

# Synthesis of cationic zinc complexes from protonated diazadienes and $ZnR_2$ ( $R = Et, N(SiMe_3)_2$ ). The crystal structures of $[Pr^iDADH][H_2N\{B(C_6F_5)_3\}_2]$ , $[\{Pr^iDADZn(\mu-OH)\}_2][H_2N\{B(C_6F_5)_3\}_2]_2$ , and $[Ph^*DADZnN(SiMe_3)_2][H_2N\{B(C_6F_5)_3\}_2]$

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Received 21 September 2004; accepted 10 November 2004

Available online 7 February 2005

Dedicated to Professor F. Gordon A. Stone, whose synthesis of  $B(C_6F_5)_3$  so enhanced synthesis and catalysis

## Abstract

Protonation of  $(MeC=NC_6H_3Pr^i_{2-2,6})_2$  ( $Pr^iDAD$ ) with  $[H(OEt_2)][H_2N\{B(C_6F_5)_3\}_2]$  affords the immonium salt  $[Pr^iDADH][H_2N\{B(C_6F_5)_3\}_2]$  (**1**) which shows intra- and inter-ionic  $NH \cdots F$  hydrogen bonding in the solid state. Protolysis of  $ZnEt_2$  with  $[Pr^iDADH][H_2N\{B(C_6F_5)_3\}_2]$  gives  $[(Pr^iDAD)ZnEt][H_2N\{B(C_6F_5)_3\}_2]$  as a reactive intermediate. Repeated recrystallizations allowed the isolation of the dimeric zinc hydroxo complex  $[\{Pr^iDADZn(\mu-OH)\}_2][H_2N\{B(C_6F_5)_3\}_2]_2$  (**2**) which shows asymmetric OH-bridges. The analogous reaction of  $[Ph^*DADH][H_2N\{B(C_6F_5)_3\}_2]$  [ $Ph^*DAD = (MeC=NC_6H_3Ph_{2-2,6})_2$ ] with  $ZnMe_2$  or  $M\{N(SiMe_3)_2\}$  gives the three-coordinate Zn and Cd compounds  $[(Ph^*DAD)ZnMe][H_2N\{B(C_6F_5)_3\}_2]$  (**5**) and  $[(Ph^*DAD)M-N(SiMe_3)_2][H_2N\{B(C_6F_5)_3\}_2]$  (**6**,  $M = Zn$ ; **7**,  $M = Cd$ ). The crystal structures of **1**, **2** and **6** are reported.

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**Keywords:** Zinc complexes; Diazadiene; Crystal structures; Alkyl complexes; Amido complexes

## 1. Introduction

Tris(pentafluorophenyl)borane [1–3] has proved to be a remarkably versatile reagent and is widely used as Lewis acid [4], as catalyst activator [5–8], and as a source of very weakly coordinating anions such as  $[B(C_6F_5)_4]^-$  [1] and  $[Z\{B(C_6F_5)_3\}_x]^{y-}$  [9–11]. Although generally chemically inert, it can also function as a smooth aryl transfer agent [12–15]. Thus the reaction of zinc dialkyls with  $B(C_6F_5)_3$  or  $[Ph_3C][B(C_6F_5)_4]$  can follow several differ-

ent pathways, depending on the nature of the solvent and of any co-ligands: In non-polar media such as toluene,  $ZnMe_2$  and  $B(C_6F_5)_3$  lead to rapid aryl exchange; this reaction is in fact a very convenient method for synthesizing  $Zn(C_6F_5)_2 \cdot$  toluene [16]. On the other hand, in the presence of diethyl ether, stable salts of cationic zinc alkyls are formed,  $[RZn(OEt)_2]^+[B(C_6F_5)_4]^-$  [16] which are active catalysts for the ring-opening polymerization of epoxides and  $\epsilon$ -caprolactone [17]. In a preliminary communication we have also shown that bulky diazadiene ligands afford three-coordinate zinc alkyl cations  $[(Pr^iDAD)ZnR]^+X^-$  [ $R = Me, Et$ ;  $Pr^iDAD = (MeC=NC_6H_3Pr^i_{2-2,6})_2$ ;  $X = MeB(C_6F_5)_3$  or  $B(C_6F_5)_4$ ] [18].

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We report here the synthesis and structures of the starting material  $[\text{Pr}^i\text{DADH}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  and of three- and four-coordinate zinc DAD complexes stabilized by the amidodiborate anion,  $[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ .

## 2. Results and discussion

Treatment of  $\text{Pr}^i\text{DAD}$  with  $[\text{H}(\text{OEt}_2)][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  [19] in dichloromethane resulted in protonation of the diazadiene and formation of  $[\text{Pr}^i$

$\text{DADH}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  (**1**). The  $[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$  anion was chosen since it often shows better crystallization properties than  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , and indeed cooling dichloromethane solutions to  $-78^\circ\text{C}$  gave crystals suitable for X-ray diffraction (Figs. 1 and 2). Selected interatomic parameters are given in Table 1. The proton of the cationic fragment was located in the plane between the two imine nitrogen atoms; it is covalently bonded to N(1) [ $\text{N}(1)\text{--H}(1^*)$  0.93(2) Å] and hydrogen-bonded to N(2), with a distance of 2.01(2) Å. The  $\text{N}(1)\text{--H}(1^*)\text{--N}(2)$  angle is  $113.3(17)^\circ$ . The  $\text{C}=\text{N}$  bond of the

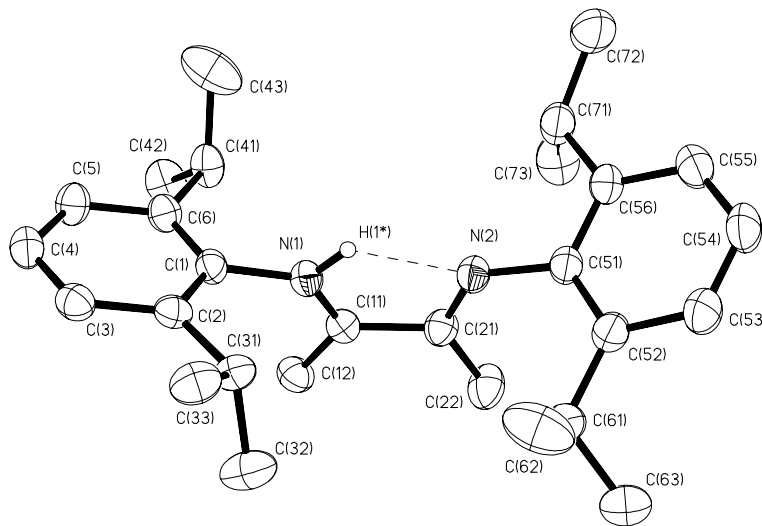


Fig. 1. Cation in  $[\text{Pr}^i\text{DADH}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$  (**1**). Thermal ellipsoids at 50% probability. Carbon-bound H atoms are omitted for clarity.

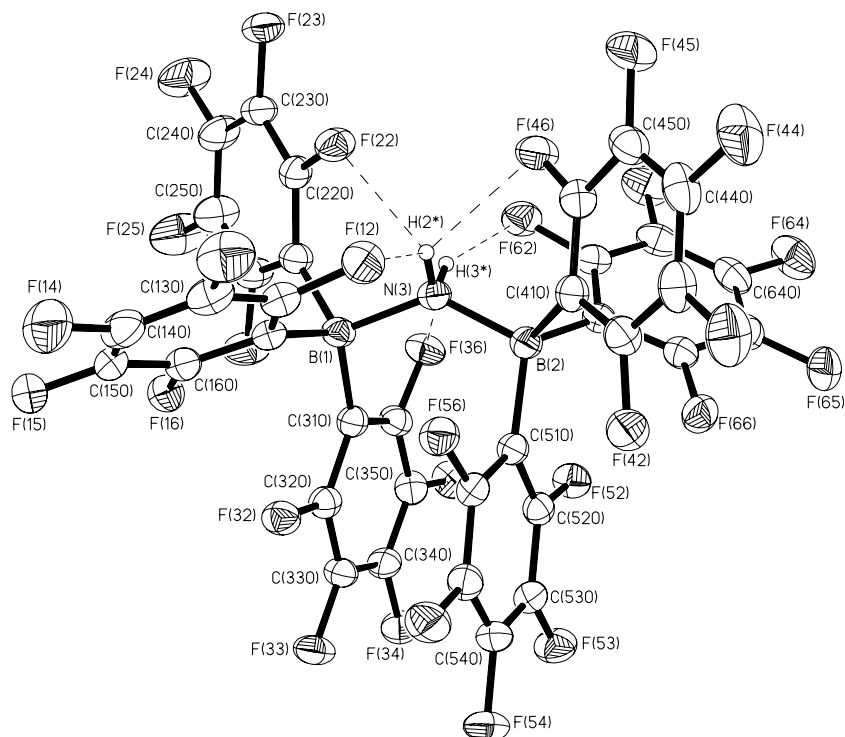


Fig. 2. Anion in **1**. Thermal ellipsoids are drawn at 50% probability.

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