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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)dititanium complex Ti2(µ-η5,η5-Pn)2 (Pn = C8H4(1,4-SiPr3)2) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the 1Pr methyl groups of a Pn 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 NH3. 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)dititanium complex Ti2(µ-η5,η5-Pn)2 (Pn = C8H4(1,4-SiPr3)2) with an N-heterocyclic carbene and subsequent hydrogolysis.

We have previously reported on the reactivity of Ti2(µ-η5,η5-Pn)2 (Pn = C8H4(1,4-SiPr3)2) (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 σ-donor ligands. When (1) was treated with an excess of PMe3 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 1Pr methyl groups of a Pn ligand by addition of the strongly donating NHC (2) was initially confirmed by NMR. In particular, the 1H-NMR spectrum showed two inequivalent pentalene ring environments, a sharp singlet at −7.91 ppm for the bridging hydride (T1: 479 ms), with one of the diastereotopic protons of the “tucked-in” CH2 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 0.137 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 Fig. 1. The NHC coordinates to one of the Ti centres (T12 in Fig. 1), while one of the methyl groups on a TIPS substituent has been cyclometallated on the other Ti centre (T1 in Fig. 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)5) and is typical of a single bond. The Ti–C(carbene) bond (2.300(2) Å; T12–C1 in Fig. 1) is within the range of 2.2–2.35 Å reported for other Ti–NHC complexes.9 The Ti–H bond lengths (i.e. T12–H1: 1.72(3) Å, T12–H2: 1.79(3) Å) are identical within esd's and are similar to previously reported monomeric10 and dimeric,6,11 titanium hydrides as well as Ti(µ) aluminoids12 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.6,10,11

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

† Dedicated to Phil on the occasion of his 65th birthday - Lá Breithe Sona!
‡ 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

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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)).

With a view to synthesising a new hydride derivative via σ-bond metathesis of the Ti–CH2 bond in (3) with dihydrogen, 2 bar of H2 was added to a C2D4 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 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” CH2 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 Toeppler 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 310 ms, with the concomitant appearance of a second doublet centred at 2.17 ppm (T1 336 ms), which is too broad to be observable at room temperature (Fig. 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 (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 structure6,15 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 H2, 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 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)
energies. For example energy of binding an NHC to a Ti$_2$Pn$_2$ dimer suggested that sterics were important in determining the reaction
‡ (ADF:BP/TZP: details are given in the ESI)
would be lessened in solution.
The presence of the base improves the energetics of the tuck-in
‡ substituents on the NHC made very little difference to its binding
depended critically on the substituents. Introduction of the methyl
between theory and X-ray diffraction experiments.
are not unusual when comparing distances to bound hydrogen
The Ti–H distances are 1.83 Å and the angle at the bridging
energy but the bulky Si$i$Pr$_3$ substituents on the pentalene ligands
of Ti$_2$Pn (Table 1).
The degree to which the tuck-in reaction was favoured in
the absence of an NHC was also investigated. The formation
(vide infra)
belongs to form
Addition of H$_2$ to 3 to form 4 is calculated to have reaction
energies $\Delta E = -0.77$ eV and $\Delta G = -31 \text{ kJ mol}^{-1}$. 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 Si$i$Pr$_3$ substituent on one of the pentalene ligands and
C$_3$H$_4$N$_2$ as the NHC for computational efficiency. The free energy
of activation was estimated as 84 kJ mol$^{-1}$ 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 H$_2$ are 2.74 and 3.24 Å, the H–H
distance being 0.76 Å. Such a geometry indicates that the tuck-
process is reversed before complete H$_2$ addition, consistent
with the lack of deuterium incorporation into iPr groups and
the conclusion that σ bond metathesis is not in play. It may be
that the steric compression induced by the mere approach of the
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 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 iPr
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 H$_2$ to produce
very cleanly a unique syn-bimetallic di-hydride complex (4) feature-
ing 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.
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**Conflicts of interest**

There are no conflicts to declare.
Notes and references

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8 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.


15 Data were collected up to 0.82 Å resolution using CuKα as well up to 0.78 Å using MoKα with identical metric parameters.