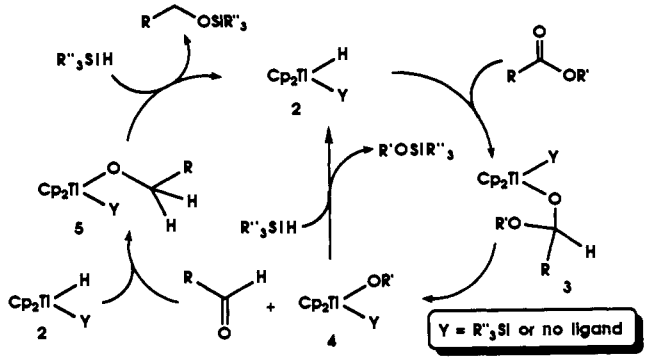
Scheme II



A surprising degree of selectivity is seen with this catalyst system. For example, ethyl 6-bromohexanoate is cleanly converted to 6-bromo-1-hexanol at −20 °C. Likewise, α,β-unsaturated esters and esters containing phenolic, amino, or cyclopropyl groups, as well as di- and trisubstituted olefins, are efficiently transformed into the corresponding primary alcohols.[6b] For substrates containing a terminal olefin or an epoxide, use of the more hindered titanocene dichloride species ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium dichloride,[7] (EBTHI)$TiCl_2$, is required for a successful transformation. Selective hydrosilylation of an ester in the presence of a ketone was not possible. However, *a methyl ester can be selectively reduced in the presence of a tert-butyl ester.*

The system is relatively insensitive to the presence of adventitious moisture or small amounts of oxygen. The reaction proceeds cleanly, even when the substrate is premixed with 10 mol % of H_2O (excess silane is used to scavenge water, which is silylated under the reaction conditions) or if the reaction is carried out in a solvent that has not been rigorously deoxygenated. Moreover, while the examples shown in Table I use 5 mol % of inexpensive Cp_2TiCl_2, the amount of titanium reagent can be reduced to as low as 0.5 mol % with no noticeable decrease in yield.

While we have not yet undertaken detailed mechanistic studies, a plausible pathway for the reaction is shown in Scheme II. Our hypothesis that the active catalyst is probably in the +3 oxidation state is based on the known propensity of Ti(IV) to be reduced,[8] on the observation of partial deoxygenation of the terminal epoxide substrate (entry 6) to the corresponding olefin,[9] and on the observed disappearance of ^1H NMR signals of the titanium species. The initial interaction of the catalyst **2** with the ester substrate leads to intermediate **3**, which expels aldehyde with concomitant production of **4**. The aldehyde reacts with a second equivalent of **2** to produce **5**. Finally, the silyl ethers of the product alcohols are liberated via a σ-bond metathesis process[10] to regenerate the catalyst. Further work is obviously necessary to verify this hypothesis.

In summary, we have developed a new catalytic hydrosilylation system for the conversion of esters to primary alcohols which utilizes inexpensive silanes as the stoichiometric reductant.[11] This procedure is efficient and selective and may represent a safer and more convenient alternative to the use of reducing agents such as $LiAlH_4$ and DIBAL on a large scale.[12] Further work is in progress to utilize this and related systems for other functional group interconversions and to map out the mechanistic course of these reaction processes.

Acknowledgment. This work was supported by the National Institutes of Health (GM 34917), the National Science Foundation (CHE-9000482), and W. R. Grace, to whom we are grateful. S.L.B. is a Fellow of the Alfred P. Sloan Foundation and a Camille & Henry Dreyfus Teacher-Scholar. We are indebted to Professors K. Barry Sharpless and Julius Rebek, Dr. Alberto Gutiêrrez, and Robert Grossman for their insightful comments.

Supplementary Material Available: Detailed experimental procedures for the preparation of and spectroscopic characterization for the products given in Table I (7 pages). Ordering information is given on any current masthead page.

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(12) CAUTION! Methoxysilanes should not be used in this reaction, as they are volatile and are known to cause blindness. Additionally, while we have performed this reaction ca. 200 times without incident using the combination *n*-BuLi/Cp_2TiCl_2 in a ratio of ~2, we note that in two reactions in which *n*-BuLi/Cp_2TiCl_2 = 4, opening of the reaction vessel to the air caused the appearance of a flame, presumably due to the known disproportionation of $(EtO)_3SiH$ to SiH_4 (see: Xin, S.; Aikten, C.; Harrod, J. F.; Mu, Y.; Samuel, E. *Can. J. Chem.* **1990**, *68*, 471). A control experiment in which *n*-BuLi was allowed to react with $(EtO)_3SiH$ in the absence of Cp_2TiCl_2 gave similar results. We have found that the liquid polymer, polymethylhydrosiloxane (a commodity material produced by Dow-Corning and available from Huls America), is a suitable substitute for $(EtO)_3SiH$; its use eliminates the chance of generating SiH_4.

Polymer-Supported Solution Synthesis of Oligosaccharides[1]

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The efficient preparation of oligosaccharides, as well as their elaboration into glycopeptides and glycolipids, is of central importance for the application of these compounds in biological sciences and medicine.[2] In an effort to develop a fundamentally new approach to oligosaccharide synthesis, we have been exploring a polymer-supported method combining the anomeric control of solution chemistry with the ease and speed of solid-state-supported workup. The solid-state-based procedure eliminates time-consuming workups and potentially reduces the time required for the synthesis of an oligosaccharide from months to days or weeks.

Despite recent dramatic advancements in the solution methodology of oligosaccharide synthesis,[3,4] yields in the key glycosidic

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linkage formation steps are still in the 80% range. Certain "difficult linkages" are accessible often below 50%.[3,4] This reflects both the low reactivity and the instability of the reactants, in particular of the glycosylating agent. The activated glycosylating agent may decompose to several products, behaving chromatographically similarly to the desired product. The excess glycosylating agent necessary to obtain an acceptable yield of coupled products often leads to reaction mixtures in which the desired compound is a relatively minor component. Thus a major obstruction to greater efficiency of glycosylation is the chromatographic purification. Solid-state methodology should, in principle, remove this obstacle.

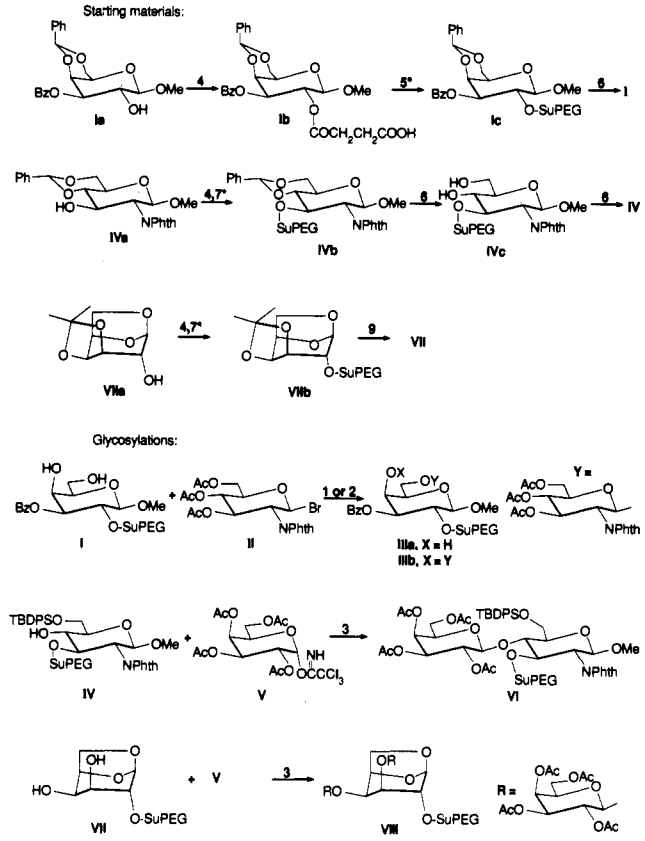
Success in the synthesis of oligonucleotides[5] and oligopeptides,[6] led to consideration of solid-state synthesis of oligosaccharides in the past.[7-9] It was clear, however, that this approach had its limitations,[7-9] and no further attempts to overcome them have appeared in the literature. Among the problems encountered were decreased glycosylation reaction rate compared to solution strategies, incomplete coupling, and lack of complete stereoselectivity. Since two C-1 epimers (anomers) can be formed, stereochemical control is mandatory, and solution methodology has already designed ways to achieve it in a variety of situations.[3,4]

Another strategy probed for the synthesis of oligomers of peptides and nucleotides is polymer-supported liquid synthesis.[10] Applied to oligosaccharide synthesis, this approach requires the polymer–carbohydrate synthon to be soluble under conditions of glycosylation and to be insoluble during the workup of reaction mixtures. The solubility of the reactants allows reaction kinetics and anomericity control similar to those observed in solution chemistry. This approach would be of particular value for syntheses of smaller oligomers in gram and larger quantities.[10a]

We have explored as the supporting polymer poly(ethylene glycol)monomethyl ether [$HOCH_2CH_2(OCH_2CH_2)_nOCH_3$, n = 80–160; PEG, average MW 5000].[11] We have linked it (i) directly to the anomeric carbon as an aglycon[19] or (ii) to different carbohydrate hydroxyl groups through ester linkages of succinic acid [$-COCH_2CH_2COOCH_2CH_2(OCH_2CH_2)_nOCH_3$; PEG–Su; cf. Ib and Ic].[12] When PEG is bound to a carbohydrate hydroxyl, the glycosylation reaction can be driven to virtual completion by repeated additions of the glycosylating agent. Normally, the use of such an excess of any glycosylating agent would create a serious problem for purification; in this procedure the nonpolar fragments resulting from the decomposition of the reactants are washed off the precipitated PEG-bound product. The more polar contaminants are removed by simple crystallization of the PEG-bound product from ethanol. Furthermore, since PEG contains a single OCH_3 group (δ = 3.380 ppm), the reaction course is easily monitored by NMR spectroscopy with the signal of this methyl being used as an internal standard.

We have examined glycosylations of several PEG-Su-bound substrates under metal and acid catalysis (cf. Scheme I).[20] In

Scheme I. Examples of Glycosylations Leading to Di- and Trisaccharides Utilizing Polymer-Supported Solution Methodology[a]



[a] Compound I was prepared through Ia–c; IV, through IVa–c; and VII through VIIa and VIIb. For reaction conditions, see footnote 18. Starting materials were prepared according to the references indicated: Ia,[15] II,[14] IVa,[16] V,[4a], VIIa.[17]

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(18) Reaction conditions (scale 0.1–2 mmol): (1) AgOTf, DBMP, CH_2Cl_2, 4A ms, 91%; (2) Ag_2CO_3, DBMP, CH_2Cl_2, 4A ms, 75%; (3) $BF_3{\cdot}Et_2O$, CH_2Cl_2, 70%; (4) succinic anhydride, DMAP, pyridine, 70%; (5) PEG, DCC, DMAP, CH_3CN, 90%; (6) 60% aqueous AcOH, 100 °C, 85%; (7) PEG, DCC, DMAP, CH_2Cl_2, 93%; (8) TBDPS-Cl, imidazole, CH_2Cl_2, 94%; (9) 60% aqueous AcOH, 60 °C, 91%. *Alternatively, the appropriate hydroxyl can be esterified by PEG–hemisuccinate using DCC activation with DMAP. Abbreviations: Ac, acetyl; AgOTf, CF_3SO_3Ag; Bz, benzoyl; DBMP, 2,6-di-*tert*-butyl-4-methylpyridine; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCC, 1,3-dicyclohexylcarbodiimide; DMAP, 4-(dimethylamino)pyridine; 4A ms, 4A molecular sieves; PEG, $-OCH_2CH_2(OCH_2CH_2)_nOCH_3$, n = 110; Phth, phthalimido; Su, $-COCH_2CH_2CO-$; Su–PEG, $-COCH_2CH_2COOCH_2CH_2(OCH_2CH_2)_nOCH_3$; TBDPS, *tert*-butyldiphenylsilyl.

(19) Unexpected complications caused by the low stability of the PEG–anomeric carbon bond made anchoring PEG to the anomeric carbon unpractical. Douglas, S. P.; Whitfield, D. M.; Krepinsky, J. J. *Tetrahedron Lett.*, submitted for publication.

all cases examined to date, PEG-Su has been linked to the acceptor. Glycosylating agents have been added several times, if required, for completion of the glycosylation (unoptimized yields of isolated products were 85-95%, or greater; small losses occurred during crystallization). The progress of glycosylation was monitored by NMR spectroscopy (cf. above). After the reaction is completed, the PEG-bound product is precipitated from solution with diethyl ether or *tert*-butyl methyl ether, is recrystallized from ethanol, and after drying is ready for the next step of the synthetic sequence. PEG-Su is eventually easily cleaved from the saccharide by DBU-catalyzed methanolysis in dichloromethane or by hydrazinolysis[21] if a phthalimido group is to be removed as in VI. Peracetylated oligosaccharides for final purification[22] are obtained from dried residues after methanolysis by acetylation with acetic anhydride in pyridine. The expected anomer[3,4] was formed in each glycosylation; the other anomer was not detected. The silyl group used for protection of hydroxyl groups was found to be compatible with this design. Regioselectivity of the glycosylation is exemplified by the formation of IIIa and IIIb.

Supplementary Material Available: Experimental details including procedures for the preparation of IIIa,b, IV, and VI and the cleavage of IIIa,b (6 pages). Ordering information is given on any current masthead page.

(20) The structures of all compounds were confirmed by NMR (500 MHz) spectroscopy and FAB mass spectrometry. Presaturation of PEG at δ 3.640 (CH_2O signals) was carried out to ensure no dynamic range overflow. We are indebted to Dr. H. Pang, Carbohydrate Research Centre, for measuring the mass spectra with a ZAB SE mass spectrometer.

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(22) Peracetylated oligosaccharides are usually more suitable for final purification by chromatography than deprotected compounds; after deacetylation pure oligosaccharides are obtained.[21]

Reactivity of a Binuclear Ruthenium(0) Complex with an Electron-Poor Alkyne. An Unusual Double Insertion of Carbon Monoxide

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Many examples of metal-catalyzed double-carbonylation reactions (eq 1) have been reported.[1] Mechanistic studies of the

$$RX + 2CO + NuH \rightarrow RC(O)C(O)Nu + HX \quad (1)$$

$$(NuH = R'NH_2, R'OH, H_2O)$$

most common palladium-catalyzed system have shown that the critical C-C bond forming step occurs via reductive elimination from a bis(acyl) complex.[2-8] Except for alkyls of lutetium[9] and thorium,[10] the alternative C-C coupling pathway involving the consecutive insertion of two carbon monoxides into a metal-carbon bond has not been observed. Only one example of a migratory insertion of CO into a d-block metal-acyl bond has been reported.[11] In this paper we describe a facile, high-yield reaction between a metal carbonyl and an alkyne that results in the net double insertion of CO into a putative metal-alkyne bond.

As shown in Scheme I, the reaction of $Ru_2(dmpm)_2(CO)_5$ (**1**)[12] with dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of three isolable products. In concentrated solutions of toluene (15-20 mmol/L), at room temperature, a red product was formed and crystallized from solution 10-15 min after mixing (isolated yield = 81%). The analytical and mass spectral data established the molecular formula as $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]_2$ (**2**).[13] Spectroscopic data alone did not allow assignment of the structure, which was established via single-crystal X-ray crystallography.[14]

The $Ru_2(dmpm)_2$ framework is nearly planar, exhibiting a twist angle (defined as the angle between planes Ru1-P12-P11-Ru2 and Ru2-P21-P22-Ru1) of 4.16°. This portion of the structure is similar to related bis(diphosphine) diruthenium compounds with the exception of the long Ru1-Ru2 distance of 3.153 (1) Å.[15-20] The surprising feature in the structure of **2** was a five-membered metallocyclic ring that appears to have resulted from the double insertion of two CO ligands into a metal-alkyne bond. This ring was found to be distinctly nonplanar, exhibiting a dihedral angle of 18° between the planes comprising Ru2-C20-C16 and C16-C13-C19-C20. Identification of C19, C20, O5, and O6 as carbons and oxygens was based on their temperature factors, bond distances, and knowledge of the overall formula of **2**. The bond distances within the α-ketoacyl portion of **2** are similar to those in the previously characterized examples of this type of ligand.[6,11,21,22] The second alkyne bridges the two Ru atoms and is bound as a cis-dimetalated alkene. Consistent with the infrared spectral data, the structure contains a semibridging carbonyl ligand. The long Ru-Ru distance suggests that there is no direct metal-metal bond, and we propose that both metals exist in the 2+ oxidation state. This implies that Ru1 would be a 16-electron

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(14) X-ray diffraction data for **2**: FW 898.64; ρ_{calcd} = 1.671 g cm^{-1}; crystal system = orthorhombic; space group = $P2_12_12_1$ (No. 19); T = -101 °C; a = 13.932 (5) Å; b = 14.360 (3) Å; c = 17.854 (3) Å; V = 3572 (3) $Å^3$; Z = 4; μ = 10.62 cm^{-1} (empirical correction applied); radiation = Mo Kα; scan range = $0 < 2\theta < 49.9°$; unique reflections collected = 6299; reflections used ($I > 2.0\sigma(I)$) = 5179; R = 0.050; R_w = 0.055. Thermal ellipsoids in Scheme I were drawn at the 50% probability level. Selected distances (Å): Ru1-C23, 2.115 (9); Ru1-C22, 2.510 (8); Ru2-C22, 1.907 (8); Ru2-C26, 2.138 (8); Ru2-C20, 2.097 (8); Ru2-C16, 2.153 (8); C23-C26, 1.33 (1); C20-C19, 1.57 (1); C20-O6, 1.197 (9); C19-C13, 1.44 (1); C19-O5, 1.21 (1); C13-C16, 1.35 (1).
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