This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: N. Tsoureas, J. Green and F. G. Cloke, Chem. Commun., 2017, DOI: 10.1039/C7CC07726B.
C-H and H-H Activation at a Di-titanium Centre†

Nikolaos Tsoureas, a Jennifer C. Greenb and F. Geoffrey N. Cloke c

Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/X000000x

www.rsc.org/

The reaction of the bis[pentane]dititanium complex Ti₂(μ-η⁵,η⁵-SiNP₃)₂ (PN₃ = C₅H₅(1,4-SiPr₃)) with the N-heterocyclic carbene 1,3,4,5-tetramethyldimidazol-2-ylidene results in intramolecular C-H activation of one of the Pr methyl groups of a PN₃ ligand and formation of a "tucked-in" bridging hydride complex. The "tuck-in" process is reversed by the addition of hydrogen, which yields a dihydride featuring terminal and bridging hydrides.

Group IV metallocene chemistry has been instrumental in the development of organometallic chemistry, elucidating fundamental aspects of bonding and reactivity, especially via the synthesis, isolation and study of low valent metallocene complexes. In this context, the synthesis and isolation of such complexes bearing hydride ligands has been important; for example, such low or mixed valence hydride complexes have been shown to promote or be involved in the fixation of N₂ to NH₄⁺. In this communication, we present the first examples of the synthesis of bridging titanium hydrides under non-reducing conditions, via the reaction of bis[pentane]dititanium complex Ti₂(μ-η⁵,SiNP₃)₂ (PN₃ = C₅H₅(1,4-SiPr₃)) with an N-heterocyclic carbene and subsequent hydrogenolysis.

We have previously reported on the reactivity of Ti₂(μ-η⁵,η⁵-PN₃)₂ (PN₃ = C₅H₅(1,4-SiPr₃)) (1) towards a variety of small molecules and π-acceptor ligands. In order to gain a better insight into the reactivity of (1), we decided to study its interaction with strong α-donor ligands. When (1) was treated with an excess of PME₅, no reaction was observed. However, addition of 1,3,4,5-tetramethyldimidazol-2-ylidene (2) to (1) in toluene at 0 °C resulted in an immediate colour change from crimson red to a dark pine green (Scheme 1).

Scheme 1: Synthesis of a new syn-bimetallic hydride titanium cluster.

The formulation of the new complex (3) as a "tucked-in" hydride resulting from C-H activation of one of the Pr methyl groups of a PN₃ induced by addition of the strongly donating NHC (2) was initially confirmed by NMR. In particular, the 1H-NMR spectrum showed two inequivalent pentane ring environments, a sharp singlet at -7.91 ppm for the bridging hydride (Ti; 479ms), with one of the diastereotopic protons of the "tucked-in" CH₃ group appearing as an overlapping dd at -2.91 ppm whilst the other was largely obscured by the complex aliphatic region of the spectrum at ca 1.37 ppm; the coordination of the NHC was confirmed by the observation of a peak at 197.78 ppm in the 13C[1H]-NMR spectrum.

The structure of (3) was confirmed by X-ray diffraction and is shown in Figure 1. The NHC coordinates to one of the Ti centres (Ti2 in Figure 1), while one of the methyl groups on a TIPS substituent has been cyclometallated on the other Ti centre (Ti1 in Figure 1) with concurrent formation of a bridging hydride. The Ti-Ti bond has been retained but lengthened to 2.5610(8) Å (from 2.399(2) Å in (1) ††) and is typical of a single bond. The Ti-C(carbene) bond (2.300(2) Å; Ti2-C1 in Figure 1) is within the range of 2.2-2.35 Å reported for other Ti-NHC complexes. The Ti-H bond lengths (ie...
COMMUNICATION

Ti2-H1: 1.72(3) Å, Ti1-H1: 1.79(3) Å) are identical within esd’s and are similar to previously reported monomeric10 and dimeric11–13 titanium hydrides as well as Ti(III) aluminates12 and borohydrides13 (1.7-1.9 Å), although it has to be noted that, probably due to the topology of the hydride ligand in (3), these Ti-H bond distances fall at the shorter end of the known range. Due to this unique topology, the Ti-H-Ti bond angle (93.4(13)°) approaches a right angle and is the most acute ever observed in dimeric titanium hydrides.11,12,64

Figure 1: ORTEP diagram of the molecular structure of (3) displaying 50% probability ellipsoids. 1Pr groups omitted for clarity

It is also worth noting that the addition of (2) to (1) results in the formal oxidation of the two Ti centres (ie from +2 to +3), and employing the CBC model each Ti has a count of 18e (16e in (1)).14

With a view to synthesising a new hydride derivative via σ-bond metathesis of the Ti-CH3 bond in (3) with dihydrogen, 2 bar of H2 was added to a C6D6 solution of (3) in an NMR tube. This indeed resulted in clean conversion of (3) (100% spectroscopic yield) to a new complex (4) (Scheme 2).

Scheme 2. Hydrogenolysis of (3) to afford (4)

Compared to the 1H NMR spectrum of (3), (4) displays a new, broader hydride peak (Δν1/2 = 29 Hz) at -8.82 ppm at room temperature, whilst the signal for the “tucked-in” CH3 group has disappeared completely; the NHC is still coordinated (13C{1H} δ 198.27 ppm). Removal of the H2 overpressure by freeze-thaw-degassing showed that (4) is persistent in solution, although some regeneration of (3) was observed (Scheme 2). Addition of H2 to a solution of (3), via a Teeppler pump, showed that for the conversion of (3) to (4) to occur quickly (minutes) 5 eq of H2 are required (when 1-2 equivalents of H2 were added, complete conversion to (4) occurred after ca 1 week). The rate of reaction was also found to be pressure dependent: when (3) was exposed to an atmosphere of 10% H2 in N2 at 1.5 bar but in an amount corresponding to only 1 equivalent of H2 the reaction was again complete in minutes.

Variable temperature 1H NMR studies showed that the broad hydride peak at -8.82 ppm in (4) becomes fully resolved into a doublet at 0 °C (with no further change below that temperature and down to -70 °C) with a T1 of 310ms, with the concomitant appearance of a second doublet centred at 2.17 ppm (T2 336ms), which is too broad to be observable at room temperature (Figure 2); these two signals are related by a coupling constant of JHH = 11 Hz. EXSY spectroscopy (in both the presence and absence of an H2 overpressure) confirmed that these two protons exchange at 30 °C while at 0 °C the process is quenched. Thus the peak at -8.82 ppm is assigned to the bridging hydride in (4) and that at 2.17 ppm to the terminal one (Scheme 2).

Initial attempts to crystallise (4) by standard methods (ie removal of volatiles and recrystallisation) were frustrated by the preferential isolation of crystalline (3) (as it is less soluble than (4)) with the mother liquor consisting of a mixture of (3) and (4) (ca 20:80 by NMR), due to the partial reversibility of the reaction. However, the solid state molecular structure15 of (4) (Figure 3) was eventually determined from single crystals grown by cooling slowly a freshly prepared solution of (4) at -78 °C under an overpressure (1.5 atm) of H2, and confirms the spectroscopic assignment.

Figure 3: ORTEP diagram of the molecular structure of (4) displaying 50% probability ellipsoids. 1Pr groups omitted for clarity.
The Ti-C(carbene) bond length in (4) is 2.291(4) Å and is identical to that found in (3). On the other hand, the Ti-Ti bond is slightly shortened in (4) from 2.5610(8) Å in (3) to 2.5413(8) Å possibly due to the negligible steric requirements of the terminal hydride ligand. The Ti-H(bridging) bond distances (Ti-H1 = 1.84(5) Å; Ti2-H1 = 1.79(5) Å) in (4) are similar within esd’s and compare with the ones found in (3); the same applies to the Ti-H(terminal) (ie Ti2-H2 = 1.74(4) Å in Figure 2) bond length. The Ti1-H1-Ti2 bond angle in (4) again approaches 90° (89(2)°) and is very similar to that found in (3).

When (3) was treated with an excess of D₂ (5 eq.), the formation of (4-D) was observed, but deuterium was found to be only incorporated in the hydridic positions, and not in the new Me group derived from the previously "tucked-in" CH₂ group (confirmed by ²H-NMR, DEPT-135 and gHSQC). Hence the reaction of (3) with H₂ to form (4) does not go via σ-bond metathesis (which would lead to D incorporation in the Me group in the reaction with D₂). Hence the formation of (4) (and also (3)) was probed computationally (ADF:B3P86/6-31G: details are given in the ESL). Preliminary studies suggested that steric factors were important in determining the reaction energies. For example energy of binding an NHC to a Ti₂P₈₂ dimer depended critically on the substituents. Introduction of the methyl substituents on the NHC made very little difference to its binding energy but the bulky S⁠(S)₃ substituents on the pentane ligands increased the Ti-Ti-C angle forcing the NHC to a less favourable binding position thus decreasing the binding energy significantly (Table 1).

<table>
<thead>
<tr>
<th>Ti pentane dimer</th>
<th>NHC</th>
<th>∆E (eV)</th>
<th>∆G (kJ/mol)</th>
<th>-C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₂(C₂H₄)₂</td>
<td>C₂H₄N₂</td>
<td>-1.31</td>
<td>-66</td>
<td>100</td>
</tr>
<tr>
<td>Ti₂(C₂H₂)₂</td>
<td>C₂Me₂N₂</td>
<td>-1.26</td>
<td>-65</td>
<td>114</td>
</tr>
<tr>
<td>Ti₃P₈₂</td>
<td>C₂Me₂N₂</td>
<td>-0.48</td>
<td>+21</td>
<td>127</td>
</tr>
</tbody>
</table>

* Calculations are on gas phase species which leads to an overestimation of the entropy change when there is a change in the number of species.

The degree to which the tuck-in reaction was favoured in the absence of an NHC was also investigated. The formation of Ti₃P₈₂(Ti₄P₈₂-H)(μ-H) from Ti₃P₈₂ was calculated to have ∆E=0.03 eV and ∆G=11 kJ/mol. However, the energies of the observed tuck-in reaction with the methylated NHC present were calculated to be ∆E=0.69 eV and ∆G=9 kJ/mol. Thus the presence of the base improves the energetics of the tuck-in reaction. The significant entropy disadvantage in the gas phase would be lessened in solution.

The HOMO of 3 (Figure 4) shows a Ti-Ti σ-bond. The calculated Ti-Ti distance is 2.56 Å in excellent agreement with experiment. The Ti-H distances are 1.83 Å and the angle at the bridging hydrogen 89°. Such discrepancies from the experimental values are not unusual when comparing distances to bound hydrogen between theory and X-ray diffraction experiments.

**Fig. 4. Isosurface for the HOMO of 3.**

Addition of H₂ to 3 to form 4 is calculated to have reaction energies ∆E=-0.77 eV and ∆G=31 kJ/mol. The calculated Ti-Ti distance for 4 is 2.54 Å reproducing the shortening from 3 found experimentally. The Ti-H(terminal) distance is 1.74 Å, the Ti-H(bridging) distances 1.81 and 1.82 Å and the Ti-H-Ti angle unchanged at 89°.

A transition state for this reaction was modelled using just one S⁠(S)₃ substituent on one of the pentane ligands and C₂H₄N as the NHC for computational efficiency. The free energy of activation was estimated as 84 kJ/mol for such a system. The transition state structure is shown in Figure 5.

**Fig. 5 Structure of the calculated transition state for H₂ addition. The reacting Hs are highlighted.**

The Ti distance to the previously bridging H is 3.53 Å and the Ti distances to the reacting H₂ are 2.74 and 3.24 Å, the H-H distance being 0.76 Å. Such a geometry indicates that the tuck-in process is reversed before complete H₂ addition, consistent with the lack of deuterium incorporation into P₃ groups and the conclusion that σ bond metathesis is not in play. It may be that the steric...
compression induced by the mre approach of the H₂ molecule is sufficient to reverse the tuck-in process, an idea given some credence by the pressure dependence of the reaction of (3) with H₂ (vide infra).

In conclusion, we have described the facile preparation of the first example of a syn-bimetallic Ti complex (3) featuring a bridging hydride, originating from the C-H activation of a 'Pr substituent induced by addition of the strong Lewis base 1,3,4,5-tetramethyldiimidazol-2-ylidene. Preliminary studies show that this transformation is also effected by other, effectively "planar" Lewis bases, e.g. dimethylaminopyridine (DMAP). The resultant C-H activation product (3) readily reacts with an excess of H₂ to produce very cleanly a unique syn-bimetallic di-hydride complex (4) featuring bridging and terminal hydride ligands. Labelling experiments and computational studies strongly suggest that the latter reaction does not proceed via a σ-bond metathesis mechanism.

Acknowledgements

We thank the EPSRC for funding (N.T.), and Dr Alexander Kilpatrick (University of Oxford) and Dr Iain Day (University of Sussex) for help with NMR experiments.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 P.J. Chiric, Organometallics, 2010, 29, 1500.
7 The hydride was found in the Fourier difference map and refined freely. We recognize the difficulties associated with the location of hydrogen atoms next to heavy atoms as Fourier ripples can be erroneously misinterpreted for hydrogen atoms due to the sharp cut-off at high angles. Nevertheless, based on the spectroscopic evidence the hydrogen atoms have been included in the supplied models.
11 (a) M.L.H. Green, G. Parkin, J. Chem. Ed., 2014, 91, 807. (b) L.C. Green, M.L.H. Green, G. Parkin, Chem. Commun., 2012, 48, 11481. (c) Data were collected up to 0.82 Å resolution using Cu/Kα as well up to 0.78 Å using Mo/Kα with identical metric parameters.
An NHC promotes intramolecular C-H activation in bis(pentalene)dititanium; this process is reversed by the addition of hydrogen, forming a dihydride.