Preparation of Cobaloxime-Substituted Unsaturated Carbonyl Compounds and Their Subsequent Conversion into 1-Cobaloxime-Substituted 1,3-Dienyl Complexes

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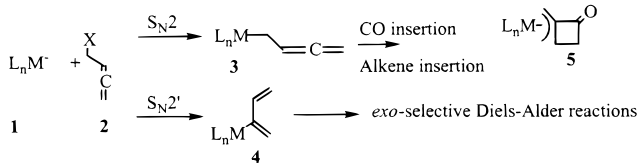
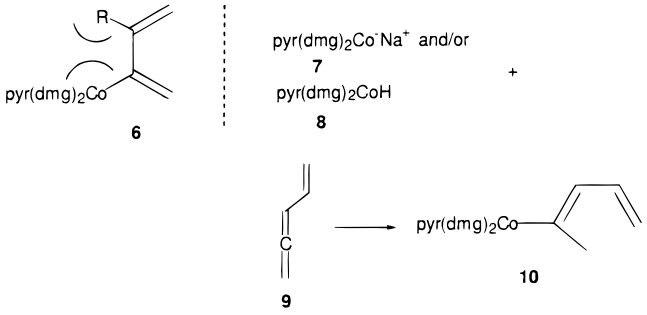
Reduced cobaloxime (cobaloxime = [(pyridine)(dimethylglyoxime)$_2$cobalt]) compounds react with a variety of oxygen-substituted allenic and propargyl electrophiles to produce cobaloxime-substituted α,β- or β,γ-unsaturated ketones and aldehydes. Two of the new unsaturated acyl complexes prepared have been characterized by X-ray crystallography. Several of the α,β-unsaturated acyl complexes were subsequently converted into 1-cobaloxime-1,3-dienyl complexes using Peterson or Petasis olefinations. One of these new dienyl complexes has also been characterized by X-ray crystallography.

Introduction

Over the last 7 years, we have reported a number of examples of transition-metal anions (**1**) which react with allenic electrophiles (**2**) to produce products that can be rationalized by S_N2'[1] and S_N2[2] reactions of **1** with **2**. We have also reported an alternative method for the preparation of 2-cobaloxime-substituted 1,3-dienyl complexes that involves hydrocobaltation reactions of enynes.[3] The 2-transition-metal-substituted 1,3-dienes (**4**)[1] are extremely reactive in Diels−Alder [4 + 2] cycloadditions,[1] and the 4-transition-metal-substituted 1,2-dienes (**3**)[2] are precursors for metal-complexed alkylidene cyclobutanone synthesis (**5**).[2a,4]



While exploring the scope and limitations of Diels−Alder reactions of 2-cobaloxime-substituted 1,3-dienes, we found that we could not effect Diels−Alder reactions of dienyl complexes that were 2,3-disubstituted (**6**).[2b] To circumvent this synthetic limitation, we began to look for methods of preparing 1-cobaloxime-substituted 1,3-dienes. Hydrocobaltation of vinyl allenes (**9**) proved successful but again suffers from the limitation of requiring the synthesis of easily polymerizable vinyl allenes (**9**) and only leads to 1,1-disubstituted 1,3-dienyl complexes (**10**).[5]



We have also previously shown that cobaloxime anions (**7**) and hydrides (**8**) react with ynones (**11**) and ynoates (**11**, R_2 = OR) to produce unsaturated acyl complexes (**12**−**14**).[6] We thought alkenation of β-cobaloxime-substituted α,β-unsaturated acyls such as **12** and **13** might provide a general solution to the diene synthesis problem outlined above. However, the most synthetically useful ynone and ynoate hydrocobaltation procedures we reported back in 1997[6] yielded the Z isomer (**13**) as the major or exclusive product, and we suspected dienes prepared from **13** might also have problems attaining the *s-cis* conformation required for Diels−Alder reactions.

Here, we report reactions of cobaloximes with allenic and alkynyl carbonyl compounds and other oxygen-substituted allenic and alkynyl electrophiles, which in

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[#] To whom inquiries concerning X-ray structure determinations should be sent.

(1) For a review of our work in this area see: Welker, M. E.; Wright, M. W.; Stokes, H. L.; Richardson, B. M.; Adams, T. A.; Smalley, T. L.; Vaughn, S. P.; Lohr, G. J.; Liable-Sands, L.; Rheingold, A. L. *Adv. Cycloaddition* **1997**, *4*, 149. For some other recent references to the primary literature see: (a) Richardson, B. M.; Day, C. S.; Welker, M. E. *J. Organomet. Chem.* **1999**, *577*, 120. (b) Adams, T. A.; Welker, M. E.; Day, C. S. *J. Org. Chem.* **1998**, *63*, 3683. For a recent review of cobaloxime chemistry see: Tada, M. *Rev. Heteroatom Chem.* **1999**, *20*, 97.

(2) (a) Vinson, N. A.; Day, C. S.; Welker, M. E.; Guzei, I.; Rheingold, A. L. *Organometallics* **1999**, *18*, 1824. (b) Stokes, H. L.; Richardson, B. M.; Wright, M. W.; Vaughn, S. M.; Welker, M. E.; Liable-Sands, L.; Rheingold, A. L. *Organometallics* **1995**, *14*, 5520. (c) Stokes, H. L.; Smalley, T. L.; Hunter, M. L.; Welker, M. L.; Rheingold, A. L. *Inorg. Chim. Acta* **1994**, *220*, 305.

(3) Stokes, H. L.; Welker, M. E. *Organometallics* **1996**, *15*, 2624.

(4) Benyunes, S. A.; Deeth, R. J.; Fries, A.; Green, M.; McPartlin, M.; Nation, C. B. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3453.

(5) Lohr, G. J.; Welker, M. E. *Inorg. Chim. Acta* **1999**, *296*, 13.

(6) Adams, T. A.; Welker, M. E. *Organometallics* **1997**, *16*, 1300.

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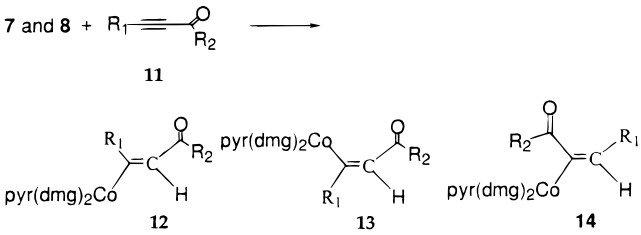
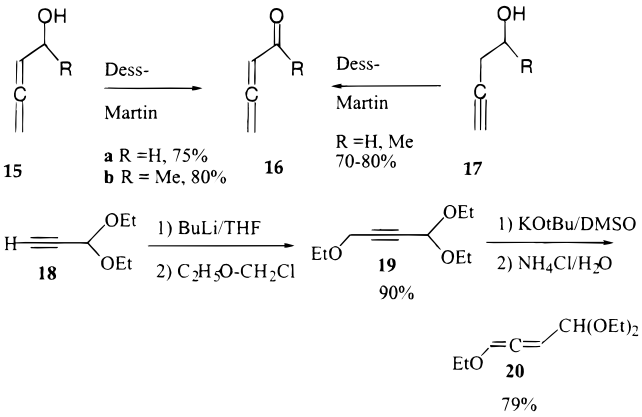


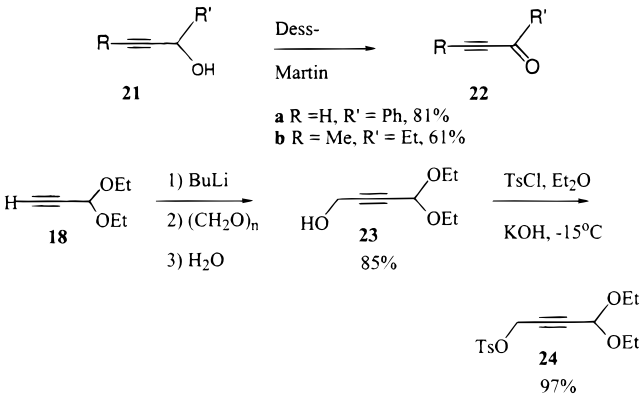
several cases provide a new route to β-cobaloxime-substituted α,β-unsaturated carbonyl compounds with the E alkene geometry, which will most likely prove best for subsequent Diels−Alder reactions. Several of these cobalt-substituted acyls are then converted into 1-cobaloxime-substituted 1,3-dienyl complexes using carbonyl olefination reactions.

Results and Discussion

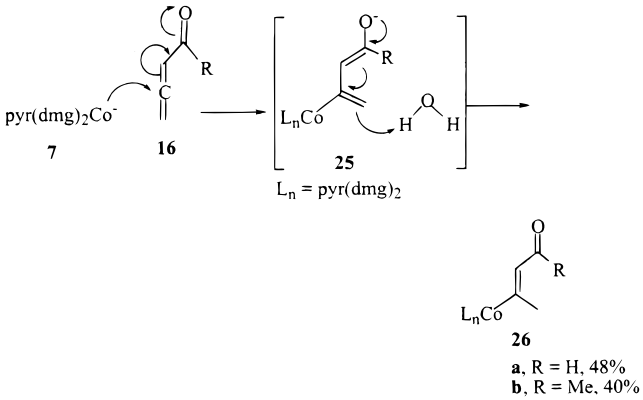
(a) Preparation of Oxygenated Allenic Electrophiles. Allenic aldehyde **16a** and allenic ketone **16b** can be prepared by Dess−Martin oxidation of the allenic alcohols[7] **15** or, even more conveniently, by a Dess−Martin oxidation/isomerization reaction of the commercially available alkynols **17**.[8] We also easily prepared propargyl ether **19** since its preparation and isomerization to the allenic ether **20** had been previously reported.[9,10]



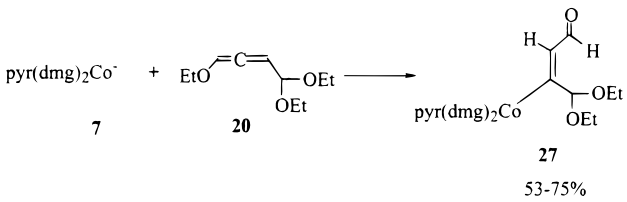
(b) Preparation of Oxygenated Alkynyl Electrophiles. Two of the alkynones we used in this study, 3-butyn-2-one and 3-hexyn-2-one, are commerically available, and the other two used (**22a** and **22b**) were easily prepared via Dess−Martin oxidation of the commercially available alkynols **21a** and **21b**.[7,8] Likewise alkynyl tosylate **24** was easily prepared from commercially available **18** by procedures analogous to those we have reported previously.[1]



(c) Reactions of Allenic Electrophiles with Cobaloximes. Following preparation of the allenic carbonyl compounds **16**, cobaloxime anion **7** was generated at −20 °C in THF, the appropriate electrophiles (**16a** or **b**) were added at −20 °C, and then the solutions were allowed to warm to 25 °C and quenched with ice water. Both substrates **16a**,**b** yielded β-cobaloxime-susbstituted α,β-unsaturated compounds **26a**,**b** in ca. 50% yield. The isolation of these products (**26**) can be rationalized via Michael reaction of the cobaloxime anion **8** with the allenic carbonyl compounds **16** followed by protonation (**25**), analogous to chemistry we have reported previously.[1]



Reactions of the oxygen-substituted allene (**20**) with cobaloxime proved much more complicated than we initially anticipated. Oxygenated allene **20** reacted with cobaloxime anion **7** in EtOH to produce α,β-unsaturated acyl complex **27** in good yield. The isolation of this complex (**27**) was unexpected since it represents a cobaloxime addition to **20** without concomitant reduction of **20**.



Complex **27** was present in the crude product of the **7** + **20** reaction, prior to chromatography, so its presence

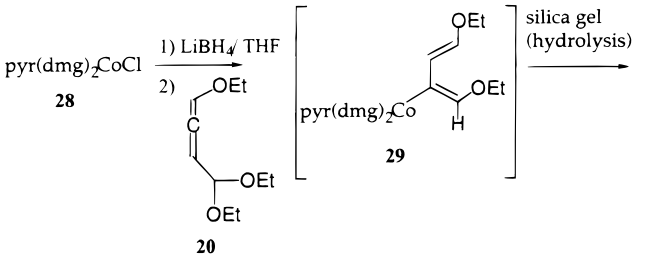
(7) (a) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550. (b) Marshall, J. A.; Wang, X. *J. Org. Chem.* **1991**, *56*, 960. (c) Marshall, J. A.; Sehon, C. A. *J. Org. Chem.* **1995**, *60*, 5966. (d) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.

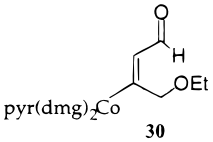
(8) Hashmi, A. S. K.; Ruppert, T. L.; Knofel, T.; Bats, J. W. *J. Org. Chem.* **1997**, *62*, 7295.

(9) (a) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier Publishing Co.: New York, 1988; pp 260−261. (b) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Actylenes, Allenes, and Cumulenes*; Elsevier Publishing Co.: New York, 1981; pp 65, 94−96, 171, 188, 238.

(10) (a) van Rijn, P. E.; Everhardus, R. H.; van der Ven, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas.* **1981**, *100*, 372. (b) Van Boom, J. H.; Montijn, P. P.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim.* **1965**, *84*, 31. (c) Montijn, P. P.; Schmidt, H. M.; Van Boom, J. H.; Bos, H. J. T.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim.* **1965**, *84*, 271. (d) Mantione, R. *Bull. Chim. Soc. Fr.* **1969**, 4514. (e) Mantione, R. *Bull. Chim. Soc. Fr.* **1969**, 4523.

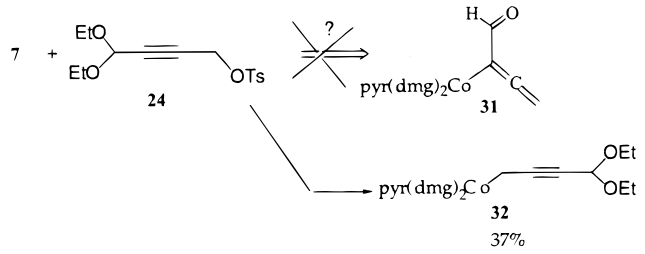
is not due to air oxidation of SiO_2.[11] We could speculate on the mechanism of formation of **27** but will not since the focus of this work is on the preparation of α,β-unsaturated acyls that can be converted to dienyl complexes. Regarding this mechanism question, we can note that switching from EtOH to the polar aprotic solvent THF (where the predominant cobaloxime species present should be **7** rather than **8**) yielded a crude product that by ^1H NMR appeared to be a 3.5:1 mixture of dienyl complex **29** [($CDCl_3$): 8.60 (d, J = 5.0 Hz, 2H), 7.75 (t, J = 5.0 Hz, 1H), 7.30 (t, J = 5.0 Hz, 2H), 6.4 (d, J = 12.8 Hz, 1H), 5.7 (s, 1H), 5.1 (d, J = 12.8 Hz, 1H), 3.7 (q, J = 6.9 Hz, 2H), 3.6 (q, J = 7.1 Hz, 2H), 2.19 (s, 12H), 1.2 (t, J = 7.1 Hz, 3H), 1.1 (t, J = 7.1 Hz, 3H)] and pyr(dmg)$_2$CoCl (**28**). However, attempts to purify **29** by recrystallization or chromatography on silica resulted in enol ether hydrolysis, and the only isolable new cobaloxime complex from this reaction proved to be another α,β-unsaturated acyl of E alkene geometry (**30**).



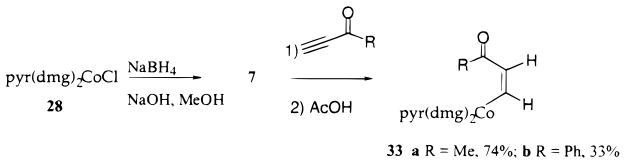


(d) Reactions of Alkynyl Electrophiles with Cobaloximes. Alkynyl electrophile **24** is included here because we suspected it would react with cobaloxime anion **7** followed by hydrolysis to generate aldehyde **31**, which could also be converted into an interesting dienyl complex. Somewhat surprisingly, from propargyl tosylate **24**, we isolated only the S_N2 product **32**. We have reported one other example of a 1,1-disubstituted allenic tosylate which also reacted with cobaloxime anion **7** to give a S_N2 rather than S_N2' product.[2b] In both of these cases where we have observed S_N2 products, the carbon α to the site of possible S_N2' attack has been disubstituted, so perhaps the two substitutents provide enough steric hindrance to direct cobaloxime addition away from the S_N2' position.

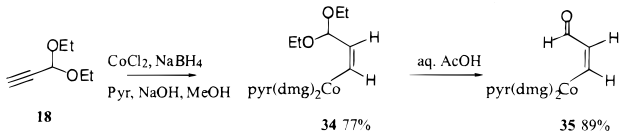
We next prepared three unsaturated acyl complexes with Z-alkene geometry (**33a**, **33b**, **35**) by analogy with chemistry we reported earlier.[6] All these preparations involve reactions of cobaloximes with terminal alkynes. Dienes prepared from these acyls would be expected to react slowly in Diels−Alder reactions unless Z to E isomerization occurred prior to cycloaddition. Since we had noted such thermal isomerizations previously in



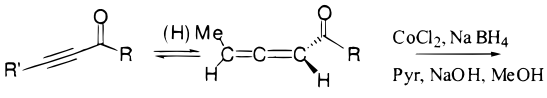
cobaloxime diene [4 + 2] cycloadditions, preparation of these substrates appeared warranted.[12]



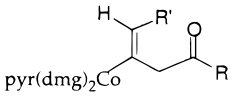
33 a R = Me, 74%; **b** R = Ph, 33%



The two isomeric internal alkynes **36a**,**b** were also subjected to similar cobaloxime addition reaction conditions. Both of these internal alkynes yielded unexpected β,γ-unsaturated cobalt acyl complexes **38** and **39**. The formation of these complexes can be rationalized by base-induced alkyne **36**−allene **37** isomerization[9,10] followed by cobaloxime addition to the central sp-hybridized carbon of the isomeric allene **37**. Both of these unusual β,γ-unsaturated acyls were characterized by X-ray crystallography.



36a R = Et, R' = Me
22b R = Me, R' = Et
37



38 R' = H, R = Et 35%
39 R' = Me, R = Me 48%

Figures 1 and 2 show the ORTEP drawings of compounds **38** and **39**. The bond lengths (Å) and the bond angles (deg) for **38** are displayed in Tables 2 and 3, and the analogous data for **39** are presented in Tables 5 and 6. As Figures 1 and 2 show, the two β,γ-unsaturated acyl cobalt complexes, **38** and **39**, show different orientations about the carbon 15−carbon 16 bond. The torsion angles (C14−C15−C16−C17) of **38** and **39** are 15° and 87°, respectively. The large torsion angle of **39** is due to the methyl substituent that lies *cis* to the remaining part of the organic R group.When comparing the cobalt−vinyl fragment of the crystal structures of **38** and **39** with that of the unsubstituted 2-cobaloxime-1,3-butadiene we have reported previously,[13] we note that the cobalt−carbon (Co1−C15) bond

(11) (a) Cohen, Z.; Keinan, E.; Mazur, Y.; Vacony, T. H. *J. Org. Chem.* **1975**, *40*, 2141. (b) Sosnowski, J. J.; Danaher, E. B.; Murray, R. K. *J. Org. Chem.* **1985**, *50*, 2759. (c) Ferreira, J. T. B.; Cruz, W. O.; Vieira, P. C.; Yonashimo, M. *J. Org. Chem.* **1987**, *52*, 3698.

(12) Wright, M. W.; Welker, M. E. *J. Org. Chem.* **1996**, *61*, 133.

(13) Wright, M. W.; Smalley, T. L.; Welker, M. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6777.

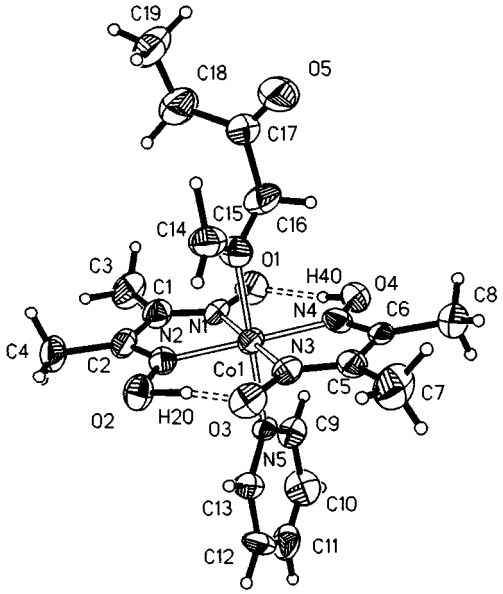


Figure 1. Molecular structure of compound **38** using 50% probability for thermal ellipsoids.

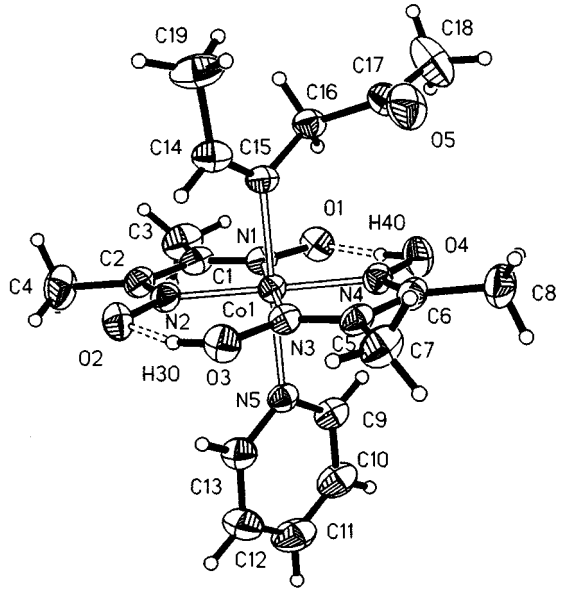


Figure 2. Molecular structure of compound **39** using 50% probability for thermal ellipsoids.

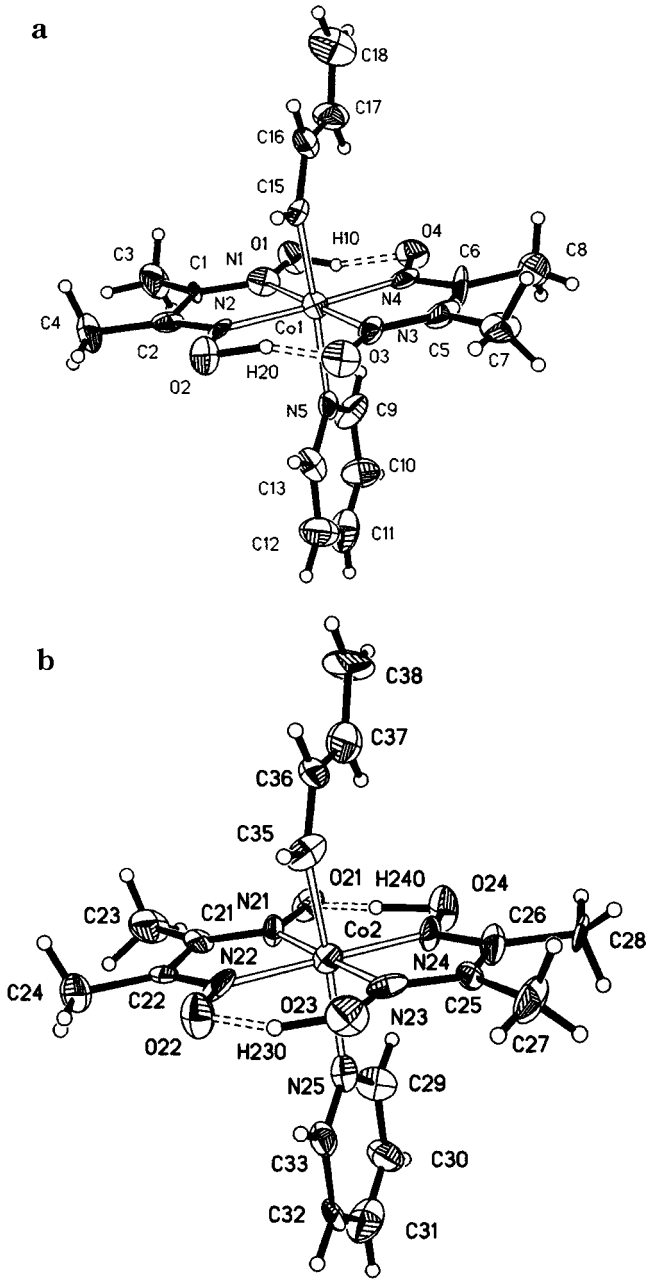


Figure 3. (a) Molecular structure of compound **45a** (molecule 1) using 50% probability for thermal ellipsoids. (b) Molecular structure of compound **45a** (molecule 2) using 50% probability for thermal ellipsoids.

length of all three compounds is approximately 2.0 Å. The carbon−carbon double bonds here, C14−C15 of **38** (1.34 Å) and C14−C15 of **39** (1.32 Å), are both within experimental error of a normal C=C bond length (1.337 Å).[14]

Last, on acyl complex synthesis, we tried a cobaloxime reduction/electrophile trapping procedure originally reported by Widdowson[15] for making cobaloxime complexes from base and polar protic solvent-sensitive α-halocarbonyl compounds. This method utilizes zinc to reduce $pyr(dmg)_2CO(III)X$ to cobalt(II) in polar aprotic solvents. In the cobaloxime generation method described above for the preparation of **7** and **8**, we reduced the cobalt with $NaBH_4$ in polar protic solvents and the acyl complexes we isolate can be rationalized by classical alkyne or allene hydrometalation. However, the Widdowson cobaloxime preparation is reported to initially generate $Co(II)(Pyr)_2(dmg)_2$ (**41**), which then reacts with electrophiles by electron-transfer chemistry rather than via cobaloxime anion (**7**) nucleophilic addition or cobaloxime hydride (**8**) hydrometalation. We find that this method of cobaloxime generation yields a cobalt species that reacts with alkynyl ketones to cleanly generate cobalt-substituted E alkenes (**43**) in high yield and stereoisomeric purity. This method failed to provide a good yield of the E unsaturated aldehyde **43a**, and we think this is partly due to the high water solubility of that compound. For our purposes this method proved complementary to the Schrauzer cobaloxime prepara-

(14) Mitchell, A. D., Cross, L. C., Eds. *Tables of Interatomic Distances and Angles*; The Chemical Society: London, 1958.

(15) Roussi, P. F.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1025.

Table 1. Crystal Data and Structure Refinement for (3-Oxo-5-hexen-5-yl)(pyridine)-bis(dimethylglyoximato) Cobalt(III) (38)

empirical formula	$C_{19}H_{28}CoN_5O_5$
fw	465.39
temperature	193(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, *Pn* (an alternate description of $Pc-C_s^2$ (No. 7))
unit cell dimens	$a = 8.3411(8)$ Å $b = 11.774(1)$ Å, $\beta = 94.202(2)°$ $c = 10.913(1)$ Å
volume	1068.88(18) Å^3
Z, calcd density	2, 1.446 g/cm^{-1}
abs coeff	0.843 mm^{-1}
$F(000)$	488
cryst size	0.13 × 0.14 × 0.24 mm
θ range for data collection	1.73−25.05°
limiting indices	$-9 \le h \le 9$, $-14 \le k \le 12$, $-12 \le l \le 8$
no. of reflns collected/unique	5654/2649 [$R_{int} = 0.0523$]
completeness to $\theta = 25.05$	99.8%
abs corr	empirical
max. and min. transmission	0.5287 and 0.4370
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2649/2/290
goodness-of-fit on F^2	0.933
final R indices	
[1874$F_o > 4\sigma(F_o)$ data]	R1 = 0.0439, wR2 = 0.0867
[all 2649 data]	R1 = 0.0715, wR2 = 0.0948
absolute structure (Flack) param	0.35(3)
largest diff peak and hole	0.440 and −0.274 e/Å^3

Table 2. Selected Bond Lengths (Å) of Compound 38

type	length, Å	type	length, Å
Co_1-N_1	1.867(6)	Co_1-N_3	1.900(6)
Co_1-N_2	1.887(6)	Co_1-N_4	1.875(6)
Co_1-N_5	2.050(6)	Co_1-C_{15}	2.008(9)
O_5-C_{17}	1.225(10)	$C_{15}-C_{16}$	1.435(11)
$C_{16}-C_{17}$	1.542(10)	$C_{17}-C_{18}$	1.484(11)
$C_{18}-C_{19}$	1.502(9)	$C_{14}-C_{15}$	1.339(11)

Table 3. Selected Bond Angles (deg) of Compound 38

type	angle, deg	type	angle, deg
$N_1-Co_1-N_4$	99.2(3)	$N_1-Co_1-N_5$	91.3(2)
$N_1-Co_1-N_2$	81.2(3)	$N_4-Co_1-N_5$	90.3(2)
$N_4-Co_1-N_3$	81.3(3)	$N_2-Co_1-N_5$	91.0(2)
$N_2-Co_1-N_3$	98.3(2)	$N_3-Co_1-N_5$	90.4(2)
$N_1-Co_1-C_{15}$	88.7(3)	$C_{15}-Co_1-N_5$	179.4(4)
$N_4-Co_1-C_{15}$	90.3(3)	$N_4-Co_1-N_2$	178.7(3)
$N_2-Co_1-C_{15}$	88.5(3)	$N_1-Co_1-N_3$	178.2(3)
$N_3-Co_1-C_{15}$	89.5(3)	$C_{14}-C_{15}-C_{16}$	121.4(8)
$C_{14}-C_{15}-Co_1$	121.3(6)	$C_{16}-C_{15}-Co_1$	116.8(6)
$O_5-C_{17}-C_{18}$	120.6(8)	$O_5-C_{17}-C_{16}$	122.6(8)
$C_{15}-C_{16}-C_{17}$	114.4(6)	$C_{18}-C_{17}-C_{16}$	116.8(8)
$C_{17}-C_{18}-C_{19}$	114.4(7)	$C_{15}-C_{14}-H_{14a}$	116(2)
$C_{15}-C_{14}-H_{14b}$	113(4)	$H_{14a}-C_{14}-H_{14b}$	130(4)

tion, which provided Z alkene acyl complexes (**33**−**35**).[16] We can rationalize the production of E alkenes by a reduction/coupling scheme proceeding through intermediate **42**, reminiscent of the intermediates proposed for dissolving metal reductions of alkynes.[17]

(e) Synthesis of 1-Cobaloxime-1,3-butadienes. Several of the new unsaturated acyl complexes prepared in this study were next subjected to olefination reac-

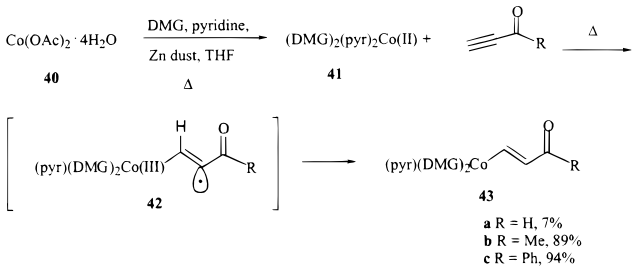
Table 4. Crystal Data and Structure Refinement for (2-Oxo-4(*E*)-hexen-4-yl)(pyridine)-bis(dimethylglyoximato) Cobalt(III)(dichloromethane) (39)

empirical formula	$C_{19}H_{28}CoN_5O_5(CH_2Cl_2)$
fw	550.32
temperature	233(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, $P2_1/c-C_{2h}^5$ (No. 14)
unit cell dimens	$a = 9.081(1)$ Å $b = 8.267(1)$ Å, $\beta = 96.01(1)°$ $c = 33.225(4)$ Å
volume	2480.5(6) Å^3
Z, calcd density	4, 1.474 g/cm^{-1}
abs coeff	0.947 mm^{-1}
$F(000)$	1144
crystal size	0.25 × 0.40 × 0.70 mm
θ range for data collection	2.26−26.37°
limiting indices	$-1 \le h \le 11$, $-10 \le k \le 1$, $-41 \le l \le 41$
no. of reflns collected/unique	6311/5081 [$R_{int} = 0.0226$]
completeness to $\theta = 26.37$	100.0%
abs corr	empirical
max. and min. transmission	0.8467 and 0.7212
refinement method	full-matrix least-squares on F^2
no. of data/params	5081/333
goodness-of-fit on F^2	1.039
final R indices	
[3866$I > 2\sigma$(I) data]	R1 = 0.0417, wR2 = 0.0946
[all 5081 data]	R1 = 0.0650, wR2 = 0.1055
largest diff peak and hole	0.451 and −0.325 e/Å^3

Table 5. Selected Bond Lengths (Å) of Compound 39

type	length, Å	type	length, Å
Co_1-N_1	1.878(2)	Co_1-N_3	1.884(2)
Co_1-N_2	1.881(2)	Co_1-N_4	1.884(2)
Co_1-N_5	2.074(2)	Co_1-C_{15}	1.992(3)
O_5-C_{17}	1.212(4)	$C_{14}-C_{19}$	1.505(4)
$C_{15}-C_{16}$	1.509(4)	$C_{16}-C_{17}$	1.500(4)
$C_{17}-C_{18}$	1.504(5)	$C_{14}-C_{15}$	1.321(4)

tions. We first treated acyl complexes with Me_3SiCH_2-Li to see if they could be converted to 1,3-dienes by Peterson olefination.[18] Acyl complexes **35**, **33a**, and **33b**



were converted to α-hydroxy silanes **44a**, **44b**, and **44c** in high yield. Base-induced trimethylsilanol elimination from **44a** and **44b** produced the desired 1,3-dienes **45a** and **45b**, but the isolated yields were only moderate and the dienes were routinely obtained as mixtures of E and Z isomers. Acid-catalyzed Me_3SiOH elimination using silica gel proved possible and provided the dienes **45a**−**c** in higher isolated yield and stereochemical purity (Z).

β,γ-Unsaturated acyl complexes (**38** and **39**) could not be olefinated using this procedure. Treatment of those complexes with Me_3SiCH_2Li lead to a complex mixture of products, which by ^{1}H NMR contained no alkene ^{1}H resonances. Those complexes (**38** and **39**) contain pro-

(16) (a) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61. (b) Bulkowski, J.; Cutler, A.; Dolphin, D.; Silverman, R. B. *Inorg. Synth.* **1980**, *20*, 127.

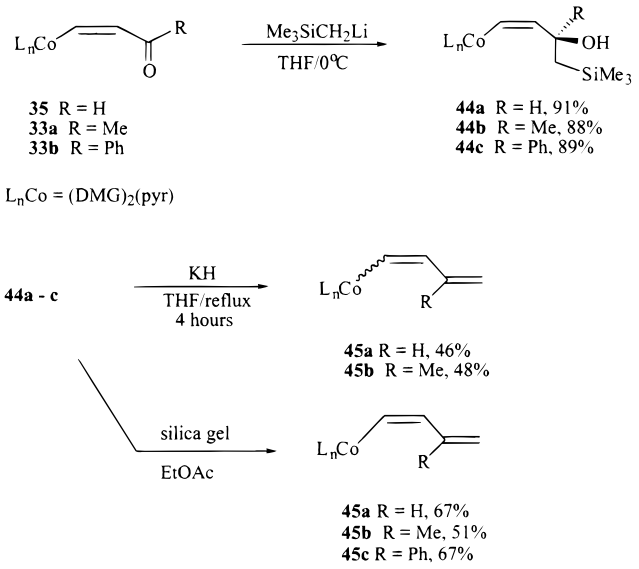
(17) House, H. O.; Kinloch, E. F. *J. Org. Chem.* **1974**, *39*, 747.

(18) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780.

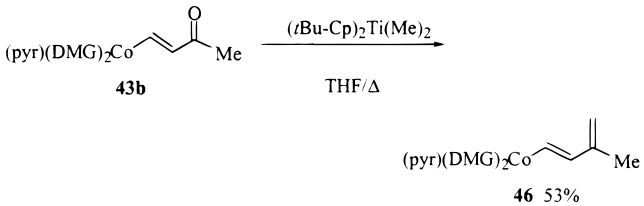
Table 6. Selected Bond Angles (deg) of Compound 39

type	angle, deg	type	angle, deg
$N_1-Co_1-N_2$	81.76(10)	$N_1-Co_1-N_5$	89.55(9)
$N_2-Co_1-N_3$	98.70(10)	$N_2-Co_1-N_5$	89.98(9)
$N_1-Co_1-N_4$	98.48(10)	$N_3-Co_1-N_5$	90.54(9)
$N_3-Co_1-N_4$	81.06(10)	$N_4-Co_1-N_5$	90.92(9)
$N_1-Co_1-C_{15}$	89.57(11)	$C_{15}-Co_1-N_5$	178.99(11)
$N_2-Co_1-C_{15}$	90.39(11)	$N_1-Co_1-N_3$	179.53(10)
$N_3-Co_1-C_{15}$	90.33(10)	$N_2-Co_1-N_4$	179.07(10)
$N_4-Co_1-C_{15}$	88.71(10)	$C_{15}-C_{14}-C_{19}$	126.3(3)
$C_{14}-C_{15}-C_{16}$	121.5(3)	$C_{14}-C_{15}-Co_1$	120.7(2)
$C_{16}-C_{15}-Co_1$	117.78(19)	$O_5-C_{17}-C_{16}$	123.6(3)
$O_5-C_{17}-C_{18}$	122.2(3)	$C_{17}-C_{16}-C_{15}$	118.0(3)
$C_{16}-C_{17}-C_{18}$	114.1(3)		

tons that are allylic and α to a ketone, so enolate formation and subsequent reactions may predominate



over olefination chemistry. Somewhat to our surprise, (*E*)-α,*β*-unsaturated acyl complex **43b** failed to react with Me_3SiCH_2Li; even refluxing **43b** with Me_3SiCH_2-Li in THF lead to the recovery of unreacted **43b**. However, treatment of **43b** with a commercially available form of Petasis' reagent [$(tBuCp)_2TiMe_2$][19] led to the formation of the desired (*E*)-1,3-dienyl complex **46** in 53% yield.



The structure of dienyl complex **45a** was confirmed by X-ray crystallography. Figures 3a and 3b show the ORTEP drawings of compound **45a**. In a single crystal, two crystallographically independent molecules were present. For both molecules, the bond lengths (Å) are displayed in Table 8 and the bond angles (deg) in Table 9. In comparing the crystal structure of the 1-cobaloxime diene (**45a**) with that of the 2-cobaloxime diene we reported earlier,[13] we observe similarities in the carbon−carbon bond lengths of the diene; all lengths are within 0.05 Å of each other. The cobalt−carbon bond lengths are similar (2.002 Å for the 2-substituted diene, 1.947 Å for **45a**). The major difference in the solid-state structures of these two compounds is the torsion angle

(19) Petasis, N. A.; Bzowej, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6392.

Table 7. Crystal Data and Structure Refinement for (1,3(*Z*)-butadien-4-yl)(pyridine)-bis(dimethylglyoximato) Cobalt(III)(chloroform) (45a)

empirical formula	$C_{17}H_{24}CoN_5O_4(Cl_3CH)$
fw	540.71
temperature	188(2) K
wavelength	0.71073 Å
cryst syst, space group	triclinic, $P1-C_1^1$ (No. 1)
unit cell dimens	$a = 8.3124(7)$ Å, $\alpha = 77.949(2)°$ $b = 11.503(1)$ Å, $\beta = 73.239(2)°$ $c = 13.374(1)$ Å, $\gamma = 71.805(2)°$
volume	1153.31(18) Å^3
Z, calcd density	2, 1.557 g/cm^{-1}
abs coeff	1.126 mm^{-1}
F(000)	556
cryst size	0.04 × 0.12 × 0.18 mm
θ range for data collection	1.60−24.10°
limiting indices	$-7 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 13$
no. of reflns collected/unique	5792/4485 [$R_{int} = 0.0702$]
completeness to $\theta = 24.10°$	98.8%
abs corr	integration
max. and min. transmission	0.9678 and 0.8342
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4485/39/618
goodness-of-fit on F^2	0.793
final *R* indices	
[$2207F_o > 4\sigma(F_o)$ data]	R1 = 0.0494, wR2 = 0.0666
[all 4485 data]	R1 = 0.1348, wR2 = 0.0815
absolute structure parameter	−0.01(3)
largest diff peak and hole	0.312 and −0.314 e/Å^3

Table 8. Selected Bond Lengths (Å) of Compound 45a

molecule 1		molecule 2	
type	length, Å	type	length, Å
Co_1-N_1	1.861(10)	Co_2-N_{21}	1.888(11)
Co_1-N_2	1.884(9)	Co_2-N_{22}	1.904(10)
Co_1-N_3	1.876(10)	Co_2-N_{23}	1.890(10)
Co_1-N_4	1.891(11)	Co_2-N_{24}	1.850(10)
Co_1-N_5	2.065(10)	Co_2-N_{25}	2.062(10)
Co_1-C_{15}	1.947(12)	Co_2-C_{35}	1.942(12)
$C_{15}-C_{16}$	1.314(15)	$C_{35}-C_{36}$	1.359(16)
$C_{16}-C_{17}$	1.471(15)	$C_{36}-C_{37}$	1.467(17)
$C_{17}-C_{18}$	1.325(16)	$C_{37}-C_{38}$	1.332(17)

Table 9. Selected Bond Angles (deg) of Compound 45a

molecule 1		molecule 2	
type	angle, deg	type	angle, deg
$N_1-Co_1-N_2$	81.0(5)	$N_{24}-Co_2-N_{21}$	98.2(5)
$N_3-Co_1-N_2$	99.2(5)	$N_{24}-Co_2-N_{23}$	81.3(5)
$N_1-Co_1-N_4$	98.2(5)	$N_{21}-Co_2-N_{22}$	80.6(5)
$N_3-Co_1-N_4$	81.6(5)	$N_{23}-Co_2-N_{22}$	99.8(5)
$N_1-Co_1-C_{15}$	94.6(4)	$N_{24}-Co_2-C_{35}$	95.8(5)
$N_3-Co_1-C_{15}$	84.9(4)	$N_{21}-Co_2-C_{35}$	93.6(5)
$N_2-Co_1-C_{15}$	83.9(4)	$N_{23}-Co_2-C_{35}$	85.2(4)
$N_4-Co_1-C_{15}$	94.0(4)	$N_{22}-Co_2-C_{35}$	85.1(5)
$N_1-Co_1-N_5$	89.6(4)	$N_{24}-Co_2-N_{25}$	89.0(4)
$N_3-Co_1-N_5$	90.9(4)	$N_{21}-Co_2-N_{25}$	91.1(4)
$N_2-Co_1-N_5$	91.6(4)	$N_{23}-Co_2-N_{25}$	90.2(4)
$N_4-Co_1-N_5$	90.6(4)	$N_{22}-Co_2-N_{25}$	90.2(4)
$N_2-Co_1-N_4$	177.7(5)	$C_{35}-Co_2-N_{25}$	172.8(5)
$C_{15}-Co_1-N_5$	173.2(5)	$N_{21}-Co_2-N_{23}$	178.6(5)
$N_1-Co_1-N_3$	179.5(5)	$N_{24}-Co_2-N_{22}$	178.6(5)
$C_{16}-C_{15}-Co_1$	137.5(10)	$C_{36}-C_{35}-Co_2$	135.6(10)
$C_{15}-C_{16}-C_{17}$	127.1(13)	$C_{35}-C_{36}-C_{37}$	130.3(14)
$C_{18}-C_{17}-C_{16}$	118.5(13)	$C_{38}-C_{37}-C_{36}$	123.4(16)

formed by the four carbon atoms of the diene. The 2-cobaloxime diene had a diene torsion angle of 54°, while that of compound **45a** is 178°. The 1-cobaloxime (**45a**) is a Z-diene that sits almost completely flat in the *s-trans* conformation.

In summary, we have shown that cobaloximes react with a variety of allenyl and alkynyl aldehydes and ketones to cleanly produce cobaloxime-substituted unsaturated acyl products of E or Z alkene geometry. These cobaloxime-substituted unsaturated acyls can be converted into 1-cobaloxime 1,3-dienyl complexes using Peterson or Petasis olefinations. Diels−Alder reactions of these new dienyl complexes will be reported in due course.

Experimental Section

General. All nuclear magnetic resonance (NMR) spectra were obtained using a Varian VXR-200 FT NMR or a Bruker AVANCE 300 FT NMR. All absorptions were expressed in parts per million relative to residual protonated solvent. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA. High-resolution mass spectral analyses were performed by the Duke University Mass Spectrometry Facility. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen. Alumina adsorption (80−200 mesh) for column chromatography was purchased from Fisher Scientific and deactivated with an acetone/water mixture (90:10) immediately prior to use.

Cobalt chloride hexahydrate used in the preparation of acyl and dienyl complexes was purchased from Strem Chemicals and used as received. Dimethylglyoxime was purchased from Fischer Scientific and recrystallized from 95% EtOH (12 mL/g) prior to use. 3-Butyne-2-one, 3-hexyn-2-one, 3-butyn-1-ol (**17**), and 4-pentyn-2-ol (**21**) were purchased from GFS Chemicals. Propioaldehyde diethyl acetal (**18**) was purchased from Lancaster. (Pyr)(dmg)$_2$CoCl (**28**) was prepared according to a literature procedure.[16] Allenic electrophiles **16a** and **16b** were prepared according to literature procedures.[7,8] Lithium borohydride in THF, sodium borohydride, and chloromethyl ethyl ether were purchased from Aldrich Chemicals and used as received. All reactions were performed under an atmosphere of nitrogen unless specified otherwise.

1,1,4-Triethoxy-2-butyne (19). This compound was prepared according to a previously reported procedure.[10] Additional spectroscopic data are included here. ^{1}H NMR ($CDCl_3$): 5.30 (s, 1H), 4.20 (s, 2H), 3.75 (m, 2H), 3.55 (m, 4H), 1.20 (m, 9H). ^{13}C NMR ($CDCl_3$): 91.6, 82.0, 81.7, 67.0, 61.5, 58.2, 15.5, 14.4.

1,4,4-Triethoxy-1,2-butadiene (20). This compound was prepared according to a previously reported procedure.[10] Additional spectroscopic data are included here. ^{1}H NMR ($CDCl_3$): 6.81 (d, J = 5.7 Hz, 1H), 5.85 (t, J = 5.7 Hz, 1H), 4.89 (d, J = 5.7 Hz, 1H), 3.62 (m, 6H), 1.23 (m, 9H). ^{13}C NMR ($CDCl_3$): 196.4, 123.4, 105.5, 101.3, 65.0, 61.7, 15.5, 14.9.

General Procedure for the Oxidation of Propargylic Alcohols. The propargylic alcohols were oxidized with the Dess−Martin reagent.[20] The secondary alcohol was dissolved in dichloromethane (100 mL). This was cooled to −78 °C in a dry ice/acetone bath. The Dess−Martin periodinane reagent (1.5 equiv) was added. The reaction mixture was allowed to warm to 25 °C over 3 h. It was then poured into saturated $NaHCO_3$ (150 mL) containing $Na_2S_2O_3$ (1 g). The organic layer was saved, and this procedure was repeated four times to remove all remaining iodine salts. The aqueous washes were back extracted with CH_2Cl_2, and the combined organic layers were dried with $MgSO_4$. The dichloromethane was removed by distillation. The resulting ynone was purified by Kugelrohr distillation.

1-Phenyl-2-propyn-1-one (22a). 1-Phenyl-2-propyn-1-ol (**21a**) (3.59 g, 27.0 mmol) was dissolved in dichloromethane (100 mL). The product was obtained as a waxy, yellow solid (**22a**) (2.85 g, 21.9 mmol, 81% yield) after following the procedure outlined above; mp 49−50 °C. This compound was previously reported with limited characterization data and no spectral data.[21] IR (NaCl): 3227, 2096, 1684, 1454, 1260, 1007 cm^{-1}. ^{1}H NMR ($CDCl_3$): 8.18 (dd, J = 7.1, 1.3 Hz, 2H), 7.65 (tt, J = 7.4, 1.3 Hz, 1H), 7.51 (tt, J = 7.8, 1.7 Hz, 2H), 3.46 (s, 1H). ^{13}C NMR ($CDCl_3$): 177.40, 136.19, 134.53, 129.71, 128.71, 80.79, 80.31. HRMS EI: calcd for C_9H_6O $(M)^+$, 130.0419; found, 130.0423.

4-Hexyn-3-one (22b). 4-Hexyn-3-ol (**21b**) (2.0 g, 20.0 mmol) was dissolved in dichloromethane (100 mL). The product was obtained as a clear liquid (**22b**) (1.18 g, 12.3 mmol, 61% yield) after following the procedure outlined above. This compound matched the previously reported boiling point of 46 °C at 10 mm[22] and the previously reported mass spectrometry data.[23] There has been no published IR and NMR spectral data on this compound. IR (NaCl): 2957, 2222, 1699, 1530, 1252, 1016 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.55 (q, J = 7.4 Hz, 2H), 2.02 (s, 3H), 1.13 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): 188.39, 89.69, 79.66, 38.37, 7.65, 3.56. HRMS EI: calcd for C_6H_8O $(M)^+$, 96.0575; found, 96.0487.

4,4-Diethoxy-2-butyn-1-ol (23). Acetal **18** (13.42 mL, 0.094 mol) was dissolved in THF (150 mL) and cooled to −78 °C. Butyllithium (52.24 mL, 0.1311 mol of a 2.5 M solution in hexanes) was added dropwise slowly over a period of 2 h. The mixture was allowed to stir for 0.5 h at −78 °C, then paraformaldehyde (9.25 g, 0.102 mol) was added, and the mixture was allowed to warm to 25 °C. Ice water (30 mL) was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 50 mL). The organic layers were combined and dried with $MgSO_4$, and the solvent was removed by rotary evaporation. The resulting liquid was vacuum-distilled to afford a viscous liquid: bp 70−75 °C, 25 mmHg; 12.58 g, 0.080 mol, 85%. ^{1}H NMR ($CDCl_3$): 5.26 (t, J = 1.4 Hz, 1H), 4.27 (br s, 2H), 3.62 (m, 4H), 2.23 (br s, 1H), 1.19 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): 91.2, 83.7, 80.8, 60.9, 50.8, 15.0. IR ($CDCl_3$): 3608.1, 3447.3, 3155.7, 2981,7, 2931.7, 2900.6, 1653.0, 1559.0, 1473.0, 1382.1, 1328.0 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.73; H, 8.92. Found: C, 60.85; H, 8.92.

1-Tosyl-4,4-diethoxy-2-butyne (24). In an adaptation of a literature procedure,[9] alkynol **23** (5.00 g, 0.032 mol) was dissolved in distilled diethyl ether (60 mL) and *p*-toluenesulfonyl chloride (5.72 g, 0.030 mol) was added. The mixture was cooled to −15 °C, and powdered KOH (5 equiv) (8.87 g, 0.158 mol) was added 1 equiv at a time over 30−45 min. The reaction mixture was then allowed to stir at −15 °C for 90 min. Ice water (80 mL) was then added, and the mixture was extracted with diethyl ether (3 × 50 mL). The combined ether layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. The remaining residue was then triturated with petroleum ether (15 mL) and cooled to −78 °C, and the solvent was decanted. The product was dried under vacuum to yield a dark brown oil (9.55 g, 0.031 mol, 97%). ^{1}H NMR ($CDCl_3$): 7.79 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.12 (t, J = 1.5 Hz, 1H), 4.72 (d, J = 1.5 Hz, 2H), 3.54 (m, 4H), 2.42 (s, 3H), 1.17 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$):

(20) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

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(22) Smith, W. N.; Kuehn, E. D. *J. Org. Chem.* **1973**, *38*, 3588.

(23) Bachiri, M.; Perros, P.; Verneuil, B.; Mouvier, G.; Carlier, P. *Org. Mass Spectrom.* **1980**, *15*, 84.

145.2, 132.9, 129.9, 128.1, 90.9, 84.3, 76.9, 61.0, 57.4, 21.7, 15.0. IR ($CDCl_3$): 3154.5, 2982.0, 2900.8, 1653.1, 1559.1, 1472.4, 1376.6, 1190.8, 1096.0 cm^{-1}. EI HRMS: *m/z* calcd for $C_{15}H_{20}O_5S$ (M^+) 312.1031, found 312.1026. Anal. Calcd for $C_{15}H_{20}O_5S$: C, 57.68; H, 6.45. Found: C, 57.96; H, 6.36.

(1-Oxo-2(*E*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (26a). Cobaloxime chloride **28** (1.00 g, 2.50 mmol) was dissolved in degassed THF (30 mL) and cooled to −20 °C. $LiBH_4$ (0.993 mL, 1.99 mmol of a 2.0 M solution in THF) was added, and the mixture was stirred (20 min). Allenyl aldehyde **16a** (1.50 g, 0.022 mol) was added, and the mixture was allowed to warm to 25 °C overnight. The THF was removed by rotary evaporation, and the remaining residue was poured into ice water (100 mL) containing pyridine (0.75 mL). The mixture was extracted with CH_2Cl_2 (4 × 50 mL) and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was chromatographed on silica (EtOAc) to yield a yellow-orange solid (**26a**) (0.525 g, 1.20 mmol, 48%); mp 158−160 °C dec. ^1H NMR ($CDCl_3$): 9.63 (d, J = 7.0 Hz, 1H), 8.60 (d, J = 6.3 Hz, 2H), 7.72 (t, J = 6.3 Hz, 1H), 7.31 (t, J = 6.3 Hz, 2H), 6.21 (d, J = 7.0 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 12H). ^{13}C NMR ($CDCl_3$): 183.0, 150.5, 150.0, 138.0, 135.5, 125.4, 23.2, 12.4. IR ($CDCl_3$): 3154.9, 2984.6, 2902.4, 1635.8, 1472.3, 1383.8, 1166.2, 1095.2 cm^{-1}. FAB HRMS: *m/z* calcd for $C_{17}H_{24}CoN_5O_5$ ($M + H^+$) 438.1109, found 438.1167. Anal. Calcd for $C_{17}H_{24}CoN_5O_5$: C, 46.69; H, 5.53. Found: C, 46.83; H, 5.61.

(1-Oxo-2(*E*)-penten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (26b). This complex was prepared using the method described above using cobaloxime chloride **28** (1.50 g, 3.72 mmol), $LiBH_4$ (1.49 mL, 2.97 mmol of a 2.0 M solution in THF), and allenyl ketone **16b** (1.50 g, 0.018 mol) to yield a dark orange solid (**26b**) (0.671 g, 1.49 mmol, 40%); mp 183−184 °C dec. ^1H NMR ($CDCl_3$): 8.61 (d, J = 5.1 Hz, 2H), 7.72 (t, J = 5.1 Hz, 1H), 7.31 (t, J = 5.1 Hz, 2H), 6.34 (s, 1H), 2.11 (s, 3H), 2.09 (s, 12H), 2.02 (s, 3H). ^{13}C NMR ($CDCl_3$): 192.2, 150.3, 150.0, 137.8, 130.1, 125.3, 31.6, 25.5, 12.2. IR ($CDCl_3$): 3155.0, 2985.8, 2902.0, 1653.1, 1558.8, 1471.4, 1382.7, 1235.4, 1094.9 cm^{-1}. Anal. Calcd for $C_{18}H_{26}CoN_5O_5$: C, 47.90; H, 5.81. Found: C, 47.83; H, 5.80.

(4,4-Diethoxy-1-oxo-2(*Z*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (27). Cobaloxime chloride **28** (1.00 g, 2.47 mmol) was suspended in degassed absolute EtOH (20 mL) and cooled to −20 °C. $LiBH_4$ (0.990 mL of a 2.0 M solution, 1.98 mmol in THF) was added, and the mixture was allowed to stir for 45 min at −20 °C. Allene **20** (0.461 g, 2.47 mmol) was added dropwise slowly, and the mixture was allowed to warm to 25 °C overnight. The mixture was then poured into ice water (100 mL) containing pyridine (0.50 mL) and then extracted with CH_2Cl_2 (4 × 25 mL). The CH_2Cl_2 extracts were combined and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The remaining residue was chromatographed on silica (EtOAc) to yield a yellow solid (0.970 g, 1.85 mmol, 75%); mp 160−162 °C dec. ^1H NMR ($CDCl_3$): 9.95 (d, J = 7.0 Hz, 1H), 8.55 (d, J = 7.0 Hz, 2H), 7.67 (t, J = 7.0 Hz, 1H), 7.27 (t, J = 7.0 Hz, 2H), 6.01 (d, J = 7.0 Hz, 1H), 5.29 (s, 1H), 3.49 (q, J = 7.1 Hz, 2H), 3.22 (q, J = 7.1 Hz, 2H), 2.04 (s, 12H), 1.02 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): 190.1, 151.2, 150.4, 138.7, 138.3, 125.8, 103.5, 63.6, 15.9, 12.7. IR ($CDCl_3$): 3155.1, 2983.5, 2901.4, 1652.8, 1559.2, 1471.8, 1382.1, 1297.3, 1216.3, 1167.2, 1098.0 cm^{-1}. FAB HRMS: *m/z* calcd for $C_{21}H_{32}CoN_5O_7$ 525.1633; found 525.1637. Anal. Calcd for $C_{21}H_{32}CoN_5O_7$: C, 48.00; H, 6.14. Found: C, 48.25; H, 6.20.

4-Ethoxy-1-oxo-2(*Z*)-buten-3-yl-(pyridine)bis(dimethylglyoximato)cobalt(III) (30). Cobaloxime chloride **28** (1.00 g, 2.47 mmol) was suspended in degassed THF (20 mL) and cooled to −20 °C. $LiBH_4$ (0.990 mL of a 2.0 M solution, 1.98 mmol in THF) was added, and the mixture was allowed to stir for 45 min at −20 °C. Allene **20** (0.461 g, 2.47 mmol) was added dropwise slowly, and the mixture was allowed to warm to 25 °C overnight. The mixture was then poured into ice water (100 mL) containing pyridine (0.50 mL) and then extracted with CH_2Cl_2 (4 × 25 mL). The CH_2Cl_2 extracts were combined and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product ^1H NMR ($CDCl_3$) was consistent with structure **29**: 8.60 (d, J = 5.0 Hz, 2H), 7.75 (t, J = 5.0 Hz, 1H), 7.30 (t, J = 5.0 Hz, 2H), 6.4 (d, J = 12.8 Hz, 1H), 5.7 (s, 1H), 5.1 (d, J = 12.8 Hz, 1H), 3.7 (q, J = 6.9 Hz, 2H), 3.6 (q, J = 7.1 Hz, 2H), 2.19 (s, 12H), 1.2 (t, J = 6.9 Hz, 3H), 1.1 (t, J = 7.1 Hz, 3H). This crude product was chromatographed on silica (EtOAc) to yield a yellow solid (**30**) (0.144 g, 0.299 mmol, 12%); mp 143−145 °C dec. ^1H NMR ($CDCl_3$): 9.73 (d, J = 7.2 Hz, 1H), 8.54 (d, J = 7.0 Hz, 2H), 7.67 (t, J = 7.1 Hz, 1H), 7.26 (t, J = 7.1 Hz, 2H), 6.10 (d, J = 7.2 Hz, 1H), 4.15 (s, 2H), 3.33 (q, J = 7.0 Hz, 2H), 2.04 (s, 12H), 1.04 (t, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): 186.9, 151.2, 150.3, 138.6, 138.3, 125.8, 71.5, 66.0, 15.6, 12.7. IR ($CDCl_3$): 3155.5, 2984.3, 2902.1, 1653.0, 1559.3, 1471.1, 1382.5, 1216.5, 1094.6 cm^{-1}. FAB HRMS: *m/z* calcd for ($M + H^+$) $C_{19}H_{28}CoN_5O_6$ 482.1371, found ($M + H^+$) 482.1437. Anal. Calcd for $C_{19}H_{28}CoN_5O_6$: C, 47.41; H, 5.86. Found: C, 47.28; H, 5.77.

(4,4-Diethoxy-2-butyn-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (32). Cobaloxime chloride **28** (1.50 g, 3.72 mmol) was dissolved in degassed THF (45 mL) and cooled to −20 °C. $LiBH_4$ (1.49 mL of a 2.0 M solution, 2.97 mmol in THF) was added, and the mixture was stirred for 20 min. Tosylate **24** (1.28 g, 4.41 mmol) was added, and the reaction mixture was allowed to warm to 25 °C overnight. The mixture was poured into ice water (200 mL) containing pyridine (0.75 mL), and the orange product was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude orange product was chromatographed on silica (EtOAc) to yield an orange solid (0.703 g, 1.380 mmol, 37%); mp 124−126 °C dec. ^1H NMR ($CDCl_3$): 8.54 (d, J = 7.6 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 4.99 (t, J = 1.8 Hz, 1H), 3.50 (m, 4H), 2.16 (s, 12H), 1.89 (m, 2H), 1.16 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): d 150.2, 150.1, 137.7, 125.3, 94.0, 92.5, 78.6, 60.7, 60.3, 15.1, 12.3. IR ($CDCl_3$): 3156.8, 2984.0, 2901.6, 1646.1, 1559.1, 1237.7, 1167.0, 1096.0 cm^{-1}. HRMS FAB: *m/z* calcd for $C_{21}H_{32}CoN_5O_6$ 509.1684, found 509.1700. Anal. Calcd for $C_{21}H_{32}CoN_5O_6$: C, 49.51; H, 6.33. Found: C, 49.65; H, 6.34.

General Procedure for the Synthesis of (Z)-Alkene-Containing Unsaturated Acyl Complexes. Cobaloxime chloride **28** was suspended in degassed MeOH (20 mL) containing NaOH (3.3 equiv) at 0 °C and was reduced with $NaBH_4$ (1.8 equiv). Ynone (2.5 equiv) was added, followed by the dropwise addition of acetic acid (approximately 7−8 drops) until the solution turned orange-red. The reaction mixture was then immediately poured into ice water containing pyridine (0.75 mL). Depending on the presence or absence of a precipitate, the product was either filtered and washed with water (500 mL) or extracted with EtOAc (4 × 100 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (EtOAc) to yield yellow-orange solids.

(1-Phenyl-1-oxo-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (33b). Cobaloxime chloride **28** (1.24 g, 3.10 mmol) was dissolved in degassed MeOH. Following reduction with $NaBH_4$, 1-phenyl-2-propyn-1-one (**22b**) (2.5 equiv) was added. After continuing with the above procedure, the reaction mixture was poured into the ice water/pyridine mixture. The product precipitated out and was vacuum filtered to yield a yellow solid (**33b**) (0.511 g, 1.02 mmol, 33% yield); decomposes at 176 °C. IR (NaCl): 2957, 2923, 1725, 1657, 1547, 1446 cm^{-1}. ^1H NMR ($CDCl_3$): 17.80 (bs, 2H), 8.34 (d, J = 6.2 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 6.9 Hz, 1H), 7.25 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 6.4 Hz, 2H), 6.17 (d, J = 10.6 Hz, 1H), 6.08 (d, J = 10.6 Hz, 1H), 1.76 (s, 12H). ^{13}C NMR ($CDCl_3$): 194.82, 150.51, 149.66, 137.89, 137.80, 137.18, 132.55, 129.34, 128.08, 125.23,

11.95. HRMS FAB (*m*/*z*): calcd for $C_{22}H_{26}O_5N_5Co$, 499.1266; found 499.1259. Anal. Calcd for $C_{22}H_{26}O_5N_5Co$: C, 52.91; H, 5.25. Found: C, 53.28; H, 5.64.

(1,1-Diethoxy-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (34) and (1-Oxo-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (35). Complex **34** was synthesized by analogy with a literature procedure.[16] Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) (5.00 g, 21.0 mmol) and dimethylglyoxime (4.87 g, 42.0 mmol) were dissolved in degassed methanol (150 mL). Sodium hydroxide (1.68 g, 42.0 mmol) in water (15 mL) was added followed by pyridine (1.66 g, 21.0 mmol). The reaction mixture was cooled to −10 °C in a dry ice/acetone bath and stirred under nitrogen for 15 min. Subsequently, another equivalent of sodium hydroxide (0.84 g, 21.0 mmol) in water (7 mL) and $NaBH_4$ (1.17 g, 32.0 mmol) in water (20 mL) were added. Propionaldehyde diethylacetal (**18**) (4.03 g, 32.0 mmol) was added by syringe, and the solution was allowed to warm gradually to 25 °C over a few hours. The reaction mixture was concentrated under reduced pressure to a volume of about 50 mL and then poured into ice water (300 mL) containing pyridine (2 mL). The orange precipitate (**34**) (7.99 g, 16.1 mmol, 77% yield) was collected by vacuum filtration and washed with water; mp 171 °C. IR (NaCl): 2974, 2948, 2872, 1556, 1446, 1287, 1227, 1083 cm^{-1}. ^1H NMR ($CDCl_3$): 18.36 (bs, 2H), 8.60 (d, J = 6.3 Hz, 2H), 7.70 (t, J = 6.2 Hz, 1H), 7.30 (t, J = 6.1 Hz, 2H), 6.27 (d, J = 7.9 Hz, 1H), 5.18 (d, J = 7.9 Hz, 1H), 5.08 (t, J = 7.9 Hz, 1H), 3.60 (q, J = 7.1 Hz, 2H), 3.46 (q, J = 7.1 Hz, 2H), 2.04 (s, 12H), 1.14 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): 150.17, 149.83, 137.74, 135.45, 125.53, 125.28, 99.81, 61.08, 15.59, 12.11. Anal. Calcd for $C_{20}H_{32}O_6N_5Co$: C, 48.29; H, 6.48. Found: C, 48.16; H, 6.36. Complex **34** (7.99 g, 16.1 mmol) was then suspended in water and cooled to 0 °C. Acetic acid was added dropwise until the solution was at pH = 4, and then the solution was warmed to 25 °C and stirred (2 h). The solution was then poured into ice water containing a few drops of pyridine, and **35** was isolated by vacuum filtration (6.028 g, 14.2 mmol, 88%). This complex (**35**) proved identical by ^1H NMR comparison with material we had prepared previously by an alternate procedure.[6]

(3-Oxo-5-hexen-5-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (38). Cobaloxime chloride **28** (1.68 g, 4.17 mmol) was dissolved in degassed MeOH. Following cobaloxime reduction with $NaBH_4$, 4-hexyn-3-one (**22b**) (2.5 equiv) was added. After continuing with the above procedure, the reaction mixture was poured into the ice water/pyridine mixture. The product was extracted with EtOAc (4 × 100 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (EtOAc) to yield a dark orange solid (**38**) (0.685 g, 1.47 mmol, 35% yield); mp 165−167 °C. IR (NaCl): 3472, 2974, 2931, 1707, 1556, 1438, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): 8.58 (d, J = 6.3 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 6.3 Hz, 2H), 4.95 (d, J = 1.7 Hz, 1H), 4.19 (d, J = 1.7 Hz, 1H), 3.07 (s, 2H), 2.34 (q, J = 7.3 Hz, 2H), 2.07 (s, 12H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): 209.52, 150.51, 150.04, 137.62, 137.37, 125.21, 119.62, 52.89, 34.64, 12.09, 8.02. DEPT ($CDCl_3$): 209.52 (C), 150.51 (C), 150.04 (CH), 137.62 (CH), 137.37 (C), 125.21 (CH), 119.62 (CH_2), 52.89 (CH_2), 34.64 (CH_2), 12.09 (CH_3), 8.02 (CH_3). HRMS FAB (*m*/*z*): calcd for $C_{19}H_{28}O_5N_5Co$, 465.1422; found 465.1431. Anal. Calcd for $C_{19}H_{28}O_5N_5Co$: C, 49.04; H, 6.06. Found: C, 48.82; H, 6.19.

(2-Oxo-4(*E*)-hexen-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (39). Cobaloxime chloride **28** (0.50 g, 1.24 mmol) was dissolved in degassed MeOH. Following cobaloxime reduction with $NaBH_4$, 3-hexyn-2-one (**36a**) (2.5 equiv) was added. After continuing with the above procedure, the reaction mixture was poured into the ice water/pyridine mixture. The product was extracted with EtOAc (4 × 100 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (EtOAc) to yield a dark orange solid (**39**) (0.277 g, 0.60 mmol, 48% yield); decomposes at 170 °C. IR (NaCl): 2957, 2923, 1708, 1556, 1438, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): 18.04 (bs, 2H), 8.56 (d, J = 6.3 Hz, 2H), 7.66 (t, J = 6.2 Hz, 1H), 7.25 (t, J = 6.4 Hz, 2H), 5.26 (q, J = 6.7 Hz, 1H), 3.13 (s, 2H), 2.03 (s, 12H), 2.02 (s, 3H), 1.48 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): 205.95, 150.51, 149.99, 137.45, 127.18, 125.23, 125.08, 47.87, 29.09, 14.84, 12.01. DEPT ($CDCl_3$): 205.95 (C), 150.51 (C), 149.99 (CH), 137.45 (CH), 127.18 (CH), 125.23 (C), 125.08 (CH), 47.87 (CH_2), 29.09 (CH_3), 14.84 (CH_3),12.01 (CH_3). HRMS FAB (*m*/*z*): calcd for $C_{19}H_{28}O_5N_5Co$, 465.1422; found 465.1429. Anal. Calcd for $C_{19}H_{28}O_5N_5Co$: C, 49.04; H, 6.06. Found: C, 49.22; H, 6.13.

1-Propen-3-al-1-ylpyridinebis(dimethylglyoximato)cobalt(III) (43a). Cobalt(II) acetate tetrahydrate (**40**) (1.001 g, 4.01 mmol), dimethylglyoxyime (0.928 g, 8.00 mmol), pyridine (1.0 mL, 12.4 mmol), and zinc dust (1.378 g, 21.1 mmol) were all combined in degassed THF (70 mL). The reaction mixture was refluxed for 15 min and then allowed to cool to room temperature. Propionaldehyde diethyl acetal (0.90 mL, 6.29 mmol) was then added. The reaction mixture was refluxed an additional hour. Upon cooling to 25° C, approximately 7−8 drops of acetic acid were added. The mixture was then poured into ice water (50 mL) containing 5 drops of pyridine. The product was extracted with EtOAc (5 × 100 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using EtOAc to yield the product as a bright yellow solid (0.121 g, 0.286 mmol, 7%); decomposes at 151−153° C. ^1H NMR ($CDCl_3$): 9.19 (d, J = 7.6 Hz, 1H), 8.61 (d, J = 4.1 Hz, 2H), 8.39 (d, J = 14.7 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 6.22 (dd, J = 14.8, 7.6 Hz, 1H), 2.13 (s, 12H). ^{13}C NMR ($CDCl_3$): 189.49, 150.57, 150.38, 141.99, 138.57, 125.92, 12.70. IR (NaCl): 2921, 2794, 2707, 1664, 1559, 1546, 1232, 1094, 1072 cm^{-1}. Anal. Calcd for $C_{16}H_{22}CoN_5O_5$: C, 45.64; H, 5.24. Found: C, 45.59; H, 5.34.

(2-Oxo-3(*E*)-buten-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (43b). Cobalt(II) acetate tetrahydrate (**40**) (1.0 g, 4.02 mmol), dimethylglyoxime (0.93 g, 8.03 mmol), pyridine (0.95 g, 12.0 mmol), and zinc dust (2.61 g, 40.2 mmol) were all combined in degassed THF (50 mL). The reaction mixture was refluxed for 10 min and then allowed to cool back down to room temperature. 3-Butyn-2-one (0.41 g, 6.02 mmol) was then added. The reaction mixture was refluxed for an additional hour. Upon cooling to 25 °C, approximately 7−8 drops of acetic acid were added. The reaction mixture was then poured into ice water containing pyridine (0.75 mL). The product was extracted with EtOAc (4 × 100 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was chromatographed on silica gel (EtOAc) to yield a bright orange solid (**43b**) (1.56 g, 3.57 mmol, 89% yield); decomposes at 228 °C. IR (NaCl): 3480, 2957, 2923, 1649, 1556, 1235 cm^{-1}. ^1H NMR ($CDCl_3$): 18.16 (bs, 2H), 8.62 (d, J = 6.3 Hz, 2H), 8.21 (d, J = 14.9 Hz, 1H), 7.78 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 6.6 Hz, 2H), 6.08 (d, J = 14.9 Hz, 1H), 2.13 (s, 12H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$): 193.07, 150.90, 150.01, 149.52, 139.36, 138.05, 125.45, 26.22, 12.23. HRMS FAB (*m*/*z*): calcd for $C_{17}H_{25}O_5N_5Co$ $(MH)^+$, 438.1188; found 438.1184. Anal. Calcd for $C_{17}H_{24}O_5N_5Co$: C, 46.69; H, 5.53. Found: C, 46.86; H, 5.59.

3-Phenyl-1-propen-3-one-1-ylpyridinebis(dimethylglyoximato)cobalt(III) (43c). Cobalt(II) acetate tetrahydrate (**40**) (1.006 g, 4.04 mmol), dimethylglyoxyime (0.930 g, 8.02 mmol), pyridine (1.0 mL, 12.4 mmol), and zinc dust (1.360 g, 20.8 mmol) were all combined in degassed THF (70 mL). The reaction was refluxed for 15 min and then allowed to cool to room temperature. 1-Phenyl-2-propyn-1-one (0.781, 6.01 mmol) was then added. The reaction mixture was refluxed an additional hour. Upon cooling to 25° C, approximately 7−8 drops of acetic acid were added. The reaction was then poured into ice water (50 mL) containing 5 drops of pyridine. The

product was extracted with (4 × 100 mL), dried with $MgSO_4$, and concentrated under pressure. The resulting sticky solid was triturated with 1:1 pentane/EtO_2 to yield a dark brown-orange solid (1.864 g, 3.77 mmol, 94%); decomposes at 99−101° C. ^{1}H NMR ($CDCl_3$): 8.65 (d, J = 5.2 Hz, 2H), 8.52 (d, J = 14.3 Hz, 1H), 7.80 (m, 3H), 7.57−7.46 (m, 1H), 7.40 (m, 4H), 6.92 (d, J = 14.3 Hz, 1H), 2.13 (s, 12H). ^{13}C NMR ($CDCl_3$): 186.53, 151.06, 150.52, 138.87, 138.54, 133.97, 132.41, 129.44, 128.61, 126.00, 12.84. IR (NaCl): 3588, 3567, 3510, 3447, 3060, 1652, 1542, 1237, 1013 cm^{-1}. Anal. Calcd for $C_{22}H_{26}CoN_5O_4$: C, 52.91; H, 5.24. Found: C, 53.36; H, 5.08.

General Procedure for the Synthesis of Cobaloxime α-Hydroxy Silane Complexes. The unsaturated acyl complex was dissolved in THF (25 mL). The reaction mixture was cooled to 0 °C in an ice bath. The (trimethylsilyl methyl)lithium or Grignard reagent (3.5 equiv) was slowly added by syringe. The solution was allowed to gradually warm to 25 °C overnight. The reaction mixture was then poured into an ice/saturated NH_4Cl solution (150 mL). The product was extracted with EtOAc (3 × 75 mL), dried with $MgSO_4$, and then concentrated under reduced pressure to yield an orange-brown oil. Attempted chromatographic purification of these compounds yielded the respective dienes; therefore inadequate HRMS and elemental analyses were obtained.

(2-Hydroxyl-1-trimethylsilyl-3(*Z*)-buten-4-yl)(pyridine)-bis(dimethylglyoximato)cobalt(III) (44a). Unsaturated acyl complex **35** (0.100 g, 0.24 mmol) was dissolved in THF (25 mL). The α-hydroxy silane complex **44a** was obtained as an orange-brown oil (0.111 g, 0.21 mmol, 91% yield) after following the procedure outlined above. IR (NaCl): 3426, 2954, 1302 cm^{-1}. ^{1}H NMR ($CDCl_3$): 8.61 (d, J = 6.4 Hz, 2H), 7.75 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 6.02 (d, J = 7.3 Hz, 1H), 5.12 (t, J = 7.4 Hz, 1H), 4.42 (q, J = 7.4 Hz, 1H), 2.07 (s, 12H), 0.90 (d, J = 7.4 Hz, 2H), −0.07 (s, 9H). ^{13}C NMR ($CDCl_3$): 150.85, 150.24, 149.73, 144.47, 137.83, 125.33, 65.06, 26.92, 12.04, −0.71.

(2-Hydroxyl-2-methyl-1-trimethylsilyl-3(*Z*)-buten-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (44b). Unsaturated acyl complex **33a** (0.100 g, 0.23 mmol) was dissolved in THF (25 mL). The hydroxy silane complex was obtained as an orange-brown oil (**44b**) (0.106 g, 0.201 mmol, 88% yield) after following the procedure outlined above. IR (NaCl): 3379, 2957, 2923, 1547, 1235, 1092 cm^{-1}. ^{1}H NMR ($CDCl_3$): 8.62 (d, J = 6.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 5.78 (d, J = 8.5 Hz, 1H), 5.22 (d, J = 8.7 Hz, 1H), 2.10 (s, 12H), 2.07 (s, 3H), 1.20 (s, 2H), −0.05 (s, 9H). ^{13}C NMR ($CDCl_3$): 150.77, 149.66, 148.62, 137.75, 137.40, 125.08, 64.66, 33.70, 12.31, 12.08, 0.42.

(2-Hydroxyl-2-phenyl-1-trimethylsilyl-3(*Z*)-buten-4-yl)-(pyridine)bis(dimethylglyoximato)cobalt(III) (44c). Unsaturated acyl complex **33b** (0.100 g, 0.20 mmol) was dissolved in THF (25 mL). The hydroxy silane complex was obtained as an orange-brown oil (**44c**) (0.105 g, 0.179 mmol, 89% yield). ^{1}H NMR ($CDCl_3$): 8.55 (d, J = 5.7 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.13 (d, J = 8.8 Hz, 1H), 5.71 (d, J = 8.8 Hz, 1H), 2.03 (s, 12H), 1.65 (s, 2H), −0.14 (s, 9H).

General Procedure for the Synthesis of 1-Cobaloxime Butadiene Complexes. (Method A) By following a method similar to the original Peterson olefination procedure,[18] the hydroxy silane complex was dissolved in THF (30 mL). Potassium hydride (35% dispersion in mineral oil) (5.0 equiv) was then added as a THF slurry. The reaction mixture was refluxed for 4 h. Upon cooling, the solution was poured into an ice/saturated NH_4Cl solution (150 mL) containing pyridine (0.50 mL). The product was extracted with EtOAc (3 × 75 mL), dried with $MgSO_4$, and then concentrated under reduced pressure to yield an orange/yellow solid. (Method B) The crude hydroxy silane was chromatographed on silica gel (EtOAc). The fraction from the orange band proved to be the dienyl complex and needed no further purification.

(1,3-(*E*)- and -(*Z*)-Butadiene-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (45a). (Method A) Hydroxy silane **44a** (0.097 g, 0.19 mmol) was dissolved in THF (30 mL). Potassium hydride (0.063 g, 0.95 mmol) was added, and the procedure outlined in the above section was followed. The dienyl complex was obtained as a yellow solid (**44a**) (0.037 g, 0.088 mmol, 46% yield) with varying E:Z ratios. Following method B, column chromatography of hydroxy silane **44a** (1.00 g, 1.96 mmol) on silica gel also provided the product (Z only) (**45a**) (0.56 g, 1.33 mmol, 67% yield); decomposes at 170 °C. IR (NaCl): 2948, 2924, 1556, 1446, 1294 cm^{-1}. ^{1}H NMR ($CDCl_3$): E isomer, 18.41 (bs, 2H), 8.62 (d, J = 6.4 Hz, 2H), 7.73 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 6.3 Hz, 2H), 6.83 (m, 1H), 6.48 (d, J = 13.8 Hz, 1H), 5.90 (dd, J = 13.8 Hz, 3.9 Hz, 1H), 4.81 (dd, J = 16.8, 0.93 Hz, 1H), 4.58 (dd, J = 9.6, 0.93 Hz, 1H), 2.10 (s, 12H); Z isomer, 18.41 (bs, 2H), 8.67 (d, J = 4.9 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 6.2 Hz, 2H), 6.83 (m, 1H), 6.25 (d, J = 7.9 Hz, 1H), 5.75 (t, J = 7.9 Hz, 1H), 5.06 (dd, J = 10.0, 1.1 Hz, 1H), 4.96 (dd, J = 16.4, 1.1 Hz, 1H), 2.09 (s, 12H). ^{13}C NMR ($CDCl_3$): 150.07, 149.85, 149.77, 149.57, 137.75, 135.67, 125.29, 116.34, 12.10. HRMS FAB (*m*/*z*): calcd for $C_{17}H_{25}O_4N_5Co$ $(MH)^+$, 422.1239; found 422.1250. Anal. Calcd for $C_{17}H_{24}O_4N_5Co$: C, 48.46; H, 5.74. Found: C, 47.97; H, 6.31.

(2-Methyl-1,3(*E*)- and -(*Z*)-butadiene-4-yl)(pyridine)-bis(dimethylglyoximato)cobalt(III) (45b). (Method A) Hydroxy silane **44b** (0.151 g, 0.29 mmol) was dissolved in THF (30 mL). Potassium hydride (0.094 g, 1.4 mmol) was added, and the procedure outlined in the above section was followed. The dienyl complex was obtained as an orange solid (**45b**) (0.60 g, 1.38 mmol, 48% yield) with varying E:Z ratios. Following method B, column chromatography of hydroxy silane **44b** (0.244 g, 0.46 mmol) on silica gel also provided the product (Z only) (**45b**) (0.102 g, 0.234 mmol, 51% yield); mp 159−162 °C. IR (NaCl): 3413, 2948, 2872, 1556, 1438, 1227 cm^{-1}. ^{1}H NMR ($CDCl_3$): E isomer, 8.56 (d, J = 6.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 6.40 (d, J = 14.1 Hz, 1H), 5.92 (d, J = 14.1 Hz, 1H), 4.61 (d, J = 1.3 Hz, 1H), 4.52 (d, J = 1.3 Hz, 1H), 2.06 (s, 12H), 1.68 (s, 3H); Z isomer, 8.53 (d, J = 6.4 Hz, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 5.71 (d, J = 8.6 Hz, 1H), 5.32 (d, J = 8.6 Hz, 1H), 4.58 (d, J = 1.3 Hz, 1H), 4.45 (d, J = 1.3 Hz, 1H), 2.08 (s, 12H), 1.65 (s, 3H). ^{13}C NMR ($CDCl_3$): 150.07, 149.89, 149.62, 149.55, 137.60, 125.27, 125.14, 110.66, 23.71, 12.22. HRMS FAB (*m*/*z*): calcd for $C_{18}H_{27}O_4N_5Co$ $(MH)^+$, 436.1395; found 436.1408. Anal. Calcd for $C_{18}H_{26}O_4N_5Co$: C, 49.66; H, 6.02. Found: C, 49.18; H, 6.22.

(2-Phenyl-1,3(*Z*)-butadiene-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (45c). Following method B, column chromatography of hydroxy silane **44c** (0.105 g, 0.179 mmol) on silica gel also provided the product (Z only) (**45c**) (0.060 g, 0.12 mmol, 67% yield); decomposes at 147 °C. IR (NaCl): 2948, 2923, 1556, 1227 cm^{-1}. ^{1}H NMR ($CDCl_3$): Z isomer, 18.29 (bs, 2H), 8.55 (d, J = 5.7 Hz, 2H), 7.68 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 5.95 (d, J = 9.0 Hz, 1H), 5.89 (d, J = 9.0 Hz, 1H), 5.54 (s, 1H), 5.07 (s, 1H), 2.03 (s, 12H). ^{13}C NMR ($CDCl_3$): 150.12, 149.73, 142.08, 139.03, 138.33, 137.59, 127.94, 126.96, 125.82, 125.14, 111.80, 11.83. HRMS FAB (*m*/*z*): calcd for $C_{23}H_{29}O_4N_5Co$ $(MH)^+$, 498.1552; found 498.1476.

(2-Methyl-1,3(*E*)-butadiene-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (46). Acyl complex **43b** (0.200 g, 0.458 mmol) was dissolved in THF (30 mL). The Petasis reagent [$(tBuCp)_2TiMe_2$] (Strem Chemical) (1.5 equiv) was added, and the reaction mixture was degassed for 10 min. The reaction was refluxed overnight. After cooling to room temperature, the reaction mixture was then poured into ice water containing pyridine (0.75 mL). The product was extracted with EtOAc (3 × 75 mL), dried with $MgSO_4$, and concentrated under

reduced pressure. The crude product was chromatographed on silica gel with EtOAc and eluted last (first orange band contains titanium byproduct) to yield a bright orange solid (**46**) (0.106 g, 0.244 mmol, 53% yield); decomposes at 171 °C. IR (NaCl): 2957, 2898, 1556, 1438, 1227 cm^{-1}. ^1H NMR ($CDCl_3$): 18.32 (bs, 2H), 8.58 (d, J = 6.3 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 6.40 (d, J = 14.0 Hz, 1H), 5.92 (d, J = 14.0 Hz, 1H), 4.61 (d, J = 1.3 Hz, 1H), 4.52 (d, J = 1.3 Hz, 1H), 2.10 (s, 12H), 1.68 (s, 3H). ^{13}C NMR ($CDCl_3$): 150.09, 149.98, 149.49, 149.00, 137.45, 125.23, 125.17, 110.92, 12.11, 11.96. HRMS FAB (m/z): calcd for $C_{18}H_{27}O_4N_5Co$ $(MH)^+$ 436.1395; found 436.1387.

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Supporting Information Available: Tables giving additional details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, and anisotropic displacement parameters for **38**, **39**, and **45a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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