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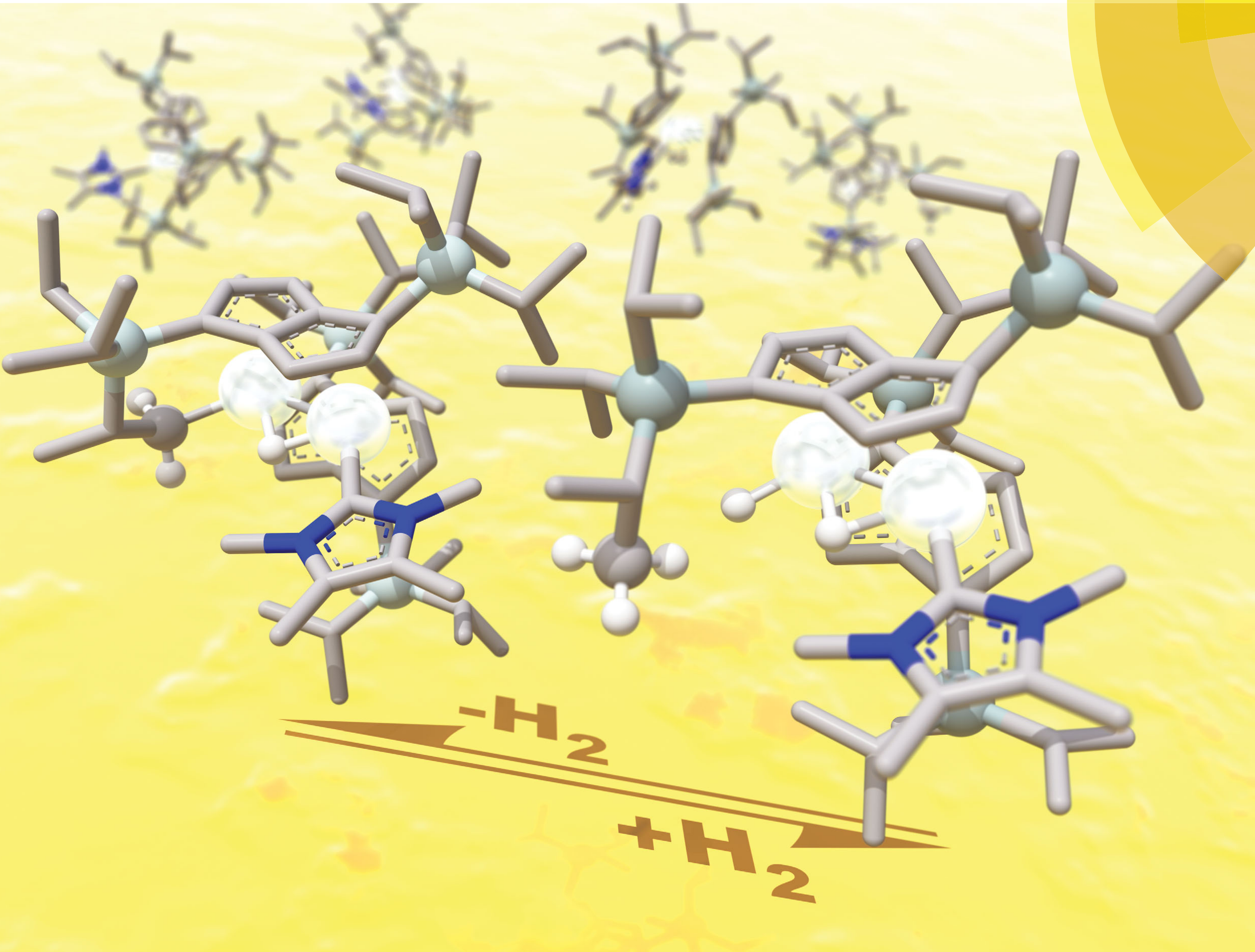

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C–H and H–H activation at a di-titanium centre†‡

Nikolaos Tsoureas,[a] Jennifer C. Green[b] and F. Geoffrey N. Cloke *[a]

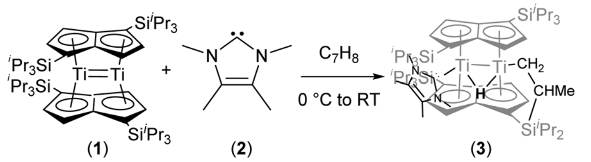
The reaction of the bis(pentalene)dititanium complex $Ti_2(\mu{:}\eta^5,\eta^5\text{-}Pn^\dagger)_2$ ($Pn^\dagger = C_8H_4(1,4\text{-}Si^iPr_3)_2$) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the ^{i}Pr methyl groups of a $Pn^\dagger$ 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,[1] elucidating fundamental aspects of bonding[2] and reactivity,[3] especially *via* the synthesis, isolation and study of low valent metallocene complexes.[1,4] In this context, the synthesis and isolation of such complexes bearing hydride ligands has been important;[5] for example, such low or mixed valence hydride complexes have been shown to promote or be involved in the fixation of N_2 to NH_3.[6] 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 $Ti_2(\mu{:}\eta^5,\eta^5\text{-}Pn^\dagger)_2$ ($Pn^\dagger$ = $C_8H_4(1,4\text{-}Si^iPr_3)_2$) with an N-heterocyclic carbene and subsequent hydrogenolysis.

We have previously reported on the reactivity of $Ti_2(\mu{:}\eta^5,\eta^5\text{-}Pn^\dagger)_2$ ($Pn^\dagger$ = $C_8H_4(1,4\text{-}Si^iPr_3)_2$) (**1**) towards a variety of small molecules and π-acceptor ligands.[7] 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 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}Pr methyl groups of a $Pn^\dagger$ induced by addition of the strongly donating NHC (**2**) was initially confirmed by NMR. In particular, the ^{1}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" 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 $^{13}C\{^1H\}$-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 (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.[8] The Ti–Ti bond has been retained but lengthened to 2.5610(8) Å (from 2.399(2) Å in (**1**)[7e]) 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.[9] 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[10] and dimeric[6d,6b,11] titanium hydrides as well as Ti(III) alumino-[12] and borohydrides[13] (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.[6b,6d,11]



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

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[a] *Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK. E-mail: f.g.cloke@sussex.ac.uk*

[b] *Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK*

† 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

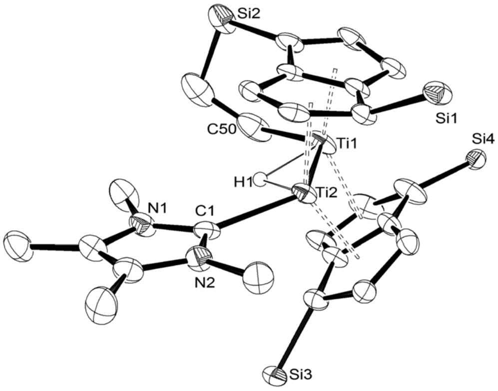
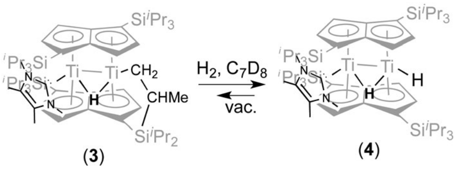


Fig. 1 ORTEP diagram of the molecular structure of (**3**) displaying 50% probability ellipsoids. ^{i}Pr groups omitted for clarity.

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**)).[14]

With a view to synthesising a new hydride derivative *via* σ-bond metathesis of the Ti–CH$_2$ bond in (**3**) with dihydrogen, 2 bar of H$_2$ was added to a C$_7$D$_8$ 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 ^{1}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$_2$ group has disappeared completely; the NHC is still coordinated (^{13}C{^{1}H} δ 198.27 ppm). Removal of the H$_2$ overpressure by freeze–thaw-degassing showed that (**4**) is persistent in solution, although some regeneration of (**3**) was observed (Scheme 2). Addition of H$_2$ 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$_2$ are required (when 1–2 equivalents of H$_2$ 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$_2$ in N$_2$ at 1.5 bar but in an amount corresponding to only 1 equivalent of H$_2$ the reaction was again complete in minutes.



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

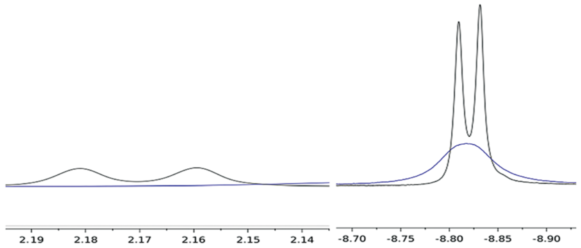


Fig. 2 Hydride peaks in (**4**) at RT (blue) and at 0 °C (black).

Variable temperature ^{1}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$_1$ of 310 ms, with the concomitent appearance of a second doublet centred at 2.17 ppm (T$_1$ 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_{HH} = 11 Hz. EXSY spectroscopy (in both the presence and absence of an H$_2$ 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[8,15] 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 H$_2$, 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$_2$ (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$_2$ group (confirmed by ^{2}H-NMR, DEPT-135 and gHSQC). Hence the reaction of (**3**) with H$_2$ to form (**4**)

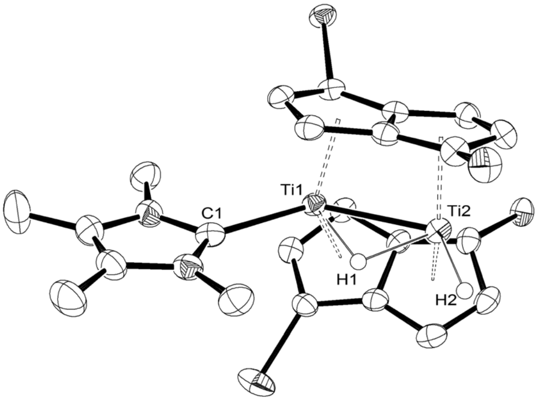


Fig. 3 ORTEP diagram of the molecular structure of (**4**) displaying 50% probability ellipsoids. ^{i}Pr groups omitted for clarity.

Table 1 Electronic binding energies (ΔE) and Gibbs energy changes (ΔG) for the reaction Ti_2Pn_2 + NHC = Ti_2Pn_2NHC

Ti pentalene dimer	NHC	ΔE (eV)	ΔG^a (kJ mol^{-1})	Ti–Ti–C (°)
$Ti_2(C_8H_6)_2$	$C_3H_4N_2$	−1.31	−66	100
$Ti_2(C_8H_6)_2$	$C_3Me_4N_2$	−1.26	−65	114
$Ti_2Pn^{\dagger}_2$	$C_3Me_4N_2$	−0.48	+21	127

[a] 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* σ-bond metathesis (which would lead to D incorporation in the Me group in the reaction with 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 Ti_2Pn_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 Si^iPr_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 $Ti_2Pn^{\dagger}(Pn^{\dagger}\text{-H})(\mu\text{-H})$ from $Ti_2Pn^{\dagger}_2$ was calculated to have ΔE = −0.03 eV and ΔG = 11 kJ mol^{-1}. However, the energies of the observed tuck-in reaction with the methylated NHC present were calculated to be ΔE = −0.69 eV and ΔG = 9 kJ mol^{-1}. 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 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.

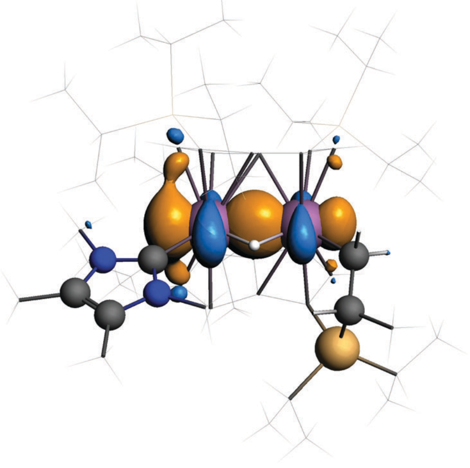


Fig. 4 Isosurface for the HOMO of **3**.

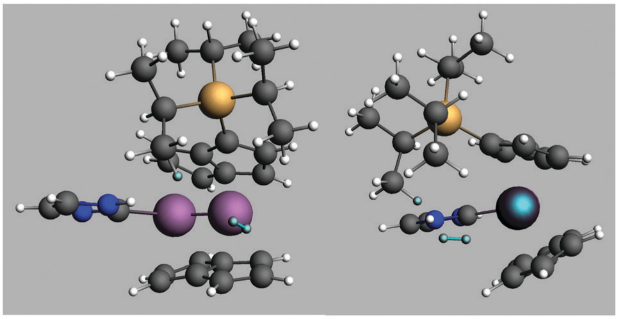


Fig. 5 Structure of the calculated transition state for H_2 addition. The reacting Hs are highlighted.

Addition of H_2 to **3** to form **4** is calculated to have reaction energies ΔE = −0.77 eV and ΔG = −31 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^iPr_3 substituent on one of the pentalene ligands and C_3H_4N 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-in process is reversed before complete H_2 addition, consistent with the lack of deuterium incorporation into ^{i}Pr 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 ^{i}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 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 σ-bond metathesis mechanism.

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Conflicts of interest

There are no conflicts to declare.

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