carbons. The averaging results from a degenerate Cope rearrangement of the homotropilidene portion of **2**. When the ^1H NMR spectrum of **2** was run at lower temperatures, the triplet at δ 4.35 (H2, H4, H6, H8) broadened and began to separate into two widely spaced signals at about −70 °C, beyond which insolubility problems precluded further study.[19]

Conclusion

The longer distal cyclopropyl bond length in crystalline **2** compared to that of cyclopropylamine can be attributed to σ-acceptor effects associated with the electronegativity of the nitrogen atom N3. σ-Acceptor effects and hybridization effects can account for the shorter adjacent bond lengths in **2** relative to cyclopropane. Special geometric constraints associated with bridging of the homotropilidine by the triazolidinedione do not account for the long distal bond lengths in **2**, since the C1–C5 internuclear distance is similar to that of bullvalene. The five bridging carbon atoms connecting N2 and N3 are compatible with the most nearly planar triazolidinedione ring yet observed.

Experimental Section

4-Phenyl-2,4,6-triazatetracyclo[6.3.2.0^{2,6}.0^{7,9}]trideca-10,12-diene-3,5-dione was prepared by the reported procedure.[1] Spectral parameters are as follows: ^{13}C NMR ($CDCl_3$, 30 °C, 25.2 MHz, $CHCl_3$ assigned as 76.91 ppm) δ 73.750 (C1/C5), 40.957 (C2/C4/C6/C8), 127.532 (C6/C9), 131.516, 127.752 (ipso/para C), 128.830, 125.435 (meta/para C), 148.573 (C=O); ^1H NMR (CD_2Cl_2, XL 200 MHz, 30 °C, tetramethylsilane) δ 7.49 (Ph), 4.92 (t, J = 7.7 Hz, H1/H5), 4.35 (major coupling t, J = 7.7 Hz, H2/H4/H6/H8), 6.08 (major coupling t, J = 7.7 Hz, H6/H9). At −10 °C the peak at δ 4.35 begins to broaden, at −70 °C it is totally flat, and below this the solute precipitates.

Crystal Structure Data. Intensity data were collected at 293 K and at 153 K on a Nicolet P3 four-circle computer-controlled diffractometer, using graphite-monochromated X-radiation (Cu Kα, λ = 1.5418 Å for 293 K and Mo Kα, λ = 0.71069 Å for 153 K). The crystals are monoclinic, space group $P2_1/c$. The structure was solved by using the 293 K data in the direct methods multiple-solution program MULTAN80.[20] The 293 and 153 K data were used in structure refinements by a full-matrix least-squares procedure[21,22] with anisotropic temperature factors for O, N, and C atoms and isotropic temperature factors for H atoms. The atomic scattering factors used are from a compilation of published values.[24]

293 K data: a = 9.030 (4) Å, b = 16.519 (6) Å, c = 8.681 (5) Å, β = 96.20 (4)°, V = 1287 (1) Å^3, Z = 4, 2059 unique data ($I \geq 2.00\ \sigma(I)$), θ range 0–69.5°, R = 0.060, R_w = 0.063.

153 K data: a = 8.849 (4) Å, b = 16.587 (5) Å, c = 8.643 (5) Å, β = 96.07 (4)°, V = 1261.4 (9) Å^3, Z = 4, 3700 unique data ($I \geq 3.00\ \sigma(I)$), θ range 0–32.5°, R = 0.062, R_w = 0.078.

Acknowledgment. This research was supported by USPHS Grants CA-10925, CA-06927, RR-05539, and CA-22780 from the National Institutes of Health, by Grant BC-242 from the American Cancer Society, and by an appropriation from the Commonwealth of Pennsylvania. We acknowledge Professors P. von R. Schleyer and Edgar F. Kiefer for helpful discussions and Professor J. E. Baldwin for the use of the facilities of Dyson Perrins Laboratory, Oxford University.

Supplementary Material Available: X-ray experimental procedures, ORTEP and stick diagrams, and listings of anisotropic thermal parameters, final atomic parameters, and torsion angles for **2** at T = 293 K and T = 153 K (11 pages); listings of observed and calculated structure factors for **2** at T = 293 K and T = 153 K (41 pages). Ordering information is given on any current masthead page.

(19) Not all exchange processes that occur in solution are observed in the solid state. Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396–7397. Macho, V.; Miller, R. D.; Yannoni, C. S. *Ibid.* **1983**, *105*, 3735–3737. Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216. For a semibullvalene that is fluctional in the crystalline state, see ref 4a and 11e. Note, also: Kobayashi, Y.; Ando, A.; Kawada, I.; Kumandaki, I. *J. Am. Chem. Soc.* **1981**, *103*, 3958–3959.

(20) Main, P. *Multan80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York: York, England, 1979.

(21) Carrell, H. L. *ICRFMLS. Modification of UCLALS4*; Institute for Cancer Research: Philadelphia, 1975.

(22) Gantzel, P. K.; Sparks, R. A.; Long, R. E.; Trueblood, K. N. *UCLAS4. Full-Matrix Least-Squares Program in FORTRAN IV*, 1969.

(23) $R = \sum||F_o| - |F_c||/\sum|F_o|$, where F_o is an observed structure factor and F_c is a structure factor calculated from a postulated structure. R is a measure of the extent to which the measured x-ray diffraction pattern of a structure agrees with that calculated from the parameters of the structure determined by analysis of the diffraction data. $R_w = (\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2)^{1/2}$ is another measure of this agreement incorporating the weight, w, of each observation. R_{obsd} is the agreement using those data considered to be "observed." R_{all} is the agreement using all data measured.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102.

Dynamic Behavior of Dicobalt Hexacarbonyl Propargyl Cations and Their Reactions with Chiral Nucleophiles

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Abstract: The dynamic behavior of several dicobalt hexacarbonyl propargyl cations has been investigated by variable temperature ^1H and ^{13}C NMR methods. Two distinct fluxional properties have been identified. The temperature-dependent NMR spectra of these cations are consistent with a lower energy antarafacial migration of an alkylidene ligand from one cobalt tricarbonyl unit to the other. This motion results in the enantiomerization of the cation. A diastereomerization process has been detected at elevated temperatures. The relevance of this fluxional behavior to the stereochemical outcome of cation alkylation reactions is discussed. For example, on treatment with a chiral, nonracemic nucleophile (Evans' boron enolate) an unusual double stereodifferentiating reaction is found to occur. The yield and stereochemistry of the reaction suggest the intermediacy of a cation that (1) racemizes at a rate that is fast relative to alkylation and (2) reacts with different rates (kinetic resolution) with the chiral nucleophile. A stereochemical model is proposed that accounts for these results and allows predictions to be made concerning the outcome of other nucleophile–electrophile combinations.

Transition-metal complexes of alkynes, as transient reaction intermediates and isolable compounds, have played a prominent role in the chemistry of acetylenes. Mononuclear[1] and dinuclear[2] complexation results in marked changes in alkyne structure and

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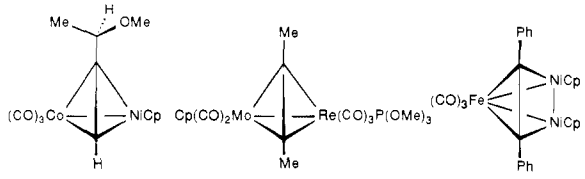
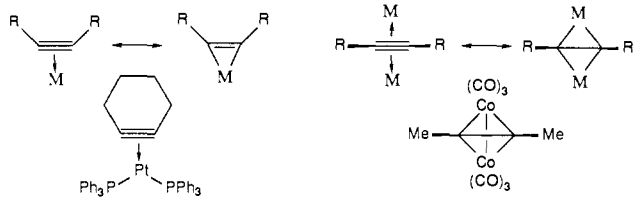


Figure 1.

reactivity.[3] Dicobalt hexacarbonyl complexes of acetylenes are among the better known members of the latter class and have been found to be of considerable value in organic synthesis. Insertion



mononuclear complex dinuclear complex

reactions of these complexes have been demonstrated to provide substituted aromatics[4] (with an acetylene), bifurandiones[5] (with carbon monoxide), and cyclopentenones[6] (with an olefin and carbon monoxide). Stable carbocationic intermediates that benefit from the β-effect of cobalt have been alkylated with several carbon nucleophiles to result in carbon–carbon bond formation (Nicholas reaction).[7] Silyl enol ethers can be stereoselectively alkylated with dicobalt hexacarbonyl complexes of propargylic ethers when treated with a Lewis acid.[8] Intramolecular alkylation reactions have been achieved with allylic silanes to provide both extra- and intraannular acetylene–cobalt complexes. The latter species represent transition-metal-stabilized cycloalkynes which were shown to participate in the Pauson-Khand insertion reaction affording products that contain the polycarbocyclic skeleton of some terpenes.[8]

One objective of our research in this area has been to identify features of the reactions of dicobalt hexacarbonyl alkynes that may be attributable to the presence of two metal centers. A considerable number of related cluster compounds are known whose reaction chemistry remains largely unexplored. Several examples that contain acetylenic ligands and heterobi- and heterotrimetallic units as components of their structure are presented in Figure 1.[9] A knowledge of the role of the cobalt–cobalt bond

(1) For a recent example and leading references, see: (a) Buchwald, S. L.; Lum, R. T.; Dervan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (b) Platinum complex (Figure 1): Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(2) Hoffman, D. M.; Hoffmann, R.; Fisel, R. C. *J. Am. Chem. Soc.* **1982**, *102*, 3858.

(3) Trinuclear and tetranuclear cobalt complexes of acetylene are also known, see: Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323.

(4) Hubel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, p 301.

(5) Sauer, J. C.; Cramer, R. D.; Englhardt, V. A.; Ford, T. A.; Holmquist, H. E.; Howk, D. W. *J. Am. Chem. Soc.* **1959**, *81*, 3677.

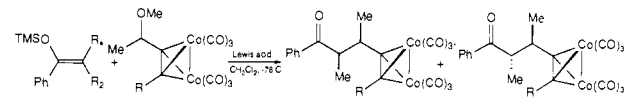
(6) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977.

(7) (a) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. *Transition Metal Organometallics*; Halper, Ed.; Academic: New York, 1978; Vol. 2, p 1. (b) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1982**, *25*, 2555. (c) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1983**, *24*, 2239. (d) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1981**, *212*, 115. (e) O'Boyle, J. E.; Nicholas, K. M. *Tetrahedron Lett.* **1980**, *21*, 1595. (f) Padmanabhan, S.; Nicholas, K. M. *Syn. Commun.* **1980**, *10*, 503. (g) Nicholas, K. M.; Mulvaney, M.; Bayer, M. *J. Am. Chem. Soc.* **1980**, *102*, 2508. (h) Hodes, H. D.; Nicholas, K. M. *Tetrahedron Lett.* **1978**, *19*, 439. (i) Lockwood, R. F.; Nicholas, K. M. *Tetrahedron Lett.* **1977**, *18*, 4163. (j) For a recent application to the total synthesis of (±)-cyclocolorenone see: Saha, M.; Bogby, B.; Nicholas, K. M. *Tetrahedron Lett.* **1986**, *27*, 915.

(8) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128.

(9) (a) Ni–Co; unpublished results of M. T. Klimas. Prepared by the procedure of: Freeland, B. H.; Hux, J. E.; Payne, N. C.; Tyers, K. G. *Inorg. Chem.* **1980**, *19*, 693. (b) Mo-Re: Beck, W.; Muller, H.-J.; Nagel, U. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 734. (c) Ni_2–Fe: Tilney-Bassett, J. F. *J. Chem. Soc.* **1963**, 4784.

Table I. Stereochemistry of Alkylation[a]



R	R_1	R_2	Lewis acid	syn/anti	yield (%)
TMS	Me	H	$BF_3{\cdot}OEt_2$	15:1	92
Ph	Me	H	$EtAlCl_2$	18:1	90
Ph	H	Me	$EtAlCl_2$	9:1	93
Me	Me	H	$BF_3{\cdot}OEt_2$	6.8:1	87
Me	H	Me	$BF_3{\cdot}OEt_2$	3.5:1	89
H	Me	H	$EtAlCl_2$	1.6:1	91

[a] See Experimental Section for details of the stereochemical correlations that serve as the basis for the structural assignments for alkylation products.

in the reactions of the simpler dicobalt alkyne complexes is hoped to guide future examinations of these more complicated systems. Evidence has been presented that the Nicholas carbocation has fluxional properties that result in an interaction of the electron-deficient propargylic carbon with *both* cobalt tricarbonyl units.[10] In order to understand the origins of the diastereoselection exhibited by these cations in their reactions with carbon nucleophiles and to guide future experiments with these and related organocluster species, we have undertaken new spectroscopic and reaction studies of dicobalt hexacarbonyl propargyl cation salts and related species. We present evidence that the presence of *two* metal centers in these dinuclear complexes gives rise to unusual chemical properties that are relevant to their reaction diastereoselection and provides a means to achieve asymmetric syntheses with *racemic* organocobalt clusters.

Treatment of a dicobalt hexacarbonyl propargyl alcohol complex with HBF_4 provides an often stable cation that has been alkylated in a subsequent reaction with carbon nucleophiles to provide a range of propargylated products.[7] This procedure works well in many cases and, since reaction at the propargylic site is insured, avoids formation of allenic products. In certain cases, we found the formation of the cationic salt under these conditions was complicated by deleterious reactions of acid-sensitive groups present in the cobalt-containing substrate (particularly in the intramolecular alkylation reaction) or by the tendency of the cation to undergo elimination of a proton when treated with a carbon nucleophile in the subsequent step. Frequently, these problems can be overcome by treating a 1:1 mixture of a carbon nucleophile and a cobalt complexed methyl propargyl ether with a Lewis acid.[8] We assume that these conditions result in the in situ generation of the cationic complex. Stereochemical results have been obtained (vide infra) that are consistent with this interpretation.

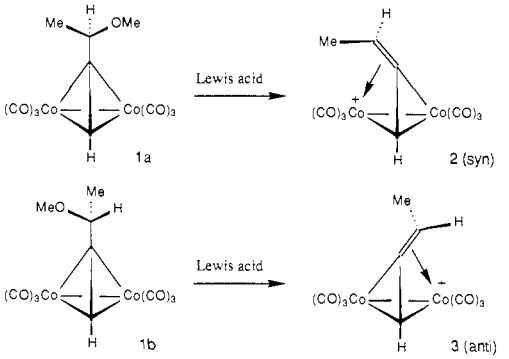
The Lewis acid promoted Nicholas reaction is particularly well suited for forming a new carbon–carbon bond between two vicinal branched carbon centers. We have examined the stereochemistry of this reaction with the (*E*)- and (*Z*)-trimethylsilyl enol ether of propiophenone and several cobalt complexes. The results of these studies are presented in Table I.

Several trends are evident from these studies. Both geometric isomers result in the preferential formation of the (*l*)-syn diastereomer (relative face selection = *lk*); the (*Z*)-enol ether provided higher levels of diastereoselection. The remote acetylenic substituent R plays a significant role in determining the degree of diastereoselection. Larger groups resulted in increased selectivity (R = $SiMe_3$, 15:1; R = Ph, 18:1) whereas a terminal acetylene exhibited a small preference for syn selectivity (R = H, 1.6:1). Only small variations in diastereomer ratios were observed upon modification of the Lewis acid structure. Reagents that were found to be effective include $BF_3{\cdot}OEt_2$, BCl_3, Bu_2BOTf, $TiCl_4$, Et_2AlCl, $EtAlCl_2$, Me_3Al, and TMSOTf. Ether groups other than methoxy undergo substitution (vide infra). The cobalt unit can be removed

(10) (a) Padmanabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1983**, *268*, 23. (b) Connor, R. G.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45.

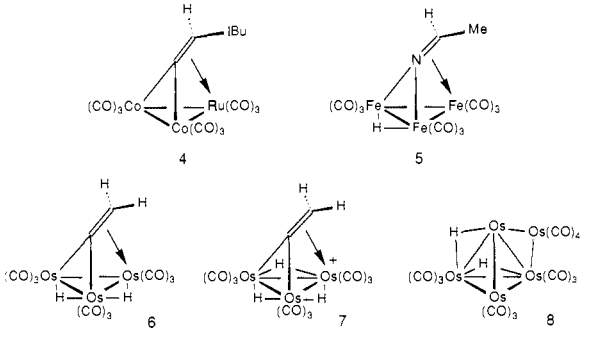
from the acetylene ligand under oxidative ($Fe(NO_3)_3$,[11] Me_3NO,[12] CAN[13]) conditions without complications of epimerization or allene formation.

Heterolysis of the carbon–oxygen bond in **1ab** should proceed with stereoelectronic control. Backside participation of one of the carbon–cobalt bonds results in the formation of two possible diastereomeric cations **2** and **3** that differ in the relationship of the ethylidene group to the carbido carbon (syn/anti). Nucleophilic attack should proceed with similar stereoelectronic control whereby the nucleophile adds to the ethylidene ligand anti to cobalt in either **2** or **3**. Two limiting cannonical forms of the cation can be considered: the positive charge can be localized on carbon (carbocation) or cobalt (cobalt cation). The latter structure is assumed to best represent the charge distribution in these complexes, and for reasons of economy, only this type of structure will be presented in subsequent discussions.

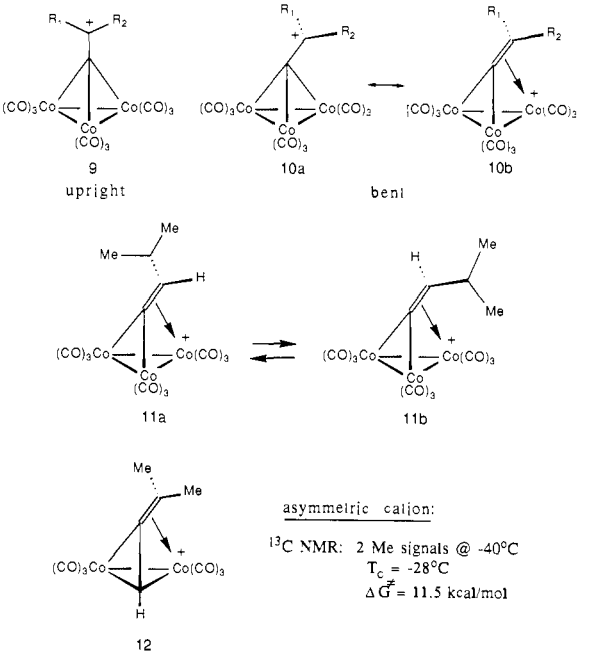


Experimental evidence for charge delocalization onto the $Co_2(CO)_6$ moiety has been obtained. For example, Nicholas and Conner have reported IR data for cations that show an increase in the carbonyl stretching frequencies (40–60 cm^{-1}) relative to the neutral complex that indicate a diminution of cobalt–carbon monoxide back-bonding.[14] The ^1H NMR spectrum of $[Co_2(CO)_6(HC{\equiv}CC(CH_3)_2]^+$ displayed a small downfield shift of the methyl groups (0.7 ppm) relative to the parent alcohol complex while the uncomplexed cation $[CH_3C{\equiv}CC(CH_3)_2]^+$ displayed a corresponding downfield shift of 2.3 ppm. Most striking are the large upfield shifts in ^{13}C NMR of the complexed cation relative to the free cation (Δppm = 124 for $-\mathbf{C}^+(Me)_2$ and 137 for Me–**C**≡).[10]

A number of cluster compounds which are isolobal to the cations **2** and **3** have been characterized and shown to have nonsymmetrical, bent structures (**4–8**).[14] Perhaps the best known isolobal complexes are the closely related alkylidynetricobalt nonacarbonyls that have been extensively studied by Seyferth.[7a] Cations adjacent



to the alkylidyne carbon in the tricobalt cluster are stabilized in a manner similar to that of dicobalt hexacarbonyl complexed propargylic cations. Hoffman has predicted that bending of the cationic carbon toward one of the cobalt atoms (**10ab**) would result in hyperconjugative stabilization and that the upright structure **9** is 17.5 kcal/mol higher in energy than **10**.[15] Mislow and Norton later provided experimental evidence for the bent structure through an ingenious ^{13}C NMR experiment that utilized cation **11**.[16] At low temperature, two distinct doublets were observed for the isopropyl substituent. These results are indicative of diastereotopic methyl groups and were interpreted as evidence for the bent structure. Coalescence of these signals at −52 °C indicated a barrier to interconversion of 10.5 kcal/mol. Two mechanisms exist for interconversion of the diastereotopic methyl groups: simple carbon–carbon bond rotation about the (formal) double bond and simultaneous rotation and migration of the alkylidene ligand from one cobalt tricarbonyl unit to the other (antarafacial migration). While both processes accomplish the same task, Hoffman's calculations predict antarafacial migration should be the lower energy process.



The fluxional nature of the cobalt acetylene cationic complexes has also been established. Of the compounds studied by Nicholas, one displayed temperature-dependent behavior in an NMR experiment. The cation **12** exhibits one methyl signal in the ^{13}C NMR spectrum at 0 °C which separates into two sharp signals below −40 °C (T_c = −28 °C).[10a] An energy barrier of 11.5 kcal/mol was calculated on the basis of these observations.[17] The existence of two methyl signals at low temperature is not consistent with a symmetrical structure and is suggestive of considerable charge delocalization onto the cobalt tricarbonyl unit.

The alkylation reactions summarized in Table I were performed with racemic propargylic ether complexes and achiral nucleophiles. Hence, the absolute stereochemistry of propargylic substitution was still unknown. At the outset of these studies we envisioned the Lewis acid promoted alkylation reaction would pass through the same cation that was preformed in the earlier investigations of Nicholas. In order to gain further understanding of the alkylation reaction, we have carried out spectroscopic studies of the cationic salts that we suspected as reaction intermediates. We have now determined that the stereochemical outcome of reactions

(11) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, *12*, 3475.
(12) (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.
(13) Seyferth, D.; Wehman, A. T. *J. Am. Chem. Soc.* **1970**, *92*, 5521.
(14) For a detailed discussion of the factors that influence the geometry in dinuclear transition-metal acetylene complexes, see ref 3a.
(15) (a) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6274. (b) Schilling, B. E. R.; Hoffmann, R. *Ibid.* **1979**, *101*, 3456.
(16) Edidin, R. T.; Norton, J.; Mislow, K. *Organometallics* **1982**, *1*, 561.
(17) The value of $\Delta G^{\neq}$ in ref 10a was reported incorrectly. We thank Professor Nicholas for a helpful exchange of information relevant to this issue. Activation energies were determined by use of the Eyring equation for site exchange, see: Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*: Brookes/Cole: Montery, 1985; p 200.

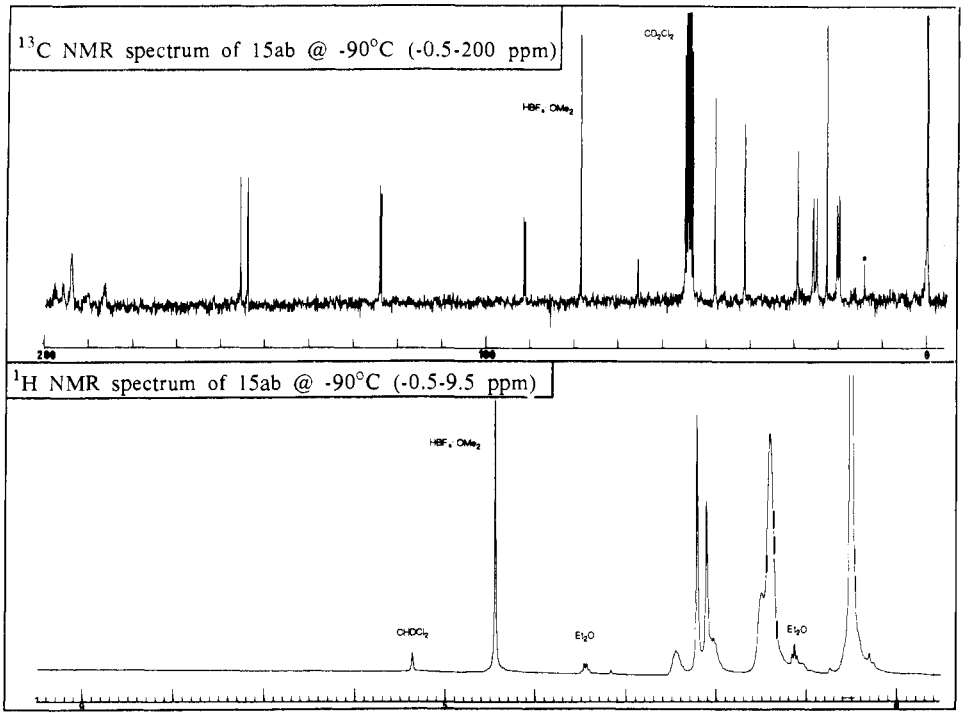
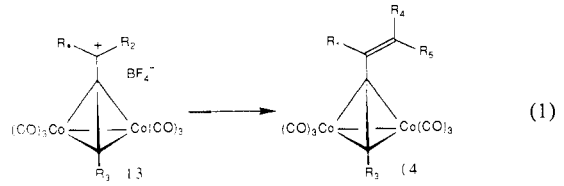


Figure 2. ^{13}C and ^{1}H NMR spectra of **15ab** at ca. −90 °C.

of chiral, nonracemic ether complexes and nucleophiles are in complete accord with the intermediacy of cobalt cations along the reaction coordinate. These new data provide a basis for speculation on the origins of the reaction diastereoselection (relative face selectivity) and stereoselection at the progargylic site.

Results

^{1}H and ^{13}C NMR experiments were employed in order to investigate the influence of cluster substituents on the dynamics of the cobalt cations. Diastereotopic groups were used to distinguish fluxional processes available to the cations including syn–anti isomerization, suprafacial migration, and antarafacial migration. These studies required the formation of isolable, stable cations of known purity. The procedure developed by Nicholas involves the treatment of complexed propargylic alcohols with tetrafluoroboric acid in propionic anhydride.[10b] Upon dilution with a large excess of diethyl ether, the tetrafluoroborate salt precipitates. This procedure, though effective for several substrates, proved inadequate for compounds that were prone to eliminate (eq 1) and resulted in the formation of propionic anhydride derived impurities that could not be removed despite several purification attempts.



(1)

Modifications of this procedure were undertaken in order to minimize these problems. Molecular sieves (4A) were added to a solution of a cobalt-complexed propargylic alcohol (or methyl ether) in diethyl ether containing a slight excess of tetrafluoroboric acid dimethyl ether complex. Reactions that utilized the methyl ether were considerably slower than those of the corresponding alcohol. The procedure with molecular sieves in an ethereal solvent has a drawback; at the low temperatures required to preserve more sensitive cations, the tetrafluoroboric acid–ether complex is insoluble and precipitates from the solution without noticable reaction. In these cases, trifluoroacetic anhydride was used as the dehydrating agent, either in an ether-based solvent or as the primary solvent followed by ether dilution to precipitate the cation. After purification, ^{13}C NMR showed no sign of residual trifluoroacetic anhydride derived byproducts.

Cation formation resulted in products that exhibited a range of thermal stabilities that were dependent on the substitution pattern at the propargylic position. The principal competing pathway in the temperature range of interest (−90 to 0 °C) was elimination of a proton to provide an alkenyl substituted cobalt complex (eq 1). At higher temperatures other degradative pathways are involved with include acetylene decomplexation. Primary cations (**13**: $R_1 = R_2 = H$) cannot eliminate; consequently, we found these systems are stable for long periods of time even at room temperature. Tertiary cations (**13**: $R_1 = R_2 =$ alkyl) are stable below −30 °C. Variations in stability of secondary cations (**13**: $R_1 = H$, $R_2 =$ alkyl) reflect the degree of substitution at the incipient olefin. The facile formation of the trisubstituted olefin derived from one cation (**13**: $R_1 = H$, $R_2 = i$-Pr) prevented the isolation of this particular tetrafluoroborate salt under a variety of conditions. In contrast, the cation (**13**: $R_1 = H$, $R_2 =$ Me) is stable to elimination up to −20 °C. In between these extremes is the case of the cation (**13**: $R_1 = H$, $R_2 =$ Et) which is isolated only with great difficulty and is unstable above −50 °C. The cation (**13**: $R_1 = H$, $R_2 = t$-Bu) is stable even at room temperature. The stability of these salts was not noticeably affected by the nature of the R_3 substituent; hydrogen, phenyl, and silyl derivatives behaved similarly.

Certain aspects of the low-temperature NMR procedure warrant discussion. In order to maintain useful concentrations of the cobalt cations for the purpose of NMR experiments, polar solvents such as sulfur dioxide or *d*-trifluoroacetic acid are required. In addition to solvating properties, it is also useful to have a deuterium lock for the purpose of shimming. Unfortunately, commonly employed halocarbons do not sufficiently solubilize the cation and some mixtures of polar solvents and deuteriated halocarbons become immiscible at low temperature. A 1:1 mixture of sulfur dioxide and deuteriomethylene chloride satisfies the criteria of cation solubilization, miscibility at low temperature, and the provision of a deuterium lock, in addition to their effect of extending the freezing points of the individual solvents. The SO_2 was distilled through H_2SO_4 and passed over P_2O_5 to remove interfering impurities and was condensed directly into the NMR tube prior to sealing.

Observing the precautions and procedural modifications outlined above and in the Experimental Section, the NMR spectra of the

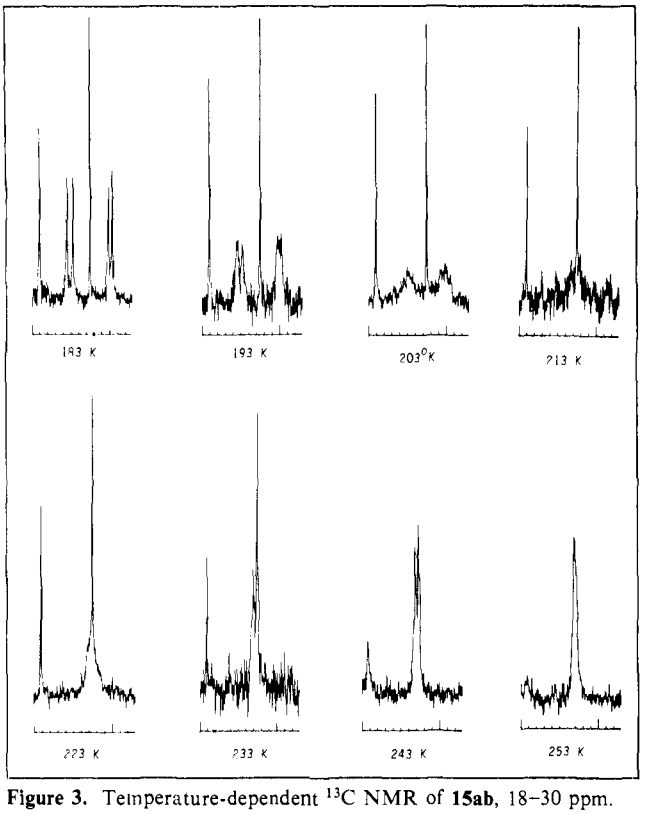


Figure 3. Temperature-dependent ^{13}C NMR of **15ab**, 18–30 ppm.

cobalt cations are free of major contaminants with the exception of small amounts of diethyl ether and tetrafluoroboric acid. A representative ^1H and ^{13}C NMR spectrum of the cation **15** (**13**: R_1 = Me, R_2 = *i*-Pr, R_3 = $SiMe_3$) is provided in Figure 2. The presence of two isomers (syn and anti) is readily discerned. Concentration limitations are imposed by the presence of cobalt derived paramagnetic impurities. To shim effectively and achieve the desired resolution, the concentration must be kept low (ca. 0.03 M). This constraint applies to all dicobalt hexacarbonyl acetylene systems; it is not unique to the cationic species.

The investigation of fluxional properties by ^{13}C NMR offered several advantages over the ^1H NMR experiment. The coalescence temperature is related to the frequency difference of the exchanging environments. Since carbon resonance differences are greater than those of proton, the exchange phenomena are easier to study by ^{13}C NMR. The ^{13}C frequency range is 6X that of ^1H and the ^{13}C signals are sharper and singlets. In fact, resolution of the diastereotopic methyl groups (vide infra) was possible only in the carbon spectrum. The main drawback to the ^{13}C NMR method concerns the length of acquisition time required to produce a high signal/noise ratio, a limitation compounded by the need for low concentrations.

The low-temperature (−90 °C) spectra of **15ab** are in accord with the existence of two isomers (syn/anti = 1.3/1) with bent (asymmetric) structures as two pair of diastereotopic methyl signals are observed. That the major isomer has the syn stereochemistry was ascertained by NOEDS experiments. For example, irradiation (ca. −90 °C) of the trimethylsilyl group of the major isomer was accompanied by enhancement of the isopropyl methine (6%) and methyl groups (1%) of the major isomer only. Similar behavior was observed in a related cation (**13**: R_1 = Me, R_2 = *i*-Pr, R_3 = H) which exists as a 1.1:1 ratio of syn and anti isomers. Two distinct fluxional processes were observed as the solutions were warmed by 10 °C increments (Figure 3). A lower energy process interconverts the diastereotopic methyl groups of each isomer. As this is the only interconversion that is evident, this process represents an enantiomerization of **15a** and **15b**. A coalescence temperature of ca. T_c = −45 °C was determined which corresponds to an activation barrier of $\Delta G^{\ddagger}$ = 10.1 kcal/mol for enantiomerization of each cobalt cation isomer at this temperature. The analogous rotational barrier in the Seyferth cation **11** is 10.5

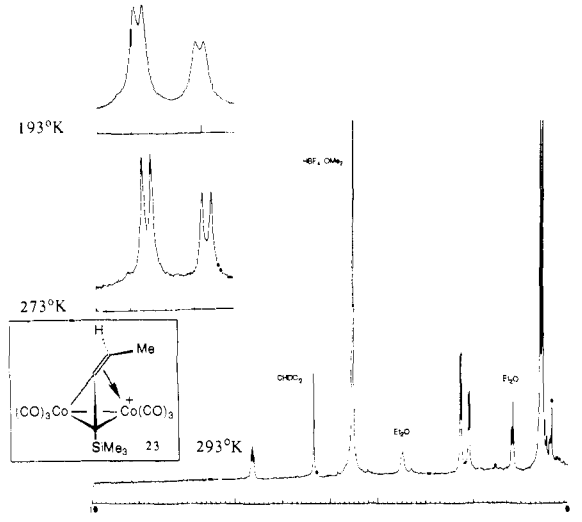
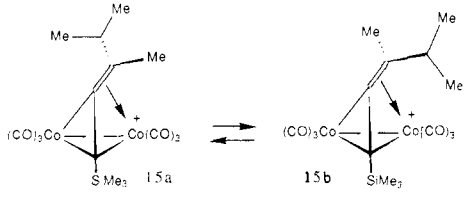


Figure 4. ^1H NMR spectrum of **23** (0.0–10.0 ppm; insert 2.0–2.4 ppm).

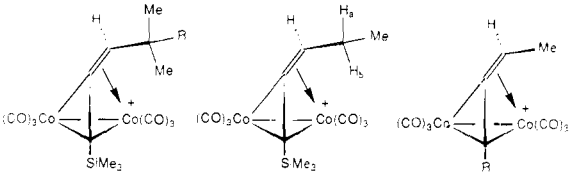
kcal/mol with a coalescence temperature of −52 °C.

A second fluxional process that results in the interconversion of syn and anti isomers (**15a** ⇔ **15b**) was detected at higher temperatures in both the proton and carbon NMR spectra.



Coalescence was observed at ca. −16 °C which corresponds to an activation barrier of $\Delta G^{\ddagger}$ = 12.9 kcal/mol at this temperature. The data derived from carbon and proton spectra are in agreement within the uncertainties of the experiment. Spin saturation transfer experiments confirmed that site exchange was taking place. These experiments entailed irradiating a particular resonance and observing a decreased intensity of its complement relative to the full spectrum at a temperature below that where complements exchange on the NMR time scale (i.e., $T_{exp} < T_c$). NOEDS experiments also displayed a temperature dependence in accord with an interconversion of isomers above −16 °C (e.g., irradiation (at $T_{exp} \cong T_c$) of the trimethylsilyl group of the major isomer enhances the isopropyl methine and methyl signals of *both* isomers **15a** and **15b**). Other tertiary cations exhibited similar temperature-dependent behavior.

Chemical and spectroscopic limitations prevented a similar study of the lower energy (enantiomerization) process in several secondary cations (**13**: R_1 = H, R_2 = alkyl). Structure **16** is the direct analogue of the previously described tertiary cation. This compound undergoes facile elimination; even with formation at low temperature, **16** was difficult to isolate and characterize. Compounds **17–19** also failed to provide useful information since



16 R = H
17 R = Ph
18 R = Et
19 R = vinyl

20

21 R = H (s/a = 3.6:1)
22 R = Me (s/a = 3.0:1)
23 R = $SiMe_3$ (s/a = 1.4:1)

the diastereotopic methyl groups were not sufficiently resolved. Likewise, the diastereotopic hydrogens (H_a, H_b) in **20** exhibited overlapping resonances in the ^1H NMR. Information concerning isomer ratios (syn/anti) and isomer interconversion dynamics could

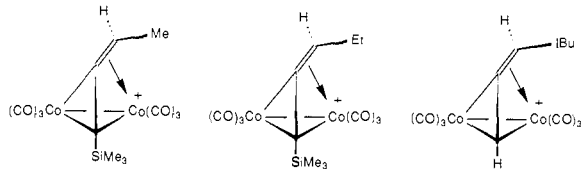


Figure 5.

be acquired with several different secondary cations. In each instance, an increase in the activation barrier to syn–anti isomerization, relative to tertiary cations, was observed. Coalescence of signals or peak broadening (e.g., the methyl resonance of the syn and anti isomers of **23**, Figure 4) did not occur at or below 20 °C. Since degradation of the cations **23** occurs within an hour at room temperature and within minutes at elevated temperatures, an accurate activation barrier could not be obtained. A spin saturation transfer experiment provided evidence that exchange takes place at room temperature. Accordingly, we conclude that at room temperature the exchange rate is slower than the NMR time scale. The absence of peak broadening at 20 °C provides a limit of $\Delta G^{\ddagger} \geq 14.7$ kcal/mol. This behavior is in contrast to the tertiary cations that exhibit a coalescence temperature of ca. −20 °C.

Syn–anti isomer ratios were determined for secondary cations **21–25** by integration of like resonances in the ^{1}H NMR spectra. Structural assignments were based on NOEDS experiments. We were particularly interested in assessing the steric demand of a cobalt tricarbonyl unit relative to the neighboring carbido substituent as viewed from the perspective of the alkylidene ligand. Cations **21–23** differ only in the identity of the carbido substituent. The data indicate the methyl group of the ethylidene ligand has a small destabilizing steric interaction with the cobalt tricarbonyl unit that is comparable to that provided by a trimethylsilyl group at the carbido carbon. In Figure 5 the effect of varying the alkylidene substituent is evident. A substantial steric interaction is uncovered in the form of cation **25**, which exists as a single, syn-diastereomer.

Discussion

The temperature-dependent changes in the NMR spectra of cobalt cations can be explained by the dynamic behavior depicted in Figure 6. The lower energy fluxional process observed with cation **15** resulted in the interconversion of diastereotopic groups only (Ra and Rb in **26–29**). This enantiomerization (**26** ⇔ **27** and **28** ⇔ **29**) results from the antarafacial migration of the alkylidene ligand from the one cobalt tricarbonyl unit to the other. The higher energy fluxional process interconverts the syn and anti isomers and can take place by 180° rotation of the alkylidene ligand (**26** ⇔ **29** and **27** ⇔ **28**) or suprafacial migration (120° rotation with migration; **26** ⇔ **28** and **27** ⇔ **29**). The transition state for the enantiomerization may resemble the upright structure **30** which is capable of maintaining partial delocalization of the carbon p-orbital into hybrid d-orbitals on the neighboring cobalt atoms.[15] The increased energetic requirements for achieving diastereomerization (syn–anti interconversion) may be associated with the requirement for achieving the rotated upright structure **31** which localizes charge on carbon.

The increased activation barrier to diasteromerization for secondary cations (**26–29**: R_1 = H) relative to tertiary cations (R_1 = alkyl) is consistent with the localized transition-state structure **31** and with the view of the salts as alkylidene complexed *cobalt* cations. Although we were not successful in attempts to observe the enantiomerization of secondary cations (vide supra) we speculate on the existence of an increased value of $\Delta G^{\ddagger}$ for this process as well. The transition state for enantiomerization (**30**) likewise results in substantial localization of charge on carbon and should be slower for secondary systems due to their increased electron demand. The isotopically labeled primary cation (C= CHD (vinylidene) ligand) might be expected to exhibit even greater decrease in dynamic behavior.

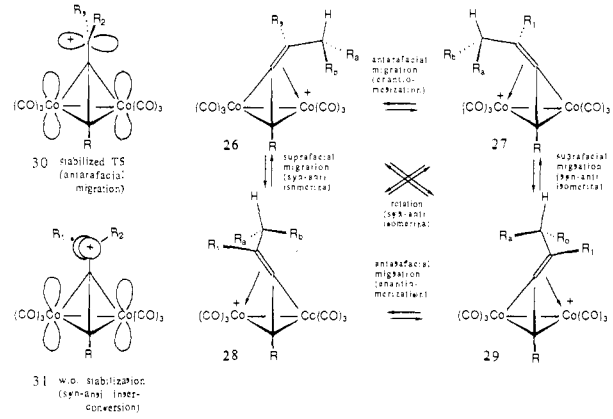


Figure 6.

The antarafacial migration of the *alkylidene* ligands is reminiscent of the dynamic behavior exhibited by Casey's μ-alkenyl diiron species **32** ⇔ **33**.[18] In these systems the *alkenyl* group was observed to migrate in a stereospecific manner (antarafacial) between the iron centers. This behavior was rationalized by the stabilized transition state **34** which allows smooth transition between **32** and **33** and results in interaction of the electron rich hybrid iron atom d-orbitals with the p-orbital of the migrating carbon. An analogous diastereomerization (via the higher energy transition state structure **35**), which would result in a *cis*-alkenyl ligand, was not observed.

The dynamic behavior of cobalt cations, especially secondary systems, has relevance to the stereochemistry of the propargylic substitution reaction. If the Lewis acid mediated alkylation reaction (Table I) passed through a static cobalt cation (2,3), retention of stereochemistry would result. Indeed, this is the normal outcome of alkylation reactions that proceed through mononuclear metal stabilized carbocation intermediates such as the benylic substitution reaction of chromium arene tricarbonyl complexes (eq. 3).[19] Notice, however, that antarafacial migration and rotation processes (Figure 6) result in exposure of the opposite enantiotopic face for attack by a nucleophile. Only the suprafacial migration preserves exposure of the kinetically formed enantioface of the ethylidene ligand. Hence, the relative rate of alkylation and, e.g., enantiomerization will determine the degree of stereospecificity in the propargylic substitution reaction. We have examined several chiral cobalt complexes and determined that the intermolecular reaction of these ether complexes with allyl trimethylsilane proceeds with racemization. We interpret this result as providing evidence for the cobalt cation as an intermediate and that antarafacial migration (enantiomerization) of the cation is fast relative to the rate of alkylation in this particular reaction.

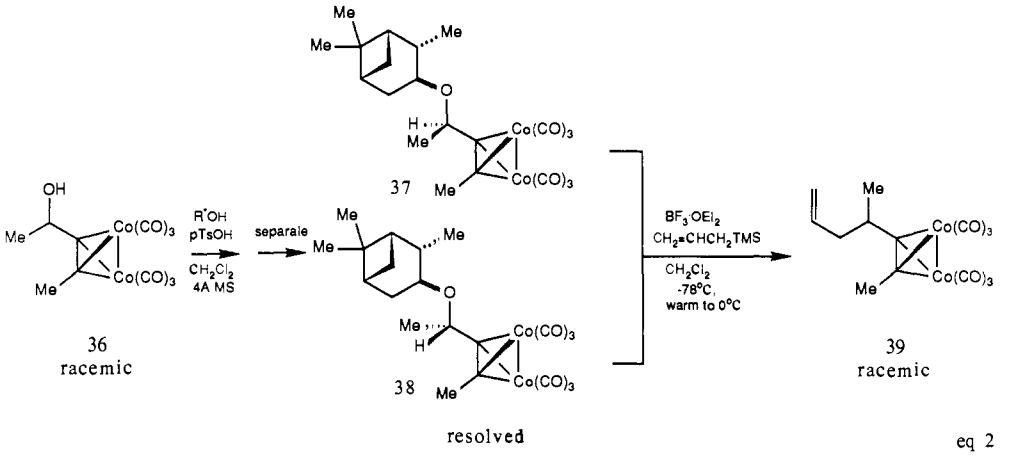
The allylation of **36** is demonstrative (eq 2). The racemic complex **36** was treated with (+)-isopinocampheol and a catalytic quantity of *p*-toluenesulfonic acid in the presence of 4 Å molecular sieves. The isopinocamphyl ethers **37** and **38** were produced in a 1:1 ratio and were separated by high-pressure liquid chromatography (HPLC). Treatment of the resolved ethers **37** and **38** with allyltrimethylsilane and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 (−78 °C → 0 °C) resulted, in each case, in the formation of racemic **39**.

The ability of the cobalt cation to enantiomerize under the conditions of the intermolecular alkylation reaction, in combination with the intrinsic relative face selectivity of the reaction (Table I), suggests that a double stereodifferentiating process may be achieved *with kinetic resolution of a racemizing cation* if a suitable chiral, nonracemic nucleophile can be found. To explore this

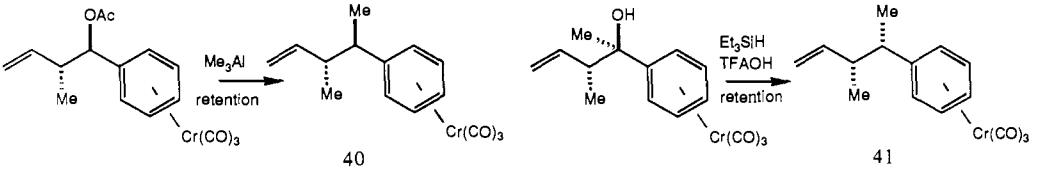
(18) Casey, C. P.; Mesnaros, M. W.; Fagan, P. S.; Bly, R. K.; Coborn, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 4053.

(19) (a) Uemura, M.; Minami, T.; Isobe, K.; Kobayashi, T.; Hayashi, Y. *Tetrahedron Lett.* **1986**, *27*, 967. (b) For a discussion of the fluxional properties of π-allyl palladium complexes, see: Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033. Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046.

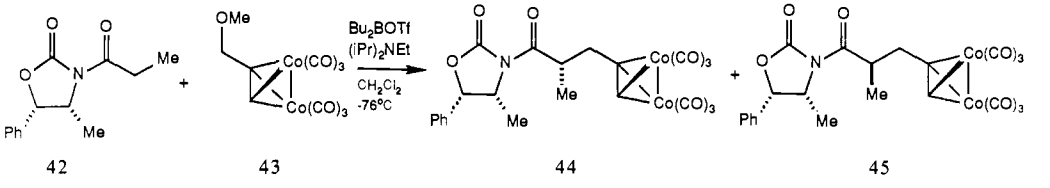
Scheme I



eq 2

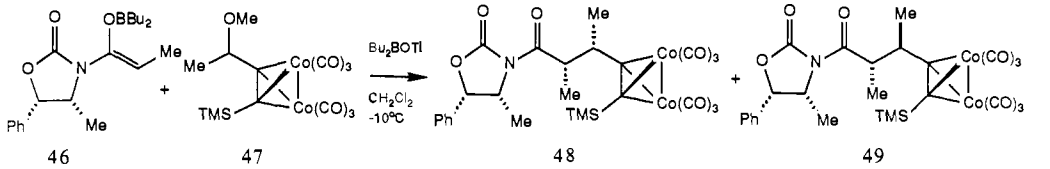


eq 3



Bu_2B enolate 35 : 1
Lewis acid=Bu_2OTf
Et_3Si enolate 2.5 : 1
Lewis acid=BF_3OEt_2

eq 4



eq 5

possibility, we have examined the utility of the boron enolates of chiral propionimides developed by Evans and his co-workers as the nucleophilic partner in the alkylation reaction.[20]

The extensive investigations into the facial selectivities exhibited by the propionimide metal enolates provided the expectation that boron derivatives would provide optimal results. A comparison of the selectivities exhibited by silicon and boron enolates in the alkylation reactions with cobalt complexes of propargylic ethers is consistent with these earlier studies (eq 4). A 1:1 mixture of the chiral boron enolate **46** and the achiral ether complex **43** was treated with 1.2 equiv of dibutylboron triflate and resulted in the formation of a 35:1 ratio of **44**:**45** in 85% yield. A result relevant to *intramolecular* alkylation reactions is that the enolate can be generated in situ: treatment of the propionimide **42** with **43** and 2.2 equiv of dibutylboron triflate and 1.1 equiv of Hunigs base resulted in a comparable reaction outcome. The facial selectivity exhibited by **46** was expected from results of Evans on the reaction of **46** with the noncoordinating electrophile Br_2.[21,22] The origins of this selectivity have been discussed elsewhere.

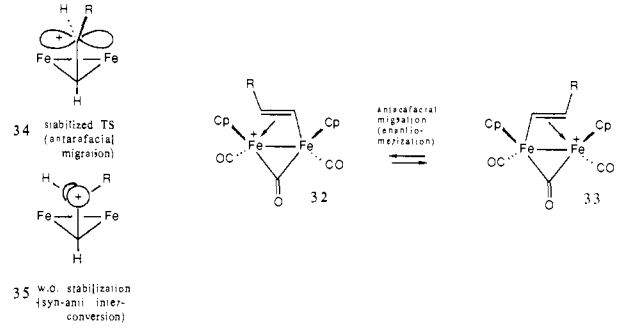


Figure 7.

(20) Evans, D. A.; Ennir, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737.

(21) Evans, D. A.; Ellman, J. A.; Dorow, R. L. *Tetrahedron Lett.* **1987**, *28*, 1123.

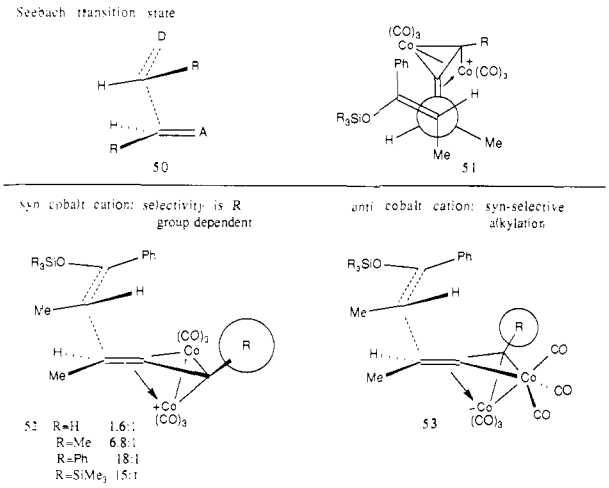
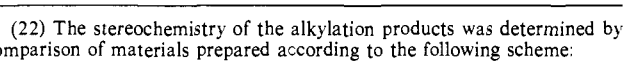


Figure 8.

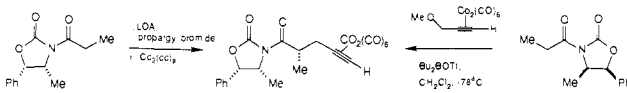
Having established the utility of the Evans' enolate in the alkylation of achiral cobalt cations, our attention was next turned to a reaction with a chiral cation. Treatment of the boron enolate **46** and the methoxyethyl-substituted cobalt complex (±)-**47** (1.8:1 ratio) with 1.2 equiv of dibutylboron triflate in CH_2Cl_2 at −10 °C afforded an 80% yield of a 12:1 mixture of **48** and **49** (eq 5).[23] In this example, the in situ generation of the boron enolate or lowering of the reaction temperature resulted in the formation of considerable amounts of the elimination product (**14**: R_1 = R_4 = R_5 = H, R_3 = $SiMe_3$). Interestingly, prior generation of the cobalt cation tetrafluoroborate salt, according to the Nicholas procedure, and subsequent reaction with **46** resulted in conversion to the elimination product **14** without any alkylation.

The stereochemical outcome of this double stereodifferentiating reaction is consistent with the diasteroselection observed previously (Table I) in the reaction of achiral nucleophiles (i.e., syn:anti = 12:1). The issue of substitution stereochemistry at the propargylic center deserves some comment since the racemic complex (1:1 mixture of isomers at the propargyl center) was converted into a 12:1 mixture in the product and in a yield (80%) that rules out the possibility of a "simple" kinetic resolution. Indeed, the yield and stereochemistry of products are strongly suggestive of the intermediacy of cations that (1) racemize at a rate that is fast relative to alkylation *and* (2) react with different rates (kinetic resolution) with the chiral nucleophile. A stereochemical model that is consistent with these results and those obtained from our studies on the alkylation of cobalt cations with achiral nucleophiles is presented in Figure 8.

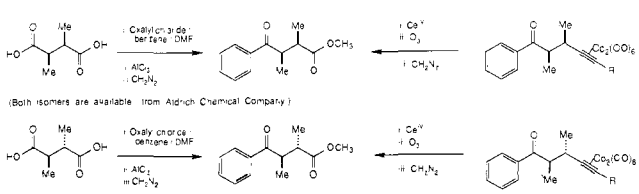
The stereochemical analysis is complicated by the fluxional behavior of the cation and the absence of a quantitative understanding of relative rates. Nevertheless, an a posteriori analysis



(22) The stereochemistry of the alkylation products was determined by comparison of materials prepared according to the following scheme:



(23) The stereochemistry of the alkylation products in Table I was determined by comparison of materials prepared according to the following scheme:



A similar correlation confirmed the stereochemistry of **48** and **49**.

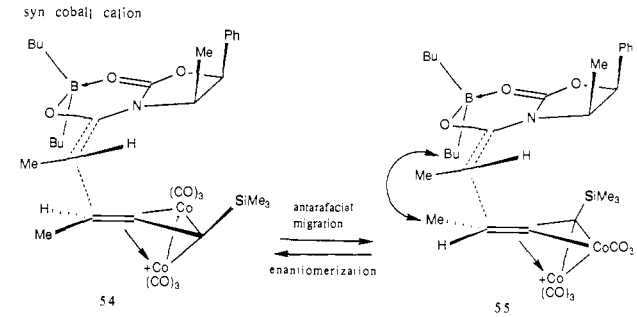


Figure 9.

of the two transition states which stagger the reacting trigonal center (antiperiplanar and synclinal) has been performed. The model that is most successful in providing a rationale for the stereochemical features of the reaction reported herein entails a synclinal relationship of the donor and acceptor II systems. Seebach has presented an analysis of the general properties of synclinal transition-state structures that provide an inherent stabilization relative to the antiperiplanar structures (see **50**).[24] The same rationale can be used to explain our results; however, the unusual steric demands of the cobalt electrophile reverse the normal sense of relative face selection (see **51**).

In Figure 8, the synclinal transition states for the reaction of the (*Z*)-enol ether of propiophenone with the syn (**52**) and anti (**53**) cobalt cations (that place the hydrogen of the ethylidene ligand in the most sterically demanding position) are presented. Whereas the anti-cobalt cation is expected to give rise to the syn-alkylation product, the stereochemical outcome of the reaction of the syn-cobalt cation is expected to be R group dependent. In accord with our observations, an increase in the size of the R group is expected to favor formation of the syn-alkylation product. The reversed sense of relative face selectivity in this reaction (*lk*) as compared to those considered by Seebach (*ul*) can be traced to the unusual topographical features of the cobalt cation: the A group (**50**) in **52** and **53** exhibits considerable steric demand.

The stereochemistry of the reaction of the Evans' chiral enolate with the racemizing cobalt cation can be accounted for as well (Figure 9). The chiral nucleophile can react with four stereoisomeric cobalt cations. To illustrate, consider the synclinal transition states of the enantiomeric syn-cobalt cations, **54** and **55**. Of course, the boron enolate exhibits the normal diastereotopic face selectivity.[21] The reaction of **46** with the syn-cation **54** is expected to be fast and leads to the normal syn-alkylation product. Antarafacial migration results in the enantiomerization of **54** into its antipode **55**. Reaction of this "mismatched" pair via the synclinal transition state would result in the anti-alkylation product but is expected to be slow due to steric interference not present in the "matched" pair (**54** and **46**). Of course, other transition-state structures (e.g., alternative synclinal transition states) are available to **55**, but each is expected to be less favorable than the one indicated. Since cations **54** and **55** undergo interconversion under the reaction conditions *and* react with different rates, the racemic pair of ethers **47** can be converted into a 12:1 mixture of diastereomers **48** and **49**. Further, the stereochemical model allows predictions to be made concerning other chiral nucleophile–racemic electrophile combinations. Of course, the model is relevant to reactions that involve an alkylation rate that is slow relative to the rate of cation stereomutation. The spectroscopic studies provide a qualitative estimate of the energetics that are involved in the latter process. Since the alkylation reaction is bimolecular and the fluxional processes are unimolecular, intramolecular alkylations present an interesting situation and may proceed in a stereospecific manner. The same result may be obtained by modification of the cation structure since substituent changes have now been demonstrated to alter the kinetics of the isomerization processes. Investigations along these avenues are underway.

(24) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413.

Experimental Section

General Methods. ^1H magnetic resonance spectra were obtained on a Bruker WM-250 (250 MHz) or WM-500 (500 or 490 MHz) spectrometer and are reported in parts per million with $CDCl_3$ (7.27) or CD_2Cl_2 (5.35) as an internal standard on a δ scale. Data are reported in the following sequence: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and integration. ^1H decoupled ^{13}C NMR spectra were recorded on a Bruker WM-250 (62.9 MHz) instrument and are reported in parts per million with $CDCl_3$ (77.2) or CD_2Cl_2 (53.8) as an internal standard on a δ scale. CD_2Cl_2 and $CDCl_3$ were dried over activated 4A molecules sieves and distilled under N_2 prior to use. SO_2 was condensed into a reaction flask containing concentrated H_2SO_4, distilled through a plug of P_2O_5, and condensed directly into the NMR tube prior to sealing. NMR samples were prepared and sealed on a vacuum line prior to analysis.

NOE experiments were performed on a Bruker WM250 instrument equipped with an Aspect 2000 computer. The Bruker program 12.5 (NOE difference, direct A-B FID accumulation) was used with the following parameters: relaxation delay of 10 s, NOE generation for 3 s (ca. 2-3X T1), repetitive cycling with accumulation of 8 scans on and off resonance and two dummy scans to assure saturation. Homogated irradiation was used to eliminate spurious noise with irradiation power of less than 0.5 W. Exponential multiplication of 2 Hz was used for data processing. Enhancements are reported in percent relative to the irradiation signal.

Infrared spectra were recorded on a Nicolet 5 SX FT-IR spectrometer (ν_{max} in cm^{-1}). Bands are characterized as strong (s), medium (m), and weak (w). Reactions were monitored by analytical thin-layer chromatographic methods (TLC) with use of E. Merck silica gel 60F glass plates (0.25 mm). Flash chromatography was carried out with the use of E. Merck silica gel 60 (230–400 mesh). High-performance liquid chromatography (HPLC) was performed with a Waters 510 liquid chromatograph equiped with a μ-porasil column. Diastereomer ratios were determined by (a) weight measurements of isolated materials, (b) NMR integration, or (c) integration of HPLC traces (assuming equivalent response factors for diastereomers).

Air-sensitive compounds were prepared and transfered with standard Schlenk techniques under argon. Diethyl ether, THF, and toluene were distilled from benzophenone ketyl solutions. CH_2Cl_2 and diisopropylethylamine were distilled from CaH_2 and trifluoroacetic acid was dried over P_2O_5 prior to distillation. Other reagents were purified by standard procedures unless otherwise indicated; all distillations were performed under an argon atmosphere.

3,4-Dimethyl-1-(trimethylsilyl)-1-pentyn-3-ol–Dicobalt Hexacarbonyl Complex (Alcohol Precursor of 15ab). Representative Formation of Cobalt-Complexed Propargyl Alcohols. $Co_2(CO)_8$ (3.11 g, 9.10 mmol) was transferred under nitrogen to a dry, preweighed 100-mL round-bottomed flask. Et_2O (50 mL) was introduced via syringe followed by an ether solution (5 mL) of 3,4-dimethyl-1-(trimethylsilyl)-1-pentyn-3-ol (2.78 g, 15.1 mmol). The solution was stirred for a 0.5 h until CO evolution was no longer visible. The solvent was removed by aspirator vacuum and the residue subjected to flash chromatography. Elution, first with straight hexanes to remove cobalt derived impurities, followed by 20/1 hexane/ethylacetate afforded 3.89 g (91%, 8.28 mmol) of the desired cobalt complex: ^1H NMR ($CDCl_3$, 250 MHz) δ 0.35 (s, 9 H), 1.00 and 1.15 (diastereotopic Me groups, d, J = 6.7 Hz, 3 H), 1.38 (s, 3 H), 1.65 (exchanges with D_2O, s, 1 H), 1.79 (q, J = 6.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 187–189 (br), 40.3, 25.6, 19.1, 17.8, 1.6 (remaining resonances not discernable); IR (film) 2967 (m), 2085 (s), 2060–1990 (br s), 1574 (s), 1250 (s), 839 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{20}Co_2O_7Si$: C, 40.87; H, 4.29. Found: C, 41.13; H, 4.19.

1-Butyn-3-ol–Dicobalt Hexacarbonyl Complex (Alcohol Precursor of 21). The complex was similarly prepared from 1-butyn-3-ol in 84% yield: ^1H NMR ($CDCl_3$, 250 MHz) δ 1.52 (d, J = 6.3 Hz, 3 H), 1.85 (d, J = 5.7 Hz, 1 H), 5.98 (d of q, J = 5.8, 6.3 Hz, 1 H), 6.07 (s, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 196–200 (br), 101.0, 71.5, 68.6, 26.0; IR (film) 3420 (br w), 2982 (w), 2096 (s), 2060–2015 (br s), 1513 (w), 1449 (w), 1369 (w), 1302 (w), 1105 (w), 872 (w) cm^{-1}. Anal. Calcd for $C_{10}H_6Co_2O_7$: C, 33.74; H, 1.70. Found: C, 33.96; H, 1.66.

Representative Alkylation of a Cobalt Complex with (*Z*)-1-Phenyl-1-(trimethylsiloxy)propene. A 15-mL flask was charged with 2-methoxy-3-pentyne–dicobalt hexacarbonyl complex (61.0 mg, 0.159 mmol), (*Z*)-1-phenyl-1-(trimethylsiloxy)propene (39 mg, 0.189 mmol), and 1.6 mL of CH_2Cl_2 and cooled to −78 °C (CO_2/acetone bath). Freshly distilled (CaH_2) $BF_3{\cdot}OEt_2$ (0.230 mL, 1.89 mmol, 10 equiv) was added and the solution was stirred at −78 °C for 3 h and then slowly warmed to room temperature. The reaction was quenched by the addition of saturated $NaHCO_3$ and ether. The organic layer was washed with brine and dried over $MgSO_4$, and the solvent was removed by rotary evaporation. Flash chromatography (hexanes, then 20/1 hexane/ethyl acetate) gave 64.4 mg (0.146 mmol, 92%) of alkylated product. Analysis of the crude NMR resulted in the determination of a diastereomeric ratio of 6.8:1. The separation of diastereomers was achieved by HPLC.

Major: ^1H NMR ($CDCl_3$, 250 MHz) δ 1.27 (d, J = 4.0 Hz, 3 H), 1.32 (d, J = 7 Hz, 3 H), 2.47 (s, 3 H), 3.60 (m, 2 H), 7.65–7.60 (m, 3 H), 7.65–8.05 (m, 2 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 202, 200 (br), 135, 133, 128.8, 128.3, 47, 38, 22, 19, 15; IR (film) 2974 (w), 2086 (s), 2043 (s), 2012 (s, br), 1083 (m), 1448 (m), 1206 (m) cm^{-1}. Minor ^1H NMR ($CDCl_3$, 250 MHz) δ 8.95–9.0 (m, 2 H), 7.48–7.64 (m, 3 H), 3.42 (m, 2 H), 2.77 (s, 3 H), 1.32 (d, J = 6.4 Hz, 3 H), 1.27 (d, J = 6.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 203.3, 136.7, 133.3, 128.8, 128.3, 48.0, 40.3, 22.3, 22.1, 17.7; IR (film) 2975 (w), 2086 (s), 2043 (s), 2012 (s, br), 1683 (m), 1448 (w), 1201 (w) cm^{-1}.

Determination of the Stereochemistry of the Alkylation Products of Table I. (A) Representative Ozonolysis of Acetylenes: Ozonolysis of 2(*R*,*S*)-3(*S*,*R*)-Dimethyl-4-alkynyl-5-(trimethylsilyl)valerophenone. The acetylene (12.7 mg, 0.049 mmol), prepared according to the literature procedure,[13] was dissolved in 1 mL of glacial acetic acid and 0.2 mL of ethyl acetate and the solution was cooled to 0 °C. Ozone was bubbled through until the reaction was judged complete by TLC (5 min). The solution was purged with nitrogen and then the solvent was removed at reduced pressure. Flash chromatography (2/1 hexane/ethyl acetate) gave 7.5 mg of the acid (78%): ^1H NMR ($CDCl_3$, 250 MHz) δ 7.95–8.0 (m, 2 H), 7.27–7.44 (m, 3 H), 3.76 (q, J = 7.6 Hz, 1 H), 3.00 (q, J = 7.6 Hz, 1 H), 1.26 (d, J = 7.4 Hz, 3 H), 1.19 (d, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 203.1, 181.5, 135.8, 133.0, 128.6, 128.4, 42.9, 41.3, 14.38 13.7; IR (film) 3000 (v, br, m), 1687 (s), 1703 (sh), 1454 (m), 1425 (m), 1327 (m), 1292 (s), 1213 (w), 1179 (w), 707 (s); MS (EI, 20 eV), m/e 206 (m^+, 2.9), 188 (1.1), 134 (1.7), 123 (23.2), 105 (100), 77 (17.6).

(B) Friedel–Crafts Acylation of Benzene with *meso* (or D,L)-2,3-Dimethylsuccinic Acid. Oxalyl chloride (17 μL, 0.202 mmol) was added to a suspension of *meso*-2,3-dimethylsuccinic acid (Aldrich Chemical Co., 24.7 mg, 0.169 mmol) in 1 mL of benzene. DMF (2 μL) was added and the reaction was allowed to stir at room temperature until all of the solid dissolved (3 h). Aluminum chloride (68 mg, 0.151 mmol) was then added, and the reaction was allowed to stir overnight. The solvent was diluted with 15 mL of ether and then the reaction was carefully quenched with water. The organic phase was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Flash chromatography (2/1 hexane/ethyl acetate) gave 31 mg (0.15 mmol, 89%) of a product which was not identical with that derived from decomplexation and ozonolysis of the major compound of the alkylation reaction in Table I. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.95–8.0 (m, 2 H), 7.48–7.61 (m, 3 H), 3.76 (qd, J = 7.0, 8.6 Hz, 1 H), 3.00 (qd, J = 7.0, 8.7 Hz, 1 H), 1.28 (d, J = 7.0 Hz, 3 H) 1.22 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 202.8, 181.1, 136.4, 133.4, 128.8, 128.4, 43.4, 42.4, 16.5, 16.0. Similarly, acylation of benzene with (D,L)-2,3-dimethyl succinic acid gave material that was identical with that derived from decomplexation and ozonolysis of the major compound of the alkylation reaction in Table I.

(4*R*,5*S*)-3-[(2*S*)-1-Oxo-2-methyl-4-pentynyl]-4-methyl-5-phenyl-2-oxazolidinone–Dicobalt Hexacarbonyl Complex (44). (*R*,5*S*)-3-Propionyl-4-methyl-5-phenyl-2-oxazolidinone (47.1 mg, 0.20 mmol) and methyl propargyl ether–dicobalt hexacarbonyl complex (65.3 mg, 0.18 mmol) were added to a 10 mL round-bottomed flask. The flask and contents were evacuated and purged with argon three times. CH_2Cl_2 (3 mL) was added to the reaction flask, and the resulting solution was cooled to −78 °C (CO_2/acetone). Freshly distilled diisopropylethylamine (37.6 μL, 0.22 mmol) and dibutylboron triflate (400 μL of a 1.0 M solution in CH_2Cl_2, 0.40 mmol) were added in sequence by syringe. The bath was removed and the solution was warmed to room temperature over 30 min. The mixture was partitioned between 5 mL of pH 7 phosphate buffer and 5 mL of CH_2Cl_2. The aqueous phase was extracted with 4 portions of CH_2Cl_2 (2 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and reduced on a rotary evaporator. The ratio of major (*S*) to minor (*R*) (35:1) alkylation products was determined by integration of their respective peaks on an HPLC trace and confirmed by analysis of the ^1H NMR of the crude reaction mixture. The mixture was subjected to flash chromatography (20/1 hexane/ethyl acetate) to yield 85.9 mg (0.15 mmol, 86%) of the major diastereomer **44**: ^1H NMR ($CDCl_3$, 250 MHz) δ 0.96 (d, J = 6.6 Hz, 3 H), 1.37 (d, J = 6.9 Hz, 3 H), 2.92 (d of d, J = 15.4, 6.0 Hz, 1 H), 3.51 (d of d, J = 15.4, 7.5 Hz, 1 H), 3.99 (septet, J = 6.8 Hz, 1 H), 4.80 (quintet, J = 6.7 Hz, 1 H), 5.70 (d, J = 7.3 Hz, 1 H), 5.95 (very tight triplet, 1 H), 7.25–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 200.0 (br), 175.6, 153.0, 133.6, 129.1, 129.0, 126.0, 94.1, 79.2, 73.9, 55.3, 38.1, 40.4, 18.1, 14.8; IR (film) 2984 (w), 2359 (w), 2093 (s), 2050 (s), 2015 (s), 1786 (m), 1698 (m), 1342 (m), 1195 (m), 1121 (w) cm^{-1}. Anal. Calcd for $C_{22}H_{17}Co_2NO_7$: C,

47.42; H, 3.08. Found: C, 47.52; H, 2.83.

(4*R*,5*S*)-3-[(2*S*,3*S*)-1-Oxo-2,3-dimethyl-5-(trimethylsilyl)-4-pentynyl]-4-methyl-5-phenyl-2-oxazolidinone–Dicobalt Hexacarbonyl Complex (48). (4*R*,5*S*)-Propionyl-4-methyl-5-phenyl-2-oxazolidinone (99.7 mg, 0.43 mmol) was transferred into a flame-dried 10-mL round-bottomed flask. The flask and contents were evacuated and purged with argon. Distilled CH_2Cl_2 (2 mL) was added, and the resultant solution was cooled to 0 °C with an ice bath. Dibutylboron triflate (855 μL of a 1.0 M CH_2Cl_2 solution, 0.86 mmol) was syringed into the reaction flask, followed by the addition of freshly distilled diisopropylethylamine (74 μL, 0.43 mmol). After being stirred at 0 °C for 15 min (to assure deprotonation), the boron enolate was cooled to −78 °C (CO_2/acetone). 3-Methoxy-1-(trimethylsilyl)-1-butyne–dicobalt hexacarbonyl complex (105.7 mg, 0.24 mmol) was added as a CH_2Cl_2 solution (1.0 mL) under Ar. The low-temperature bath was replaced with an ice bath to bring the reaction temperature to 0 °C. The bath was removed and the reaction was stirred for 35 min. The reaction was then partitioned between 5 mL of pH 7 phosphate buffer and 5 mL of CH_2Cl_2. The aqueous phase was extracted with 4 portions of CH_2Cl_2 (3 mL). The organic extracts were combined, dried over $MgSO_4$, filtered, and reduced on a rotary evaporator. Diastereomer ratios (12:1) were determined by analysis of the NMR of the crude reaction mixture. Following flash chromatography (15/1 hexane/ethyl acetate), 121.2 mg of the major diastereomer was recovered (0.19 mmol, 80%). Major diastereomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.37 (s, 9 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 1.25 (d overlapping, *J* = 7.0 Hz, 6 H), 3.61 (d of q, *J* = 7.0, 8.4 Hz, 1 H), 4.08 (d of q, *J* = 7.0, 8.4 Hz, 1 H), 4.82 (quintet, *J* = 6.9 Hz, 1 H), 5.69 (d, *J* = 7.4 Hz, 1 H), 7.28–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 175.1, 152.8, 133.7, 129.1, 129.0, 126.0, 79.1, 55.1, 43.9, 39.9, 14.8, 1.3; IR (film) 2981 (m), 2086 (s), 2052–2005 (br s), 1789 (s), 1698 (s), 1456 (m), 1367 (s), 1343 (s), 1250 (s), 1197 (s), 839 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_3Si$: C, 67.19; H, 7.61. Found: C, 67.29; H, 7.81.

General Aspects of Cation Formation. In order to preserve sensitive substrates at a high purity level the following modifications of the Nicholas procedure were undertaken. A modified Schlenk apparatus attached to an NMR tube served as the reaction vessel. This system could be purged or evacuated as required. Typically, the cobalt complex was preweighed into the flame-dried system and the solvent was distilled under argon directly into the reaction flask. After the entire assemblage (including the attached NMR tube) was cooled to the desired temperature, the dehydrating agent (in the case of TFAA) and tetrafluoroboric acid were introduced via syringe. After the cation precipitated stirring was discontinued and the solid was allowed to settle. The mother liquor, which contained unreacted starting materials and elimination products, was syringed from the solid and replaced with an equivalent amount of cold, freshly distilled diethyl ether. This procedure was repeated several times to effect a colorless rinse, which indicated that the cation tetrafluoroborate salt was free of unreacted starting material, eliminated product, and solvent-based impurities. A portion of the fine suspension was transferred to the hitherto empty NMR tube. Solvent was removed from the settled solid first via syringe and then in vacuo. NMR solvents were distilled into the tube containing the purified solid, the contents were freeze–thawed (3×), and the tube was vacuum sealed.

3,4-Dimethyl-1-(trimethylsilyl)-1-pentyn-3-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (15). Representative Cation Formation from an Alcohol Precursor with 4A Molecular Sieves as the Desiccant. To a flame-dried flask equipped with a magnetic stir bar, rubber septum, vacuum sidearm and an attached NMR tube was charged 3,4-dimethyl-1-(trimethylsilyl)-1-pentyn-3-ol–dicobalt hexacarbonyl complex (127.9 mg, 0.27 mmol). The cobalt complex was filtered over silica to remove any cobalt impurities immediately prior to cation formation. An excess of activated 4A molecular sieves was added to the solid. The reaction vessel was evacuated and purged with argon three times. Et_2O (10 mL) was distilled directly into the reaction flask from benzophenone ketyl under argon. The solution was then cooled to −35 °C (CH_3CN/CO_2). Tetrafluoroboric acid–dimethyl ether complex (53 μL, 0.54 mmol) was added via gas-tight syringe, and the resulting suspension was stirred slowly at ca. −35 °C (to avoid fracture of the molecular sieves) for 15 min. The reaction mixture was then diluted with 15 mL of dry Et_2O, being careful to maintain the reaction temperature indicated above. After the solid tetrafluoroborate salt settled, the supernatent liquid was removed via syringe and replaced with an equivalent amount of fresh, cold Et_2O. After four such cycles, the supernatent was clear of ether soluble byproducts that include starting material and the result of several degradative pathways (i.e., elimination of a proton). On the final rinse the entire assembly (reaction flask, sidearm, and NMR tube) was immersed in the cold bath. The suspension was swirled and the heavier molecular sieves settled quickly. A portion of the suspended, finer solid was then transferred to the NMR tube. Solvent was removed via syringe and then by high vacuum for 2 h at the reaction temperature of −35 °C to yield a free-flowing, temperature-sensitive solid. CD_2Cl_2 (150 μL) was syringed into the NMR tube side of the reaction flask. SO_2 (150 μL), distilled from H_2SO_4 and passed through a plug of P_2O_5, was condensed into the NMR tube. The NMR sample was freeze–thawed three times and sealed under vacuum. No attempt was made to quantitate the overall yield because only a small portion was used for spectroscopic studies. Qualitatively, the yields varied between 60 and 80%. ^{1}H NMR (1/1 $CDCl_2/SO_2$ 250 MHz, −90 °C) ratio of isomers 1.3/1 [minor in brackets] δ 0.48 (s, 18 H), 1.39 (br s, 9 H), 1.48 (br s, 3 H), 2.20 (s, 3 H), [2.09 (s, 3 H)], 2.01 (m, 1 H), [2.43 (m, 1 H)]; ^{13}C NMR (1/1 CD_2Cl_2/SO_2 62.9 MHz, −90 °C) δ 186–200 (br), 155.4, [153.8], 123.9, [123.6], 91.3, [90.9], 47.9, [41.0], 22.4, [29.0], 19.6, [20.0], 24.7, [25.4], −0.5, [−0.4].

1-(Trimethylsilyl)-1-butyn-3-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (23). Similarly prepared from 1-(trimethylsilyl)-1-butyn-3-ol–dicobalt hexacarbonyl complex at −25 °C. ROH: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.33 (s, 9 H), 1.53 (d, *J* = 6.3 Hz, 3 H), 1.79 (d, *J* = 5.2 Hz, 1 H), 5.01 (d, of q, *J* = 6.3, 5.2 Hz, 1 H). Cation: ^{1}H NMR (1/1 $CD_2Cl_2OSO_2$, 250 MHz, −20 °C) ratio of isomers 1.4/1 [minor in brackets] δ 0.54 (s, 9 H), [0.59 (s, 9 H)], 2.26 (d, *J* = 6.4 Hz, 3 H), [2.09 (d, *J* = 6.6 Hz, 3 H)], 6.65 (q, *J* = 6.4 Hz, 1 H), [6.62 (q, *J* = 6.6 Hz, 1 H)].

3-Pentyn-2-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (22). Similarly prepared from 3-pentyn-2-ol dicobalt hexacarbonyl complex at −25 °C. ROH: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.52 (d, *J* = 6.3 Hz, 3 H), 1.78 (d, *J* = 5.1 Hz, 1 H), 2.68 (s, 3 H), 5.02 (d of q, *J* = 6.3, 5.1 Hz, 1 H). Cation: ^{1}H NMR (1/1 CD_2Cl_2/SO_2, 250 MHz −40 °C) ratio of isomers 3.0/1 [minor in brackets] δ 2.17 (d, *J* = 6.4 Hz, 3 H), [2.09 (d, *J* = 6.6 Hz, 3 H)], 2.89 (s, 3 H), [2.99 (s, 3 H)], 6.66 (q, *J* = 6.4 Hz, 1 H), [6.40 (q, *J* = 6.6 Hz, 1 H)].

2,2-Dimethyl-4-pentyn-3-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (25). Similarly prepared from 2,2-dimethyl-4-pentyn-3-ol–dicobalt hexacarbonyl complex at −20 °C. ROH: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.04 (s, 9 H), 1.83 (d, *J* = 5.4 Hz, 1 H), 4.47 (d, *J* = 5.3 Hz, 1 H), 6.06 (s, 1 H). Cation: ^{1}H NMR (1/1 CD_2Cl_2/SO_2, 250 MHz, −20 °C) one isomer δ 1.29 (s, 9 H), 6.63 (s, 1 H), 7.78 (s, 1 H); ^{13}C NMR δ 189–195 (br m), 131.4, 110.0, 85.2, 40.7, 28.6.

1-(Trimethylsilyl)-1-pentyn-3-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (20). The cation was similarly prepared from 1-(trimethylsilyl)-1-pentyn-3-ol–dicobalt hexacarbonyl complex at −50 °C, but it resulted in a very low yield of poor quality solid. ROH: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.33 (s, 9 H), 1.16 (br t, *J* = 7.4 Hz, 3 H), 1.66 (br d of q, *J* = 7.4, 3.4 Hz, 1 H), 1.71 (br d of q, *J* = 7.4, 3.4 Hz, 1 H), 1.78 (d, *J* = 5.7 Hz, 1 H), 4.67 (d of d of d, *J* = 5.7, 3.4 Hz, 1 H). Cation: ^{1}H NMR (1/1 CD_2Cl_2/SO_2, 250 MHz, −70 °C) ratio of isomers 2.2/1 [minor in brackets] δ 0.46 (s, 9 H), [0.50 (s, 9 H)], 1.04 (br t, 3 H), [1.17 (br t, 3 H)], 2.09 (quintet, *J* = 6.6 Hz, 2 H), [1.94 (quintet, *J* = 6.6 Hz, 2 H)], 6.41 (br t, 1 H), [6.21 (br t, 1 H)].

1-Butyn-3-yl Tetrafluoroborate–Dicobalt Hexacarbonyl Complex (21). Representative Cation Formation from an Ether Precursor Using Trifluoroacetic Anhydride as the Desiccant. To a flame-dried flask equipped with a magnetic stir bar, rubber septa, vacuum sidearm, and an attached NMR tube was added 3-methoxy-1-butyne–dicobalt hexacarbonyl complex (191.3 mg, 0.52 mmol). Trifluoroacetic anhydride (300 μL) was added to the complex, and the solution was cooled to −40 °C under argon (CH_3CN/CO_2). Distilled Et_2O (500 μL) was added to keep the anhydride solution from freezing. After the addition of tetrafluoroboric acid–dimethyl ether (102 μL, 1.04 mmol), the solution was stirred for 15 min, during which time the solid tetrafluoroborate salt precipitated. While the temperature was maintained at −40 °C, 10 mL of distilled Et_2O was added to enhance the precipitation of the salt from the solution. Purification and transfer of the cation tetrafluoroborate were achieved in an identical manner to that described in the previous procedure. Methyl ether: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.52 (d, *J* = 6.3 Hz, 3 H), 3.47 (s, 3 H), 4.47 (d of q, *J* = 0.8, 6.2 Hz, 1 H), 6.11 (d, *J* = 0.8 Hz, 1 H). Cation: ^{1}H NMR (1/1 CD_2Cl_2/SO_2, 250 MHz, −30 °C) ratio of isomers 3.6/1 [minor in brackets] δ 2.20 (d, *J* = 6.4 Hz, 3 H), [2.08 (d, *J* = 6.6 Hz, 3 H)], 6.65 (d of q, *J* = 1.3, 6.4 Hz, 1 H), [6.61 (q, 1 H)], 7.83 nd, *J* = 1.4 Hz, 1 H), [7.96, (s, 1 H)]; ^{13}C NMR δ 189–195 (br), 118.7, 109.4, [111.7], 83.9, [84.3], 21.7, [27.7].

(1*S*,2*S*,3*S*,5*R*)-3-Pinanyl 1-Butyn-3-yl Ether–Dicobalt Hexacarbonyl Complex (37, 38). 1-Butyn-3-ol–dicobalt hexacarbonyl complex (419.3 mg, 1.18 mmol) was transferred into a 25-mL flame-dired round-bottomed flask under nitrogen. CH_2Cl_2 (15 mL), a catalytic amount of *p*-toluenesulfonic acid (30 mg), and an excess of freshly activated 4A molecular sieves were added to the reaction flask. (+)-Isopinocampheol (455 mg, 2.9 mmol) was then added, and the solution was purged with argon. After the solution was stirred overnight (12 h), no starting material was evident by TLC. The suspension was filtered over Celite (to remove molecular sieve dust), reduced, and subjected to flash chroma-

tography (10/1 hexane/ethyl acetate). This procedure yielded the desired mixture of **37** and **38** (563 mg, 1.14 mmol) in 97% yield. The ethers were separated by subjecting the mixture to HPLC with heptane as the eluant. Spectral data for both diastereomers are given. Higher R_f diastereomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.94 (s, 3 H), 1.13 (d, J = 7.5 Hz, 3 H), 1.22 (s, 2 H), 1.46 (d, J = 6.2 Hz, 3 H), 1.57 (s, 3 H), 1.75–2.2 (m, 3 H), 2.3–2.5 (m, 2 H), 3.94 (quintet, J = 4.6 Hz, 1 H), 4.69 (q, J = 6.1 Hz, 1 H), 6.06 (s, 1 H). Lower R_f diastereomer: δ 0.95 (s, 3 H), 1.13 (d, J = 7.4 Hz, 3 H), 1.23 (s, 2 H), 1.51 (d, J = 6.4 Hz, 3 H), 1.55 (br s, 3 H), 1.80–2.15 (m, 3 H), 2.3–2.53 (m, 2 H), 4.01 (quintet, J = 4.7 Hz, 1 H), 4.70 (q, J = 6.3 Hz, 1 H), 6.11 (s, 1 H). Higher R_f diastereomer: ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 75.8, 72.1, 71.6, 48.0, 44.8, 41.7, 38.7, 35.9, 33.3, 27.7, 24.0, 23.3, 21.5. Lower R_f diastereomer: δ 77.1, 73.2, 72.3, 48.0, 44.9, 41.8, 38.6, 36.7, 33.5, 27.7, 24.4, 24.0, 21.5. Higher R_f diastereomer: IR (film) 2973 (m), 2908 (m), 2880 (m), 2095 (s), 2051 (s), 2016 (s), 1367 (w), 1113 (w), 1076 (m), 1048 (w) cm^{-1}. Lower R_f diastereomer: IR (film) 2984 (m), 2921 (m), 2874 (m), 2094 (s), 2050–2006 (br s), 1451 (w), 1372 (w), 1096 (m), 1047 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{22}Co_2O_7$: C, 48.80; H, 4.50. Found: C, 48.90; H, 4.48.

4-Methyl-1-hepten-5-yne–Dicobalt Hexacarbonyl Complex (39). The higher R_f diastereomer of the **37,38** pair (136.8 mg, 0.28 mmol) was filtered over silica with CH_2Cl_2 as eluant and placed into a flame-dried 25-mL round-bottomed flask. CH_2Cl_2 (8 mL) was syringed into the flask, and the system was evacuated and purged with dry nitrogen. After the mixture was cooled to −78 °C (CO_2/acetone), allyltrimethylsilane (134 μL, 0.84 mmol) was added followed by the addition of distilled (CaH_2) boron trifluoride etherate (103 μL, 0.84 mmol). The reaction was warmed to room temperature over 45 min. Once at ambient temperature, the Lewis acid was quenched with excess triethylamine. The reaction mixture was diluted with 50 mL of hexane and filtered over silica gel. The silica was rinsed with solvent until all cobalt-containing species were eluted. The solution was concentrated and then subjected to flash chromatography (hexanes). This reaction was repeated with the (lower R_f) diastereomeric isopinocampheyl ether as well. The allylated product derived from both ethers exhibited no optical rotation in CH_2Cl_2 or hexane. This procedure yielded 105.0 mg of **39** (98% of theoretical). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.29 (d, J = 6.7 Hz, 3 H), 2.15–2.45 (m, 2 H), 2.94 (hextet, J = 6.7 Hz, 1 H), 5.08 (s, 1 H), 5.14 (d of d, J = 1.4, 3.3 Hz, 1 H), 5.8–6.0 (m, 1 H), 6.07 (d, J = 0.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 136.6, 117.2, 73.6, 43.6, 37.7, 22.7; IR (film) 2977 (w), 2931 (w), 2093 (s), 2049–2017 (br s), 1642 (w), 1454 (w), 1375 (w), 992 (w), 917 (m) cm^{-1}.

(4*R*,5*S*)-3-[(2*S*,3*S*)-1-Oxo-2,3-dimethyl-5-(trimethylsilyl)-4-pentynyl]-4-methyl-5-phenyl-2-oxazolidinone. Representative Decomplexation with Cerric Ammonium Nitrate. The cobalt complex **48** (28.7 mg; 0.045 mmol) was dissolved in 5 mL of reagent grade methanol. Cerric ammonium nitrate was added in portions with stirring until evolution of CO_2 ceased and the CAN color persisted. This solution was then partitioned between 30 mL of Et_2O and 30 mL of distilled H_2O. The aqueous phase was extracted an additional two times. The combined organic extracts were dried over $MgSO_4$, filtered, reduced, and subjected to flash chromatography (5/1 hexane/ethyl acetate). This procedure yielded decomplexed **48** (12.5 mg, 0.035 mmol) in 78% yield: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.10 (s, 9 H), 0.92 (d, J = 6.6 Hz, 3 H), 1.22 (d, two very close sets, J = 7.1 Hz, 6 H), 2.85 (d of q, J = 7.0, 8.4 Hz, 1 H), 3.95 (d of q, J = 7.0, 8.4 Hz, 1 H), 4.83 (quintet, J = 6.7 Hz, 1 H), 5.68 (d, J = 7.4 Hz, 1 H), 7.28–7.47 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 188.0, 152.7, 133.6, 128.8, 125.7, 109.3, 78.6, 54.7, 42.6, 29.5, 17.3, 14.6, 14.4, 0.01; IR (film) 2975 (m), 2962 (m), 2939 (m), 2169 (w), 1779 (s), 1703 (s), 1456 (m), 1343 (s), 1197 (s), 1121 (m), 843 (s) cm^{-1}.

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Registry No. 15a, 109530-46-3; **15b**, 109583-46-2; *syn*-**20**, 109530-36-1; *anti*-**20**, 109583-48-4; *syn*-**21**, 109530-38-3; *anti*-**21**, 109583-50-8; *syn*-**22**, 109530-40-7; *anti*-**22**, 109583-52-0; *syn*-**23**, 109530-42-9; *anti*-**23**, 109583-54-2; *syn*-**25**, 109530-44-1; **36**, 109530-27-0; **37**, 109530-28-1; **38**, 109583-42-8; **39**, 109530-29-2; **42**, 77877-20-4; **43**, 65966-21-4; **44**, 109530-30-5; **45**, 109583-43-9; **46**, 82507-40-2; **47**, 102286-03-3; **48**, 109530-31-6; **49**, 109583-44-0; $Co_2(CO)_6$(TMSC≡CC(CH_3)(OH)CH(CH_3)$_2$), 109530-25-8; $Co_2(CO)_6$(HC≡CCH(CH_3)OH), 40687-04-5; *syn*-[$Co_2(CO)_6$(CH_3C≡CCH(CH_3)CH(CH_3)COPh)], 102286-07-7; *anti*-[$Co_2(CO)_6$(CH_3C≡CCH(CH_3)CH(CH_3)COpH)], 102341-10-6; *syn*-[$Co_2(CO)_6$(TMSC≡CCH(CH_3)CH(CH_3)COPh)], 102418-50-8; *anti*-[$Co_2(CO)_6$(TMSC≡CCH(CH_3)CH(CH_3)COpH)], 102286-09-9; *syn*-[$Co_2(CO)_6$(PhC≡CCH(CH_3)CH(CH_3)COPh)], 109530-26-9; *anti*-[$Co_2(CO)_6$(PhC≡CCH(CH_3)CH(CH_3)COPh)], 109583-41-7; *syn*-[$Co_2(CO)_6$(HC≡CCH(CH_3)CH(CH_3)COPh)], 102286-08-8; *anti*-[$Co_2(CO)_6$(HC≡CCH(CH_3)CH(CH_3)COPh)], 102341-11-7; (±)-(*R*,*S*)-PhCOCH(CH_3)CH(CH_3)CO_2H, 109583-55-3; (±)-(*R*,*R*)-PhCOCH(CH_3)CH(CH_3)CO_2Me, 109530-48-5; (±)-(*R*,*S*)-PhCOCH(CH_3)CH(CH_3)CO_2Me, 109530-49-6; $Co_2(CO)_6$(TMSC≡CCH(CH_3)OH), 109530-32-7; $Co_2(CO)_6$(HC≡CCH(OH)C(CH_3)$_3$), 109530-33-8; $Co_2(CO)_6$(TMSC≡CCH(OH)CH_2CH_3), 109530-34-9; $Co_2(CO)_6$(HC≡CCH(OMe)CH_3), 102286-06-6; $Co_2(CO)_6$(PhC≡CCH(OMe)CH_3), 102286-04-4; (*Z*)-1-phenyl-1-(trimethylsiloxy)-propene, 66323-99-7; (*E*)-1-phenyl-1-(trimethylsiloxy)propene, 71268-59-2; 3,4-dimethyl-1-(trimethylsilyl)-1-pentyn-3-ol, 109530-47-4; 1-butyn-3-ol, 2028-63-9; (4*R*,5*S*)-3-[(2*S*,3*S*)-1-oxo-2,3-dimethyl-5-(trimethylsilyl)-4-pentynyl]-4-methyl-5-phenyl-2-oxazolidinone, 109530-50-9; (*D*,*L*)-2,3-dimethylsuccinic acid, 608-39-9; benzene, 71-43-2; (+)-isopinocampheol, 24041-60-9; allyltrimethylsilane, 762-72-1; *meso*-2,3-dimethylsuccinic acid, 608-40-2.