

Pb(IV)-P bonds in  $\text{Pb}(\text{CH}_3)_4$  (2.238 (9) Å)<sup>12</sup> and  $\text{Pb}(\text{C}_6\text{H}_5)_4$  (2.19 (3) Å),<sup>13</sup> and the Pb(II)-P bonds in **3** are slightly longer than the Pb(IV)-P bonds (2.611 Å) in  $\text{P}_7(\text{PbMe}_3)_3$ .<sup>11</sup>

For **2** the <sup>31</sup>P NMR spectrum at 0 °C (toluene) shows two triplets with <sup>119</sup>Sn and <sup>117</sup>Sn satellites at  $\delta_1$  -10.3 (<sup>3</sup>J(P,P) = 25 Hz, <sup>2</sup>J(Sn,P) = 276, 336 Hz (C-bound ligand)) and  $\delta_2$  -15.9 (<sup>3</sup>J(P,P) = 25 Hz, <sup>2</sup>J(Sn,P) = 1106, 1158 Hz (chelating ligand)). The <sup>31</sup>P NMR spectrum of **3** at -20 °C shows two equally intense resonances with <sup>207</sup>Pb satellites at  $\delta_1$  -4.7 (<sup>1</sup>J(Pb,P) = 1970 (chelating ligand)) and  $\delta_2$  -11.6 (<sup>2</sup>J(Pb,P) = 165 Hz (C-bound ligand)). The complex changes occurring at other temperatures are under investigation. However since the spectrum of **3** at 30 °C consists of a single-bond resonance at -8.0 ppm, it is clear that a path for ligand interchange exists. This mechanism is under study.

We view these substances as potential ligands with the three-coordinate phosphorus atoms, the three-coordinate carbon, and the metal (tin or lead) centers as binding sites. The coordination properties of **2** and **3** toward transition-metal ions are under active investigation.

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**Supplementary Material Available:** Listings of the final atomic coordinates, bond distances and angles, and thermal parameters (12 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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## Zinc-Promoted Reductive Coupling Reactions.

### Reaction of Sodium

### Methoxyalkenyldialkylborates(1-) with Alkenylzinc Chlorides or Zinc Chloride<sup>†</sup>

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**Summary:** Sodium methoxyalkenyldialkylborates(1-) react with alkenylzinc chlorides or zinc chloride to provide excellent yields of symmetrical 1,3-dienes in an unprecedented reductive coupling process.

As part of an ongoing synthetic project in our laboratories, we sought entries into alkenylzinc halide reagents which would allow incorporation of a variety of functional groups within the alkenylzinc halide itself. One potential route to alkenylzinc halides we envisioned involved transmetalation from corresponding alkenylboron "ate" complexes.<sup>1</sup> Alkenylboron "ate" complexes can be stereoselectively accessed and utilized in ways permitting

<sup>†</sup> Dedicated to Professor George Zweifel, on the occasion of his 60th birthday.

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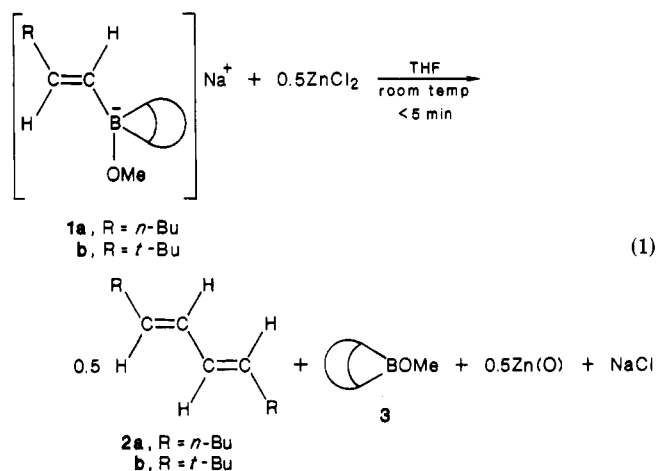
**Table I. Synthesis of Symmetrical Dienes via Zinc-Promoted Reductive Coupling Reactions<sup>a</sup>**

alkyne	% GC yield (isolated) of <b>2</b>
1-hexyne	100
3,3-dimethyl-1-butyne	80
5-chloro-1-pentyne	93
phenylacetylene	80 (75)

<sup>a</sup> Reactions performed according to eq 2. Yields are based on 1-alkyne. Satisfactory spectral data were obtained for all compounds.<sup>1c</sup>

incorporation of a number of sensitive functional groups (e.g., halides, esters, and nitriles) within these species.<sup>2</sup> Success of the procedure was expected to greatly expand general routes to functionalized, stereodefined alkenylzinc halides.

In our first attempt, the boron "ate" complex derived by addition of (*E*)-*B*-1-hexenyl-9-borabicyclo[3.3.1]nonane [(*E*)-*B*-1-hexenyl-9-BBN, **1a**] to NaOMe in THF was added to 1 equiv of ZnCl<sub>2</sub>. To our surprise, an immediate precipitate of Zn(0) appeared. Detailed analysis of the reaction mixture revealed the presence of (*E,E*)-5,7-dodecadiene (**2a**) in virtually quantitative yield, along with *B*-methoxy-9-BBN (**3**) and (presumably) NaCl. As suggested by the stoichiometry of the reaction, reductive coupling can be achieved with 0.5 equiv of ZnCl<sub>2</sub>. This protocol, too, provides quantitative generation of symmetrical dienes. Although similar coupling reactions



utilizing copper salts<sup>3</sup> and silver salts<sup>4</sup> are well-known, the present result represents an unprecedented example of zinc-promoted reductive coupling.<sup>5</sup> Synthesis of a number of conjugated dienes can be accomplished without isolation of intermediates by utilizing dicyclohexylborane in THF as the hydroborating agent in conjunction with 1-alkynes.<sup>6</sup> Addition of the (*E*)-1-alkenyldicyclohexylborane solution

(2) (a) Brown, H. C.; Campbell, J. B., Jr. *Aldrichim. Acta* **1981**, *14*, 3. (b) Campbell, J. B., Jr.; Molander, G. A. *J. Organomet. Chem.* **1978**, *156*, 71. (c) Arase, A.; Hoshi, M.; Masuda, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 209.

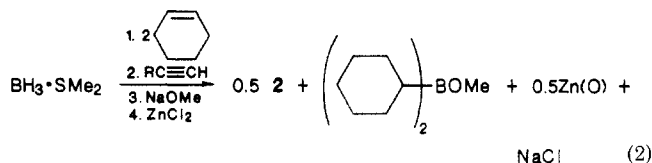
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(5) Reductive coupling of dialkylzinc compounds is precedented. However, temperatures in excess of 100 °C are required. Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103.

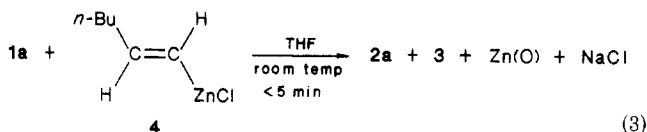
(6) Plamondon, J.; Snow, J. T.; Zweifel, G. *Organomet. Chem. Synth.* **1971**, *1*, 249.

to a slurry of dry, methanol-free NaOMe in THF generates the corresponding sodium methoxy-(*E*)-1-alkenyldicyclohexylborates(1-). Transfer of this resulting solution to zinc chloride in THF affords dienes in excellent overall yield (Table I).<sup>7</sup> Unfortunately, the zinc-promoted reaction is

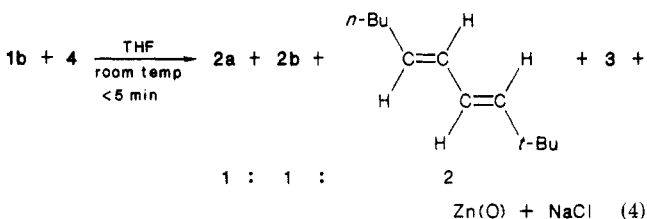


not nearly as general as the copper-promoted version of the reaction.<sup>3</sup> For example, stereochemical integrity of the alkenyl unit is not retained in the present case, as sodium methoxy-(*Z*)-1-alkenyldialkylborates(1-) provide nearly pure (*E,E*)-conjugated dienes on reaction with ZnCl<sub>2</sub>.

Perhaps the most intriguing aspect of this process is the mechanism by which coupling occurs. Believing that initial transmetalation from alkenyl boron "ate" complex to the alkenylzinc reagents had occurred, we attempted to couple **1a** with an alkenylzinc chloride derived by transmetalation with ZnCl<sub>2</sub> from the corresponding alkenyllithium reagent.<sup>8</sup> In fact, reductive coupling proceeded instantaneously, providing a quantitative yield of diene as in previous reactions with ZnCl<sub>2</sub>. Curiously, alkenylboron "ate" com-



plexes derived ultimately from internally substituted alkynes (e.g., 4-octyne) do not undergo reductive coupling with either the corresponding alkenylzinc chloride or ZnCl<sub>2</sub>. Protonolysis of reaction mixtures with glacial acetic acid in these instances revealed quantitative recovery of *cis*-4-octene. Efforts to achieve cross-coupling also failed, as reaction of **1b** with **4** provided a nearly statistical mixture of three dienes.



In instances where silver salts or copper salts promote dimerization reactions of boron "ate" complexes, the actual reductive coupling is believed to arise through thermal decomposition of corresponding organosilver or organocopper reagents, produced as intermediates in these reactions.<sup>3,4</sup> As mentioned above, there is little precedence for this process in organozinc chemistry. Indeed, we have prepared distyrylzinc reagents by addition of 2 equiv of alkenyllithium to 1 equiv of ZnCl<sub>2</sub>. As expected, no reductive coupling occurs over a period of 24 h. However, when methyl dialkylborinates (e.g., *B*-methoxy-9-BBN) are added to the reaction mixture, a slow reaction occurs (72 h), providing 54% of coupled product. Stronger Lewis

(7) A simple workup procedure allowed isolation of pure dienes. Thus, THF removed *in vacuo* was replaced by pentane. Ethanolamine (1 equiv) was added to the reaction mixture, precipitating the ethanolamine dicyclohexylborinate ester. The resulting slurry was filtered through a thin pad of Celite to remove the borinate esters, along with the Zn and NaCl. Removal of pentane and simple distillation or recrystallization provided pure dienes.

(8) Negishi, E.; Luo, F. T. *J. Org. Chem.* 1983, 48, 1560.

acids (e.g., BF<sub>3</sub>·Et<sub>2</sub>O) were ineffective in promoting reductive coupling. Neither sodium methoxytrialkylborates(1-) nor corresponding sodium methoxyaryldialkyl- or methoxyalkenyldialkylborates(1-) undergo reaction with ZnCl<sub>2</sub>. Finally, a variety of Cd(II) and Hg(II) salts are clearly less effective than Zn(II) salts in promoting the desired reaction with sodium methoxyalkenyldialkylborates(1-).<sup>9</sup>

It is tempting to suggest that electron transfer from the electron-rich, readily oxidizable alkenylboron "ate" complex<sup>10</sup> to the alkenylzinc halide<sup>11</sup> somehow initiates reductive coupling. Similar processes have previously been reported for other organometallic pairs of reagents involved in reductive coupling reactions.<sup>12</sup> However, detailed mechanistic postulates for this unique reaction must await further studies.

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(9) Less than 50% yields of symmetrical 1,3-dienes were realized upon addition of a variety of cadmium(II) and mercury(II) salts to the sodium methoxyalkenyldialkylborates(1-).

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## Isolation and Characterization of the First Simple Tantalacyclobutane Complexes<sup>1</sup>

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**Summary:** *cis,mer*-Ta(CHCMe<sub>3</sub>)Cl<sub>3</sub>(THF)<sub>2</sub> reacts with LiO-2,6-C<sub>6</sub>H<sub>3</sub>(CHMe<sub>2</sub>)<sub>2</sub>·Et<sub>2</sub>O(LiDIPP·Et<sub>2</sub>O) to give Ta-(CHCMe<sub>3</sub>)(DIPP)<sub>3</sub>(THF). Ta(CHCMe<sub>3</sub>)(DIPP)<sub>3</sub>(THF) reacts with ethylene to give colorless TaCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(DIPP)<sub>3</sub> and with styrene to give orange TaCHPhCH(CMe<sub>3</sub>)CH<sub>2</sub>(DIPP)<sub>3</sub>. TaCHPhCH(CMe<sub>3</sub>)CH<sub>2</sub>(DIPP)<sub>3</sub> crystallizes in the space group *P*2<sub>1</sub>/*n* with *a* = 21.338 (11) Å, *b* = 11.699 (5) Å, *c* = 37.198 (23) Å, β = 102.66 (5)°, *Z* = 8, and *V* = 9060.1 Å<sup>3</sup>. TaCHPhCH(CMe<sub>3</sub>)CH<sub>2</sub>(DIPP)<sub>3</sub> reacts with THF to give solely Ta(CHPh)(DIPP)<sub>3</sub>(THF). Addition of *cis*-2-pentene to Ta(CHCMe<sub>3</sub>)(DIPP)<sub>3</sub>(THF) leads to rapid, but relatively short-lived metathesis. Tantalacyclobutane complexes react with ketones and aldehydes to give a Wittig-like reaction of an incipient alkylidene complex and/or oxytantalacyclohexane complexes, the products of insertion of the carbonyl bond into the Ta-C<sub>α</sub> bond.

(1) Multiple Metal-Carbon Bonds. Part 44. For part 43 see ref 3.