H_2 Activation

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Hydrogen Activation by an Intramolecular Boron Lewis Acid/Zirconocene Pair**

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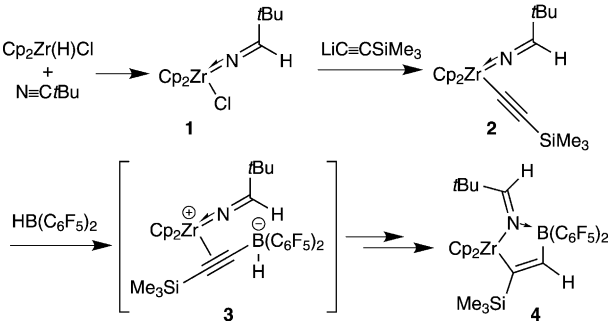
Small-molecule activation is a very important feature in stoichiometric synthetic chemistry as well as in catalysis. The cleavage and activation of dihydrogen is a typical example.[1] In many molecular systems hydrogen activation is carried out by oxidative addition of the H_2 molecule to a single transition-metal center, the Wilkinson catalyst being a typical example.[2] Alternatively transition-metal centers can split dihydrogen heterolytically with the assistance of a proton accepting main-group-element Lewis base, variants of the Noyori catalysts being typical examples.[3] We have now prepared a system featuring an inverse pair of functionalities, namely a bifunctional Group 4 metallocene/borane system where the main-group-element component may serve as a hydride acceptor. Herein we describe the synthesis of this new zirconocene/$RB(C_6F_5)_2$ pair and its reaction with dihydrogen under mild conditions.

We first treated the aldimido zirconocene complex **1**[4] with trimethylsilylethynyl lithium. Product **2** (see Scheme 1) was isolated in over 90% yield as a yellow solid. It was characterized by X-ray diffraction (see the Supporting Information) and shown to contain a close to linear "metalla-2-aza allene" type unit.

Subsequent treatment of compound **2** with one molar equivalent of "Piers' borane" $[HB(C_6F_5)_2]$[5] gave complex **4** (isolated in over 80% yield; see Scheme 1 and Figure 1). Apparently, compound **4** is the product of a 1,1-hydroboration reaction[6,7] of $HB(C_6F_5)_2$ with the pendant trimethylsilyl acetylide σ-ligand. This reaction is typically initiated by σ-alkynyl ligand transfer from zirconium to the boron Lewis acid.[7] Hydride shift from boron to carbon followed by coordination of the imino nitrogen atom to the boron Lewis acid then straightforwardly leads to **4**.

We then investigated the formally related, but in some essential aspects decidedly different reaction of the σ-alkenyl/



Scheme 1. Preparation of complexes **2** and **4**; $Cp = C_5H_5$.

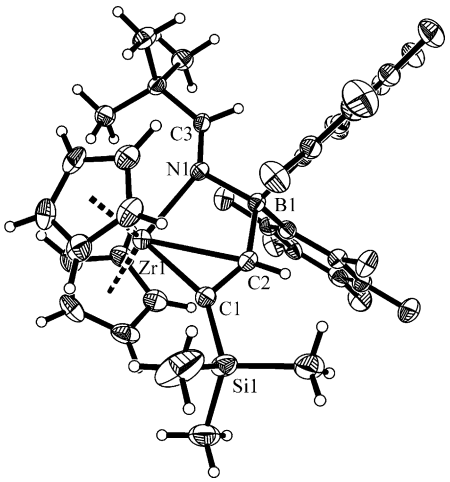


Figure 1. Molecular structure of compound **4**. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.165(4), Zr1–C2 2.513(4), Zr1–N1 2.277(3), C1–C2 1.338(5), B1–C2 1.693(5), Si1–C1 1.872(4), N1–C3 1.269(4), B1–N1 1.578(5); C1-Zr1-N1 101.8(1), B1-N1-Zr1 93.2(2), C1-Zr1-C2 32.1(1), N1-Zr1-C2 69.7(1), C2-C1-Si1 121.5(3), C2-C1-Zr1 88.4(2), B1-C2-Zr1 82.5(2).[19]

σ-alkynyl zirconocene complex **5** with $HB(C_6F_5)_2$.[8] Complex **5** was prepared by hydrozirconation of *tert*-butylacetylene[9] followed by treatment with the Li-C≡C-$SiMe_3$ reagent (see Scheme 2). It was then treated with one molar equivalent of $HB(C_6F_5)_2$ in benzene at room temperature (12 h). Workup gave the product **7** as a dark red solid in 86% yield. The X-ray crystal structure analysis revealed that one equivalent of *tert*-butylethene had apparently been eliminated during the reaction leaving the substituted 2-boryl-1-silylacetylene zirconocene complex **7** behind (see Figure 2). Both the acetylenic carbon atoms are strongly bonded to zirconium (Zr1–C1: 2.275(2), Zr1–C2: 2.390(2), C1–C2: 1.281(3) Å). The C1–

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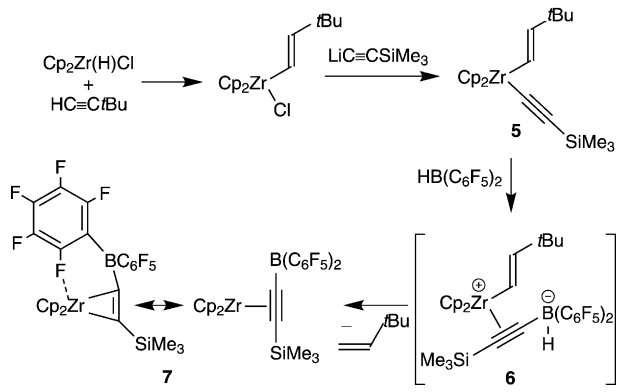


Scheme 2. Synthesis of compound **7**.

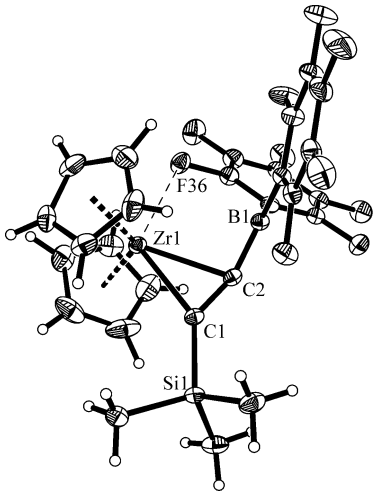


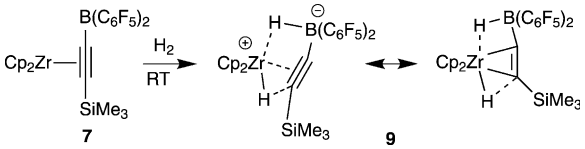
Figure 2. A view of the molecular structure of compound **7** featuring a weak Zr···F contact. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.275(2), Zr1–C2 2.390(2), Si1–C1 1.857(2), Zr1–F36 2.512(1), C1–C2 1.281(3), C2–B1 1.455(3); C1-Zr1-C2 31.7(6), C1-Zr1-F36 121.5(5), B1-C2-Zr1 94.6(1).[19]

Si1 vector is bent away from the zirconocene unit (angle C2-C1-Si1: 136.3(2)°). Most remarkable is that the C2–B1 vector is slightly leaning toward the zirconocene moiety (angle C1-C2-B1: 162.61(2)°). A close inspection of the coordination sphere of the central zirconium atom revealed a weak interaction with a fluorine atom of one of the C_6F_5 groups at boron Zr1–F36: 2.512(1) Å.[10] The Zr1···B1 separation is 2.896(2) Å.

In solution complex **7** features ^{1}H and ^{13}C NMR signals of the Cp_2Zr core at $\delta = 5.42$ (s, 10H) ppm and $\delta = 110.7$ ppm, respectively. The acetylene ligand ^{13}C NMR resonances occur at $\delta = 173.9$ (≡C[Si]) and $\delta = 178.6$ ppm ([B]C≡). Compound **7** shows a ^{11}B NMR resonance at $\delta = 15.5$ ppm and the ^{29}Si NMR signal of the -$SiMe_3$ group at $\delta = -6.0$ ppm (with a corresponding ^{1}H NMR singlet at $\delta = 0.16$ ppm). In [D_8]THF solution the spectrum of compound **7** features three sharp ^{19}F NMR signals at $\delta = -130.2$ (4F, *ortho*), −160.9 (2F, *para*), −166.3 ppm (4F, *meta*) for the C_6F_5 substituents at boron. In the non-coordinating solvent [D_8]toluene we observed decoalescence of the averaged *o*-C_6F_5 ^{19}F NMR resonance at $\delta = -145.2$ ppm (4F, 363 K) to a broad "normal" *o*-C_6F_5 signal at $\delta = -126.7$ ppm (2F, 233 K), and a broad *o*-C_6F_5 signal at $\delta = -167.1$ ppm (2F, 233 K; the spectra are shown in the Supporting Information). The $\delta = -167.1$ ppm resonance is an averaged ^{19}F NMR signal of the bridging Zr-F-C(Ar) with the remaining non-bridged *o*-F resonance of the one *o*-C_6F_5 ring. Consequently, this signal starts to decoalesce upon further lowering the temperature without reaching a fully resolved ^{19}F spectrum (temperature limit 193 K). Finally, the pair of *m*-F atoms of the two C_6F_5 rings at boron give rise to a pair of signals at $\delta = -158.7$, −163.2 ppm (each 2F, 193 K).

We can safely assume that the initial step of the reaction of **5** with $HB(C_6F_5)_2$ is again acetylide transfer from zirconium to boron[7] (to generate **6**). In contrast to the nitrogen case described above (see Scheme 1) the intermediate **6** apparently disfavors entering into the 1,1-hydroboration route but chooses stabilization by hydride transfer and reductive coupling to eventually yield **7** and *tert*-butylethene (see Scheme 2).

Compound **7** reacted rapidly with dihydrogen at ambient conditions in benzene solution (1.5 bar H_2 pressure, RT, 15 min) to give the H_2 addition product **9** (see Scheme 3). The



Scheme 3. Preparation of the hydrogen-addition product **9**.

hydrido zirconocene/hydrido borate complex **9** was isolated as a pale yellow solid in over 80% yield. The X-ray crystal structure analysis (Figure 3) shows the presence of a [Cp_2ZrH^+] cation moiety to which a [$HB(C_6F_5)_2^-$]-C≡C-$SiMe_3$ anion is π-coordinated. The resulting structure features a C1–C2 bond length of 1.265(5) Å (there are two chemically equivalent crystallographically independent molecules in the

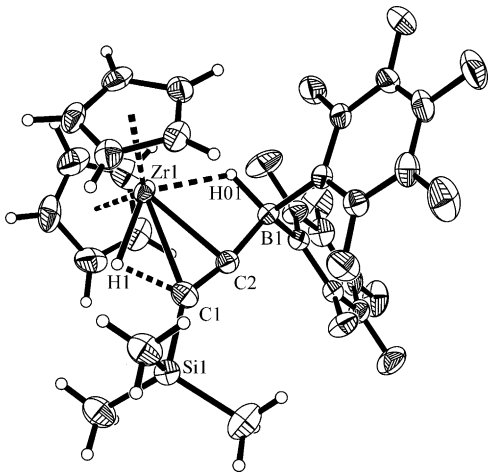


Figure 3. A projection of the molecular structure of the zwitterionic hydrogen-addition product **9**. Selected bond lengths [Å] and angles [°]: Zr1–C1 2.516(4), Zr1–C2 2.327(3), Zr1–H1 1.86(4), Zr1–H01 2.04(3), B1–C2 1.554(5), B1–H01 1.24(3), C1–C2 1.265(5), C1–H1 1.54(4); C1-Zr1-C2 29.9(1), C1-Zr1-H1 37.5(1), C2-Zr1-H01 60.3(8), C2-C1-Si1 143.2(3), C2-C1-Zr1 66.7(2), Si1-C1-Zr1 149.4(2).[19]

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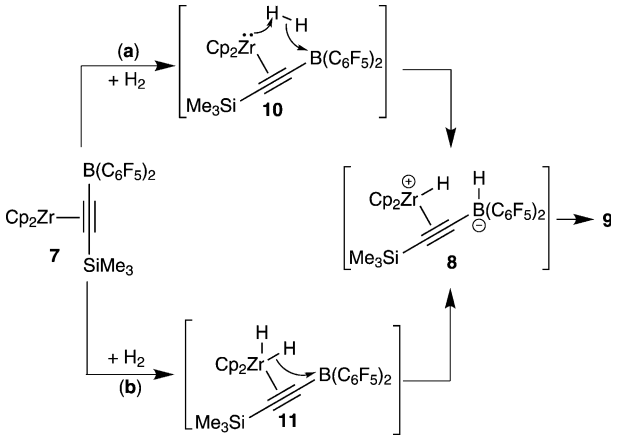
crystal; the values of molecule **A** are given here) which is slightly shorter than found in its precursor **7** (see above). In **9** the C1–Si1 vector is markedly pointing away from the zirconocene unit (angle C2-C1-Si1: 143.2(3)°) and there seems to be a weak interaction of the zirconium-hydride with C1. The C2–B1 vector is slightly oriented toward the metallocene (angle C1-C2-B1: 169.8(3)°) and the hydride at B is oriented toward the Zr atom; it is probably unsymmetrically bridging. Complex **9** shows a pronouncedly unsymmetrical coordination of the substituted acetylene ligand to the [Cp_2ZrH^+] moiety with a short Zr1–C2 bond (2.327(3) Å) and a markedly longer Zr1–C1 linkage (2.516 (4) Å), as is often observed in related alkene or alkyne units coordinated to alkyl zirconocene cations.[11]

In solution complex **9** shows a ^{1}H NMR Cp singlet at $\delta =$ 4.94 (^{13}C: $\delta = 104.1$ ppm). The B-H-Zr hydrogen atom was detected at $\delta = -2.29$ ppm, the Zr-H-C hydrogen atom at $\delta =$ 3.80 ppm (d, $^2J_{HH} = 5.5$ Hz).[12,13] We observe the large chemical shift difference of the alkyne ligand carbon NMR signals ([Si]C≡: $\delta = 79.8$ ppm ($^1J_{CH} \approx 44$ Hz); ≡C[B]: $\delta = 151.4$ ppm) that is typical for the unsymmetrical bonding situation of an acetylene ligand π-coordinated to a [Cp_2ZrR^+] cation moiety.[11] We also detect a single set of three ^{19}F NMR signals at $\delta = -129.5$ (*o*), -157.2 (*p*), and -162.9 ppm (*m*) with a small $\delta_{p,m}$ shift difference [^{11}B NMR: $\delta = -22.8$ ppm (d, $^1J_{BH} \approx 60$ Hz)].

Our study shows that the borane $HB(C_6F_5)_2$ readily and selectively abstracts a σ-acetylide ligand from a zirconocene complex. The resulting zwitterionic intermediate then has several competing choices for stabilization. In the imido zirconocene case (**3**) the rarely observed 1,1-hydroboration reaction is preferred, whereas in the alkenyl zirconocene analogue (**6**) hydride transfer to zirconium followed by reductive coupling prevails to yield the unique product **7**. Although π-alkene and π-alkyne zirconocenes are known to sometimes exhibit a pronounced metallacyclopropene σ-complex character,[14] the system **7** formally may be regarded as a Cp_2Zr^{II} derivative. Two pathways for the reaction of **7** with dihydrogen can thus be formulated. Pathway (b) in Scheme 4 describes a "conventional stepwise route" where both the zirconocene and the borane functionalities act separately in two consecutive steps, namely oxidative H–H addition to zirconium (to give **11**) followed by hydride abstraction by the borane to generate **8**.

DFT calculations (TPSS-D3/def2-TZVP)[15] have been performed on the intermediates and the transition structure of H_2 cleavage in Scheme 4. We have tried to identify a product (**11**) of oxidative H_2 addition to the zirconocene complex **7** (pathway (b)) without success. However, pathway (a) in Scheme 4 has been found to be a facile and exothermic process (Figure 4 and Table 1): Side-on coordination of H_2 at the metal center is enthalpically favored by -6.1 kcal mol^{-1} at 298 K. Coordination of H_2 at the side of the boron atom (**10a**) is preferred over the alternative coordination at the silyl-substituted side (**10b**, -0.8 kcal mol^{-1}). The transition structure of H_2 cleavage (see Figure 4) does not require extensive geometrical changes of **10a** except the elongation of the H–H bond to 1.043 Å, accompanied by an almost vanishing enthalpic barrier ($\Delta H^{\neq}(298\text{ K}) = 0$ kcal mol^{-1}, $\Delta H^{\neq}(220\text{ K}) = 0.1$ kcal mol^{-1}) of the activation. Rearrangement of the zwitterionic intermediate **8** to its isomer **9b** is exothermic again by -4.7 kcal mol^{-1} (at 298 K). Interestingly, our DFT optimizations in the gas phase identified two isomers of **9**: Besides the structure found in the solid state (**9b**), a second, slightly more stable isomer exhibits a long H1–Zr1 and a shorter C1–H1 bond (**9a**) [see the Supporting Information].



Scheme 4. Mechanistic pathways for the formation of zwitterionic compound **9**.

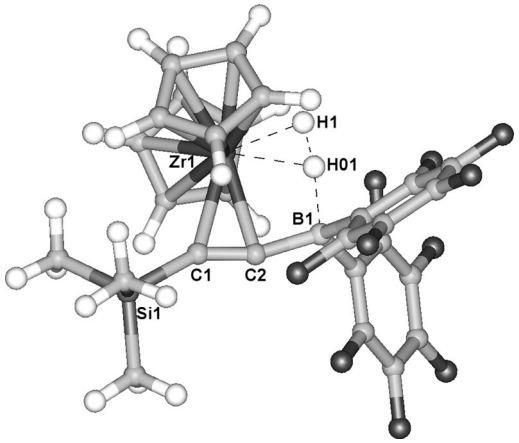


Figure 4. Calculated transition-state structure of the **7** + H_2 → **8** reaction.

Table 1: DFT calculated (TPSS-D3/def2-TZVP) relative energies (in kcal mol^{-1}) of intermediates and the H_2 cleavage transition structure in the formation of compound **9** from **7**.[a]

Structure	ΔE	$\Delta H(298\text{ K})$[b]	$\Delta H(220\text{ K})$[b]
10a	−9.8	−6.1	−5.9
10b	−4.9	−0.8	−0.7
TS(10a-8)	−8.8	−6.1	−5.8
8	−12.3	−8.4	−8.1
9a	−17.6	−13.3	−12.9
9b (= "**9**")	−17.0	−13.1	−12.8

[a] Referenced to the sum of energies of complex **7** and H_2. [b] Includes ZPVE, H_{vib}, H_{rot}, H_{trans} at the given temperature and 1 atm.

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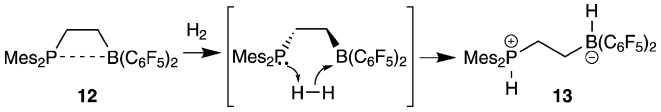
It seems that the synergistic oxidative addition pathway (a)[16] involving both the formally low-oxidation state zirconium and the borane Lewis acid in the actual step of heterolytic cleavage of the H–H molecule leading to **8** (and subsequently **9**) is favored over the conventional stepwise mechanism pathway (b).

It is interesting to note that the heterolytic splitting of dihydrogen by a variety of "frustrated Lewis pairs",[17] such as the recently reported very reactive hydrogen activating system **12** (see Scheme 5,)[18] resembles the synergistic pathway (a) in Scheme 4 conceptually. It seems that currently



Scheme 5. Formation of zwitterionic compound **13**.

examples are increasingly found where transition-metal complexes and main-group-element-derived frustrated Lewis pairs show some remarkably similar chemical behavior.

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[19] CCDC 888636 (**1**), 888637 (**2**), 888638 (**4**), 888639 (**7**), and 888640 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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