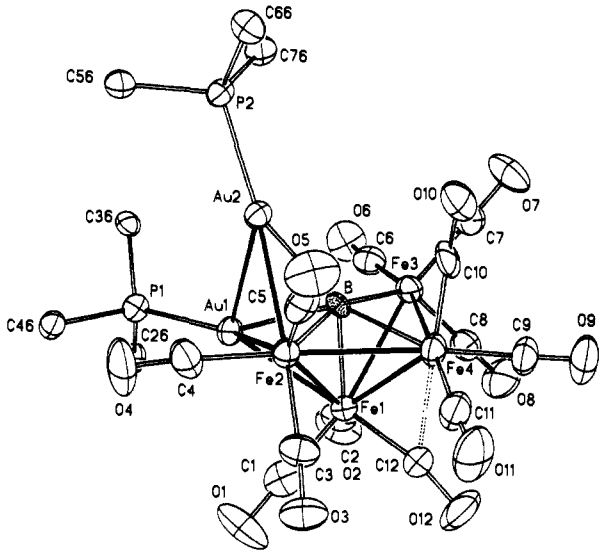

Figure 1. Molecular structure and labeling scheme for I. Phenyl rings depicted as ipso-carbon atoms only.

One AuL (L = PPh_3) unit, Au(1), caps the Fe(1)Fe(2)B face and the second AuL unit caps the Fe(2)Au(1)B face. The hydrogen atom on boron was not located, but its ^1H NMR shift (−9.1 ppm) and observed coupling to boron implies an Fe–H–B bridge position. The cluster skeleton can be regarded as a pair of facially fused trigonal bipyramids if all metal atoms plus the boron are regarded as vertex atoms, although structural parameters (viz., position of B with respect to the iron butterfly and the latter's dihedral angle of 113.4 (1)°) suggest that a more appropriate description is an *arachno* cluster as previously presented for III.[14,16,17]

Although I is prepared from anion II, it is formally derived from III by replacing two H atoms by AuL fragments. However, in contrast to many previous examples of H/AuL replacement,[4-7] this turns out not to be a straightforward structural analogy. Taking the H/AuL isolobal analogy at face value, the increased degree of boron encapsulation in going from III to I is brought about by the migration of one "proton" (in the form of $Au(PPh_3)$) from the base of the iron skeleton toward the boron. A similar situation arises in comparing $HFe_4(CO)_{12}CH$[18] (IV) with $Fe_4(CO)_{12}(AuL)_2C$ (L = PEt_3, PPh_3)[19] (V). Again, although the preparative route to V is not via direct H/AuL substitution in IV, the net result is a "proton" migration toward the main-group element and away from the metal framework. In V, however, the carbide is sited within a near octahedron of metal atoms. Whether or not the structural difference between I and V is due entirely to the requirements of the additional proton in I is currently under investigation.

It is noteworthy that, compared to III, one of the hinge $Fe(CO)_3$ units in I is twisted through 60° and forms a semibridging CO along the Fe(1)–Fe(4) hinge bond, the site occupied by a bridging hydride in II and III. The steric requirements of the Fe(1)Fe(2)B face bridging $Au(PPh_3)$ group presumably cause the hinge $Fe(CO)_3$ rearrangement. It is interesting, however, that in a closely related butterfly cluster, $[Fe_4(CO)_{13}(AuL)]^-$ (L = PPh_3, PEt_3), the AuL fragment occupies the hinge position,[20] just as the hydrogen atom did in the analogous $[HFe_4(CO)_{13}]^-$.[21]

The positions of the $Au(PPh_3)$ groups in the solid-state structure of I are inequivalent (Figure 1). However, at −70 °C, the ^{31}P NMR spectrum exhibits only one resonance. Assuming an intramolecular process, this equivalence can be explained by either a simple site exchange or a "rocking" motion of the $[Au(PPh_3)]_2$ unit across the Fe(2)–B bond. A related dynamic skeletal rearrangement involving the $[Pt(PMe_2Ph)_2]$ unit in $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$ has been invoked by Adams et al.[22]

Finally, whereas the ^{11}B NMR shift is very sensitive to the presence of B–H or Fe–H–B vs. direct Fe–B bonds,[11,23] it does not appear sensitive to association of the boron with $AuPR_3$ moieties. Thus in going from II to I no prominent change in ^{11}B NMR shift is observed, even though the boron is increasing its degree of metal encapsulation.

Acknowledgment. This research was supported by a grant from Research Corporation which is gratefully acknowledged. NSF provided support for the purchase of the University of Delaware diffractometer.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates for I (7 pages); table of observed and calculated structure factors for I (33 pages). Ordering information is given on any current masthead page.

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Enzyme-Catalyzed Regioselective Deacylation of Protected Sugars in Carbohydrate Synthesis

Henri M. Sweers and Chi-Huey Wong*†

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received May 1, 1986

Selective deprotection of acylated sugars and nucleosides or nucleotides has been a problem and an area of extensive research.[1] The preparation of protected sugars with free primary hydroxyl group, for example, is very often carried out through several steps including selective tritylation, esterification, and acid-catalyzed detritylation (which may cause complicated acyl migration) followed by tedious chromatographic purifications.[2,3]

As part of our interest in the application of enzymes in organic synthesis, particularly in carbohydrate synthesis,[4] we wish to report here the regioselective deacylation of methyl 2,3,4,6-tetra-*O*-acyl-D-hexopyranosides to give the 6-OH derivatives in high yields (80–90%) using the lipase from *Candida cylindracea* (Scheme I). Enzymatic approaches to this type of reactions were attempted but yielded a mixture of products.[5]

†Searle Scholar (1985–1988), Presidental Young Investigator (1986–1991).
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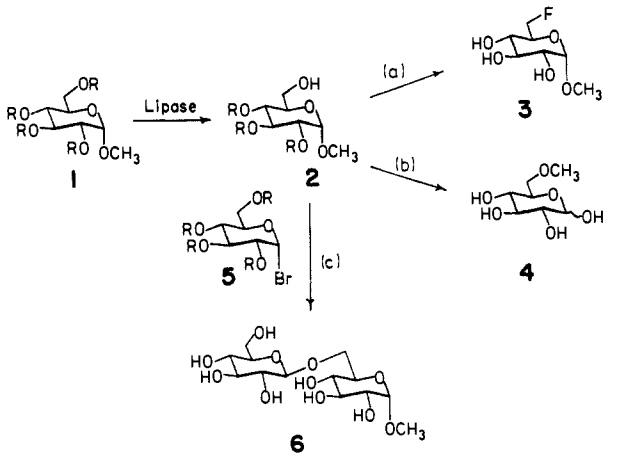
0002-7863/86/1508-6421$01.50/0

Scheme I. Enzymatic and Chemical Synthesis of Sugar Derivatives[a]



[a] (a) 1, DAST; 2, CH_3ONa (catalytic)/CH_3OH. (b) 1, CH_2N_2; 2, CH_3ONa (catalytic)/CH_3OH; 3, H^+. (c) 1, CF_3SO_3Ag; 2, CH_3ONa (catalytic)/CH_3OH. R = acetyl for **1a**, **2a**, and **5a**, pentanoyl for **1b** and **2b**, and octanoyl for **1c** and **2c**.

Of different acyl sugars tested, the octanoyl derivatives are the best substrates but for technical consideration the pentanoyl derivatives are the best to work with.[6] The sugar derivatives with 6-OH functionality prepared in this study are useful synthons in carbohydrate chemistry. The glucose derivatives, for example, can be converted chemically to other useful compounds such as methyl 6-deoxy-6-fluoro-α-D-glucopyranoside (**3**)[7] and 6-*O*-methyl-D-glucose (**4**)[8] and the disaccharide methyl 6-*O*-β-D-glucopyranosyl-α-D-glucopyranoside (**6**).[9] We compare this enzymatic procedure with the existing methods[2,3] and conclude that the lipase-catalyzed reactions offer a better process for the synthesis of 6-substituted or 6-modified hexopyranoses. In addition to the α-D-glucosides, the β-derivatives and the other sugars including D-galactose and D-mannose derivatives containing the same protecting groups are good substrates for the enzyme and deacylated selectively at the primary hydroxyl positions.[6,10]

The regioselectivity observed in the hydrolytic reactions indicates that the reverse reactions, i.e., esterification of free sugars, may also be regioselective. An attempted esterification of methyl glucoside with pentanoic acid in hexane using the *Candida* lipase, however, showed only little reaction (2-3%), probably due to the poor solubility of substrate in the organic solvent. Acylation of free sugars via transesterification using the enzyme also resulted in a poor yield, and the products were not isolated. The transesterification, however, did work when pancreatic lipase was used in the presence of isopropenyl acetate as acyl donor. The detailed procedures will be published separately.

In a representative procedure for the preparation of **2b**, compound **1b** (0.48 g, 1 mmol) was dissolved in acetone (1 mL) and added to 10 mL of phosphate buffer (0.1 M, pH 7) containing $CaCl_2$ (3 mM) and NaCl (0.2 M). Lipase (10 mg from Sigma) was added and the reaction mixture was stirred at room temperature and titrated automatically with NaOH (0.02 M) to keep the mixture at pH 7. After 3 days the suspension was extracted with $CHCl_3$ (3 × 40 mL) and the organic layer dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (ether/hexane = 1/1, v/v) to give 0.41 g of **2b** as a syrup; yield 90%; $[\alpha]^{22}_D$ +98.2° (*c* 0.55, $CHCl_3$). Analysis of the product with NMR indicates that the 6-position is specifically deacylated.[9] By increasing each component proportionally, a 50-mmol-scale preparation has been carried out and the results are essentially the same as those in small-scale preparations. The free OH group of **2b** was replaced with F by reaction with (diethylamino)sulfur trifluoride (DAST)[11] to give the F-derivative which upon deacylation with CH_3ONa (catalytic)/CH_3OH[12] gave **3** in 56% yield based on **2b**: mp 102-104 °C, $[\alpha]^{22}_D$ +146° (*c* 1.0, H_2O) [lit.[11] mp 102-104 °C, $[\alpha]^{25}_D$ +148.6° (*c* 1, H_2O)]. Treatment of **2b** with CH_2N_2 followed by deacylation and acid hydrolysis gave **4** in 60% overall yield: mp 147-149 °C (EtOH/EtOAc), $[\alpha]^{25}_D$ +56° (*c* 1, H_2O). The NMR data are consistent with those reported.[8]

Acknowledgment. Support of this research by the National Science Foundation (CHE 8318217) and the Searle Scholars Program is gratefully acknowledged.

Supplementary Material Available: Experimental details for the preparation of compounds **1-4**, galactose and mannose derivatives, and physical constants (^1H and ^{13}C NMR data, melting points, and specific rotations) (6 pages). Ordering information is given on any current masthead page.

(6) We have tested acetyl, pentanoyl, and octanoyl derivatives of D-glucose and pentanoyl derivatives of D-mannose and D-galactose. The octanoyl derivatives cause emulsion when extracted with organic solvents. The acetyl derivatives are not substrates for the enzyme. The pentanoyl glucopyranoside derivative is hydrolyzed by the enzyme with a specific activity of 30 units/g, compared to 250 units/g with the octanoyl derivatives. The α-form is hydrolyzed 5 times as fast as the β form (1 unit = 1 μmol of substrate hydrolyzed per min. The enzyme cost is $50/100 g).

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Reactive Chromium Methylidene Cations: Intramolecular Migration of Methylene from Chromium into a C-H Bond of the Cyclopentadienyl Ligand

John L. Hubbard* and William K. McVicar

Department of Chemistry, University of Vermont
Burlington, Vermont 05405

Received May 27, 1986

While considerable attention has been directed to the study of cationic alkyidene complexes $(\eta\text{-}C_5R_5)MLL'\text{-}CH_2^+$ (M = Fe, Ru; L, L' = CO, PR_3; M = Re, L = NO, R' = PR_3),[1] there has been no report of isoelectronic $(\eta\text{-}C_5R_5)M(NO)_2\text{-}CH_2^+$ analogues (M = Cr, Mo, W). We report here a facile, high-yield synthesis of the $CpCr(NO)_2\text{-}CH_2X$ complexes (Cp = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4CH_3$, $\eta\text{-}C_5(CH_3)_5$; X = Cl, Br) which serve as precursors for generating the $(\eta\text{-}C_5R_5)Cr(NO)_2\text{-}CH_2^+$ species upon halide abstraction.[2] Remarkably, the methylidene cation complexes produced in such a manner from $(\eta\text{-}C_5H_5)Cr(NO)_2\text{-}CH_2X$ and $(\eta\text{-}C_5H_4\text{-}CH_3)\text{-}Cr(NO)_2\text{-}CH_2X$ directly undergo an unprecedented rearrange-

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