Selective propargylic C(sp³)–H activation of methyl-substituted alkynes versus [2 + 2] cycloaddition at a titanium imido template†

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The reaction of the titanium imido complex 1b with 2-butyne leads to the formation of the titanium azadiene complex 2a at ambient temperature instead of yielding the archetypical [2 + 2] cycloaddition product (titanaazacyclobutene) which is usually obtained by combining titanium imido complexes and internal alkynes. The formation of 2a is presumably caused by an initial propargylic C(sp³)–H activation step and quantum chemical calculations suggest that the outcome of this unexpected reactivity is thermodynamically favored. The previously reported titanaazacyclobutene I (which is obtained by reacting 1b with 1-phenyl-1-propyne) undergoes a rearrangement reaction at elevated temperature to give the corresponding five-membered titanium azadiene complex 2b.

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. Among these multiply bonded compounds, early transition metal imido complexes bearing [RN=]2− ligands (formally the dianion of a primary amine) are arguably one of the most important and well-understood. 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. 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. Furthermore, titanium imido complexes continue to gain momentum in stoichiometric and catalytic hydroamination, nitrene transfer, and oxidative amination reactions. 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. 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). Mashima, Tsurugi, and co-workers reported the activation of ortho C(sp³)–H aryl bonds at the N-aryl-substituent in imido bridged titanium complexes IV when reacted with 1-(trimethylsilyl)propyne to give the six-membered dinuclear titanium complex V (Scheme 1, third from top). 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...
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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**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 monoamine 1a and the titanium imido complex 1b. Enclosed reactivity studies of 1a/1b with multiple bond substrates furnished a broad range of [2 + 2] cycloaddition products. As a representative example, the reaction of 1a/1b with 1-phenyl-1-propyne regioselectively yielded the corresponding titanaazacyclobutene 1, 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 1 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. The hitherto only reported procedure of preparing TiCH2 substituted titanium azadiene complexes employs allylamines and (Piv)2Ti. 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 δ13C{1H} = 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. The signals of the respective chemically non-equivalent Ti–CH2 hydrogen atoms are localized at δH = 0.82 and 2.37 ppm. Both signals couple in the 1H/1H COSY spectrum to a multiplet signal at δH = 5.10 ppm with the corresponding 13C{1H} NMR signal at δ13C{1H} = 111.6 ppm. The remaining signals of the methyl group and the olefinic hydrogen atoms show coupling to the nitrogen atom in the 1H/15N HMBC spectrum (δ15N = 266.3 ppm). All these chemical shifts are in good agreement to other structurally characterized titanium azadienes, e.g. the recently reported complex VI† (Table 1).

The presence of eight signals in the 1H NMR spectrum (δ1H = 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 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 τ4/τ5 values of τ4 = 0.83 and τ5 = 0.69, respectively (the centroids of the Cp ligands have been used for the calculation). 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). The Ti1–N1 bond length of 2.020(1) Å and the Ti1–C43 bond length of 2.1840(9) Å are in reasonable accordance to the respective sums of covalent radii (∑cov(Ti–N) = 2.02 Å, ∑cov(Ti–C) = 2.11 Å (ref. 13)). 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(sp2)–C(sp3) single bond and a N–C(sp3)–C(sp3) = 1.51 Å, N–C(sp3) = 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.
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). I has been comprehensively characterized before. 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

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

| Complex | $\delta^1$H/$\delta^{13}$C($^1$H), TiCH$_2$ | $\delta^1$H/$\delta^{13}$C($^1$H), HC=C$_q$ | $\delta^{13}$C($^1$H), HC=C$_q$(R) | $\delta^{15}$N |
|---------|---------------------------------|---------------------------------|---------------------------------|-------------|
| 2a      | 0.82, 2.37/64.9                  | 5.10/111.6                     | 140.6                           | 266.3       |
| VI$^{13}$ | 1.35–1.95/57.3                  | 5.35/112.1                    | 132.2                           | 248.7       |

$^a$ Values are given in ppm. Measurements were carried out in C$_6$D$_6$ at room temperature. $^b$ Overlap with CH$_{ad}$/CH$_{2,ad}$ signals.

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**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 85.89(3), C11–Ti1–C12 128.3, $\Sigma$ N1 359.9, $\Sigma$ C44 359.4, $\Sigma$ C45 359.5, Ti1–C43–H43A/H43B/H43D–C43–C44 70.4, Ti1–C43–H43B/H43D–C43–C44 86.5 (C11 = centroid of C1–C5, C12 = centroid of C16–C20).
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 \( \tau_d/\tau_{d} \) values of \( \tau_d = 0.78 \) and \( \tau_{d} = 0.71 \), 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 \( \text{Ti}1-\text{N}1 \) and \( \text{Ti}1-\text{C}45 \) bond lengths of 2.034(2) Å and 2.107(3) Å are in good accordance to the respective single bond covalent radii (\( \text{P}^\text{cov}(\text{Ti}-\text{N}) = 2.07 \) Å, \( \text{P}^\text{cov}(\text{Ti}-\text{C}) = 2.11 \) Å (ref. 15)), the \( \text{C}44-\text{C}45 \) 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 \( \text{N}1-\text{C}44 \) bond length of 1.413(3) Å constitutes an elongated N–C(sp2) single bond (N–C(sp2) = 1.38 Å (ref. 8)), indicative for electron donation from the nitrogen lone pair to the electronegative 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 \( ^1\text{H} \) 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 \( \text{C}_6\text{D}_6 \) 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 titana-propargyl XI. A precoordination of the alkyne to the titanium center to give an alkyne-titanium π-complex (X) is
suggested to lower the pKᵢ of the propargylic hydrogen atom(s) in the first place. Even though this type of reactivity is very rare for titanium imido complexes, it was observed for reversible C(sp³)–H activation processes in the case of alkanes. Just recently, Tonks et al. also observed propargylic C–H activation of 3-hexyne by a titanium bisamido complex. Subsequently, the carbon–carbon triple bond inserts into the Ti–N bond which leads to the formation of the titanacyclopropane derivative X with an enamine functionality in the

Scheme 5  Thermally induced formation of 2b from 1.

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 (Å) 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), Ct1–Ti1–Ct2 128.6, ΣN1 359.6, ΣC44 360.0, ΣC45 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, and is common for group 3 metals. Enamine–imine tautomerization and ring expansion, similar to the chemistry of group 4 cumulene complexes, 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 XI 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 1 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(sp^3)–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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