Chemical
Science

ROYAL SOCIETY
OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Sci.*, 2021, **12**, 13711

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 8th August 2021
Accepted 27th September 2021

DOI: 10.1039/d1sc04334j

rsc.li/chemical-science

Selective propargylic C(sp^3)–H activation of methyl-substituted alkynes *versus* [2 + 2] cycloaddition at a titanium imido template†

Malte Fischer, ‡*[ac] Manfred Manßen, ‡*[bc] Marc Schmidtmann,[c]
Thorsten Klüner *[c] and Rüdiger Beckhaus *[c]

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(sp^3)–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.[1] 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.[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(sp^2)–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).[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

---

[a] Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK. E-mail: malte.fischer@chem.ox.ac.uk

[b] Anorganische Chemie Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: manfred.manssen@anorg.uni-tuebingen.de;

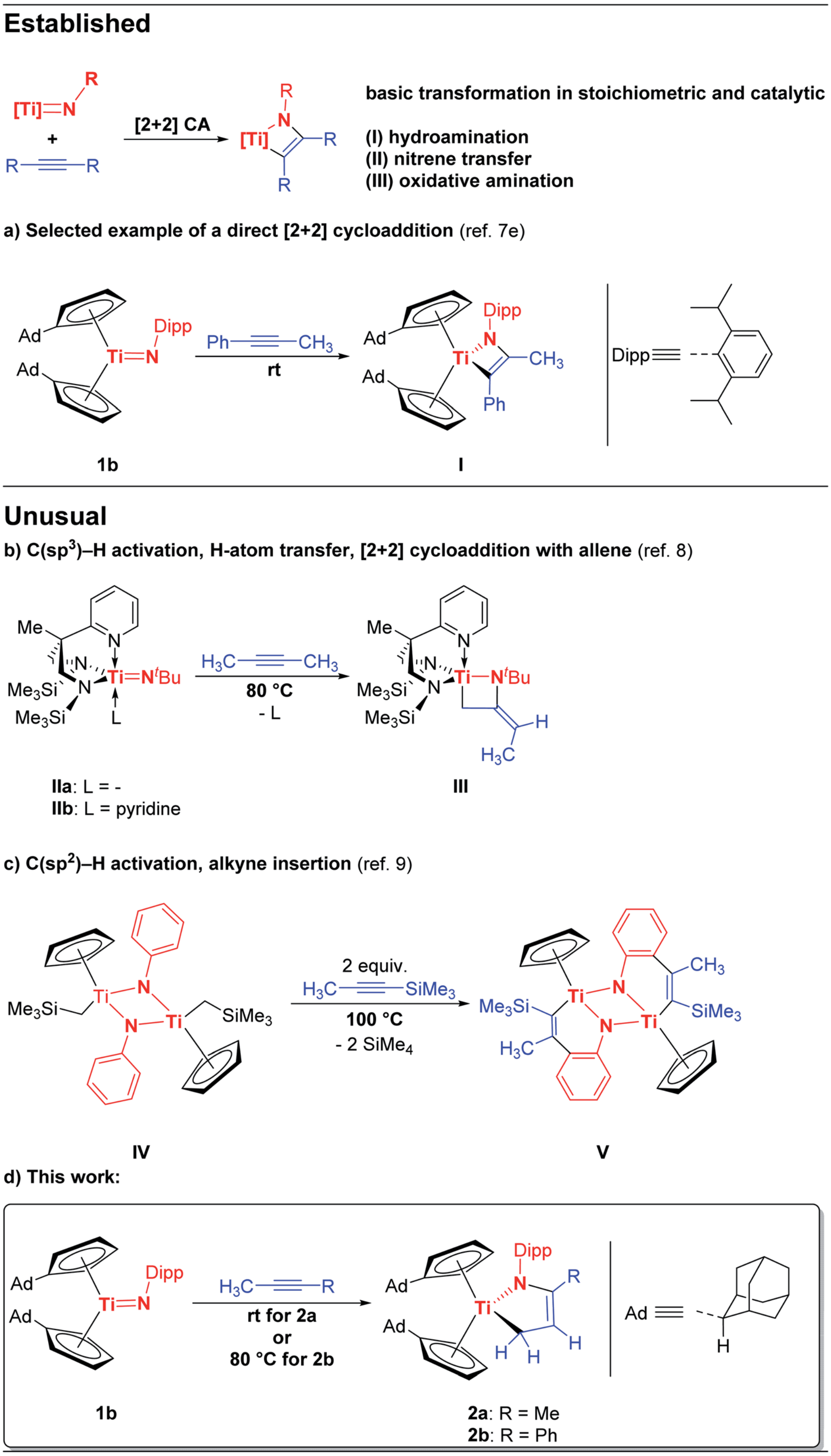
[c] Institut für Chemie, Fakultät für Mathematik und Naturwissenschaften, Carl von Ossietzky Universität Oldenburg, Postfach 2503, D-26111 Oldenburg, Germany. E-mail: ruediger.beckhaus@uni-oldenburg.de

† Electronic supplementary information (ESI) available. CCDC 2070445–2070447. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc04334j

‡ Equal contribution.

alkynes lead to the formation of five-membered titanium azadiene 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.



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 ^{1}H 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).

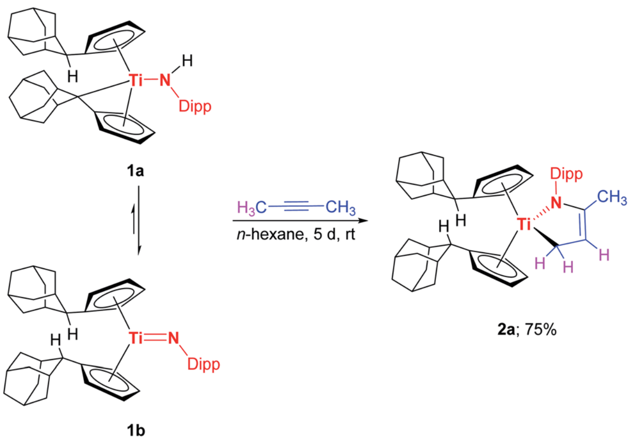
Noteworthy, titanium azadiene complexes are typically prepared by reductive complexation of azadiene ligand precursors and, due to the unavailability of CH_2 terminated azadienes, only α-C-substituted titanium azadiene complexes are synthetically available by this route.[11,12] The hitherto only other reported procedure of preparing $TiCH_2$ 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 $^{13}C\{^1H\}$ NMR signal at $\delta^{13}C\{^1H\} = 64.9$ ppm with a negative phase in the $^{13}C\{^1H\}$ DEPT 135 NMR spectrum, being in the typical region for methylene groups in position α to titanium.[13] The signals of the respective chemically nonequivalent Ti–CH_2 hydrogen atoms are localized at $\delta^1H = 0.82$ and 2.37 ppm. Both signals couple in the $^1H/^1H$ COSY spectrum to a multiplet signal at $\delta^1H = 5.10$ ppm with the corresponding $^{13}C\{^1H\}$ NMR signal at $\delta^{13}C\{^1H\} = 111.6$ ppm. The remaining signals of the methyl group and the belonging quaternary carbon atom at $\delta^1H = 1.69$ ppm ($\delta^{13}C\{^1H\} = 20.6$ ppm) and $\delta^{13}C\{^1H\} = 140.6$ ppm, together with the expected cross peaks in the 2D NMR spectra already allow for the assignment of connectivity in **2a**. Additionally, both the ^{1}H NMR signals of the methyl group and the olefinic hydrogen atoms show coupling to the nitrogen atom in the $^1H/^{15}N$ HMBC spectrum ($\delta^{15}N = 266.3$ 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 ^{1}H NMR spectrum ($\delta^1H = 4.93–5.93$ 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 ^{1}H NMR spectrum of **2a** in the temperature range from 213 K to 353 K (excerpt of the VT ^{1}H 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 ($\sum$cov(Ti–N) = 2.02 Å, $\sum$cov(Ti–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 $C(sp^3)–C(sp^2)$ single bond and a $N–C(sp^2)$ single bond ($C(sp^3)–C(sp^2) = 1.51$ Å, $N–C(sp^2) = 1.38$ Å (ref. 16)), respectively. The C44–C45 bond length of 1.3807(13) Å is elongated compared to a typical double bond between two sp^2-hybridized carbon atoms ($C(sp^2){=}C(sp^2) = 1.32$ Å (ref. 16)).

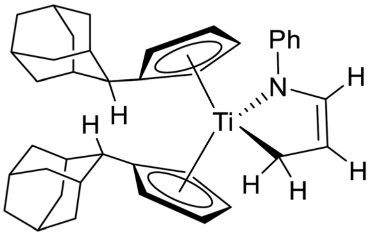
To gain further insight into the significantly different reactivity of **1a**/**1b** toward 2-butyne compared to the reactions of internal alkynes with other titanium imido complexes, quantum chemical calculations were performed.[17]



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

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

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



VI

[a] Values are given in ppm. Measurements were carried out in C_6D_6 at room temperature. [b] Overlap with $CH_{Ad}/CH_{2,Ad}$ signals.

The Gibbs free enthalpy difference Δ_rG for the formation of **2a** was found to be $\Delta_rG = -0.63$ eV which is significantly more exergonic as compared to the corresponding [2 + 2] cycloaddition product ($\Delta_rG = -0.16$ eV). The formation of a titanaazetidine (*cf.* **III**) could further be excluded being only slightly exergonic ($\Delta_rG = -0.10$ 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 $\Delta_rG = -0.52$ eV for the formation of the titanium azadiene complex, and $\Delta_rG = -0.26$ 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

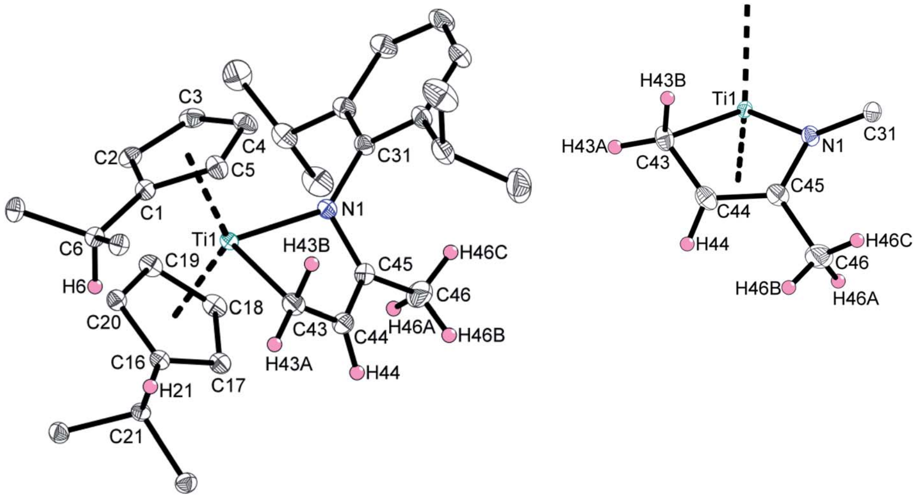
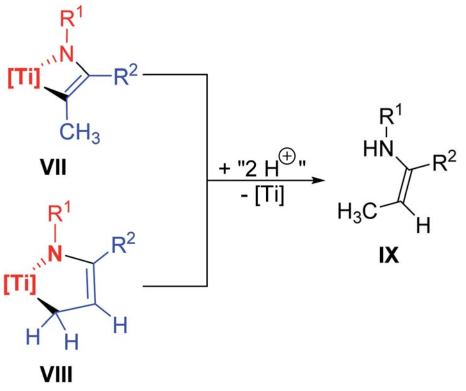
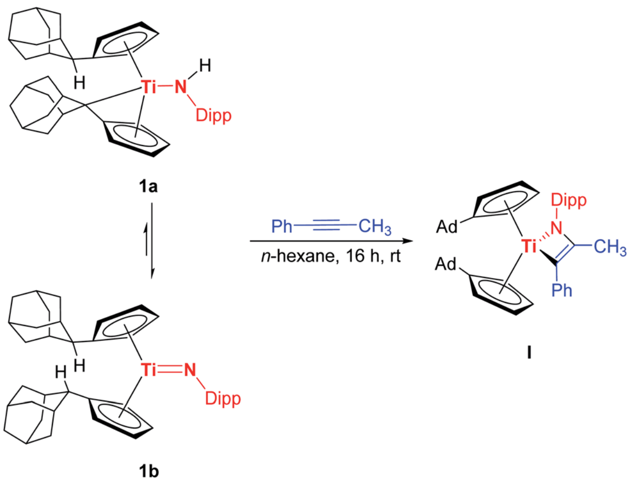


Fig. 1 Molecular structure of **2a**. Hydrogen atoms (except H6, H21, and those of the central five-membered ring system) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 2.0201(7), 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, $\Sigma\angle$N1 359.9, $\Sigma\angle$C44 359.4, $\Sigma\angle$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 $\tau_4 = 0.78$ ($\tau_d = 0.71$), 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 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 ($\sum$cov(Ti–N) = 2.07 Å, $\sum$cov(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 ($C(sp^2){=}C(sp^2)$ = 1.32 Å (ref. 16)), and the N1–C44 bond length of 1.413(3) Å constitutes an elongated $N{-}C(sp^2)$ single bond ($N{-}C(sp^2)$ = 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 ^{1}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 C_6D_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 titanapropargyl **XI**. A precoordination of the alkyne to the titanium center to give an alkyne-titanium π-complex (**X**) is

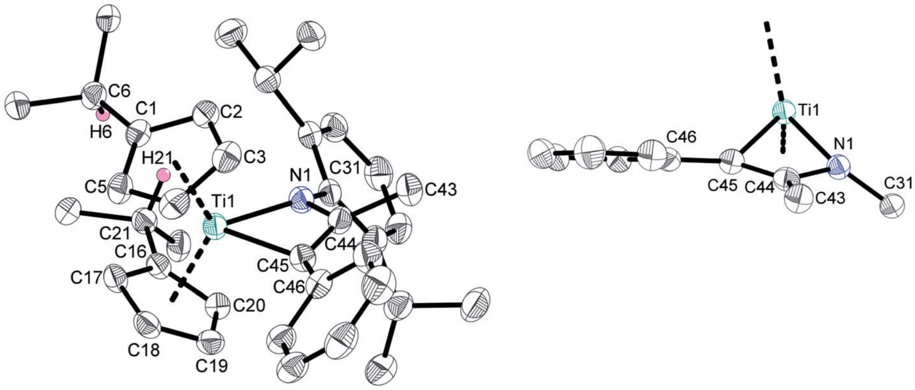
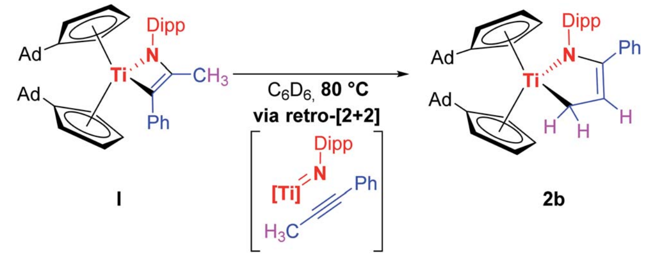


Fig. 2 Molecular structure of I. Hydrogen atoms (except H6 and H21) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 2.034(2), Ti1–C45 2.107(3), N1–C44 1.413(3), C44–C45 1.364(4), N1–Ti1–C45 67.47(10), Ct1–Ti1–Ct2 130.9, Σ∠N1 355.1, Σ∠C44 359.1, Σ∠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 pK_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 C(sp^3)–H activation processes in the case of alkanes.[2b,20] Just recently, Tonks *et al.* also observed propargylic C–H activation of 3-hexyne by a titanium bisamido complex.[21] Subsequently, the carbon–carbon triple bond inserts into the Ti–N bond which leads to the formation of the titanacyclopropane derivative **XII** with an enamine functionality in the

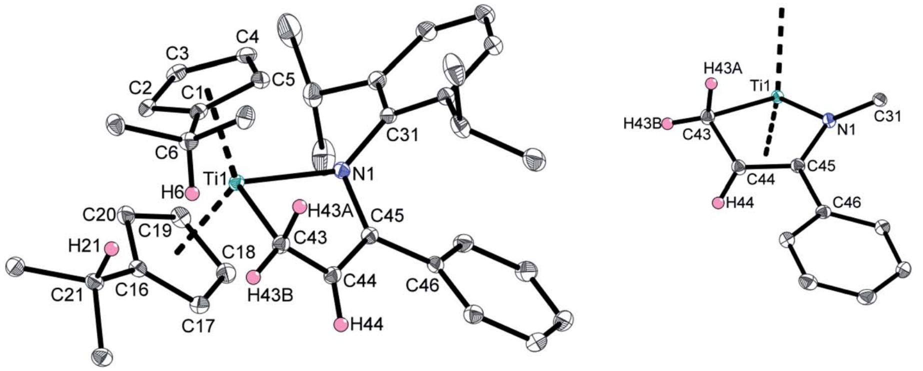
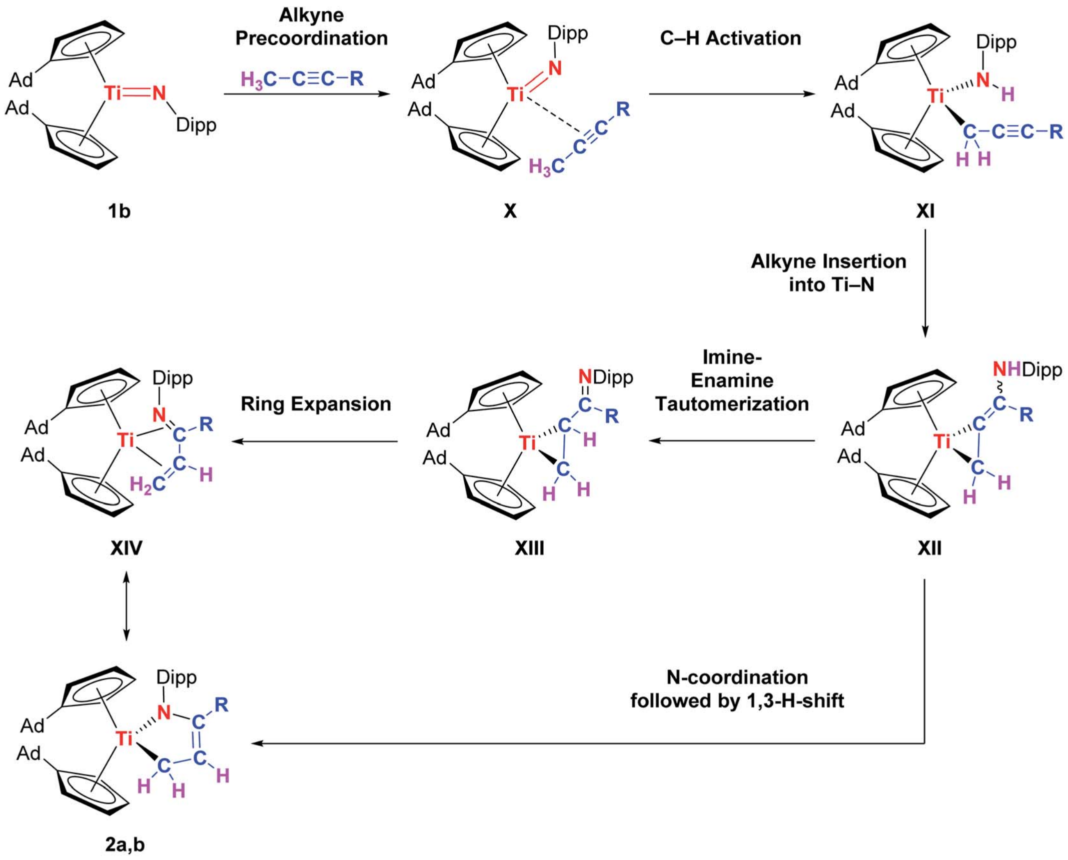


Fig. 3 Molecular structure of **2b**. Hydrogen atoms (except H6, H21, and except those of the central five-membered ring system) and fragments of the adamantyl groups are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti1–N1 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, $\Sigma\angle$N1 359.6, $\Sigma\angle$C44 360.0, $\Sigma\angle$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(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.

Acknowledgements

M. F. and M. M. are thankful to the Alexander von Humboldt Foundation for funding and support. The simulations were performed at the HPC Cluster CARL, located at the University of Oldenburg (Germany) and funded by the DFG through its Major Research Instrumentation Programme (INST 184/157-1 FUGG) and the Ministry of Science and Culture (MWK) of the State of Lower Saxony. M. F. would like to thank his friend Vladyslav Kukulevskyy for the drawing of the table of content.

References

1 (*a*) W. A. Herrmann, *Angew. Chem. Int. Ed.*, 1986, **25**, 56–76; *Angew. Chem.*, 1986, **98**, 57–77; (*b*) E. Rivard and P. P. Power, *Inorg. Chem.*, 2007, **46**, 10047–10064.
2 (*a*) P. D. Bolton and P. Mountford, *Adv. Synth. Catal.*, 2005, **347**, 355–366; (*b*) N. Hazari and P. Mountford, *Acc. Chem. Res.*, 2005, **38**, 839–849; (*c*) D. N. Zarubin and N. A. Ustynyuk, *Russ. Chem. Rev.*, 2006, **75**, 671–707; (*d*) A. R. Fout, U. J. Kilgore and D. J. Mindiola, *Chem.–Eur. J.*, 2007, **13**, 9428–9440; (*e*) R. R. Schrock, *Chem. Rev.*, 2009, **109**, 3211–3226; (*f*) T. L. Gianetti, H. S. La Pierre and J. Arnold, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3771–3783; (*g*) K. Kawakita, B. F. Parker, Y. Kakiuchi, H. Tsurugi, K. Mashima, J. Arnold and I. A. Tonks, *Coord. Chem. Rev.*, 2020, **407**, 213118.
3 (*a*) C. T. Owen, P. D. Bolton, A. R. Cowley and P. Mountford, *Organometallics*, 2007, **26**, 83–92; (*b*) R. Arteaga-Müller, J. Sánchez-Nieves, J. Ramos, P. Royo and M. E. G. Mosquera, *Organometallics*, 2008, **27**, 1417–1426.
4 T. Hanna, *Coord. Chem. Rev.*, 2004, **248**, 429–440.
5 Selected reviews: (*a*) T. E. Müller and M. Beller, *Chem. Rev.*, 1998, **98**, 675–703; (*b*) R. Severin and S. Doye, *Chem. Soc. Rev.*, 2007, **36**, 1407–1420; (*c*) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795–3892; (*d*) A. L. Odom and T. J. McDaniel, *Acc. Chem. Res.*, 2015, **48**, 2822–2833; (*e*) M. Manßen and L. L. Schafer, *Chem. Soc. Rev.*, 2020, **49**, 6947–6994.
6 Selected examples for nitrene transfer reactions with group 4 complexes: (*a*) A. I. Nguyen, R. A. Zarkesh, D. C. Lacy, M. K. Thorson and A. F. Heyduk, *Chem. Sci.*, 2011, **2**, 166–169; (*b*) A. A. Dissanayake and A. L. Odom, *Chem. Commun.*, 2012, **48**, 440–442; (*c*) C. M. Pasko, A. A. Dissanayake, B. S. Billow and A. L. Odom, *Tetrahedron*, 2016, **72**, 1168–1176; (*d*) Z. W. Gilbert, R. J. Hue and I. A. Tonks, *Nat. Chem.*, 2016, **8**, 63–68; (*e*) S. P. Heins, P. T. Wolczanski, T. R. Cundari and S. N. MacMillan, *Chem. Sci.*, 2017, **8**, 3410–3418; (*f*) Z. W. Davis-Gilbert, L. J. Yao and I. A. Tonks, *J. Am. Chem. Soc.*, 2016, **138**, 14570–14573; (*g*) A. J. Pearce, X. Y. See and I. A. Tonks, *Chem. Commun.*, 2018, **54**, 6891–6894; (*h*) H.-C. Chiu and I. A. Tonks, *Angew. Chem. Int. Ed.*, 2018, **57**, 6090–6094; *Angew. Chem.*, 2018, **130**, 6198–6202; (*i*) Z. W. Davis-Gilbert, X. Wen, G. D. Goodpaster and I. A. Tonks, *J. Am. Chem. Soc.*, 2018, **140**, 7267–7281; (*j*) Z. W. Davis-Gilbert, K. Kawakita, D. R. Blechschmidt,

H. Tsurugi, K. Mashima and I. A. Tonks, *Organometallics*, 2018, **37**, 4439–4445; (*k*) E. P. Beaumier, M. E. McGreal, A. R. Pancoast, R. H. Wilson, K. T. Moore, B. J. Graziano, J. D. Goodpaster and I. A. Tonks, *ACS Catal.*, 2019, **9**, 11753–11762; (*l*) A. J. Pearce, R. P. Harkins, B. R. Reiner, A. C. Wotal, R. J. Dunscomb and I. A. Tonks, *J. Am. Chem. Soc.*, 2020, **142**, 4390–4399; (*m*) E. P. Beaumier, A. A. Ott, X. Wen, Z. W. Davis-Gilbert, T. A. Wheeler, J. J. Topczewski, J. D. Goodpaster and I. A. Tonks, *Chem. Sci.*, 2020, **11**, 7204–7209.

7 Further selected examples in which group 4 azacyclobutenes were isolated: (*a*) P. J. Walsh, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729–8731; (*b*) P. J. Walsh, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 1708–1719; (*c*) N. Vujikovic, B. D. Ward, A. Maisse-Francois, H. Wadepohl, P. Mountfourd and L. Gade, *Organometallics*, 2007, **26**, 5522–5534; (*d*) P. D. Bolton, M. Feliz, A. R. Cowley, E. Clot and P. Mountford, *Organometallics*, 2008, **27**, 6096–6110; (*e*) M. Manßen, S. de Graaff, M. F. Meyer, M. Schmidtmann and R. Beckhaus, *Organometallics*, 2018, **37**, 4506–4514; (*f*) M. Fischer, M. C. Wolff, E. del Horno, M. Schmidtmann and R. Beckhaus, *Organometallics*, 2020, **39**, 3232–3239.

8 (*a*) A. Bashall, M. McParlin, P. E. Collier, P. Mountford, L. H. Gade and D. J. M. Trösch, *Chem. Commun.*, 1998, 2555–2556; (*b*) D. J. M. Trösch, P. E. Collier, A. Bashall, L. H. Gade, M. McPartlin, P. Mountford and S. Radojevic, *Organometallics*, 2001, **20**, 3308–3313.

9 H. Nagae, W. Hato, K. Kawakita, H. Tsurugi and K. Mashima, *Chem.–Eur. J.*, 2017, **23**, 586–596.

10 The corresponding titanium imido pyridine adduct of **1a**/**1b** proved to be completely inert in reactions with multiple bond substrates.[7e]

11 (*a*) M. Fischer, M. Schmidtmann and R. Beckhaus, *Organometallics*, 2017, **36**, 4779–4793; (*b*) F. Loose, I. Plettenberg, D. Haase, W. Saak, M. Schmidtmann, A. Schäfer, T. Müller and R. Beckhaus, *Organometallics*, 2014, **33**, 6785–6795; (*c*) S. Kahlert, H. Görls and J. Scholz, *Angew. Chem. Int. Ed.*, 1998, **37**, 1857–1861; *Angew. Chem.*, 1998, **37**, 1857–1861; (*d*) J. Scholz, S. Kahlert and H. Görls, *Organometallics*, 1998, **17**, 2876–2884; (*e*) J. Scholz, M. Nolte and C. Krüger, *Chem. Ber.*, 1993, **126**, 803–809; (*f*) J. M. Davis, R. J. Whitby and A. Jaxa-Chamiec, *J. Chem. Soc., Chem. Commun.*, 1991, 1743–1745.

12 H. K. Hall, *Makromol. Chem., Macromol. Symp.*, 1992, **54–55**, 73–81.

13 (*a*) M. Manßen, I. Töben, C. Kahrs, J.-H. Bölte, M. Schmidtmann and R. Beckhaus, *Organometallics*, 2017, **36**, 2973–2981; (*b*) M. Manßen, C. Kahrs, I. Töben, J.-H. Bölte, M. Schmidtmann and R. Beckhaus, *Chem.–Eur. J.*, 2017, **23**, 15827–15833.

14 (*a*) M. H. Reineke, M. D. Sampson, A. L. Rheingold and C. P. Kubiak, *Inorg. Chem.*, 2015, **54**, 3211–3217; (*b*) L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964.

15 (*a*) P. Pyykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 12770–12779; (*b*) P. Pyykkö and M. Atsumi, *Chem.–Eur. J.*, 2009, **15**, 186–197.

16 M. B. Smith and J. March, *Advanced Organic Chemistry*, 6th edn, Wiley, New York, 2007.

17 All calculations were performed using version ES64L-G16RevA.03 of Gaussian 16. Using a cc-pVTZ basis set, the geometry of all species were optimized within density functional theory using the B97D3 functional for exchange and correlation. Subsequent frequency calculations were performed to exclude imaginary frequencies of all obtained structures and to obtain thermodynamic properties (T = 298, 15 K, p = 1 atm). M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas,J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

18 Selected examples for this reactivity: (*a*) D. C. Leitch, C. S. Turner and L. L. Schafer, *Angew. Chem. Int. Ed.*, 2010, **49**, 6382–6386; *Angew. Chem.*, 2010, **122**, 6526–6530; (*b*) D. V. Gribkov and K. C. Hultzsch, *Angew. Chem. Int. Ed.*, 2004, **43**, 5542–5546; *Angew. Chem.*, 2004, **116**, 5659–5663.

19 Y. Wang, J. Zhu, A. C. Durham, H. Lindberg and Y.-M. Wang, *J. Am. Chem. Soc.*, 2019, **141**, 19594–19599.

20 J. L. Bennett and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1997, **119**, 10696–10719.

21 A. J. Pearce, Y. Cheng, R. J. Dunscomb and I. Tonks, *Organometallics*, 2020, **39**, 3771–3774.

22 C. Müller, R. Koch and S. Doye, *Chem.–Eur. J.*, 2008, **14**, 10430–10436.

23 (*a*) F. Lauterwasser, P. G. Hayer, S. Bräse, W. E. Piers and L. L. Schafer, *Organometallics*, 2004, **23**, 2234–2237; (*b*) L. J. E. Stanlake and L. L. Schafer, *Organometallics*, 2009, **28**, 3990–3998.

24 U. Rosenthal, V. V. Burlakov, M. A. Bach and T. Beweries, *Chem. Soc. Rev.*, 2007, **36**, 719–728.