Formation of (σ-Butatrienyl)- and (σ-Enynyl)cobaloxime Complexes via Reaction of (Dimethylglyoximato)(pyridine)cobalt Anion, $[Co(dmgH)_2py]^-$, with Alkynylvinyl Triflates. Stereochemistry and Mechanism of Formation†

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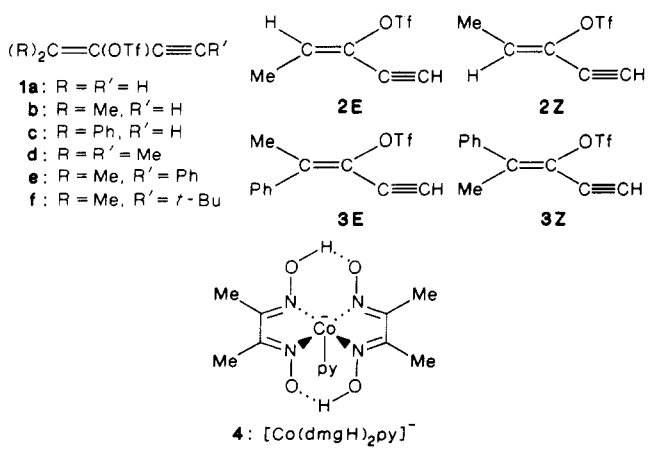
Alkynylvinyl triflates readily react with $[Co(dmgH)_2py]^-$ (**4**) to give either (σ-enynyl)- or (σ-butatrienyl)cobaloxime complexes depending upon the substitution pattern of the starting triflate. Reaction of either isomeric vinyl triflate **2E** or **2Z** gives only a single product enynyl complex **13E**. In contrast reaction of isomeric vinyl triflates **3E** and **3Z** with **4** is stereospecific, presumably with retention of olefin geometry, giving only the respective (σ-butatrienyl)cobaloxime complexes. A double nucleophilic vinylic substitution is invoked to rationalize these results.

The interaction of low-valent transition-metal systems with unsaturated organic substrates can lead to a wide variety of interesting organotransition-metal species as typified by σ- and π-olefin and acetylene complexes.[2] σ- as well as π-allenyl and butadienyl transition-metal complexes are also reasonably well established.[2] In contrast, despite the fact that highly unsaturated organic functionalities such as enynes, polyenes, polyynes, and cumulenes are well-known,[3,4] little, if anything, is known[5] about their interaction with transition metals.

Recently we reported[6] the reaction of Vaska's complex with ethynylvinyl triflates and the formation of novel, stable (σ-butatrienyl)iridium complexes, the first examples of extended σ-cumulenyl transition-metal species. With the aim of exploring the generality of this simple methodology for the ready formation of diverse σ-butatrienyl complexes, we undertook a systematic investigation of the reactions of alkynylvinyl triflates with a variety of transition-metal nucleophiles. In this and the following paper we wish to report the results of the reaction with $[Co(dmgH)_2py]^-$ and $(Ph_3P)_4Pt$, respectively.

Results and Discussion

Alkynylvinyl triflates **1–3** were prepared by standard literature procedure[7] from the corresponding known alkynyl ketones. The cobaloxime anion **4** was prepared from commercial $CoCl_2 \cdot 6H_2O$ under oxygen-free conditions by standard procedure.[8] Interaction of alkynylvinyl triflates



† Dedicated to Professor Dietmar Seyferth on the occasion of his 60th birthday.

Table I. Summary of Products of Reaction of 1 and 4

starting triflate	overall yield,[a] %	mp, °C dec	ratio of products % 5	% 6
1a	25	183–185	100	
1b	11	149–151		100
1c	13	157–159		100
1d	40	140–143		100
1e	43	*b*	80	20
1f	54	153–155	100	

[a] Isolated yields. [b] Not obtained on mixture.

1 with anion **4** in methanol/water (9:1, v/v) occurred in a matter of minutes, or less, at 0 °C yielding σ-enynyl, **5**, and/or σ-butatrienyl, **6**, cobaloxime complexes[9] as orange microcrystalline solids in 11–54% isolated yields (Table I). The reaction was conveniently followed by the color change of the solution from the deep blue color of the anion **4** to an orange-brown color. This color change occurred essentially upon mixing of the reagents (like a titration) and reaction was instantaneous, although stirring was maintained at 0 °C for an additional 5–10 min to assure completion. The product σ-enynyl, **5**, and σ-butatrienyl, **6**, cobaloxime complexes are reasonably stable in the solid-state (decomposition occurs after several days at room

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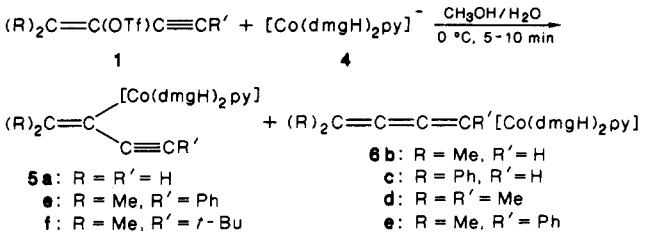
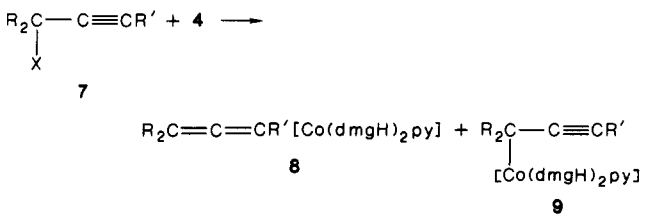


temperature) but decompose faster (several hours) in chlorinated solvents.

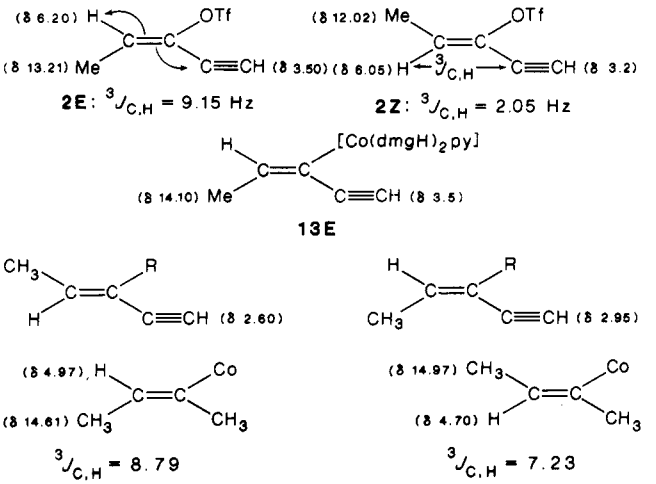
Cobaloxime complexes **5** and **6** were characterized by selected analytical and spectral means. The FAB mass spec showed molecular ions (and MH^+) for 1:1 adducts and a characteristic fragment ion at M^+ – pyridine (and MH^+ – py). The infrared, besides the absorptions characteristic of the C=N group of the dimethylgyoximato moiety at around 1550 and 1450 cm^{-1}, showed weak absorptions between 2060 and 2195 cm^{-1} for the C≡C enyne complexes **5** and between 1990 and 2030 cm^{-1} for the cumulenic stretch of **6**. The proton NMR, besides the absorptions due to the various enyne, **5**, σ-butatrienyl, **6**, units showed characteristic signals for the dmg methyl groups between 2.05 and 2.20 ppm and in the aromatic region for the complexed pyridine.[10] Most useful and characteristic were the ^{13}C NMR and in particular the location of the acetylenic carbons of **5** and the low-field cumulenic carbons of **6**. The signal due to the carbon directly attached to Co in either **5** or **6** was not observed because of the presence of the spin active (7/2) cobalt nucleus.[10,11]

Mechanistic Considerations. A number of alkylcobaloxime complexes are known,[12-14] formed by a simple S_N2 process between **4** and an alkyl halide. Likewise the reaction of propargyl halides, **7**, with **4** to give (σ-allenyl)cobaloxime (**8**) or (σ-propargyl)cobaloxime (**9**) complexes has been ascribed to an S_N2' process.[15-17]



Pasto and Timmers[17] observed that the formation of **8** vs **9** from **7** strongly depended on the terminal acetylenic substituent R' in **7**. When R' = H, only **8** was observed,[15] whereas when R' = CH_3 only **9** was observed.[17] These results were ascribed to the steric effects of R' and the relatively greater steric crowding in **8**, due to a shorter C_{sp^2}–Co bond distance than in **9**.[17] Our data (Table I) with the homologous enyne triflates **1** indicate that the picture is not so simple. The relative ease of formation of **5** and **6** depends upon both the β-substituents R in **1** and the acetylenic substituent R'. When there is a hydrogen in the β-position as in **1a** and **2**, only enyne products **5** are observed, whereas with **1b–d** and **3** only σ-butatrienyl products **6** are found. The terminal phenyl-substituted system **1e** results in a mixture of products, and only the very bulky *tert*-butyl group in **1f** forces the formation of exclusively enyne product **5f**. Hence to get further insight into the mechanism of reaction of enyne triflates **1** with **4**, we carried out careful stereochemical investigations of the reaction of **4** with **2** and **3**.

Chart I



Stereochemical Studies. Preparative GC was used to separate the respective geometric isomers **2E** and **2Z** in greater than 99% isomeric purity. The stereochemistry of **2E** and **2Z** has previously been assigned[6] on the basis of ^1H and ^{13}C NMR data briefly summarized in Chart I along with data for model compounds. Specifically, the relative $^3J_{C,H}$ coupling constants (i.e., $^3J_{trans} > {}^3J_{cis}$),[18] the relative proton chemical shifts of the acetylenic hydrogens,[19] and the relative carbon-13 chemical shifts of the β-methyls[20] are all consistent with the stereochemical assignments.

Reaction of either pure isomer, **2E** or **2Z**, with **4** gave only a *single* enyne product, **13E** and no isomeric **13Z** or σ-butatrienyl complex was observed,[21] as summarized in Scheme I. The stereochemistry of the product (enyne)-cobaloxime complex was assigned on the basis of the same spectral criteria as the starting materials discussed above. In particular the ^{13}C chemical shift of the β-methyl and the proton signal of the acetylenic hydrogen are all consistent with an *E* stereochemistry.

Since we have recently shown[1a,10] that vinylic nucleophilic substitution (S_NV)[22] by an addition–elimination process in the reaction of simple alkylvinyl triflates with **4** results in mostly stereoconvergence, this process is ruled out for the reaction of enynyl triflates with **4**. Moreover, such a process with enynyl triflates **1–3** would have to result in loss of conjugation between the alkene–alkyne π-system in the transition state and/or intermediate, an unlikely prospect. Hence, we believe that these results are best *rationalized* by the mechanism outlined in Scheme I.

Syn-S_N2' attack of the Co^-, **4**, on **2E** and **2Z** results in σ-butatrienyl compounds **11E** and **11Z**, respectively, either

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(20) Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617.
(21) As detected by ^1H and ^{13}C NMR, we estimate that ~3% of the isomeric products would have been easily observed.
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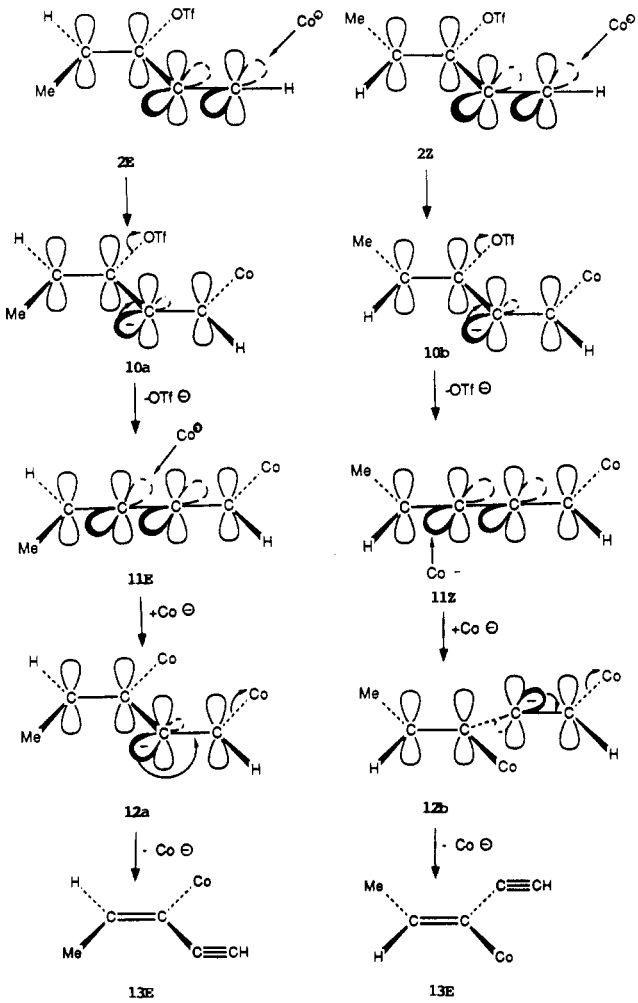
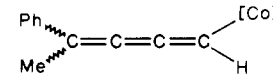
Scheme I



via vinyl anion like intermediates of **10a** and **10b** or in a more or less concerted process. Syn attack is postulated on the basis of the known[6] *retention* of olefin stereochemistry in the reaction of **2E** and **2Z** with Vaska's complex to give the stable, isolable (σ-butatrienyl)iridium complexes analogous to **11E** and **11Z**. However, $[Co(dmgH)_2py]^-$ is known to be a much more powerful nucleophile (by about 10^7) than Vaska's complex.[23] Moreover, a nucleophile is simultaneously a reasonable leaving group.[24] Therefore, **11E** and **11Z** can be attacked by a second $[Co(dmgH)_2py]^-$ present in the medium. In order to preserve conjugation as well as to maintain the proper relative orientation of the incoming and leaving groups, this attack must occur in the plane of the olefin substituents as seen in Scheme I. Preferential attack should occur from the less hindered side (i.e., the side of H in both **11E** and **11Z**) resulting in retention of olefin geometry in the case of **2E** but inversion of olefin geometry in the case of **2Z** and hence the observation of a single identical product **13E** from either pure starting isomer.

This mechanism would predict that introduction of a second substituent into the β-position of **2** should (a) block the second attack by Co and result in a σ-butatrienyl complex, as is indeed observed with **1b–d**, and (b) the initial reaction should be stereospecific with *retention* of olefin geometry. To test this prediction we also examined the reaction of the individual isomeric vinyl triflates **3E** and **3Z** with **4**. Reaction of the individual isomers of **3** with **4** is indeed stereospecifc and gives *only* σ-butatrienyl complexes **14** as products as indicated by the spectral data.



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Specifically these products showed characteristic cumulene absorptions in the infrared at 2020 cm^{-1} (and no absorptions for C≡C or C≡CH) and low-field ^{13}C NMR signal, between 148 and 165 ppm for the C_{sp} carbons characteristic of cumulenes (and no signals for C≡C); likewise the ^1H NMR showed only cumulenic C=CH at 6.5 ppm and no C≡CH signals (see Experimental Section for full spectral details). Unfortunately, both the starting ethynylvinyl triflates **3** and the product (σ-cumulenyl)cobaloxime complexes **14** are tetra or "fully" substituted olefins, and short of X-ray crystallography there are no techniques presently known that allow unambiguous stereochemical assignments of such systems. Since to date we have been unable to grow suitable single crystals of either product and since the starting triflates are liquid, we unfortunately do not know the stereochemistry of either starting material or product. However, as predicted, the reactions are definitely stereospecific giving only σ-butarienyl complexes we *suspect* of retained olefin geometry.

Conclusion. A variety of alkynylvinyl triflates **1–3** react with $[Co(dmgH)_2py]^-$ resulting in reasonably stable, isolable, microcrystalline, orange σ-enynyl, **5**, or σ-butatrienyl, **6**, cobaloxime complexes. Reaction takes place at 0 °C in CH_3OH/H_2O in a few minutes or even seconds. The formation of either **5** or **6** is dependent upon both the β and acetylenic substituents; the presence of either a β-hydrogen or a *bulky* substituent on the acetylenic carbon results in (σ-enyne)cobaloxime complexes **5** whereas β,β-dialkyl groups give σ-butatrienyl complexes **6**. A double nucleophilic vinylic displacement reaction is invoked to rationalize these results. The first reaction occurs via a syn-S_N2' process, analogous to the formation of (σ-butatrienyl)iridium complexes,[6] resulting in (σ-butatrienyl)-cobaloxime complexes (with retained olefin geometry where relevant). A second in-plane nucleophilic attack from the less hindered side by a second Co anion, with $[Co(dmgH)_2py]^-$ as a leaving group, accounts for the formation of the enyne products **5**.

Experimental Section

General Data. 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 SC-300 and XL-300 spectrometer and are reported in parts per million (ppm) relative to internal Me_4Si (0.00); for ^{13}C NMR the locks were on deuterated solvents. Mass spectra were obtained on a Varian MAT731 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. and $CoCl_2 \cdot 6H_2O$ and dimethylglyoxime from MCB. Alkynylvinyl triflates **1a–f** are known compounds and were prepared by standard literature procedures.[7,25,26] The

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(24) The ability of metal centers to function as leaving groups is not widely recognized. For a recent cogent example see: Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 215 and references therein.

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preparation, isolation, separation, and characterization of the isomeric alkynylvinyl triflates **2E** and **2Z** have been described elsewhere.[6] The isomeric vinyl triflates **3E** and **3Z** were prepared as follows.

1-(Trimethylsilyl)-4-phenylpentyn-3-one. Reaction[7] of 2-phenylpropinoyl chloride (25.3 g, 150 mmol), commercial (Petrarch) bis(trimethylsilyl)acetylene (25.5 g, 150 mmol), and anhydrous $AlCl_3$ (20.0 g, 150 mmol) in 500 mL of dry CH_2Cl_2 at 0–5 °C for 3 h gave, after workup, 31 g (90%) of the title ketone as a pale yellow oil: bp 110 °C (1 mm); IR (neat), 3060 (w, ArH), 2145 (m, C≡C), 1670 (s, C=O), 850 (s, $SiMe_3$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.1 (s, 9 H), 1.48 (d, 3 H), 3.78 (q, 1 H), 7.15–7.40 (m, 5 H).

1-(Trimethylsilyl)-4-phenyl-3-penten-1-yn-3-yl Triflate. The above ketone (5.75 g, 25 mmol) was reacted with $(CF_3SO_2-)_2O$ (10.6 g, 37.5 mmol) and *N,N*-diisobutyl-2,4-dimethyl-3-pentylamine (Fluka) (7.1 g, 31 mmol) in dry CH_2Cl_2 (250 mL) at 25 °C for 24 h.[7] Workup, including column chromatography (SiO_2/hexane), gave 7.24 g (80%) of the title triflate as an 60:40 mixture (analytical GC; 0.125 in. × 6 ft 10% QF-1 on 100/120 chromosorb W, 200 °C) of geometric isomers: IR (neat, mixture) 2150 (w, C≡C), 1680 (w, C=C), 1400, 1210, 1130 (OSO_2CF_3) 840 (s, $SiMe_3$) cm^{-1}; ^1H NMR ($CDCl_3$) *major isomer* δ 0.17 (s, 9 H), 2.24 (s, 3 H), 7.2–7.6 (m, 5 H), *minor isomer* δ 0.3 (s, 9 H), 2.32 (s, 3 H), 7.2–7.6 (m, 5 H).

4-Phenyl-3-penten-1-yn-3-yl Triflates (3E and 3Z). The above *mixture* of silyl triflates (3.0 g, 8.3 mmol) and $KF·2H_2O$ (2.4 g, 25 mmol) were stirred in MeOH (80 mL) at 25 °C for 30 min.[7] Workup and column chromatography (SiO_2/hexane) gave 2.1 g (84%) of a 60:40 mixture of **3E** and **3Z**. The two isomers were separated by HPLC by using a Varian micropack normal phase column [hexanes (HPLC grade), λ = 220 nm, flow rate = 2 mL/min]. Since we were unable to assign stereochemistry to the individual isomers (see text), they are referred to as *major isomer* (first fraction or **3F**) and *minor isomer* (second fraction or **3S**). For *major isomer* **3F** (**3E** or **3Z**): ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 3.21 (s, 1 H), 7.37–7.51 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.23 (CH_3), 75.13, 83.94 (C≡C), 118.1 (q, OSO_2CF_3) 126.70, 127.90, 128.28, 129.03, 136.60, 142.05. *Minor isomer* **3S** (**3E** or **3Z**): ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 3.60 (s, 1 H), 7.28–7.47 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 21.28 (CH_3), 74.94, 86.10 (C≡C), 118.0 (q, OSO_2CF_3), 124.97, 127.65, 128.38, 128.91, 135.66, 141.37.

General Procedure for the Reaction of Alkynylvinyl Triflates 1–3 with $[Co(dmgH)_2py]^-$ (4). Formation of 5f. Cobaloxime anion **4** was generated[10,27] in 20 mL of 9:1, CH_3OH/H_2O, from dimethylglyoxime (1.16 g, 10 mmol), $CoCl_2·6H_2O$ (1.19 g, 5 mmol), pyridine (0.4 g, 5 mmol), 0.60 g (15 mmol) of NaOH, and 0.05 g (1.3 mmol) of $NaBH_4$. To the cooled, 0 °C, blue solution of **4** was added 1.14 g (4 mmol) of triflate **1f**, and the mixture was stirred at 0 °C for 5–10 min. After cooling to −20 °C for 2 h, filtration, and column chromotgraphy (activated SiO_2/dry THF, dry hexanes) (enyne)cobaloxime complex **5f** was obtained as a yellow-orange solid: IR (KBr) 2180 cm^{-1} (C≡C); MS *m/e* 504 (MH^+, 2), 503 (M^+, 1), 425 (MH^+ − py, 25), 424 (M^+−py, 15), 368 (12), 290 (47), 273 (100); ^1H NMR ($CDCl_3$) δ 1.26 (s, 9, *t*-Bu), 1.82 (s, 3, Me), 2.01 (s, 3, Me), 2.08 (s, 12, dmg Me), 7.21 (m, 2, β-py), 7.62 (m, 1, γ-py), 8.61 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.32 (dmg Me), 22.33, 28.66 (Me), 28.73 (q C of *t*-Bu), 30.88 (Me of *t*-Bu), 84.27, 104.0 (C≡C), 124.89, 137.29, 143.20, 149.89, 150.29 (C=N).

(Enyne)cobaloxime Complex 5a. Reaction of 10 mmol of **1a**, as above, gave **5a** as an orange microcrystalline solid: IR (KBr) 3220 (C≡CH), 2063 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 2.1 (s, 12, dmg Me), 3.4 (s, 1, C≡CH), 5.1 (s, 1, C=CH_2), 5.2 (s, 1, C=CH_2), 7.3 (m, 2 β-py), 7.7 (m, 1, γ-py), 8.6 (m, 2, α-py); ^{13}C NMR (DMSO-d_6) δ 12.3 (dmg Me), 82.6, 88.2 (C≡C), 126.0, 128.0, 139.1, 149.5, 150.3. Anal. Calcd for $C_{17}H_{22}N_5O_4Co$: Co, 14.0; C, 48.69; H, 5.29. Found: Co, 13.3; C, 48.94, H, 5.33.

Enyne, 5e, and σ-Butatrienyl, 6e, Cobaloxime Complexes. Reaction of 5 mmol of **1e**, as above, and workup gave a *mixture* of **5e** and **6e** as an orange, powdery solid. The mixture could not be separated by HPLC or recrystallization and was characterized by spectra as the *mixture*: MS *m/e* 524 (MH^+, 4), 523 (M^+, 2), 460 (12), 445 (MH^+ − py, 29), 444 (M^+ − py, 15), 368 (5), 290 (73), 273 (100); IR (KBr, mixture) 2195 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) for **5e**, δ 1.99 (s, 3, Me), 2.14 (s, 12, dmg Me), 2.17 (s, 3, Me), 6.95–7.75 (m, 8) 8.70 (m, 2, α-py); for **6e**, δ 1.97 (s, 6, Me), 2.06 (s, 12, dmg Me), 6.90–7.70 (m, 8), 8.50 (m, 2, α-py); ^{13}C NMR ($CDCl_3$, for **5e** and **6e** jointly) δ 12.25, 19.25, 21.28, 23.21, 29.62, 79.74, 95.08, 95.91, 121.41, 125.05, 125.17, 126.16, 126.50, 126.67, 126.76, 127.20, 127.92, 128.44, 129.26, 130.39, 131.40, 137.50, 137.68, 146.73, 149.81, 150.07, 150.72.

(σ-Butatrienyl)cobaloxime Complex 6b. Reaction of 10 mmol of **1b**, as above, and workup gave **6b** as an orange solid: IR (KBr) 2028 cm^{-1} (C=C=C=C); ^1H NMR ($CDCl_3$) δ 1.8 (s, 3, Me), 1.9 (s, 3, Me), 2.2 (s, 12, dmg Me), 5.9 (s, 1, =CH), 7.3 (m, 2, β-py), 7.7 (m, 1, γ-py), 8.6 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.3 (dmg Me), 22.6, 24.0 (Me), 109.7, 125.3, 137.9, 149.5, 150.2, 156.4, 164.4. Anal. Calcd for $C_{19}H_{26}N_5O_4Co$: Co, 13.2; C, 51.01; H, 5.86. Found; Co, 12.5; C, 50.72; H, 5.97.

(σ-Butatrienyl)cobaloxime Complex 6c. Reaction of 10 mmol of **1c**, as above, gave after workup **6c** as an orange solid: IR (KBr), 1990 cm^{-1} (C=C=C=C); ^1H NMR ($CDCl_3$) δ 2.1 (s, 12, dmg Me), 6.9 (s, 1, =CH), 7.3–8.0 (m, 13), 8.8 (m, 2, α-py); ^{13}C NMR ($CDCl_3$) δ 12.2 (dmg Me), 118.3, 125.4, 126.7, 127.0, 128.0, 128.3, 129.6, 138.0, 138.4, 138.8, 150.0, 150.1, 156.7, 170.9. Anal. Calcd for $C_{29}H_{30}N_5O_4Co$: Co, 10.3; C, 60.95; H, 5.29. Found: Co, 9.76; C, 60.89, H, 5.34.

(σ-Butatrienyl)cobaloxime Complex 6d. Reaction 1.0 mmol of **1d**, as above, and workup gave **6d** as an organe-yellow solid: IR (KBr) 2030 cm^{-1} (C=C=C=C); ^1H NMR ($CDCl_3$) δ 8.65 (m, 2, α-py), 7.7 (m, 1, γ-py) 7.3 (m, 2, β-py), 2.15 (s, 12, dmg Me), 2.05 (s, 3, Me), 1.95 (s, 3, Me), 1.80 (s, 3, Me), ^{13}C NMR (50:50 $C_2D_6CO/CDCl_3$) δ 149.38, 149.09, 139.10, 137.47, 124.71, 124.53, 109.96, 23.86 (Me), 23.26 (Me), 18.94 (Me), 11.36 (dmg Me).

Reaction of Pure 2E and 2Z with 4. Formation of 13E. Separate reactions of 0.5 mmol each of pure **2E** and **2Z**, as above, gave after a workup a single product, enyne complex **13E** as an orange solid: IR (KBr) 3240 (C≡CH), 2060 cm^{-1} (C≡C); ^1H NMR ($CDCl_3$) δ 8.50 (m, 2, α-py), 7.6 (m, 1, γ-py), 7.2 (m, 2, β-py), 5.4 (q, 1), 3.55 (s, 1), 2.1 (s, 12), 1.85 (d, 3); ^{13}C NMR ($CDCl_3$) δ 150.43, 150.29, 138.46, 137.83, 125.31, 85.33, 84.33, 18.63 (Me), 12.19, (dmg, Me).

Reaction of Pure 3E and 3Z with 4. Formation of 14. Separate reactions of 0.28 mmol each of pure **3E** and **3Z**, as above, gave, after workup, two distinct isomers of **14**. Reaction of the major isomer (99% pure) **3F**, gave 60 mg (42%) of **14**: mp 155–160 °C dec; IR (KBr) 2020 cm^{-1} (C=C=C=C); ^1H NMR ($CDCl_3$) δ 2.10 (s, 12, dmg Me), 2.12 (s, 3, Me), 6.5 (s, 1, =C=CH), 7.00–7.75 (m, 8), 8.6 (m, 2, α-py). Reaction of the minor isomer **3S** gave 52 mg (38%) of **14**: mp 150–153 °C dec; IR (KBr) 2020 cm^{-1} (C=C=C=C); ^1H NMR ($CDCl_3$) δ 2.13 (s, 3, Me), 2.17 (s, 12, dmg Me), 7.00–7.8 (m, 8), 8.62 (m, 2, α-py).

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Registry No. **1a**, 71451-06-4; **1b**, 71451-07-5; **1c**, 71451-08-6; **1d**, 100109-00-0; **1e**, 100108-99-4; **1f**, 75700-32-2; **2E**, 106211-71-6; **2Z**, 106211-72-7; **3E**, 119072-34-3; **3Z**, 119072-35-4; **4**, 53790-02-6; **5a**, 77945-97-2; **5e**, 119325-91-6; **5f**, 119325-90-5; **6b**, 77932-77-5; **6c**, 77932-78-6; **6d**, 119325-93-8; **6e**, 119325-92-7; **13E**, 119325-94-9; **14** (isomer 1), 119325-95-0; **14** (isomer 2), 119365-53-6; $CoCl_2$, 7646-79-9; $(CF_3SO_2)_2O$, 358-23-6; 1-(trimethylsilyl)-4-phenylpentyn-3-one, 119296-70-7; 2-phenylpropinoyl chloride, 22414-26-2; bis(trimethylsilyl)acetylene, 14630-40-1; 1-(trimethylsilyl)-4-phenyl-3-penten-1-yn-3-yl triflate, 119296-71-8; *N,N*-diisobutyl-2,4-dimethyl-3-pentylamine, 54561-97-6; dimethylglyoxime, 95-45-4.

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