Lineweaver-Burk analysis of initial velocities suggest that the inhibition by **4** is competitive with respect to either substrate with K_i values of 134 μM and 220 μM for ApA and ApU, respectively (Table I).[12] The inclusion of uridine (4 mM) in the assay for ApU hydrolysis resulted in no detectable loss of activity, indicating that the observed inhibition is not due to product inhibition. A similar experiment with adenosine (4 mM) for ApA hydrolysis resulted in an inhibition of activity similar to that for the case of addition of 60 μM **4**. In a separate experiment, ribonuclease U2 was incubated with a radiolabeled RNA substrate (5'-AAGUAAGAGACAAGAUACAU-3'), and the products were separated on a denaturing polyacrylamide gel and visualized by autoradiography. Inclusion of adenosine to 2 mM or free technetium-99 (54 mM) in the limit digests resulted in no observable loss of activity. Addition of 600 μM **4** to the limit digests, however, resulted in a 95% loss of ribonuclease activity (data not shown). These findings strongly suggest that inhibition is caused by the complex and is not due to inhibition by either free adenosine or adventitious binding of technetium-99 to the enzyme.

Lindquist et al.[2a] have calculated the K_i for cyclic UMP hydrolysis by RNase A by uridine-vanadate complexes to be 8-12 μM. The strength of binding is attributed to the resemblance of the complexes to the transition state for the hydrolysis reaction. A solved X-ray crystal structure of a ribonuclease-uridine-vanadate complex indicates that the uridine-vanadate ester assumes a distorted trigonal-bipyramidal geometry in the active site of RNase A with an angle of 162° between the apical substituents.[4] Thus, the uridine-vanadate ester most likely resembles a complex formed along the reaction path for the hydrolysis reaction. While the parent technetium complexes are known to exist as square-pyramidal species, our constrained technetium-ribonucleoside complex may assume a geometry intermediate between a square-pyramidal and a trigonal-bipyramidal structure. The K_i values we have determined are only 13-28-fold weaker than the K_i calculated for the uridine-vanadate complex, which corresponds in a loss of binding energy of 1.6-2.1 kcal/mol. This suggests that the technetium complex may also resemble a complex formed along the reaction path of phosphodiester hydrolysis, albeit further away from the idealized transition state.[13] A crystallographic analysis of **4** should shed light on this hypothesis.[14]

We have synthesized a technetium-based hapten that appears to be a reasonable approximation of the putative transition state as judged by its potent, competitive inhibition of ribonuclease U2 activity. Our experimentally determined K_i values are only an order of magnitude less than the calculated K_i for the uridine-vanadate complexes, which are generally regarded as excellent mimics of the transition state for phosphodiester hydrolysis. This, coupled with the fact that the technetium-complex is stable in aqueous solution, makes them ideal candidates for use in immunization protocols for the purpose of generating catalytic antibodies capable of phosphodiester hydrolysis. These complexes, and others like them, would have potential as general inhibitors of ribonucleases in preparative RNA isolation or as inhibitors of other enzymes that catalyze phosphoryl-transfer reactions such as 3',5'-cAMP phosphodiesterase. We are currently exploring such opportunities.

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(11) The assay mixture contained 10 units of sequencing-grade ribonuclease U2 (Pharmacia-LKB), 16.5 mM sodium citrate (pH 3.5), 0.85 mM EDTA, 3.5 M urea, and the desired concentration of substrate and inhibitor in a final volume of 50 μL. Assays were performed at 52 °C ± 1 °C; 5-μL aliquots were removed and products separated on an Alltech Adsorbosphere HS C-18 reverse-phase column using a mixed isocratic-gradient elution system. The mobile phase contained 4% acetonitrile/96% 50 mM NH_4OAc, pH 4.5, at a flow rate of 1 mL/min with a gradient to 50% acetonitrile from 10 to 20 min. Products were monitored at 260 nm and quantitated by comparison to standard curves derived by injection of authentic compounds. Initial velocities for cAMP, adenosine (or uridine), and ApA (or ApU) were used for the kinetic plots. All velocities were observed to be linear within this range; no product inhibition was observed under the assay conditions. The range of substrate concentrations used to determine K_m and V_{max} values was 63.8 μM to 3.88 mM for ApA (Sigma) and 382 μM to 18.3 mM for ApU (Sigma). K_i values were determined from Dixon plots using inhibitor concentrations ranging from 40 to 300 μM. ApA, adenylyl(3'-5')adenosine; ApU, adenylyl(3'-5')uridine.

(12) Since these values represent a mixture of the diastereomers of **4**, the K_i values for the isomer recognized by the enzyme could be at least one-half of the reported values.

(13) One can also argue that the presence of the methylene moieties in **4** contribute to the hydrophobicity of the molecule and would disfavor binding of the complex in the hydrophilic pocket of the active site. If this is indeed the case, then the geometry of the complex would in fact more closely approximate a trigonal-bipyramidal species.

(14) It is interesting to note that the K_i value for free vanadium(IV), 60-65 μM, is not significantly different from the K_i value for the uridine-vanadate complex (8-12 μM). In our compound, both the ribonucleoside and the technetium are necessary for inhibition.

Reactions of Bis(indenyl)dimethyltitanium with Phenylsilane: Synthesis of a Novel μ-Indenyl μ-Dihydrido Mixed-Valence Ti(III)/Ti(II) Compound

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Bis(cyclopentadienyl) complexes of titanium and zirconium have a remarkable ability to catalyze the dehydrocoupling of organosilanes.[1-4] Dimethyltitanocene (DMT) has been studied in some detail, and a number of novel silyltitanium(III) complexes have been prepared, either by direct reaction of silanes with DMT[1c] or by addition of ligands to such reactions.[5]

The chemistry of indenyl complexes is of interest because of their potential application as stereoselective catalysts.[6-8] It was found that bis(indenyl)dimethyltitanium complexes function relatively poorly as catalysts for dehydrocoupling, compared to their zirconium analogues[8] or to DMT. Initially, the reaction of bis(indenyl)dimethyltitanium (**1**) with phenylsilane is very similar to that observed with DMT.[1c] Following mixing of a catalytic amount of **1** with phenylsilane, there is an induction period of a few minutes, during which there is no observable reaction. The end of the induction period is signaled by a sudden change in color from orange to blue/green, accompanied by a vigorous gas evolution and the complete disappearance of NMR signals due to **1**. In contrast to the case of DMT, no new NMR signals due to bimetallic Ti(III) complexes are observed. In addition, the initial activity of the catalyst rapidly declines to a very low level. During the period of declining activity, dark colored crystalline material deposits on the wall of the reaction vessel and the initially broad NMR signals of organic and organosilicon products sharpen. One

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(1) (a) Aitken, C. A.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (b) Harrod, J. F. *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 7. (c) Aitken, C. A.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(2) (a) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (b) Woo, H.-S.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H.-S.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757.

(3) (a) Corey, J. Y.; Chang, L. S.; Corey, E. G. *Organometallics* **1987**, *6*, 1596. (b) Chang, L. S.; Corey, J. Y. *Organometallics* **1989**, *8*, 1885. (c) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C. Organosilicon Symposium, 23rd, Midland, MI, April 20-21, 1990; Abstract D1.

(4) Campbell, W. H.; Hilty, T. K.; Yurga, L. *Organometallics* **1989**, *8*, 2615.

(5) Samuel, E.; Mu, Y.; Harrod, J. F.; Dromzee, Y.; Jeannin, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3435.

(6) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

(7) Kaminsky, W.; Kulper, K.; Brintzinger, H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(8) Gauvin, F.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1638.

0002-7863/92/1514-1489$03.00/0

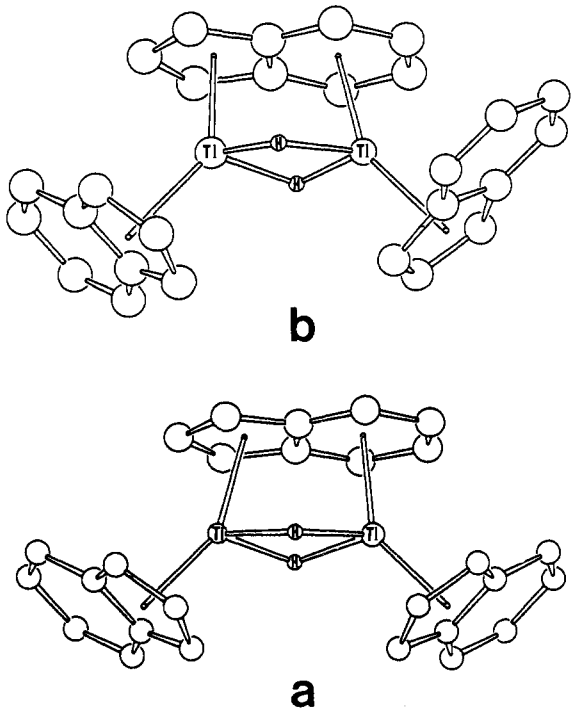

Figure 1. Ball-and-stick models of the molecules **2a** and **2b**. The C and Ti positions are established by X-ray crystallography; the positions of the bridging hydrides are conjectural.

unusual product which is evident at the end of the reaction is indane.

A reaction of **1** with 2.5 equiv of phenylsilane on a preparative scale yielded 0.5 equiv of indane, estimated by its ^{1}H NMR spectrum, and about a 30% isolated yield of well-formed crystals of a new compound, **2**.[9] The presence of methane, phenylmethylsilane, and small amounts of oligophenylsilanes was also evident from the NMR spectra. The structure of **2**, shown in Figure 1, is based on X-ray crystallography and EPR and IR spectra.[10] The crystal contains two equally populated sublattices of the molecules with syn (**2a**) and anti (**2b**) disposition of the terminal indenyl ligands, as illustrated in Figure 1. Both of the isomers have C_s symmetry, and the two μ-hydrogens are diastereotopic in both. Although the crystallographic study gave the overall structure, it was not possible to accurately determine molecular parameters related to the bridging indenyl group, nor to locate the bridging hydride ligands, because of a 50:50 disorder involving random packing of the two enantiomers of **2a** and **2b**. In both cases the enantiomers differ by a rotation of the bridging indenyl ligand about a pseudo-2-fold axis passing through the center of, and perpendicular to, the Ti_2H_2 plane.

The presence of the bridging hydrogens was confirmed by comparison of the EPR and IR spectra of the hydrido and deuterido analogues.[9] The IR band at 1300 cm^{-1}, shifted to 945 cm^{-1} by deuterium substitution, is in the region previously observed for compounds containing the Ti–H–Ti group.[11] The EPR spectrum consists of a well-resolved 1:2:1 triplet resulting from coupling of the unpaired electron to two hydrogens, with further unresolved splitting, attributable to the inequivalence of these two hydrogens. These splittings collapse in the deuterio compound due to the reduction of the hyperfine coupling, as expected. Satellites due to hyperfine interaction with Ti nuclei [$I = {}^7/_2$, ^{49}Ti (5.5%); $I = {}^5/_2$, ^{47}Ti (7.75%)] were observed. The isotropic values a_H and a_{Ti} are approximately half those previously reported for other paramagnetic, monomeric titanium compounds,[12-14] indicating that the unpaired electron is exchanging sites between a low-spin Ti(II) center and Ti(III).

To our knowledge, the indenyl bridging mode found in **2** has only been observed previously in bis(indenyl)divanadium(I).[15] There are two reported examples of bimetallic complexes in which two transition metals occupy antifacial sites on a bridging indenyl ligand (Rh/Re and Rh/Cr).[16,17] The Ti–Ti distance (average value for **2a** and **2b** = 2.745 Å) is the shortest so far observed[18] and is significantly shorter than that of metallic α-Ti (2.896 Å).[19] This short distance is perhaps indicative of a Ti–Ti bond, as well as of a fairly strong Ti(II)–arene bond forcing a shorter metal–metal separation. The only other example of a structurally characterized Ti(II)/Ti(III) dimer is $(C_5H_5)Ti(C_4H_8O)(\mu\text{-}C_5H_4)Ti(C_5H_5)_2$.[20] The two fragments of this molecule are attached through a μ-η^1,η^5-C_5H_4 ligand, and the large Ti–Ti separation (3.336 Å) does not suggest any significant interaction between the metal centers. Although the paramagnetism of the molecule was demonstrated by the temperature-dependent chemical shift of the ^{1}H NMR resonance, no EPR measurements have been reported.

The provenance of **2** is clearly relevant to the rapid loss of activity when **1** is used to catalyze the dehydrocoupling of phenylsilane. The key appears to be the susceptibility of the indenyl ligand to hydrogenation by the catalytic intermediates. The ability of reduced titanocene derivatives to catalyze olefin hydrogenation is well documented.[21] We have also reported the facile transfer of hydrogen to olefins under DMT-catalyzed dehydrocoupling conditions.[22] In the present work we have also observed the cohydrogenation of styrene in the presence of phenylsilane and a catalytic amount of **1**. This points to the conclusion that the loss of indene from the metal may occur with the simultaneous generation of a Ti(II) species, which can no longer sustain two η^5 ligands. One possible mechanism for such a reaction would be the reductive elimination of indene from a mixed-valence Ti(III)/Ti(IV) trihydride, **3**, as shown in the equation, followed by a hydrogenation of indene to indane (Ind = η^5-indenyl):

$$\underset{\mathbf{3}}{(\mathrm{Ind})_2\mathrm{TiH}(\mu\text{-H})\mathrm{HTi}(\mathrm{Ind})_2} \rightarrow (\mathrm{Ind})\mathrm{Ti}(\mu\text{-Ind})(\mu\text{-H})_2\mathrm{Ti}(\mathrm{Ind}) + \mathrm{IndH}$$

A mixed-valence hydride analogous to **3** is the ubiquitous end product of the reactions of silanes with DMT.[1c] However, we have never seen any indication of CpH loss in the latter case, nor any

(9) Dry, oxygen-free toluene (20 mL) containing **1** (500 mg; 1.6 mmol) was cooled to 0 °C. Phenylsilane, or deuteriosilane (0.410 mL; 3.29 mmol), was added, and the solution, after thorough mixing, was left to stand unperturbed for 15 h. The supernatant solution was decanted, and the crystalline residue was washed twice with cold toluene and dried under vacuum. Yield: 110 mg (30%). Mp 245–250 °C dec. Anal. Found: C, 69.78; H, 5.01; Ti, 24.26; Si, 0.30. Calcd for $C_{27}H_{23}Ti_2$: C, 73.15; H, 5.23; Ti, 21.61. IR: 1300 cm^{-1} (TiH_2Ti); 945 cm^{-1} (TiD_2Ti). EPR in toluene: (TiH_2Ti) triplet, g = 1.9885; $a_{iso,H}$ = 0.48 mT; $a_{iso,Ti}$ = 0.4 mT; (TiD_2Ti) singlet (ΔB = 0.32 mT), g_{iso} = 1.9887; g_x = 2.0020; g_y = 1.9895; g_z = 1.9762 at 130 K. Due to the rather broad features of the signals, only satellites due to the (^{48}Ti–^{48}Ti), (^{48}Ti–^{47}Ti), and (^{48}Ti–^{49}Ti) pairs were observed; the others were not detected due to their much lower intensity.

(10) An X-ray structure report for **2** has been deposited as supplementary material.

(11) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301. Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182.

(12) Pattiasina, J. W.; Bolhuis, F. v.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*(4), 330.

(13) Krusic, P.; Tebbe, F. N. *Inorg. Chem.* **1982**, *21*, 2900.

(14) Samuel, E.; Harrod, J. F. *J. Am. Chem. Soc.* **1984**, *106*, 1859.

(15) (a) Jonas, K.; Rüsseler, W.; Angermund, K.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*(10), 927. (b) Poumbga, C.; Daniel, C.; Bēnard, M. *J. Am. Chem. Soc.* **1991**, *113*, 1090.

(16) Green, M. L. H.; Lowe, N. D.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1547.

(17) Ceccon, A.; Gambaro, A.; Santi, S.; Valle, G.; Venzo, A. *J. Chem. Soc., Chem. Commun.* **1989**, 51.

(18) To our knowledge, the hitherto shortest reported Ti–Ti bond in an organometallic complex (2.910 Å) is that reported in the following: Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 7870. These authors conclude that the short bond is indicative of metal–metal bonding.

(19) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072.

(20) *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emēleus, H. J., Nyholm, R., Trottman Dickenson, A. F., Eds.; Pergamon Press: New York, 1973; Vol. 3, p 358.

(21) (a) Pez, G. P.; Kwan, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 8079. (b) Samuel, E. *J. Organomet. Chem.* **1980**, *198*, C65.

(22) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381.

evidence for ligand hydrogenation. On the other hand, styrene is extremely rapidly hydrogenated in the DMT/$PhSiH_3$ system.[22]

We are pursuing the synthesis of analogues of **2** with alkyl-substituted indenyl ligands, in an attempt to circumvent the disorder problem and get more precise structural parameters for this type of molecule. We are also undertaking a more general development of the chemistry of Cp(arene)TiX complexes.

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Registry No. 1, 49596-02-3; **2a**, 136910-76-4; **2a**-d_2, 136910-77-5; **2b**, 137036-29-4; **2b**-d_2, 137036-30-7; indane, 496-11-7; styrene, 100-42-5; phenylsilane, 694-53-1; deuteriosilane, 13587-51-4.

Supplementary Material Available: A complete crystal structure report for **2** including experimental details, positional and thermal parameters, bond distances and angles, least-squares planes, and atomic coordinates (27 pages); listing of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Palladium(0) to the Anomeric Center of Carbohydrate Electrophiles

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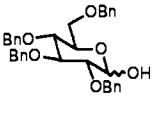
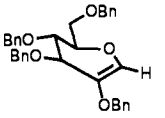
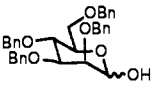
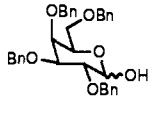
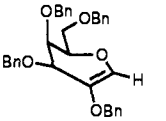
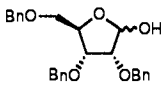
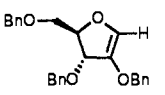
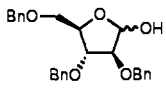
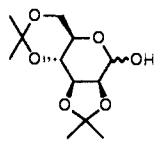
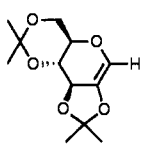
Palladium-mediated processes have been applied to the synthesis of biologically active carbohydrates in a variety of ways.[1-3] Daves[1] and others[2] have explored the use of Heck-type reactions using 1,2-anhydro sugars (glycals) as the olefin moiety. Glycals have also been metalated at the anomeric center and then coupled with aryl electrophiles using palladium(0) catalysts under classic cross-coupling conditions.[4,5] Earlier studies by this group[6] and others[7] led to the hypothesis that unactivated α-alkoxy electrophiles should be sufficiently reactive to allow oxidative addition to occur. Herein we wish to report the first use of a palladium-catalyzed process involving oxidative addition into the anomeric center of a carbohydrate derivative.

Table I. Two-Step Oxyglycal Synthesis

entry	carbohydrate	glycal	^{1}H NMR δ H-1	isolated yield (%)
1	 **1**	 **2**	6.31	87
2	 **3**	**2**		53
3	 **4**	 **5**	6.17	21[a]
4	 **6**	 **7**	6.17	60
5	 **8**	**7**		58
6	 **9**	 **10**	6.22	15

[a] dppfPd(0) (10 mol % dppfPdCl$_2$, 12 mol % *n*-BuLi) was used in place of $Pd(PPh_3)_4$.

Sulfonate esters have been employed as electrophiles in Heck olefinations and cross-coupling reactions.[6d,8] Treatment of tetra-*O*-benzylglucopyranose with freshly prepared[9] methanesulfonic anhydride in the presence of *s*-collidine yielded the corresponding mesylate.[10] Subsequent treatment with 0.9–5 mol % $Pd(PPh_3)_4$ at 50 °C resulted in oxidative addition followed by β-hydride elimination to afford tetra-*O*-benzylglucal **2** in high yield (Table I).[11] Oxyglycal **2** is readily identified by the vinyl hydrogen resonance at 6.31 ppm in the ^{1}H NMR spectrum.[12,13] In the absence of palladium, no glycal formation was observed.

To probe the generality of this reaction, a variety of protected sugars were subjected to the reaction conditions. Tetrabenzylmannose **3** underwent the two-step dehydration to give oxyglycal

(1) (a) Farr, R. N.; Outten, R. A.; Cheng, J. C.-Y.; Daves, G. D., Jr. *Organometallics* **1990**, *9*, 3151–3156. (b) Daves, G. D., Jr. *Acc. Chem. Res.* **1990**, *23*, 201–206. (c) Outten, R. A.; Daves, G. D., Jr. *J. Org. Chem.* **1989**, *54*, 29–35.

(2) (a) Tius, M. A.; Gu, X.-q.; Gomez-Galeno, J. *J. Am. Chem. Soc.* **1990**, *112*, 8188–8189. (b) Tius, M. A.; Gomez-Galeno, J.; Gu, X.-q.; Zaidi, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 5775–5783.

(3) (a) Brakta, M.; Lhoste, P.; Sinou, D. *J. Org. Chem.* **1989**, *54*, 1890–1896. (b) Czernecki, S.; Bellosta-Dechavanne, V. *Can. J. Chem.* **1985**, *63*, 491–494. (c) Yougai, S.; Miwa, T. *J. Chem. Soc., Chem. Commun.* **1983**, 68–69.

(4) (a) Friesen, R. W.; Sturnio, C. F.; Daljeet, A. K.; Kolaczewska, A. *J. Org. Chem.* **1991**, *56*, 1944–1947. (b) Friesen, R. W.; Sturino, C. F. *J. Org. Chem.* **1990**, *55*, 5808–5810.

(5) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986. (c) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis: Practical Applications of Transition Metals*; Plenum Press: New York, 1984. (d) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(6) (a) Yuan, K.; Scott, W. J. *Tetrahedron Lett.* **1991**, *32*, 189–192. (b) Yuan, K.; Scott, W. J. *Tetrahedron Lett.* **1989**, *30*, 4779–4782. (c) Scott, W. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1755–1756. (d) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47–54.

(7) For oxidative addition into (a) activated thioacetals, see (1) Yang, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 2261–2262; (2) Ni, Z.-J.; Yang, P.-F.; Ng, D. K. P.; Tzeng, Y.-L.; Luh, T.-Y. *J. Am. Chem. Soc.* **1990**, *112*, 9356–9364; (3) Shi, X.; Luh, T.-Y. *Organometallics* **1990**, *9*, 3019–3020; (b) acetals, see (1) Mukaiyama, T.; Soga, T.; Takenoshita, H. *Chem. Lett.* **1989**, 997–1000; (2) Mukaiyama, T.; Takenoshita, H.; Yamada, M.; Soga, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3122–3131.

(8) (a) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271–2274. (b) Scott, W. J.; Peña, M. R.; Swärd, K.; Stoessel, S. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302–2308.

(9) Owen, L. N., Whitelaw, S. P. *J. Chem. Soc.* **1953**, 3723.

(10) Leroux, J.; Perlin, A. S. *Carbohydr. Res.* **1967**, *67*, 163–178.

(11) General procedure: A solution of tetra-*O*-benzylglucose (1.08 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was treated with Ms_2O (0.70 g, 4.0 mmol) and collidine (0.80 mL, 6.0 mmol) and allowed to stir at room temperature for 1 h. To the clear, dark brown solution was added $Pd(PPh_3)_4$ (23 mg, 1 mol %), and the mixture was heated under argon at 50 °C overnight. The solution was then diluted with CH_2Cl_2 (20 mL), washed with 10% HCl (25 mL) and a saturated NaCl solution (25 mL), dried over $MgSO_4$, filtered through a plug of silica gel (1 × 2.5 cm), and purified by radial chromatography (SiO_2, 10% EtOAc in hexanes) to give 0.91 g of the oxyglucal (87%) as a white solid. (NOTE: Yields drop precipitously if the Ms_2O is even *slightly* decomposed; best results were obtained if the Ms_2O had been prepared[9] within 1 week of use.)

(12) Nicotra, F.; Ronchetti, F.; Russo, G. *J. Org. Chem.* **1982**, *47*, 4459–4462.

(13) For previous syntheses of oxyglycals, see: (a) Maurer, K.; Mahn, H. *Chem. Ber.* **1927**, *60*, 1316–1320. (b) Rao, D. R.; Lerner, L. M. *Carbohydr. Res.* **1972**, *22*, 345–350. (c) Ekberg, G.; Garegg, P. J.; Josephson, S. *Carbohydr. Res.* **1978**, *65*, 301–306.

0002-7863/92/1514-1491$03.00/0