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C–H and H–H activation at a di-titanium centre



## C–H and H–H activation at a di-titanium centre†‡

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**The reaction of the bis(pentalene)ditanium complex  $\text{Ti}_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$  ( $\text{Pn}^\dagger = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the  $^i\text{Pr}$  methyl groups of a  $\text{Pn}^\dagger$  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,<sup>1</sup> elucidating fundamental aspects of bonding<sup>2</sup> and reactivity,<sup>3</sup> especially *via* the synthesis, isolation and study of low valent metallocene complexes.<sup>1,4</sup> In this context, the synthesis and isolation of such complexes bearing hydride ligands has been important;<sup>5</sup> for example, such low or mixed valence hydride complexes have been shown to promote or be involved in the fixation of  $\text{N}_2$  to  $\text{NH}_3$ .<sup>6</sup> In this communication, we present the first examples of the synthesis of bridging titanium hydrides under non-reducing conditions, *via* the reaction of bis(pentalene)ditanium complex  $\text{Ti}_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$  ( $\text{Pn}^\dagger = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) with an N-heterocyclic carbene and subsequent hydrogenolysis.

We have previously reported on the reactivity of  $\text{Ti}_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$  ( $\text{Pn}^\dagger = \text{C}_8\text{H}_4(1,4\text{-Si}^i\text{Pr}_3)_2$ ) (**1**) towards a variety of small molecules and  $\pi$ -acceptor ligands.<sup>7</sup> In order to gain a better insight into the reactivity of (**1**), we decided to study its interaction with strong  $\sigma$ -donor ligands. When (**1**) was treated with an excess of  $\text{PMe}_3$  no reaction was observed. However, addition of 1,3,4,5-tetramethylimidazol-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).

The formulation of the new complex (**3**) as a “tucked-in” hydride resulting from C–H activation of one of the  $^i\text{Pr}$  methyl groups of a  $\text{Pn}^\dagger$  induced by addition of the strongly donating NHC (**2**) was initially confirmed by NMR. In particular, the  $^1\text{H}$ -NMR spectrum showed two inequivalent pentalene ring environments, a sharp singlet at  $-7.91$  ppm for the bridging hydride ( $T_1$  479 ms), with one of the diastereotopic protons of the “tucked-in”  $\text{CH}_2$  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  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum.

The structure of (**3**) was confirmed by X-ray diffraction and is shown in Fig. 1. The NHC coordinates to one of the Ti centres (Ti2 in Fig. 1), while one of the methyl groups on a TIPS substituent has been cyclometallated on the other Ti centre (Ti1 in Fig. 1) with concurrent formation of a bridging hydride.<sup>8</sup> The Ti–Ti bond has been retained but lengthened to 2.5610(8) Å (from 2.399(2) Å in (**1**)<sup>7e</sup>) and is typical of a single bond. The Ti–C(carbene) bond (2.300(2) Å; Ti2–C1 in Fig. 1) is within the range of 2.2–2.35 Å reported for other Ti–NHC complexes.<sup>9</sup> The Ti–H bond lengths (*i.e.* Ti2–H1: 1.72(3) Å, Ti1–H1: 1.79(3) Å) are identical within esd's and are similar to previously reported monomeric<sup>10</sup> and dimeric<sup>6d,6b,11</sup> titanium hydrides as well as Ti(III) alumino-<sup>12</sup> and borohydrides<sup>13</sup> (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.<sup>6b,6d,11</sup>

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

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† Dedicated to Phil on the occasion of his 65th birthday. Lá Breithe Soná!

‡ Electronic supplementary information (ESI) available: Full experimental and computational details, and X-ray data. CCDC 1577130–1577132. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc07726b





Fig. 1 ORTEP diagram of the molecular structure of **(3)** displaying 50% probability ellipsoids. <sup>1</sup>Pr 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 (*i.e.* from +2 to +3), and employing the CBC model each Ti has a count of 18 e (16 e in **(1)**).<sup>14</sup>

With a view to synthesising a new hydride derivative *via*  $\sigma$ -bond metathesis of the Ti–CH<sub>2</sub> bond in **(3)** with dihydrogen, 2 bar of H<sub>2</sub> was added to a C<sub>7</sub>D<sub>8</sub> 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).

Compared to the <sup>1</sup>H NMR spectrum of **(3)**, **(4)** displays a new, broader hydride peak ( $\Delta\nu_{1/2}$  = 29 Hz) at –8.82 ppm at room temperature, whilst the signal for the “tucked-in CH<sub>2</sub> group has disappeared completely; the NHC is still coordinated (<sup>13</sup>C{<sup>1</sup>H}  $\delta$  198.27 ppm). Removal of the H<sub>2</sub> overpressure by freeze–thaw–degassing showed that **(4)** is persistent in solution, although some regeneration of **(3)** was observed (Scheme 2). Addition of H<sub>2</sub> to a solution of **(3)**, *via* a Toepler pump, showed that for the conversion of **(3)** to **(4)** to occur quickly (minutes) 5 eq of H<sub>2</sub> are required (when 1–2 equivalents of H<sub>2</sub> 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% H<sub>2</sub> in N<sub>2</sub> at 1.5 bar but in an amount corresponding to only 1 equivalent of H<sub>2</sub> the reaction was again complete in minutes.

Variable temperature <sup>1</sup>H 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 T<sub>1</sub> of 310 ms, with the concomitant appearance of a second doublet centred at 2.17 ppm (T<sub>1</sub> 336 ms), which is too broad to be observable at room temperature (Fig. 2); these two signals are related by a coupling constant of J<sub>HH</sub> = 11 Hz. EXSY spectroscopy (in both



Fig. 2 Hydride peaks in **(4)** at RT (blue) and at 0 °C (black).

the presence and absence of an H<sub>2</sub> 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 (*i.e.* 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 structure<sup>8,15</sup> of **(4)** (Fig. 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 H<sub>2</sub>, and confirms the spectroscopic assignment.

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 (Ti1–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) (*i.e.* Ti2–H2 = 1.74(4) Å in Fig. 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 D<sub>2</sub> (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” CH<sub>2</sub> group (confirmed by <sup>2</sup>H-NMR, DEPT-135 and gHSQC). Hence the reaction of **(3)** with H<sub>2</sub> to form **(4)**



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



Fig. 3 ORTEP diagram of the molecular structure of **(4)** displaying 50% probability ellipsoids. <sup>1</sup>Pr groups omitted for clarity.





**Table 1** Electronic binding energies ( $\Delta E$ ) and Gibbs energy changes ( $\Delta G$ ) for the reaction  $\text{Ti}_2\text{Pn}_2 + \text{NHC} = \text{Ti}_2\text{Pn}_2\text{NHC}$ 

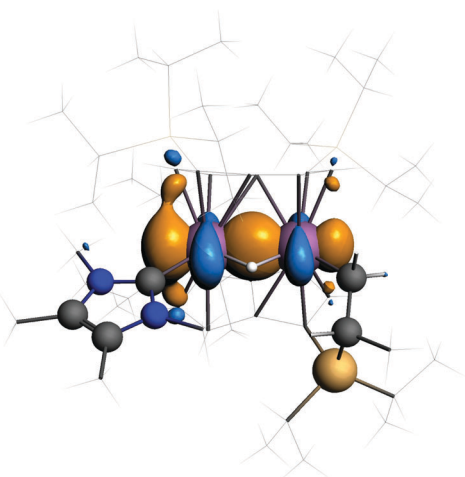
| Ti pentalene dimer                    | NHC                               | $\Delta E$ (eV) | $\Delta G^a$ (kJ mol <sup>-1</sup> ) | Ti-Ti-C (°) |
|---------------------------------------|-----------------------------------|-----------------|--------------------------------------|-------------|
| $\text{Ti}_2(\text{C}_8\text{H}_6)_2$ | $\text{C}_3\text{H}_4\text{N}_2$  | -1.31           | -66                                  | 100         |
| $\text{Ti}_2(\text{C}_8\text{H}_6)_2$ | $\text{C}_3\text{Me}_4\text{N}_2$ | -1.26           | -65                                  | 114         |
| $\text{Ti}_2\text{Pn}^\dagger_2$      | $\text{C}_3\text{Me}_4\text{N}_2$ | -0.48           | +21                                  | 127         |

<sup>a</sup> 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.

does not go *via*  $\sigma$ -bond metathesis (which would lead to D incorporation in the Me group in the reaction with  $\text{D}_2$ ). Hence the formation of (4) (and also (3)) was probed computationally (ADF:BP/TZP: details are given in the ESI†). Preliminary studies suggested that sterics were important in determining the reaction energies. For example energy of binding an NHC to a  $\text{Ti}_2\text{Pn}_2$  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  $\text{Si}^i\text{Pr}_3$  substituents on the pentalene ligands increased the Ti-Ti-C angle forcing the NHC to a less favourable binding position thus decreasing the binding energy significantly (Table 1).

The degree to which the tuck-in reaction was favoured in the absence of an NHC was also investigated. The formation of  $\text{Ti}_2\text{Pn}^\dagger(\text{Pn}^\dagger\text{-H})(\mu\text{-H})$  from  $\text{Ti}_2\text{Pn}^\dagger_2$  was calculated to have  $\Delta E = -0.03$  eV and  $\Delta G = 11$  kJ mol<sup>-1</sup>. However, the energies of the observed tuck-in reaction with the methylated NHC present were calculated to be  $\Delta E = -0.69$  eV and  $\Delta G = 9$  kJ mol<sup>-1</sup>. 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 (Fig. 4) shows a Ti-Ti  $\sigma$ -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.**Fig. 5** Structure of the calculated transition state for  $\text{H}_2$  addition. The reacting Hs are highlighted.

Addition of  $\text{H}_2$  to 3 to form 4 is calculated to have reaction energies  $\Delta E = -0.77$  eV and  $\Delta G = -31$  kJ mol<sup>-1</sup>. 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  $\text{Si}^i\text{Pr}_3$  substituent on one of the pentalene ligands and  $\text{C}_3\text{H}_4\text{N}$  as the NHC for computational efficiency. The free energy of activation was estimated as 84 kJ mol<sup>-1</sup> for such a system. The transition state structure is shown in Fig. 5.

The Ti distance to the previously bridging H is 3.53 Å and the Ti distances to the reacting  $\text{H}_2$  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  $\text{H}_2$  addition, consistent with the lack of deuterium incorporation into  $^i\text{Pr}$  groups and the conclusion that  $\sigma$  bond metathesis is not in play. It may be that the steric compression induced by the mere approach of the  $\text{H}_2$  molecule is sufficient to reverse the tuck-in process, an idea given some credence by the pressure dependence of the reaction of (3) with  $\text{H}_2$  (*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  $^i\text{Pr}$  substituent induced by addition of the strong Lewis base 1,3,4,5-tetramethylimidazol-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  $\text{H}_2$  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  $\sigma$ -bond metathesis mechanism.

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## Conflicts of interest

There are no conflicts to declare.



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