*ipso*-C_6H_5), 147.5 (C^6), 149.9 (C=*C*H_a), 151.6 (*C*=CH_b), 152.2 (*ipso*-C_6H_4-Me), 160.3 (C^2), 228.9 (C=*C*H_b) ppm. Anal. Found (calcd for $C_{43}H_{46}N_4Ti$): C, 77.2 (77.5); H, 7.2 (6.9); N, 8.1 (8.4).

[Ti($N_2^{Tol}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol)=CH}] (5b). To a solution of [Ti(N^{t}Bu)($N_2^{Tol}N_{py}$)(py)] (1,00 g, 1.85 mmol) in toluene (50 mL) was added 3 equiv of tolylacetylene (0.70 μL, 1.81 mmol) via syringe. The resulting brown solution was stirred for 60 min at 100 °C. Removing the volatiles under reduced pressure produced a brown, waxy solid, which was redissolved into diethyl ether (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Diffraction-quality single crystals were grown from a saturated diethyl ether solution at 5 °C (400 mg in 4 mL of diethyl ether). Yield 379 mg (30%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.16 (9 H, s, CMe_3), 1.19 (3 H, s, Me of N_2N_{py}), 2.04 (12 H, s, C_6H_3*Me*), 2.06 (3 H, s, 4-C_6H_4*Me*), 2.12 (3 H, s, 4-C_6H_4*Me*), 3.27 (2 H, d, C*H*HN, ^3J = 12.5 Hz), 3.69 (2 H, d, CH*H*N, ^3J = 12.5 Hz), 6.42 (1 H, ddd, H^5, $^3J(H^4H^5)$ = 7.4 Hz, $^3J(H^6H^5)$ = 5.4 Hz, $^4J(H^3H^5)$ = 1.1 Hz), 6.76 (1 H, d, H^3, ^3J = 7.9 Hz), 6.88−7.04 (13 H, overlapping m, H^4, C_6H_3Me and *m*-4-C_6H_4-Me), 7.56 (4 H, dd, *o*-4-C_6H_4Me, ^3J = 8.1 Hz, ^4J = 5.3 Hz), 8.09 (1 H, s, H_a), 9.35 (1 H, d, H_6, ^3J (H^5H^6) = 5.2 Hz), 10.46 (1 H, s, H_b) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 20.7 (C_6H_4*Me*), 21.1 (4-C_6H_4*Me*), 21.2 (4-C_6H_4*Me*), 25.3 (Me of N_2N_{py}), 31.7 (C*Me*$_3$), 42.0 [*C*(CH_2NTol)$_2$], 62.4 (*C*Me$_3$), 63.5 [(*C*H_2NTol)$_2$], 115.9 (*o*-C_6H_4Me), 119.9 (C^3), 1218 (*C*=CH_a), 122.5 (C^5), 128.6 (*m*-4-C_6H_4Me), 129,1 (*m*-4-C_6H_4Me), 129.3 (*p*-C_6H_4Me), 129.5 (*m*-C_6H_4Me), 130.1 (*o*-4-C_6H_4Me), 130,3 (*o*-4-C_6H_4Me), 133.3 (*p*-4-C_6H_4Me), 135.3 (*p*-4-C_6H_4Me), 138.3 (C^4), 142.7 (*ipso*-4-C_6H_4Me), 143.2 (*ipso*-4-C_6H_4Me), 147.6 (C^6), 149.5 (C=*C*H_a), 151.5 (*C*=CH_b), 152.3 (*ipso*-C_6H_4Me), 160.3 (C^2), 229.6 (C=*C*H_B) ppm. Anal. Found (calcd for $C_{45}H_{50}N_4Ti$): C, 77.3 (77.8); H, 7.4 (7.3); N, 7.9 (8.1).

[Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH=C(Ph)C(Ph)=CH}] (5c). To a solution of [Ti(N^{t}Bu)($N_2^{Xyl}N_{py}$)(py)] (1.03 mg, 1.8 mmol) in toluene (50 mL) was added 3 equiv of phenylacetylene (0.60 mL, 5.4 mmol) via syringe. The resulting brown solution was stirred for 60 min at 100 °C. Removing the volatiles under reduced pressure produced a brown, waxy solid, which was redissolved into diethyl ether (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Yield 492 mg (39%). ^{1}H NMR (C_6D_6, 399.9 MHz, 296 K): δ 1.14 (9 H, s, CMe_3), 1.18 (3 H, s, Me of N_2N_{py}), 2.15 (12 H, s, 3,5-C_6H_3*Me*$_2$), 3.30 (2 H, d, C*H*HN, ^3J = 12.5 Hz), 3.71 (2 H, d, CH*H*N, ^3J = 12.5 Hz), 6.48−6.52 (3 H, overlapping m, H^5 and *p*-3,5-$C_6H_3Me_2$), 6.85 (1 H, d, H^3, ^3J = 7.9 Hz), 6.89 (4 H, s, *o*-3,5-$C_6H_3Me_2$), 6.99−7.12 (3 H, overlapping m, $H^4$and *p*-C_6H_5), 7.26 (4 H, m obscured by the solvent, *o*-C_6H_5), 7.70 (4 H, t, *m*-C_6H_5, ^3J = 8.2 Hz), 8.07 (1 H, s, H_a), 9.29 (1 H, d, H^6, ^3J (H^5H^6) = 5.9 Hz), 10.16 (1 H, s, H_b) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.5 MHz, 296 K): δ 21.8 (3,5-C_6H_3*Me*$_2$), 25.3 (Me of N_2N_{py}), 31.5 (C*Me*$_3$), 42.0 [*C*(CH_2NXyl)$_2$], 62.4 (*C*Me$_3$), 63.1 [(*C*H_2NXyl)$_2$], 113.8 (*o*-3,5-$C_6H_3Me_2$), 119.9 (C^3), 122.3 (*C*=CH_a), 122.5 (C^5), 122.6 (*p*-3,5-$C_6H_3Me_2$), 124.2 (*p*-C_6H_5), 126.1 (*p*-C_6H_5), 127.9 (*o*-C_6H_5), 128.1 (*o*-C_6H_5), 129.7 (*m*-C_6H_5), 130.2 (*m*-C_6H_5), 137.8 (*m*-3,5-$C_6H_3Me_2$), 138.4 (C^4), 145.5 (*ipso*-C_6H_5), 145.9 (*ipso*-C_6H_5), 147.6 (C^6), 149.2 (C=*C*H_a), 151.4 (*C*=CH_b), 154.2 (*ipso*-3,5-C_6H_3-Me_2), 160.3 (C^2), 228.2 (C=*C*H_b) ppm. Anal. Found (calcd for $C_{45}H_{50}N_4Ti$): C, 77.2 (77.8); H, 7.3 (7.3); N, 7.9 (8.1).

[Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH=C(Tol)C(Tol)=CH}] (5d). To a solution of [Ti(N^{t}Bu)($N_2^{Xyl}N_{py}$)(py)] (1.18 g, 2.1 mmol) in toluene (50 mL) was added 3 equiv of tolylacetylene (0.79 mL, 6.2 mmol) via syringe. The resulting brown solution was stirred for 60 min at 100 °C. Removing the volatiles under reduced pressure produced a brown, waxy solid, which was redissolved into diethyl ether (20 mL). After 2 days at −4 °C, the title compound was formed as a black crystalline solid. Yield 275 mg (18%). Diffraction-quality single crystals were grown from a saturated diethyl ether solution at 5 °C (600 mg in 4 mL of diethyl ether). ^{1}H NMR (C_6D_6, 600.1 MHz, 296 K): δ 1.17 (9 H, s, CMe_3), 1.19 (3 H, s, Me of N_2N_{py}), 2.07 (3 H, s, 4-C_6H_4*Me*), 2.11 (3 H, s, 4-C_6H_4*Me*), 2.17 (12 H, s, 3,5-C_6H_3*Me*$_2$), 3.32 (2 H, d, C*H*HN, ^3J = 12.4 Hz), 3.72 (2 H, d, CH*H*N, ^3J = 12.4 Hz), 6.44 (3 H, overlapping m, H^5 and *p*-3,5-$C_6H_3Me_2$), 6.78 (1 H, d, H^3, ^3J = 7.6 Hz), 6.83 (4 H, s, *o*-3,5-$C_6H_3Me_2$), 6.94 (1 H, td, H^4 ^3J = 7.8 ,^4J = 1.8), 7.01 (4 H, t, *m*-4-C_6H_4Me, ^3J = 8.4 Hz), 7.58 (4 H, dd, *o*-4-C_6H_4Me, ^3J = 8.1 Hz, ^4J = 6.4 Hz), 8.08 (1 H, s, H_a), 9.36 (1 H, dd, H_6, ^3J (H^5H^6) = 5.4 Hz, ^4J (H^4H^6) = 1.6 Hz), 10.25 (1 H, s, H_b) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150.9 MHz, 296 K): δ 21.1 (4-C_6H_4*Me*), 21.2 (4-C_6H_4*Me*), 21.8 (3,5-C_6H_3*Me*$_2$), 25.3 (Me of N_2N_{py}), 31.5 (C*Me*$_3$), 42.0 [*C*(CH_2NXyl)$_2$], 62.3 (*C*Me$_3$), 63.1 [(*C*H_2NXyl)$_2$], 113.8 (*o*-3,5-$C_6H_3Me_2$), 119.9 (C^3), 122.4 (*C*=CH_a), 122.5 (C^5 and *p*-3,5-$C_6H_3Me_2$ overlapping), 128.7 (*m*-4-C_6H_4Me), 128.9 (*m*-4-C_6H_4Me), 129.7 (*o*-4-C_6H_4Me), 130.2 (*o*-4-C_6H_4Me), 133.1 (*p*-4-C_6H_4Me), 135.3 (*p*-4-C_6H_4Me), 137.8 (*m*-3,5-$C_6H_3Me_2$), 138.4 (C^4), 142.9 (*ipso*-4-C_6H_4Me), 143.1 (*ipso*-4-C_6H_4Me), 147.6 (C^6), 148.7 (C=*C*H_a), 151.3 (*C*=CH_b), 154.3 (xyl-ipso-C), 160.4 (C^2), 227.5 (C=*C*H_B) ppm. ^{15}N{^{1}H} NMR (C_6D_6, 60.8 MHz, 296 K): δ 246.2 (N_2N_{py}), 287.0 (N^tBu), 288.3 (N_2N_{py}) ppm. Anal. Found (calcd for $C_{47}H_{54}N_4Ti$): C, 78.5 (78.1); H, 7.7 (7.5); N, 7.8 (7.8).

Kinetic Studies of the {2 + 2} Addition of Phenylacetylene to the Ti Imido Complex 3c and of the Reaction of the Azatitanacycle 4a with *tert*-Butylamine. A solution of [Ti(N^{t}Bu)-($N_2^{Xyl}N_{py}$)(py)] (**3c**) (5.7 mg, 10 μmol) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in toluene-d_8 (0.5 mL) was transferred to a J. Young NMR tube. After cooling the sample to −20 °C, 0.5 to 4 equiv of phenylacetylene (5 to 40 μmol) was added. The tube was transferred to an NMR spectrometer probe that had been precooled to 0 °C. ^{1}H NMR spectra were recorded every 3 min for a period of up to 30 min. The concentration of the reaction product was plotted against time, and the conversion curve was line-fitted to a first-order exponential decay $Ae^{-x/b}$. The initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for x = 0. A plot of the initial rate versus alkyne concentration indicated a linear relationship.

A solution of [Ti(N^{t}Bu)($N_2^{Xyl}N_{py}$)(py)] (**3c**) (5 to 25 μmol) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in toluene-d_8 (0.5 mL) was transferred to a J. Young NMR tube. After the sample was cooled to −20 °C, 20 equiv of phenylacetylene (0.1−0.5 mmol) was added. The tube was transferred to an NMR spectrometer probe that had been precooled to 0 °C. ^{1}H NMR spectra were recorded

Table 3. X-ray Data for 2a, 2b, 3c, 5b, and 5d

	2a	2b	3c	5b	5d
empirical formula	$C_{27}H_{37}N_5Ti \cdot C_7H_8$	$C_{29}H_{41}N_5Ti$	$C_{34}H_{43}N_5Ti$	$C_{45}H_{50}N_4Ti$	$C_{47}H_{54}N_4Ti$
formula weight	571.67	507.58	569.65	694.82	722.84
crystal size /mm	0.16 × 0.08 × 0.03	0.10 × 0.15 × 0.25	0.15 × 0.15 × 0.15	0.25 × 0.25 × 0.25	0.10 × 0.20 × 0.20
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C2/c$	$C2/c$
a /Å	10.7877(2)	10.637(2)	8.650(6)	30.081(6)	31.3967(18)
b /Å	11.6261(3)	22.176(4)	20.362(13)	13.029(3)	12.6357(8)
c /Å	25.8717(7)	11.572(2)	17.777(11)	21.530(4)	22.2022(13)
α /deg	90	90	90	90	90
β /deg	98.831(5)	91.32(3)	93.924(14)	102.73(3)	114.867(1)
γ /deg	90	90	90	90	90
V /Å^3	3206.3(1)	2729.1(9)	3124(3)	8231(3)	7991.4(8)
Z	4	4	4	8	8
D_c /Mg m^{-3}	1.180	1.235	1.211	1.121	1.202
μ /mm^{-1}	0.297	0.340	0.304	0.242	0.252
max, min trans.	0.995, 0.968	0.97, 0.95	0.959, 0.952	0.942, 0.929	0.7464, 0.6786
index ranges,	0 to 14,	−15 to 15,	−10 to 10,	−41 to 40,	−40 to 36,
h,k,l	0 to 15,	0 to 31,	0 to 25,	0 to 18,	0 to 16,
	−33 to 33	0 to 16	0 to 22	0 to 29	0 to 28
θ /deg	1.8 to 27.5	1.8 to 30.5	1.5 to 26.7	1.7 to 29.6	1.7 to 27.5
T /K	173(2)	100(2)	100(2)	100(2)	100(2)
F(000)	1224	1088	1216	2960	3088
reflns collected	7708	26059	77092	203516	80120
reflns independent [R_{int}]	7708 [0.04]	8335 [0.051]	6633 [0.094]	11545 [0.0749]	9162 [0.0840]
data/rest./par.	7708/0/343	8335/0/316	6606/0/361	11514/0/451	9162/0/479
GOF on F^2	1.009	0.9674	0.8625	1.035	1.087
final R indices	$R_1 = 0.087$	$R_1 = 0.056$	$R_1 = 0.056$	$R_1 = 0.099$	$R = 0.050$
[$I > 2\sigma(I)$]	$wR_2 = 0.101$	$wR_2 = 0.141$	$wR_2 = 0.127$	$wR_2 = 0.230$	$wR2 = 0.133$
R indices (all data)	$R_1 = 0.087$	$R_1 = 0.082$	$R_1 = 0.083$	$R_1 = 0.123$	$R = 0.079$
	$wR_2 = 0.101$	$wR_2 = 0.161$	$wR_2 = 0.155$	$wR_2 = 0.237$	$wR2 = 0.148$
Larg. res. peak /e. Å^{-3}	1.071 and −0.876	0.83 and −0.87	0.60 and −0.76	0.79 and −1.21	0.457 and −0.536

every 3 min for a period of up to 30 min. The concentration of the reaction product was plotted against time, and the conversion curve was line-fitted to a first-order exponential decay $Ae^{-x/b}$. The initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for $x = 0$. A plot of the initial rate versus titanium concentration indicated a linear relationship, from which the rate coefficient was obtained from the slope of the graph as 1.9×10^{-3} s^{-1}.

To a solution of [Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH═CPh}] (**4a**) (5.9 mg, 10 μmol) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in toluene-d8 (0.5 mL) was added 0.5−4 equiv of *tert*-butylamine (5 to 40 μmol). The mixture was transferred to a J. Young NMR tube and then to an NMR spectrometer. ^{1}H NMR spectra were recorded every 3 min for a period of up to 30 min. The concentration of the reaction product was plotted against time, and the conversion curve was line-fitted to a first-order exponential decay $Ae^{-x/b}$. The initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for $x = 0$. A plot of the initial rate versus amine concentration indicated a linear relationship.

A solution of [Ti($N_2^{Xyl}N_{py}$){κ^2-N(^{t}Bu)CH═CPh}] (**4a**) (5−25 μmol) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in toluene-d_8 (0.5 mL) was transferred to a J. Young NMR tube. After the sample was cooled to 0 °C, 20 equiv of *tert*-butylamine (0.1−0.5 mmol) was added. The tube was transferred to an NMR spectrometer probe that had been precooled to 0 °C. ^{1}H NMR spectra were recorded every 3 min for a period of up to 30 min. The concentration of the reaction product was plotted against time, and the conversion curve was line-fitted to a first-order exponential decay $Ae^{-x/b}$. The initial rate was estimated from $-A/b$, derived from differentiation of the fitted line for $x = 0$. A plot of the initial rate versus titanium concentration indicated a linear relationship, from which the rate coefficient was obtained from the slope of the graph as 1.1×10^{-3} s^{-1}.

Catalytic Hydroamination of Phenylacetylene with *tert*-Butylamine. To a solution of [Ti(N^tBu)($N_2^{Ar}N_{py}$)(py)] (**3a** and **3c**) (10 μmol, 0.5−10 mol %) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in C_6D_6 (0.5 mL) was added 10−500 equiv of *tert*-butylamine (0.1 to 5 mmol). The mixture was transferred to a J. Young NMR tube and then to an NMR spectrometer. ^{1}H NMR spectra were recorded at 1 h intervals for up to 48 h.

To a solution of [Ti(N^tBu)($N_2^{Ar}N_{py}$)(py)] (**3a** and **3c**) (10 μmol, 10 mol %) and 1,4-dimethoxybenzene (3.0 mg, internal standard) in C_6D_6 (0.5 mL) was added 10 equiv of *tert*-butylamine (0.1 mmol). The mixture was transferred to a J. Young NMR tube and then to an NMR spectrometer probe that had been preheated to 50 °C. ^{1}H NMR spectra were recorded at 1 h intervals for up to 24 h.

Crystal Structure Determinations Suitable crystals of **2a**, **2b**, **3c**, **5b**, and **5d** were obtained from saturated solutions at 0 °C. Intensity data were collected at low temperature on a Bruker AXS Smart 1000 CCD (**2b**, **3d**, **5b**, **5d**) or a Enraf-Nonius Kappa-CCD (**2a**) diffractometer. The structures were solved using direct methods with absorption corrections being applied as part of the data scaling procedure.[53] After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms. They were introduced as fixed contributors in the structure factor calculations and treated with a riding model, with isotropic temperature factors but not refined. A final difference map revealed no significant maxima of residual electron density. Structure solution and refinement were performed by using the programs SIR,[54] SHELXS-86,[55] SHELXL-97,[56] or CRYSTALS.[57] The crystal of **5b** was found to possess a disordered molecule of diethyl ether. Various models were em-

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ployed to model this molecule, of which none adequately fitted the electron density. Therefore it was removed and the corresponding electron density was modeled with SQUEEZE[58] in the advanced mode, with the A and B parts of the structure factors being passed back to CRYSTALS for inclusion in F_c, rather than being removed from F_o. Crystal data and experimental details are provided in Table 3.

Computational Details

All calculations were performed using the Gaussian 03 program.[59] All calculated structures were optimized without geometry constraints, with each optimization being followed by a frequency calculation (for quantum mechanical calculations) to confirm the nature of the located extrema (minimum or transition state). Where possible, molecular parameters of optimized structures were compared to available X-ray data and exhibited no significant differences. For ONIOM calculations involving the $N_2^{Xyl}N_{py}$ ligand, the apical methyl group and the aryl methyl groups were calculated at the UFF level, with the remainder of the molecule calculated with the B3PW91 method, in which the metal, the coordinated atoms, and the alkyne C≡C fragment were modeled with the 6-311G(d,p) basis set, with the remainder of the atoms modeled with the 6-31G basis set.

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Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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