

Insertions into Azatitanacyclobutenes: New Insights into Three-Component Coupling Reactions Involving Imidotitanium Intermediates

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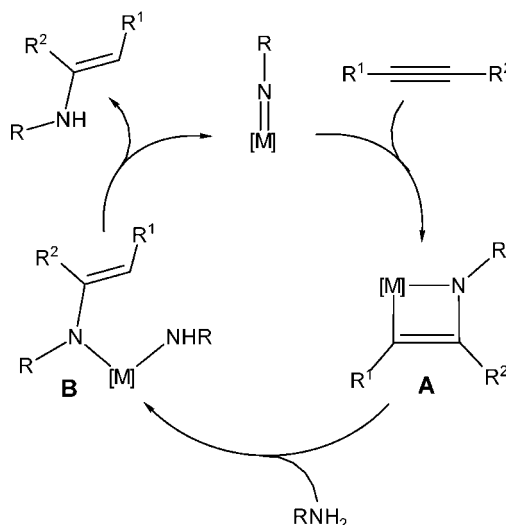
Reaction of the titanium imido complexes $[\text{Ti}(\text{NR})(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})(\text{L})]$ ($\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}} = \text{MeC}(2\text{-C}_5\text{H}_4\text{N})\{\text{CH}_2\text{N}(3,5\text{-C}_6\text{H}_3\text{Me}_2)\}_2$) with aryl acetylenes afforded the $\{2+2\}$ cycloaddition products $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{Bu})\text{CH}=\text{C}(\text{Ar})\}]$ ($\text{Ar} = \text{Ph}$: **1a**, Tol : **1b** ($\text{Tol} = 4\text{-C}_6\text{H}_4\text{Me}$)). Complex **1a** was found to insert sulfur and selenium atoms into the Ti–C bond of the strained azatitanacyclobutene unit to give the five-membered metallacyclic systems $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(t\text{Bu})\text{CH}=\text{C}(\text{Ph})\text{E}\}]$ ($\text{E} = \text{S}$: **2**, Se : **3**). Likewise, isonitriles were found to insert into the Ti–C bonds to give $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{Bu})\text{CH}=\text{C}(\text{Ar})\text{C}=\text{NR}\}]$ ($\text{Ar} = \text{Ph}$, $\text{R} = \text{xylyl}$: **4**, Cy : **5**, $t\text{Bu}$: **6a**; $\text{Ar} = \text{C}_6\text{H}_5\text{Me}$, $\text{R} = t\text{Bu}$: **6b**), one example of which (**4**) has been characterized by X-ray crystallography. The latter species is thought to be a key intermediate in the titanium-mediated three-component coupling of primary amines with acetylenes and isonitriles (“iminoamination”). Reaction of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{Bu})\text{CH}=\text{C}(\text{Ph})\text{C}=\text{NR}\}]$ with $t\text{BuNH}_2$ gave $t\text{BuN}=\text{CHC}(\text{Ph})\text{CHNHR}$, which have been previously identified as the major reaction products in the catalytic aminoamination of alkynes.

Introduction

Azametallacyclobutenes of the Group 4 elements are key intermediates in a range of stoichiometric and catalytic C–N and C–C coupling reactions mediated by these metals.^{1,2} The most intensely studied catalytic transformation involving such species is the hydroamination of alkynes.^{3–8} The azametallacycles have been identified as the $\{2+2\}$ cycloaddition products of Ti or Zr imidocomplexes with alkynes, the key step of this catalytic cycle (Scheme 1).

Scheme 1. Catalytic Cycle for the Group 4 Metal Catalyzed Hydroamination of Alkynes Originally Proposed by Bergman et al.

Catalytic hydroamination of alkynes:



The four-membered metallaheterocycle **A** is able to react further with the primary amine, opening up to give an enamido

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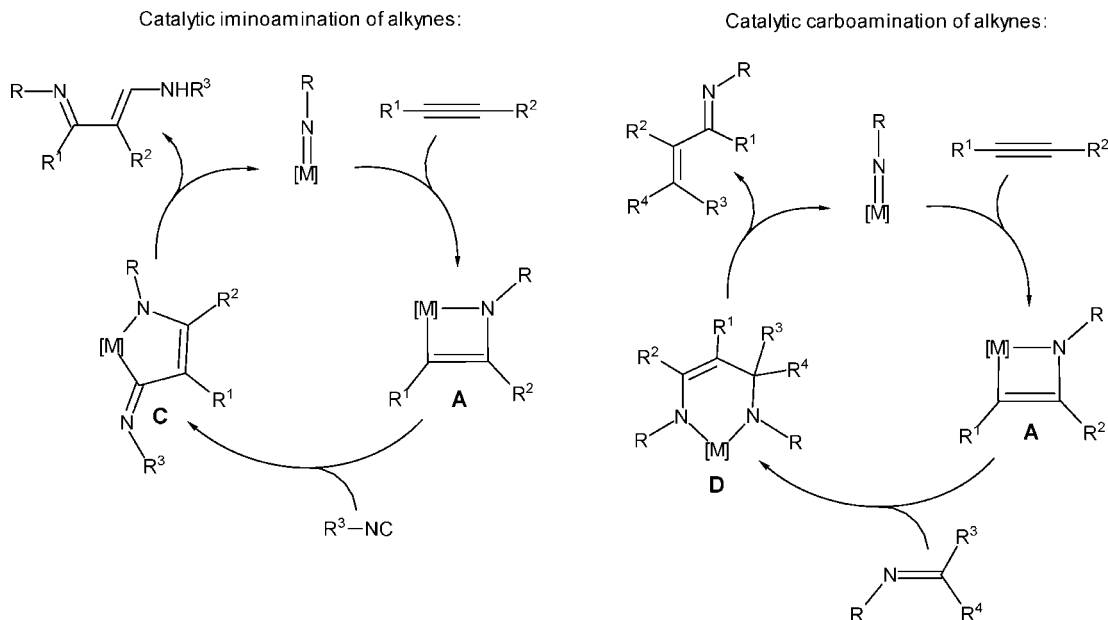
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Scheme 2. Catalytic Cycle of the Iminoamination (left) and the Carboamination (right) of Alkynes. In the final step aminolysis with R-NH₂ occurs (not shown)

complex **B**, which rapidly eliminates the enamine to regenerate the active imido catalyst. Alternatively, insertion of a third, unsaturated substrate such as an isocyanide into the reactive M–C bond has been thought to give a metallapentacycle **C**, which has been postulated as an intermediate in the Ti-catalyzed iminoamination of alkynes reported by Odom et al. (Scheme 2).⁹ A similar M–C insertion of an imine has been invoked by Bergman and co-workers for the Zr-catalyzed carboamination of alkynes with imines,¹⁰ a process extended to Ti-imides in Mindiola's group (Scheme 2).¹¹

We introduced a tridentate diamido-pyridyl ligand [N₂R^{N_{py}}]²⁻ as a supporting ligand to early transition metal chemistry,¹² a system that has been particularly suitable for the stabilization of complexes containing reactive M=N bonds.^{13,14} We recently reported the preparation and characterization of azatitanacyclobutene complexes supported by this ligand system.¹⁵ Using the N-arylated derivatives [N₂Ar^{N_{py}}]²⁻ as ancillary ligands, we

were able to demonstrate that such azatitanacyclobutenes act as hydroamination catalysts, which allowed a detailed mechanistic investigation of this process.¹⁶ The possibility to isolate such species has led us to investigate their reactivity, in particular with regard to insertions into the Ti–C bond. Starting with an analysis of the bonding in these azatitanacyclobutenes, we report in this work on the insertion of chalcogenide atoms as well as isocyanides, the latter leading to the hitherto elusive intermediate **C** in the Ti-catalyzed iminoamination of alkynes.

Results and Discussion

Determination and Description of the Molecular Structures of the Azatitanacyclobutenes [Ti(N₂^{Xyl}N_{py}){κ²-N(*t*Bu)-CH=CPh}] (1a) and [Ti(N₂^{Xyl}N_{py}){κ²-N(*t*Bu)CH=C*Tol*}] (1b). The synthesis and spectroscopic characterization of azatitanacyclobutenes [Ti(N₂^{Xyl}N_{py}){κ²-N(*t*Bu)CH=CAr}] (Ar = Ph: **1a**, Tol: **1b**) have been previously described,¹⁶ and both have been shown to be key intermediates in the catalytic hydroamination of arylalkynes, which was chosen as the test reaction. A first indication of the reactivity of their Ti–C bonds was the insertion of a second equivalent of alkyne, leading to azatitanacyclohexadienes. In order to analyze the structure and bonding in **1a** and **1b** and the potential reactive behavior that might result from it, single-crystal X-ray structure analyses of both complexes have been carried out. These were thought to provide the structural point of reference for subsequent theoretical modeling of the bonding in the metallacycles. Their closely related molecular structures are depicted in Figure 1a,b and confirm the previous structural proposal derived from the NMR data. Moreover, they proved to be very similar to the *N*-trimethylsilylated derivative previously characterized by X-ray diffraction.¹⁵ Selected bond lengths and angles are listed in Table 1.

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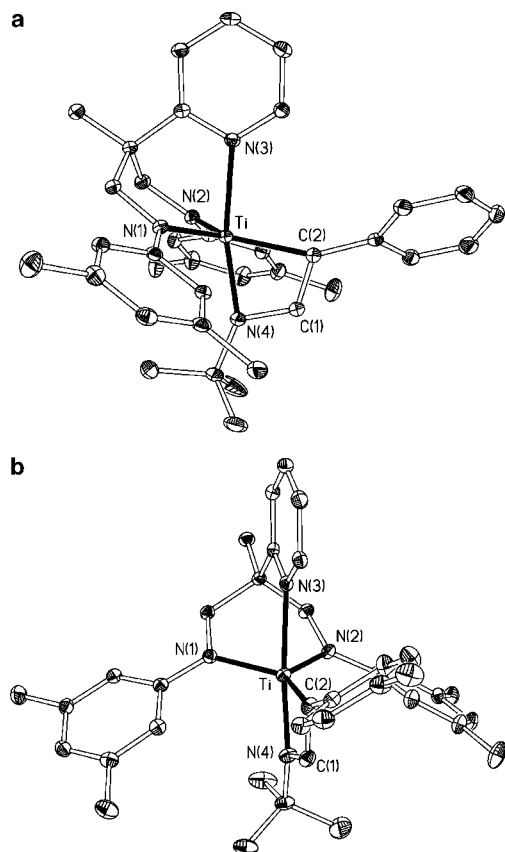


Figure 1. (a) Molecular structure of $[\text{Ti}(\text{N}_2^{\text{XylNpy}})\{\kappa^2\text{-N}'(\text{Bu})\text{CH}=\text{CPh}\}]$ (**1a**). (b) Molecular structure of $[\text{Ti}(\text{N}_2^{\text{XylNpy}})\{\kappa^2\text{-N}'(\text{Bu})\text{CH}=\text{CTol}\}]$ (**1b**). Thermal ellipsoids are drawn at 30% probability. A comparative listing of selected bond lengths and angles of both structures is provided in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ti}(\text{N}_2^{\text{XylNpy}})\{\kappa^2\text{-N}'(\text{Bu})\text{CH}=\text{CAr}'\}]$ ($\text{Ar}' = \text{Ph: 1a, 4-C}_6\text{H}_4\text{Me: 1b}$)

	1a	1b
Ti–N(1)	1.912(2)	1.960(2)
Ti–N(2)	1.930(2)	1.923(2)
Ti–N(3)	2.231(2)	2.232(2)
Ti–N(4)	1.943(2)	1.929(2)
Ti–C(2)	2.091(2)	2.097(2)
C(1)–C(2)	1.370(3)	1.363(3)
C(1)–N(4)	1.380(3)	1.393(2)
N(1)–Ti–N(2)	103.66(7)	102.84(7)
N(1)–Ti–N(3)	82.90(7)	83.40(6)
N(1)–Ti–N(4)	105.36(8)	105.85(7)
N(1)–Ti–C(2)	127.21(8)	128.35(7)
N(2)–Ti–N(3)	82.87(7)	83.64(6)
N(2)–Ti–N(4)	103.73(8)	104.64(7)
N(2)–Ti–C(2)	128.83(8)	128.38(8)
N(3)–Ti–N(4)	167.53(7)	165.47(6)
N(3)–Ti–C(2)	96.80(7)	94.85(7)
N(4)–Ti–C(2)	70.80(8)	70.63(7)
Ti–C(2)–C(1)	82.6(1)	83.9(1)
C(2)–C(1)–N(4)	116.7(2)	115.6(2)
C(1)–N(4)–Ti	88.2(1)	89.8(1)

The titanium atom in both structures adopts a pentacoordinate coordination geometry in which the diamidopyridyl ligand is facially bound to the central metal atom, which itself occupies a corner of the four-membered titanacycle. The bond length between the two carbon atoms C(1)–C(2) of the titanacycle is 1.370(3) Å for **1a** (1.363(3) for **1b**), which is consistent with a C=C double bond. On the other hand, the Ti–C(2) (**1a**: 2.091(2), **1b**: 2.079(2) Å) and Ti–N(4) (**1a**:

1.943(2); **1b**: 1.929(2) Å) distances indicate sp^2 -type single bonds to the metal center.

DFT Study of Compound 1a. In order to obtain insight into the properties of the azametallacyclobutenes, compound **1a** was theoretically modeled using the DFT computational B3PW91 method with a 6.31G(d) basis set.^{17–20} Of particular interest were the molecular orbitals (Cartesian (MO) as well as natural linear molecular orbitals (NLMO)), involved in the C(2)–C(1)–N(4) π -system of the azametallacyclobutene unit.²⁰ The chemical interpretation of the Cartesian molecular orbitals (CMOs) is limited by the symmetry-imposed delocalization, while NLMOs provide a more localized picture and interpretability of the bonding. The semilocalized character of the NLMO offers direct insight into the nature of the “delocalization tails”. The MO orbitals contributing to the π -system (HOMO, HOMO–2, HOMO–12) are depicted in Figure 2, and an alternative representation of the π -bonding is provided by the NLMO orbitals NLMO_{HOMO–15}, NLMO_{HOMO–12}, and NLMO_{HOMO–2}. Furthermore, selected NPA charges of the Ti-bonded ligands and the metallacycle are also provided. The Cartesian molecular orbitals MO_{HOMO–12}, MO_{HOMO–2}, and MO_{HOMO} depict the π -bonding, nonbonding, and π C(2)–C(1)/ π^* C(1)–N(4) situation between C(2)–C(1)–N(4) atoms, respectively. It is evident that the Ti–C(2)–C(1)–N(4) cycle is adequately described as containing a C(2)–C(1) double bond and an amido-type N(4) atom. In addition, the NLMO analysis indicates significant delocalization of the lone electron pair of N(4) into the titanium atom (ca. 10%), which is consistent with amide π -donation.¹⁶

Martins et al. have reported a combined experimental and theoretical (DFT) study of the insertion of isocyanides into titanium–carbon and titanium–nitrogen bonds in $[\text{Ti}(\eta^5\text{-Ind})(\text{NMe}_2)_2\text{Me}]$ and related complexes in which neither the Ti–C nor the Ti–N bonds are part of strained structural units.²¹ Not unexpectedly, they found a clear preference of the insertion into the Ti–C bond over insertion into the Ti–N bond, a consequence of the difference in bond strength of the Ti–CH₃ and Ti–NR₂ bonds. NLMO analysis of complex **1a** has established a Ti–N bond ($E_{\text{NLMO}(\sigma(\text{Ti}-\text{N}(4)))} = -10.3$ eV) that is more stable than the Ti–C bond ($E_{\text{NLMO}(\sigma(\text{Ti}-\text{C}(1)))} = -8.4$ eV)

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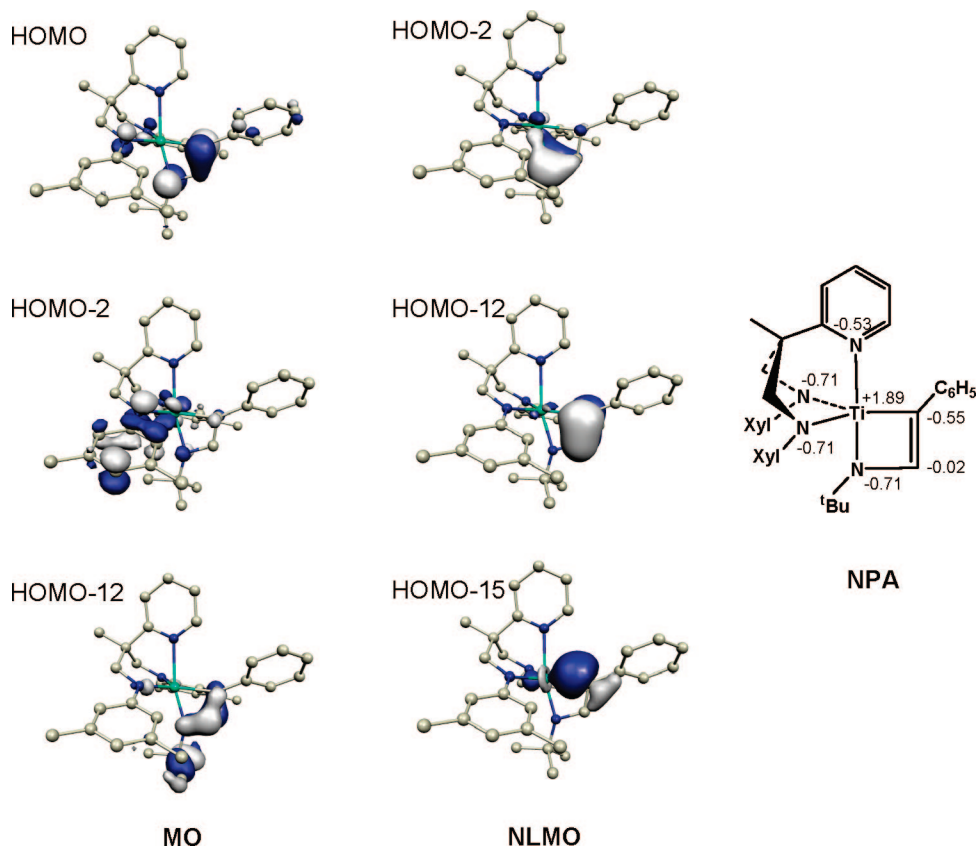


Figure 2. Molecular Kohn–Sham orbitals involved in the π -system of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{CPh}\}]$ (**1a**) (left column) displayed along with an NLMO analysis (middle column). Selected NPA charges are shown in the line drawing on the right.

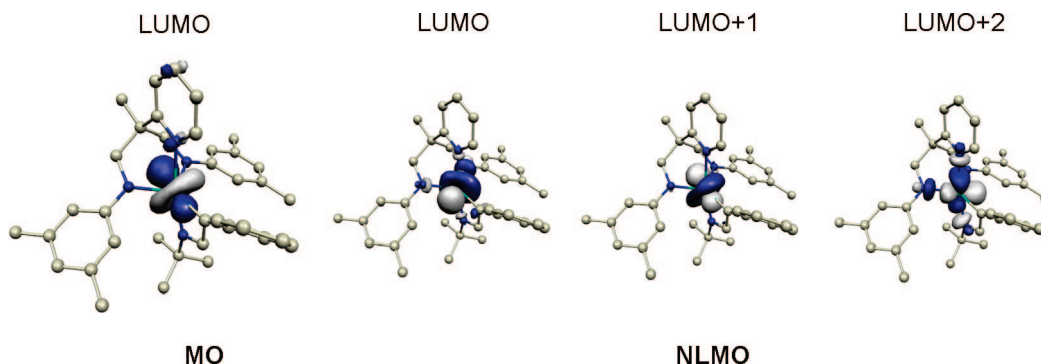


Figure 3. Lowest unoccupied Kohn–Sham molecular orbital (left). The corresponding LUMO, LUMO+1, and LUMO+2 NLMO orbitals (right).

in the metallacycle, thus leading us to anticipate similar reactivity to the system referred to above.

Since the Cartesian and NLMO-LUMO orbitals are mainly located on the titanium atom (Figure 3), it is reasonable to assume that the inserting reagent first coordinates to the Ti atom, giving a six-coordinate intermediate (or five-coordinate if the pyridyl unit dissociates). Subsequently, the lower stability of the σ_{NLMO} orbital representing the equatorial Ti–C(2) bond ($E = -8.4$ eV) compared to the σ_{NLMO} (Ti(1)–N(4)) bond ($E = -10.3$ eV) in the axial coordination site would explain the observed selectivity (*vide infra*).

Insertion of Chalcogen Atoms into Azatitanacyclobutene Compound 1a. Reaction of the azatitanacyclobutene complex $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{CPh}\}]$ (**1a**) with 1 molar equiv of

the chalcogen atom transfer reagent propylene sulfide^{13,22h} or triphenylphosphine selenide^{13,23h} gave the complexes $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{C}(\text{Ph})\text{E}\}]$ (E = S: **2**, Se: **3**) (Scheme 3).

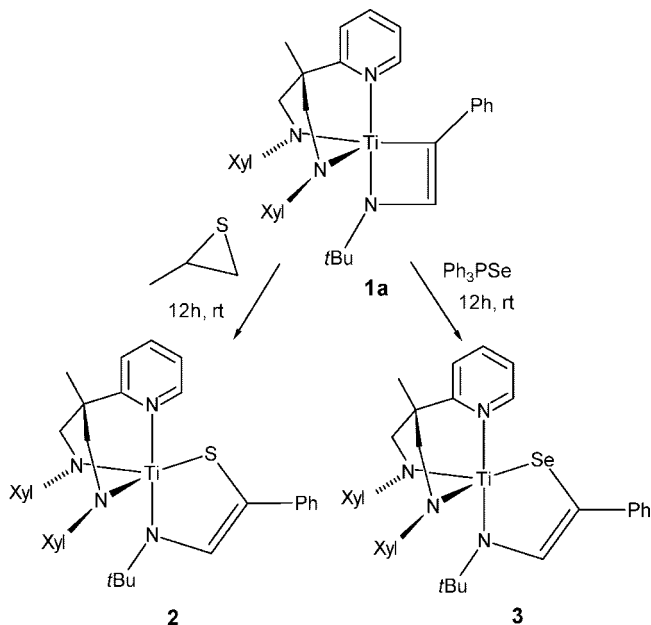
The conversion was monitored by ^1H NMR spectroscopy, which indicated the formation of new titanium species, com-

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Scheme 3. Reaction of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})]\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{CPh}\}$ (1a**) with Chalcogen-Atom Donors to Give Products **2** and **3**.**



pounds **2** and **3**, in both reactions as well as the concomitant generation of the byproduct propene and triphenylphosphine, respectively. Upon removal of the organic volatiles from the reaction with propylene sulfide *in vacuo*, $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})]\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{C}(\text{Ph})\text{S}\}$ (**2**) was isolated in quantitative yield. The analytically pure selenacyclic complex $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})]\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{C}(\text{Ph})\text{Se}\}$ (**3**) was obtained through recrystallization from a concentrated toluene solution at 10 °C.

The NMR data of complexes **2** and **3** are consistent with the overall molecular C_s symmetry of the complexes depicted in Scheme 3. A methyne proton is observed as a singlet at 7.5 for **2** and 7.7 ppm for **3** and thus at significantly higher field than the corresponding signal in the azatitanacyclobutene complex **1a** (10.0 ppm). On the other hand, the signal of the H^6 pyridyl proton of the $\text{N}_2\text{N}_{\text{py}}$ ligand is observed at lower field (10.1 ppm for **2**, 9.8 for **3** compared to 9.2 for **1a**), which is consistent with the pyridyl unit remaining coordinated to the Lewis acidic Ti center. The $^1\text{H}-^1\text{H}$ NOESY NMR spectra of **2** and **3** indicate that the *tert*-butyl resonance is in close proximity to the xyl groups of the $\text{N}_2\text{N}_{\text{py}}$ ligand, while the *ortho*-phenyl proton has moved away from H^6 . The NMR data are thus consistent with an S and Se insertion into the $\text{Ti}-\text{C}$ bond.

Single-crystal X-ray structure analyses of both complexes **2** and **3** confirm the structural proposals derived from the NMR data. Their molecular structures are depicted in Figures 4 and 5, respectively, along with the principal bond lengths and angles. The titanium atom is pentacoordinate with the diamidopyridyl-supporting ligand adopting facial tricoordination. The thia and selenacyclic metallacycles incorporating the metal centers deviate slightly from planarity. The $\text{C}(1)-\text{C}(2)$ distance (1.351(2) Å for **2** and 1.352(2) Å for **3**) is consistent with there being a double bond between these two carbon atoms in the metallacycles, while the $\text{Ti}-\text{N}(4)$ bond length indicates sp^2 -type single bonding to the metal center. The $\text{Ti}-\text{S}$, $\text{Ti}-\text{Se}$, $\text{C}-\text{S}$, and $\text{Se}-\text{C}$ bond lengths were in the expected ranges on comparison with the Cambridge Structural Database ($\text{Ti}-\text{S}$: 2.191–2.983 Å for 366 examples; $\text{Ti}-\text{Se}$: 2.369–2.796 Å, mean 2.569 Å for 36 examples; $\text{C}-\text{S}$: 1.218–2.178 Å for 12 736 examples; $\text{Se}-\text{C}$: 1.695–2.174 Å, mean 1.891 Å for 711 examples).²⁴

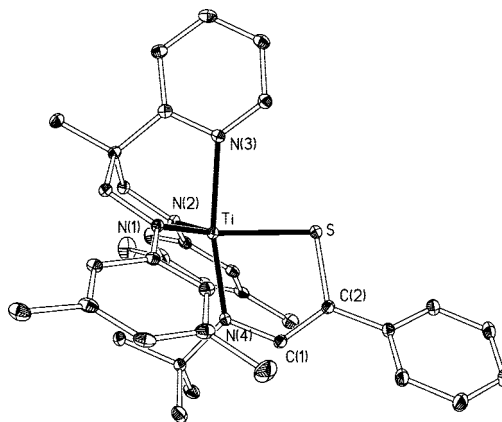


Figure 4. Molecular structure of complex **2**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): $\text{Ti}-\text{S}$ 2.3796(6), $\text{Ti}-\text{N}(1)$ 1.9136(14), $\text{Ti}-\text{N}(2)$ 1.9223(14), $\text{Ti}-\text{N}(3)$ 2.2355(15), $\text{Ti}-\text{N}(4)$ 2.0019(15), $\text{S}-\text{C}(2)$ 1.7521(18), $\text{C}(2)-\text{C}(1)$ 1.351(2), $\text{C}(1)-\text{N}(4)$ 1.378(2), $\text{N}(1)-\text{Ti}-\text{S}$ 126.44(5), $\text{N}(1)-\text{Ti}-\text{N}(2)$ 109.51(6), $\text{N}(1)-\text{Ti}-\text{N}(3)$ 85.29(6), $\text{N}(1)-\text{Ti}-\text{N}(4)$ 98.41(6), $\text{N}(2)-\text{Ti}-\text{S}$ 122.34(5), $\text{N}(2)-\text{Ti}-\text{N}(3)$ 85.53(6), $\text{N}(2)-\text{Ti}-\text{N}(4)$ 104.00(6), $\text{N}(3)-\text{Ti}-\text{S}$ 86.17(4), $\text{N}(3)-\text{Ti}-\text{N}(4)$ 167.78(6), $\text{N}(4)-\text{Ti}-\text{S}$ 82.27(4).

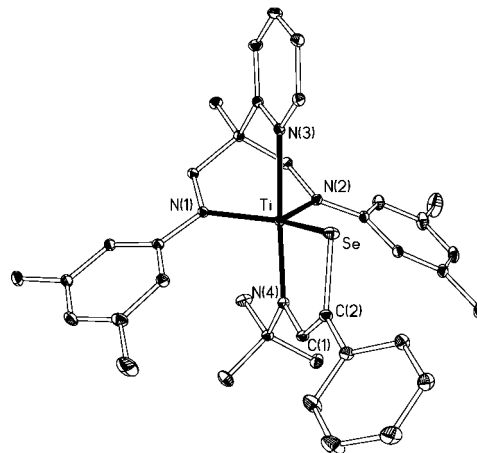


Figure 5. Molecular structure of complex **3**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): $\text{Ti}-\text{Se}$ 2.5019(4), $\text{Ti}-\text{N}(1)$ 1.9148(13), $\text{Ti}-\text{N}(2)$ 1.9265(13), $\text{Ti}-\text{N}(3)$ 2.2524(14), $\text{Ti}-\text{N}(4)$ 2.0077(13), $\text{Se}-\text{C}(2)$ 1.8986(16), $\text{C}(2)-\text{C}(1)$ 1.352(2), $\text{C}(1)-\text{N}(4)$ 1.3810(19), $\text{N}(1)-\text{Ti}-\text{Se}$ 126.27(4), $\text{N}(1)-\text{Ti}-\text{N}(2)$ 109.86(5), $\text{N}(1)-\text{Ti}-\text{N}(3)$ 85.22(5), $\text{N}(1)-\text{Ti}-\text{N}(4)$ 98.92(5), $\text{N}(2)-\text{Ti}-\text{Se}$ 121.82(4), $\text{N}(2)-\text{Ti}-\text{N}(3)$ 85.09(5), $\text{N}(2)-\text{Ti}-\text{N}(4)$ 103.99(5), $\text{N}(3)-\text{Ti}-\text{Se}$ 85.47(3), $\text{N}(3)-\text{Ti}-\text{N}(4)$ 167.87(5), $\text{N}(4)-\text{Ti}-\text{Se}$ 82.89(4).

Insertion of Isocyanides into Azatitanacyclobutene Complexes **1a and **1b**.** Treatment of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})]\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{C}(\text{Ar})\}$ (Ar = Ph: **1a** or Tol: **1b**) with 1 molar equiv of CNR (R = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$, Cy, and tBu), at room temperature selectively gave the complexes $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})]\{\kappa^2\text{-N}(\text{tBu})\text{CH}=\text{C}(\text{Ar})\text{C}=\text{N}(\text{R})\}$ (Ar = Ph, R = 2,6- $\text{C}_6\text{H}_3\text{Me}_2$ (**4**), R = Cy (**5**), or R = tBu (**6a**); Ar = Tol, R = tBu (**6b**)) in quantitative yields (Scheme 4).

The NMR data of the resulting complexes are consistent with an insertion of the RNC group into the $\text{Ti}-\text{C}$ bond similar to the chalcogen atom insertion described above as well as the previously observed insertion of a second alkyne. In the ^1H NMR spectra of **4–6a,b** the metallacyclic CH proton resonance is observed between 8.76 and 9.07 ppm. ^1H NOESY spectra established its position *between* the $\text{N}(\text{tBu})$ group and the C-Ph

Scheme 4. Reaction of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{C}(\text{Ar})\}]$ **1a** ($\text{Ar} = \text{Ph}$) and **1b** ($\text{Ar} = \text{Tol}$) with Isonitriles to Give Products $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})=\text{CHC}(\text{Ar})=\text{CNR}\}]$ ($\text{Ar} = \text{Ph}$) **4** ($\text{R} = 2,6\text{-C}_6\text{H}_3\text{Me}_2$), **5** ($\text{R} = \text{Cy}$), or **6a** ($\text{R} = \text{'Bu}$) and ($\text{Ar} = \text{Tol}$) **6b** ($\text{R} = \text{'Bu}$)

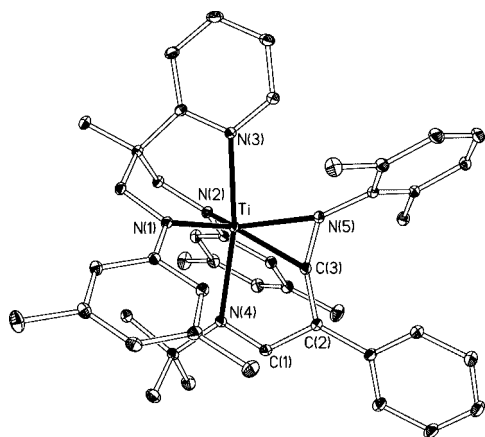
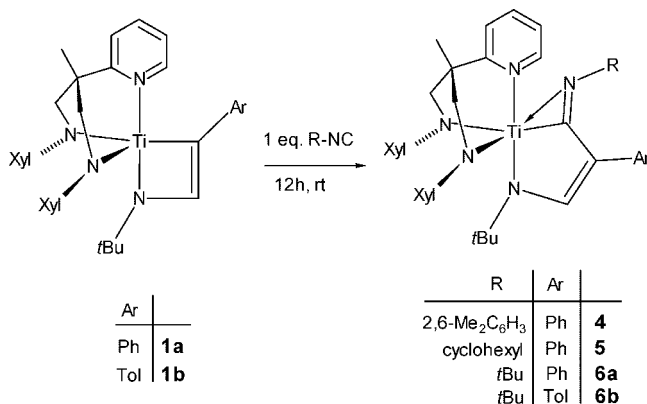


Figure 6. Molecular structure of complex **4**. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ti–N(1) 1.9521(8), Ti–N(2) 1.9550(8), Ti–N(3) 2.2737(8), Ti–N(4) 2.3455(8), Ti–N(5) 2.1399(8), Ti–C(3) 2.0185(9), N(5)–C(3) 1.2916(11), C(3)–C(2) 1.3816(12), C(2)–C(1) 1.4314(13), C(1)–N(4) 1.3101(12), N(1)–Ti–N(2) 104.28(3), N(1)–Ti–N(3) 82.74(3), N(1)–Ti–N(4) 91.47(3), N(1)–Ti–N(5) 124.05(3), N(1)–Ti–C(3) 125.63(3), N(2)–Ti–N(3) 81.83(3), N(2)–Ti–N(4) 90.56(3), N(2)–Ti–N(5) 127.25(3), N(2)–Ti–C(3) 125.91(3), N(3)–Ti–N(4) 168.96(3), N(3)–Ti–N(5) 84.40(3), N(3)–Ti–C(3) 120.39(3), N(4)–Ti–N(5) 106.61(3), N(4)–Ti–C(3) 70.59, N(5)–Ti–C(3) 36.04(3), C(3)–N(5)–Ti 66.85(5), N(5)–C(3)–Ti 77.11(5), N(5)–C(3)–C(2) 153.96(9), C(3)–C(2)–C(1) 107.12(8), C(2)–C(1)–N(4) 121.72(8), C(1)–N(4)–Ti 111.59(6), C(2)–C(3)–Ti 128.93(7).

group and thus proved the regiochemistry of the insertion indicated in Scheme 4. Moreover, the NOE cross-peaks between the signals of the isocyanide substituent R and the resonances of the C-Ph group as well as the H⁶ pyridyl proton of the ancillary ligand is explained by the orientation of the metallacycle represented in Scheme 4. Finally, the characteristic ¹H NMR chemical shift of the H⁶ proton of the pyridyl donor of the N₂N_{py} ligand is observed between 9.00 and 9.31 ppm, indicating the coordination of the pyridyl donor to the metal center.

Additional proof of the connectivity in the metallacycles has been obtained by an X-ray crystallographic study of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{C}(\text{Ph})\text{C}=\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (**4**). Its molecular structure is depicted in Figure 6 along with the principal bond lengths and angles. The establishment of the structural details allowed

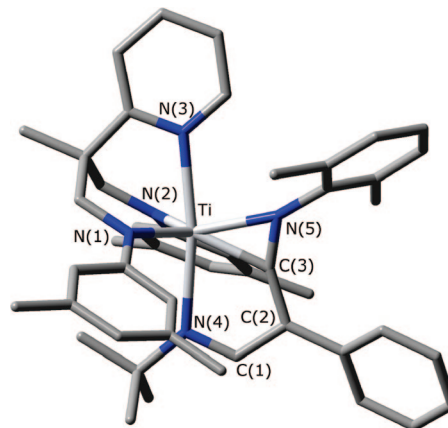


Figure 7. Optimized structure of complex **4**. (DFT calculation with B3PW91 functional and 6-31G(d) basis set for all atoms.)

closer inspection of the bonding situation in the metallacyclic insertion product, which proved to be particularly interesting. The N(4)–C(1) and N(5)–C(3) distances of 1.310(1) and 1.292(1) Å, respectively, indicate substantial C=N double-bond character, likewise with the C(2)–C(3) bond length of 1.382(1) Å. This, along with the C(2)–C(3)–N(5) angle of 153.96(9)°, renders this unit to some extent an η^2 -bonded heteroallene (iminoketene). Notable is also the C(1)–C(2) distance of 1.431(1) Å, which also indicates some multiple-bond character (bond order of ca. 1.5 due to conjugation of the adjacent double bonds, *vide infra*). The Ti–C(3) and Ti–N(5) distances of 2.0185(9) and 2.1399(8) Å lie in the range of alkyl–Ti and amido–Ti single bonds, whereas the Ti–N(4) bond length of 2.3455(8) Å is in the range for an N-donor–acceptor interaction of a ligand with the metal center as also observed for the pyridyl bonding of the ancillary ligand in the trans axial position [Ti–N(3) 2.2737(8) Å].¹³

DFT Study of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{C}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (4**).** The metric parameters of the coupled organometallic fragment ligated to the Ti center discussed in the previous section raised the question of the overall bonding situation and the interpretation of the resulting bond lengths. Similar to the chosen approach for complex **1a**, the insertion product $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{C}(\text{Ph})\text{C}=\text{N}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (**4**) has been modeled by DFT methods using the B3PW91 functional and a 6-31G(d) basis set for all atoms.^{17–19} The optimized structure of complex **4** represented in Figure 7 is in good agreement with the experimental X-ray data, as is shown in Table 2 for selected bond lengths and angles.

The average difference of the calculated and experimental Ti–N and Ti–C bond lengths is less than 0.02 Å, with the exception of the axial pyridyl N(3)–Ti distance, for which the calculated and experimental values deviate by 0.049 Å, which we have noticed in previous modeling studies of related systems. The excellent agreement between theory and experiment for the $\kappa^2\text{-N}(\text{'Bu})\text{CHC}(\text{Ph})\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ fragment of complex **4** (deviations of <0.003 Å, well within typical error limits for X-ray crystallographic analyses) allowed a closer inspection of its bonding.

Since the physical (particularly magnetic) properties of complex **4** are consistent with a formal oxidation state of Ti^{IV} for the central atom, the $\kappa^2\text{-N}(\text{'Bu})\text{CHC}(\text{Ph})\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ unit is supposed to be formally dianionic. However, as for many other organometallic complexes such formal oxidation states do not necessarily reflect the partial charges calculated for the respective atoms or molecular fragments. The entire N('Bu)CH-

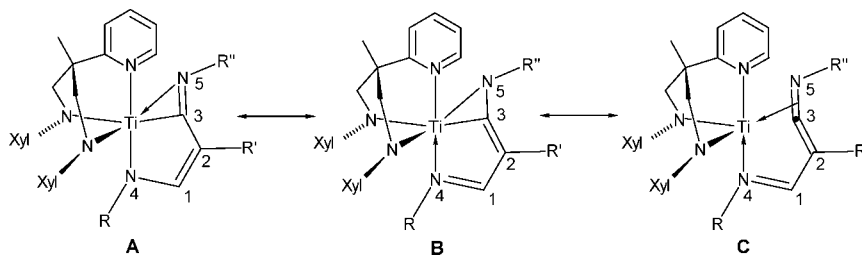


Figure 8. Resonance structures describing the bonding situation in $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})=\text{CHC}(\text{Ph})=\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (**4**).

Table 2. Selected Experimental and Theoretical Angles (deg) and Distances (Å) for Compounds **1a** and **4**

	1a		4	
	exptl	calcd	exptl	calcd
$d(\text{Ti}-\text{N}(1))$	1.912	1.941	1.952	1.940
$d(\text{Ti}-\text{N}(2))$	1.930	1.953	1.955	1.958
$d(\text{Ti}-\text{N}(3))$	2.231	2.275	2.274	2.323
$d(\text{Ti}-\text{N}(4))$	1.943	1.942	2.346	2.358
$d(\text{Ti}-\text{C}(2))$	2.091	2.069	$d(\text{Ti}-\text{N}(5))$	2.140
$d(\text{N}(4)-\text{C}(1))$	1.380	1.382	$d(\text{Ti}-\text{C}(3))$	2.019
$d(\text{C}(1)-\text{C}(2))$	1.370	1.375		1.310
				1.431
			$d(\text{C}(2)-\text{C}(3))$	1.382
			$d(\text{C}(3)-\text{N}(5))$	1.292
$\alpha(\text{N}(1)-\text{Ti}-\text{N}(2))$	103.7	104.1		1.294
$\alpha(\text{N}(4)-\text{C}(1)-\text{C}(2))$	116.7	116.8	$\alpha(\text{C}(2)-\text{C}(3)-\text{N}(5))$	104.3
				154.0
				153.4

$\text{C}(\text{Ph})\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ fragment is planar, suggesting a highly delocalized π -system spread across the five atoms. It is instructive to begin an analysis of the data in terms of the limiting resonance structures **A–C** depicted in Figure 8.

Given the way in which complex **4** was formed, i.e., as an insertion product of an isocyanide and an azatitanacyclobutene, resonance structure **A** appears reasonable. However, the bond length pattern described above, with short $\text{C}(2)-\text{C}(3)$ and $\text{N}(4)-\text{C}(1)$ as well as a longer $\text{C}(1)-\text{C}(2)$ distances, does not agree with this resonance form. The alternative resonance structure **B** appears to reflect the metric parameters better, as does the formulation of the side-on bound cumulene unit in resonance form **C**. The latter, however, implies the formulation of $\text{N}(\text{'Bu})\text{CHC}(\text{Ph})\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ as a neutral fragment and thus the Ti center as formally divalent. A natural population analysis (NPA) performed for **4** established the partial charge pattern represented in Figure 9.

Notable is the low partial charge at titanium, which may be explained by the high degree of covalency of the metal–ligand bonding in this complex and, in particular, the alternating charge distribution pattern in $\text{N}(\text{'Bu})\text{CHC}(\text{Ph})\text{CNR}$, with the highest electron density being located in the middle ($\text{C}(2)$) and at extreme ends ($\text{N}(4)$, $\text{N}(5)$) of the chain. This is very similar to the charge distribution in a pentadienyl monoanion, and this analogy is also apparent in an analysis of the conjugated π -system in the metallacyclic fragment.

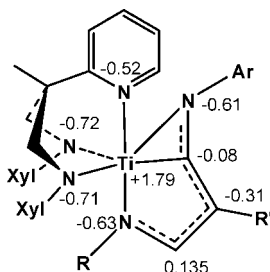


Figure 9. Selected NPA charges in $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})\{\kappa^2\text{-N}(\text{'Bu})=\text{CHC}(\text{Ph})=\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)\}]$ (**4**).

In Figure 10 an orbital analysis of the π -bonding in the pentadienide reference system (column a) as well as the metallacyclic unit (columns b and c) is provided. An all in-phase conjugated π -bonding of the NC_3N fragment is evident in HOMO–20, whereas HOMO–14 clearly represents the π -bonding interaction between $\text{N}(5)-\text{C}(3)$ and $\text{N}(4)-\text{C}(1)$. The HOMO itself represents the third nonbonding combination (with some constructive overlap reinforcing the $\text{C}(2)-\text{C}(3)$ bond). Calculation of the Wiberg indices, which provide a semiquantitative measure of the bond multiplicity,²⁵ for the bonds within this fragment revealed a higher bond order between the atoms $\text{C}(2)-\text{C}(3)$ (1.35) than between carbons $\text{C}(1)-\text{C}(2)$ (1.21), while the bond orders between $\text{N}-\text{C}$ atoms are significantly greater than unity (1.50 and 1.60) (Table 3).

Three-Component Coupling to Generate α,β -Unsaturated β -Iminoamines. Compounds **4–6a,b** are models for the key intermediate of the catalytic cycle for the three-component coupling of alkynes, isocyanides, and amines to generate α,β -unsaturated β -iminoamines, which has been reported by Odom and co-workers.⁹ In order to determine whether compounds **4–6a** reported in this work do in fact display the reactivity postulated for this type of intermediate, we investigated their reaction with *tert*-butylamine (Scheme 5).

Compounds **4–6a** were reacted with 2 molar equiv of *tert*-butylamine at room temperature to give a titanium imido species along with the respective three-component iminoamination coupling products **7a–c**. This reaction represents the final step in the catalytic cycle. The ^1H NMR spectra of the reaction mixture showed the characteristic signals from the previously described titanium imido complex stabilized by *tert*-butylamine $[\text{Ti}(\text{N}(\text{'Bu})\text{N}_2^{\text{Xyl}}\text{N}_{\text{py}})(\text{NH}_2\text{'Bu})]$ (**8**).¹⁶ After filtration through silica, the crude reaction mixtures were analyzed by GC-MS, HR-MS, and NMR spectroscopy. For each reaction, the three-component coupling products have been identified as sole reaction products according to high-resolution mass spectrometry.

Attempts to develop the sequence of stoichiometric reactions described in this work into a catalytic process failed. We

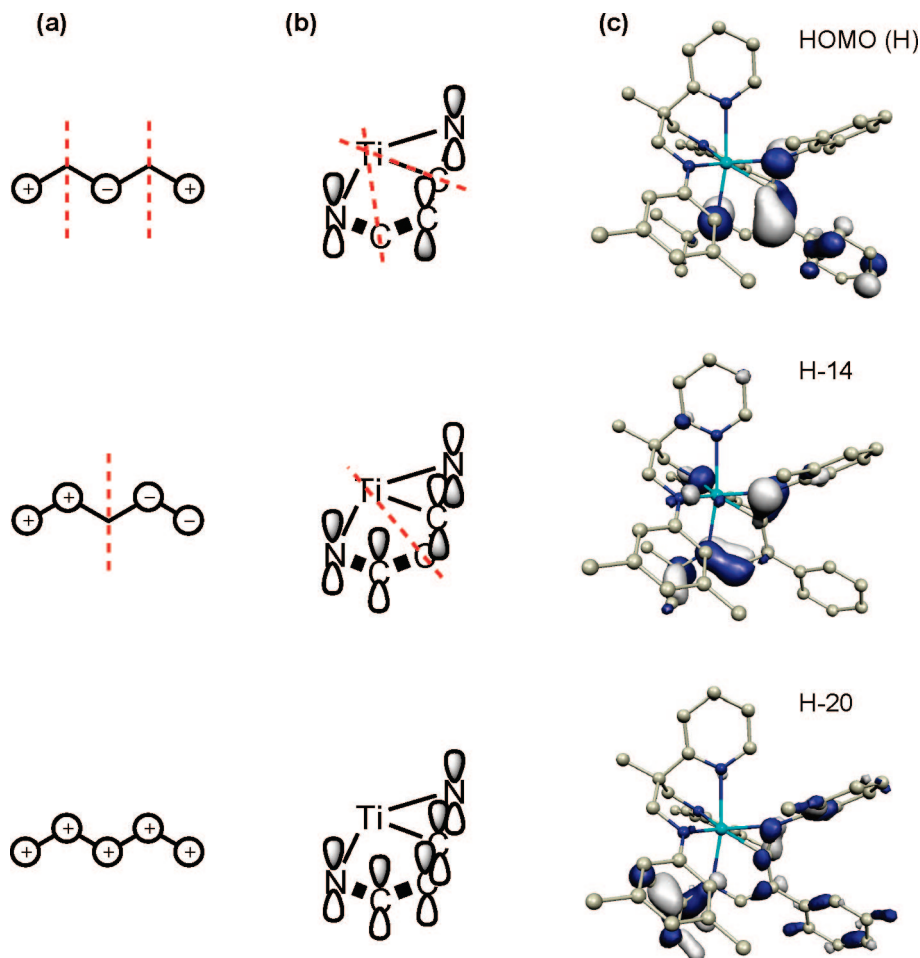


Figure 10. Schematic π orbitals in $\text{CH}_2(\text{CH})_3\text{CH}_2$ and in the $\text{Ti}-\kappa^2\text{-N}(\text{'Bu})=\text{CHC}(\text{Ph})=\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ fragment of complex **4** (columns a and b, respectively). Molecular orbitals of complex **4** involving the π -system in the $\kappa^2\text{-N}(\text{'Bu})=\text{CHC}(\text{Ph})=\text{CN}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ fragment are presented in column c.

Table 3. Bond Orders (WI)^a and Bond Lengths of the π -System $\text{N}(\text{'Bu})\text{CH}=\text{C}(2,6\text{-C}_6\text{H}_3\text{Me}_2)$ in Complex **4**

	N(4)–C(1)	C(1)–C(2)	C(2)–C(3)	C(3)–N(5)
WI	1.50	1.21	1.35	1.60
<i>d</i> (Å)	1.294	1.432	1.384	1.309

^a The Wiberg indices (WI) are used as a measure of the bond order.²⁵

tentatively attribute this to the more rapid imido–isocyanide coupling as compared to the essential {2+2} cycloaddition of the imide with the alkyne. We have studied such rapid (multiple) reactions with isonitriles previously in some detail for a closely related imidotitanium complex.^{13a,13b} However, in the case at hand, we were unable to identify such products unambiguously.

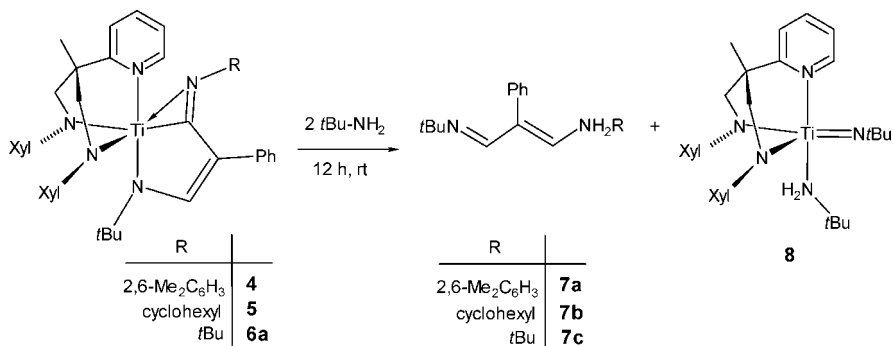
Conclusion

The stable azatitanacyclobutene complexes **1a** and **1b** have been shown to readily undergo Ti–C bond insertion reactions. This has allowed us to synthesize and fully characterize the intermediates of the three-component iminoamination of alkynes to give α,β -unsaturated β -iminoamines. Furthermore, a DFT study has provided some insight into the bonding in a previously postulated but unobserved key intermediate of this process along with the qualitative rationalization of the observed Ti–C selectivity in the insertion reaction step converting compounds **1a** and **1b** to **2–6a,b**.

Experimental Section

General Experimental Procedures. 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. Toluene was dried over sodium, distilled, and degassed prior to use. C_6D_6 was dried over potassium, vacuum distilled, and stored in Teflon valve ampules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. ^1H , ^{13}C , ^{15}N , and ^{77}Se spectra were recorded on Bruker Avance 200, 400, and 600 NMR spectrometers and were referenced using the residual protio solvent (^1H) or solvent (^{13}C) resonances or externally to $^{15}\text{NH}_3$ and $^{77}\text{SeMe}_2$. Mass spectra and elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department. The azametallacyclobutenes $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{Npy})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{CAr}'\}]$ ($\text{Ar}' = \text{Ph}$: **1a** 4- $\text{C}_6\text{H}_4\text{Me}$: **1b**) were prepared according to published procedures.¹⁶ All other reagents were obtained from commercial sources and used as received unless explicitly stated otherwise.

Preparation of the Compounds. $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{Npy})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{C}(\text{Ph})\text{S}\}]$ (**2**). To a solution of $[\text{Ti}(\text{N}_2^{\text{Xyl}}\text{Npy})\{\kappa^2\text{-N}(\text{'Bu})\text{CH}=\text{CPh}\}]$ (211 mg, 0.36 mmol) in toluene (10 mL) was added an equimolar amount of propenesulfide (28 μL , 0.36 mmol) via syringe. The resulting dark green solution was stirred overnight before removing the solvent *in vacuo* to yield the title compound as a dark green solid. Quantitative yield. Diffraction-quality single crystals were grown from a saturated toluene solution at 10 °C. ^1H NMR (C_6D_6 , 600.1 MHz, 296 K): δ 1.10 (3 H, s, Me of N_2Npy), 1.17 (9 H, s, CMe_3), 2.19 (12 H, s, $\text{C}_6\text{H}_3\text{Me}_2$), 3.13 (2 H, d, CHH , $^3J = 12.6$

Scheme 5. Formation of α,β -Unsaturated β -Iminoamines (R = Cy, 2,6-C₆H₃Me₂, or ^tBu)

(Hz), 4.75 (2 H, d, CHH, ³J = 12.6 Hz), 6.46 (1 H, ddd, H⁵, ³J(H⁴H⁵) = 7.5 Hz, ³J(H⁶H⁵) = 5.5 Hz, ⁴J(H³H⁵) = 1.2 Hz), 6.51 (2 H, s, *p*-C₆H₃Me₂), 6.71 (1 H, d, H³, ³J = 7.6 Hz), 6.91 (1 H, td, H⁴, ³J(H³H⁴H⁵) = 7.9 Hz, ⁴J(H⁴H⁶) = 1.7 Hz), 6.94 (4 H, s, *o*-C₆H₃Me₂), 7.07 (1 H, tt, *p*-C₆H₅, ³J = 7.3 Hz, ⁴J = 1.2 Hz), 7.37 (2 H, app. t, *m*-C₆H₅, ³J = 7.4 Hz), 7.47 (1 H, s, C=CH), 8.01 (2 H, dd, *o*-C₆H₅, ³J = 8.1 Hz, ⁴J = 1.2 Hz), 10.07 (1 H, dd, H⁶, ³J(H⁵H⁶) = 5.5 Hz, ⁴J(H⁴H⁶) = 1.6 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 21.7 (C₆H₃Me₂), 25.4 (Me of N₂Npy), 31.7 (CMe₃), 42.1 [C(CH₂NXyl)₂], 62.3 (CMe₃), 62.8 [(CH₂NXyl)₂], 107.0 (C=CH), 114.7 (*o*-C₆H₃Me₂), 120.5 (C³), 123.1 (C⁵), 123.7 (*p*-C₆H₃Me₂), 123.8 (*p*-C₆H₅), 126.0 (*o*-C₆H₅), 128.5 (*m*-C₆H₅), 135.6 (C=CH), 137.9 (*m*-C₆H₃Me₂), 139.3 (C⁴), 142.3 (*ipso*-C₆H₅), 149.6 (C⁶), 153.5 (*ipso*-C₆H₃Me₂), 159.9 (C²) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 261.0 (N₂Npy), 280.4 (N₂Npy), 314.2 (N^tBu) ppm. Anal. Found (calcd) (%) for C₃₇H₄₄N₄STi: C 71.5 (71.1); H 7.1 (7.1); N 8.6 (9.0).

[Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=C(Ph)Se}] (**3**). To a solution of [Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=CPh}] (185 mg, 0.27 mmol) in toluene (10 mL) was added an equimolar amount of triphenylphosphine selenide (91 mg, 0.27 mmol). The resulting dark green solution was stirred overnight. Removing the volatiles under reduced pressure produced a dark green waxy solid, which was redissolved into toluene (5 mL). After 2 days at 10 °C, the title compound was formed as a black crystalline solid. Yield: 38 mg (21%). Diffraction-quality single crystals were grown from a saturated toluene solution at 10 °C. ¹H NMR (C₆D₆, 600.1 MHz, 296 K): δ 1.09 (3 H, s, Me of N₂Npy), 1.14 (9 H, s, CMe₃), 2.21 (12 H, s, C₆H₃Me₂), 3.12 (2 H, d, CHH, ³J = 12.5 Hz), 3.71 (2 H, d, CHH, ³J = 12.5 Hz), 6.41 (1 H, ddd, H⁵, ³J(H⁴H⁵) = 7.2 Hz, ³J(H⁶H⁵) = 5.6 Hz, ⁴J(H³H⁵) = 1.2 Hz), 6.53 (2 H, s, *p*-C₆H₃Me₂), 6.71 (1 H, d, H³, ³J = 7.9 Hz), 6.90 (1 H, td, H⁴, ³J(H³H⁴H⁵) = 7.8 Hz, ⁴J(H⁴H⁶) = 1.6 Hz), 7.03 (5 H, m, *o*-C₆H₃Me₂ and *p*-C₆H₅), 7.34 (2 H, app. t, *m*-C₆H₅, ³J = 7.5 Hz), 7.71 (1 H, s, C=CH), 7.99 (2 H, app. d, *o*-C₆H₅, ³J = 8.3 Hz), 9.85 (1 H, dd, H⁶, ³J(H⁵H⁶) = 5.5 Hz, ⁴J(H⁴H⁶) = 1.2 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 21.7 (C₆H₃Me₂), 25.7 (Me of N₂Npy), 31.8 (CMe₃), 41.9 [C(CH₂NXyl)₂], 62.5 (CMe₃), 62.7 [(CH₂NXyl)₂], 104.2 (C=CH), 114.4 (*o*-C₆H₃Me₂), 120.3 (C³), 122.8 (C⁵), 123.7 (*p*-C₆H₃Me₂), 123.9 (*p*-C₆H₅), 126.4 (*o*-C₆H₅), 128.4 (*m*-C₆H₅), 137.6 (*m*-C₆H₃Me₂), 138.0 (C=CH), 138.9 (C⁴), 143.4 (*ipso*-C₆H₅), 150.1 (C⁶), 152.7 (*ipso*-C₆H₃Me₂), 159.7 (C²) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 265.1 (N₂Npy), 281.0 (N₂Npy), 314.2 (N^tBu) ppm. ⁷⁷Se NMR (76 MHz, C₆D₆, 296 K): δ 926.2 ppm. Anal. Found (calcd) (%) for C₃₇H₄₄N₄SeTi (+C₇H₈): C 68.8 (69.2); H 6.8 (6.9); N 7.3 (7.3).

[Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=C(Ph)C=N(2,6-C₆H₃Me₂)}] (**4**). To a solution of [Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=CPh}] (229 mg, 0.39 mmol) in toluene (10 mL) was added an equimolar amount of 2,6-dimethylphenyl isocyanide (50 mg, 0.39 mmol). The resulting dark red solution was stirred overnight before removing the solvent *in vacuo* to yield the title compound as a brown solid. Quantitative yield. Diffraction-quality single crystals were grown from a

saturated toluene solution at 10 °C. ¹H NMR (C₆D₆, 600.1 MHz, 296 K): δ 1.01 (9 H, s, CMe₃), 1.27 (3 H, s, Me of N₂Npy), 2.15 (6 H, s, 2,6-C₆H₃Me₂), 2.21 (12 H, s, C₆H₃Me₂), 3.22 (2 H, d, CHH, ³J = 12.7 Hz), 3.76 (2 H, d, CHH, ³J = 12.7 Hz), 6.35 (1 H, ddd, H⁵, ³J(H⁴H⁵) = 7.4 Hz, ³J(H⁶H⁵) = 5.5 Hz, ⁴J(H³H⁵) = 1.2 Hz), 6.41 (4 H, s, *o*-C₆H₃Me₂), 6.44 (2 H, s, *p*-C₆H₃Me₂), 6.84 (1 H, d, H³, ³J = 7.9 Hz), 6.90 (1 H, app. t, *p*-C₆H₅), 7.94 (1 H, td, H⁴, ³J(H³H⁴H⁵) = 7.6 Hz, ⁴J(H⁴H⁶) = 1.6 Hz), 7.05 (3 H, m, 2,6-C₆H₃Me₂), 7.13 (2 H, app. t, *m*-C₆H₅, ³J = 7.8 Hz), 7.18 (2 H, dd, *o*-C₆H₅, ³J = 8.3 Hz, ⁴J = 1.1 Hz), 9.07 (1 H, s, N=CH), 9.31 (1 H, dd, H⁶, ³J(H⁵H⁶) = 5.5 Hz, ⁴J(H⁴H⁶) = 1.6 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 19.1 (2,6-C₆H₃Me₂), 21.6 (C₆H₃Me₂), 24.7 (Me of N₂Npy), 31.6 (CMe₃), 43.3 [C(CH₂NXyl)₂], 57.4 (CMe₃), 61.7 [(CH₂NXyl)₂], 93.7 (C-CH), 112.3 (*o*-C₆H₃Me₂), 119.1 (C³), 120.7 (*p*-C₆H₃Me₂), 122.1 (C⁵), 122.8 (*p*-C₆H₅), 124.2 (*o*-C₆H₅), 125.0 (*o/p*-2,6-C₆H₃Me₂), 128.5 (*m*-C₆H₅), 128.6 (*o/p*-2,6-C₆H₃Me₂), 132.7 (*m*-2,6-C₆H₃Me₂), 137.5 (*m*-C₆H₃Me₂), 137.6 (*ipso*-C₆H₅), 138.2 (C⁴), 148.3 (*ipso*-2,6-C₆H₃Me₂), 149.0 (C⁶), 153.5 (*ipso*-C₆H₃Me₂), 162.0 (C²), 175.8 (C-CH), 199.2 (C-N) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 193.8 (CNC₆H₃Me₂), 252.6 (N₂Npy), 259.8 (N^tBu), 290.3 (N₂Npy) ppm. Anal. Found (calcd) (%) for C₄₆H₅₃N₅Ti (+C₇H₈): C 77.8 (78.0); H 7.7 (7.5); N 8.7 (8.6).

[Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=C(Ph)C=N(Cy)}] (**5**). To a solution of [Ti(N₂^{Xyl}Npy){κ²-N(^tBu)CH=CPh}] (215 mg, 0.36 mmol) in toluene (10 mL) was added an equimolar amount of cyclohexyl isocyanide (45 μL, 0.36 mmol) via syringe. The resulting dark green solution was stirred overnight before removing the solvent *in vacuo* to yield the title compound as a brown solid. Quantitative yield. ¹H NMR (C₆D₆, 600.1 MHz, 296 K): δ 0.90 (1 H, m, *p*-C₆H₁₁), 1.01 (2 H, m, obscured by CMe₃, *m*-C₆H₁₁), 1.02 (9 H, s, CMe₃), 1.29 (3 H, s, Me of N₂Npy), 1.33 (1 H, app. d, *p*-C₆H₁₁, ³J = 11.7 Hz), 1.49 (2 H, app. d, *m*-C₆H₁₁, ³J = 13.5 Hz), 1.64 (2 H, app. dq, *o*-C₆H₁₁), 2.04 (2 H, app. d, *o*-C₆H₁₁, ³J = 12.5 Hz), 2.25 (12 H, s, C₆H₃Me₂), 3.24 (2 H, d, CHH, ³J = 12.6 Hz), 3.71 (2 H, d, CHH, ³J = 12.6 Hz), 3.86 (1 H, app. tt, *isopropyl*-C₆H₁₁), 6.38 (4 H, s, *o*-C₆H₃Me₂), 6.45 (2 H, s, *p*-C₆H₃Me₂), 6.69 (1 H, ddd, H⁵, ³J(H⁴H⁵) = 7.4 Hz, ³J(H⁶H⁵) = 5.5 Hz, ⁴J(H³H⁵) = 1.2 Hz), 6.93 (1 H, d, H³, ³J = 7.9 Hz), 7.12 (2 H, m, H⁴ and *p*-C₆H₅), 7.39 (2 H, app. t, *m*-C₆H₅, ³J = 7.7 Hz), 7.68 (2 H, dd, *o*-C₆H₅, ³J = 8.2 Hz, ⁴J = 1.2 Hz), 8.82 (1 H, s, N=CH), 9.27 (1 H, dd, H⁶, ³J(H⁵H⁶) = 5.4 Hz, ⁴J(H⁴H⁶) = 1.2 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 21.7 (C₆H₃Me₂), 24.6 (Me of N₂Npy), 27.7 (*p*-C₆H₁₁), 25.9 (*m*-C₆H₁₁), 31.7 (CMe₃), 33.6 (*o*-C₆H₁₁), 43.5 [C(CH₂NXyl)₂], 57.6 (CMe₃), 61.9 [(CH₂NXyl)₂], 63.8 (*ipso*-C₆H₁₁), 95.9 (C-CH), 112.2 (*o*-C₆H₃Me₂), 119.3 (C³), 120.4 (*p*-C₆H₃Me₂), 121.2 (C⁵), 123.2 (*p*-C₆H₅), 126.4 (*o*-C₆H₅), 128.7 (*m*-C₆H₅), 137.3 (*m*-C₆H₃Me₂), 138.1 (C⁴), 140.1 (*ipso*-C₆H₅), 149.6 (C⁶), 154.2 (*ipso*-C₆H₃Me₂), 162.1 (C²), 173.6 (C-CH), 206.4 (C-N) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 212.6 (CNCy), 242.0 (N₂Npy), 254.5 (N^tBu), 291.1 (N₂Npy) ppm. Anal. Found (calcd) (%) for C₄₄H₅₅N₅Ti: C 75.4 (75.3); H 8.1 (7.9); N 9.9 (10.0).

Table 4. Details of the Crystal Structure Determinations of the Complexes 1a, 1b, 2a, 3, and 4

	1a	1b	2a	3	4
formula	C ₃₇ H ₄₄ N ₄ Ti	C ₃₈ H ₄₆ N ₄ Ti	C ₃₇ H ₄₄ N ₄ STi · 0.5C ₇ H ₈	C ₃₇ H ₄₄ N ₄ SSeTi · 0.5C ₇ H ₈	C ₅₃ H ₆₁ N ₅ Ti
cryst syst		orthorhombic		monoclinic	triclinic
space group		<i>Pbca</i>		<i>P2₁/c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	20.6472(16)	21.266(4)	11.1455(13)	11.210(1)	11.434(2)
<i>b</i> /Å	12.203(1)	12.788(2)	12.2427(15)	12.180(1)	14.483(3)
<i>c</i> /Å	25.668(2)	24.435(4)	25.737(3)	25.940(3)	14.939(3)
α /deg					95.761(4)
β /deg			97.782(2)	97.311(2)	103.409(4)
γ /deg					108.459(3)
<i>V</i> /Å ³	6467.3(9)	6645(2)	3479.5(7)	3513.0(7)	2241.9(8)
<i>Z</i>		8		4	2
<i>M_r</i>	592.66	606.69	670.79	717.69	815.97
<i>d_c</i> /Mg · m ⁻³	1.217	1.213	1.281	1.357	1.209
<i>F</i> ₀₀₀	2528	2592	1428	1500	872
μ (Mo K α) /mm ⁻¹	0.296	0.289	0.341	0.314	0.232
max., min. transmn factors	0.7464, 0.6898	0.7464, 0.6499	0.0514, 0.1128	0.6700, 0.7464	0.7464, 0.6850
range/deg	2.1 to 27.9	1.9 to 29.1	2.3 to 30.5	1.8 to 32.3	2.0 to 32.1
index ranges (indep set) <i>h,k,l</i>	−27 ... 0, 0 ... 16, −33 ... 0	−29 ... 0, 0 ... 17, −33 ... 0	−15 ... 15, 0 ... 17, 0 ... 36	−16 ... 16, 0 ... 18, 0 ... 38	−16 ... 15, −20 ... 20, 0 ... 22
no. of reflns measd	131 850	148 273	84 423	88 720	55 273
unique, <i>R</i> _{int}	7701, 0.0970	8936, 0.0992	10622, 0.0946	11743, 0.0547	14532, 0.0274
observed [<i>I</i> 2 σ (<i>I</i>)]	5369	6032	7602	8927	12817
no. of params refined	389	453	435	438	582
<i>R</i> indices [<i>F</i> > 4 σ (<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0545, 0.1411	0.0509, 0.1229	0.0514, 0.1128	0.0390, 0.1005	0.0377, 0.1081
<i>R</i> indices (all data) <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0828, 0.1549	0.0877, 0.1370	0.0824, 0.1239	0.0583, 0.1071	0.0433, 0.1127
Goof on <i>F</i> ²	1.09	1.08	1.07	1.10	1.10
largest residual peaks/e · Å ⁻³	0.429, −0.802	0.412, −0.464	0.506, −0.441	0.921, −0.510	0.560, −0.3

[Ti(N₂^{Xy}N_{py}){κ²-N'(Bu)CH=C(Ph)C=N'(Bu)}] (**6a**). To a solution of [Ti(N₂^{Xy}N_{py}){κ²-N'(Bu)CH=CPh}] (190 mg, 0.27 mmol) in toluene (10 mL) was added an equimolar amount of *tert*-butyl isocyanide (30 μL, 0.27 mmol) via syringe. The resulting dark red solution was stirred overnight before removing the solvent *in vacuo* to yield the title compound as a brown solid. Quantitative yield. ¹H NMR (C₆D₆, 600.1 MHz, 296 K): δ 1.08 (9 H, s, CMe₃), 1.25 (9 H, s, CN(CMe₃)), 1.28 (3 H, s, Me of N₂N_{py}), 2.24 (12 H, s, C₆H₃Me₂), 3.28 (2 H, d, CHH, ³*J* = 12.6 Hz), 3.65 (2 H, d, CHH, ³*J* = 12.6 Hz), 6.43 (2 H, s, *p*-C₆H₃Me₂), 6.46 (4 H, s, *o*-C₆H₃Me₂), 6.54 (1 H, ddd, H⁵, ³*J*(H⁴H⁵) = 7.4 Hz, ³*J*(H⁶H⁵) = 5.6 Hz, ⁴*J*(H³H⁵) = 1.2 Hz), 6.89 (1 H, d, H³, ³*J* = 7.9 Hz), 7.06 (1 H, td, H⁴, ³*J*(H³H⁴H⁵) = 7.7 Hz, ⁴*J*(H⁴H⁶) = 1.7 Hz), 7.11 (1 H, app. t, *p*-C₆H₅), 7.39 (2 H, app. t, *m*-C₆H₅, *J* = 7.8 Hz), 7.61 (2 H, dd, *o*-C₆H₅, ³*J* = 7.1 Hz, ⁴*J* = 1.0 Hz), 8.78 (1 H, s, N=CH), 9.00 (1 H, dd, H⁶, ³*J*(H⁵H⁶) = 5.3 Hz, ⁴*J*(H⁴H⁶) = 1.2 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 21.6 (C₆H₃Me₂), 24.6 (Me of N₂N_{py}), 30.0 (CN(CMe₃)), 31.6 (CMe₃), 43.6 [C(CH₂NXyl)₂], 57.8 (CMe₃), 61.2 (CN(CMe₃)), 61.9 [(CH₂NXyl)₂], 98.4 (C-CH), 112.3 (*o*-C₆H₃Me₂), 119.3 (C³), 120.4 (*p*-C₆H₃Me₂), 120.5 (C⁵), 123.1 (*p*-C₆H₅), 126.0 (*o*-C₆H₅), 128.7 (*m*-C₆H₅), 137.3 (*m*-C₆H₃Me₂), 137.9 (C⁴), 140.7 (*ipso*-C₆H₅), 149.1 (C⁶), 154.4 (*ipso*-C₆H₃Me₂), 161.7 (C²), 171.6 (C-CH), 211.1 (C-N) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 229.4 (CN^oBu), 238.6 (N₂N_{py}), 254.7 (N^oBu), 290.3 (N₂N_{py}) ppm. Anal. Found (calcd) (%) for C₄₂H₅₃N₅Ti: C 74.9 (74.7); H 7.7 (7.9); N 10.2 (10.4).

[Ti(N₂^{Xy}N_{py}){κ²-N'(Bu)CH=C(Tol)C=N'(Bu)}] (**6b**). To a solution of [Ti(N₂^{Xy}N_{py}){κ²-N'(Bu)CH=CTol}] (175 mg, 0.29 mmol) in toluene (10 mL) was added an equimolar amount of *tert*-butyl isocyanide (33 μL, 0.29 mmol) via syringe. The resulting dark green solution was stirred overnight before removing the solvent *in vacuo* to yield the title compound as a brown solid. Quantitative yield. ¹H NMR (C₆D₆, 600.1 MHz, 296 K): δ 1.08 (9 H, s, CMe₃), 1.26 (9 H, s, C-NCMe₃), 1.28 (3 H, s, Me of N₂N_{py}), 2.26 (12 H, s, C₆H₃Me₂), 2.28 (3 H, s, C₆H₄Me), 3.28 (2 H, d, CHH, ³*J* = 12.6 Hz), 3.66 (2 H, d, CHH, ³*J* = 12.6 Hz), 6.42 (2 H, s, *p*-C₆H₃Me₂), 6.46 (4 H, s, *o*-C₆H₃Me₂), 6.54 (1 H, ddd, H⁵, ³*J*(H⁴H⁵) = 7.4 Hz, ³*J*(H⁶H⁵) = 5.4 Hz, ⁴*J*(H³H⁵) = 1.1 Hz), 6.89 (1 H, d, H³, ³*J* = 8.0 Hz), 7.06 (1 H, td, H⁴, ³*J*(H³H⁴H⁵) = 7.7 Hz, ⁴*J*(H⁴H⁶) = 1.7 Hz), 7.20 (2 H, d, *m*-C₆H₄Me, ³*J* = 7.7 Hz),

7.54 (2 H, d, *o*-C₆H₄Me, ³*J* = 8.0 Hz), 8.76 (1 H, s, N=CH), 9.01 (1 H, dd, H⁶, ³*J*(H⁵H⁶) = 5.3 Hz, ⁴*J*(H⁴H⁶) = 1.2 Hz) ppm. ¹³C{¹H} NMR (C₆D₆, 150.9 MHz, 296 K): δ 21.2 (C₆H₄Me), 21.8 (C₆H₃Me₂), 24.8 (Me of N₂N_{py}), 30.2 (CN(CMe₃)), 31.8 (CMe₃), 43.8 [C(CH₂NXyl)₂], 57.9 (CMe₃), 61.3 (CN(CMe₃)), 62.1 [(CH₂NXyl)₂], 98.3 (C-CH), 112.5 (*o*-C₆H₃Me₂), 119.5 (C³), 120.6 (*p*-C₆H₃Me₂), 120.7 (C⁵), 125.6 (*p*-C₆H₄Me), 126.4 (*o*-C₆H₄Me), 129.7 (*m*-C₆H₄Me), 132.3 (*ipso*-C₆H₄Me), 137.4 (*m*-C₆H₃Me₂), 138.1 (C⁴), 149.3 (C⁶), 154.7 (*ipso*-C₆H₃Me₂), 161.9 (C²), 171.9 (C-CH), 210.7 (C-N) ppm. ¹⁵N{¹H} NMR (C₆D₆, 60.8 MHz, 296 K): δ 228.4 (CN^oBu), 238.1 (N₂N_{py}), 254.0 (N^oBu), 290.4 (N₂N_{py}) ppm. Anal. Found (calcd) (%) for C₄₃H₅₅N₅Ti: C 74.9 (74.9); H 8.1 (8.0); N 9.6 (10.1).

General Procedure for the Preparation of Three-Component Iminoamination Products. To a solution of [Ti(N₂^{Xy}N_{py}){κ²-N'(Bu)=CHC(Ph)=C(NR)}] (0.025 mmol) in toluene (0.5 mL) was added 2 equiv of *tert*-butylamine (0.05 mmol) via syringe. The reaction mixture was stirred overnight at room temperature, affording an orange solution, which was filtered through silica. **7a**: ¹H NMR (CD₂Cl₂, 600.1 MHz, 296 K): δ 1.39 (9 H, s, CMe₃), 2.23 (6 H, s, 2,6-C₆H₃Me₂), 6.89 (1 H, t, *p*-2,6-C₆H₃Me₂, ³*J* = 7.5 Hz), 7.06 (2 H, d, *m*-2,6-C₆H₃Me₂, ³*J* = 7.5 Hz), 7.12 (1 H, app. t, *p*-C₆H₅, ³*J* = 7.0 Hz), 7.25–7.30 (4 H, m, *o*-C₆H₅ and *m*-C₆H₅), 7.38 (1 H, d, ³*J* = 3.0 Hz), 8.10 (1 H, d, ³*J* = 3.0 Hz) 11.04 (1 H, br s, NH). ¹³C{¹H} NMR (CD₂Cl₂, 150.9 MHz, 296 K): δ 18.6 (2,6-C₆H₃Me₂), 30.1 (CMe₃), 52.0 (CMe₃), 104.3 (C_b), 122.7 (*p*-2,6-C₆H₃Me₂), 124.1 (*p*-C₆H₅), 124.9 (C₆H₅), 128.0 (*m*-2,6-C₆H₃Me₂), 128.3 (*o*-2,6-C₆H₃Me₂), 128.5 (C₆H₅), 141.4 (*ipso*-C₆H₅), 143.7, 151.8 (*ipso*-2,6-C₆H₃Me₂), 162.2. HRMS (EI): *m/z* (%) calcd for C₂₁H₂₆N₂ [M⁺] 306.2096, found: 306.2115 (100). **7b**: ¹H NMR (CD₂Cl₂, 600.1 MHz, 296 K): δ 1.30 (9 H, s, H_aNCMe₃), 1.39 (9 H, s, H_cNCMe₃), 7.26–7.37 (6 H, m, H_a and C₆H₅), 9.47 (1 H, d, H_c, ³*J* = 3.8 Hz), 10.87 (1 H, br s, NH). HRMS (EI): *m/z* (%) calcd for C₁₇H₂₆N₂ [M⁺] 258.2096, found 258.2096 (100). **7c**: ¹H NMR (CD₂Cl₂, 600.1 MHz, 296 K): δ 1.30 (9 H, s, H_aNCMe₃), 1.39 (9 H, s, H_cNCMe₃), 7.26–7.37 (6 H, m, H_a and C₆H₅), 9.47 (1 H, d, H_c, ³*J* = 3.8 Hz), 10.87 (1 H, br s, NH). HRMS (EI): *m/z* (%) calcd for C₁₉H₂₈N₂ [M⁺] 284.2252, found 284.2269 (100).

X-ray Crystal Structure Determinations. Crystal data and details of the structure determinations are listed in Table 4. Intensity data were collected at 100(2) K with a Bruker AXS

Smart 1000 CCD diffractometer (Mo K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). Data were corrected for Lorentz, polarization, and absorption effects (semiempirical, SADABS).²⁶ The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors²⁷ and refined by full-matrix least-squares methods based on F^2 .²⁸ All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms were taken from difference Fourier syntheses and refined.

Computational Methods. All the calculations have been carried out with the Gaussian 03 program.¹⁷ DFT calculations with the nonlocal hybrid B3PW91 functional and 6-31G(d) basis set for all atoms were performed. This approach is widely used for computational studies of transition metal complexes, yielding consistent results. The electronic structures were studied using natural bond orbital (NBO) analysis, with the NBO 3.0 facilities built into

Gaussian 03. In particular, linear natural molecular orbitals (NLMO) ("delocalization tails") as well as natural population analysis (NPA) (charge distribution) were determined and analyzed. As a semi-quantitative measure of the bond order, the Wiberg bond index was used. All the orbital visualizations have been obtained with GaussView¹⁹ and MOLEKEL²⁹ programs. The molecular structures were optimized starting from X-ray diffraction data. Following geometry optimization, frequency calculations were performed on all calculated structures to ensure that there were no imaginary frequencies and thus confirm their character as that of energy minima.

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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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