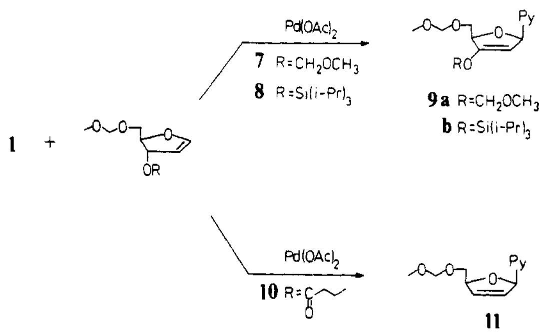
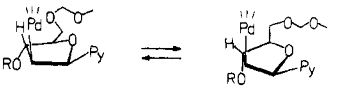
However, if the 3-hydroxyl substituent of this glycal was converted to an ester[21] (**10**), the directing effect on adduct formation[1] was retained while the improved leaving group changed the relative energetics for adduct decomposition modes. The observed product, formed by anti loss of palladium carboxylate, was (2′*R*)-*cis*-5-[2′,5′-dihydro-5′-[(methoxymethoxy)methyl]-2′-furanyl]-1,3-dimethyl-2,4-(1*H*,3*H*)pyrimidinedione[17] (**11**) which is a direct precursor to various important ribofuranosyl C-nucleosides.[22,23]



In the five-membered ring series, unlike the six, it is typical that multiple, essentially isoenergetic conformations coexist in solution.[24] The nature, number, and position of substituents on the furanosyl ring affect conformational preferences significantly,[25] making difficult the prediction of favored conformation(s) for specific molecules. In conformation B, which has the large groups at $C_{1'}$ and $C_{4'}$ in favorable pseudoequatorial positions, palladium and β-hydrogen are essentially syn-periplanar[26] as required for syn β-hydride elimination (which is facile in furanoid systems).[1,5] However, the favorable leaving ability of carboxylate diverts the reaction to anti palladium carboxylate elimination, presumably following a suitable conformational change to B′.



B **B′**

The combination of regio- and stereocontrol of adduct formation previously achieved and stereoelectronic control of adduct decomposition provides an effective and versatile synthetic approach to C-nucleosides. Continued experimental and theoretical[27] study of mechanistic details of organometallic reactions foreshadows the development of synthetic procedures of increasingly impressive specificity.

Acknowledgment. We thank the American Cancer Society for financial support. We thank H. Henrik Johnsson for preparation of starting materials for pyranoid glycals.

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Additions and Corrections

Robert W. Armbruster, Michael M. Morgan, James L. Schmidt, Chun Man Lau, Rose M. Riley, Daniel L. Zabrowski, and Harold A. Dieck*: Palladium-Catalyzed Additions of Amines to Conjugated Dienes: Alteration of Behavior of (Triphenylphosphine)palladium Catalysts with Amine Hydroiodide Salts. **1986**, *5*, 234–237.

On page 236, left column, line 51, the word "not" should be deleted. Thus the sentence beginning on line 49 should read: "After 9 h, greater than 85% conversion (GLC) to the 1,4-addition product *N*-(1-buten-1-yl)-*p*-toluidine had occurred."

T. K. Dutta, J. C. Vites, and T. P. Fehlner*: On the Mechanism of the Hydrogenation/Dehydrogenation of a C_2 Fragment on a Triiron Site. **1986**, *5*, 385–386.

In the caption to Figure 1 the calculated mass for $HD_2Fe_3(CO)_9CCH_3$ should read 451.8186.