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Introduction

The formation of multiple bonds between d- and p-block elements and their resulting reactivities have always excited chemists, and have lead (and presumably will always lead) to novel groundbreaking discoveries which ask fundamental questions in the analyses of structure and bonding.¹ Among these multiply bonded compounds, early transition metal imido complexes bearing $[\text{RN}=\text{]}^{2-}$ ligands (formally the dianion of a primary amine) are arguably one of the most important and well-understood.² In this context, solely for the chemistry of titanium imido complexes diverse reactivities have been reported ranging from metathesis reactions, insertions, and cycloadditions to C–H bond activations.² With regard to catalysis, imido complexes have been employed as robust supporting ligands in Ziegler–Natta type olefin polymerization, ring-opening metathesis, and are used in the industrial production of acrylonitrile.^{2e,3,4} Furthermore, titanium imido complexes continue to gain momentum in stoichiometric and catalytic hydroamination, nitrene transfer, and oxidative amination reactions.^{5,6} The fundamental initial

reaction step of these last mentioned transformations is the [2 + 2] cycloaddition of a multiple bond substrate (e.g. an alkyne) to the titanium imido fragment to give four-membered systems which can then be further functionalized (e.g. by subsequent insertion of another substrate). These [2 + 2] cycloaddition products of alkynes and terminal imido complexes were observed, isolated, and characterized on several occasions, and undoubtedly the early work by Bergman and co-workers laid the foundation for the later developed catalytic applications.⁷ Although the [2 + 2] cycloaddition reaction between titanium imido complexes and alkynes is by far the most dominantly observed pathway for early transition metals (selected example Scheme 1, top), two unusual reaction pathways between these compounds were unveiled in recent years. These exceptions might be particularly interesting in the future because they might lead to novel catalytic transformations, give additional mechanistic insight, and allow the isolation of heterocycles which are not accessible by the [2 + 2] cycloaddition route. For terminal titanium imido complexes, Mountford *et al.* reported the formation of a titanaazetidine (e.g. **III**) with an exocyclic carbon–carbon double bond by reacting titanium imido complexes (**II**) bearing tridentate *N,N,N*-supporting ligands with methyl-substituted alkynes (Scheme 1, second from top).⁸ Mashima, Tsurugi, and co-workers reported the activation of *ortho* C(sp²)–H aryl bonds at the *N*-aryl-substituent in imido bridged titanium complexes **IV** when reacted with 1-(trimethylsilyl)propane to give the six-membered dinuclear titanium complex **V** (Scheme 1, third from top).⁹ Herein, we report on another exception to the perceived well-understood chemistry of early transition metal imido complexes. The reactions of the bis(cyclopentadienyl)-based titanium imido complex **1b** with methyl-substituted

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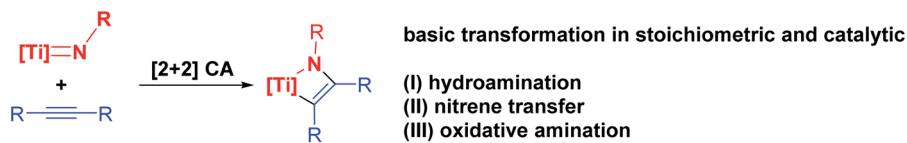
[‡] Equal contribution.



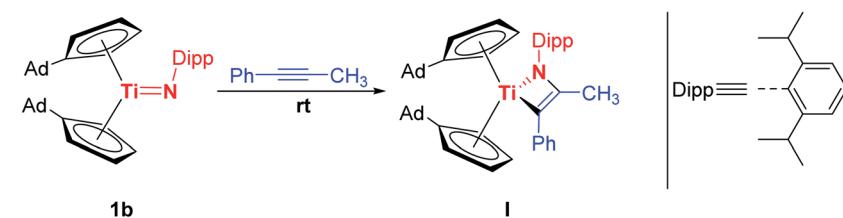
alkynes lead to the formation of five-membered titanium aza-diene complexes **2a,b** by initial C–H activation of an internal alkyne (Scheme 1, bottom).

These results are supported by multinuclear NMR experiments, single crystal X-ray diffraction and quantum chemical calculations.

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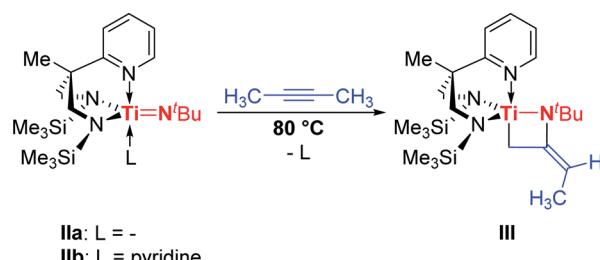


a) Selected example of a direct [2+2] cycloaddition (ref. 7e)

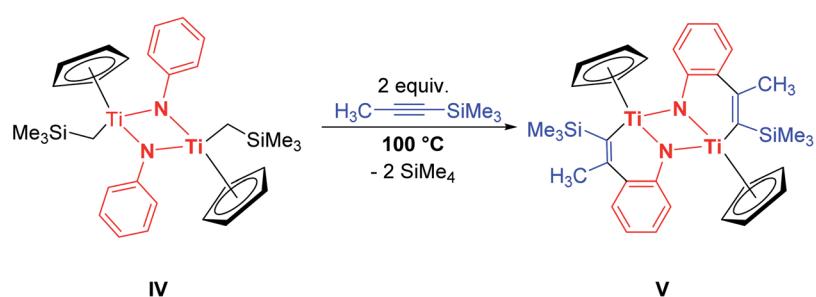


Unusual

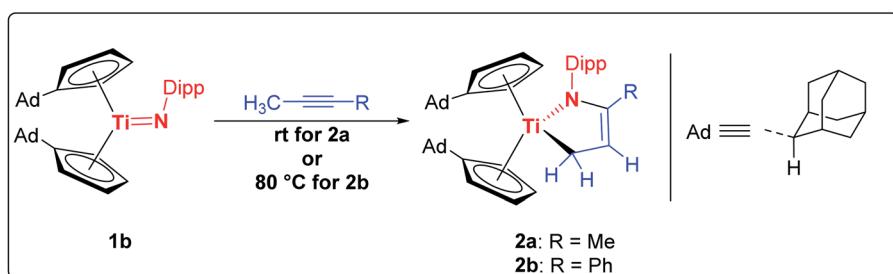
b) C(sp³)–H activation, H-atom transfer, [2+2] cycloaddition with allene (ref. 8)



c) C(sp²)–H activation, alkyne insertion (ref. 9)



d) This work:



Scheme 1 Overview of the reactivity of titanium imido complexes with internal alkynes.



Results and discussion

In a recent work we reported the preparation of the chemical equilibrium between the titanium monoamide **1a** and the titanium imido complex **1b**.^{7e} Enclosed reactivity studies of **1a/1b** with multiple bond substrates furnished a broad range of [2 + 2] cycloaddition products.^{7e,10} As a representative example, the reaction of **1a/1b** with 1-phenyl-1-propyne regioselectively yielded the corresponding titatanaazacyclobutene **I**, in which the phenyl substituent is localized in position α to the titanium centre (Scheme 1, top). Interestingly, the reaction of **1a/1b** with 2-butyne under the same reaction conditions as the reaction of **1a/1b** with 1-phenyl-1-propyne (*n*-hexane, 20 h, rt) was already being probed at the same time, but quite complex reaction mixtures were obtained and the expected [2 + 2] cycloaddition product was not observed, which naturally inspired us to take a closer look at this outcome.

Accordingly, the equilibrium of **1a/1b** was reacted with 2-butyne in *n*-hexane over a significantly increased time period of five days at room temperature which was accompanied by an observable color change of the reaction mixture from red to maroon. Gratifyingly, removal of all volatile components and subsequent ¹H NMR analysis revealed, that the starting material **1a/1b** was completely consumed and a new complex was formed. Unexpectedly, **3** was unequivocally identified as the titanium azadiene complex **2a** (Scheme 2), thus the reaction of **1a/1b** with 2-butyne neither yielded the expected [2 + 2] cycloaddition product comparable to **I** nor a titanaazetidine (*cf.* **III**) which was previously observed by Mountford *et al.* (Scheme 1).

Noteworthy, titanium azadiene complexes are typically prepared by reductive complexation of azadiene ligand precursors and, due to the unavailability of CH₂ terminated azadienes, only α -C-substituted titanium azadiene complexes are synthetically available by this route.^{11,12} The hitherto only other reported procedure of preparing TiCH₂ substituted titanium azadiene complexes employs allylamines and (Fv^{Ad})₂Ti.¹³ Complex **2a** is obtained in a good isolated yield of 75% and shows good solubilities in aliphatic and aromatic hydrocarbons

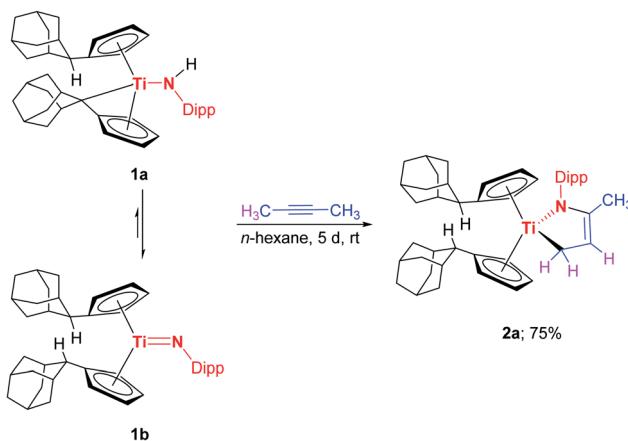
such as *n*-hexane, toluene, and tetrahydrofuran. Multinuclear NMR spectroscopy is already indicative for the formation of the five-membered heterocycle **2a** (Fig. S1–S7†). Highly characteristic is the ¹³C{¹H} NMR signal at $\delta^{13}\text{C}^{1\text{H}} = 64.9$ ppm with a negative phase in the ¹³C{¹H} DEPT 135 NMR spectrum, being in the typical region for methylene groups in position α to titanium.¹³ The signals of the respective chemically non-equivalent Ti-CH₂ hydrogen atoms are localized at $\delta^1\text{H} = 0.82$ and 2.37 ppm. Both signals couple in the ¹H/¹H COSY spectrum to a multiplet signal at $\delta^1\text{H} = 5.10$ ppm with the corresponding ¹³C{¹H} NMR signal at $\delta^{13}\text{C}^{1\text{H}} = 111.6$ ppm. The remaining signals of the methyl group and the belonging quaternary carbon atom at $\delta^1\text{H} = 1.69$ ppm ($\delta^{13}\text{C}^{1\text{H}} = 20.6$ ppm) and $\delta^{13}\text{C}^{1\text{H}} = 140.6$ ppm, together with the expected cross peaks in the 2D NMR spectra already allow for the assignment of connectivity in **2a**. Additionally, both the ¹H NMR signals of the methyl group and the olefinic hydrogen atoms show coupling to the nitrogen atom in the ¹H/¹⁵N HMBC spectrum ($\delta^{15}\text{N} = 266.3$ ppm). All these chemical shifts are in good agreement to other structurally characterized titanium azadienes,^{11,13} *e.g.* the recently reported complex **VI**¹³ (Table 1).

The presence of eight signals in the ¹H NMR spectrum ($\delta^1\text{H} = 4.93$ –5.93 ppm) for the cyclopentadienyl hydrogen atoms and distinct signals for the Dipp (2,6-diisopropylphenyl) moiety are caused by the different chemical environments above and below the central five-membered ring system. In this context, the inhibition of the characteristic envelope rearrangement of titanium azadiene complexes^{11,13} is not observed in the ¹H NMR spectrum of **2a** in the temperature range from 213 K to 353 K (excerpt of the VT ¹H NMR experiment: Fig. S8†).

Crystals of **2a** suitable for single crystal X-ray diffraction were obtained by slow evaporation of an *n*-hexane solution of **2a**. The molecular structure is shown in Fig. 1 and confirms the information obtained from the solution NMR analyses.

The central titanium atom is in a trigonal pyramidal coordination environment with respect to the τ_4/τ_δ values of $\tau_4 = 0.83$ and $\tau_\delta = 0.69$, respectively (the centroids of the Cp ligands have been used for the calculation).¹⁴ The above mentioned envelope structure of this diene type complex is demonstrated by a fold angle of the central five-membered ring system of 49.3° which is in good agreement to other structurally characterized titanium azadiene complexes (*e.g.* 44.4° for **VI**).^{11,13} The Ti1–N1 bond length of 2.0201(7) Å and the Ti1–C43 bond length of 2.1840(9) Å are in reasonable accordance to the respective sums of covalent radii ($\sum \text{cov}(\text{Ti}-\text{N}) = 2.02$ Å, $\sum \text{cov}(\text{Ti}-\text{C}) = 2.11$ Å (ref. 15)). The C43–C44 bond length of 1.4561(14) Å and the N1–C45 bond length of 1.3851(11) constitute a slightly shortened C(sp³)–C(sp²) single bond and a N–C(sp²) single bond (C(sp³)–C(sp²) = 1.51 Å, N–C(sp²) = 1.38 Å (ref. 16)), respectively. The C44–C45 bond length of 1.3807(13) Å is elongated compared to a typical double bond between two sp²-hybridized carbon atoms (C(sp²)=C(sp²) = 1.32 Å (ref. 16)).

To gain further insight into the significantly different reactivity of **1a/1b** toward 2-butyne compared to the reactions of internal alkynes with other titanium imido complexes, quantum chemical calculations were performed.¹⁷

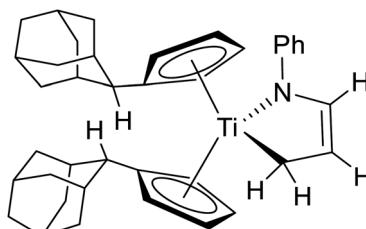


Scheme 2 Reaction of **1a/1b** with 2-butyne to yield the titanium azadiene complex **2a**.



Table 1 Selected ^1H , ^{13}C , and ^{15}N NMR data of **2a** and **VI**^a ¹³

Complex	$\delta^1\text{H}/\delta^{13}\text{C}\{^1\text{H}\}$, TiCH_2	$\delta^1\text{H}/\delta^{13}\text{C}\{^1\text{H}\}$, $\text{HC}=\text{C}_q$	$\delta^{13}\text{C}\{^1\text{H}\}$, $\text{HC}=\text{C}_q(\text{R})$	$\delta^{15}\text{N}$
2a VI ¹³	0.82, 2.37/64.9 1.35–1.95 ^b /57.3	5.10/111.6 5.35/112.1	140.6 132.2	266.3 248.7



VI

^a Values are given in ppm. Measurements were carried out in C_6D_6 at room temperature. ^b Overlap with $\text{CH}_{\text{Ad}}/\text{CH}_{2,\text{Ad}}$ signals.

The Gibbs free enthalpy difference $\Delta_r G$ for the formation of **2a** was found to be $\Delta_r G = -0.63$ eV which is significantly more exergonic as compared to the corresponding [2 + 2] cycloaddition product ($\Delta_r G = -0.16$ eV). The formation of a titanaazetidine (*cf.* **III**) could further be excluded being only slightly exergonic ($\Delta_r G = -0.10$ eV). Thus, the formation of **2a** is thermodynamically favored.

With regard to titanium catalyzed hydroamination reactions, this unexpected titanium azadiene formation could add another discussable part to the selectivity of this reaction type since both a typical [2 + 2] cycloaddition product **VII** and the corresponding titanium azadiene complex **VIII** would (in principle) give the same enamine **IX** after formal twofold protonation (Scheme 3).

Intriguingly, the quantum chemical calculations showed that even in the previously reported reaction of **1a/1b** with 1-phenyl-1-propyne, the corresponding titanium azadiene complex should be the thermodynamically favored product of this reaction and not the [2 + 2] cycloaddition product **I**. Here, a Gibbs free energy difference of $\Delta_r G = -0.52$ eV for the formation of the titanium azadiene complex, and $\Delta_r G = -0.26$ eV for the formation of **I** was found.

To verify this quantum chemical results, **I** was synthesized according to the literature procedure (Scheme 4).^{7e}

I has been comprehensively characterized before.^{7e} In the course of this work crystals of **I** suitable for single crystal X-ray diffraction could be obtained with the molecular structure being shown in Fig. 2, unambiguously verifying that indeed the formal [2 + 2] cycloaddition product is formed with the

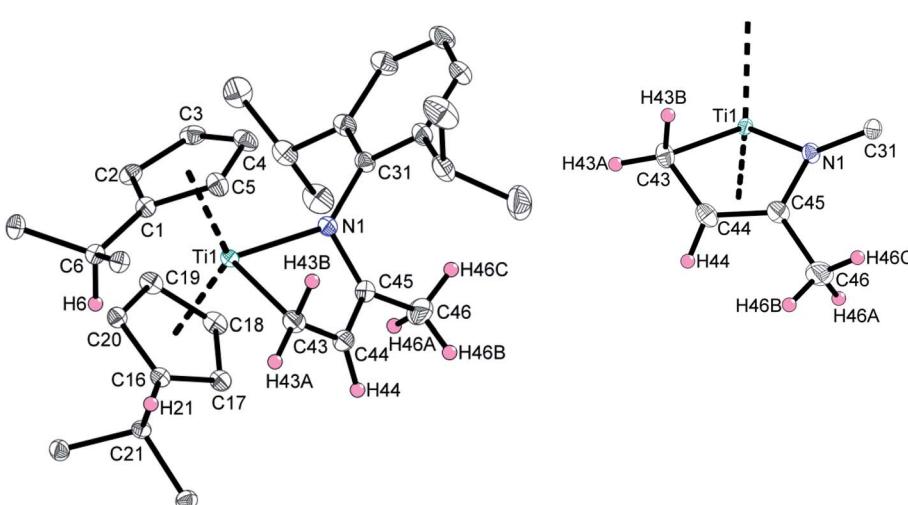
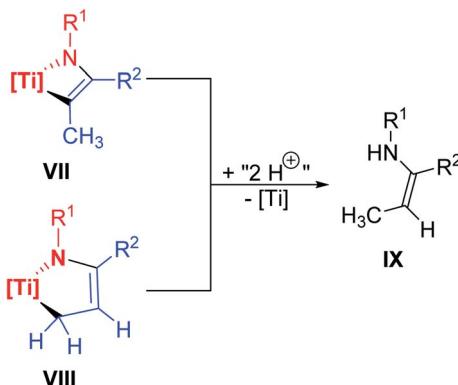
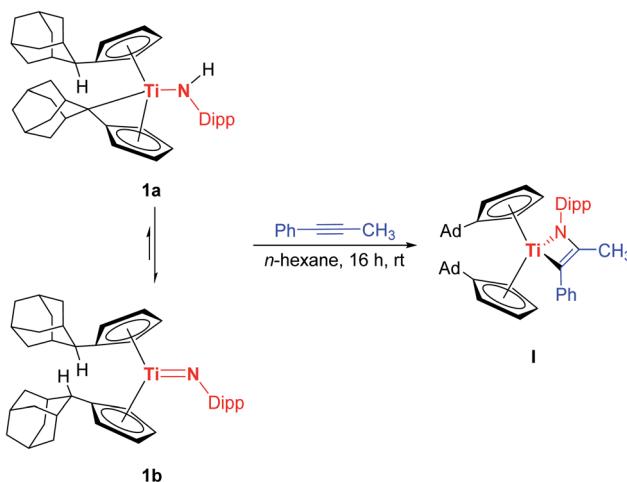


Fig. 1 Molecular structure of **2a**. Hydrogen atoms (except H6, H21, and those of the central five-membered ring system) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 2.0201(7), Ti1–C43 2.1840(9), N1–C45 1.3851(11), C43–C44 1.4561(14), C44–C45 1.3807(13), N1–Ti1–C43 83.89(3), Ct1–Ti1–Ct2 128.3, Σ N1 359.9, Σ C44 359.4, Σ C45 359.5, Ti1–C43–H43A/H43A–C43–C44 70.4, Ti1–C43–H43B/H43B–C43–C44 86.5 (Ct1 = centroid of C1–C5; Ct2 = centroid of C16–C20).





Scheme 3 Formal twofold protonation of both a typical [2 + 2] cycloaddition product VII and of a corresponding titanium azadiene VIII to yield the same enamine IX.



Scheme 4 Reaction of 1a/1b with 1-phenyl-1-propyne to yield the titanaazacyclobutene I.

phenyl substituent being in position α to the titanium centre. It should be mentioned here, although we consider it unlikely, that in principle a formal σ -bond insertion starting

from the titanium amide **1a** could also lead to the formation of **I**.¹⁸

According to the τ_4/τ_δ values of $\tau_4 = 0.78$ ($\tau_\delta = 0.71$), the coordination environment at the titanium centre is best described as trigonal pyramidal and the central four-membered ring system forms a nonplanar kite shape.¹⁴ The bond lengths within the four-membered ring are as one would expect. The Ti1–N1 and Ti1–C45 bond lengths of 2.034(2) Å and 2.107(3) Å are in good accordance to the respective single bond covalent radii ($\sum \text{cov}(\text{Ti–N}) = 2.07$ Å, $\sum \text{cov}(\text{Ti–C}) = 2.11$ Å (ref. 15)), the C44–C45 bond length of 1.364(4) Å is in the range of the respective double bond ($\text{C}(\text{sp}^2)=\text{C}(\text{sp}^2) = 1.32$ Å (ref. 16)), and the N1–C44 bond length of 1.413(3) Å constitutes an elongated N–C(sp²) single bond ($\text{N–C}(\text{sp}^2) = 1.38$ Å (ref. 8)), indicative for electron donation from the nitrogen lone pair to the electropositive metal centre.

Given the results of the quantum chemical calculations, and the energy difference of 0.26 eV between **I** and the to **2a** corresponding titanium azadiene complex **2b**, a solution of **I** in deuterated benzene was first heated to 50 °C for several hours, and subsequently to 80 °C due to the slow reaction process at 50 °C (Fig. S17†). This variable temperature ¹H NMR experiment showed a quite clean and irreversible conversion of **I** to the corresponding titanium azadiene complex **2b** (Scheme 5).

Multinuclear NMR experiments (Fig. S10–S16†) show excellent agreement of the significant signals to those observed for **2a**. Furthermore, crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of a C₆D₆ solution of **2b** at room temperature, unambiguously verifying this thermally induced rearrangement (Fig. 3).

Since the structural parameters and solution NMR data of **2a** and **2b** are in very good agreement, and have been comprehensively discussed for **2a**, no detailed discussion for **2b** is given here.

Mechanistically, we think that the initial step of the reaction is the C–H activation of the methyl group of the alkyne by the titanium imido complex to give the corresponding titanopropargyl **XI**. A precoordination of the alkyne to the titanium center to give an alkyne–titanium π -complex (**X**) is

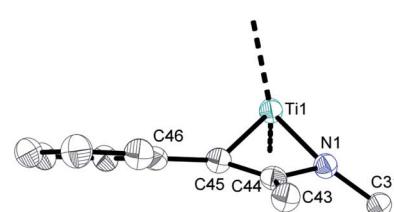
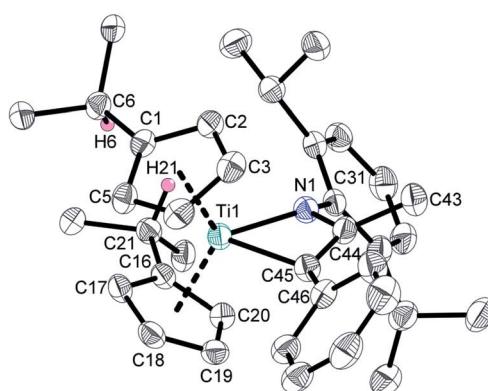
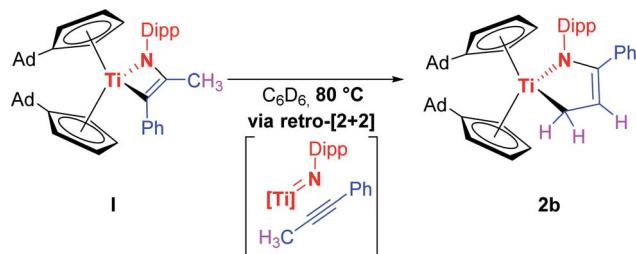
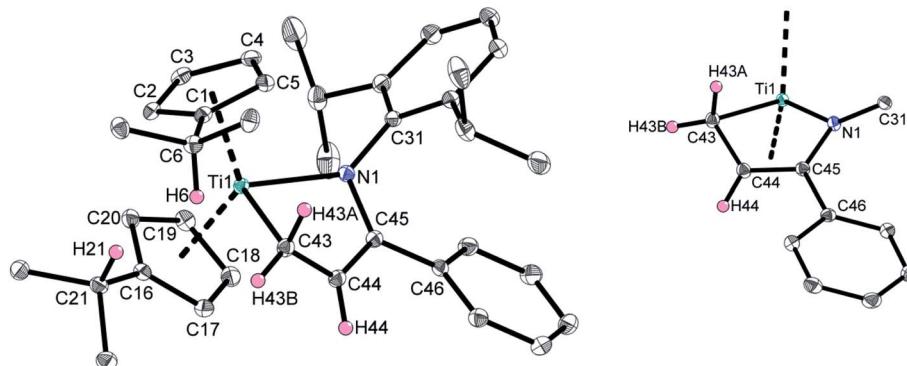
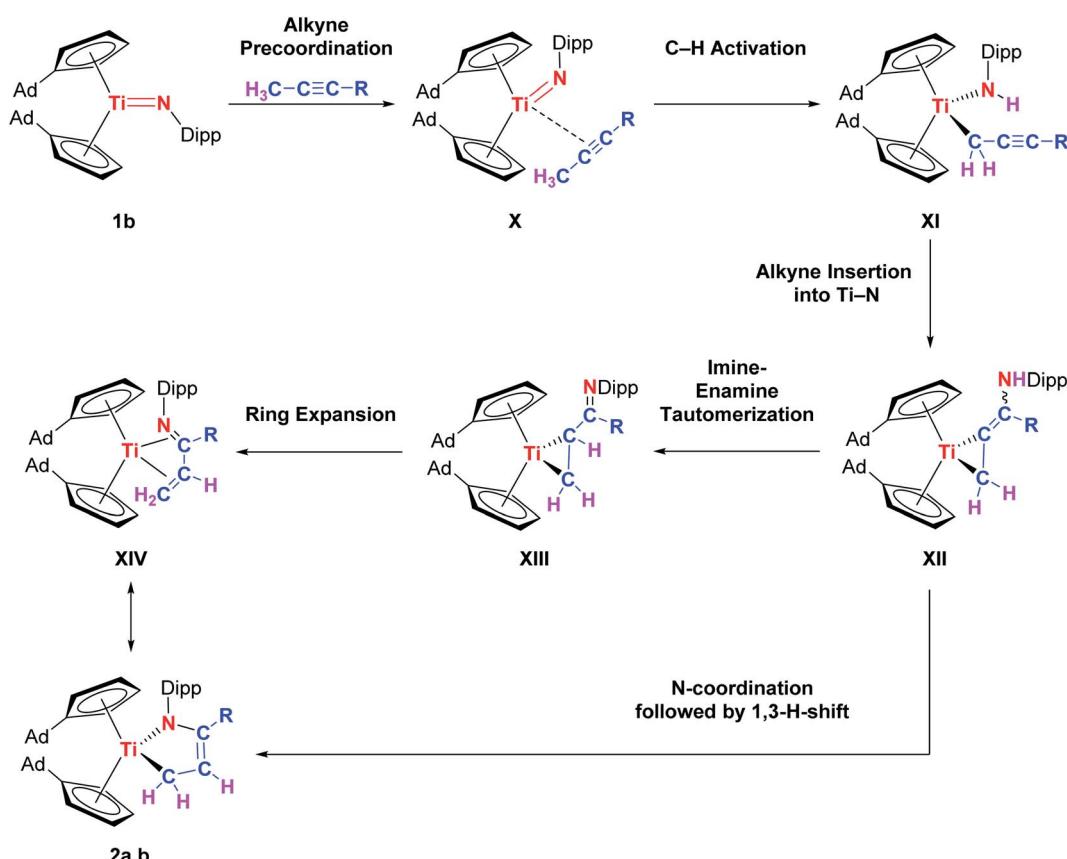


Fig. 2 Molecular structure of I. Hydrogen atoms (except H6 and H21) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 2.034(2), Ti1–C45 2.107(3), N1–C44 1.413(3), C44–C45 1.364(4), N1–Ti1–C45 67.47(10), C1–Ti1–Ct2 130.9, $\Sigma \angle \text{N1}$ 355.1, $\Sigma \angle \text{C44}$ 359.1, $\Sigma \angle \text{C45}$ 356.0 (Ct1 = centroid of C1–C5; Ct2 = centroid of C16–C20).



Scheme 5 Thermally induced formation of **2b** from **I**.

suggested to lower the $\text{p}K_{\text{a}}$ of the propargylic hydrogen atom(s) in the first place.¹⁹ Even though this type of reactivity is very rare for titanium imido complexes, it was observed for reversible $\text{C}(\text{sp}^3)\text{–H}$ activation processes in the case of alkanes.^{2b,20} Just recently, Tonks *et al.* also observed propargylic $\text{C}\text{–H}$ activation of 3-hexyne by a titanium bisamido complex.²¹ Subsequently, the carbon–carbon triple bond inserts into the $\text{Ti}\text{–N}$ bond which leads to the formation of the titanacyclopropane derivative **XII** with an enamine functionality in the

Fig. 3 Molecular structure of **2b**. Hydrogen atoms (except H6, H21, and except those of the central five-membered ring system) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (\AA) and angles (deg): Ti1–N1 2.0761(10), Ti1–C43 2.1724(12), N1–C45 1.3861(14), C43–C44 1.4535(16), C44–C45 1.3851(16), N1–Ti1–C43 82.50(4), C1–Ti1–Ct2 128.6, $\Sigma \angle \text{N1}$ 359.6, $\Sigma \angle \text{C44}$ 360.0, $\Sigma \angle \text{C45}$ 360.0 (Ct1 = centroid of C1–C5; Ct2 = centroid of C16–C20).Scheme 6 Proposed mechanism for the formation of **2a,b**.

backbone. This insertion step was already discussed by the Doye group as a possible alternative reaction pathway for titanium catalyzed hydroamination reactions,²² and is common for group 3 metals.^{5c,23} Enamine-imine tautomerization and ring expansion, similar to the chemistry of group 4 cumulene complexes,²⁴ finally yields the titanium azadiene complex **2a**. The thermally induced rearrangement of **I** to give **2b** suggests that in this case a [2 + 2] retro-cycloaddition is the first step (Scheme 5). Alternatively, a loose coordination of the nitrogen lone pair to the metal centre in **XII** could trigger a 1,3-H-shift to directly give **2a,b**. Noteworthy, the general possibility for a [2 + 2] cycloaddition pathway followed by multiple H-shifts can not be ruled out completely at this point. The proposed mechanism is shown in Scheme 6.

Conclusion

In this contribution an exception from the so far observed reactivity between titanium imido complexes and internal alkynes is reported. By employing the bis(cyclopentadienyl) titanium imido complex **1b**, the formation of the titanium azadienes **2a,b** can be achieved in reactions with the methyl-substituted alkynes 2-butyne and 1-phenyl-1-propyne, respectively. Whereas, in the case of 2-butyne the reaction proceeds at room temperature, the formation of the titanium azadiene complex **2b** is realized by heating a solution of the known [2 + 2] cycloaddition product **I** for a prolonged time. The titanium azadiene complexes were comprehensively characterized in solution by multinuclear NMR spectroscopy and in the solid state by single crystal X-ray diffraction. These unusual reactions between an early transition metal imido complex and internal alkynes *via* an initial C(sp³)-H activation step might induce new possibilities in hydroamination and nitrene transfer chemistry in the near future. Currently, extensive experimental and theoretical investigations on the proposed mechanism are being investigated in our laboratories.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

M. F.: conceptualization, experimentation, data analysis, drafting the manuscript and writing the final version with contributions from all authors; M. M.: conceptualization, experimentation, data analysis; M. S.: single crystal X-ray diffraction; T. K.: computational analysis; R. B.: conceptualization, project coordination.

Conflicts of interest

There are no conflicts to declare.

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