(−78 °C) slurry of CuI (0.143 g, 0.75 mmol) in THF (2 mL), followed by the addition of MeLi (0.48 mL, 0.75 mmol). The mixture was then warmed until a colorless, homogeneous solution formed. The solution was recooled to −78 °C and transferred to an NMR tube in the manner described above.

Preparation of $Me(MeOCMe_2C{\equiv}C)CuLi{\cdot}2BF_3$. $Me(MeOCMe_2C{\equiv}C)CuLi$ was prepared in the same manner as described above. The following amounts of reagents were used: 3-methyl-3-methoxy-1-butyne, 0.093 mL, 0.75 mmol; THF, 4 mL; MeLi, 0.888 mL, 1.5 mmol; and CuI, 0.143 g, 0.75 mmol. An aliquot (0.45 mL, 0.068 mmol) was transferred to an NMR tube as described above. A 0.976 M solution (−78 °C) of $BF_3{\cdot}Et_2O$/THF (2 equiv, 0.136 mL, 0.132 mmol) was also added via a syringe and the NMR tube was sealed for use as described above.

Figure 4. Reaction of 3-Methyl-2-cyclohexenone and $Me_3Cu_2Li{\cdot}BF_3$. Me_3Cu_2Li was prepared in the same manner as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2 mL; MeLi, and 0.73 mL, 1.125 mmol. An aliquot (0.45 mL, 0.063 mmol) of the colorless, homogeneous solution was transferred to a dry NMR tube as described above. One equivalent (0.062 mL, 0.060 mmol) of a 0.976 M solution (−78 °C) of $BF_3{\cdot}Et_2O$/THF was also added via a syringe followed by the addition of 1 equiv of 3-methyl-2-cyclohexenone (0.007 mL, 0.06 mmol). The NMR tube was then sealed and used in the NMR experiment at −80 °C.

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Registry No. 1, 15681-48-8; **3**, 61303-82-0; **4**, 110140-36-8; **5**, 79135-33-4; **6** (R = $H_2C{=}CH$), 22903-99-7; **6** (R = Ph), 23402-69-9; **6** (R = *n*-Bu), 24406-16-4; **7** (R = $H_2C{=}CH$), 118398-08-6; **7** (R = Ph), 118376-86-6; **7** (R = *n*-Bu), 118376-85-5; **8**, 65139-98-2; (*E*)-$H_3CCH{=}CHCO_2Et$, 623-70-1; $H_3CCH(Ph)CHO$, 93-53-8; $H_3CC(CH_3)(Ph)CH_2COCH_3$, 7403-42-1; $H_3C(CH_2)_3CH(CH_3)CH_2CO_2Et$, 37492-08-3; $PhCH_2CH(OH)CH_2I$, 86151-59-9; $PhCH_2CH(OH)CH_2CH{=}CH_2$, 61077-65-4; (*R*,R**)-$H_3CCH(Ph)CH(OH)(CH_2)_3CH_3$, 96929-99-6; (*R*,S**)-$H_3CCH(Ph)CH(OH)(CH_2)_3CH_3$, 96930-05-1; $BF_3{\cdot}Et_2O$, 109-63-7; MeCu, 1184-53-8; PhCu, 3220-49-3; $H_2C{=}CHCu$, 37616-22-1; $MeLi{\cdot}BF_3$, 82977-34-2; $Me(2\text{-Th})_2Cu_2Li$, 118376-87-7; $Me_2(2\text{-Th})Cu_2Li$, 118376-88-8; $Me(MeOC(CH_3)_2C{\equiv}C)_2Cu_2Li$, 118376-89-9; $Me_2(MeOC(CH_3)_2C{\equiv}C)Cu_2Li$, 118376-90-2; $H_2C{=}CH\text{-}Cu{\cdot}BF_3$, 104747-24-2; CuI, 7681-65-4; 3-methyl-2-cyclohexenone, 1193-18-6; 4-isopropyl-2-cyclohexenone, 500-02-7; mesityl oxide, 141-79-7; isophorone, 78-59-1; 1,2-epoxy-3-phenylpropane, 4436-24-2; 3,3-dimethylcyclohexanone, 2979-19-3; *trans*-3-vinyl-4-isopropylcyclohexanone, 118376-84-4; 3,5,5-trimethyl-3-vinylcyclohexanone, 27749-07-1; 3,5,5-trimethyl-3-butylcyclohexanone, 41601-84-7; allylbenzene, 300-57-2; thiophene, 110-02-1; 2-thienyllithium, 2786-07-4; 3-methyl-3-methoxy-1-butyne, 13994-57-5; 3-methyl-3-methoxy-1-butynyllithium, 76320-69-9.

Interaction of the (Dimethylglyoximato)(pyridine)cobalt Anion, $[Co(dmgH)_2py]^-$, with Vinyl Triflates. Stereochemistry and Mechanism of Formation of Vinyl–Cobaloxime Complexes†

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Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112. *Received August 18, 1988*

Abstract: Reaction of $[Co(dmgH)_2py]^-$ with simple alkylvinyl triflates occurs at 0 °C in CH_3OH/H_2O (9:1) in less than 10 min to give stable, crystalline σ-vinyl–cobaloxime complexes in 18–51% isolated yields. The reaction of isomeric (*E*)- and (*Z*)-vinyl triflates results in stereoconvergence. The data indicate that reaction most likely occurs by a stepwise addition–elimination process with an anionic intermediate of sufficient lifetime to undergo bond rotation before elimination.

A large variety of organic substrates, alkyl, benzyl, allyl, propargyl, acyl, aryl, and some vinyl systems (usually halides), react with low valent transition metal nucleophiles, resulting in diverse carbon–metal σ-bond complexes.[2,3] From a classical organic chemical prospective these reactions may be viewed as the alkylation, acylation, arylation, etc., via the appropriate electrophiles, of transition-metal complexes with the metal serving as a nucleophile. Hence, in parallel with organic chemistry, the reactions of alkyl, acyl, benzyl, allyl, propargyl, and aryl systems are extensively investigated and reasonably well understood. However, in classical organic as well as organometallic chemistry, nucleophilic vinyl substitutions (S_NV),[4-6] i.e. displacements at a C_{sp^2} center, are much less common and, until recently, less understood. The reason for this anomaly is generally attributed to the inertness of *simple alkylvinyl* substrates (usually halides) to S_NV processes, even under forcing conditions with powerful nucleophiles.[4] Therefore, in organic[4] as well as organometallic[7,8] chemistry, nucleophilic vinylic substitutions usually require "activated", i.e. halo, cyano, carbonyl, aryl, etc., substituted vinylic systems for reaction to occur. For example, with one exception,[9] even the supernucleophilic[10] $[Co(dmgH)_2py]^-$ anion only reacts with β-chloroacrylate[11] and β-bromostyrene[12] and not with simple alkylvinyl halides.

The ready availability[13] and high reactivity, $k_{CF_3SO_3^-}/k_{X^-} \cong 10^6$–$10^9$, of vinyl triflates offers a potential solution to this problem, as exemplified by the easy generation of both alkylidenecarbenes[14]

† Dedicated to Professor Donald J. Cram on the occasion of his 70th birthday.

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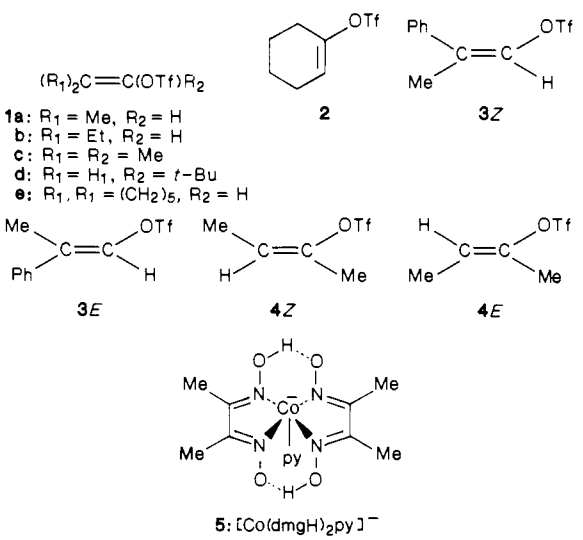
0002-7863/89/1511-1358$01.50/0

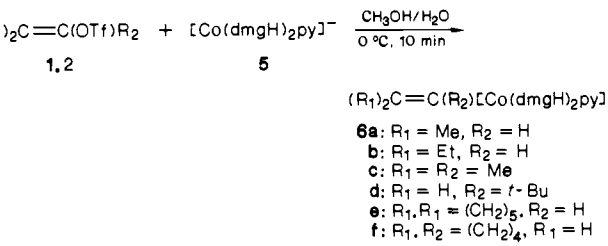
and alkylvinyl cations[15] via these substrates. Yet despite the emergence of vinyl (enol) triflates as premeier reagents[16] in organic chemistry, including metal-mediated vinylic cross-coupling reactions,[16] little, if anything, is known[17] about their reaction with organometallic nucleophiles. Hence, in this paper we report our results on the reaction of alkylvinyl triflates with $[Co(dmgH)_2py]^-$ and the ready formation of stable vinyl-cobaloxime complexes.

Results and Discussion

Vinyl triflates **1–4** were prepared by standard procedures[13] from the corresponding ketone or aldehyde for **1–3** and 2-butyne for **4**. The cobaloxime anion **5** was prepared from $CoCl_2 \cdot 6H_2O$ by



standard literature procedure.[12] Interaction of **1** and **2** with a 10% excess of **5** in CH_3OH/H_2O (9:1 v/v) at 0 °C occurred in a few



minutes, yielding orange-yellow microcrystalline σ-vinyl-cobaloxime complexes **6** in 18–51% isolated yields. The extent of reaction could be conveniently followed by the color change of the solution from the deep, intense blue of anion **5** to orange for **6**. Reaction occurred essentially upon mixing of the reagents and the solution was stirred an additional few minutes only for convenience and to assure completion.

The σ-vinyl-cobaloxime complexes **6** were characterized by analytical and spectral means. FAB mass spectra clearly indicated a 1:1 adduct and showed the M^+ and MH^+ in 2–22% abundance for each adduct. Characteristically high abundance signals for each compound were the $M^+ - py$ and $MH^+ - py$ fragments. The infrared spectra had characteristic absorptions centered around 1600, 1560, and 1450 cm^{-1} due to the various C=C and C=N bonds. The proton NMR spectra had uniquely characteristic signals between 2.05 and 2.11 ppm, due to the four equal methyls of the dimethylglyoximato moiety, and three signals around 7.3, 7.7, and 8.7 ppm, due to the protons of the complexed pyridine along with the absorptions of the various alkenyl units. In the ^{13}C NMR, spectra the signal due to the α-vinylic carbon (C=C—Co) was not observed in any of the adducts **6** due to the high splitting as a consequence[21] of the $^7/_2$ spin of Co. Characteristic signals were observed at 149.6 ± 0.3 ppm for the equivalent C=N carbons of the glyoximato units and between 113 and 151 ppm for the three pyridine carbons and the remaining olefinic carbon.

Mechanistic Considerations. The interaction of **5** with alkylvinyl triflates **1** and **2** is a remarkable reaction. There are few, *if any*, nucleophilic vinylic substitutions known[4-6] that occur essentially instantaneously or at most in a matter of minutes at 0 °C. Moreover, there are few, if any, nucleophilic vinyl substitutions known with simple *alkylvinyl* substrates; S_NV reactions generally require "activated" (i.e. anion stabilizing) substituents.[4-6] For example, even the reaction of **5** with *cis*- and *trans*-β-halostyrenes (an activated substrate) requires reaction times of 2–12 h at 25–45 °C.[12,22-24] Likewise, the reaction of a highly activated β-chloroacrylate with **5** requires 4 h at 25 °C for completion.[11] Hence, the vinyl triflate reactions are several orders of magnitude faster,[25] even with **5**, than the few known[11,12] comparable reactions of vinyl halides with **5**, undoubtedly due to the aforementioned superior leaving ability[13] of the triflate compared to that of halides. The superior leaving ability of OTf^- compared to that of X^- cannot, however, alone account for these remarkable reactions, as even alkylvinyl triflates do not react[26] with ordinary nucleophiles such as N_3^-, PhS^-, CN^-, etc., even under forcing conditions. Hence, both the high reactivity of triflates and the superior nucleophilicity[8,9] of the cobalt anion **5** are required for S_NV reaction with simple alkylvinyl substrates.

The reaction seems to be remarkably insensitive to the substitution pattern of the olefin; mono, 2,2-di-, 1,2-di-, and trisubstituted, as well as cyclic, systems react with equal facility.[25] This likely rules out prior complexation of the olefin and anion, as such complexation should vary as a function of substitution and concomitant steric hindrance, with the least substituted systems reacting faster than the hindered, fully substituted ones.

Stereochemical Investigations. To get some insight into the mechanism of this remarkable reaction, we undertook a careful stereochemical investigation of the reaction of the two isomeric pairs of vinyl triflates **3** and **4**. Preparative GC allowed separation of the two pairs of geometric isomers, **3*E*** and **3*Z***, and **4*E*** and **4*Z***, respectively, in greater than 99% isomeric purity. The stereochemistry of the isomeric starting vinyl triflates as well as the isomeric product vinyl-cobaloximes was assigned by careful NMR analyses,[1] as summarized in Table I. Two highly characteristic features of the NMR data allow unambiguous assignments of the olefin geometry of each individual isomer. A large body of evidence[27-35] indicates that in *all* mono-, di-, and tri-

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(15) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic: New York, 1979.
(16) Scott, W. J.; McMurray, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.
(17) Outside of our own recent reports on the reactions of enynyl triflates, >C=C(OTf)C≡C—, with cobalt[18] and iridium,[19] respectively, and a preliminary report[20] on the reaction of alkylvinyl triflates with $(Ph_3P)_4Pt$, and their recent use in coupling reactions,[16] we are not aware of any reaction of vinyl triflates with organometallic complexes.
(18) Stang, P. J.; Wistrand, L. *J. Organomet. Chem.* **1981**, *204*, 405.
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(23) Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *22*, 473.
(24) Naumburg, M.; Duong, K. N. V.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *25*, 231.
(25) Because of both the remarkably rapid rate of these reactions as well as the conditions of preparing $[Co(dmgH)_2py]^-$, **5**, it is impossible to do kinetic measurements and obtain any kind of rates under these conditions.
(26) Unpublished observations, Stang, P. J.; Treptow, W. See also: Treptow, W. Ph.D. Dissertation, The University of Utah, 1979.
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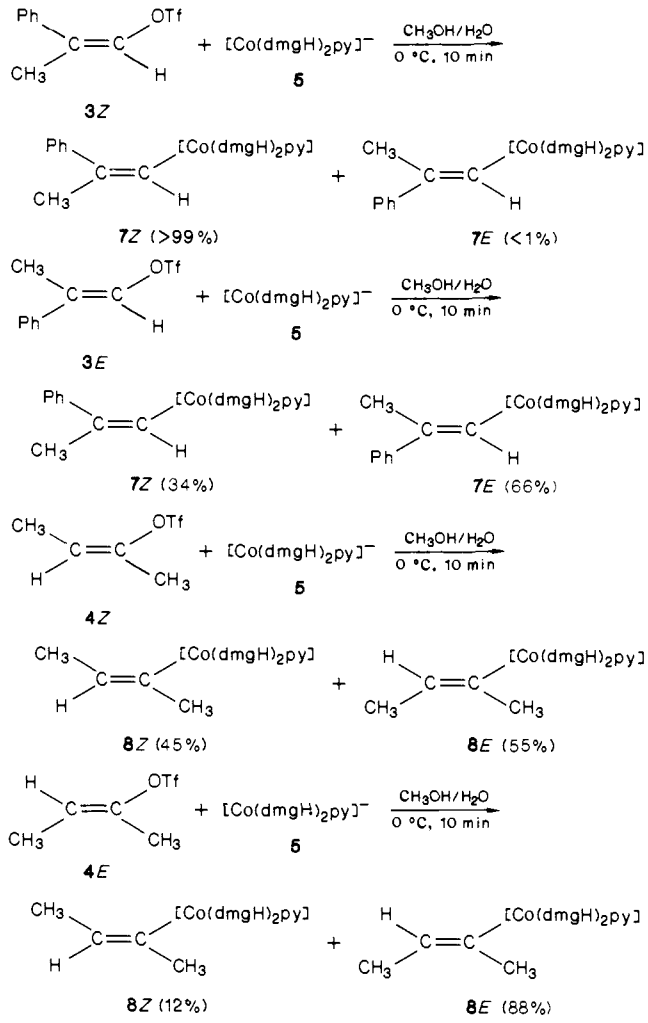
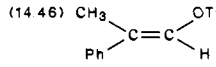
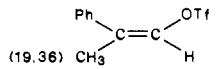
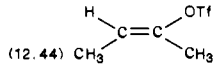
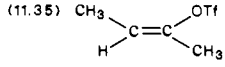
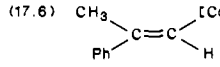
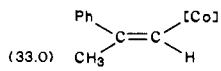
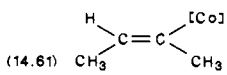
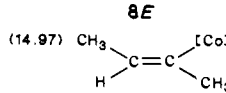
Scheme I. Summary of Stereochemical Results of Reaction of **3** and **4** with **5**



substituted alkenes examined to date the long-range vicinal carbon–hydrogen coupling is always larger in the trans arrangement than in the cis one; $^3J_{C,H}(trans) \gg {}^3J_{C,H}(cis)$. Likewise, a large body of data[29,36-39] indicates that the carbon-13 chemical shifts of carbon atoms in spatially crowded (perturbed) alkyl groups are always further *upfield* than the shifts of similar carbon atoms in an uncrowded (unperturbed) environment. For example, the β-CH_3 in isomer **3*E*** resonates at 14.46 ppm whereas the unperturbed CH_3 in **3*Z*** absorbs at 19.36 ppm. Likewise, the highly crowded CH_3 in **7*E*** resonates at 17.6 ppm whereas the unperturbed CH_3 in isomer **7*Z*** occurs at 33.0 ppm. Similarly, $^3J_{C,H}(trans)$ = 4.2 and 8.79 Hz for **4*E*** and **8*E***, respectively; whereas, the $^3J_{C,H}(cis)$ = 2.27 and 7.23 Hz for the isomeric **4*Z*** and **8*Z*** compounds, respectively. Hence, inspection of all the data in Table I leaves no doubt about the appropriate stereochemical assignments.

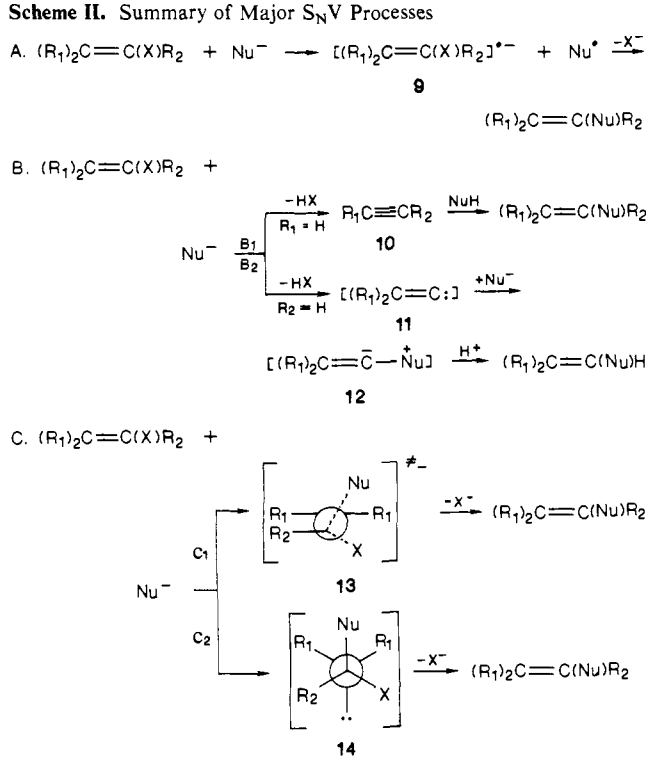
The results of the reactions of the *individual* isomeric vinyl triflates **3** and **4** with **5** are summarized in Scheme I. In contrast to the reactions of β-halostyrenes[12,22-24] and β-chloroacrylate[11] as well as the reaction of 1-bromooctene[10] with 5, which occurred *exclusively with complete retention of olefin geometry*, the reactions of vinyl triflates (with the possible exception of **3*Z***) occur with various degrees of stereoconvergence of the olefin geometry.

Table I. Summary of Selected Coupling Constants and the CH_3-Carbon Chemical Shifts of Isomeric Vinyl Triflates and Cobaloximes[a]

compound (δ, CH_3)	$^4J_{H,H}$, Hz	$^3J_{C,H}$, Hz (CH_3,H)
(14.46)  **3*E***	1.65 ± 0.1	5.60 ± 0.1
 (19.36) **3*Z***	1.64 ± 0.1	3.80 ± 0.1
 (12.44) (16.38) **4*E***	1.0 ± 0.1	4.2 ± 0.1
(11.35)  (19.67) **4*Z***	1.2 ± 0.1	2.27 ± 0.1
(17.6)  **7*E***	0.90 ± 0.1	9.88 ± 0.1
 (33.0) **7*Z***	1.35 ± 0.1	7.70 ± 0.1
 (14.61) (19.54) **8*E***	1.55 ± 0.1	8.79 ± 0.1
(14.97)  (31.05) **8*Z***	1.70 ± 0.1	7.23 ± 0.1

[a] [Co] = [Co(dmgH)$_2$py].

Scheme II. Summary of Major S_NV Processes



Careful control experiments established that the starting isomeric vinyl triflates **3** and **4** and product vinyl–cobaloximes **7** and **8** are stable under the reaction conditions and hence no stereorandom-

(36) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315. Wool-Fenden, W. R.; Grant, D. M. *Ibid.* **1966**, *88*, 1496.
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(38) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.
(39) Uriac, P.; Bonnic, J.; Huet, J. *Tetrahedron* **1985**, *41*, 5051.

ization was observed in the starting materials or products.

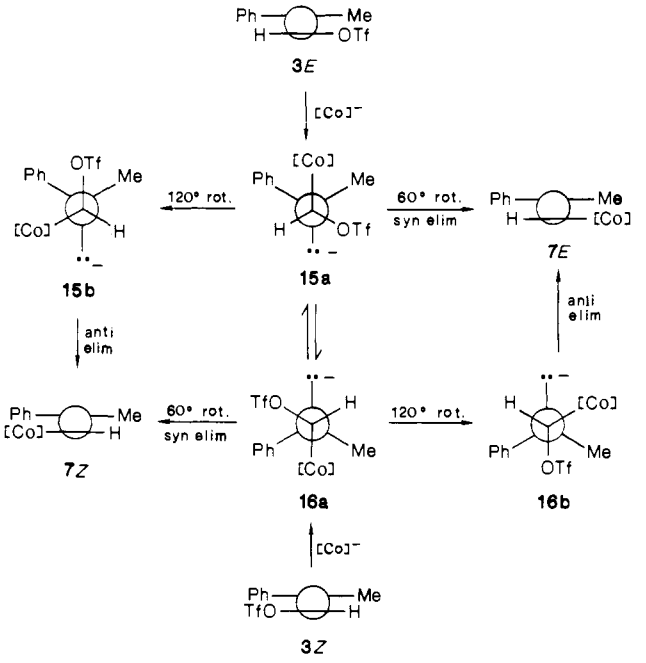
The direct in-plane S_N2 analogue of nucleophilic vinylic substitutions has been shown[40] to be of prohibitively high energy and therefore not likely to occur. Hence a wide variety of other mechanistic pathways have been considered for S_NV reactions.[4,5] These generally fall into three categories: (A) single-electron transfer (SET) processes, (B) elimination–addition pathways, and (C) addition–elimination routes as summarized in Scheme II. Besides the mechanisms in Scheme II, two other pathways must be briefly considered. The S_N1-like formation of vinyl cations can be ruled out by the fact that (a) the generation of these intermediates[15] requires much more stringent reaction conditions even from vinyl triflates and (b) there are no "primary" (i.e., α-H substituted such as from **1a** and **1b**) vinyl cations known.[15] Gaudemer and co-workers[11] proposed an unusual concerted three-centered displacement of the chlorine by the cobalt anion **5** on their chiral β-chloroacrylate to account for the complete retention of both axial chirality and olefin geometry. Such a process is ruled out in the reaction of vinyl triflates with **5** by the observed alkene stereorandomization.

The SET process, A, although consistent with the stereochemical observations, is usually observed with halides. There are no known SET processes with sulfonate esters[41] and triflates[42] in particular and hence they are very unlikely in this case. The elimination–addition pathways, B, either via alkyne **10** (path B_1) or via alkylidenecarbene **11** (path B_2), although well precedented,[5,14] can be easily ruled out by (i) the fact that triflate **2** cannot eliminate yet readily reacts and (ii) the fact that either pathway, contrary to the experimental observations, would require *identical* product isomer distributions from the respective pairs of individual isomeric vinyl triflates **3** and **4**.

Addition–elimination can occur in a more or less concerted single-step process (path C_1) if the lifetime of the "intermediate" or transition state (**13**) is short compared to the time needed for molecular rotation around the C–C bond. Such a process is characteristic of moderately activated olefins of the general formula RYC=CXR (Y = activating substituent, e.g. Ph; X = leaving group) and results in complete (or nearly complete) *retention* of starting olefin stereochemistry.[43,44] Alternatively, the intermediate, **14**, may have a significant lifetime (path C_2) and hence rotate around the C–C bond to form product(s) with partial or complete stereoconversion of the starting alkene geometry (i.e. multistep process).[4,5] This last process is characteristic of highly activated, strongly electrophilic alkenes of general structure YY'C=CXR (Y, Y' = activating substituents, e.g. CN, CO_2Me, NO_2, etc.; X = leaving group, e.g. halides).[45,46]

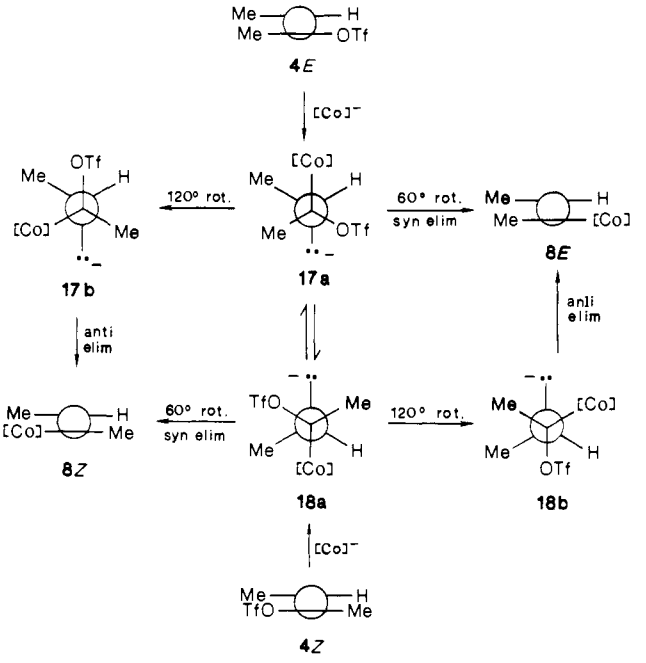
Nucleophilic vinylic substitutions are generally considered to proceed via a variable transition state and the exact nature of the intermediate is strongly dependent upon the alkene substituent, the nucleophile, the leaving group, and the reaction conditions.[4,5,43] Alkylvinyl triflates are not activated in the classical sense and hence it is not really clear why they should react via a stepwise process involving relatively long-lived intermediates with sufficient lifetimes to undergo C–C bond rotation and stereoconversion. However, Co^- and OTf^- are not the common nucleophiles or leaving groups normally employed in S_NV or substitution reactions in general, and this may account in some way for these unusual reactions and observations. Further insight into these reactions might be gained by a more detailed examination of the specific reactions of **3** and **4** with **5** as outlined in Schemes III and IV, respectively.

Scheme III. Mechanism of the Reaction of Isomeric Vinyl Triflates **3** with $[Co(dmgH)_2py]^-$[a]



[a] [Co] = $[Co(dmgH)_2py]$.

Scheme IV. Mechanism of Reaction of Isomeric Vinyl Triflates **4** with $[Co(dmgH)_2py]^-$[a]



[a] [Co] = $[Co(dmgH)_2py]$.

Attack of Co^- on **3*E*** and **3*Z*** leads to the formation of intermediates **15a** and **16a**, respectively. A 60° rotation of the substituents aligns the lone pair and nucleofuge in a cisoid conformation, for syn elimination, resulting in *retention* of olefin stereochemistry. However, a 120° rotation of **15a** and **16a** leads to conformers **15b** and **16b**, respectively. Anti elimination from **15b** and **16b**, respectively, affords products of inverted olefin geometry. Exactly analogous considerations hold for reaction of **4*E*** and **4*Z*** with Co^- as shown in Scheme IV. Normally 60° rotation is preferred over 120° rotation [$k_{rot}(60°) > k_{rot}(120°)$][5,43] due to minimum rotation, less steric interaction, and possible stabilizing hyperconjugative interaction between the substituents and the lone-pair electrons.[43] However, if the resulting carbanion has a significant lifetime and the steric strain (eclipsing effect) during

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rotation is not very severe, then a 120° rotation, anti elimination, and inversion can occur. The experimental data (Scheme I) shows formation of 66% of **7*E*** and 34% of **7*Z*** from **3*E***. The preferential formation of **7*E*** and concomitant retention of olefin stereochemistry is accounted for by the favored minimal 60° rotation involved. Similar arguments account for the observed retention of olefin geometry in the reaction of Co^- with β-styryl halides.[12,22] Likewise, reaction of **3*Z*** with **5** gives 99% **7*Z*** (Scheme I), and this is accounted for by a similar preferential minimal 60° rotation as well as possible favorable electronic effects[47] arising from the interaction of the electropositive cobalt atom and the π-electrons of the aromatic ring. This latter effect also plays a significant role in the formation of the 34% of **7*Z*** from **3*E*** and probably accounts for the lack of stereospecificity in the reaction of **3*E***.

The results of the reactions of **4*E*** and **4*Z*** with **5** (Scheme I) are accountable in terms of steric interactions (Scheme IV) as there are no π-electrons (such as in the phenyl case of **3**) and hence little if any electronic effects. Specifically, the eclipsing interactions between substituents (Co, Me), (Co, H), and (Me, Me) are important and dominant. Hence, the 88% formation of **8*E*** from **4*E*** via **17a** is favored both by the 60° minimal rotation and the preferred Co, H over the Co, Me (in the 120° rotation and formation of **17b**) eclipsing interactions. The small amount, 12%, of **8*Z*** observed might be the result of the unfavorable Me, Me interaction in the above 60° (syn elimination) process leading to the formation of the dominant product, **8*E***. Likewise, the small preference (55:45) for formation of **8*E*** from **4*Z*** and the concomitant inversion of olefin stereochemistry is accounted for by the unfavorable Co, Me eclipsing interaction in the generally preferred 60° rotation from **18a** leading to **8*Z***. Hence, as observed, reaction of **4*E*** leads predominantly to retained product **8*E*** whereas reaction of **4*Z*** leads to predominantly inverted product **8*E*** for the same steric reasons, namely the unfavorable Co, Me eclipsing interactions. Finally, it is obvious that the observed stereochemical preferences, with the exception of the reaction of **3*Z***, are very small and hence small effects might account for and might even change the experimental outcome.

Conclusion

A wide variety of simple alkylvinyl triflates react with $[Co(dmgH)_2py]^-$, resulting in stable, microcrystalline alkylvinylcobaloxime complexes. Reaction takes place at 0 °C in CH_3OH/H_2O in less than 10 min and represents one of the most remarkable nucleophilic vinylic substitution reactions as a consequence of the supernucleophilicity of $[Co(dmgH)_2py]^-$ and the superior leaving ability of $CF_3SO_3^-$. Careful examination of the stereochemistry of reaction of **5** with two isomeric pairs of vinyl triflates shows partial stereoconversion as the predominant mode of reaction. These results are best accounted for by a two-step addition–elimination process, with an anionic intermediate of sufficient lifetime to allow rotation around the C–C bond.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere. All boiling and melting points are uncorrected. IR spectra were recorded on either a Perkin-Elmer 289 or a Nicolet 600 FT spectrophotometer. NMR were recorded on a Varian EM-360 or -390 FT80A or XL-300 or XL-400 spectormeter and are reported in parts per million (ppm) relative to internal Me_4Si (0.00); for ^{13}C NMR the locks were on deuteriated solvents. Mass spectra were obtained on a Varian MAT112 or a VG Micromass spectrometer. Analytical GC was carried out with a HP-5710A flame-ionization GC with a HP-3380-A integrator. Preparative GC utilized a Varian-Aerograph 90P chromatograph. Solvents and reagents were purified and dried by standard procedures immediately prior to use.

Starting Materials. Trifluoromethanesulfonic acid was purchased from 3M Co. Necessary aldehydes and ketones as well as 2-butyne were purchased from Aldrich and redistilled prior to use; $CoCl_2·6H_2O$ and dimethylglyoxime were obtained from MCB. All alkylvinyl triflates are well-known[13] compounds and were prepared according to standard literature procedures; vinyl triflates **1–3** were prepared from the corresponding aldehydes or ketones via the hindered-base method,[48] and **4** was prepared from 2-butyne by addition[49] of CF_3SO_3H. The isomeric vinyl triflates **3*E*** and **3*Z*** were separated by preparative GC on a 0.25 in. × 15 ft, 15% SF-96 on 45/60 Chromosorb W, column at 120 °C, and **4*E*** and **4*Z*** were separated on a 0.375 in. × 15 ft, 20% Carbowax 20 M on 45/60 Chromosorb W, column at 80 °C.

General Procedure for the Reaction of Vinyl Triflates with 5. Reaction of 2 with 5. Dimethylglyoxime (1.16 g, 5 mmol) and $CoCl_2·6H_2O$ (1.1 g, 5 mmol) were magnetically stirred in MeOH (20 mL) for 30 min under an argon atmosphere in a round-bottomed flask. Aqueous NaOH (0.40 g, 10 mmol in 2 mL of H_2O) and pyridine (0.40 g, 5 mmol) were added, and the mixture was stirred at 0 °C for 15–20 min. Additional amounts of aqueous NaOH were added (0.2 g, 5 mmol in 1 mL of H_2O), and then aqueous $NaBH_4$ (0.05 g in 0.5 mL of H_2O) was added and shortly afterward the mixture turned deep blue. The blue solution was stirred an additional 5 min at 0 °C, and then 1.04 g (4.5 mmol) of cyclohexenyl triflate **2** was added via a syringe and the resulting orange-brown mixture was stirred for 10 min at 0 °C. The reaction mixture was transferred to an Erlenmeyer flask and 20 mL of degassed H_2O was added and then the mixture was stored at −20 °C for 2 h. The crude product was filtered and subjected to column chromatography on activated silica gel (1.5 × 30 cm column) using dry THF/hexanes (4:1) as eluent. The orange-yellow fractions were combined, and after evaporation of the solvent via a rotary evaporator and drying, 0.91 g (45%) of **6f** was obtained as an orange, powdery (microcrystalline) solid: mp 200–205 °C dec; MS, *m/z* 450 (MH^+, 10), 449 (M^+, 9), 371 (MH^+ − py, 63), 370 (M^+ − py, 100), 368 (5), 290 (25), 273 (7); IR (KBr) 3110 (w), 3040 (w), 2930 (s), 1600 (s), 1560 (w), 1445 (m), 1230 (s), 1070 (s), 800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (m, 4, CH_2), 2.04 (m, 4, CH_2), 2.10 (s, 12, dmg Me), 5.06 (m, 1, C=CH), 7.30 (m, 2, β-py), 7.72 (m, 1, γ-py), 8.66 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.2 (dmg Me), 23.6 (CH_2), 26.5 (CH_2), 28.6 (CH_2), 33.6 (CH_2), 124.6, 125.1, 137.4, 149.4 (C=N), 150.0. Anal. Calcd for $C_{19}H_{28}N_5O_4Co$: C, 50.78; H, 6.28. Found: C, 50.13; H, 5.91.

Bis(dimethylglyoximato)(pyridine)(2-methyl-1-propenyl)cobalt Complex (6a). Reaction of 5 mmol of **5** with 4.5 mmol of **1a** and workup gave 720 mg (38%) of **6a** as an orange, powdery solid: mp 150–155 °C dec; MS, *m/z* 424 (MH^+, 22), 423 (M^+, 12), 345 (MH^+ − py, 80), 344 (M^+ − py, 100), 368 (4), 290 (46); IR (KBr) 3060 (w), 3020 (w), 2950 (s), 1600 (w), 1560 (s), 1450 (m), 1260 (s), 1235 (s), 1080 (s), 800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (d, *J* = 1.0 Hz, 3, Me), 1.75 (d, *J* = 1.0 Hz, 3, Me), 2.05 (s, 12, dmg Me), 5.26 (m, 1, C=CH), 7.25 (m, 2, β-py), 7.68 (m, 1, γ-py), 8.62 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.0 (dmg Me), 19.6 (Me), 28.8 (Me), 125.0, 136.1, 137.4, 149.6 (C=N), 149.8. Anal. Calcd for $C_{17}H_{26}N_5O_4Co$: C, 48.23, H 6.19. Found: C, 48.29, H, 6.21.

Bis(dimethylglyoximato)(pyridine)(2-ethyl-1-butenyl)cobalt Complex (6b). Reaction of 4.5 mmol of **1b** with 5 mmol of **5** and workup gave 0.73 g (36%) of **6b** as an orange, powdery solid: mp 142–144 °C dec; MS, *m/z* 452 (MH^+, 10), 451 (M^+, 6), 373 (MH^+ − py, 83), 372 (M^+ − py, 100), 368 (2), 290 (78), 273 (8); IR (KBr) 3105 (w), 3035 (w), 2930 (s), 1600 (w), 1555 (s), 1485 (w), 1440 (m), 1230 (s), 1080 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (m, 6, 2 CH_3), 1.96 (q, 2, CH_2), 2.05 (s, 12, dmg Me), 2.15 (q, 2, CH_2), 5.36 (m, 1, C=CH), 7.30 (m, 2, β-py), 7.67 (m, 1, γ-py), 8.63 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.2 (dmg Me), 14.2, 14.7, 23.8, 30.7, 125.0, 137.3, 148.0, 149.4, 149.7 (C=N). Anal. Calcd for $C_{19}H_{30}N_5O_4Co$: C, 50.53; H, 6.70; N, 15.61. Found: C, 49.67; H, 6.73; N, 15.12.

Bis(dimethylglyoximato)(pyridine)(2-methyl-2-butenyl)cobalt Complex (6c). Reaction of 1 mmol of **5** with 0.9 mmol of **1c** gave after workup 74 mg (18.7%) of **6c** as an orange, powdery solid: mp 150–152 °C dec; MS, *m/z* 438 (MH^+, 15), 437 (M^+, 10), 359 (MH^+ − py, 19), 358 (M^+ − py, 22), 290 (100), 273 (19); IR (KBr) 3110 (w), 3060 (w), 2960 (s), 1600 (w), 1560 (s), 1450 (s), 1360 (m), 1260 (s), 1230 (s), 1100 (s), 1030 (s), 800 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (s, 3, Me), 1.78 (s, 3, Me), 1.84 (s, 3, Me), 2.11 (s, 12, dmg Me), 7.21 (m, 2, β-py), 7.62 (m, 1, γ-py), 8.59 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.3 (dmg Me), 23.4 (Me), 23.9 (Me), 24.9 (Me), 124.9, 129.9, 137.1, 149.4 (C=N), 150.6.

Bis(dimethylglyoximato)(pyridine)(3,3-dimethyl-2-butenyl)cobalt Complex (6d). Reaction of 5 mmol of **5** with 4.5 mmol of **1d** gave upon workup 0.92 g (45%) of **6d** as an orange, microcrystalline solid: mp 149–152 °C dec, MS, *m/z* 452 (MH^+, 1.2), 451 (M^+, 2.3), 373 (MH^+ − py, 4), 372 (M^+ − py, 10), 341 (6), 290 (100), 273 (30); IR (KBr) 3110 (w), 3070 (w), 2960 (s), 1600 (w), 1560 (s), 1445 (m), 1230 (s), 1080 (s), 1030 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 9, *t*-Bu), 2.10 (s, 12, dmg Me), 4.0 (d, *J* = 4.2 Hz, 1, C=CH), 4.80 (d, *J* = 4.2 Hz, 1, C=CH), 7.25 (m, 2, β-py), 7.62 (m, 1, γ-py), 8.61 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.4 (dmg Me), 32.0 (*t*-Bu, Me), 43.7 (*t*-Bu) 113.8,

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124.9, 137.2, 149.2 (C=N), 150.9.

Bis(dimethylglyoximato)(pyridine)(cyclohexylmethylidene)cobalt Complex (6e). Reaction of 5 mmol of **5** with 4.5 mmol of **1e** gave after workup 1.05 g (51%) of **6e** as an orange, powdery solid: mp 150-152 °C dec; MS, *m/z* 464 (MH^+, 20), 463 (M^+, 11), 385 (MH^+ - py, 86), 384 (M^+ - py, 100), 368 (7), 359 (18), 290 (45); IR (KBr) 3110 (w), 3050 (w), 2920 (s), 1600 (w), 1560 (s), 1490 (w), 1440 (s), 1360 (m), 1270 (m), 1230 (s), 1080 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (m, 4, CH_2), 1.45 (m, 2, CH_2), 2.08 (m, 2, CH_2), 2,10 (s, 12, dmg Me), 2.20 (m, 2, CH_2), 5.36 (s, 1, C=CH), 7.32 (m, 2, β-py), 7.71 (m, 1, γ-py), 8.67 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.2 (dmg Me), 27.1, 29.06, 30.05, 30.50, 40.0, 125.0, 137.3, 145.1, 149.45 (C=N), 149.70.

Reaction of 5 with Vinyl Triflate 3*Z*. Formation of 7*Z*. Treatment of 400 mg (1.5 mmol) of pure triflate **3*Z*** with 1.6 mmol of **5** (freshly generated from 380 mg of $CoCl_2 \cdot 6H_2O$, 370 mg of dimethylglyoxime, 126 mg of pyridine, 200 mg of NaOH, and 17 mg of $NaBH_4$ in 6 mL of CH_3OH/H_2O) and workup according to the above general procedure gave 420 mg (58%) of **7*Z*** as an orange, microcrystalline product: mp 170-175 °C dec; NMR showed no other product and no **7*E*** could be detected by either ^1H or ^{13}C NMR; IR (KBr) 3110, 3040, 2930, 1600, 1560, 1445, 1290, 1230, 1085, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.88 (s, 12, dmg Me), 1.96 (d, 3, Me), 4.98 (m, 1, C=CH), 7.0-7.2 (m, 7), 7.70 (m, 1, γ-py), 8.47 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.0 (dmg Me), 33.0 (Me), 124.99, 127.44, 128.21, 137.54, 144.43, 145.56, 149.42, 149.96. See the text and Table I for assignment of olefin stereochemistry.

Reaction of 5 with Vinyl Triflate 3*E*. Formation of a Mixture of 7*Z* and 7*E*. Treatment of 170 mg (0.66 mmol) of pure triflate **3*E*** with 0.70 mmol of **5** and workup as above gave 180 mg (56%) of a *mixture* of **7*E*** and **7*Z*** (66:34). The mixture could not be separated by chromatography, HPLC, or crystallization. All spectra were recorded on the mixture of product isomers (**7*E*** and **7*Z***). ^1H NMR [$CDCl_3$, **7*E*** only (by substraction of signals for **7*Z***)] δ 2.10 (dmg Me), 2.15 (d, 3, Me), 6.46 (m, 1, C=CH), 7.15-7.40 (m, 7), 7.74 (m, 1, γ-py), 8.72 (m, 2, α-py); ^{13}C NMR ($CDCl_3$, mixture of **7*E*** and **7*Z***) δ 12.0 (dmg Me), 17.6, 33.0, 124.99, 125.14, 125.74, 127.44, 127.55, 128.21, 137.54, 140.03, 144.43, 144.91, 145.56, 149.38, 149.42, 149.86, 149.90, 149.96. See the text and Table I for assignment of olefin stereochemistry.

Reaction of 5 with Vinyl Triflate 4*Z*. Formation of 8*Z* and 8*E*. Treatment of 250 mg (1.22 mmol) of pure isomeric **4*Z*** with 1.33 mmol of **5**, as above, and workup gave 300 mg (59%) of a mixture of **8*E*** and **8*Z*** (55:45). The mixture could not be separated by chromatography, HPLC, or crystallization. All spectra were obtained on the mixture and compared to the spectra of the product mixture from the reaction of pure **4*E***. See the text and Table I for assignment of olefin stereochemistry.

Reaction of 5 with Vinyl Triflate 4*E*. Formation of 8*Z* and 8*E*. Treatment of 125 mg (0.61 mmol) of pure isomeric **4*E*** with 0.7 mmol of **5**, as above, and workup gave 155 mg (60%) of a mixture of **8*E*** and **8*Z*** (88:12). The mixture could not be separated by chromatography, HPLC, or crystallization. All spectra were obtained on this mixture and compared to the spectra of the product mixture from the above reaction of pure **4*Z***. See the text and Table I for assignment of olefin stereochemistry. IR (KBr, 88:12 mixture of **8*E*** and **8*Z***) 3105, 3060, 3020, 3000, 2900, 2850, 1600, 1550, 1445, 1370, 1230, 990 cm^{-1}. For **8*E***: ^1H NMR ($CDCl_3$, recorded for 88:12 mixture of **8*E*** and **8*Z***) δ 1.47 (m, 3, Me), 1.66 (m, *J* = 6.72 Hz, 3, Me), 2.10 (s, 12, dmg Me), 4.97 (m, *J* = 6.72 Hz, 1.55 Hz, 1, C=CH), 7.30 (m, 2, β-py), 7.70 (m, 1, γ-py), 8.65 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.21 (dmg Me), 14.61 (Me), 19.54 (Me), 121.10, 124.95, 137.23, 149.42, 149.78. For **8*Z***: ^1H NMR ($CDCl_3$, recorded on a 55:45 mixture of **8*E*** and **8*Z***) δ 1.65 (m, 3, Me), 1.76 (m, *J* = 7.1 Hz, 3, Me), 2.10 (s, 12, dmg Me), 4.70 (m, *J* = 7.1, 1.70 Hz, 1, C=CH), 7.32 (m, 2, β-py), 7.70 (m, 1, γ-py), 8.68 (m, 2, α-py); ^{13}C NMR ($CDCl_3$, **8*E*** and **8*Z*** jointly) δ 12.21 (dmg Me), 14.61 (Me), 14.97 (Me), 19.54 (Me), 31.05 (Me), 121.10, 124.95, 124.98, 125.67, 137.23, 149.30, 149.42, 149.76, 150.15.

Test for the Isomerization of Starting Vinyl Triflates 3 and 4 under the Reaction Conditions. A 2-fold excess of *each* pure, isomeric vinyl triflate **3*E*** and **3*Z***, and 4E and 4Z was treated with **5** exactly as above. After the reaction was over, the unreacted starting triflates were analyzed on an analytical GC using a 0.125 in. × 6 ft, 10% UCW-982 on 80/100 Chromosorb W, column for **3*E*** and **3*Z*** and a 0.125 in. × 6 ft, 10% QF-1 on 100/120 Chromosorb W, column for **4*E*** and **4*Z***. In no case was any isomerization of the starting triflate observed.

Test for the Stability of the Isomeric Product Vinyl-Cobaloxime Complexes. Each of the cobaloxime products (0.1 mmol), **7*E***, **7*Z***, **8*E***, and **8*Z*** (or mixture of products, see above) from the reaction of the individual pure isomeric vinyl triflates **3** and **4** was refluxed for 2 h in a 1/1 CH_3OH:$CHCl_3$ mixture. After removal of the solvent, the residue was reanalyzed by ^1H NMR. No change was observed in any product ratios. Likewise, each of the previously isolated product mixtures was subjected to reaction with additional fresh **5**, $[Co(dmgH)_2py]^-$, under the general reaction conditions. Reisolated products, after standard workup, showed no change in isomer ratios by ^1H NMR analyses. Hence, all product ratios observed are the result of the actual reactions and not due to workup, prior, or post isomerization.

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Stereochemical Mechanism of Iodoacetic Acid Mediated Decomposition of L-Methionine to L-Homoserine Lactone

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Abstract: (2*S*,3*S*,4*S*)-, (2*R*,3*R*,4*R*)-, (2*S*,3*R*,4*R*)-, and (2*R*,3*S*,4*S*)-[3,4-$^2H_2$]methionine and (2*S*,3*S*,4*R*)-, (2*R*,3*R*,4*S*)-, (2*S*,3*R*,4*S*)-, and (2*R*,3*S*,4*R*)-[3,4-$^2H_2$]methionine were synthesized from (*E*)-[$^2H_2$]ethylene and (*Z*)-[$^2H_2$]ethylene, respectively, and were utilized to determine the stereochemical mechanism of the iodoacetic acid mediated decomposition of methionine to homoserine lactone. Additionally, a stereochemical mechanism for the conversion of protected tosyl derivatives of L-homoserine derivatives, chiral at the C-4 position due to isotopic substitution, to their corresponding methionine derivatives by reaction with sodium methanethiolate is also proposed.

Investigation of the stereochemical reaction mechanisms of enzymes responsible for the interconversion of four-carbon amino acids has necessitated the syntheses of regio- and stereospecific deuteriated four-carbon amino acids.[1-3] The key step in the synthesis of (4*S*)- and (4*R*)-[4-^2H]-L-methionine employs the direct displacement of a tosylate anion from an appropriately

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