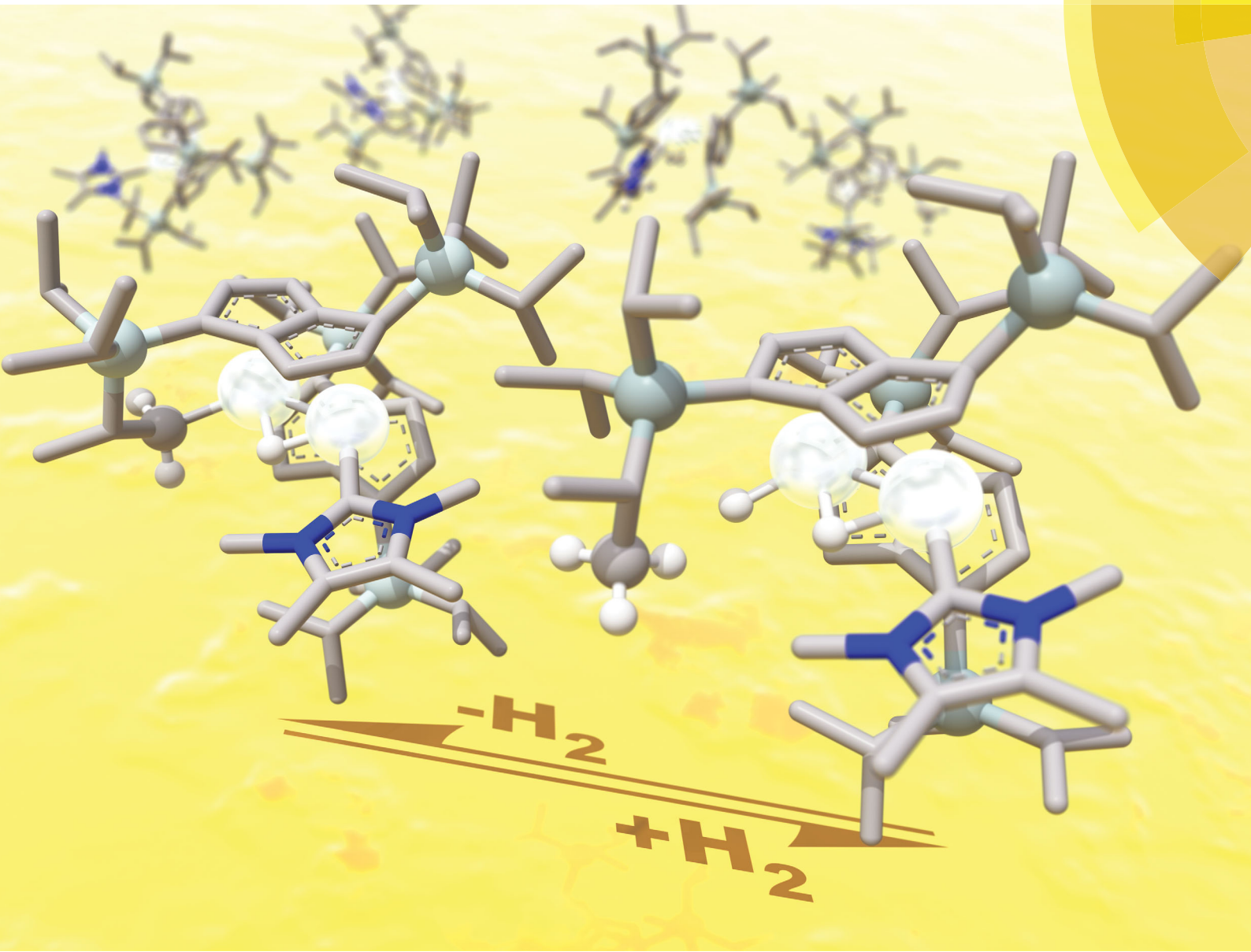
Volume 53 | Number 98 | 21 December 2017 | Pages 13085–13182

ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

F. Geoffrey N. Cloke *et al.*

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

ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2017, 53, 13117

Received 5th October 2017,
Accepted 25th October 2017

DOI: 10.1039/c7cc07726b

rsc.li/chemcomm

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

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

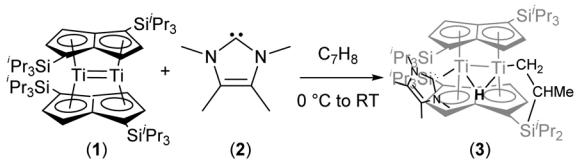
The reaction of the bis(pentalene)dititanium complex $Ti_2(\mu{:}\eta^5,\eta^5\text{-}Pn^\dagger)_2$ ($Pn^\dagger$ = $C_8H_4(1,4\text{-}Si^iPr_3)_2$) with the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene results in intramolecular C–H activation of one of the ^{i}Pr methyl groups of a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

[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

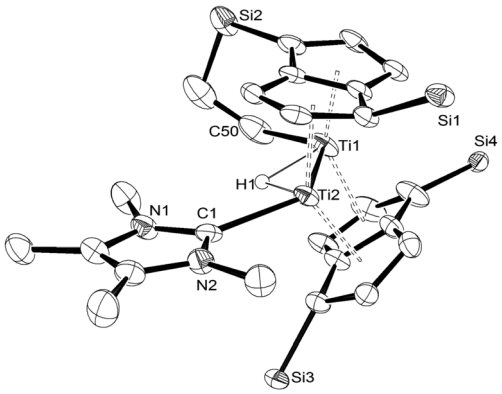


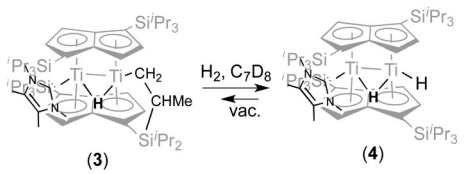
Fig. 1 ORTEP diagram of the molecular structure of (**3**) displaying 50% probability ellipsoids. ^{i}Pr groups omitted for clarity.

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_7D_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.

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



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

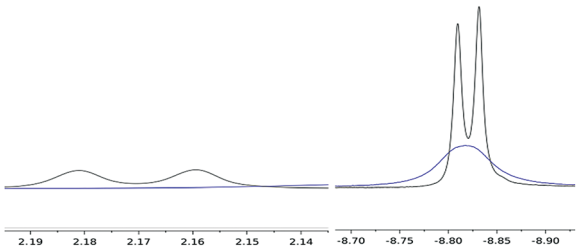


Fig. 2 Hydride peaks in (**4**) at RT (blue) and at 0 °C (black).

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**)

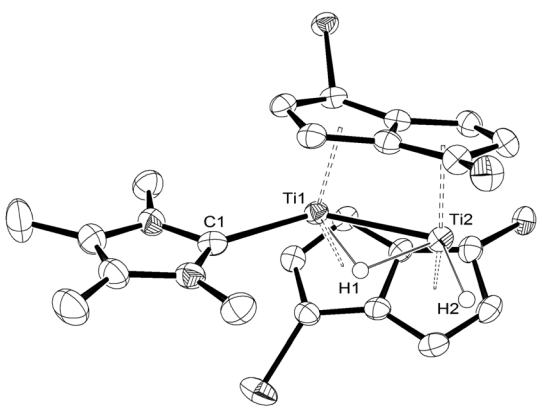


Fig. 3 ORTEP diagram of the molecular structure of (**4**) displaying 50% probability ellipsoids. ^{i}Pr groups omitted for clarity.

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 $Ti_2Pn^\dagger(Pn^\dagger$-H)(μ-H) from $Ti_2Pn^\dagger_2$ was calculated to have $\Delta E = -0.03$ eV and $\Delta G = 11$ kJ mol^{-1}. 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^{-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.

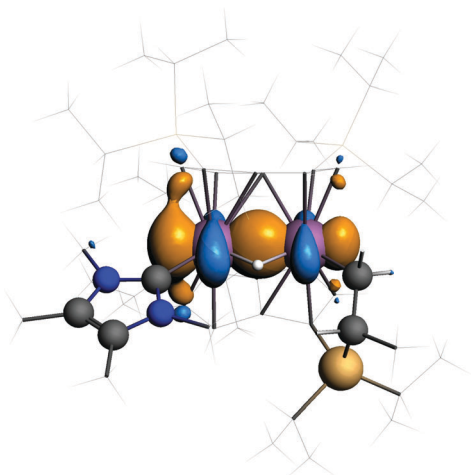


Fig. 4 Isosurface for the HOMO of **3**.

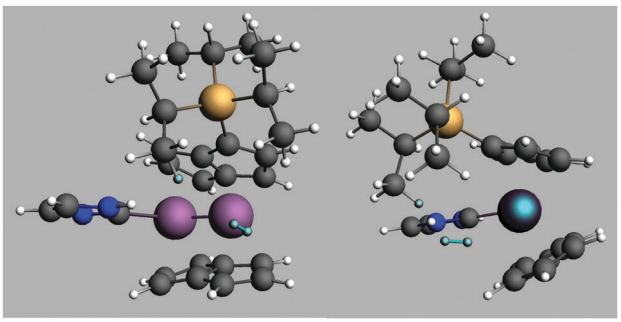


Fig. 5 Structure of the calculated transition state for H_2 addition. The reacting Hs are highlighted.

Addition of H_2 to **3** to form **4** is calculated to have reaction energies $\Delta E = -0.77$ eV and $\Delta G = -31$ 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.

We thank the EPSRC for funding (N. T.), Dr Graham Tizzard (National Crystallography Service, University of Southampton), 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.
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. Salzmann, *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. Olivè and G. S. Olivè, *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. Chirik, *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. Chirik, *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. Chirik, *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. Manβen, 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. Lebuis, 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. Gugenbereger 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.

