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First Example of Stable 1,1-Bimetalloalkenes of Boron and Zirconium: Synthesis, Reactivity, X-ray Analysis, and NMR Studies

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This communication describes the synthesis, chemistry, X-ray analysis, and NMR studies of a new class of 1,1-bimetalloalkenes based on dioxaborolanes and zirconocene, **2**.[1] The chemistry of carbon–zirconium[2] and carbon–boron[3] bonds differs considerably and should allow a sequential route to substituted alkenes. In addition, the cleavage of the C(sp^2)–Zr and C(sp^2)–B bonds generally occurs with retention of geometry.[4,5] It is thus reasonable to presume that a union of boron and zirconium organometallic chemistry should be synergistic, affording products and chemistry not attainable by each reagent itself. 1,1-Bimetalloalkenes that have been prepared in the past, including aluminum and titanium,[6] aluminum and zirconium,[6] and zinc and zirconium,[7] behave as alkylidene-transfer reagents. Lipshutz and co-workers have described 1,1-bimetalloalkenes based on tin and zirconium that displayed selective hydrolysis of the carbon–zirconium bond to provide (*Z*)-vinylstannanes.[8] Other 1,1-bimetalloalkenes containing aluminum and zirconium,[9] aluminum and hafnium,[10] gallium and zirconium,[11] zinc and boron,[12a] copper and boron,[12a] and tin and boron[12b] have also been described. Our own interests in this area center around 1,1-bimetalloalkenes based on boron and zirconium that would take advantage of their different electronegativities and bond polarities. Recently, we synthesized a series of boron–zirconium 1,1-bimetalloalkanes[13,14] and showed that they undergo selective cleavage of the carbon–zirconium bond with a series of halogen-based electrophiles.[15,16] In this communication we describe our initial results on the preparation, characterization, and reactions of 1,1-bimetalloalkenes based on dioxaborolanes and zirconium.

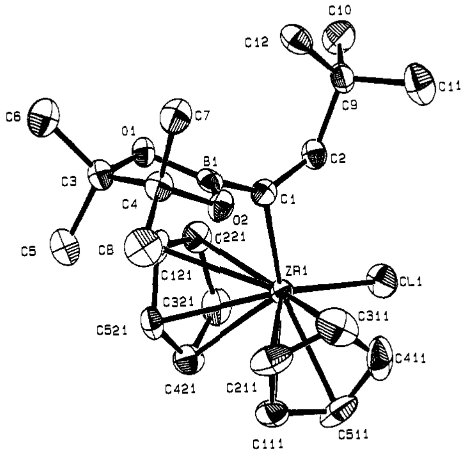
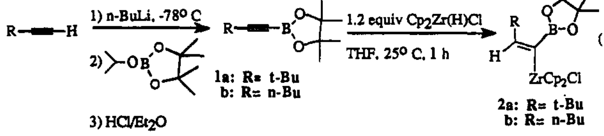


Figure 1. An ORTEP[29] drawing of **2a** (molecule A) with 50% probability thermal ellipsoids.

As representative of this class of compounds, we prepared one hindered and one nonhindered 1,1-bimetalloalkene. Their synthesis is outlined in eq 1. The 1-alkynyldioxaborolanes **1** were



(1)

synthesized in high yield according to the method of Brown[17] by the reaction of 1-lithium acetylides with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[18] at –78 °C, followed by treatment with ethereal hydrogen chloride. Hydrozirconation of **1** with 1.2 equiv of zirconocene hydrochloride[19] afforded the desired products. In both cases the zirconium was placed on C1 (eq 1). The *tert*-butyl derivative **2a** was isolated as a pale greenish crystalline solid (81.5% yield).

The X-ray analysis of **2a**[20] confirmed the configuration of the four-coordinated Zr complex with two cyclopentadienyl rings, Cl, and C(sp^2) as four ligands (Figure 1). There are two molecules in the asymmetric part of the unit cell. Their configurations are identical, although the conformations differ in details. All bond distances and angles in both molecules agree within experimental error and show very good agreement with the values quoted for similar structures.[16,21,22] In both molecules the coordination spheres of zirconium form almost regular tetrahedrons. The mean distances from the central Zr ions to their ligands are as follows: to Cl, 2.520(1) Å; to C(sp^2), 2.242(4) Å; to Cp1 and Cp2, 2.22(1) Å, where Cp here means the center of the cyclopentadienyl ring. Both heterocyclic rings resemble the typical envelope conformations,[23] with O–B–O–C in the plane and the remaining fifth C atom out of plane (0.46 and 0.42 Å for C3 in molecule A and C15

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[20] X-ray analysis: The light green crystal (0.48 × 0.32 × 0.21mm) was mounted on a glass fiber and placed immediately in a cold stream of nitrogen. Crystal: $C_{22}H_{32}BO_2ClZr$, $M = 465.98$, triclinic, $P\bar{1}$ (No. 2), $a = 14.384(3)$ Å, $b = 15.888(3)$ Å, $c = 11.021(1)$ Å, $\alpha = 93.35(1)°$, $\beta = 94.22(1)°$, $\gamma = 66.96(1)°$, $V = 2310(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.34$ g cm^{-3}. The structure was solved by direct methods in TEXSAN 5.0 and refined to $R = 0.033$ ($R_w = 0.057$) for 5226 reflections with $I > 3\sigma(I)$ measured at –100 °C on a Rigaku AFC6S diffractometer (Mo Kα radiation, $\lambda = 0.710\,69$ Å). The absorption corrections were introduced by applying ψ scans of several reflections. All hydrogen atoms were located in difference Fourier maps but not refined.

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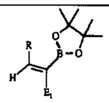
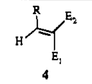
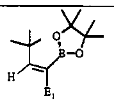
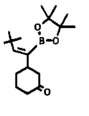
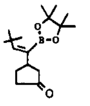
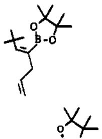
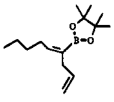
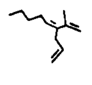
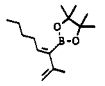
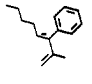
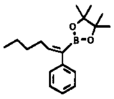
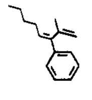
Table 1. Reactions of Dioxaborolane Zirconocene 1,1-Bimetallics with Various Electrophiles

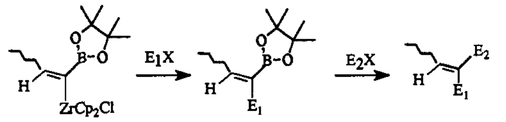
Bimetallic	E_1X	 3	% Isolated Yield 3	E_2X	 4	% Isolated Yield 4
2a						
	NBS	E_1 = Br	97			
	NCS	Cl	87			
	NIS	I	93			
	Pivaloyl chloride[a]	t-BuCO	76			
	Benzoyl chloride[a]	PhCO	83			
2a	Cyclohexenone[b]		73			
2a	Cyclopentenone[b]		64			
2a	Allyl bromide[c]		87			
2b	Allyl bromide[c]		90	Phenyl iodide[e]		82
2b	Allyl bromide[c]	''	90	2-Bromopropene[e]		86
2b	2-Bromopropene[d]		62	Phenyl iodide[e]		84
2b	Phenyl iodide[d]		69	2-Bromopropene[e]		87

[a] Reaction conditions: **2** (1.05 mmol), acid chloride (1.05 equiv), CuBr·SMe_2, 0.1 equiv), THF, 25 °C, 1 h. See: Wipf, P.; Xu, W. *Synlett* **1992**, 718. [b] Reaction conditions: **2** (0.83 mmol), enone (1.0 equiv), CuBr·SMe_2 (0.1 equiv), THF, 25 °C, 1 h. See: Wipf, P.; Smitrovich, J. H.; Moon, C.-H. *J. Org. Chem.* **1992**, *57*, 3178. [c] Reaction conditions: **2** (0.9 mmol), allyl bromide (1.0 equiv), CuCN (0.1 equiv), THF, 25 °C, 12 h. See: Venanzi, L. M.; Lehman, R.; Keil, R.; Lipshutz, B. H. *Tetrahedron Lett.* **1992**, *33*, 5857. [d] Reaction conditions: **2** (1.24 mmol), $ZnCl_2$ (1 equiv), $Pd(PPh_3)_4$ (0.05 equiv), vinyl or aryl halide (1 equiv), THF, 25 °C, 2 h. See: Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. [e] Reaction conditions: **3** (0.72 mmol), $Pd(PPh_3)_4$ (0.5 equiv), vinyl or aryl halide (1 equiv), EtONa in EtOH (1.5 equiv), reflux 3 h. See: (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (b) Miyaura, N.; Satoh, M.; Suzuki, A. *Tetrahedron Lett.* **1986**, *27*, 3745. (c) Satoh, M.; Miyaura, N.; Suzuki, A. *Chem. Lett.* **1986**, 1329.

in molecule **B**, respectively). However, C3 bends toward the metallocene moiety, while C15 points outwardly. Also, in molecule **A** the planar part of the heterocyclic ring makes almost a right angle (86°) with the plane defined by the cis-substituted BC═CC olefin part of the complex while in molecule **B** the same dihedral angle is only 72°. These two observations are in contrast to the structures of D-mannitol tris(phenylboronic ester),[24] two derivatives of streptovaricin C,[25] and a derivative of sarcophytol B,[26] where in all cases the boron-containing rings are fairly planar and conjugated with the phenyl rings attached to boron.

The absence in **2a** of C–B(pp)–π overlap in solution is indicated by the ^{11}B chemical shift (δ = 32.3) since this is in the same region (δ = 31.1) as the resonance for the corresponding boron zirconium 1,1-dimetalloalkane, chlorobis(cyclopentadienyl)[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethylbutyl]zirconium(IV).[13,15] Metals with abundant isotopes that have spin quantum numbers exceeding $^1/_2$ can broaden ^{13}C resonances for directly attached (and sometimes remote) carbons in organometallic compounds. In some cases where this scalar spin–spin relaxation occurs, ^{13}C signals may not be observed at all, such as for C1 of **2a** in $CDCl_3$. However, in [D_8]THF at 25 °C, a resonance is visible for C1 (δ = 187.8, $W_{1/2}$ = 145 Hz) of **2a**. The magnitude of this shift is outside of the normal range (80–145 ppm) for substituted alkenes not bonded to a metal through the alkenyl carbons. These effects are currently under investigation.

Compounds **2** were reacted with various electrophiles (Table 1). The carbon–zirconium bond always reacted first. *N*-Halosuccinimides reacted with **2a** to give (α-halo alkenyl)boronates.[27] Using our method, we can access (*E*)-(α-haloalkenyl)boronic esters. Consequently, our approach complements hydroboration of 1-haloalkynes that provides only the *Z*-isomer.[28] Carbon–carbon bond formation also occurred readily with various carbon electrophiles. No dialkylated products were observed with 1 equiv of electrophile. Conjugate addition provided alkenylboronates not available by other methodologies. Reaction with carboxylic acid chlorides afforded α-boryl α,β-unsaturated ketones. Sequential addition of electrophiles is possible (eq 2). Thus reaction of **2b** with 2-bromopropene followed by coupling with phenyl iodide provided **4** (E_1 = propenyl, E_2 = phenyl). The same starting material, **2b**, leads to the isomeric product **4** (E_1 = phenyl, E_2 = propenyl) by reversing the sequence of addition of electrophiles.



(2)

This communication presents a number of firsts: (i) the description of a new class of 1,1-bimetalloalkenes; (ii) a single-crystal X-ray analysis of a representative compound; (iii) a demonstration of the more reactive nature of C(sp^2)–Zr, thus enabling sequential coupling sequences with various electrophiles; and (iv) the preparation of alkenylboronates hitherto not accessible.

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Supplementary Material Available: General experimental procedures, representative spectra for compounds in Table 1, and crystallographic data and an ORTEP drawing of molecule B (67 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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