molecules per unit cell. **2** is a $(Et_2N)_2P$-substituted 4,5-benzo-1,3,2-diazaphosphole[12] in which a P_3N_2 triphosphazane unit is stabilized by bonding of the ortho-C_6H_4 ring to nitrogen atoms N(1) and N(2). **2** has approximate C_s point group symmetry, with a symmetry plane passing through P(2) perpendicular to and bisecting the $C_6H_4N_2$ ring, consistent with that observed for **1** in solution. The $(Et_2N)_2P(S)$ units are oriented around the P(1)-N(1) and P(3)-N(2) bonds such that the P=S bond vectors are approximately perpendicular to the $C_6H_4N_2$ plane and trans to the P(2) lone pair electrons. The N(1)-P(2)-N(2) and $C_6H_4N_2$ planes are close to coplanar; the interplane dihedral angle (bend along the N···N axis) of the PN_2C_2 ring is 21.4°. Phosphorus atoms P(1) and P(3) are displaced out of the $C_6H_4N_2$ plane by 0.28 Å. P(2) is displaced in the opposite direction by 0.46 Å. P(2) is in a protected "cleft" in the molecule and consequently is relatively inaccessible to attack by external reagents. The mean ring P(2)-N(1,2) distance [1.753 (5) Å] is considerably longer than the exo ring P(1)-N(1), P(3)-N(2) distance [1.668 (6) Å], although both are in the range of P-N distances observed for other phosphazane[2] and 1,3,2-diazaphosphole[8,9] systems.

Triphosphazanes **1** and **2** display high thermal and chemical stability and phosphorus atom reaction selectivity. Thermolysis of **1** or **2** for 1 day in vacuo at 100 °C produced no decomposition. In contrast to the selective exo phosphorus atom [P(2) and P(3)] reaction of **1** with S_8 which yields **2**, **1** with H_2O in CH_2Cl_2 reacts at the central phosphorus [P(2)] to form phosphine oxide **3**[10] in 80-85% yield. Cleavage of the P(2)-N(5) bond occurs without significant cleavage of other P-N bonds in the system. Reaction of **2** with anhydrous gaseous HCl yields chlorophosphine **4**,[11] again with barely detectable cleavage of skeletal or exo P-N bonds. It appears the nucleophilicity of P atoms in **1** and **2** is generally reduced, but more so for P(2) than for P(1) and P(3). Conversely, the H_2O-**1** reaction suggests that P(2) is activated electrophilically relative to P(1) and P(3). This difference in P(1,3) vs. P(2) reactivity might be a function both of the specific conformation assumed by **1** and the protected nature of P(2), a premise that can be tested only after other conformationally characterized acyclic phosphazanes become available.

Since the new triphosphazanes **1-4** contain a functional phosphorus atom [P(2)] in an unusually protected position, given the novel phosphorus atom selective reactivity these molecules display, and they contain functionally useful groups on the terminal [P(1) and P(3)] phosphorus atoms, it is expected that further derivative chemistry will be developed. Related studies, including efforts to incorporate these phosphazanes into new phosphazane macromolecules, are in progress currently.

Acknowledgment. Support for this work by National Science Foundation Grant CHE-8312856 is gratefully acknowledged. The assistance of Dr. C. Campana and the Nicolet Instrument Co., Madison, WI, in obtaining low-temperature X-ray diffraction data is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, positional, isotropic, and anisotropic thermal parameters, hydrogen coordinates, temperature factors, and bond distances and angles for **2** (6 pages). Ordering information is given on any current masthead page.

(8) Malavaud, C.; Boisdon, M. T.; Charbonnel, Y.; Barrans, J. *Tetrahedron Lett.* **1979**, *20*, 447.

(9) Malavaud, C.; N'Gando M'Pondo, T.; Lopez, L.; Barrans, J.; Legros, J.-P. *Can. J. Chem.* **1984**, *62*, 43.

(10) **3**: ^{31}P NMR (C_6D_6) δ 111.9 (d, $^2J_{PP}$ = 22.4 Hz, area 2), 8.8 (d of t, $^1J_{PH}$ = 664.0 Hz, area 1); MS, parent at *m/e* 502, $C_{22}H_{45}N_6OP_3^+$; ^1H NMR (C_6D_6) δ 7.16-6.84 (m, area 4, C_6H_4), 3.66-2.63 (m, area 16, CH_2CH_3), 1.10 (m, area 24, CH_2CH_3); IR (NaCl), characteristic absorption at 2418 cm^{-1} (P-H).

(11) **4**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 143.9 (t, $^2J_{PP}$ = 66.7 Hz, area 1), 64.5 (d, area 2); ^1H NMR δ 7.65 and 6.93 (multiplets, area 4, C_6H_4), 3.20 (m, area 16, CH_2CH_3), 0.96 (m, area 24, CH_2CH_3); MS, parent ion at *m/e* 684, $C_{22}H_{44}N_6P_3S_2Cl^+$; IR (KBr), characteristic absorption at 604 cm^{-1} (P=S).

(12) (a) Lehousse, C.; Haddad, M.; Barrans, J. *Tetrahedron Lett.* **1982**, *23*, 4171. (b) Kalinin, A. E.; Andrianov, V. G.; Stuckhov, Y. T. *Zhur. Strukt. Khim.* **1974**, *15*, 1132. (c) Schmidpeter, A.; Luber, J. *Chem. Ber.* **1975**, *108*, 820.

Lewis Acid Mediated Version of the Nicholas Reaction: Synthesis of Syn-Alkylated Products and Cobalt-Complexed Cycloalkynes

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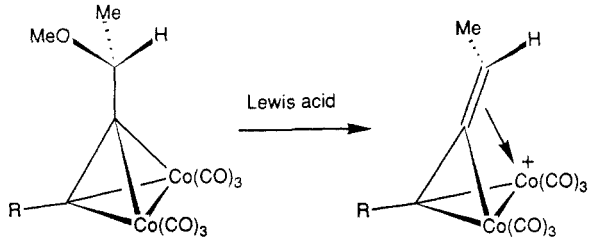
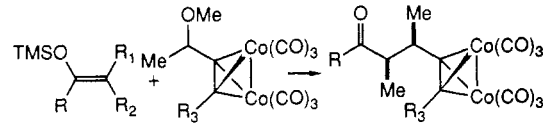
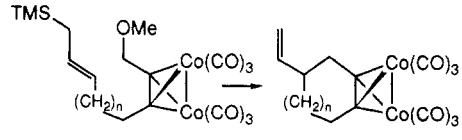
The reaction of cobalt complexed propargylic alcohols with HBF_4 provides a cobalt-stabilized carbocation that can be treated with a variety of carbon nucleophiles to provide alkylated products (Nicholas reaction).[1] The application of this reaction to systems with acid-sensitive functionality or where 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.[2] 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).



(1)



(2)



(3)

The intermolecular version of this reaction provides high levels of diastereoselection for syn-alkylated products provided certain stereocontrol elements are maintained. The intramolecular alkylation reaction with allylic silanes affords either intra- or extraannular 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 dicobalt 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

(1) (a) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. *Transition Metal Organometallics*; Halper Ed.; Academic Press: New York, 1978; Vol. 2, p 1. (b) Hodes, H. D.; Nicholas, K. M. *Tetrahedron Lett.* **1978**, 4349. (c) Nicholas, K. M.; Mulvaney, M.; Bayer, M. *J. Am. Chem. Soc.* **1980**, *102*, 2508. (d) Nicholas, K. M.; Siegel, J. *J. Am. Chem. Soc.* **1985**, *107*, 4999. (e) Mikaelian, G. S.; Gybin, A. S.; Smit, W. A.; Caple, R. *Tetrahedron Lett.* **1985**, *26*, 1269.

(2) Unpublished results from these laboratories. For a BF_3·OEt_2-promoted alkylation of cobalt-complexed propargylic alcohols with several carbon nucleophiles, see: (a) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1982**, *25*, 2555. For the alkylation and alkynylation of cobalt-complexed propargylic acetates with aluminum reagents, see: (b) Padmanabhan, S.; Nicholas, K. M.; *J. Organomet. Chem.* **1981**, *212*, 115. (c) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1983**, *24*, 2239.

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Scheme I

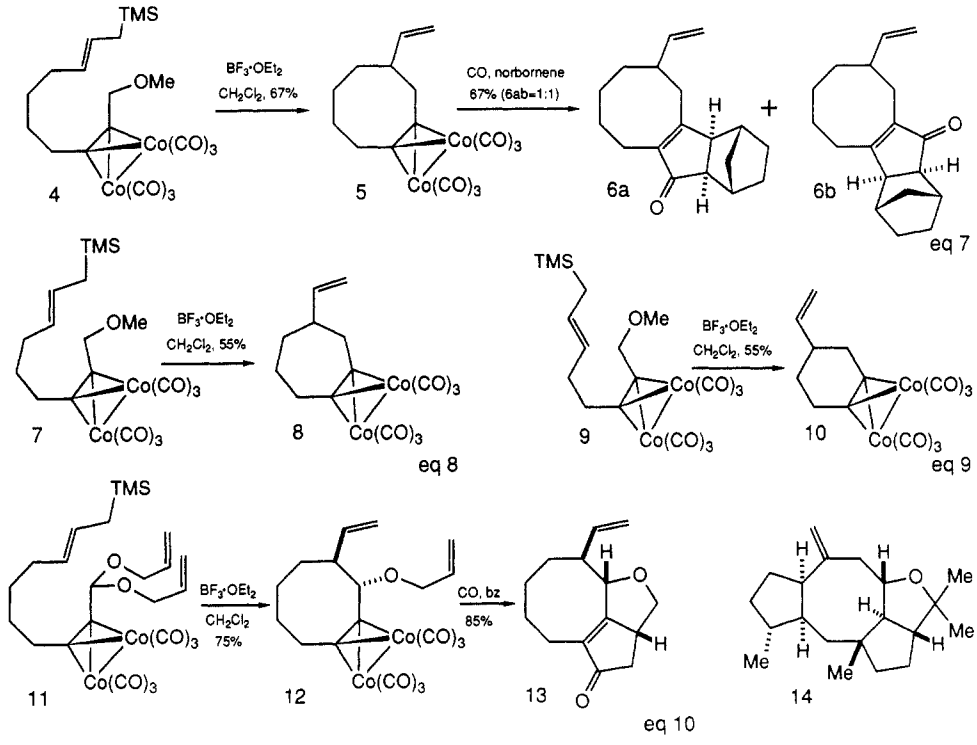
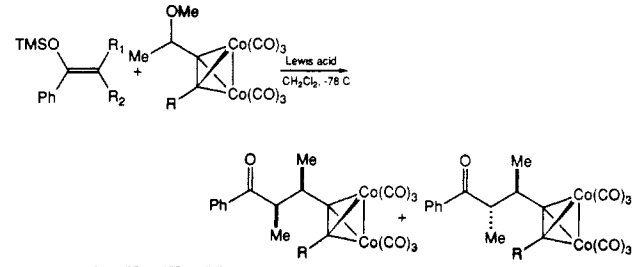


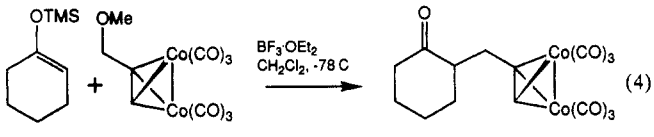
Table I. Stereochemistry of Alkylation[a]



R	R_1	R_2	Lewis acid	syn/anti
Me_3Si	Me	H	BF_3·OEt_2	15:1
Ph	Me	H	$EtAlCl_2$	18:1
Ph	H	Me	$EtAlCl_2$	9:1
Me	Me	H	BF_3·OEt_2	6.8:1
Me	H	Me	BF_3·OEt_2	3.5:1
H	Me	H	$EtAlCl_2$	1.6:1

[a] See 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 ste-



reochemical 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.[3] 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 = $SiMe_3$, 15:1).[4] The latter result is significant since the silylacetylene 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[5] or ferric nitrate.[6] An interesting decomplexation with concomitant desilylation occurred upon treatment of the trimethylsilyl-substituted cobalt complex with tetrabutylammonium fluoride (eq 5).

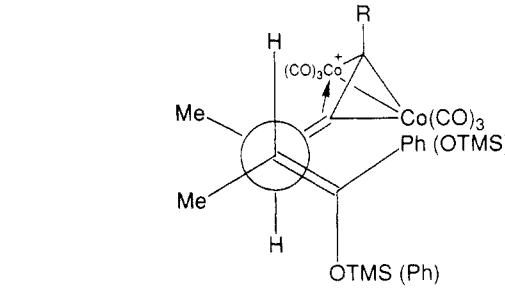
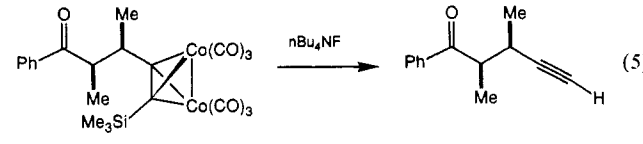


Figure 1.



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).[7] The syn complex that

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

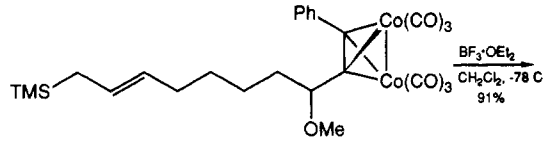
(4) A related effect of a trimethylsilyl group in a Pauson–Khand cyclization has been reported: Magnus, P.; Principle, M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(5) (a) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336. (b) Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640.

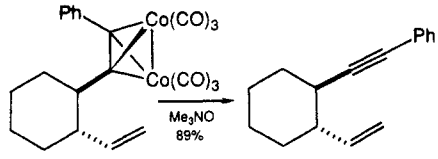
(6) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475.

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 ethylidene group (resulting in syn-anti isomerization).[8] A transition state with a synclinal alignment of the two Π systems and with the methyl groups antiperiplanar to the Π systems (relative face selection = *lk*) will result in the syn-alkylated (*l*) products that are observed to predominate (Si-Si alignment is illustrated).[9] 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 $\Delta\Delta G^{\ddagger}$ for diastereomeric 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)



1



2 3

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-allyl cation equivalent with a regiochemical imperative for reaction at its terminus. Oxidative removal of the cycloacetylenic ligand with Me_3NO 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 norbornene 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 slugglishly 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 ^{1}H NMR experiments (NOE difference, *J* value measurements). Comparison of structure **13** with epoxydictymene **14**,[13] a representative member of the fusicoccin class of diterpenes, 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 Dox 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.

(7) Evidence in support of the cannonical structure with charge localized on cobalt is found in the increase in the carbonyl stretching frequency in the cationic complexes (Connor, R. G.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45) and by analogy with the isolobal tricobalt alkylidyne cluster compounds (Ediden, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561).

(8) NMR studies implicate a significant barrier to rotation about the C-C+R_2 bond and to suprafacial migration of the ethylidene group: Padmonbahan, S; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, C23.

(9) Compare to: (a) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413. (b) Denmark, S.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (c) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (d) Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2794. (e) Faller, J. W.; Lambert, C. *Tetrahedron* **1985**, *41*, 5755.

(10) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1976**, 30. Although it is likely that **6a** and **6b** exist as a mixture of stereoisomers (at the carbon bearing the vinyl group), we were not able to confirm this point.

(11) These two compounds were separated by SiO_2 chromatography. The major trans isomer was employed in the subsequent cyclization reaction.

(12) (a) Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2093, 2101. (b) Majetich, G.; Hull, K.; Defauru, J.; Shawe *Tetrahedron Lett.* **1985**, *26*, 2755.

(13) Enoki, N.; Furusaki, A.; Suehiro, K.; Ishida, R.; Matsumoto, T. *Tetrahedron Lett.* **1983**, *24*, 4341.

Electrochemical and ESR Characterization of the Redox Behavior of Bis[tris(trimethylsilyl)methyl]diphosphene, $(Me_3Si)_3C-P=P-C(SiMe_3)_3$ (TsiP=PTsi)

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An explosive growth of interest and activity in the area of synthesis and characterization of diphosphenes followed the 1981' report of Yoshifuji and co-workers[1] on the synthesis of the first stable compound featuring a phosphorus-phosphorus 3p(π)-3p(π) double bond. Since then, some symmetrically as well as unsymmetrically substituted diphosphenes and diarsenes have been

[†] Université de Provence.
[‡] Université P. Sabatier.

(1) Yoshifuji, M.; Shima, I.; Inamoto, N. J.; Hirota, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. Bertrand, G.; Couret, C.; Escudié, J.; Majid, S.; Majoral, J. P. *Tetrahedron Lett.* **1982**, *23*, 3567. Couret, C.; Escudié, J.; Satgé, J. *Tetrahedron Lett.* **1982**, *23*, 4941. Cowley, A. H.; Kilduff, J. E.; Newman, T. J.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. Review: Cowley, A. H. *Polyhedron* **1984**, *3*, 389.

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