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Construction of a Borole Ligand from Coordinated Diene and $B(C_6F_5)_3$ via Successive C−H Activation Steps: A Case of Catalyst Self-Activation

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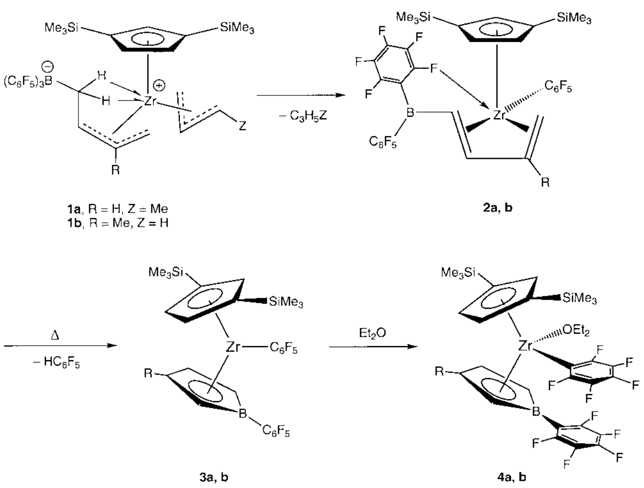
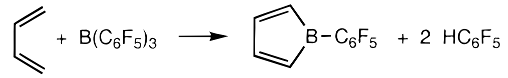
Complexes of the borole dianion $[C_4H_4BR]^{2-}$ are usually made via dehydrogenation of 2,5-dihydro-1*H*-boroles with various transition metal compounds[1] or by the reaction of the preformed borole dianion with metal halides.[2] Some early transition metal derivatives have recently attracted attention in the context of metallocene-catalyzed alkene polymerizations.[3] We now find that borole complexes are formed from zirconium 1,3-diene complexes and $B(C_6F_5)_3$ by successive C−H activation steps within the metal coordination sphere. Unusually, tris(pentafluorophenyl)borane, widely used as an activator of metallocene polymerization catalysts because of its resistance to aryl transfer reactions,[4,5] acts as the boron source.

As we have shown recently,[6] the zwitterionic 14-electron bis(allyl)zirconium complexes **1** are readily accessible from Cp″Zr(η^3-allyl)(η^4-1,3-diene) [Cp″ = 1,3-$(Me_3Si)_2C_5H_3$] and $B(C_6F_5)_3$ and are active ethene polymerization catalysts; their activities and lifetimes are however limited by their thermal stability, which depends on the degree of substitution of the diene-derived allyl ligand. Thus **1a** is readily converted to **2a** via activation of one of the C−H bonds of the $B-CH_2$ moiety and elimination of butene even at −60 °C, while the analogous reaction of **1b** requires higher temperatures.[6b] The formation of **2** is associated with catalyst deactivation.

Scheme 1



However, we find that compounds of type **2** are not the end products of the reaction sequence. Monitoring the reaction by NMR in toluene-d_8 over a period of two weeks indicated the formation of pentafluorobenzene together with new products **3a** and **3b** which contain the new pentafluorophenyl-substituted borole ligands $[C_4H_4BC_6F_5]^{2-}$ and $[3\text{-}MeC_4H_3BC_6F_5]^{2-}$, respectively (Scheme 1). Compound **3a** can be made directly from Cp″Zr(η^3-C_4H_7)(η^4-C_4H_6)[6b] and $B(C_6F_5)_3$ without the isolation of any intermediates and is separated from side-products by the addition of diethyl ether to give **4a** as a red solid. The decomposition of red **2b** in diethyl ether proceeds more cleanly at ambient temperature to give a purple solution from which blue microcrystals of **4b** precipitate. Overall, the zirconium mediated formation of pentafluorophenylborole from a 1,3-diene corresponds to the reaction:



(1)

In toluene solution at 25 °C the chiral complexes **4** are fluxional, with rapid interchange of the ether ligand. In the case of **4b** the presence of the 3-methyl substituent on the borole ligand leads to two diastereomers, in a ratio of 1:0.6 at −50 °C. No such fluxionality is observed for the ether-free complexes **3** over the temperature range from 20 to −90 °C.

At ambient temperature the ^{19}F NMR spectra of **4a** and **4b** show two different C_6F_5 groups. The zirconium C_6F_5 ligands show hindered rotation, and even at room temperature the *o*-F atoms are inequivalent. At −40 °C the $Zr-C_6F_5$ groups show characteristic *o*-F high-field chemical shifts (e.g. **4a**: −106.9 and −119.2).[6] The rotation of the $B-C_6F_5$ group is more facile but is slow below −60 °C. In the ether-free complexes **3** the low-temperature limit for $Zr-C_6F_5$ rotation is reached only on cooling to −90 °C. For **3b** the two ^{19}F signals are found at δ −118.1 and −148.9, the latter being most probably indicative of Zr··· *o*-F coordination.[6a,7] The ^{11}B NMR spectra show broad peaks at δ 44 (**3b**), 36 (**4a**), and 38 (**4b**), respectively, which are high-

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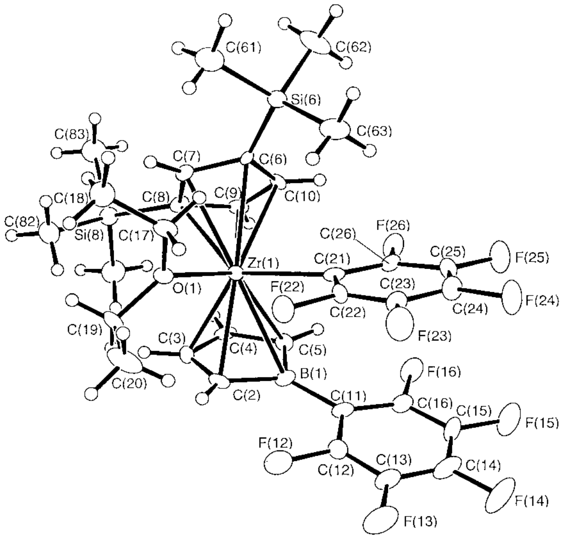

Figure 1. Molecular structure of **4b**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability. Selected interatomic distances (Å) and angles (deg): Zr−O(1) 2.266(3); Zr−C(21) 2.351(5); Zr−B(1) 2.662(6); Zr−C(2) 2.488(5); Zr−C(3) 2.396(4); Zr−C(4) 2.430(4); Zr−C(5) 2.507(5); O−Zr−C(21) 105.4(2); C(2)−B−C(5) 103.0(5); C(2)−B−C(11) 127.3(5); C(5)−B−C(11) 129.6(5).

field shifted by ca. 10−20 ppm compared to complexes of C_6H_5-substituted boroles[1a,c,e,g−i] and reflect the electron-withdrawing nature of the C_6F_5 substituent.

The structure of **4a** was confirmed by X-ray diffraction (Figure 1).[8] The compound adopts a conformation in which the B−C_6F_5, the Zr−C_6F_5, and one of the $SiMe_3$ substituents are almost eclipsed, with one of the $SiMe_3$ methyl groups resting above the plane of the Zr−C_6F_5 ligand. The Zr−C distances to the C_4H_4-BC_6F_5 ligand are short (average Zr−C 2.455 Å) and indicate strong bonding to borole, compared to the bonding of the cyclopentadienyl group (average Zr−C 2.554 Å). Despite the coplanar arrangements of the C_4B and the B−C_6F_5 rings the B−C(21) distance of 1.595(8) Å is typical of a B−C single bond and gives no indication of a π-bonding contribution,[6a,9] unlike the situation in related aminoborole complexes.[3]

The conversion of **1** into **2** is a catalyst deactivation process.[6b,10] Standard tests for ethene polymerization (1 bar, 5 min) of toluene solutions of **2** in the presence or absence of trimethylaluminum showed no catalytic activity. However, after an induction period of ca. 10 min at 60 °C under 6 bar of ethene pressure in the presence of $AlMe_3$ the onset of some polymerization is noted, and the activity increases slowly with time.[11] This behavior is indicative of the slow buildup of a catalytically active species.

Table 1. Ethene Polymerizations[a]

catalyst precursor	Al alkyl	Zr (μmol)	Al/ Zr ratio	temp (°C)	time (min)	polym yield (g)	productivity[b]	M_w[c]	M_w/M_n
4b	$AlMe_3$	30.5	26	60	50	23.1	151	d	d
4b	$AlMe_3$	30.5	26	60	110	33.6	110	49 700	6.0
4b	$AlMe_3$	31.5	15	60	50	17.5	110	53 600	5.6
$ZrCp_2Cl_2$	$AlMe_3$	57	30	60	50	traces			
4b	MAO	39	37	60	50	22	113	d	d
4b	MAO	39	37	60	110	30	70	100 700	18
4b	MAO	31	500	60	110	42	123	225 000	26

[a] Polymerization conditions: A 1 L stainless steel Büchi autoclave was charged with 200 mL of toluene. The required amount of aluminum alkyl was injected under 6 bar of ethene presure and equilibrated at 60 °C, followed by the injection of the Zr complex. Polymerizations were terminated by injecting 20 mL of methanol. [b] Productivity is in 10^3 g PE (mol Zr)$^{-1}$ h^{-1} bar^{-1}, based on isolated polymer yields. [c] By GPC relative to polystyrene standards. [d] Not determined.

In this case the reaction is explained by Scheme 1, i.e., the conversion of the inactive half-sandwich complex **2** into a 14-electron metallocene derivative of type **3**. Compound **3** is of course isoelectronic with the well-known active species in metallocene catalysts, $[Cp_2ZrR]^+$. We are therefore observing the unusual situation where a catalyst deactivation product undergoes a controlled further rearrangement into a species that on contact with $AlMe_3$ gives an active metallocene complex, a case of *catalyst "self-reactivation"*.

Solutions of isolated **4b** in toluene did not show catalytic activity, no doubt since ethene insertion into the stable Zr−C_6F_5 bond is unfavorable. However, addition of $AlMe_3$ to **4b** at Al/Zr ratios of 15:1 to 30:1 gave immediate polymerization *without an induction period*.[11] NMR studies confirm that under these conditions Zr−C_6F_5/CH_3 exchange takes place, to give a catalytically active Zr−Me species.[12] It is noteworthy that under identical conditions Cp_2ZrCl_2 is inactive (Table 1). The activities obtained with methylalumoxane (MAO) closely resemble those achieved with $AlMe_3$ alone; there is no significant productivity increase on raising the Al/Zr ratio in the MAO system from 37:1 to 500:1.

The results illustrate the importance of C−H activation pathways not only in the deactivation of metallocene-based polymerization catalysts but also as a novel route to new catalyst systems, the formation of which could not have been anticipated.

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Supporting Information Available: Experimental details of synthetic procedures, X-ray structure determination, and crystal data of **4b** (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(8) Crystal data: $C_{31}H_{35}BF_{10}OSi_2Zr$; space group $P2_1/n$; monoclinic; $a = 11.9588(14)$ Å; $b = 18.750(5)$ Å; $c = 15.2003(11)$ Å; $\beta = 106.125(7)°$, $\gamma = 90°$ at 160 K.; volume = 3274.2(9) Å^3; $Z = 4$; final R indices [$I > 2\sigma(I)$] $R_1 = 0.0416$, $wR_2 = 0.0694$ for 4595 absorption-corrected reflections.

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(11) The activity profile was monitored over a 60 min period. See Supporting Information for gas comsumpton vs time diagrams.

(12) (a) On adding $AlMe_3$ to a solution of **4b** in toluene-d_8 at 25 °C the color changed from brown to red. The NMR spectra showed a complex product mixture containing $AlMe_3$, $AlMe_3{\cdot}Et_2O$, and $AlMe_2C_6F_5{\cdot}Et_2O$, as well as two resonances for Zr−Me signals tentatively assigned to $Cp''(C_4H_3MeBC_6F_5)Zr(\mu\text{-}Me)_2AlMe_2$, in analogy to the known catalyst $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$.[12b] See Supporting Information. (b) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.