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Titanium-catalyzed iminohydrazination of alkynes

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Abstract

Titanium pyrrolyl complexes $Ti(NMe_2)_2(dap)_2$ (**1**), where dap is 2-(*N*,*N*-dimethylaminomethyl)pyrrolyl, and $Ti(NMe_2)_3(bap)$ (**3**), where bap is 2,5-bis(*N*,*N*-dimethylaminomethyl)pyrrolyl, were found to be effective catalysts for the iminohydrazination of alkynes, a new multicomponent coupling reaction involving an alkyne, hydrazine, and isonitrile. A brief study on the scope of the reaction suggests that it is applicable to internal and terminal alkynes, alkyl and aryl isonitriles, and alkyl- and aryl-containing 1,1-disubstituted hydrazines. The best yields were obtained with terminal alkynes and alkyl isonitriles. The regioselectivity of the reactions is quite sensitive to catalyst structure, and, in all cases, we were able to obtain one regioisomer of the iminohydrazination product with either **1** or **3** as catalyst. The conformation of the products was probed by NMR spectroscopy and DFT calculations, which suggest that the *s-cis* isomer of the hydrazone–enamine tautomer is the most favorable configuration. However, several configurations are probably accessible in solution at room temperature. Reaction of **1** with 2 equivalents of H_2NNMe_2 results in the formation of a dinuclear complex $Ti_2(dap)_3(NNMe_2)_2(NHNMe_2)$ (**4**), where one dap ligand was removed protolytically. Examination of regioselectivities in iminohydrazination reactions using **4** and mono(dap) complex $Ti(dap)(NMe_2)_3$ (**5**) are consistent with these species using the same catalytic cycle as **1**. Consequently, the active species is likely a mono(dap) titanium complex. Current mechanistic information is consistent with a hydrazido(2−) intermediate and a pathway reminiscent of the Bergman hydroamination mechanism. $Ti(NMe_2)_3(bap)$ (**3**) and $Ti_2(dap)_3(NNMe_2)_2(NHNMe_2)$ (**4**) were characterized by X-ray diffraction.

Keywords: Hydroamination; Hydrohydrazination; Iminoamination; Iminohydrazination; Titanium; Catalysis

1. Introduction

The synthesis of complex and functional group-rich organic products from simple building blocks [1] is an important goal for transition metal catalysis and is aided by multicomponent coupling reactions [2]. In this vein, we recently reported that readily available titanium complexes catalyze the 3-component coupling of an amine, isonitrile, and alkyne in a new reaction that is the formal iminoamination of an alkyne (Scheme 1). [3] The products of these reactions were tautomers of 1,3-diimines, α,β-unsaturated β-iminoamines.

Using titanium catalysts, alkynes can be hydrohydrazinated [4] (Scheme 2) with 1,1-disubstituted hydrazines, a process that generates hydrazones and indoles (after Fischer cyclization) [5,6]. This procedure recently has been elegantly expanded by Ackermann [7] and Beller [8] using alternative titanium catalysts to generate a variety of indole derivatives.

Here we report that titanium complexes will also catalyze the 3-component coupling of an isonitrile, 1,1-disubstituted hydrazine, and alkyne. The alkyne is formally iminohydrazinated during this process. The products are tautomers of 3-imino-1-hydrazones, α,β-unsaturated β-aminohydrazones, which are useful as intermediates in organic synthesis and are derivatives of the invaluable 1,3-diketone core [9]. In addition, these compounds are related to 1,3-diimines, which are

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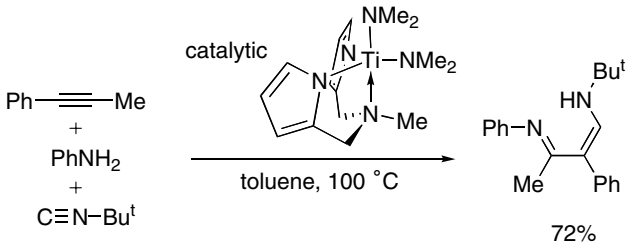
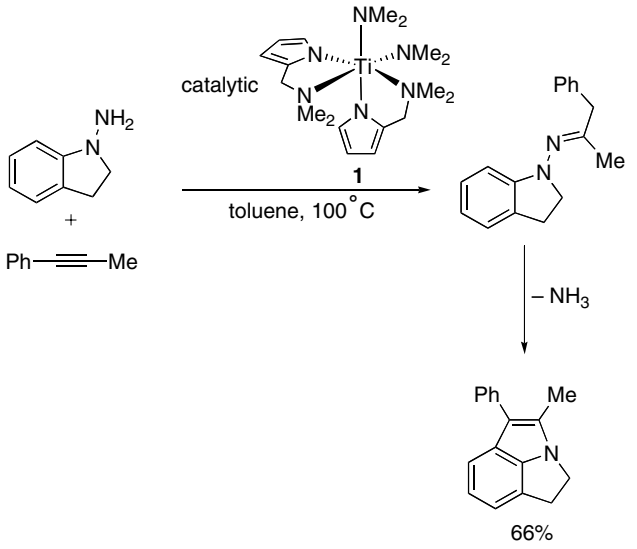


Scheme 1. Example of iminoamination catalyzed by a titanium pyrrolyl complex.



Scheme 2. Hydrohydrazination of an alkyne catalyzed by **1** and Fischer cyclization.

common ligands for metal complexes [10]. However, these unsymmetrical 1,3-iminohydrazones have not been extensively utilized, perhaps due to the multistep procedures that would ordinarily be required for their synthesis. Using the iminohydrazination methodology, these unsymmetrical compounds are available in a single, multicomponent coupling step. In addition, some preliminary explorations into the mechanism of the iminohydrazination reaction are detailed.

2. Results and discussion

2.1. Iminohydrazination results

The iminohydrazination reaction is a modification of hydrohydrazination of alkynes [5–8] catalyzed by some titanium complexes where a 1,1-disubstituted hydrazine is added to an alkyne to generate a hydrazone (Scheme 2). In a previous study, we developed two catalysts for alkyne hydrohydrazination, a titanium pyrrolyl complex $Ti(NMe_2)_2(dap)_2$ (**1**), where dap is 2-(*N*,*N*-dimethylaminomethyl)pyrrolyl, and thiolate-containing $Ti(NMe_2)_2(SC_6F_5)_2(NHMe_2)$ (**2**) (Chart 1).

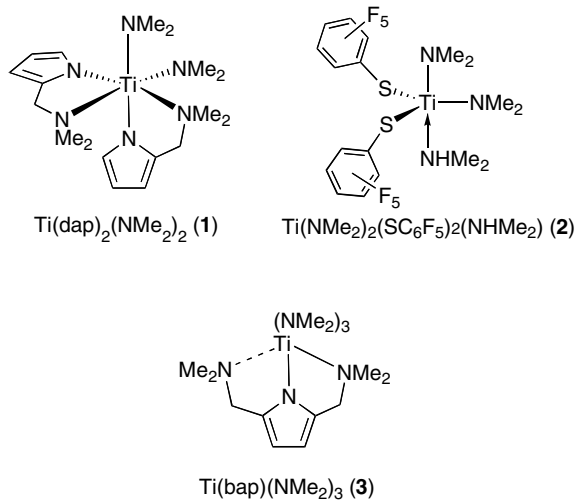


Chart 1. Examples of titanium catalysts employed in these studies.

For the current study, we also investigated the use of the pyrrolyl ancillary ligand *bis*-2,5-(*N*,*N*-dimethylaminomethyl)pyrrolyl, bap. Addition of 1 equivalent of Hbap to $Ti(NMe_2)_4$ results in the formation of $Ti(NMe_2)_3$(bap) (**3**). The two arms of the bap ligand are equivalent by NMR spectroscopy in fluid solution. However, only one arm is coordinated in the solid-state (Fig. 1). In fact, the uncoordinated amine nitrogen is 4.1 Å from titanium, and the equivalency of the two dimethylamine donors in solution is likely due to fast exchage processes. The *tris*(dimethylamido) $Ti(NMe_2)_3$(bap) (**3**) was advantageous for some substrates (vide infra). [11]

The anticipated route (Scheme 3) of the hydrohydrazination was a modification of the Bergman mechanism [12] for hydroamination [13,14] developed for zirconocene catalysis. In the presence of isonitrile, the azatitanacyclobutene [15] intermediate is trapped with C–C bond formation to generate a new 5-membered metallacycle. Protonolysis of the 4-membered metallacycle leads to the hydrohydrazination product, and protonolysis of the 5-membered metallacycle affords the iminohydrazination product.

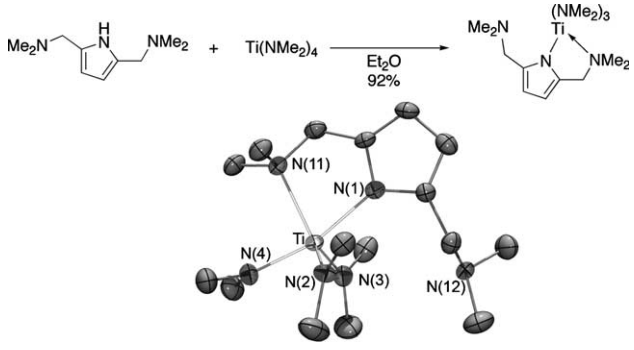
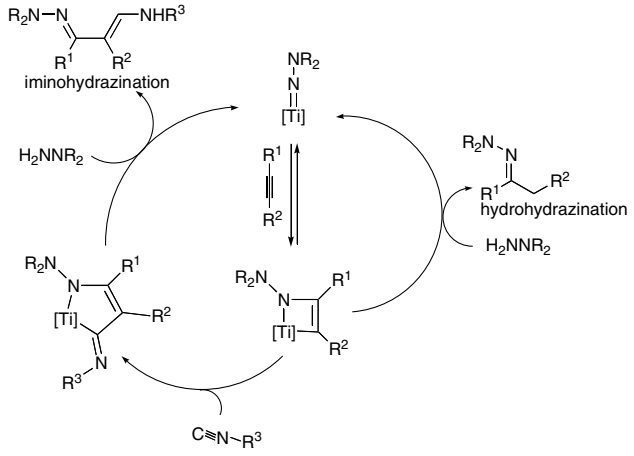


Fig. 1. Synthesis and solid-state structure of $Ti(bap)(NMe_2)_3$ (**3**) from X-ray diffraction.



Scheme 3. Titanium-catalyzed hydrohydrazination versus iminohydrazination.

Some results of the iminohydrazination study using **1** and **3** as catalysts are shown in Table 1. The reactions utilized a variety of terminal and internal alkynes, alkyl and aryl hydrazines, and alkyl and aryl isonitriles to demonstrate the scope of the catalysis. The purified yields in this fairly broad but short study varied from 12% to 73%.

In our initial studies on hydrohydrazination [5], the thiolate-based catalyst **2** was quite efficient for many different types of substrates, often exceeding the pyrrolyl-based catalyst **1** in activity for certain combinations. However, **2** was ineffective for most substrate combinations in iminohydrazination, often providing no observed products. The one combination for which **2** was effective was for that shown in Entry 5 of Table 1, which used the quite reactive phenylacetylene as substrate. However, the reaction also showed a significant amount of hydrohydrazination product making it less desirable than **3** for the same reaction. Some activity was observed with the substrates in Entry 1 involving 1-hexyne. However, the major product was one having a mass consistent with a 4-component coupling involving 2 equivalents of *tert*-butylisonitrile, 1 equivalent of 1-hexyne, and 1 equivalent of 1,1-dimethylhydrazine. The oily product seems unstable to both distillation and column chromatography; consequently, its structure is currently unknown.

Some problems observed with amine substrates were not observed with hydrazines. For example, with amine substrates the carbon adjacent to the isonitrile group was required to be quaternized for effective catalysis. [3] With hydrazines, substrates such as cyclohexylisonitrile worked quite well (Entry 2, Table 1). The major side reaction observed with amines was the production of formamidine by two-component coupling of the amine and isonitrile; we did not observe the analogous reaction with hydrazines. Hydrohydrazination is observed as a side reaction with some substrates. However, the hydrazones are readily removed from the iminohydrazination products by column chromatography or distillation. Reactions with 1,1-diphenylhydrazine resulted in quite low yields of multicomponent product, and the major product observed was diphenylamine. While reactions with 2,6-xylyl isonitrile were successful, yields were generally low with this substrate. Attempts to use acetylene as the alkyne, which was very effective in our initial hydrohydrazination studies, did not result in multicomponent coupling products with **1** as catalyst.

2.2. Studies on the conformation and tautomers of 1,3-iminohydrazones

In all of the reactions in Table 1, only one isomer is observed by NMR. (However, see Section 2.6 for some discussion of regioselectivity versus catalyst structure.) From previous studies on related tautomers and conformers [16,9c], we assumed that the conformers shown in Table 1 would be favored. The *s-cis* isomers are believed to be more favorable in most cases due to potential hydrogen bonding between the two nitrogens. From our NMR studies, the favored tautomeric form is the hydrazone–enamine.

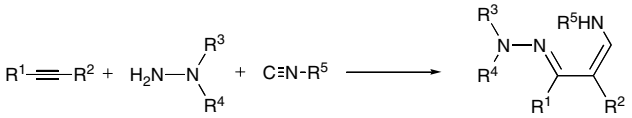
Computational studies on the product of Entry 1 in Table 1 were carried out to probe the energy differences between some of the conformers and in an attempt to confirm the *s-cis* conformer as the most stable species. To insure that the sterics of the molecule were accurately depicted, the entire molecule without truncation was used in the study. Four of the expected isomers were minimized (*s-cis* amine, *s-trans* amine, *s-cis* imine, and *s-trans* imine) with DFT(B3LYP) using the 6-31++G** basis set and local minima were found for each. The minimized conformation and calculated energy for each isomer are shown in Fig. 2.

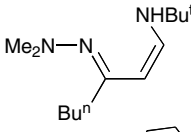
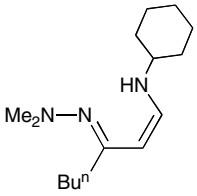
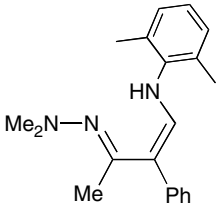
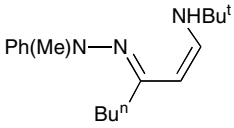
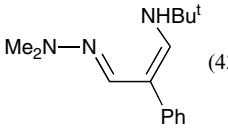
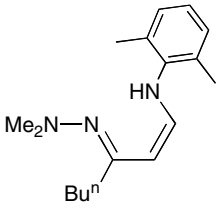
Consequently, the experimental and computational studies suggest that the *s-cis* amine isomer is preferred. While the accuracy of the energy differences calculated are unknown, the ~2 kcal/mol gap, assuming Arrhenius behavior and no entropy difference between the two molecules, would result in a solution that was ~97% *s-cis* amine. As a result, this magnitude of gap, though small, is consistent with the *s-cis* imine being the only conformer observed by NMR.

2.3. Possible 1,2-insertion mechanism

An alternative mechanism to the one shown in Scheme 1 is certainly plausible. The reaction could proceed through a route involving 1,2-insertion of the alkyne into a hydrazido(1−) intermediate (Scheme 4), a pathway extensively studied by Marks and coworkers [17]. The Marks hydroamination mechanism likely is

Table 1
Examples of alkyne iminohydrazination



Entry	R^1, R^2	R^3, R^4	R^5	Conditions[a]	product (% yield)
1	Bu^n, H	Me, Me	Bu^t	**A**,16 h	 (63)
2	Bu^n, H	Me, Me	Cy[b]	**A**, 16 h	 (73)
3	Me, Ph	Me, Me	Ar[c]	**B**, 43 h	 (14)
4	Bu^n, H	Ph, Me	Bu^t	**A**, 16 h	 (27)
5	H, Ph	Me, Me	Bu^t	**C**, 16 h	 (43)
6	Bu^n, H	Me, Me	Ar[c]	**A**, 16 h	 (12)

[a] **A** is 10 mol% **1** in toluene at 100 °C, **B** is 10 mol% **1** in toluene at 130 °C, **C** is 10 mol% **3** in toluene at 100 °C.
[b] Cy is cyclohexyl.
[c] Ar = 2,6-dimethylphenyl.

operative for some Group-4 [18], lanthanide [19], and Group-3 hydroamination catalysts [20]. If the isonitrile traps a resulting vinyl complex due to 1,1-insertion in our system, the same iminohydrazination product would result. For this mechanism, only hydrazido(1−) intermediates are required and reactions with trimethylhydrazine would be expected to give products similar to those shown in Table 1.

A reaction under the same conditions as those used in Entry 1 of Table 1 with trimethylhydrazine in place of 1,1-dimethylhydrazine was carried out, which resulted in no observed reaction (Scheme 5) when monitored by GC/FID. The inactivity of trimethylhydrazine is inconsistent with the 1,2-insertion mechanism shown in Scheme 4, which only requires access to hydrazido(1−) intermediates. This result suggests that

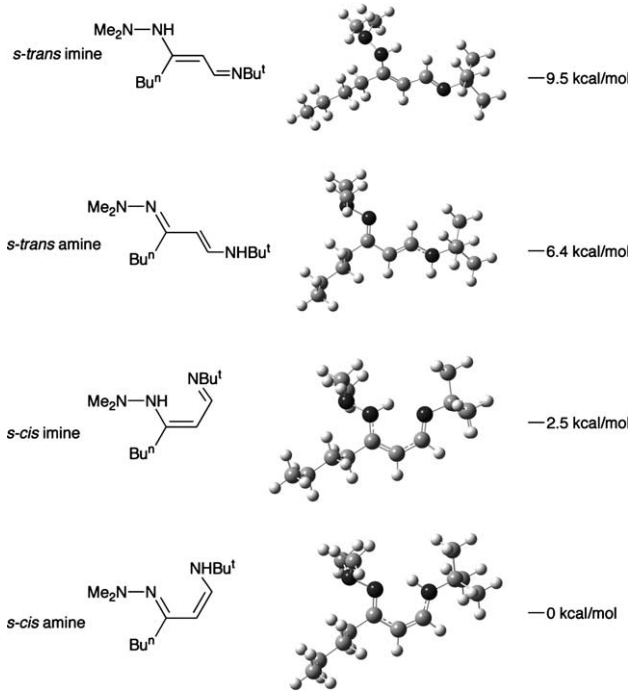
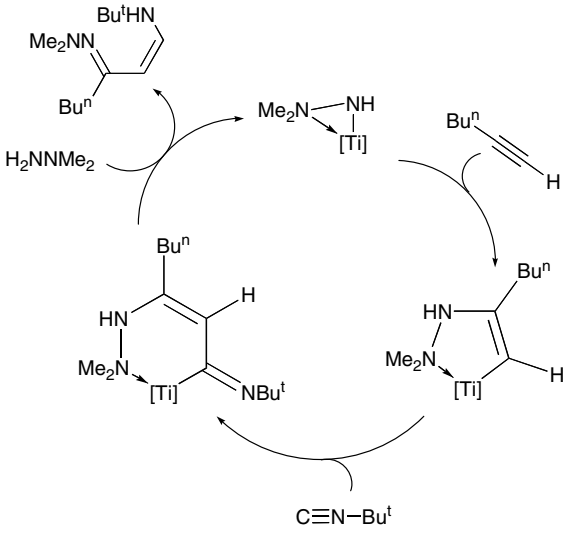


Fig. 2. Minimized conformations and energies of the product in Entry 1 of Table 1 by DFT. The energies listed are relative to the s-*cis* amine isomer, which is defined as 0 kcal/mol.

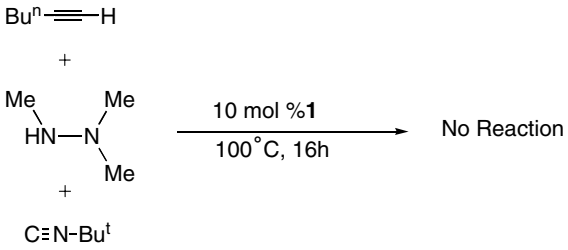


Scheme 4. Possible 1,2-insertion mechanism for iminohydrazination.

hydrazido(2−) intermediates are a requirement for the catalysis.

2.4. Reactions between $Ti(NMe_2)_2(dap)_2$ (1) and 1,1-dimethylhydrazine

The stoichiometric reaction of **1** with hydrazine was carried out in an attempt to see what may be gleaned



Scheme 5. Attempted reaction of trimethylhydrazine, 1-hexyne, and *tert*-butyl isonitrile with added **1**.

about the route of the catalysis. Treatment of **1** with 1,1-dimethylhydrazine results in the generation of a new dinuclear complex $Ti_2(dap)_3(\mu_2{:}\eta^1,\eta^2\text{-}NNMe_2)(\mu_1{:}\eta^1\text{-}NHNMe_2)$ (**4**), which has two bridging hydrazido(2−) ligands and where one dap has been protolytically replaced with a hydrazido(1−). The synthesis and structure from X-ray diffraction are shown in Fig. 3; in that figure, the α-nitrogen for the hydrazido(1−) ligand is labeled N(11) and is attached to Ti(2). From the isolated dinuclear complex, it is obvious that at least one of the dap ligands is protolytically labile in the presence of 1,1-dimethylhydrazine. However, the active species probably does contain at least one dap ligand considering $Ti(NMe_2)_4$ is not a catalyst for hydrohydrazination or iminohydrazination under any conditions we have found.

In order to determine if the complex **4** is competent to be involved in the catalytic cycle, kinetic experiments were attempted using **1** and **4** as catalysts. However, the reaction is apparently not suitable for a detailed kinetic study, probably due to somewhat low yields, and the results were highly variable even using **1** as catalyst. Values for rate constants had very large errors. Consequently, we resorted to the use of a reaction that provides a mixture of regioisomers (see

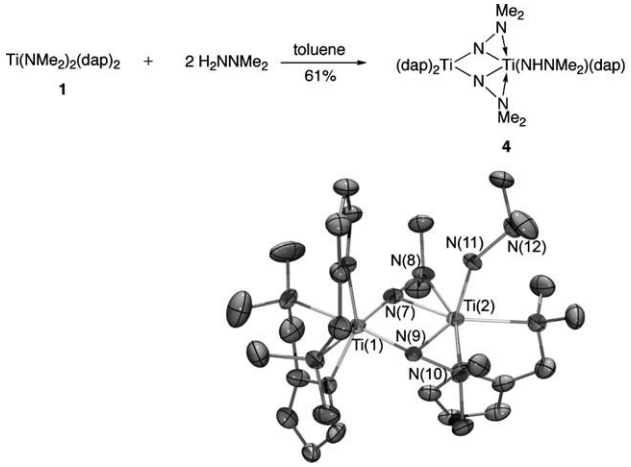


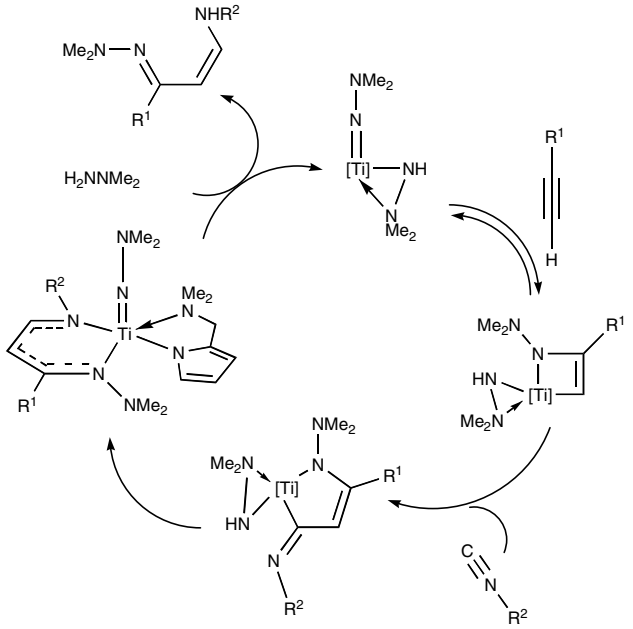
Fig. 3. Synthesis and structure from X-ray diffraction of $Ti_2(dap)_3(\mu_2{:}\eta^1,\eta^2\text{-}NNMe_2)(\mu_1{:}\eta^1\text{-}NHNMe_2)$ (**4**).

Section 2.6). With **1** as catalyst, the iminohydrazination of phenylacetylene provides a mixture of regioisomers along with small amounts of hydrohydrazination products. This catalysis was run six times, and the crude GC/FID ratios were obtained. The ratio of iminohydrazination products was found to be 0.453 ± 0.177, where the error is at the 99% confidence level. The ratio of hydrohydrazination products observed was 0.443 ± 0.339. If the dinuclear complex gives catalysis resulting in the same ratios within error, this is reasonably good evidence for its involvement during catalyses involving **1**. The ratio found for dinuclear complex **4** was 0.383 for iminohydrazination and 0.172 for hydrohydrazination products, which is consistent with its involvement when **1** is used.

Considering the apparent protolytic lability of one dap in **1**, we generated and isolated the mono(dap) complex $Ti(dap)(NMe_2)_3$ (**5**) by reaction of Lidap with $ClTi(NMe_2)_3$ [21]. Attempts to synthesize **5** by addition of one equivalent of Hdap to $Ti(NMe_2)_4$ provided mostly the bis(dap) complex **1**. The mono(dap) compound **5** appears to be comparable in catalytic activity to **1**. It provided a comparable yield when used instead of **1** for the reaction shown in Entry 1 of Table 1. In addition, its regioisomeric ratio for the reaction involving phenylacetylene, 1,1-dimethylhydrazine, and *tert*-butylisonitrile was 0.478 for iminohydrazination products and 0.238 for hydrohydrazination products, the same within error as the ratios for **1**. Consequently, our current evidence is consistent with an active species only bearing one dap ligand.

2.5. A working model for the catalytic cycle

From the information known about the mechanism thus far, one can postulate the catalytic cycle shown in Scheme 6. Here we assume based on the evidence above that a hydrazido(2−) intermediate is involved in a similar capacity as in the Bergman mechanism for hydroamination [12]. Considering the mild conditions under which **4** is formed relative to the catalytic conditions and catalysis results using **5**, it is likely that the active species has only one dap ligand. The dinuclear complex **4** has 6-coordinate and 7-coordinate titanium centers making it unlikely to be involved directly in the catalytic cycle. Consequently, we assume that it is an intermediate between **1** and the active species, which is likely a lower coordinate, monomeric titanium complex with one dap ligand. When possible, the β-nitrogen of hydrazido complexes is often acting as a donor towards titanium, e.g., complex **4** above, and is depicted as doing so below. Additional experimental evidence concerning the mechanism of iminoamination and iminohydrazination will be sought in future investigations [22].

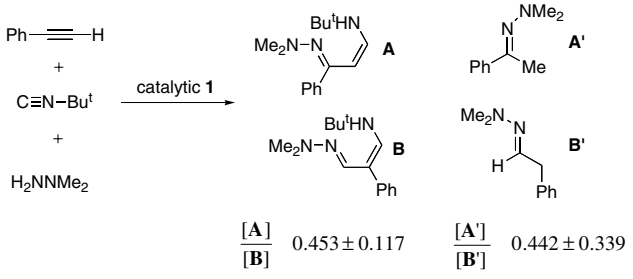


Scheme 6. Working model for iminohydrazination catalyzed by **1**. [Ti] = Ti(dap).

2.6. Some experimental observations on regioselectivities

The multicomponent coupling reaction between *tert*-butylisonitrile, phenylacetylene, and 1,1-dimethylhydrazine using **1** as catalyst results in a mixture of hydrohydrazination and iminohydrazination due to competitive protonolysis and 1,1-insertion (Scheme 7). In addition, both regioisomers are observed for both of the two product types. As a result, the reaction provides the opportunity to compare hydrohydrazination and iminohydrazination regioselectivity in a single system.

For the 3-component coupling reaction, the isomer having the phenyl group in the 2-position of the 1,3-hydrazonylimine (same product as that shown in Entry 5 of Table 1) is favored. The reaction was run six times with **1** as catalyst. The ratio of amounts of 3-component coupling products was found to be 0.453 ± 0.117 (99% confidence level, $\nu = 5$). The range for the ratio of regioisomers in the reactions run under the same conditions was fairly large from 0.351 to 0.510. For the



Scheme 7. Results of iminohydrazination of phenylacetylene when catalyzed by **1**.

same experiments, the ratio of hydrohydrazination products was 0.442 ± 0.339 with a range from 0.236 to 0.750. While the errors are large on these ratios, it should be kept in mind that the values are quite sensitive to catalyst structure. For example, the ratios of regioisomers when using the closely related catalyst Ti(bap)$(NMe_2)_3$ (**3**) for the same reaction are <0.01 for both the hydrohydrazination and iminohydrazination products, only one regioisomer is observed for each product.

Admittedly, the errors are quite large, but the mean values are remarkably close. This suggests that, to a first approximation, the ratio of the different isomers is nearly the same for the hydrohydrazination and iminohydrazination reactions. The similar regioselectivities are consistent with an important regiochemical event being associated with a step prior to protonolysis or 1,1-insertion (Scheme 3), e.g., [2 + 2] cycloaddition and/or alkyne coordination. This is in agreement with a recent assertion from the Beller group that titanium hydroamination regioselectivities correlate with calculated relative energies associated with alkyne coordination regioselectivity [23]. However, the experimental protonolysis and 1,1-insertion regioselectivities may or may not be identical, since the gross regioselectivity-determining events are the same (the [2 + 2] cycloaddition) but other factors still contribute to the final value. In other words, the equilibrium between the two azametallacycles contributes to the regioselectivities in both reactions, but the relative trapping rates of the two metallacycles may be slightly different with protons and isonitriles.

Switching the ancillary ligands on titanium can favorably affect the regioselectivities. Using **3** as catalyst provides only one regioisomer; however, both hydrohydrazination and iminohydrazination products are still observed. In fact, they are observed in a similar ratio as when using catalyst **1**, suggesting that the regioselectivity of the [2 + 2] cycloaddition was dramatically effected, but the relative rate of protonation versus 1,1-insertion was not greatly perturbed by the change in ancillary ligand in this particular case.

3. Concluding remarks

Titanium pyrrolyl complexes have allowed the examination of a new reaction, iminohydrazination of an alkyne. The reaction seems to have a fairly large substrate scope. Attempts to use trimethylhydrazine in place of 1,1-dimethylhydrazine, which would prevent formation of the terminal hydrazido(2−) ligand, resulted in no multicomponent coupling product being observed. If a 1,2-insertion pathway (cf. the Marks Hydroamination mechanism and Scheme 4) was accessible, one might expect that some product would be formed using this substrate. Initial indications, albeit based on circumstantial evidence, are that the mechanism involves terminal hydrazido(2−) complexes that undergo [2 + 2] cycloaddition with the alkyne. In addition, current evidence suggests that the active species is a mono(dap) complex, which maybe formed under relatively mild conditions when Ti$(dap)_2(NMe_2)_2$ is reacted with H_2NNMe_2.

As can be seen from the content of Table 1, the reactions are significantly enhanced by having terminal alkynes. Many attempted substrate combinations were quite sluggish due to the relatively low activity of these initial catalysts. It is hoped that additional studies will lead to improved catalyst performance and enable the use of internal alkynes on a routine basis. However, these results suggest that iminohydrazination is an effective methodology for 3-imino-1-hydrazones with some substrates even using these initially discovered catalyst architectures.

4. Experimental

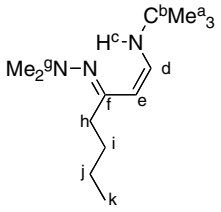
4.1. General considerations

All manipulations of air sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Anhydrous ether was purchased from Columbus Chemical Industries Inc. and freshly distilled from purple sodium benzophenone ketyl. Toluene was purchased from Spectrum Chemical Mfg. Corp. and purified by refluxing over molten sodium under nitrogen for at least 2 days. Pentane (Spectrum Chemical Mfg. Corp.), tetrahydrofuran (JADE Scientific), and benzene (EM Science) were distilled from purple sodium benzophenone ketyl. Dichloromethane (EM Science) and acetonitrile (Spectrum Chemical) were distilled from calcium hydride. Hydrazines were purchased from Aldrich Chemical Company and dried by distillation from KOH under dry nitrogen. Alkynes were distilled under dry nitrogen. Ti$(NMe_2)_4$ [24] and TiCl$(NMe_2)_3$ [21] were prepared using the literature procedures. The Hdap ligand was prepared as described in the literature [25,26]. Lidap was prepared by addition of 1.1 equivalents of $LiBu^n$ to a toluene solution of Hdap; the Lidap was collected by filtration and washed with pentane to afford the colorless product. Hbap was prepared using the literature procedure [26]. *tert*-Butyl isonitrile [27] and 2,6-xylyl isonitrile [28] were prepared from the amine using published methods. Cyclohexyl isonitrile was purchased from Aldrich Chemical Company and distilled under dry nitrogen prior to use. Deuterated solvents were dried over purple sodium benzophenone ketyl (C_6D_6) or phosphoric anhydride ($CDCl_3$) and distilled under nitrogen. ^1H and ^{13}C spectra were recorded on Inova-300 or VXR-500 spectrometers. ^1H and ^{13}C assignments were confirmed when necessary

with the use of two-dimensional ^{1}H–^{1}H and ^{13}C–^{1}H correlation NMR experiments. All spectra were referenced internally to residual protiosolvent (^{1}H) or solvent (^{13}C) resonances. Many common coupling constants are not listed. Chemical shifts are quoted in ppm and coupling constants in Hz.

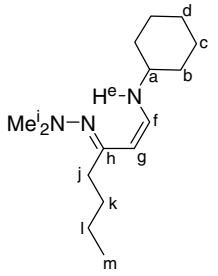
4.2. Synthesis and characterization of compounds in Table 1

4.2.1. Entry 1 of Table 1



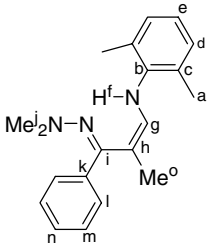
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (6 mL), Ti(dap)$_2$(NMe$_2$)$_2$ (0.458 g, 1.20 mmol), 1,1-dimethylhydrazine (910 μL, 12 mmol), 1-hexyne (1399 μL, 12.00 mmol), and *tert*-butyl isocyanide (1355 μL, 12.00 mmol). The tube was sealed with a Teflon cap and heated at 100 °C for 16 h. The solvent was removed under vacuum. The product was isolated by distillation under vacuum (~65 °C, 0.65 Torr) in 63% yield (1.702 g, 7.564 mmol) as red oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.82$ (br s, 1H, NH^{c}), 6.88 (t, 1H, $J_{HH} = 6.2$ Hz, CH^{d}), 4.68 (d, 1H, $J_{HH} = 8.1$ Hz, CH^{e}), 2.71 (m, 8H, CH_3^{g} and CH_2^{j}), 1.77 (m, 2H, CH_2^{h}), 1.64 (m, 2H, CH_2^{i}), 1.52 (s, 9H, CH_3^{g}), 1.17 (t, 3H, $J_{HH} = 8.0$ Hz, CH_3^{k}). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): $\delta = 171.5$ (NNC^{f}), 139.6 (C^{d}H), 89.5 (C^{e}H), 51.5 ($C^{g}H_3$), 48.9 ($C^{h}H_2$), 47.5 ($C^{i}H_2$), 31.2 ($C^{j}H_2$), 30.4 ($C^{b}(CH_3)_3$), 23.1 ($C^{k}H_3$), 13.9 ($C^{a}H_3$). Elemental analysis; Experimental (Calc.), C: 69.41 (69.33). H: 12.35 (12.00). N: 18.85 (18.67). MS (EI) $m/z = 225(M^+)$.

4.2.2. Entry 2 of Table 1



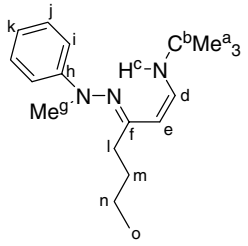
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (6 mL), Ti(dap)$_2$(NMe$_2$)$_2$ (0.457 g, 1.20 mmol), 1,1-dimethylhydrazine (910 μL, 12 mmol), 1-hexyne (1399 μL, 12.00 mmol), and cyclohexyl isocyanide (1790 μL, 14.4 mmol). The tube was sealed with a Teflon cap and heated at 100 °C for 16 h. The solvent was removed under vacuum. The product was isolated by distillation under vacuum (~110 °C, 0.65 Torr) in 73% yield (2.205 g, 8.785 mmol) as brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.61$ (br s, 1H, NH^{e}), 6.74 (d, 1H, $J_{HH} = 8.1$ Hz, CH^{f}), 4.61 (d, 1H, $J_{HH} = 8.1$ Hz, CH^{g}), 2.68 (m, 8H, CH_3^{i} and CH_2^{j}), 2.09–1.93 (m, 11H, a, b, c, d), 1.73 (m, 2H, CH_2^{k}), 1.57 (m, 2H, CH_2^{l}), 1.14 (t, 3H, $J_{HH} = 7.1$ Hz, CH_3^{m}). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): $\delta = 171.9$ (C^{h}N), 142.5 (C^{f}H), 89.9 (C^{g}H), 56.0 ($C^{j}H_2$), 49.8 ($C^{i}H_3$), 47.9 ($C^{k}H_2$), 34.8 ($C^{l}H_2$), 31.5 ($C^{m}H_3$), 26.2 (C^{a}NH), 24.9 ($C^{b}H_2$), 23.0 ($C^{c}H_2$), 13.9 ($C^{d}H_2$). Elemental analysis; experimental (Calc.), C: 71.71 (71.71). H: 11.96 (11.55). N: 16.80 (16.73). MS (EI) $m/z = 251(M^+)$.

4.2.3. Entry 3 of Table 1



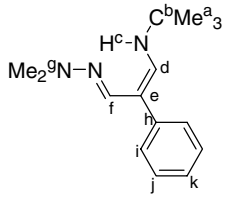
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (4.5 mL), Ti(dap)$_2$(NMe$_2$)$_2$ (0.344 g, 0.900 mmol), 1,1-dimethylhydrazine (1024 μL, 13.50 mmol), 1-phenylpropyne (1078 μL, 9 mmol), and xylyl isocyanide (1.769 g, 13.50 mmol). The tube was sealed with a Teflon cap and heated at 130 °C for 43 h. The volatiles were removed under vacuum. The product was then isolated by column chromatography on Florisil. The impurities were removed as the first fraction using 1:1 pentane:ethyl acetate mixture. The product was then isolated with pure ethyl acetate in 15% yield (0.401 g, 1.31 mmol) as a dark brown viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 11.31$ (br s, 1H, NH^{f}), 7.35–6.69 (m, 8H, Ph, d, e, l, m, n), 6.82 (d, 1H, $J_{HH} = 7.3$ Hz, CH^{g}), 2.66 (s, 6H, CH$_3^{j}$), 2.43 (s, 6H, CH$_3^{a}$), 2.23 (s, 3H, CH$_3^{o}$). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): $\delta = 166.3$ (C^{i}N), 142.7 (C^{g}H), 142.0–118.0 (Ph), 108.3 (H$_3$CC^{h}), 48.2 (N($C^{j}H_3$)$_2$), 19.5 ($C^{o}H_3$), 17.9 ($C^{a}H_3$). Elemental analysis; experimental (Calc.), C: 77.88 (78.17). H: 8.33 (8.14). N: 13.49 (13.68). MS (EI) $m/z = 307(M^+)$.

4.2.4. Entry 4 of Table 1



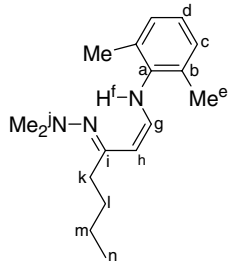
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (4.5 mL), Ti(dap)$_2$(NMe$_2$)$_2$ (0.344 g, 0.900 mmol), 1-methyl-1-phenylhydrazine (1059 μL, 9.00 mmol), 1-hexyne (1119 μL, 9.00 mmol), and *tert*-butyl isocyanide (1018 μL, 9.00 mmol). The tube was sealed with a Teflon cap and heated at 100 °C for 13 h. The solvent was removed under vacuum. The product was isolated by distillation under vacuum (~110 °C, 0.65 Torr) in 27% yield (0.693 g, 2.414 mmol) as dark brown oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.69 (br s, 1H, N*H*^{c}), 7.27–6.83 (m, 5H, Ph, i, j, k), 6.93 (m, 1H, C*H*^{d}), 4.57 (d, 1H, J_{HH} = 8.1 Hz, C*H*^{e}), 3.11 (s, 3H, CH_3^g), 2.36 (t, 2H, J_{HH} = 7.7 Hz, CH_2^l), 1.50 (m, 2H, CH_2^m), 1.39 (m, 2H, CH_2^n), 1.29 (s, 9H, CH_3^g), 0.89 (t, 3H, J_{HH} = 7.2 Hz, CH_3^o). ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$): δ = 176.3 (*C*^{f}N), 152.2 (*C*^{d}H), 140.9 (*C*^{h}N), 128.5 (*C*^{i}N), 118.0 (*C*^{j}H), 113.9 (*C*^{k}H), 89.1 (*C*^{e}H), 51.0 (*C*^{g}H$_3$), 42.8 (*C*^{l}H$_2$), 32.0 (*C*^{m}H$_2$), 30.3 (*C*^{n}H$_2$), 30.1 (*C*^{b}(CH$_3$)$_3$), 22.8 (*C*^{o}H$_3$), 13.8 (*C*^{a}H$_3$). Elemental analysis; Experimental (Calc.), C: 75.29 (75.26). H: 10.49 (10.10). N: 14.72 (14.63). MS (EI) *m*/*z* = 287(M$^+$).

4.2.5. Entry 5 of Table 1



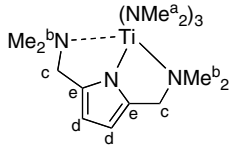
Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (4.9 mL), Ti(bap)(NMe$_2$)$_3$ (0.353 g, 0.980 mmol), 1,1-dimethylhydrazine (743 μL, 9.80 mmol), phenylacetylene (1075 μL, 9.80 mmol), and *tert*-butyl isocyanide (1107 μL, 9.80 mmol). The tube was sealed with a Teflon cap and heated at 100 °C for 16 h. The solvent was removed under vacuum. The product was isolated by distillation under vacuum (~125 °C, 0.65 Torr) in 43% yield (1.030 g, 4.20 mmol) as a red oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 9.03 (br d, 1H, J_{HH} = 13.0 Hz, N*H*^{c}), 7.65 (s, 1H, C*H*^{f}), 7.40–7.15 (m, 5H, Ph, i, j, k), 6.89 (d, 1H, J_{HH} = 2.3 Hz, C*H*^{d}), 2.83 (s, 6H, CH_3^g), 1.36 (s, 9H, CH_3^g). ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$): δ = 143.0 (*C*^{f}N), 142.0 (Ph, h), 136.0 (*C*^{d}H), 128.5 (Ph, i), 125.0 (Ph, j), 124.0 (Ph, k), 102.9 (*C*^{e}Ph), 50.9 (*C*^{b}Me$_3$,), 42.0 (*C*^{g}H$_3$), 30.0 (*C*^{a}H$_3$). Elemental analysis; experimental (Calc.), C: 73.58 (73.47). H: 9.26 (9.39). N: 17.05 (17.14). MS (EI) *m*/*z* = 245(M$^+$).

4.2.6. Entry 6 of Table 1



Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (6 mL), Ti(dap)$_2$(NMe$_2$)$_2$ (0.432 g, 1.20 mmol), 1,1-dimethylhydrazine (910 μL, 12 mmol), 1-hexyne (1399 μL, 12 mmol), and xylyl isocyanide (1.573 g, 12 mmol). The tube was sealed with a Teflon cap and heated at 100 C for 16 h. The volatiles were removed under vacuum. The product was then isolated by column chromatography on Florisil. The impurities were removed as the first fraction using 1:1 dichloromethane:ethyl acetate mixture. The product was then isolated with ethyl acetate as the eluent in 12% yield (0.401 g, 1.47 mmol) as a viscous oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 10.89 (br s, 1H, N*H*^{f}), 7.15–6.85 (m, 3H, Ph, c, d), 6.78 (d, 2H, J_{HH} = 7.8 Hz, C*H*^{g}), 4.62 (d, 1H, J_{HH} = 8.0 Hz, C*H*^{h}), 2.58 (m, 8H, CH_3^j and CH_3^k), 2.38 (s, 6H, CH_3^e), 1.59 (m, 2H, CH_2^l), 1.41 (m, 2H, CH_2^m), 0.99 (t, 3H, J_{HH} = 7.3 Hz, CH_3^n). ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$): δ = 170.4 (*C*^{i}N), 143.1 (*C*^{g}H), 141.8–117.9 (Ph), 92.0 (*C*^{h}H), 48.8 (*C*^{j}H$_3$), 46.6 (*C*^{k}H$_2$), 31.4 (*C*^{l}H$_2$), 23.0 (*C*^{e}H$_3$), 19.3 (*C*^{m}H$_2$), 14.0 (*C*^{n}H$_3$). High resolution MS (EI) *m*/*z* = 273.2200, calc. = 273.2205.

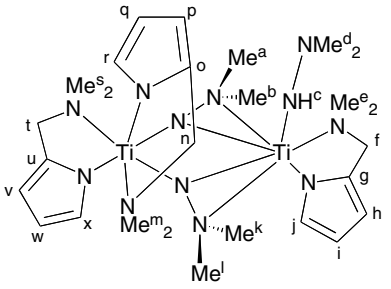
4.3. Synthesis and characterization of Ti(bap)(NMe$_2$)$_3$ (**3**)



Under an atmosphere of dry nitrogen, a solution of Ti(NMe$_2$)$_4$ (2.00 g, 8.90 mmol) in ether (20 mL) was

frozen in a liquid nitrogen cooled cold well. The solution was allowed to warm enough to be stirred. Then, a cold solution of Hbap (1.610 g, 8.90 mmol) in 10 mL ether was added to the above solution dropwise over a period of 20 min. It was allowed to warm up to room temperature and stir overnight. The volatiles were removed under vacuum. The solid was purified by crystallization as orange–red crystals from pentane (2.950 g, 8.20 mmol) in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.34 (s, 2H, CH^{d}), 3.48 (s, 4H, $CH_2{}^{c}$), 3.13 (s, 12 H, $N(CH_3)_2{}^{b}$), 2.07 (s, 18 H, $N(CH_3)_2{}^{a}$). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): δ = 137.9 (pyrrole, **e**), 106.9 (pyrrole, **d**), 60.0 ($C^{c}H_2$), 47.1 ($N(CH_3)_2{}^{b}$), 45.8 ($N(CH_3)_2{}^{a}$). Elemental analysis; experimental (Calc.), C: 53.19 (53.33). H: 10.09 (10.07). N: 22.82 (23.32).

4.4. Synthesis and characterization of $Ti_2(dap)_3(NHNMe_2)(NNMe_2)_2$ (**4**)



All the manipulations were done inside a nitrogen filled glove-box. In a vial, $Ti(dap)_2(NMe_2)_2$ (0.200 g, 0.500 mmol) was dissolved in toluene (250 μL). It was then cooled in a liquid nitrogen-cooled cold well. To this solution was added 1,1-Me_2NNH_2 (76 μL, 1.00 mmol). Then, the solution was allowed to warm up to room temperature and stir for 1 h. The solution was kept in the refrigerator at −35 °C overnight. The volatiles were removed in vacuo, and the reddish-brown residue was crystallized from a 1:1 mixture of dichloromethane:pentane to obtain **4** as yellow plates in 61% yield (0.195 g, 0.305 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.68 (br, 1H, c), 6.89 (br, 1H, r or x), 6.56 (t, 1H, J_{HH} = 2.7 Hz, q or w), 6.40 (t, 2H, J_{HH} = 2.5 Hz, q or w and r or x), 6.34 (br, 1H, p or v), 6.22 (br, 1H, j), 6.17 (t, 1H, J_{HH} = 2.6 Hz, i), 6.08 (br, 1H, p or v), 5.77 (br, 1H, h), 3.99 (d, 1H, f, J_{HH} = 13.8 Hz), 3.87 (d, 1H, n or t, J_{HH} = 13.8), 3.78 (d, 1H, n or t, J_{HH} = 13.4), 3.57 (d, 1H, n or t, J_{HH} = 13.4), 3.52 (d, 1H, n or t, J_{HH} = 13.8), 3.12 (d, 1H, f, J_{HH} = 13.8), 2.95 (br, 3H, a or b or k or l), 2.85 (br, 6H, m or s), 2.68 (br, 3H, a or b or k or l), 2.42 (br, 6H, d), 2.32 (br, 3H, a or b or k or l), 2.29 (br, 3H, a or b or k or l), 2.26 (br, 6H, m or s), 1.86 (br, 6H, e). $^{13}C\{^{1}H\}$ NMR (500 MHz, C_6D_6): δ = 137.2 (pyrrole, u), 136.1 (pyrrole, o), 133.5 (pyrrole, g), 130.6 (pyrrole, x or r), 129.5 (pyrrole, h), 108.0 (pyrrole, j), 107.3 (pyrrole, q or w), 106.7 (pyrrole, q or w), 102.1 (pyrrole, p or v), 101.8 (pyrrole, i), 101.4 (pyrrole, p or v), 65.5 (CH_2, n), 63.0 (CH_2, t), 62.9 (CH_2, f), 54.4 (CH_3, a or b or k or l), 54.3 (CH_3, a or b or k or l), 51.0 (CH_3, e), 50.6 (CH_3, a or b or k or l), 50.3 (CH_3, a or b or k or l), 49.8 (CH_3, m or s), 49.4 (CH_3, m or s). Elemental analysis; experimental (Calc.), C: 50.93 (50.64). H: 8.48 (8.12). N: 26.07 (26.25).

4.5. Synthesis and characterization of $Ti(dap)(NMe_2)_3$ (**5**)

Under an atmosphere of dry nitrogen, $Ti(NMe_2)_3(Cl)$ (0.200 g, 0.929 mmol) was dissolved in 15 mL ether in a filter flask. Lidap (0.121 g, 0.931 mmol) was dissolved in 5 mL ether in a vial. Both of them were cooled in the cold well. Then Lidap solution was added to the solution of $Ti(NMe_2)_3(Cl)$ and allowed to warm up to the room temperature and stir overnight. Then the solvent was pumped down, and the residue was purified by crystallization from ether as reddish-brown crystals in 77% yield (0.218 g, 0.719 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (q, 1H, 5-pyrrolyl), 6.02 (t, 1H, J_{HH} = 2.6 Hz, 4-pyrrolyl), 5.82 (m, 1H, 3-pyrrolyl), 3.51 (s, 2H, CH_2), 3.22 (s, 18H, amido CH_3), 2.36 (s, 6H, amine CH_3). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$): δ = 142.9 (2-pyrrolyl), 133.3 (5-pyrrolyl), 122.0 (4-pyrrolyl), 107.5 (3-pyrrolyl), 65.2 (CH_2), 53.3 (amido CH_3), 51.6 (amine CH_3).

4.6. Attempted reaction of 1-hexyne, N,N,N′-trimethylhydrazine, tert-butylisocyanide in presence of $Ti(dap)_2(NMe_2)_2$ (**1**)

Under an atmosphere of dry nitrogen, a threaded pressure tube was loaded with toluene (300 μL), $Ti(dap)_2(NMe_2)_2$ (**1**) (0.023 g, 0.06 mmol), *N*,*N*,*N*′-trimethylhydrazine (0.044 g, 0.60 mmol), 1-hexyne (0.070 μL, 0.61 mmol), and *tert*-butyl isocyanide (68 μL, 0.60 mmol). The tube was sealed with a Teflon cap and heated at 100 °C for 16 h. The residue was analyzed with GC-FID. Only starting materials were observed, and no product was detected under these reaction conditions.

4.7. X-ray crystallography

Crystals grown from concentrated solutions at −35 °C were moved quickly from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample

Table 2
Crystallographic data and structure refinement parameters for $Ti(NMe_2)_3(bap)$ (**3**) and $Ti_2(dap)_3(NHNMe_2)(NNMe_2)_2$ (**4**)

	3	4
Formula	$C_{16}H_{36}N_6Ti$	$C_{27}H_{52}N_{12}Ti_2$
Formula weight	360.41	640.61
Crystal size (mm)	$0.32 \times 0.68 \times 0.71$	$0.59 \times 0.84 \times 0.96$
Crystal shape	Parallelpiped	Parallelpiped
Temperature (K)	174(2)	174(2)
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P(–1)
Unit cell dimensions		
a (Å)	9.3023(11)	10.090(3)
b (Å)	11.1907(14)	10.859(4)
c (Å)	19.610(2)	17.152(5)
α (°)	90	75.86(3)
β (°)	93.075(3)	79.47(3)
γ (°)	90	65.23(3)
V (Å^3)	2038.4(4)	1647.8(9)
Z	4	2
D (g cm^{-3})	1.174	1.291
μ (mm^{-1})	0.429	0.522
θ range (°)	2.08–23.28	2.10–23.29
Reflections measured	17217	7483
Independent reflections (R_{int})	2937 (0.0782)	4697 (0.0668)
Number of parameters	208	385
$R(F)$ for $I > 2\sigma(I)$	0.0592	0.0556
$wR(F^2)$ (all data)	0.1566	0.1430
GOF(F^2)	1.049	1.043
Maximum, minimum $\Delta\rho$ (e Å^{-3})	0.543, −0.474	1.345, −0.515

temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced utilizing the program SAINT-PLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques Table 2.

4.8. Computational details

The calculated molecular structures were obtained by geometry optimizations at the DFT level using the B3LYP functional using Gaussian's default grid size [29]. The geometry optimizations on Entry 1 of Table 1 were initially carried out using the STO3G basis set and further refined with the 6-31++G** basis set to obtain the listed energies. The molecules shown in Fig. 1 were placed near the desired geometry and optimized to the local or global minimum for that conformation. All calculations used the Gaussian-03M program [30] as implemented on a G5 Macintosh desktop with dual processors.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic tables from X-ray diffraction experiments. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 264853 **3** and 264854 for **4**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2005.03.025.

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