

**Figure 1.** ORTEP diagram of the molecular structure of  $(C_5Me_5)_2Ta_2(\mu-Br)_2(B_2H_6)$  (**2b**) viewed perpendicular to the Ta=Ta bond. Key bond distances (Å) and bond angles (deg) not given in the text are as follows: Ta(1)–Br(1), 2.649 (2); Ta(1)–Br(2), 2.641 (2); Ta(2)–Br(1), 2.627 (2); Ta(2)–Br(2), 2.645 (2); Ta(1)–Br(1)–Ta(2), 65.11 (5); Ta(1)–Br(2)–Ta(2), 64.99 (5).

bridges (a data set with lower  $\sigma$ 's is needed to substantiate this) since a Ta<sup>III</sup>–B distance can be estimated at 2.35 Å.<sup>8,15</sup> All non-Cp\* hydrogens except H(6) were found during refinement, with H(6) calculated and placed between Ta(1)/B(1) because of the marginally longer Ta(1)–B(1) separation. Acute TaBrTa angles are consistent<sup>8</sup> with a Ta=Ta interaction. The Ta(1)=Ta(2) distance is in the single-bond range, whereas a double bond of  $\sigma^2\delta^2$  configuration would be expected for  $B_2H_6^{2-}$  bonded to a Cp\*<sub>2</sub>Ta(III)<sub>2</sub>(μ-X)<sub>2</sub><sup>2+</sup> fragment. Metal–metal bond length–order correlations can be unreliable in complexes with bridging ligands, and M–M bonds lengthen substantially upon substitution of a μ-hydride by a μ-halide.<sup>8,16</sup> We ascribe the Ta=Ta lengthening to the  $B_2H_6^{2-}$  ligand.

Addition of 4 equiv of LiBH<sub>4</sub> to **1** or 2 equiv to **2** results in halogen substitution, H<sub>2</sub> elimination, and formation of the violet  $(C_5Me_4R)_2Ta_2(B_2H_6)_2$ , **3**, in 60% yield (eq 1).<sup>17</sup> This complex has chemically equivalent C<sub>5</sub>Me<sub>4</sub>R groups, through which pass a mirror plane, and two <sup>1</sup>H resonances for BH<sub>i</sub> and TaHB groups; a singlet is seen in the <sup>11</sup>B NMR spectrum. There is no NMR-detectable exchange between TaHB and BH<sub>i</sub> hydrogens, with invariant chemical shifts between –83 and 95 °C. These data are consistent with symmetric bridging (μ-H)<sub>2</sub>H<sub>1</sub>B–BH<sub>i</sub>(μ-H)<sub>2</sub> moieties.

The mechanism of formation of **2** and **3** has been probed in several ways. Reaction of excess LiBH<sub>4</sub> with a Cp\*<sub>2</sub>Ta<sub>2</sub>Cl<sub>4</sub>/(C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Ta<sub>2</sub>Cl<sub>4</sub> mixture yields Cp\*<sub>2</sub>Ta<sub>2</sub>(B<sub>2</sub>H<sub>6</sub>)<sub>2</sub> and (C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Ta<sub>2</sub>(B<sub>2</sub>H<sub>6</sub>)<sub>2</sub> with no cross product (C<sub>5</sub>Me<sub>4</sub>Et)–Cp\*Ta<sub>2</sub>(B<sub>2</sub>H<sub>6</sub>)<sub>2</sub> by NMR, thus ruling out mononuclear intermediates. Kinetic studies by UV/vis show that both reactions in eq 1 are first-order in organoditantalum reactant and zero-order in LiBH<sub>4</sub>.<sup>18</sup> The zero-order [LiBH<sub>4</sub>] dependence and near-zero  $\Delta S^\ddagger$  for both reactions suggest that the organoditantalum reactants rearrange prior to BH<sub>4</sub><sup>–</sup> reaction, perhaps by opening of two μ-halides.

Complexes with B<sub>2</sub>H<sub>6</sub> ligands are rare.<sup>13,19–22</sup> Fe<sub>2</sub>(CO)<sub>6</sub>(B<sub>2</sub>–

H<sub>6</sub>)<sup>13</sup> possesses an unsymmetrical (μ-H)<sub>2</sub>H<sub>1</sub>BHBH<sub>i</sub>(μ-H)<sub>2</sub><sup>2–</sup> group and Fe–B bond as shown by NMR. The byproduct Cp\*<sub>2</sub>Nb<sub>2</sub>(B<sub>2</sub>H<sub>6</sub>)<sub>2</sub> (4% yield), from synthesis<sup>23</sup> of Cp\*<sub>2</sub>Nb(BH<sub>4</sub>), possesses a structure<sup>22</sup> analogous to **3** and presumably arises from reaction of BH<sub>4</sub><sup>–</sup> with adventitious Cp\*<sub>2</sub>Nb<sub>2</sub>Cl<sub>4</sub> formed under the reducing conditions.

The dimetalladiboranes **2** and **3** are novel in several aspects: (1) they are obtained from BH<sub>4</sub><sup>–</sup>, which shows that early metal dinuclear complexes can act as templates for B–H activation and BH<sub>4</sub><sup>–</sup> oligomerization;<sup>3a,24</sup> (2) the isoelectronic relationships between BH<sub>4</sub><sup>–</sup> and CH<sub>4</sub> and between the arachno anion B<sub>2</sub>H<sub>6</sub><sup>2–</sup> and C<sub>2</sub>H<sub>6</sub> suggest that the formation of **2** or **3** can serve as models for dehydrodimerization of CH<sub>4</sub> to H<sub>3</sub>CCH<sub>3</sub> and that **2** and **3** are structural models<sup>25</sup> for C<sub>2</sub>H<sub>6</sub> surface coordination; (3) they are novel examples of early-transition-metal metallaboranes with low boron content, an unexplored area (other than BH<sub>4</sub><sup>–</sup> and Group 6 B<sub>3</sub>H<sub>8</sub><sup>–</sup> complexes.<sup>3b,26</sup>)

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**Supplementary Material Available:** Tables of coordinates, thermal parameters, and bond lengths and angles (13 pages); listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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## Serial Radical Reactions of Enol Ethers: Ready Routes to Highly Functionalized C-Glycosyl Derivatives<sup>1</sup>

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Carbohydrate derivatives, because of their highly functionalized nature, have been favorite substrates for testing the viability of free-radical reactions for synthetic operations.<sup>3–8</sup> By corollary,

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(17) Characterization data for Cp\*<sub>2</sub>Ta<sub>2</sub>(B<sub>2</sub>H<sub>6</sub>)<sub>2</sub>, **3**: Anal. Calcd for C<sub>20</sub>H<sub>42</sub>B<sub>4</sub>Ta<sub>2</sub>: C, 34.92; H, 6.11. Found: C, 34.85; H, 6.45. <sup>1</sup>H NMR (δ, 25°, C<sub>6</sub>D<sub>6</sub>): –10.5 (br, TaHB), 2.26 (s, Cp\*), 4.4 (br, BH); at 75° (partial correlation time decoupling): –10.5 (br d, TaHB) and 4.28 (1:1:1:1 q, BH<sub>i</sub>, <sup>1</sup>J<sub>BH</sub> ≈ 110 Hz). <sup>13</sup>C NMR (δ, C<sub>6</sub>D<sub>6</sub>): 13.5 (s, C<sub>5</sub>Me<sub>5</sub>), 109.6 (s, C<sub>5</sub>Me<sub>5</sub>). <sup>11</sup>B NMR (δ, C<sub>6</sub>D<sub>6</sub>): –4.0. Mass spectrum (E1): *m/e* 688, M<sup>+</sup>. IR (Nujol, cm<sup>–1</sup>): 2417 (s, BH<sub>i</sub>), 1784 (s, TaHB); 1800, 1328 for LiBD<sub>4</sub>-derived product.

(18) Pseudo-first-order (in Ta<sub>2</sub>, s<sup>–1</sup>) rate constants and activation parameters: **1** → **2b** (24.7°): 3.04 × 10<sup>–4</sup>,  $\Delta H^\ddagger$  = 90.5 (1.9) kJ mol<sup>–1</sup>,  $\Delta S^\ddagger$  = –8 (6) J mol<sup>–1</sup> K; **2b** → **3** (25.1°): 4.54 × 10<sup>–5</sup>,  $\Delta H^\ddagger$  = 83.1 (5.8),  $\Delta S^\ddagger$  = –49 (19).

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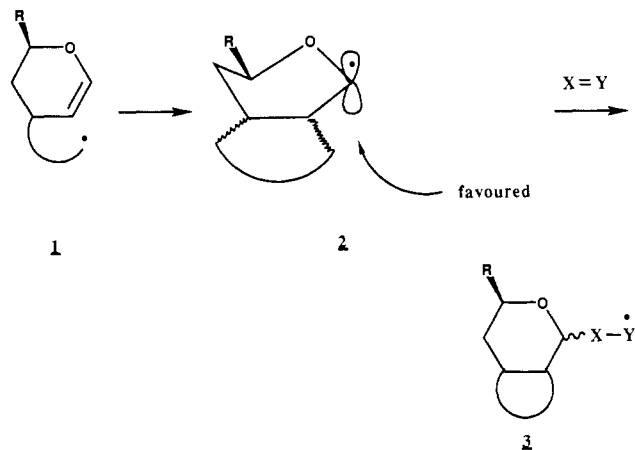
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Scheme I



such procedures are particularly well suited for carbohydrate manipulations because of their mildness,<sup>9</sup> their ability to tolerate unprotected hydroxy groups, and the attendant low incidence of  $\beta$ -elimination of oxygen functionalities.<sup>10</sup> The unsaturated sugar derivatives, known as glycols, which are commercially available or readily prepared, are popular starting materials for synthesizing modified sugars<sup>11</sup> or natural product chirons.<sup>12</sup> However, we are unaware of any studies of carbon-centered radical addition to these substrates. We report herein some recent studies relating to the potential of such processes for ready access to versatile polyfunctionalized C-glycosyl derivatives through serial radical cyclizations.<sup>13</sup>

Although intermolecular addition of a nucleophilic, carbon-centered radical to an electron rich vinyl ether is not favored,<sup>14</sup> studies by Newcomb<sup>15</sup> and Beckwith<sup>16</sup> have shown that intramolecular versions proceed at rates which are comparable to those of the corresponding reaction of olefins.<sup>29</sup> In the case of the cyclic ether **1**, the radical formed by ring closure, **2**, is (a) stabilized<sup>17,18</sup>

and (b) susceptible to facial selectivity in its reactions not only because of normal steric factors but also because of the radical anomeric effect.<sup>19,20</sup> Thus, as a result of the latter, addition from the  $\alpha$ -face, anti to the lone pair on the ring oxygen,<sup>19d</sup> is preferred. Trapping of intermediate **2** by a suitable reagent,  $X = Y$ , should therefore afford **3**, in which stereocontrolled, vicinal 1,2-substitution of the glycol double bond has occurred.

Our first task was to demonstrate that the first step could be carried out efficiently. The readily available glycols **4a**<sup>21</sup> and **5a**<sup>22</sup> were converted into the mixed acetals **4b** and **5b**, respectively, using the method of Stork<sup>23</sup> and Ueno.<sup>24</sup> Treatment of **4b** and **5b** with tri-*n*-butyltin hydride and AIBN in benzene solutions afforded the bicyclic compounds **6a** and **7a** in 85% and 80% yields, respectively, which showed that the intramolecular addition step could be carried out efficiently.

The reaction was then repeated on compound **4b** in the presence of a 10-fold excess of acrylonitrile. The C-glycosyl compounds **6b** were obtained in 76% yield without evidence of the reduced products **6a**. Replacing the bromide of **4b** with iodine<sup>25</sup> prior to cyclization improved the yield of **6b** to 87%.

Attempts to trap the radical intermediate with tertiary butylisocyanide under similar conditions, or under the conditions recommended by Stork<sup>26</sup> ( $\text{Bu}_3\text{SnCl}$ ,  $\text{NaCNBH}_3$ ,  $t\text{BuOH}$ ), afforded a mixture of the glycosyl cyanide **6c** and the reduced product **6a** in 1.4:1 ratio.

Another example of the ready introduction of a functionalized alkyl substituent at C1 was obtained by using allyl tributyltin as a radical trap in an  $\text{SH}_2'$  process,<sup>5</sup> which afforded **6d** in 70% yield. Evidence for the rapid rate of the intramolecular cyclization step **1**  $\rightarrow$  **2** in this experiment comes from the failure to detect products from the reaction of **1** with allyltributyltin.<sup>27</sup>

A final example involves using the hex-2-enopyranosid-4-ulose **8**<sup>28</sup> as the radical trap (Scheme III). This substrate has often been used in this laboratory for a variety of synthetic and mechanistic studies involving radical reactions.<sup>10a-d</sup> In the present study, isolation of the highly functionalized product, **9** in 70% yield, is a most encouraging result.

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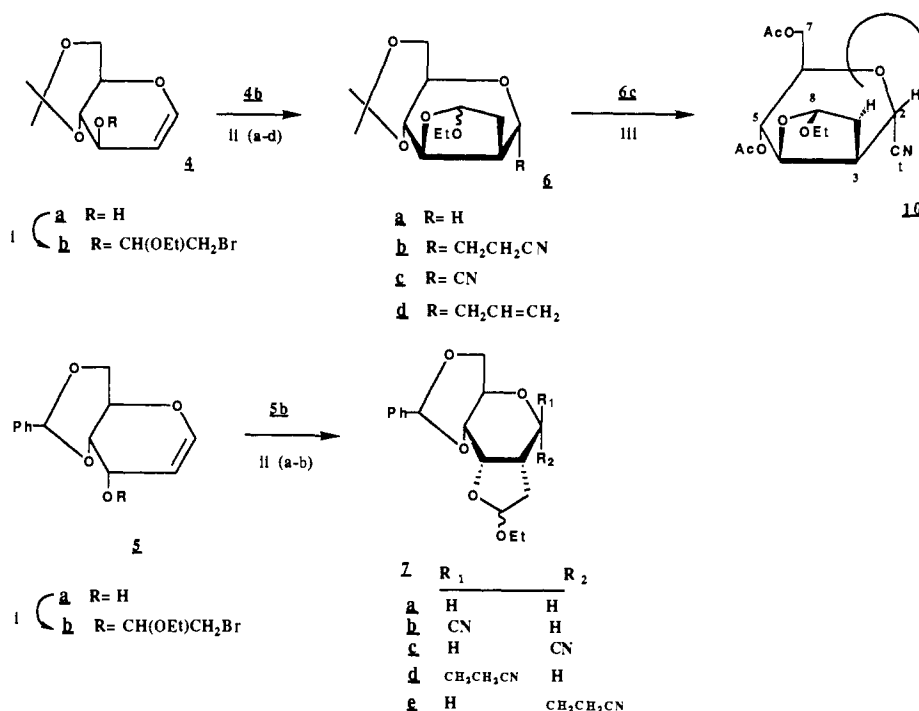
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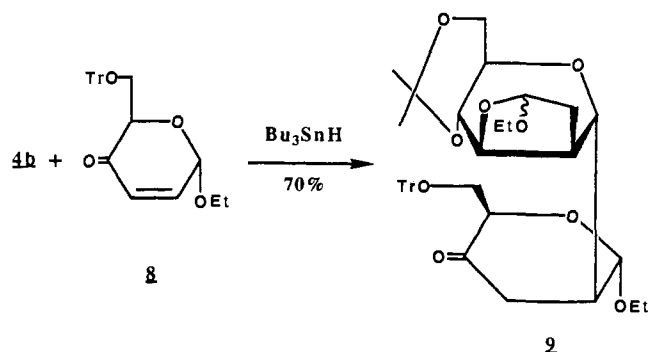
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(27) For example, Giese has shown that acyloxy migration to the anomeric carbon is faster than radical allylation described by Keck:<sup>5</sup> Giese, B., in ref 3, p 101.

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Scheme II<sup>a</sup>

Scheme III



The configurations at the anomeric center in compounds **6b–d** and **9** were expected to be  $\alpha$ , and this was supported by the range of values for  $J_{1,2} = 1.5\text{--}3.9$  Hz for these compounds. This assignment was further verified, as indicated in Scheme II. Although the C8 epimers of **6c** could not be separated chromatographically, hydrolysis and acetylation afforded **10**, which was isolated as a pure diastereomer. An NOE effect between H2 and H9 endo confirmed the  $\alpha$  orientation at anomeric center.

Reactions of **5b** were expected to be less stereocontrolled because steric effects favor the trans product with  $\beta$  anomeric orientation, whereas the radical anomeric effect favors  $\alpha$  orientation. Indeed, products from the trapping experiments gave the anomeric mixtures of **7b/7c** and **7d/7e** in 5:1 and 3:1 ratios, respectively. In the case of the former pair, the reduced material **7a** was obtained in equal amounts as the nitriles **7b/7c**. The assignment of the  $\beta$  anomers as the major products was made readily on the basis of their  $^1\text{H}$  NMR spectra.

**Note Added in Proof.** Since submission of this manuscript, three radical cyclizations involving carbohydrates have appeared:

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**Supplementary Material Available:** Preparation and spectral data ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) for **4b,d**, **6a–d**, **12**, **9**, **5b**, and **7a–e** (12 pages). Ordering information is given on any current masthead page.

## The First d–d Fluorescence of a Six-Coordinate Copper(II) Ion

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The structural diversity and relatively simple electronic structure have made copper(II) complexes a spectroscopic favorite.<sup>1</sup> However, metal-centered (d–d) emission of copper(II) complexes has only been observed in tetrahedral sites (in ZnS and CdS type semiconductors<sup>2</sup>). The improbability of observable emission in six-coordinate copper(II) complexes can be rationalized by the existence of a low-lying excited state, arising from the Jahn–Teller split component of the (octahedral)  $^2\text{T}_g(\text{E}_g)$  state which will be strongly coupled with the ground state, providing an efficient pathway for radiationless relaxation. Notwithstanding this argument, we report the unambiguous structured fluorescence for copper(II)-doped  $\text{KZnF}_3$  and  $\text{K}_2\text{ZnF}_4$  crystals.

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