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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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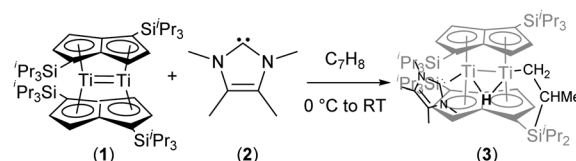
The reaction of the bis(pentalene)ditanium complex $Ti_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$ ($Pn^\dagger = C_8H_4(1,4\text{-Si}^iPr_3)_2$) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the iPr methyl groups of a Pn^\dagger 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 bonding² 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)ditanium complex $Ti_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$ ($Pn^\dagger = C_8H_4(1,4\text{-Si}^iPr_3)_2$) with an N-heterocyclic carbene and subsequent hydrogenolysis.

We have previously reported on the reactivity of $Ti_2(\mu\text{-}\eta^5, \eta^5\text{-Pn}^\dagger)_2$ ($Pn^\dagger = C_8H_4(1,4\text{-Si}^iPr_3)_2$) (**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 iPr methyl groups of a Pn^\dagger induced 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 (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 monomeric¹⁰ and dimeric^{6d,6b,11} titanium hydrides as well as Ti(III) alumino-¹² 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.^{6b,6d,11}

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. 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 (*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-CH₂ bond in (3) with dihydrogen, 2 bar of H₂ was added to a C₇D₈ 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 ($\Delta\nu_{1/2}$ = 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 Toepler 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 J_{HH} = 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 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 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 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)



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

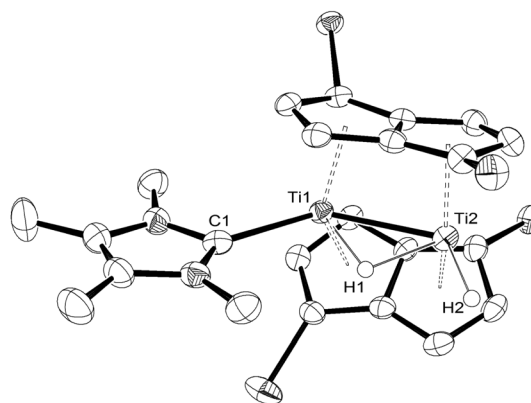


Fig. 3 ORTEP diagram of the molecular structure of (4) displaying 50% probability ellipsoids. ¹Pr groups omitted for clarity.

Notes and references

- 1 P. J. Chiric, *Organometallics*, 2010, **29**, 1500.
- 2 (a) G. Wilkinson and A. K. Fischer, *J. Inorg. Nucl. Chem.*, 1956, **2**, 149; (b) H. H. Brintzinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1970, **92**, 6182; (c) A. Davison and S. S. Wreford, *J. Am. Chem. Soc.*, 1974, **96**, 3017; (d) E. Bercaw, *J. Am. Chem. Soc.*, 1974, **96**, 5087; (e) S. I. Troyanov, H. Antropinsova and K. Mach, *J. Organomet. Chem.*, 1992, **427**, 49; (f) P. Mosimann and J. J. Salzmänn, *Helv. Chim. Acta*, 1967, **50**, 1831; (g) M. D. Walter, C. D. Sofield and R. A. Andersen, *Organometallics*, 2008, **27**, 2959.
- 3 (a) S. A. Cohen, P. R. Auburn and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 1136; (b) U. Rosenthal, V. V. Burlacov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics*, 2003, **22**, 884; (c) I. Pappas and P. J. Chiric, *J. Am. Chem. Soc.*, 2016, **138**, 13379; (d) I. Pappas and P. J. Chiric, *J. Am. Chem. Soc.*, 2015, **137**, 3498; (e) K. T. Tarantino, D. C. Miller, T. A. Callon and R. R. Knowles, *J. Am. Chem. Soc.*, 2015, **137**, 6440; (f) M. Mori, *Heterocycles*, 2009, **78**, 281; (g) M. E. Vol'pin and B. V. Shur, *Nature*, 1966, **209**, 1236; (h) G. H. Olivé and G. S. Olivé, *Angew. Chem., Int. Ed.*, 1969, **8**, 650.
- 4 (a) M. Horáček, V. Jupfer, U. Thewalt, P. Stepnicka, M. Polasek and K. Mach, *Organometallics*, 1999, **18**, 3572; (b) L. Lukesová, M. Horáček, P. Stepnicka, K. Fejfarová, R. Gyepes, I. Gisorová, J. Kubišta and K. Mach, *J. Organomet. Chem.*, 2002, **663**, 134; (c) L. Lukesová, J. Pinkas, M. Horáček, R. Gyepes, I. Gisorová, J. Kubišta and K. Mach, *J. Organomet. Chem.*, 2006, **691**, 748; (d) P. B. Hitchcock, F. M. Kerton and G. A. Lawless, *J. Am. Chem. Soc.*, 1998, **120**, 10264; (e) T. E. Hanna, E. Lobkovsky and P. J. Chiric, *J. Am. Chem. Soc.*, 2004, **126**, 14688; (f) T. E. Hanna, E. Lobkovsky and P. J. Chiric, *J. Am. Chem. Soc.*, 2006, **128**, 6018.
- 5 (a) J. E. Bercaw and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1971, **93**, 2045; (b) J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, *J. Am. Chem. Soc.*, 1972, **94**, 1219.
- 6 (a) J. A. Pool, E. Lobkovsky and P. J. Chiric, *Nature*, 2004, **427**, 527; (b) T. Shima, S. Hu, G. Luo, X. Kang, Y. Luo and Z. Hou, *Science*, 2013, **340**, 1549; (c) T. E. Hanna, E. Lobkovsky and P. J. Chiric, *J. Am. Chem. Soc.*, 2006, **128**, 6018; (d) S. P. Semproni, C. Milsman and P. J. Chiric, *Organometallics*, 2012, **31**, 3672.
- 7 (a) A. F. R. Kilpatrick and F. G. N. Cloke, *Chem. Commun.*, 2014, **50**, 2769; (b) A. F. R. Kilpatrick, J. C. Green and F. G. N. Cloke, *Organometallics*, 2015, **34**, 4816; (c) A. F. R. Kilpatrick, J. C. Green and F. G. N. Cloke, *Organometallics*, 2015, **34**, 4830; (d) A. F. R. Kilpatrick, J. C. Green and F. G. N. Cloke, *Organometallics*, 2017, **36**, 352; (e) A. F. R. Kilpatrick, J. C. Green, F. G. N. Cloke and N. Tsoureas, *Chem. Commun.*, 2013, **49**, 9434; (f) F. G. N. Cloke, J. C. Green, A. F. R. Kilpatrick and D. O'Hare, *Coord. Chem. Rev.*, 2017, **344**, 238.
- 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.
- 9 (a) A. Doddi, C. Gemel, R. W. Seidel, M. Winter and R. A. Fischer, *Polyhedron*, 2013, **52**, 1103; (b) G. B. Nikivorov, H. W. Roesky, P. G. Jones, J. Magull, A. Ringe and R. B. Oswald, *Inorg. Chem.*, 2008, **47**, 2171; (c) M. Manßen, C. Adler and R. Beckhaus, *Chem. – Eur. J.*, 2016, **22**, 4405; (d) C. Lorber and L. Vendier, *Organometallics*, 2008, **27**, 2774; (e) J. Li, C. Schulzke, S. Merkel, H. W. Roesky, P. P. Samuel, A. Döring and D. Stalke, *Z. Anorg. Allg. Chem.*, 2010, **636**, 511.
- 10 J. M. de Wolf, A. Meetsma and J. H. Teuben, *Organometallics*, 1995, **14**, 5466.
- 11 (a) J. B. Love, H. C. S. Clark, F. G. N. Cloke, J. C. Green and P. B. Hitchcock, *J. Am. Chem. Soc.*, 1999, **121**, 6843; (b) L. Hao, J. F. Harrod, A.-M. Lebus, Y. Mu, R. Shu, E. Samuel and H.-G. Woo, *Angew. Chem., Int. Ed.*, 1998, **37**, 3126; (c) S. R. Frecichs, B. K. Stein and J. E. Ellis, *J. Am. Chem. Soc.*, 1987, **109**, 559; (d) J. R. Haragorn and M. J. McNevin, *Organometallics*, 2003, **22**, 609; (e) S. I. Troyanov, K. Mach and V. Varga, *Organometallics*, 1993, **12**, 3888; (f) G. Bai, P. Wei and D. W. Stephan, *Organometallics*, 2006, **25**, 2650; (g) E. G. Perevalova, I. F. Urazowski and D. A. Lemenovskii, *J. Organomet. Chem.*, 1985, **289**, 319.
- 12 (a) E. B. Loblovskii, G. L. Soloveichik, A. I. Sizov and B. M. Bulychev, *J. Organomet. Chem.*, 1985, **280**, 53; (b) L. J. Gugenberger and F. N. Tebbe, *J. Am. Chem. Soc.*, 1973, **95**, 7870; (c) F. N. Tebbe and L. J. Gugenberger, *J. Chem. Soc., Chem. Commun.*, 1973, 227.
- 13 K. H. Melmed, D. Coucouvanis and S. J. Lippard, *Inorg. Chem.*, 1973, **12**, 232.
- 14 (a) M. L. H. Green and G. Parkin, *J. Chem. Educ.*, 2014, **91**, 807; (b) J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481.
- 15 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.

