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Cationic Ethylzinc Compound: A Benzene Complex with Catalytic Activity in Hydroamination and Hydrosilylation Reactions

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Ⓢ *Supporting Information*

ABSTRACT: The tight ion pair $[EtZn(\eta^3\text{-}C_6H_6)][CHB_{11}Cl_{11}]\cdot C_6H_6$ ($\mathbf{1}\cdot C_6H_6$) was obtained through β-hydrogen abstraction and concomitant ethene elimination from Et_2Zn with the trityl salt $[Ph_3C][CHB_{11}Cl_{11}]$. This ionlike species shows catalytic activity in hydrosilylation and intramolecular hydroamination reactions. The amine adduct $\{CH_2CHCH_2C(Ph_2)CH_2NH_2\}_3ZnCB_{11}Cl_{11}$ (**3**), which features a rare transition metal–carborane σ bond, was isolated from a hydroamination experiment.

Zinc salts have long been used as mild Lewis acids in organic synthesis.[1] While complexes with traditional Lewis bases such as ethers and amines are well-known,[2] stable isolable adducts with neutral π bases including olefins,[3,4] alkynes,[5] or arenes[6] are relatively rare. They usually require increased Lewis acidity at the zinc center brought about by electronegative substituents or weakly coordinating counterions. For example, the arene complexes $Zn(SbF_6)_2\cdot C_6Me_6$ and $Zn(SbF_6)_2\cdot C_6HMe_5$ were characterized using NMR spectroscopy in liquid SO_2.[7] The first crystallographically authenticated compound with intramolecular zinc arene interactions was the terphenylthiolate $Zn(SC_6H_3\text{-}Mes_2\text{-}2,6)_2$ (Mes = 2,4,6-$Me_3C_6H_2$),[8] and the crystal structure of a toluene adduct was finally reported for $(C_6F_5)_2Zn\cdot C_7H_8$.[9] It has been pointed out in a recent review[6] that cationic arene complexes such as $[MeZn(\eta^6\text{-}C_6Me_6)]^+$ are isoelectronic with the cyclopentadienide MeZnCp.[10,11] However, the known lability[12] of the weakly coordinating anion $[B(C_6F_5)_4]^-$ toward strong Lewis acids prevented isolation of the target cation, and C_6F_5 transfer products were observed instead. As part of our work on cationic, strongly Lewis acidic organoaluminum[13,14] and -gallium[15,16] compounds, we became interested in the synthesis of simple cationic organozinc species. The application of chemically inert carborane anions such as $[CH_6B_{11}X_6]^-$ (X = Cl, Br) and $[CHB_{11}Cl_{11}]^-$ [17] was expected to afford room temperature stable cationic organozinc compounds. Here, we report the synthesis of the first such compound, $[EtZn((\eta^3\text{-}C_6H_6)][CHB_{11}Cl_{11}]$ (**1**), and a preliminary reactivity study.

$[EtZn(\eta^3\text{-}C_6H_6)][CHB_{11}Cl_{11}]\cdot C_6H_6$ ($\mathbf{1}\cdot C_6H_6$; Figure 1) was obtained through β-hydrogen abstraction and concomitant ethene elimination from Et_2Zn with the trityl salt $[Ph_3C][CHB_{11}Cl_{11}]$[18] in a benzene/hexane solution at room temperature according to eq 1 in 61% yield as a colorless crystalline solid.

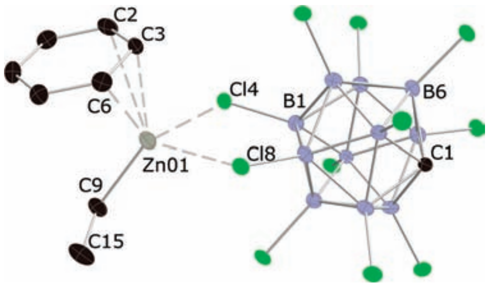

Figure 1. Thermal ellipsoid (50%) plot of **1**. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Zn01–C9 1.964(6), Zn01···C3 2.346(5), Zn01···C6 2.569(5), Zn01···C2 2.673(5), Zn01···Cl8 2.592(2), Zn01···Cl4 2.635(2); C9–Zn01–C3 138.4(2), Cl4–Zn01–Cl8 87.54(4), B1–Cl4–Zn01 104.50(19), B2–Cl8–Zn01 105.2(2).

$$Et_2Zn + [Ph_3C][CHB_{11}Cl_{11}] \xrightarrow[\text{RT, 2 h}]{C_6H_6} [EtZn(\eta^3\text{–}C_6H_6)][CHB_{11}Cl_{11}] + Ph_3CH + CH_2{=}CH_2 \quad (1)$$

The ^1H, ^{13}C, and ^{11}B NMR spectra showed the presence of an EtZn unit and the carborane anion in a 1:1 ratio in addition to about 2 equiv of benzene per EtZn unit, suggesting the formation of **1**. This was confirmed by single-crystal X-ray diffraction.[19] The structure of **1** consists of an intimate ion pair[20] in which the zinc is coordinated by one ethyl group, two chlorine donors from the anion, and three carbon atoms from a benzene molecule in an η^3 fashion. Coordination to the carborane anion involves one chlorine donor from the meta belt and one from the para position. The Zn–C distance with a value of 1.964(6) Å is identical with the one observed in the cation $[EtZn(OEt_2)_3]^+$ [21] and longer than 1.930(4) Å reported for $[EtZn(Bz_3TAC)]^+$ (Bz_3TAC = 1,3,5-tribenzyl-1,3,5-triazacyclohexane).[22]

The Zn···C(benzene) contacts with values of 2.346(5), 2.569(5), and 2.673(5) Å are the shortest ones reported to date for zinc···arene complexes,[6] an indication for the electrophilic nature of the $[EtZn]^+$ fragment. Furthermore, **1** is the first crystallographically characterized benzene complex of zinc. The

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previously reported zinc⋯arene complexes contained electron-richer arenes such as toluene[9] or hexamethylbenzene.[23] The hapticity of the arene ligand in organozinc complexes is highly variable. An η^1 coordination was observed for $(C_6F_5)_2Zn{\cdot}C_7H_8$, an η^2 coordination for the closely related perfluorobiphenyl species $(2\text{-}C_6F_5C_6F_4)_2Zn{\cdot}C_7H_8$, and an η^3 coordination for $\{C_6F_5Zn(\mu\text{-}Cl){\cdot}C_6Me_6\}_2$ and compound **1**. The Zn⋯Cl distances with values of 2.592(2) and 2.635(2) Å are significantly longer than those in the chlorine-bridged dimer $\{C_6F_5Zn(\mu\text{-}Cl){\cdot}C_6Me_6\}_2$, which average 2.337 Å, but are closer to the longer ones observed for EtZnCl with values of 2.5408(7) and 2.5248(6) Å.[24] The B−Cl distances of the ortho belt average 1.754 Å and those of the meta belt 1.784 Å, and the para B−Cl bond length is 1.809(6) Å. These distances are very close to those found in $\{CH_2CHCH_2C(Ph_2)CH_2NH_2\}_3ZnCB_{11}Cl_{11}$ (**3**; Figure 2) (ortho, 1.776 Å; meta, 1.789 Å; para, 1.804(6) Å) and in $[Et_3Sn][CHB_{11}Cl_{11}]$ (ortho, 1.764 Å; meta, 1.773 Å; para, 1.775(2) Å).[25] The B−Cl bond lengths are not affected by the Zn⋯Cl contacts, underlining the weakness of these interactions.

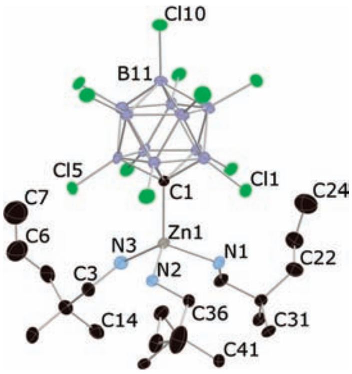
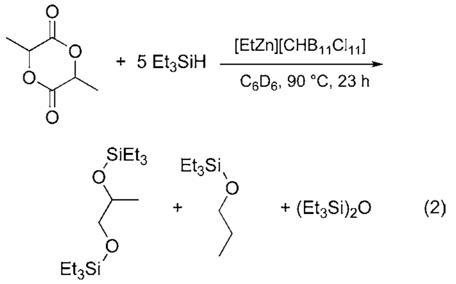


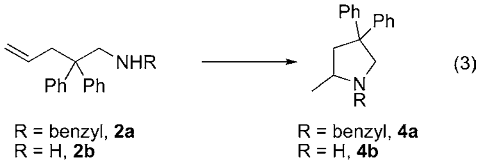
Figure 2. Thermal ellipsoid (50%) plot of **3**. Hydrogen atoms and the phenyl groups have been omitted for clarity. Selected distances (Å) and angles (deg): Zn1−C1 2.049(5), Zn1−N1 2.081(4), Zn1−N2 2.069(4), Zn1−N3 2.086(4); C1−Zn1−N1 111.6 (2), C1−Zn1−N2 115.0 (2), C1−Zn1−N3 115.9 (2), N1−Zn1−N2 104.4 (2), N1−Zn1−N3 106.6(2), N2−Zn1−N3 102.2(2).

Compound **1** is readily soluble in benzene, toluene, and tetrachloroethane and practically insoluble in hexanes, and it decomposes in chloroform. It does not react with 1-hexene at room temperature, and even at elevated temperatures (80 °C, 2 h), only a small amount of isomerization (5%) is observed. However, we have found that **1** is an active hydrosilylation catalyst. 1-Hexene is cleanly converted into $Et_3Si(CH_2)_5CH_3$ at room temperature using Et_3SiH, but higher temperatures are required for cyclohexene (75−80 °C). Benzophenone was reduced to diphenylmethane with 2 equiv of Et_3SiH at room temperature. A weak singlet at 5.75 ppm in the ^1H NMR spectrum can be observed during the reaction, which may be attributed to the silyl ether $Ph_2C(H)OSiEt_3$, the first step in the reduction of benzophenone. A small amount of a yellow oil separated after the benzophenone addition. This oil catalyzes the rapid reduction of benzophenone with Et_3SiH, but attempts to identify it have been unsuccessful so far.

Although Lewis acids have been reported to catalyze the polymerization of lactide,[26] no reaction was observed when lactide was added to a benzene solution of **1**. Similarly, no reaction took place at room temperature after the addition of Et_3SiH. Heating at 90 °C for 23 h led to lactide reduction according to eq 2. Similar to the benzophenone reduction, a small amount of a yellow oil separated, which catalyzed the reduction of additional lactide. Efforts to identify this oil are ongoing.



Intramolecular hydroamination of aminopentenes or aminohexenes is a convenient method for the construction of five- or six-membered nitrogen heterocycles, pyrrolidines, and pyrimidines.[27,28] Complexes of almost any metal in the periodic table have been tested for their ability to catalyze this reaction. Recently, in situ generated $[EtZn]^+$ was found to be an effective catalyst for the intramolecular hydroamination of secondary aminopentenes at room temperature.[29] Hence, we were curious whether **1** would show similar reactivity. In fact, a solution of **1** in C_6D_6 readily catalyzed the conversion of $CH_2CHCH_2C(Ph_2)CH_2N(H)CH_2Ph$ (**2a**; 6.2 equiv, 16% catalyst loading) at room temperature within 2 h. The solution remained active after 20 h at room temperature. An additional 28 equiv (4% catalyst loading) was converted to the pyrrolidine **4a** within 2.5 h. Interestingly, **1** did not show any reactivity toward the closely related primary aminopentene $CH_2CHCH_2C(Ph_2)CH_2NH_2$ (**2b**; 11% catalyst loading) at room temperature. Even heating at 139 °C for 37 h resulted in only a conversion of 16% of **2b**.



After standing at room temperature for 1 day, colorless crystals of a new compound, **3**, were obtained from this solution in 58% yield. ^1H and ^{11}B NMR spectroscopic analysis showed broadened signals of coordinated aminopentene and the presence of the carborane anion. On the basis of the amount of recovered aminopentene and pyrrolidine from the mother liquor, a 3:1 ratio of aminopentene/zinc was estimated. Crystals of $\mathbf{3}{\cdot}0.5CDCl_3$ suitable for X-ray diffraction were obtained by crystallization from a $CDCl_3$ solution, and it was identified as the complex $\{CH_2CHCH_2C(Ph_2)CH_2NH_2\}_3ZnCB_{11}Cl_{11}$, whose major feature is the metalated carborane.[30] The zinc center is coordinated in a slightly distorted tetrahedral fashion by three aminopentene ligands and the dianionic carborane $[CB_{11}Cl_{11}]^{2-}$.

The Zn−C bond [2.049(5) Å] in **3** is about 0.1 Å longer than those in **1** and the previously mentioned $[EtZn(OEt_2)_3]^+$[21] and $[EtZn(Bz_3TAC)]^+$,[22] but the Zn−N distances are significantly shorter than those in the TAC compound: 2.079 vs 2.244 Å. Compound **3** is a rare example of a structurally authenticated *closo*-monocarborane (CB_{11} core) with an exo carbon−transition metal bond. Some other examples include $[Et_4N]_2[Hg(CB_{11}F_{11})_2(NCMe)]$, $[Et_4N]$-

$[PhHgCB_{11}F_{11}]$,[31] $[nBu_4N]_2[ClCuCB_{11}F_{11}]$,[32] $\{[(MeCN)_4Ag_3][Ag(CB_{11}I_5Br_6)_2]\}_n$,[33] and $Ph_3PAuCB_{11}H_{11}$.[34] Although strong bases such as alkyllithium compounds readily deprotonate carborane anions,[35,36] compounds such as Et_3Al do not do so. We hypothesize that the presence of an excess of amine during the formation of **3** may have increased the basicity and reactivity of the zinc-bonded ethyl group, leading to metalation of the carborane anion.

Using the carborane anion $[CHB_{11}Cl_{11}]^-$, a novel benzene-coordinated cationic organozinc compound could be synthesized. The high Lewis acidity of the metal center led to active hydrosilylation catalysis, and a rare transition-metal-substituted deprotonated carborane dianion $[CB_{11}Cl_{11}]^{2-}$ was obtained during hydroamination catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and NMR spectra for **1** and **3** and X-ray crystallographic data for **1** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data for $\mathbf{1}\cdot C_6H_6$: monoclinic, space group $P2_1/c$, a = 15.272(1) Å, b = 15.451(1) Å, c = 14.401(1) Å, β = 114.629(5)°, V = 3089.0(4) $Å^3$, Z = 4, μ(Cu Kα) = 9.938 mm^{-1}, D_c = 1.661 Mg/m^3, $F(000)$ = 1520, GOF on F^2 = 1.009, R1 = 0.0515, wR2 = 0.1364 (F^2, all data), data/restraints/parameters 5336/0/347.

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(30) Crystal data for **3**: triclinic, space group $P\bar{1}$, a = 13.7222(4) Å, b = 14.7137(4) Å, c = 19.2699(8) Å, α = 95.465(2)°, β = 107.795(3)°, γ = 117.551(2)°, V = 3152.80(21) $Å^3$, Z = 2, μ(Cu Kα) = 5.114 mm^{-1}, D_c = 1.368 Mg/m^3, $F(000)$ = 1324, GOF on F^2 = 1.035, R1 = 0.0676, wR2 = 0.1708 (F^2, all data), data/restraints/parameters 10441/47/723.

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