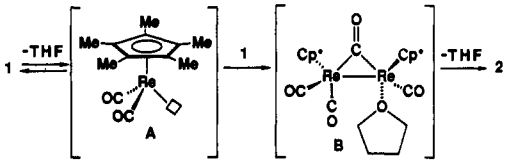
group 6 $Cp^*(CO)_2M{\equiv}M(CO)_2Cp^*$ compounds.[11]

The rhenium-rhenium double bonded compound **2** is extremely reactive in ligand addition and in oxidative addition reactions. When a green solution of **2** in THF at -80 °C was exposed to 1 atm of CO, the color of the solution changed to yellow in less than 1 min. In a preparative reaction, **2** (30 mg, 40 μmol) reacted with CO at room temperature to give the known $Cp^*(CO)_2Re(\mu\text{-}CO)Re(CO)_2Cp^*$ (**3**)[9] in 95% yield after flash chromatography.

Similarly, a green solution of **2** in THF at -80 °C turned yellow in less than 1 min upon exposure to H_2. In a preparative reaction, **2** (30 mg, 40 μmol) in THF reacted with H_2 at room temperature to produce the new dihydride $Cp^*(CO)_2Re(\mu\text{-}H)_2Re(CO)_2Cp^*$ (**4**) in 90% yield after flash chromatography. The ^1H NMR spectrum of **4** established a 1:1 ratio of Cp* to ReH units, and the IR spectrum established that only terminal CO groups were present.[12] An X-ray crystal structure of **4** (Figure 2) showed a long Re-Re distance of 3.143 (1) Å and indicated a staggered arrangement of the Cp* and CO ligands with anti Cp* groups. The arrangement of the Cp* and CO ligands is consistent only with bridging hydride ligands. Symmetrically bridged hydrides were located close to the plane perpendicular to the plane of the Re atoms and the Cp* centroids. **4** has two more valence electrons than the related tungsten compound $Cp^*(CO)_2W(\mu\text{-}H)_2W(CO)_2Cp^*$;[13] this gives **4** an unusual formal electron count of >18e at each Re. The long Re-Re distance is consistent with the presence of two three-center two-electron Re(μ-H)Re bonds and a Re--Re antibond, for a net bond order of 1. This type of bonding was first suggested by Dahl[14] for compounds such as $[L_2H_2Re]_2(\mu\text{-}H)_4$ (**5**)[15] and $[Co_2L_6(\mu\text{-}H)_3]^+$.[16] The bridging hydride ^1H NMR chemical shift of **4** (δ -6.19) is downfield from normal μ-H ligands but is similar to that seen for the unusual μ-H ligands of **5**. The facile oxidative addition of H_2 across multiple metal-metal bonds is unusual, but Sattelberger[17] and Messerle[18] have reported H_2 addition across Ta=Ta double bonds at room temperature.

While Re=Re compound **2** is the formal dimer of the high-energy coordinatively unsaturated 16e d^6 fragment **A**, it is highly unlikely that it is formed by dimerization of **A**. We suggest that



unsaturated intermediate **A** adds to a Re=CO unit of THF complex **1** to form the bridging CO intermediate **B**, which then loses THF to form **2**. The reactions of **2** with CO and other donor ligands may proceed by reactions related to the microscopic reverse of the loss of THF from **B**. We are actively pursuing the reactions of **2** and the synthesis of new M=M systems.

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Supplementary Material Available: X-ray crystallographic data for $2{\cdot}C_6D_6$ and **4** (17 pages); tables of observed and calculated structure factors for $2{\cdot}C_6D_6$ and **4** (24 pages). Ordering information is given on any current masthead page.

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Carbohydrates as Chiral Auxiliaries: Asymmetric Cyclopropanation Reaction of Acyclic Olefins

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The importance of chiral, nonracemic cyclopropane subunits in a number of natural and unnatural products[2] as well as in molecules used to probe biological processes[3] has led to intensive efforts to develop efficient methods for their construction. One synthetic strategy involves the stereoselective cyclopropanation reactions of substituted allylic alcohols or α,β-unsaturated carbonyl compounds linked to a number of well-known chiral auxiliaries.[4] However, in most cases these reactions show some severe drawbacks that include the limited availability of the chiral auxiliary and the general scope of the reaction. A highly diastereoselective cyclopropanation reaction of substituted allylic alcohols linked to a carbohydrate[5] readily available from D-glucose is reported herein.

The design of a new chiral auxiliary for this reaction is based on the observation that oxygen atoms proximal to the alkene can undergo direct attack by the reagent via prior coordination of the zinc atom.[6] It was initially anticipated that a suitably protected carbohydrate derivative would be an ideal chiral template for this purpose since it possesses a number of proximal oxygens that can direct the attack by the reagent. The ability for chelation of the oxygen at the C-2 position can, in principle, be modified by selecting an appropriate protecting group, R'. It was hoped that stereoselective delivery of the reagent from one side of the diastereotopic double bond or the other could be favored by ade-

(1) NSERC (Canada) University Research Fellow, 1989-1994; Bio-Méga Young Investigator, 1991-1993.

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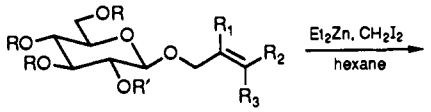
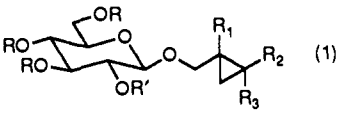
quately changing the nature of R′.

Our initial results were fairly disappointing. When fully protected glycosides **1a–d** were treated with excess diethylzinc/diiodomethane only moderate diastereoselectivities were observed for a number of different protecting groups at the 2 position (eq 1).[7] These results suggested that the ring and the C-2 oxygen atoms might not be involved in the delivery of the reagent and that the exocyclic oxygen might be the exclusive coordinating site.



R, R′ = Bn (**1a**), Ac (**1b**), Piv (**1c**)
R = Bn, R′ = TIPS (**1d**)



(1)

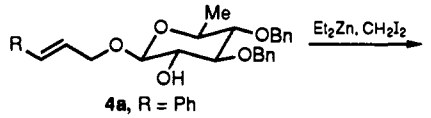
diastereoselectivities ca. 2:1–3.5:1

R_1 = H, R_2 = H, R_3 = propyl and R_1 = H, R_2 = propyl, R_3 = H

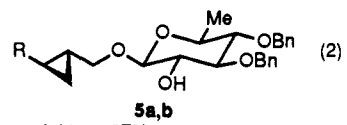
These observations prompted us to use the hydroxy group at the 2 position as an anchor for a "tethered" reagent. The precursors, 2-hydroxyglucopyranosides (**2a-g**), were readily accessible using Danishefsky's glycosylation method with commercially available tri-*O*-benzyl-D-glucal and a number of allylic alcohols.[8]

When 2-hydroxyglucopyranoside **2a** was treated with 1 equiv of the reagent generated from Et_2Zn (1 equiv) and CH_2I_2 (15 equiv) at 25 °C a 1.7:1 ratio of diastereomers was obtained. However, increasing the number of equivalents of the reagent resulted in a drastic improvement in the diastereoselection. After considerable optimization, it was found that treatment of **2a** with excess reagent (10 equiv) in toluene at −35 to 0 °C produced a >50:1 diastereomeric mixture of cyclopropanes in virtually quantitative yield. Interestingly, the increase in the diastereoselection was observed when 2 equiv or more of the reagents was used. One might presume from that observation that the delivery of the methylene group occurs via a coordinatively bonded carbenoid with the C-2 oxygen rather than a covalently bonded reagent. The scope of the reaction is very broad as illustrated by the high level of asymmetric induction observed with a number of differently substituted allylic alcohols (Table I).

The other enantiomer of the cyclopropane is also equally available by using a pseudo mirror image of D-glucose, 6-deoxy-L-glucose, readily available from L-rhamnose, as chiral auxiliary (eq 2).[9]



4a, R = Ph
4b, R = Pr



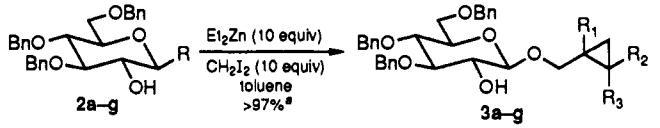
(2)

5a,b
yields: >97%
diastereoselectivities: >50:1

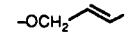
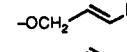
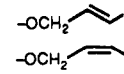
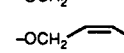
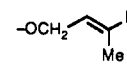
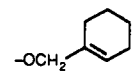
Preliminary results in the α-anomer series indicate that the cyclopropane of *opposite relative configuration* is obtained with a good level of asymmetric induction (α-**2a**, diastereoselection: 12:1[10]). *This observation is quite significant since it implies ready access to both enantiomers of the cyclopropane from the same chiral auxiliary simply by changing the anomeric configuration.*

Chiral, nonracemic substituted cyclopropylmethanols can be liberated in high yield by a novel fragmentation reaction of 2-hydroxyglucopyranosides.[11] The cyclopropanated material **3c** was converted into triflate **6** (Tf_2O, pyridine) which underwent ring contraction, upon heating in aqueous DMF in the presence of pyridine (eq 3). The desired cyclopropane carbinol **7** ($[\alpha]_D$ +86° (*c* 1.3, EtOH); 98.4% ee by cap. GC analysis) was then isolated in 90% yield along with aldehyde **8** (79%).[12]

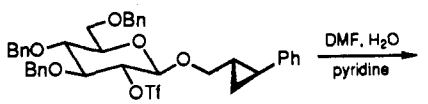
Table I. Cyclopropanation of Substituted Allylic Ethers



2a–g **3a–g**

allylic ether	R	temp,[b] °C	diastereoselectivity[c]
2a		−35 → 0	>50:1 (124:1)
2b		−35 → 0	>50:1
2c		−35 → 0	>50:1 (130:1)[d]
2d		−35 → 0	>50:1 (114:1)
2e		−20 → 0	>50:1
2f		−50 → −20	>50:1 (111:1)
2g		−35 → 0	>50:1 (100:1)

[a] Isolated yields of purified products. [b] Detailed procedures for all experiments are given in the supplementary material. [c] The diastereomeric ratios were determined by ^{13}C NMR by comparison with a 1:1 mixture. The ratios in parentheses were obtained by capillary GC after prior derivatization into the tetra(trimethylsilyl) ether: 1. HCO_2NH_4, Pd-C; 2. TMSCl, pyr (see supplementary material). [d] The absolute stereochemistry was determined to be (1*S*,2*S*) by conversion into authentic (1*S*,2*S*)-*trans*-1-hydroxymethyl-2-phenylcyclopropane: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726–728. The absolute stereochemistry of the other cyclopropanated products will be reported in the full account of this work.



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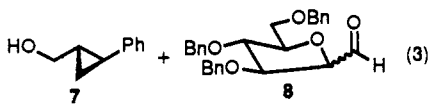

(3)

7 **8**

Further work to elucidate the mechanism of the asymmetric induction is in progress and will be reported in due course. We are also currently pursuing the use of this new chiral auxiliary in a number of hydroxyl-directed reactions.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, F.C.A.R. (Québec), and Bio-Méga Inc.. J.-F.M. thanks the NSERC for a postgraduate fellowship and B.C. thanks the Université Laval for a Georges Elie Amyot bursary.

Supplementary Material Available: Full experimental details for the cyclopropanation reactions, determination of diastereomeric excesses, and spectroscopic data of reaction products (7 pages). Ordering information is given on any current masthead page.

(7) Details will be provided in the full account of this work.
(8) Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661–6666.
(9) For the synthesis of 6-deoxy-L-glucal from L-rhamnose see: Roth, W.; Pigman, W. *Methods in Carbohydrate Chemistry*; Academic Press: New York, 1963; Vol. II, p 405.
(10) Preliminary results show that the diastereomeric ratio can be increased to >25:1 by recrystallization.
(11) For ring contraction reactions of glucopyranosides see: (a) Binkley, R. W.; Ambrose, M. G.; Hehemann, D. G. *J. Carbohydr. Chem.* **1987**, *6*, 203–219. (b) Hanessian, S.; Tyler, P. C.; Demailly, G.; Chapleur, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6243–6246.
(12) When this deglycosylation procedure is used, the chiral auxiliary is consumed. The conversion of **10** to tri-*O*-benzyl-D-glucal will be reported separately.