ChemComm

COMMUNICATION



Cite this: Chem. Commun., 2014, 50, 12753

Received 29th July 2014, Accepted 26th August 2014

DOI: 10.1039/c4cc05905k

www.rsc.org/chemcomm

Bypassing a highly unstable frustrated Lewis pair: dihydrogen cleavage by a thermally robust silylium-phosphine adduct[†]

Thomas J. Herrington, Bryan J. Ward, Laurence R. Doyle, Joe McDermott, Andrew J. P. White, Patricia A. Hunt* and Andrew E. Ashley*

The thermally robust silvlium complex $[iPr_3Si-PtBu_3]^+[B(C_6F_5)_4]^-$ (1) activates H_2/D_2 at 90 °C (PhCl); no evidence for dissociation into the separated Lewis pair is found. DFT calculations show H_2 cleavage proceeds *via* Si-P bond elongation to form an encounter complex directly from the adduct, thus avoiding the non-isolable iPr_3Si^+ -PtBu_3 FLP.

Since their discovery in 2006, 'frustrated Lewis pairs' (FLPs) have continued to provide a fresh and novel approach to the field of bond activation chemistry.1 FLPs can be defined as combinations of a Lewis acid and base which, by dint of steric hindrance, are unable to datively bind in the classical manner, leading to unquenched reactivity capable of activating small molecules. One of the most exciting properties of FLPs is their ability to induce heterolytic cleavage of H₂ into protic and hydridic components $(H^+/H^-)^2$, which can subsequently be transferred to reducible substrates either stoichiometrically $(e.g. \text{ carbonyls, } CO_2)^3$ or catalytically (e.g. imines, silvl enol)ethers, alkenes).⁴ By far the most commonly used Lewis acids are organometallics of the Group 13 elements (e.g. R_3E ; E = B or Al, R = electron-deficient organyl), among which $B(C_6F_5)_3$ remains prevalent. Silvlium ions (R₃Si⁺) are both isoelectronic and isolobal with this class of compounds and, because of their potent electrophilicity,⁵ can demonstrate similar FLP reactivity when employed as the Lewis acid partner. However, there are few reports of stable R₃Si⁺ cations, which is attributed to the difficulties in stabilising the diffuse 3p Si valence orbital either through hyper- or π -conjugation.⁶ This property explains, in part, their voracious affinity for nucleophiles; even traditionally 'inert' arene solvents⁷ and weakly coordinating anions (WCAs)⁸ can demonstrate interactions with the silicon centre. The work of Ozerov *et al.* reflects this extreme appetite for σ and π donors,

in which decomposition of the robust $[B(C_6F_5)_4]^-$ WCA was observed when heated in the presence of Et₃Si^{+,9} presumably via [C₆F₅]⁻ abstraction or C-F activation.¹⁰ Such indiscriminate reactivity may be suppressed via incorporation of intramolecular donors which moderate the potent electrophilicity while preserving sufficient reactivity for catalysis. In this respect, Oestreich and co-workers used the ferrocene-stabilised silvlium ion $[(C_5H_5)Fe(C_5H_4SitBuMe)]^+$ to selectively and catalytically hydrosilylate various ketones to the corresponding alkyl/silyl ethers (RR'CH-O-SiR₃; R/R' = alkyl);¹¹ by contrast the fully reduced alkanes $R-CH_2-R'^{12}$ can be isolated when the 'untamed' '[R₃Si]⁺' is used as catalyst. Steric protection of the Si centre has also been adopted to prevent undesired silvlation of aromatic solvents, as documented by Müller et al. Here, bulky triarylsilylium compounds (Ar_3Si^+ ; $Ar = C_6H_{6-x}Me_x$, x = 3-5), in conjunction with phosphine (R_3P ; R = alkyl, aryl) or silvlene bases,¹³ are shown to generate FLPs that engage in H₂ cleavage. Nonetheless, eventual solution-phase decomposition of these FLPs under ambient conditions was attributed to the long-term instability of the Ar₃Si⁺ ions, which leads to protonated arene products.14

View Article Online

Herein we report the synthesis and characterisation of a *classical* donor–acceptor complex between tBu_3P and the less sterically encumbered, highly reactive, silylium ion iPr_3Si^+ . We show that the use of a Lewis adduct considerably stabilises the R_3Si^+ moiety, in comparison with the previously studied Ar_3Si^+ species. Furthermore, this species is shown to heterolytically cleave H_2 , the mechanism of which avoids the formation of a presumably highly unstable iPr_3Si^+ –PtBu₃ separated Lewis pair.

Treatment of iPr₃SiH with $[Ph_3C][B(C_6F_5)_4]$ (Bartlett–Condon– Schneider hydride transfer)¹⁵ in chlorobenzene afforded solutions of $[iPr_3Si \cdot ClPh]^+$, as previously described.¹⁶ Subsequent *in situ* reaction with tBu_3P furnished $[iPr_3Si-PtBu_3]^+[B(C_6F_5)_4]^-$ (1), upon precipitation with hexanes and recrystallisation from PhCl, in excellent yield (Scheme 1). 1 has been characterised by ¹H, ¹³C, ²⁹Si and ³¹P NMR spectroscopy, high resolution MS (ES+), and elemental analysis (see ESI†).

Slow cooling of a PhF solution of 1 to -25 °C produced large colourless plates which were suitable for single crystal X-ray diffraction,‡ and the solid state structure is shown in Fig. 1.

Department of Chemistry, Imperial College London, Exhibition Road,

London SW7 2AZ, U.K. E-mail: a.ashley@imperial.ac.uk;

Web: http://www3.imperial.ac.uk/people/a.ashley

[†] Electronic supplementary information (ESI) available: Experimental section including computational details, characterisation data and copies of the NMR spectra compounds and reactions. CCDC 970728. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc05905k



Scheme 1 Synthesis of **1** and subsequent reactivity with H_2/D_2 (C_6D_5Cl or C_6H_5Cl solution, 0.096 M; H_2 and D_2 experiments respectively, 4 bar). *Reagents and conditions*: (a) (i) [Ph₃C][B(C_6F_5)₄], PhCl, RT, -Ph₃CH; (b) tBu₃P added *in situ*.



Fig. 1 ORTEP plot of the X-ray structure of 1. C atoms blue, P atom orange, B atom pink, F atoms green and Si atom light brown. H atoms have been removed for clarity, and thermal ellipsoids are shown at 50% probability; Si1–P1 = 2.4843(5) Å.

The $[iPr_3Si-PtBu_3]^+$ fragment in 1 is derived from a donoracceptor interaction between the iPr_3Si^+ moiety and tBu_3P , as exemplified by the pyrimidalisation about the Si atom (0.5765(11) Å deviation from the plane of the three C atoms in the C₃Si unit). The C-Si-C bond angles, which range between 110.51(8) and 111.86(9)°, are much closer to the idealised tetrahedral angle (109.5°) than those found in iPr₃Si(CHB₁₁H₅Cl₆) (117.3°),⁸ which possesses significant silvlium character and hence approaches a trigonal geometry. The $[B(C_6F_5)_4]^-$ anions are well separated from the cations, with no close Si to F contacts, and hence are non-coordinating. However, the Si-P bond distance is rather long (2.4843(5) Å; within the top 2% of those reported in the CSD), and may be compared to $[PhMe_2Si-PtBu_3]^+[HB(C_6F_5)_3]^-$ (Si-P = 2.376(2) Å), which has been prepared from reaction of PhMe₂SiH and the FLP system $tBu_3P/B(C_6F_5)_3$.¹⁷ This increased distance may be attributed to the higher degree of steric strain due to crowding between the organic groups along the Si-P axis.

PhCl solutions of **1** proved to be stable for at least several months at room temperature, and these can be heated at 90 °C for 24 h without evidence of decomposition. ¹H and ¹³C NMR spectra (C₆D₅Cl; 298 K) of **1** are commensurate with the solid state structure, and the upfield ²⁹Si resonance (δ = 43.1 ppm, ¹J_{SiP} = 23 Hz) reveals the Si–P bond to be intact in solution.

However, the coupling constant is noticeably smaller than those reported for $[(C_6Me_5)_3Si-PEt_3]^+[B(C_6F_5)_4]^-$ or zwitterionic $[Mes_2(SiPh_2H)P^+CH_2CH_2B^-H(C_6F_5)_2]$ (${}^1J_{SiP} = 41.2$ and 48.5 Hz, respectively), 14,18 and the ${}^{31}P$ NMR resonance ($\delta = 57.3$ ppm, 298 K) is close to that observed for free *t*Bu₃P ($\delta = 62.0$ ppm, 298 K); collectively these data would suggest a weak Si–P bond.

In contrast to the results obtained using the silylium FLPs, $(C_6Me_5)_3Si^+/PR_3^{14}$ admission of H₂ to 1 (4 bar, C₆D₅Cl solvent) at room temperature led to no discernible reaction. However, heating these solutions to 90 °C led to complete consumption of the adduct (8 hours; Scheme 1), concomitant with formation of iPr₃Si-H (¹H NMR, δ = 3.43 ppm) and phosphonium borate $[tBu_{3}P-H]^{+}[B(C_{6}F_{5})_{4}]^{-}$ (¹H NMR, $\delta = 4.17$ ppm, ¹ $J_{HP} = 430$ Hz; ³¹P 1 H} NMR, δ = 60.3 ppm) in high conversion (90–94%, four runs).¹⁹ Conducting these experiments under D_2 (C₆H₅Cl solvent) gave the deuterated products iPr_3Si-D and $[tBu_3P-D]^+$, as shown by ²H, ³¹P and ²⁹Si NMR spectroscopy (see ESI⁺ for details);²⁰ this conclusively shows that H_2/D_2 is the source of H/D atoms in the formally hydridic silane, and protic phosphonium ion.²¹ Upon reaction completion, ¹⁹F and ¹¹B NMR spectra showed only resonances corresponding to the $[B(C_6F_5)_4]^-$ counterion, demonstrating that silylium-mediated decomposition of the anion had not occurred. Since neither [H-B(C₆F₅)₃]⁻ nor B(C₆F₅)₃ could be observed in solution, the possibility that H2 cleavage involves the known tBu3P/ $B(C_6F_5)_3$ FLP pathway¹⁷ may be discounted.

In order to investigate the possibility that 1 may dissociate in PhCl solution to generate tBu3P and solvated silylium ion, [iPr3Si-ClPh]⁺, a variable temperature (VT) ³¹P NMR experiment was conducted (Ph₃P internal capillary reference; see Fig. S7 in ESI⁺). At low temperature the spectrum shows a very broad resonance $(\delta = 54.5 \text{ ppm}, -40 ^{\circ}\text{C})$ which moves progressively downfield (δ = 60.6 ppm, 100 °C), and markedly sharpens. However, it should be noted that the ³¹P NMR resonance for *t*Bu₃P also moves by *ca*. $\Delta \delta$ = 6 ppm over the same temperature range and the behaviour is likely due to a temperature-induced shift for both species. Furthermore, addition of tBu₃P (1-10 eq., PhCl, 100 °C) to 1 produced ³¹P NMR spectra consisting only of their separate respective resonances; neither a discernible change in the lineshape nor chemical shift position of the adduct was observed. If rapid exchange between 1 and appreciable concentrations of dissociated products were indeed occurring, introduction of extraneous tBu₃P would be expected to lead to a significant perturbation of the ³¹P NMR resonance of **1**. Finally, we synthesised $[iPr_3Si \cdot ClPh]^+[B(C_6F_5)_4]^-$ in order to investigate its reactivity under the conditions of H2 activation, in the absence of added phosphine: at 90 °C this species degraded (40 min) via decomposition of the anion, producing $B(C_6F_5)_3$, iPr_3SiF (¹⁹F NMR $\delta = -185.0$ ppm; ¹ $J_{FSi} = 298$ Hz) and other unidentified products. This implies that, if dissociation of *t*Bu₃P from **1** were to occur and generate iPr₃Si⁺ or (more likely) $[iPr_3Si \cdot ClPh]^+$, the rate at which this cation reacts with $[B(C_6F_5)_4]^$ would greatly exceed the observed rate of H₂ activation.

In order to determine whether thermally-induced dissociation of **1** (and hence a typical FLP-mediated mechanism) was responsible for H_2 heterolysis, we examined this system further using DFT calculations. The results of our computational calculations (M06-2X/6-311+G(d,p) level of theory; see ESI[†])



Scheme 2 Solvent-phase enthalpy (ΔH) and Gibbs free energy (ΔG) profile for H₂ activation mediated by **1** in PhCl solution, showing intermediates and transition states along the reaction coordinate (T = 363 K). P atom orange and Si atom pale green.

which took into account secondary (conductor-like polarizable continuum model; C-PCM) solvent interaction, are presented in Scheme 2 (and Table S1, ESI[†]). Various conformations of **1** were identified (Table S2, ESI[†]), which are separated in free energy by only *ca.* 13–30 kJ mol⁻¹; this lends support to the solution-phase VT ³¹P NMR data whereby the dynamic lineshape observed for **1** at low temperatures can be explained through interconversion between conformers. In total, two intermediates (**A** and **B**), and a single transition state for their interconversion (**TS**_{AB}) were located along the reaction coordinate for H₂ activation, starting from the lowest energy conformer of **1**.

On progressing to the transition state for H_2 activation, TS_{AB} , the Si \cdots P distance lengthens considerably (Table 1), to an extent that is greater than the sum of the van der Waals radii of the elements (3.90 Å).²² The incipient cavity accompanying this bond elongation permits entry of a molecule of H_2 while attractive electrostatic P \cdots Si and secondary van der Waals interactions between iPr₃Si and *t*Bu₃P fragments lead to binding beyond covalent distances, thus retarding *t*Bu₃P dissociation. This factor explains the experimental observation that the rate of H_2 activation outcompetes decomposition, (which would be anticipated to be the faster process if dissociation to a true FLP were to occur at these elevated temperatures). A range of van der Waals interactions give rise to QTAIM bond critical points (BCP) between C-H \cdots H–C and C–H \cdots P (Tables S3 and S4, ESI[†])

	$Si{\cdots}P$	$H{\cdot}{\cdot}{\cdot}H$	$Si{\cdots}H$	$P{\cdots}H$
1	2.50	0.74^{a}		
Α	2.50	0.74	5.36	6.09
TSAB	4.10	0.74	2.87	2.98
В	4.63	2.34	1.50	1.41
Products	—	—	1.50	1.40

^a Bond length corresponding to free H₂.

which appear to hold the fragments in place, fulfilling a similar role to those of the C-H···F H-bonds reported for the frustrated encounter complex $[tBu_3P] \cdots [B(C_6F_5)_3]$ (the precursor species to H_2 cleavage by that FLP system).²³ It is notable that the $B \cdots P$ distance in the latter (4.20 Å) compares well with the Si--P length in TS_{AB} , yet both are appreciably shorter than that those calculated for the 'encounter complexes' in Müller's (C₆Me₅)₃Si⁺/ PR_3 systems (R = alkyl, aryl; range 4.45–5.73 Å); this likely reflects the much greater steric bulk of the Ar₃Si⁺ fragment in these 'true' FLPs.¹⁴ Heterolytic cleavage of H₂ subsequently proceeds to give $[tBu_3P-H]^+$ and H-SiiPr₃ as a dihydrogen bonded intermediate (B), after which dissociation to form the free products is strongly entropically driven. The TS molecular orbitals exhibit H₂ contributions (Fig. S19, ESI[†]) while BCPs from H₂ to both P and Si are obtained (Table S5, ESI⁺). Moreover, the early TS exhibits nascent NBO P \rightarrow H₂(σ^*) and H₂(σ) \rightarrow Si electron transfer, approximately equal to 8 and 34 kJ mol⁻¹ respectively, which are expected to increase as the reaction proceeds. Heterolysis of H₂ in this manner is consistent with the electron transfer model,²⁴ with no observable deviation in H-H distance between that in TS_{AB} and free H₂, denoting an early transition state.

Formation of \mathbf{TS}_{AB} is both enthalpically unfavourable owing to the weakening of the Si–P interaction, and entropically unfavourable due to the increased ordering as a result of H₂ coordination (Table S1, ESI†). The substantial energy barrier (122.53 kJ mol⁻¹; $\mathbf{A} \rightarrow \mathbf{TS}_{AB}$) associated with H₂ activation is testament to the strong Si–P dative bond in 1 and explains the elevated temperatures required experimentally to achieve bond elongation and access the encounter complex. Comparable rate-determining steps have been observed elsewhere in the literature; Lammertsma *et al.* report that the experimentally observed insertion of CO₂ into dimeric P/Al-based Lewis pairs proceeds at room temperature, despite having computed a significant energy barrier (*ca.* 140 kJ mol⁻¹).²⁵

Whilst a number of Lewis pairs have been documented that exhibit classical/frustrated borderline reactivity with H_2 or alkynes,²⁶ spectroscopic evidence for the existence of the dissociated constituents has always been demonstrated, due to the stability of the Lewis acid as an independent entity. In our particular example, however, we have shown that the critical development of an encounter complex prior to H_2 activation can be achieved directly from the Lewis pair adduct *via* simple bond elongation and weakening, obviating the need for the formation of a true FLP; this is especially important when the Lewis acid partner (in our case iPr_3Si^+) is too reactive to isolate in the free form.

In conclusion, we have shown that a classical donor-acceptor adduct incorporating a highly electrophilic trialkylsilylium ion can activate H_2 ; this reaction is thus not rigidly confined to truly separated R_3Si^+ /base FLP combinations. Indeed, the formation of a stable adduct incorporating such species may provide a general strategy towards the protection of highly reactive Lewis acids/bases in Lewis pair systems, without excluding such systems from participating in characteristic FLP-type chemistry. We are currently exploring the small molecule reactivity of other $[R_3Si-(base)]^+$ adducts, in addition to investigating their potential use in the catalytic hydrogenation of unsaturated substrates.

The authors wish to acknowledge the Royal Society for a University Research Fellowship (AEA), the EPSRC for studentship funding (TJH and BJW), and Dr Richard Matthews for his assistance with the QTAIM analysis.

Notes and references

‡ Crystallographic data for 1: C₄₅H₄₈BF₂₀PSi, *M* = 1038.70, triclinic, *a* = 11.6772(5) Å, *b* = 12.5736(4) Å, *c* = 17.0286(6) Å, *α* = 79.442(3)°, *β* = 75.102(3)°, *γ* = 77.292(3)°, *U* = 2335.61(15) Å³, *T* = 173 K, space group *P*I (no. 2), *Z* = 2, ρ_{calcd} = 1.477 g cm⁻³, μ (Cu_{Kα}) = 1.792 mm⁻¹, colourless blocks, Agilent Xcalibur PX Ultra A diffractometer; 8923 independent measured reflections (R_{int} = 0.0180), *F*² refinement, ²⁷ R_1 (obs) = 0.0354, wR₂(all) = 0.0948, 7708 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 147°$], 613 parameters. CCDC 970728.

- 1 (a) G. Erker and D. W. Stephan, *Frustrated Lewis Pairs I: Uncovering and Understanding*, Top. Curr. Chem., Springer GmbH, Berlin, 2013, pp. 1–350; (b) G. Erker and D. W. Stephan, *Frustrated Lewis Pairs II: Expanding The Scope*, Top. Curr. Chem., Springer GmbH, Berlin, 2013, pp. 1–350.
- 2 (a) D. W. Stephan and G. Erker, Angew. Chem., Int. Ed., 2010, 49, 46;
 (b) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, Science, 2006, 314, 1124.
- 3 (a) A. E. Ashley, A. L. Thompson and D. O'Hare, Angew. Chem., Int. Ed., 2009, 48, 9839; (b) G. Menard and D. W. Stephan, J. Am. Chem. Soc., 2010, 132, 1796; (c) V. Sumerin, F. Schulz, M. Nieger, M. Leskela, T. Repo and B. Rieger, Angew. Chem., Int. Ed., 2008, 47, 6001.
- 4 (a) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie,
 S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and
 M. Ullrich, *Inorg. Chem.*, 2011, 50, 12338; (b) L. Greb, S. Tussing,
 B. Schirmer, P. Ona-Burgos, K. Kaupmees, M. Lokov, I. Leito,
 S. Grimme and J. Paradies, *Chem. Sci.*, 2013, 4, 2788.
- 5 C. A. Reed, Acc. Chem. Res., 1998, 31, 325.
- 6 A. Schulz and A. Villinger, Angew. Chem., Int. Ed., 2012, 51, 4526.
- 7 J. B. Lambert, S. H. Zhang, C. L. Stern and J. C. Huffman, *Science*, 1993, **260**, 1917.
- 8 Z. W. Xie, J. Manning, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 2922.
- 9 C. Douvris and O. V. Ozerov, Science, 2008, 321, 1188.
- 10 M. F. Ibad, P. Langer, A. Schulz and A. Villinger, J. Am. Chem. Soc., 2011, 133, 21016.
- 11 K. Muether and M. Oestreich, Chem. Commun., 2011, 47, 334.
- 12 M. Kira, T. Hino and H. Sakurai, Chem. Lett., 1992, 555.
- 13 (a) A. Schaefer, M. Reissmann, A. Schaefer, W. Saak, D. Haase and T. Mueller, *Angew. Chem., Int. Ed.*, 2011, 50, 12636; (b) A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann and T. Müller, *Chem. – Eur. J.*, 2014, 20, 9381.
- 14 M. Reißmann, A. Schäfer, S. Jung and T. Müller, *Organometallics*, 2013, **32**, 6736.
- 15 P. D. Bartlett, F. E. Condon and A. Schneider, J. Am. Chem. Soc., 1944, 66, 1531.

- 16 A. Schaefer, W. Saak, D. Haase and T. Mueller, *Angew. Chem., Int. Ed.*, 2012, **51**, 2981.
- 17 G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880. 18 W. Nie, H. F. T. Klare, M. Oestreich, R. Froehlich, G. Kehr and
- G. Erker, Z. Naturforsch., B: Chem. Sci., 2012, 67, 987.
- 19 1 proved to be highly reactive to even trace amounts of H₂O. Accordingly, the synthesis and solution-phase studies required meticulous drying of solvents, conducting reactions in Teflon^(B) vials, and performing NMR experiments in Teflon^(B) inserts. Reactions in dilute solution, such as those under H₂, invariably become exposed to trace amounts of H₂O, leading to [*t*Bu₃PH]⁺[B(C₆F₅)₄]⁻ and (iPr₃Si)₂O (2:1). The yield for H₂ conversion is most reliably calculated *via* relative integration of ¹H NMR signals for the iPr₃Si-H resonance against that of *t*Bu₃P-H (1:1 from H₂). Accordingly, hydrolysis produces twice the amount of phosphonium salt than the reaction with H₂, and accounts for the slightly sub-quantitative yields (90–94%). In support of this conclusion, ²H NMR spectroscopy of the D₂ cleavage reaction shows a 1:1 *t*Bu₃P-D:D-Si*i*Pr₃ ratio, since adventitious moisture is introduced as H₂O, and not D₂O (see Fig. S8 in ESI⁺).
- 20 A full kinetic study by ¹H NMR was hampered by iPr₃SiH interaction with **1**, which masks the actual amount of silane produced until reaction completion (*i.e.* complete conversion of **1**). This phenomenon has been noted for R₃Si(μ-H)SiR₃⁺ species,²⁸ wherein the silane proton is rendered invisible to ¹H NMR spectroscopy. It is plausible that a similar bridging silane interaction is also operational here.
- 21 Heating solutions of independently prepared $[tBu_3P-H]^+[B(C_6F_5)_4]^$ with iPr₃SiH (PhCl, 90 °C, 60 h) led to no reaction, demonstrating that the H₂ cleavage reaction is irreversible. Furthermore, conducting the same experiments under D₂ did not produce any HD, which would be expected to form due to H/D scrambling.
- 22 A. Bondi, J. Phys. Chem., 1964, 68, 441.
- 23 T. A. Rokob, A. Hamza, A. Stirling, T. Soós and I. Pápai, Angew. Chem., Int. Ed., 2008, 47, 2435.
- 24 T. A. Rokob, I. Bakó, A. Stirling, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2013, **135**, 4425.
- 25 F. Bertini, F. Hoffmann, C. Appelt, W. Uhl, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, *Organometallics*, 2013, **32**, 6764.
- (a) S. J. Geier and D. W. Stephan, J. Am. Chem. Soc., 2009, 131, 3476;
 (b) S. Schwendemann, R. Fröhlich, G. Kehr and G. Erker, Chem. Sci., 2011, 2, 1842;
 (c) C. Jiang and D. W. Stephan, *Dalton Trans.*, 2013, 42, 630;
 (d) T. Voss, T. Mahdi, E. Otten, R. Frohlich, G. Kehr, D. W. Stephan and G. Erker, Organometallics, 2012, 31, 2367;
 (e) S. J. Geier, A. L. Gille, T. M. Gilbert and D. W. Stephan, Inorg. Chem., 2009, 48, 10466;
 (g) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan and J. Paradies, Angew. Chem., Int. Ed., 2012, 51, 10164;
 (h) E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, Chem. Eur. J. 2012, 18, 16938;
 (i) C. Jiang, O. Blacque, T. Fox and H. Berke, Organometallics, 2011, 30, 2117;
 (j) M. Ullrich, A. J. Lough and D. W. Stephan, Organometallics, 2010, 29, 3647;
 (k) M. A. Dureen, C. C. Brown and D. W. Stephan, Organometallics, 2010, 29, 6594.
- 27 SHELXTL, *SHELX-2013*, Bruker AXS, Madison WI, http://shelx.uni-ac.gwdg.de/SHELX/index.php.
- 28 (a) M. Nava and C. A. Reed, Organometallics, 2011, 30, 4798; (b) S. P. Hoffmann, T. Kato, F. S. Tham and C. A. Reed, Chem. Commun., 2006, 767.