The reaction of cobalt complexed propargylic alcohols with HBF₄ provides a cobalt-stabilized carboxylation that can be treated with a variety of carbon nucleophiles to provide alkyalted products (Nicholas reaction). The application of this reaction to systems with acid-sensitive functionality or where the nucleophile is part of the cobalt cluster (intramolecular reaction) is complicated by the action of the tetrafluoroboric acid on these groups in preference to the propargylic alcohol. We have investigated a Lewis acid-mediated version of this reaction on cobalt-complexed propargylic ethers that can be carried out by adding a Lewis acid to a 1:1 mixture of the carbon nucleophile and cobalt cluster (eq 1-3).

The intermolecular version of this reaction provides high levels of diasteroselection for syn-alkylated products provided certain stereocontrol elements are maintained. The intramolecular alkylation reaction with allylic alanes affords either intras- or extranuclear cobalt alkyne complexes. This reaction process, in combination with the Pauson-Khand annelation protocol, provides a method for the construction of polycycles containing a medium-sized ring. The attempted alkylation of 1-(trimethylsiloxy)cyclohexene by treatment of 1:1 mixture of the enol ether and the propargylic alcohol diocarbonyl hexacarbonyl complex with tetrafluoroboric acid or various Lewis acids was unsuccessful. The alkylation of this silyl enol ether with the cobalt complex of the corresponding

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Communications to the Editor


Scheme I

Table I. Stereochemistry of Alkylation

<table>
<thead>
<tr>
<th>R</th>
<th>R₁</th>
<th>Lewis acid</th>
<th>syn/anti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me3Si</td>
<td>Me</td>
<td>BF₄⁻OEt₂</td>
<td>15:1</td>
</tr>
<tr>
<td>Ph</td>
<td>Me</td>
<td>BF₄⁻OEt₂</td>
<td>15:1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>BF₄⁻OEt₂</td>
<td>15:1</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>BF₄⁻OEt₂</td>
<td>15:1</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>BF₄⁻OEt₂</td>
<td>15:1</td>
</tr>
</tbody>
</table>

4See supplementary material for experimental procedures. All reactions proceeded in greater than 85% yield. All cobalt complexes were prepared in racemic form and purified by silica gel chromatography prior to use in the alkylation reaction.

propargylic methyl ether resulted in efficient conversion to the alkylated cyclohexanone (92% yield, eq 4). The results of stereochemical studies that employed the E and Z trimethylsilyl enol ether of propiophenone are summarized in Table I. In all systems that were examined, the syn diastereomer predominated. The Z enol ether provided higher levels of diastereoselection than the E isomer, a result that is reminiscent of the aldol reaction. The substituent (R) on the cobalt complex exerts substantial influence on the stereochemical course of this reaction (e.g., R = H, 1:6:1; R = SiMe₃, 15:1). The latter result is significant since the sily-

lacetylene can serve as a surrogate for the simple acetylene. The alkylated products could be separated and purified by HPLC. The stereochemical assignments were secured by chemical conversion of each product to compounds of known configuration. The details of these transformations are provided in the supplementary material. Decomplexation could be achieved with preservation of the stereochemical integrity of the products and in high yield with trimethylamine N-oxide or ferric nitrate. An interesting decomposition with concomitant desilylation occurred upon treatment of the trimethylsilyl-substituted cobalt complex with tetrabutylammonium fluoride (eq 5).

Several transition-state models have been considered that rationalize the results of these studies. The one that we prefer is depicted in Figure 1. The cationic complex can exist in two stereoisomeric forms, differing in the relationship of the ethylidene group to the carbido carbon (syn or anti). The syn complex that

(3) The ratio of products was largely insensitive to the identity of Lewis acid.


is shown could be formed preferentially by selective cobalt participation in the Lewis acid assisted heterolysis of the methoxyl or through nonselective cobalt participation and a subsequent suprafacial migration of the ethylene group (resulting in syn-anti isomerization). A transition state with a synclinal alignment of the two II systems and with the methyl groups antiperiplanar to the II systems (relative face selection = /k) will result in the syn-alkylated (II) products that are observed to predominate (Si-Si alignment is illustrated). The model serves to rationalize the aforementioned features of this reaction, including the role of the substituent attached to the acetylene-cobalt complex. The larger substituent would serve to increase the value of $\Delta AG^\circ$ for dia stereomeric transition states leading to syn and anti alkylated products. If the anti product were obtained through the related synclinal transition state (Re-Si alignment in Figure 1), van der Waals strain would result from the interaction of the methyl group on the enol ether with the substituent (R) on the cobalt acetylene complex.

The exocyclic internal alkylation of the allylic silane 1 (eq 6)

\[
\begin{align*}
\text{TMS} & \quad \text{Me} \\
\text{Ph} & \quad \text{C} = \text{O} \\
\text{Ph} & \quad \text{Me} \\
\end{align*}
\]

conforms to the same transition-state model. In this reaction the six-membered ring 2 is formed with complete stereocontrol (trans) with respect to the two appendages on the newly formed ring. Oxidative decomplexation of the extraannular cobalt complex provided acetylene 3.

Endocyclic internal alkylation to provide intraannular cobalt complexes of cycloalkynes has also been achieved and in combination with the Pauson-Khand cyclization provides polycycles of interest to natural and unnatural products synthesis. Examples of this process that afford six-, seven-, and eight-membered products are illustrated in Scheme I (eq 7-10). Complexation of the precursor acetylene with dicobalt octacarbonyl in each of these examples results in a substantial change in bond angles at the sp carbon centers. The intermediate can be viewed as a cis-allylic cation equivalent with a reagent invoking a relative requirement for activation at its terminus. Oxidative removal of the cycloacetylenic ligand with Me$_2$NO does not lead to the cycloalkyne product. This reaction proceeds along alternative paths that have not been fully elucidated. The intraannular cobalt complexes are excellent participants in the Pauson-Khand cyclization reaction. For example, cyclooctyne 5 gave rise to a 1:1 mixture of cyclopentenones 6a and 6b in 67% yield on treatment with norborne and 1 atm of carbon monoxide in refluxing benzene (eq 7). 10

In order to eliminate the formation of unwanted isomers in the second cyclization process, the internal Nicholas reaction can be coupled to a subsequent internal Pauson-Khand reaction as depicted in eq 10. The allyloxy acetal 11 reacts more sluggishly than the corresponding ether but proceeds at room temperature (10 min) to afford a 5:1 mixture of 12 and the cis isomer in 75% yield. 11,12 Treatment of 12 with 1 atm of carbon monoxide in benzene at 60 °C for 4 h provided a single tricyclic material 13 in 85% yield. The assignment of stereochemistry follows from NMR experiments (NOE difference, $\delta$ value measurements). Comparison of structure 13 with ethylene glycol 14 is a representation of the fusococcin class of dipterigenes, suggests this reaction sequence may prove to be of value in the synthesis of members of this class of compounds.

**Acknowledgment.** This investigation was supported by the NSF (Presidential Young Investigator Award), Dreyfus Foundation (Dreyfus Teacher-Scholar Grant), A.P. Sloan Foundation, and Pfizer, Inc., to whom we are grateful. Fellowship support (for T.S.) was contributed by the Berlex Laboratories in the form of a Berlex Predoctoral Fellowship. A Dow Fellowship (for W.E.C.) is gratefully acknowledged.

**Supplementary Material Available:** Experimental procedures as well as NMR, IR, and mass spectral data for the compounds studied (11 pages). Ordering information is given on any current masthead page.

**Electrochemical and ESR Characterization of the Redox Behavior of Bis[tris(trimethylsilyl)methyl]diphosphene, \((\text{Me}_3\text{Si})_3\text{C}=\text{P}=	ext{P}=(\text{SiMe}_3)_3\) (TspP=PTsp)**

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Received November 12, 1985

An explosive growth of interest and activity in the area of synthesis and characterization of diphosphenes followed the 1981 report of Yosifluji and co-workers on the synthesis of the first stable compound featuring a phosphorus–phosphorus 3p(σ)–3p(σ) double bond. Since then, some symmetrically as well as unsymmetrically substituted diphosphines and diarsines have been