First Example of a Stable 1,1-Bidentate Lewis Acid Based on Boron and Zirconium: Synthesis, Reactivity, X-Ray Analysis and NMR Studies

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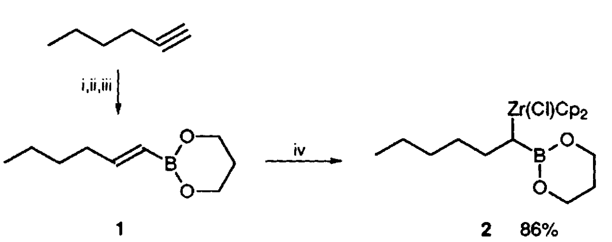
Chlorobis(cyclopentadienyl)[1-(1,3,2-dioxaborinane-2-yl)hexyl]zirconium(IV) **2**, fully characterized by X-ray, ^1H–^1H double-quantum-filtered COSY and ^{13}C-^1H heteronuclear chemical shift correlation NMR studies, IR and elemental analysis, reacts selectively with electrophilic reagents, *N*-bromo- and *N*-chlorosuccinimide and bromine to give α-haloboronic esters; it also polymerizes styrene without the aid of a co-catalyst.

Organozirconium compounds are undergoing active study for cleavage[1] and insertion reactions,[2] conjugation addition,[3] olefin cross-coupling,[4] Grignard-type addition[5] and especially catalysis of olefin polymerization.[6] 1,1-Dimetallo compounds including a transition metal are important reagents with a wide of range of applications.[7] However, such compounds containing zirconium are rare, and only a few reports have appeared in the literature, including compounds of zirconium and zinc,[4c,e] and zirconium and aluminum.[4b–d] Recently, we reported the preparation and cleavage of zirconium–boron bimetallic derivatives based on 9-borabicyclo[3.3.1]nonane.[8] However, this type of bimetallic derivative has the disadvantage of poor thermal and solution stability. Here we report the synthesis, structure and reactivity of a bimetallic compound based on zirconocene and a boronic ester, compound **2**, which, to our knowledge is the first isolated zirconium–boronic ester 1,1-dimetallo compound.

The synthesis of **2** is outlined in Scheme 1. Treatment of hex-1-yne with $HBBr_2 \cdot Me_2S$ followed by conversion of the dibromoboronic ester to the corresponding alkenylboronic acid and esterification with propane-1,3-diol provided alkenylboronic ester **1**. Hydrozirconation of **1** with 3 equiv. of Schwartz's reagent,[9] $[Zr(Cp)_2(Cl)H]$, afforded the desired product **2** (86% isolated yield), as a yellow crystalline solid. Compound **2** appears to be stable to dry air in the solid state, but softens and decomposes at 96 °C.†

The reactive nature of compound **2** is illustrated by several transformations in Scheme 2, in which its Zr–C bond selectively reacts with electrophilic reagents. Compound **2** catalyses the polymerization of styrene, as demonstrated by polymerization in solution. The resulting polymers had weight-average molecular masses in the range 75 000–110 000 with polydispersities of 1.8–2.1. GPC traces are unimodal with well-formed symmetric peaks. No co-catalyst was required to obtain these samples.[10] Further synthetic investigations of such bimetallic compounds are underway in our laboratories.



Scheme 1 *Reagents and conditions*: i, $HBBr_2 \cdot Me_2S$; ii, H_2O_2, NaOH; iii, $HO[CH_2]_3OH$; iv, $[Zr(Cp)_2(Cl)H]$ (3 equiv.), CH_2Cl_2, 0 °C (Cp = C_5H_5)

The X-ray analysis of **2** has proven it to be a complex of four-coordinated Zr with two cyclopentadienyl rings, Cl and the aliphatic C(1) as the ligands (Fig. 1).‡ There are no intra- or inter-molecular interactions between Zr and boron or oxygen atoms. The coordination sphere of zirconium approximates a tetrahedron with a dihedral angle between Cl–Zr–C(1) and Cp(1)–Zr–Cp(2)§ planes being 88.4(1)°; the dihedral angle between the planes of the cyclopentadienyl rings is 53.0(2)°, both cyclopentadienyl moieties are planar and twisted by 17.7(4)° from the fully eclipsed conformation. The distances of Zr to Cp(1) and Cp(2) are 2.205(1) and 2.208(1) Å respectively. The bond length Zr–Cl is 2.459(1) Å and Zr–C(1) is 2.306(4) Å. The conformation of the six-membered heterocyclic ring resembles an envelope[12] with C(9) being 0.619(6) Å out of the plane of the five other atoms. A search of the Cambridge Structural Database[13] revealed 22 structures with a similar coordination sphere for Zr [fragment

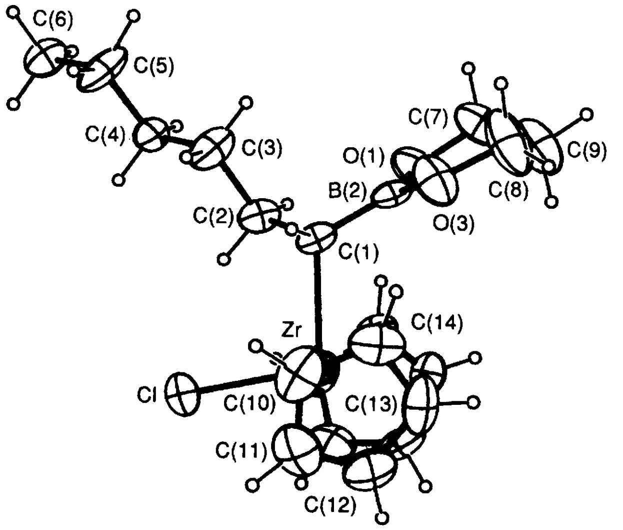
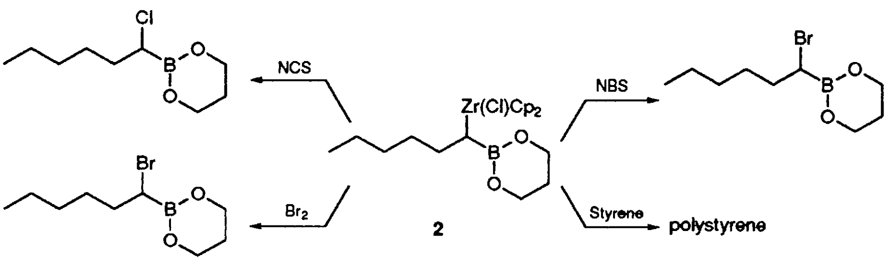


Fig. 1 An ORTEP drawing of the molecule with 50% thermal ellipsoids



Scheme 2 NCS = *N*-chlorosuccinimide; NBS = *N*-bromosuccinmide

Cl(C)ZrCp$_2$] and three structures having the same 6-membered heterocyclic ring with a CB(O)O fragment. All bond lengths and angles for **2** agree well with the mean values calculated for other comparable structures (distances within 1σ, angles within 2σ).

Compound **2** was also unambiguously characterized by ^{1}H–^{1}H double-quantum-filtered COSY,[14] ^{13}C, and ^{13}C–^{1}H heteronuclear chemical shift correlation[15] NMR spectroscopy.¶ Accurate ^{1}H chemical shifts were measured for multiplets (arising in the 1-D ^{1}H NMR) using the ^{1}H cross-sections (after two zero-fills to ensure sufficient digital resolution) from the ^{13}C–^{1}H shift correlation experiment.

Both ^{1}H and ^{13}C NMR data revealed considerable differences in the chemical shifts of the diastereotopic Cp groups. Other interesting features were the marked non-equivalence of the two groups of methylene protons 2-H and 3-H in the ^{1}H NMR, and the width together with concomitant low intensity of the C(1) resonance in the ^{13}C NMR spectrum.

We are grateful to the University of Toledo for the support of this work, and the State of Ohio Academic Challenges Program for providing funds for a high field NMR spectrometer. We also thank Nichole Jagodzinski (high school student), the participant of Research Apprenticeship Summer Program, for her help in a statistical evaluation of the crystallographic data.

Received, 13th September 1993; Com. 3/05493D

Footnotes

† *Preparation of* **2**: a suspension of [Zr(Cp)$_2$(Cl)H] (0.51 g, 2.0 mmol) in dry CH$_2$Cl$_2$ (4.0 ml) was stirred at ambient temperature under argon. The boronate **1** (0.65 mmol) in CH$_2$Cl$_2$ (0.5 mol l^{-1}; 1.3 ml) was then added. The mixture was stirred for 15 min, and became a clear green-yellow solution. After evaporation of solvents, addition of dry hexanes (4 × 10 ml), filtration and evaporation afforded **2** as a yellow solid (0.24 g, 86%).

‡ *Crystal data* (at −80 °C): C$_{19}$H$_{28}$BO$_2$ZrCl; $M_r = 425.92$; monoclinic, $P2_1/n$; $a = 10.305(2)$, $b = 16.396(5)$, $c = 11.613(2)$ Å, $\beta = 90.69(1)°$; $V = 1962(1)$ Å^3; $Z = 4$; $D_c = 1.44$ g cm^{-3}; λ(Mo-Kα) = 0.71073 Å; $\mu = 7.0$ cm^{-1}; $F(000) = 880$; $R = 0.045$, $R_w = 0.056$ for 217 variables, 2743 observed reflections [$F_o^2 > 3.0\sigma(F_o^2)$] out of 3999 unique and 4698 total data. Crystal covered by oil (Paratone–Nujol, 1 : 1) mounted on glass fibre, data collected on Enraf-Nonius CAD4 diffractometer using ω-scan technique, $2\theta_{max} = 52°$, empirical absorption and anisotropic decay corrections applied, solution by Patterson and Foutier methods, refinement by full-matrix least-squares, hydrogen atoms refined as riding atoms. All calculations done employing the MolEN software package[11] running on Micro VAX3100. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Cp(1) and Cp(2) are the centroids of the cyclopentadienyl rings defined by the atom C(10)–C(14) and C(15)–C(19) respectively.

¶ *Key data for* **2**: ^{1}H NMR (400 MHz; CDCl$_3$) δ 6.32 [s, 5H, Cp(1)], 6.28 [s, 5H, Cp(2)], 3.99 (t, $^3J_{HH} = 5.4$ Hz, 4H, 7-H, 8-H), 1.96, 1.39 (m, 2H, 2-H), 1.86 (m, 2H, 9-H), 1.86 (m, partially obscured by 9-H, 1H), 1.23 (m, 2H, 5-H), 1.15 (m, 2H, 4-H), 1.06, 0.93 (m, 2H, 3-H), 0.84 (t, $^3J_{HH} = 7.1$ Hz, 3H, 6-H); ^{13}C NMR (100.6 MHz; CDCl$_3$) δ 113.1 [Cp(1)] 112.2 [Cp(2)], 67.4 (br, $w_{\frac{1}{2}} = 49$ Hz, C-1), 61.3 (C-7, C-8), 34.1 (C-3), 33.2 (C-2), 31.9 (C-4), 28.1 (C-9), 22.7 (C-5), 14.1 (C-6); The numbering system is that in Fig. 1. FTIR (KBr pellet), ν_{max}/cm^{-1} 1407m, 1326s, 1260vs, 1179s, 751m, 668m.

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