University, Hans Paulsen of the University of Hamburg (Germany), and Klaus Bock of Carlsberg Laboratories, Copenhagen.

The *n*-pentenyl glycoside methodology developed by Fraser-Reid and coworkers enables the direct stereoselective conversion of glycosides to *N*-linked glycopeptides (glycopeptides in which the saccharide is linked to the peptide by an *N*-glycosidic bond). Danishefsky and coworkers developed a chemical route to *N*-glycopeptides from glycals. And Paulsen, Bock, and coworkers developed a solid-phase method to form the peptide backbone of *O*-glycopeptides (glycopeptides in which the sugar is attached via an *O*-glycosidic linkage).

Asked to comment on the work of Wong and coworkers, Kunz critiques the premise that forming peptide bonds in glycopeptides was a problem that needed to be solved, saying that glycopeptides can simply be made by synthesizing a peptide with an attached single sugar by chemical means, and then extending the saccharide side chain from the single-sugar attachment point using glycosyltransferases. This strategy avoids a lot of protecting group chemistry, he says. He calls Wong's technique "a good idea intellectually," but adds that "it is not the only method we will follow in the future."

Wong agrees with Kunz that small-scale glycopeptide synthesis "is not at all a problem today." But he points out that the strength of the new technique is that it can be used for large-scale synthesis. This is because the peptide-bond-forming reactions can be carried out in aqueous solution without the need for protecting group chemistry, and because followup glycosyltransferase reactions can be done under compatible conditions—that is, in aqueous solution with no protecting groups.

Danishefsky tells C&EN that Wong's paper is "symptomatic of what is the right direction for the field, which is creative confluence of chemistry and enzymology. People should be very skeptical about any arguments to the effect that one or the other method is better," referring to the tendency of some to favor conventional chemical synthesis as the true religion, or enzymology as the wave of the future that will sweep away all else before it. "Results come from a willingness to borrow from all sorts of disciplines. What Wong and coworkers have shown is the power of the enzymological method in cahoots with chemistry."

Thanks to the new findings, Danishefsky adds, the use of modified enzymes to form peptide bonds is a strategy that will now have to be considered by researchers contemplating the synthesis of glycopeptide structures.

Stu Borman

New routes to carbon-metal complexes found

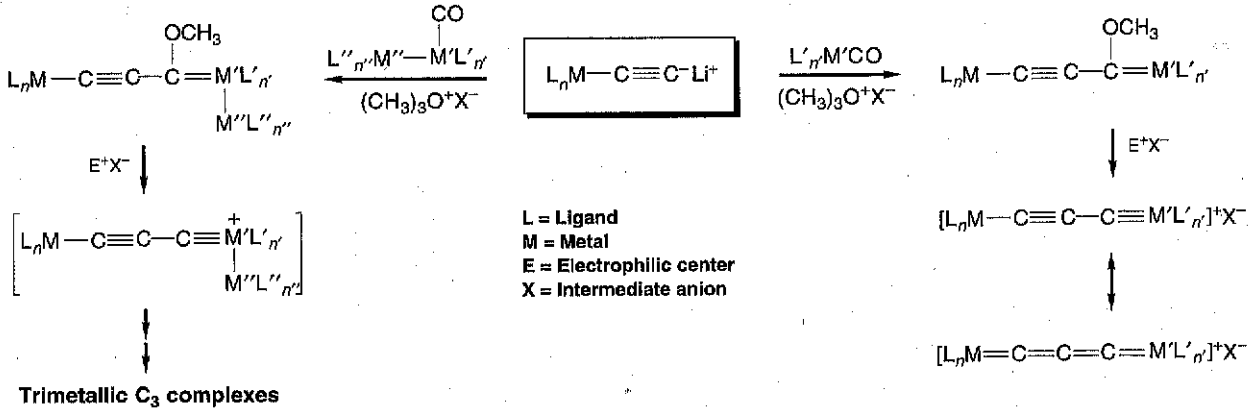
Many forms of carbon can now be stabilized in transition-metal complexes. The forms include single carbon atoms, C_{60} and other allotropes bound as π-complexes, and unsupported carbon chains that span transition-metal atoms. Such compounds are attractive as possible catalytic materials.

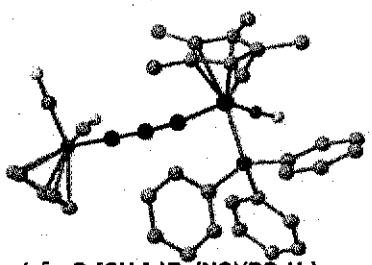
A research group at the University of Utah, Salt Lake City, has been particularly interested in preparing and characterizing those complexes with carbon chains that span the metal atoms. Under the direction of chemistry professor John A. Gladysz, the group has developed a new methodology to access such compounds and a general procedure for preparing this kind of complex. The idea is to be able to synthesize complexes with any number of carbon atoms in the bridging chain of a given complex.

The transition-metal complexes of carbon are of considerable value in modeling the carbide species generated on industrial heterogeneous catalysts. They are also of interest in the study of the many new allotropes of carbon that have recently been detected.

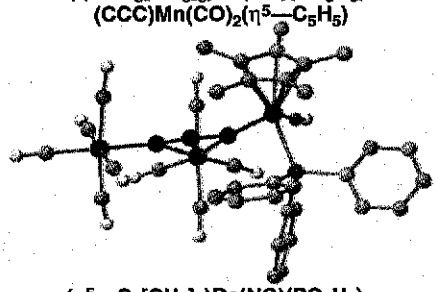
At Utah, particular attention has been focused on compounds of the type $L_nM(C)_xM'L'_n$ (where L is a ligand atom and M is a metal atom) in which one or more carbon atoms, in a chain, span two metal atoms. The chain may be inserted between the metal atoms or bridge around at least one of them. Gladysz notes a lack of general routes to synthesize these compounds, and his research was aimed at finding such routes.

Synthetic strategies lead to C_3 complexes





$(\eta^5\text{—}C_5[CH_3]_5)Re(NO)(PC_6H_5)$-
$(CCC)Mn(CO)_2(\eta^5\text{—}C_5H_5)$



$(\eta^5\text{—}C_5[CH_3]_5)Re(NO)(PC_6H_5)$-
$(\mu\text{—}\eta^1{:}\eta^3{:}\eta^1\text{—}CCC)(Re[CO]_4)Re(CO)_5$

Specifically, the Utah group sought and accomplished syntheses using conjugate bases of terminal acetylide complexes of the type $L_nMC \equiv CH$ ($x = 2$). This success was followed by appending a third carbon atom by elaboration to bimetallic Fischer carbene complexes. Still further elaboration to a C_3 chain has also been achieved. The chain is anchored by a transition-metal atom at each end and spanned by a third.

Gladysz believes that the transition-metal auxiliaries provide the best possibilities for modifying the acid-base properties for hydrogen bonds. Previous work has been centered on the complexes made from organic terminal acetylenes, $RC \equiv CH$, but the deprotonation of the complexes is difficult. The Utah group has developed alternative procedures using terminal alkyne complexes. These procedures have been used to synthesize cyclopentadienyl complexes and methyl cyclopentadienyl complexes. More than a dozen different complexes have been produced by these methods.

Most recently, the methodology has been extended to compounds in which linear unsaturated chains of elemental carbon span two transition metals—that is, compounds for which $x = 4$. In particular, a ReC_4Re complex that exhibited multiple resonance forms was produced. The reactivity of the ReC_4Re with changes in the oxidation state is one of the next problems to be tackled by the Utah researchers.

Joseph Haggin