Synthesis of Cobaloxime-Substituted α,β-Unsaturated Acyl Complexes via Reactions of Cobaloxime Anions and/or Hydrides with Ynones, Ynoates, and α,β-Unsaturated Acyl Electrophiles

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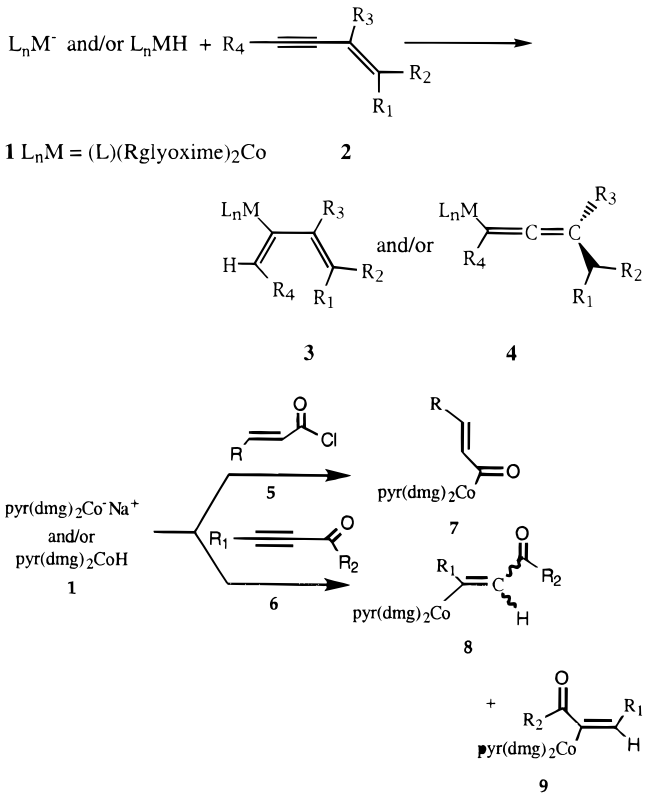
Cobaloxime anions ($pyr(dmg)_2Co^-Na^+$) and/or hydrides ($pyr(dmg)_2CoH$) react with cinnamoyl chloride and a variety of ynones and ynoates to produce cobaloxime-substituted α,β-unsaturated acyl complexes. The stereochemistry of the alkene produced by the ynone and ynoate hydrometalations can be controlled through choice of hydrometalation reaction conditions. Two of these new acyl complexes have been characterized by X-ray crystallography.

Introduction

Recently we reported an alternative method for the preparation of dienyl cobaloxime complexes which involves reactions of cobaloxime anions and/or hydrides (**1**) with enynes (**2**).[1e] This new dienyl complex preparative method led to cobalt-substituted 1,3- (**3**) or 1,2-dienes (**4**), depending on the enyne substitution pattern chosen. We and Tada et al. have been interested in preparing cobaloxime dienyl complexes **3** so that their reactivity in Diels−Alder cycloadditions could be investigated.[1,2] Here, we report analogous reaction chemistry of cobaloxime anions and hydrides (**1**) with unsaturated acid chlorides (**5**), ynones (**6**), and ynoates (**6**, R_2 = OR) to produce acyl complexes (**7**, **8**, or **9**).



Experimental Section

General Methods. For a description of instrumentation and chromatographic adsorbents used, see ref 1b. Cobalt chloride hexahydrate 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. Cinnamoyl chloride was purchased from Aldrich. 3-Butyn-2-one (**19a**) and 4-phenyl-3-butyn-2-one (**19c**) were purchased from Wiley. Ethyl propiolate (**19b**), ethyl 2-butynoate (**19d**), and ethyl 3-phenylpropiolate (**19e**) were purchased from Farchan. Propiolaldehyde diethyl acetal (**24**) was purchased from Lancaster. All ynones and ynoates were used as received, and $pyr(dmg)_2CoCl$ (**23**) was prepared according to literature procedures.[3]

(1-Oxo-3-phenyl-2(*E*)-propen-1-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (18). Cobalt chloride **23** (0.505 g, 1.25 mmol) was dissolved in degassed DMF (15 mL) and cooled to −20 °C. $NaBH_4$ (0.052 g, 1.38 mmol) was added, and the reaction mixture was allowed to stir (2 h). Cinnamoyl

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chloride (0.425 g, 2.55 mmol) was then added, and the solution was warmed to 25 °C overnight and then poured into water (100 mL) containing pyridine (0.75 mL). The product formed was collected by filtration, and the filtrate was extracted with CH_2Cl_2 until the extracts were colorless. The dichloromethane extracts were washed with water (5 × 200 mL) to remove the DMF, dried with $MgSO_4$, and then concentrated under reduced pressure. Solid from the filtrate and the filtration were combined and chromatographed on silica (EtOAc) to yield a yellow solid after solvent removal under vacuum (0.245 g, 0.491 mmol, 39%); mp: 165 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.65 (d, J = 5.1 Hz, 2H), 7.71 (t, J = 5.1 Hz, 1H), 7.50 (t, J = 5.1 Hz, 2H), 7.45 (d, J = 15.4 Hz, 1H), 7.31 (m, 5H), 6.83 (d, J = 15.6 Hz, 1H), 2.04 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 193.9, 171.9, 167.1, 153.0, 159.6, 146.7, 134.1, 130.6, 128.5, 117.8, 12.2. IR ($CDCl_3$): 3154.8, 2983.5, 2901.2, 1710.8, 1387.1, 1364.2, 1091.2 cm^{-1}. Anal. Calcd for $C_{22}H_{26}CoN_5O_5$: C, 52.91; H, 5.25. Found: C, 53.04; H, 5.30.

Method A. (2-Oxo-4-phenyl-3(*E*)-buten-4-yl)(pyridine)-bis(dimethylglyoximato)cobalt(III) (20c). Cobalt chloride **23** (1.00 g, 2.48 mmol) was dissolved in degassed DMF (20 mL) and cooled to −20 °C. $LiBH_4$ (1.36 mL of a 2.0 M solution in THF, 2.72 mmol) was added dropwise. The mixture was allowed to stir at −20 °C (20 min), and then ynone **19c** (0.484 mL, 6.19 mmol) was added dropwise. The solution was allowed to warm to 25 °C overnight and then poured into ice water (400 mL) containing pyridine (0.75 mL). The product was collected by vacuum filtration and purified by chromatography on silica (EtOAc) to yield a dark orange solid (0.380 g, 0.740 mmol, 30%); mp 220 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.45 (d, J = 5.1 Hz, 2H), 7.68 (t, J = 5.1 Hz, 1H), 7.24 (t, J = 5.1 Hz, 2H), 7.12 (m, 3H), 6.65 (m, 2H), 5.60 (s, 1H), 2.01 (s, 12H), 1.42 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 194.1, 152.3, 150.6, 149.9, 149.2, 146.9, 139.4, 137.9, 134.3, 127.1, 125.6, 29.8, 12.4. IR ($CDCl_3$): 3154.9, 2985.2, 2901.8, 1734.1, 1635.9, 1559.3, 1472.3, 1450.8, 1168.7 cm^{-1}. Anal. Calcd for $C_{23}H_{28}CoN_5O_5$: C, 53.80; H, 5.50. Found: C, 53.84; H, 5.54.

(1-Ethoxy-1-oxo-2(*E*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (20d). Cobalt chloride **23** (1.00 g, 2.47 mmol) was dissolved in degassed DMF (15 mL) and cooled to −20 °C. $NaBH_4$ (0.131 g, 2.75 mmol) was added, and the reaction mixture was allowed to stir (2 h). Ynoate **19d** (0.578 mL, 4.95 mmol) was then added, and the solution was warmed to 25 °C overnight and then poured into water (200 mL) containing pyridine (0.75 mL). The product was collected by vacuum filtration, and the filtrate was extracted with CH_2Cl_2 until the extracts were colorless. The dichloromethane extracts were washed with water (5 × 200 mL) to remove the DMF, dried with $MgSO_4$, and then concentrated under reduced pressure. Solid from the filtrate and the filtration were combined and chromatographed on silica (EtOAc) to yield a yellow solid after solvent removal (0.565 g, 1.17 mmol, 47%); mp 240 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.60 (d, J = 5.1 Hz, 2H), 7.70 (t, J = 5.1 Hz, 1H), 7.30 (t, J = 5.1 Hz, 2H), 5.79 (s, 1H), 4.03 (q, J = 7.2 Hz, 2H), 2.12 (br s, 3H), 2.08 (s, 12H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 161.2, 150.3, 150.0, 137.8, 125.3, 120.2, 59.0, 24.4, 14.4, 12.2. IR ($CDCl_3$): 3155.1, 2985.0, 2902.0, 1717.9, 1653.0, 1216.3 cm^{-1}. Anal. Calcd for $C_{19}H_{28}CoN_5O_6$: C, 47.41; H, 5.86. Found: C, 47.50; H, 5.85.

Crystallographic Structural Determination of Complex 20d. Crystal, data collection, and refinement parameters are given in Table 2. A suitable crystal for single-crystal X-ray diffraction was selected and mounted with epoxy cement in a nitrogen-flushed, thin-walled capillary. No evidence of symmetry higher than triclinic was observed. The *E*-statistics suggested the centrosymmetric space group option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. No absorption corrections were required because there was <10% variation in the integrated ψ-scan intensities. The asymmetric unit consists of the complex and a solvent molecule of 1,2-dichloroethane. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (Version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

(1-Ethoxy-1-oxo-phenyl-2(*E*)-propen-3-yl)(pyridine)-bis(dimethylglyoximato)cobalt(III) (20e). This compound was prepared by method A using $LiBH_4$ in THF (0.680 mL of a 2.0 M solution, 1.36 mmol), cobalt chloride **23** (0.500 g, 1.24 mmol), and ynoate **19e** (0.511 mL, 3.10 mmol) as described above. The crude product was purified by chromatography on silica (EtOAc) to yield an orange solid after solvent removal under vacuum (0.262 g, 0.482 mmol, 39%); mp 200−202 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.48 (d, J = 5.1 Hz, 2H), 7.68 (t, J = 5.1 Hz, 1H), 7.27 (t, J = 5.1 Hz, 2H), 7.15 (m, 3H), 6.62 (m, 2H), 5.41 (s, 1H), 3.78 (q, J = 7.2 Hz, 2H), 2.03 (s, 12H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 160.7, 150.4, 149.9, 147.2, 137.9, 126.6, 125.0, 121.9, 59.0, 14.0, 12.3. IR ($CDCl_3$): 3155.8, 3077.8, 2984.9, 2902.3, 1714.7, 1653.0, 1238.5, 1185.4 cm^{-1}. Anal. Calcd for $C_{24}H_{30}CoN_5O_6$: C, 53.04; H, 5.56. Found: C, 53.31; H, 5.62.

(1-Oxo-2(*Z*)-Propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (25). Cobalt chloride **23** (1.500 g, 3.72 mmol) was dissolved in degassed 95% EtOH (20 mL) and cooled to −20 °C. $NaBH_4$ (0.112 g, 2.97 mmol) dissolved in H_2O (0.5 mL) was added and stirred (20 min). Acetal **24** (1.07 mL, 7.43 mmol) was then added, the solution was allowed to warm to 25 °C overnight and then poured into ice water (200 mL) containing pyridine (0.75 mL). The product was collected by vacuum filtration to yield a yellow solid (**25**, 1.19 g, 0.282 mmol, 76%); mp 220 °C dec. ^{1}H NMR ($CDCl_3$): δ 9.80 (d, J = 7.8 Hz, 1H), 8.63 (d, J = 6.7 Hz, 2H), 8.09 (d, J = 9.2 Hz, 1H), 7.78 (t, J = 6.7 Hz, 1H), 7.36 (t, J = 6.7 Hz, 2H), 5.79 (br t, J = 8.5 Hz, 1H), 2.10 (s, 12H). ^{13}C NMR ($CDCl_3$) 196.7, 150.7, 149.6, 141.6, 138.2, 125.5, 12.2. IR ($CDCl_3$) 3155.2, 29.85.0, 2901.5, 1734.0, 1652.7, 1602.7, 1238.4, 1167.1 cm^{-1}. Anal. Calcd for $C_{16}H_{22}CoN_5O_5$ C: 45.40; H: 5.24. Found: C, 45.45; H: 5.23.

(1-Oxo-2(*E*)- and -2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (25). This mixture of compounds was prepared by method A in DMF (20 mL) using cobalt chloride **23** (1.500 g, 3.715 mmol), $NaBH_4$ (0.1124 g, 2.972 mmol), and acetal **24** (1.17 mL, 7.43 mmol) as described above. The crude product was chromatographed on silica (EtOAc) to yield a 2:1 mixture of *E:Z* **25** after solvent removal under vacuum (0.122 g, 0.288 mmol, 8%). ^{1}H NMR ($CDCl_3$) for the *E* isomer (2*Z* isomer ^{1}H NMR data and complete characterization reported above): δ 9.16 (d, J = 7.6 Hz, 1H), 8.51 (d, J = 6.7 Hz, 2H), 8.37 (d, J = 14.8 Hz, 1H), 7.75 (t, J = 6.7 Hz, 1H), 7.35 (t, J = 6.7 Hz, 2H), 6.22 (dd, J = 14.8, 7.6 Hz, 1H), 2.10 (s, 12H).

(2-Oxo-3(*Z*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (22a) and (2-Oxo-3(*Z*)-buten-4-yl)-(pyridine)bis(dimethylglyoximato)cobalt (III) (21a). This mixture of compounds was prepared by method A in 95% EtOH (25 mL) using cobalt chloride **23** (1.500 g, 3.715 mmol), $NaBH_4$ (0.1124 g, 2.972 mmol), and ynone **19a** (0.581 mL, 7.43 mmol) as described above. The crude product was chromatographed on silica (EtOAc) to yield compounds **22a** and **21a** as a dark orange solid (4:1 mixture) after solvent removal under vacuum (0.71 g, 1.623 mmol, 44%). ^{1}H NMR ($CDCl_3$) for **22a** (complete characterization of **21a** is reported below): δ 8.51 (d, J = 5.1 Hz, 2H), 7.70 (t, J = 5.1 Hz, 1H), 7.29 (t, J = 5.1 Hz, 2H), 4.46 (d, J = 1.2 Hz, 1H), 4.22 (d, J = 1.2 Hz, 1H), 2.157 (s, 12H), 2.012 (s, 3H).

(1-Ethoxy-1-oxo-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21b) and (1-Ethoxy-1-oxo-2(*Z*)-propen-2-yl)(pyridine)bis(dimethylglyoximato)-cobalt(III) (22b). This mixture of compounds was prepared by method A in DMF (20 mL) using cobalt chloride **23** (1.500

g, 3.715 mmol), $NaBH_4$ (0.1124 g, 2.972 mmol), and ynoate **19b** (0.7530 mL, 7.43 mmol) as described above. The crude product was chromatographed on silica (EtOAc) to yield compounds **21b** and **22b** as a yellow solid (5:1 mixture) after solvent removal under vacuum (0.433 g, 0.926 mmol, 25%). Complete characterization data for complexes **21b** and **22b** are reported below.

Method B. (2-Oxo-3(*Z*)-buten-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21a). Cobalt chloride **23** (0.300 g, 0.75 mmol) was suspended in 20 mL of degassed MeOH containing NaOH (0.100 g, 2.5 mmol) at 0 °C and was reduced with $NaBH_4$ (0.050 g, 1.32 mmol). Ynone **19a** was added, followed by the dropwise addition of acetic acid (ca. 7−8 drops) until the solution turned orange-red. The mixture was then immediately poured into ice water (100 mL) containing pyridine (0.75 mL) and extracted with EtOAc (4 × 100 mL), dried ($MgSO_4$), and concentrated. The crude product was chromatographed on silica (EtOAc) to yield an orange solid (0.240 g, 0.549 mmol, 74%); mp 122−123 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.55 (d, J = 7.2 Hz, 2H), 7.73 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 6.09 (d, J = 10.5 Hz, 1H), 5.97 (d, J = 10.5 Hz, 1H), 2.18 (br s, 3H), 2.10 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 203.4, 150.9, 150.0, 149.6, 140.9, 137.9, 125.9, 31.0, 12.2. IR ($CDCl_3$): 3154.3, 2984.4, 1734.1, 1653.0, 1465.0, 1096.3 cm^{-1}. Anal. Calcd for $C_{17}H_{24}CoN_5O_5$: C, 46.69; H, 5.53. Found: C, 46.57; H, 5.52.

(1-Ethoxy-1-oxo-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21b). This complex was prepared using method B with ynoate **19b** (0.081 mL, 0.80 mmol) to yield a yellow solid (0.281 g, 0.601 mmol, 81%); mp 182−183 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.60 (d, J = 7.0 Hz, 2H), 7.74 (t, J = 7.0 Hz, 1H), 7.33 (t, J = 7.0 Hz, 2H), 6.61 (d, J = 10.5 Hz, 1H), 5.71 (d, J = 10.5 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.10 (s, 12H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.6, 150.5, 150.1, 137.8, 130.7, 125.2, 60.1, 14.1, 12.2. IR ($CDCl_3$): 3155.0, 2985.3, 2901.4, 1733.9, 1700.3, 1472.1, 1465.9, 1167.6 cm^{-1}. Anal. Calcd for $C_{18}H_{26}CoN_5O_6$: C, 46.24; H, 5.61. Found: C, 46.27; H, 5.59.

(2-Oxo-4-phenyl-3(*Z*)-buten-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21c). This complex was prepared using method B with ynone **19c** (0.117 mL, 0.80 mmol) to yield a dark orange solid (0.233 g, 0.454 mmol, 61%); mp 130−132 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.40 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.07 (m, 3H), 6.90 (m, 2H), 5.50 (s, 1H), 2.23 (br s, 3H), 1.89 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 204.1, 152.2, 150.7, 149.1, 139.3, 137.9, 126.4, 126.2, 125.1, 124.6, 30.7, 12.1. IR ($CDCl_3$): 3154.9, 2985.8, 2901.8, 1717.9, 1684.0, 1559.1, 1470.9, 1168.3 cm^{-1}. Anal. Calcd for $C_{23}H_{28}CoN_5O_5$: C, 53.80; H, 5.50. Found: C, 54.08; H, 5.54.

(1-Ethoxy-1-oxo-2(*Z*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21d). This complex was prepared using method B with ynoate **19d** (0.093 mL, 0.80 mmol) to yield a dark orange solid (0.274 g, 0.569 mmol, 77%); mp 122−123 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.58 (d, J = 5.0 Hz, 2H), 7.68 (t, J = 5.0 Hz, 1H), 7.25 (t, J = 5.0 Hz, 2H), 5.36 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.19 (br s, 3H), 2.09 (s, 12H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 168.4, 151.3, 150.1, 149.4, 137.7, 125.2, 124.8, 60.4, 31.5, 13.9, 12.2. IR ($CDCl_3$): 3154.9, 2984.1, 2901.9, 1717.8, 1646.1, 1216.3, 1166.0 cm^{-1}. Anal. Calcd for $C_{19}H_{28}CoN_5O_6$: C, 47.41; H, 5.86. Found: C, 47.68; H, 5.89.

(1-Ethoxy-1-oxo-3-phenyl-2(*Z*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21e). This complex was prepared using method B with ynoate **19e** (0.132 mL, 0.80 mmol) to yield a dark orange solid (0.215 g, 0.396 mmol, 53%); mp 140−141 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.41 (d, J = 6.6 Hz, 2H), 7.67 (t, J = 6.6 Hz, 1H), 7.25 (t, J = 6.6 Hz, 2H), 7.05 (m, 3H), 6.85 (m, 2H), 5.38 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.93 (s, 12H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.8, 151.9, 150.9, 149.2, 137.8, 129.9, 129.4, 126.3, 125.0, 124.7, 60.2, 14.2, 12.2. IR ($CDCl_3$): 3154.3, 2984.7, 2901.9, 1717.8, 1646.3, 1239.4 cm^{-1}. Anal. Calcd for $C_{24}H_{30}CoN_5O_6$: C, 53.04; H, 5.56. Found: C, 52.96; H, 5.55.

Method C. (1-Ethoxy-1-oxo-2(*Z*)-buten-3-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (21d). Cobalt dichloride hexahydrate (1.181 g, 4.964 mmol) and dimethylglyoxime (1.406 g, 12.11 mmol) were combined in degassed 95% EtOH (20 mL). The solution was stirred (10 min), and then NaOH (0.484 g, 12.10 mmol) and pyridine (0.4 mL, 4.95 mmol) were added. The solution was allowed to stir at 25 °C overnight. $NaBH_4$ (0.10 g, 2.64 mmol) in H_2O (0.2 mL) was added at −20 °C and stirred (1 h). Acetic acid (0.250 mL, 4.35 mmol) was added, and 10 min later ynoate **19d** (1.16 mL, 9.927 mmol) was added. The reaction was warmed to 25 °C overnight and then poured into ice water (200 mL) containing pyridine (0.75 mL). The product was collected by vacuum filtration and chromatographed on silica (EtOAc) to yield a dark orange solid (0.991 g, 2.059 mmol, 42%), identical by ^{1}H NMR comparison to **21d** reported above.

(1-Ethoxy-1-oxo-2(*Z*)-propen-2-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (22b). This complex was prepared in a manner analogous to the procedure for **21d** above using $CoCl_2 \cdot 6H_2O$ (2.00 g, 8.41 mmol), dimethylglyoxime (1.952 g, 16.81 mmol), NaOH (0.672 g, 16.81 mmol), pyridine (0.68 mL, 8.41 mmol), $NaBH_4$ (0.123 g, 3.25 mmol), acetic acid (0.200 mL, 3.48 mmol), and ynoate **19b** (0.937 mL, 9.246 mmol) to yield a yellow-orange solid (**22b**, (0.663 g, 1.42 mmol, 17%); mp 210 °C dec. ^{1}H NMR ($CDCl_3$): δ 8.56 (d, J = 5.1 Hz, 2H), 7.70 (t, J = 5.1 Hz, 1H), 7.28 (t, J = 5.1 Hz, 2H), 4.78 (d, J = 1.2 Hz, 1H), 4.56 (d, J = 1.2 Hz, 1H), 4.03 (q, J = 7.2 Hz, 2H), 2.14 (s, 12H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 173.5, 152.6, 150.7, 150.1, 137.9, 125.3, 120.1, 60.4, 14.2, 12.4. IR ($CDCl_3$): 3154.0, 2984.5, 2901.6, 1739.9, 1653.0, 1216.5, 1166.4 cm^{-1}. Anal. Calcd for $C_{18}H_{26}CoN_5O_6$: C, 46.34; H, 5.61. Found: C, 45.67; H, 5.50.

Crystallographic Strucure Determination of Complex 22b. Crystal, data collection, and refinement parameters are given in Table 4. Suitable crystals were selected and mounted on the tip of a glass fiber with epoxy cement. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 25°$). The systematic absences in the diffraction data are consistent with the monoclinic space groups $P2_1$ or $P2_1/m$. The E-statistics and the absence of a molecular mirror plane indicated $P2_1$; this was verified by chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Absorption corrections were not required because the variation in integrated ψ-scan intensities was <10%. The Flack parameter refined to 0.02(2), indicating that the correct absolute hand of the structure was determined. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (Version 5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

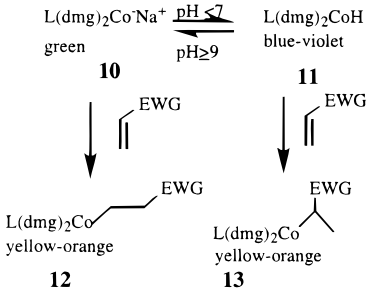
(2-Oxo-4-phenyl-3(*E*)-buten-4-yl)(pyridine)bis(dimethylglyoximato)cobalt(III) (20c). This complex was prepared using the method C cobaloxime generation described above using ynone **19c** (0.816 mL, 5.6 mmol) to yield a dark orange solid (0.467 g, 0.910 mmol, 16%), identical by ^{1}H NMR spectroscopic comparison to **20c** reported above.

(1-Ethoxy-1-oxo-3-phenyl-2(*E*)-propen-3-yl)(pyridine)bis(dimethylglyoximato)cobalt (III)(20e). This complex was prepared using the method C cobaloxime generation described above using ynoate **19e** (1.527 mL, 9.246 mmol) to yield an orange solid (1.26 g, 2.319 mmol, 28%), identical by ^{1}H NMR spectroscopic comparison to **20e** reported above.

Results and Discussion

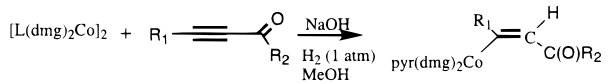
Hydrometalation of alkynes as a route to transition-metal alkenyl complexes has been studied for over 20

years.[4,5] The most well known transition-metal alkyne hydrometalation agent is bis(cyclopentadienyl)zirconium chlorohydride ("Schwartz's reagent").[6] Hydrometalation of both alkenes and alkynes involving cobaloxime chemistry has also been reported, and the product outcomes of these experiments were heavily pH dependent.[7] Cobaloxime anions **10** are typically generated by one of two methods: (i) in situ by way of reduction of the dark red cobalt(II) dimer, $[pyr(dmg)_2Co]_2$ or (ii) via reduction of the yellow-brown preformed cobalt(III) chloride, $pyr(dmg)_2CoCl$.[3] At pH ≥ 9, these aqueous alcohol solutions contain predominantly the deep green cobaloxime anion **10**, but as the pH of the solution is lowered to 7, the deep blue-violet cobalt hydrides **11** are formed.[8] When L = phosphine, these cobalt hydrides



can be isolated; however, when L = a nitrogen base, they decompose fairly rapidly at 20 °C in these solutions.[8] The cobaloxime anions **10** react with electron-deficient alkenes to give products substituted by cobalt at the β-carbon (Michael-type addition reactions) (**12**), and the cobaloxime hydrides react with these same substrates to give α-substituted cobaloximes **13**, which can be further reduced (demetalated) to the saturated esters.[8]

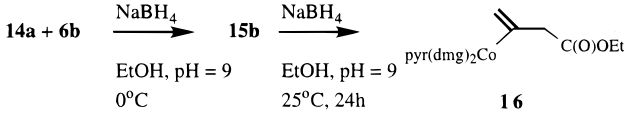
Hydrometalation of the alkyne of two ynoates via cobaloxime chemistry has been reported previously. In 1967, Schrauzer and Windgassen reported the reaction of $(H_2O)(dmg)_2CoH$ at pH = 7 with ethyl propiolate. They reported $(H_2O)(dmg)_2CoCH{=}CHCO_2Et$ with presumed *E* double bond geometry in the product but did not report ^1H NMR data for this compound.[8c] In 1970, Van Duong and Gaudemer reported that reduction of the cobaloxime dimer **14a** under 1 atm of hydrogen in MeOH at pH = 8 followed by treatment with methyl propiolate (**6a**) produced *cis*-substituted propenoate **15a** (J_{H2-H3} = 10.4 Hz) in 32% yield.[9] Later that same year, these authors also reported that ethyl 2-butynoate (**6b**) reacted with the aniline rather than pyridine-substituted cobaloxime **14b** (generated under identical conditions) to also produce the *Z* isomer **15b** (60%). The *Z*



14a L = pyr	**6a** R_1 = H, R_2 = OMe	**15a** (32%)
14b L = aniline	**6b** R_1 = Me, R_2 = OEt	**15b** (60%)
	6c R_1 = H, R_2 = OEt	**15c** (60%)

stereochemistry of the product **15b** was proposed on the basis of their observation that axial aniline ligand exchange for trimethyl phosphite produced a complex with $J_{P-\beta H}$ (*trans* to Co) of 30.5 Hz. These authors had shown that $J_{P-\beta H}$ (*cis* to Co) would be expected to be only 12−15 Hz.[10]

In 1976, these same authors along with Johnson and co-workers[11] reported that the cobaloxime anion **10** generated by $NaBH_4$ reduction of the dimer **14a** at pH = 9 reacted with ethyl propiolate (**6c**) to yield the *cis* isomer **15c**. They also reported that ethyl 2-butynoate (**6b**) reacted with the cobaloxime anion **10** at pH = 9 to initially produce **15b** but that with prolonged stirring they isolated rearranged product **16** (35%).



In our cobaloxime hydrometalation of enynes,[1e] as well as other cobaloxime dienyl syntheses,[1] we had noted significant changes in product outcomes depending on pH, solvent, and amount of reducing agent present. Therefore, we decided to reinvestigate the two ynoates reported above as well as several other ynone and ynoate hydrocobaltations at both near-neutral and strongly basic pH ranges in polar protic and aprotic solvents. We were interested in preparing a variety of cobaloxime acyl complexes where cobalt was substituted at both the acyl carbonyl (prepared via reactions of cobaloxime anions with acid chlorides, anhydrides, or acylimidazoles) and the α or β alkene carbon (prepared via hydrocobaltation of a variety of ynones and ynoates) so that these complexes could be investigated as heterodienes in Diels−Alder reactions. The results of our cobaloxime acyl complex preparations using both of the methods outlined above are presented here.

Reaction of Cobaloxime Anions with Acid Chlorides, Anhydrides, and Acylimidazoles. Reactions of acyl electrophiles (acid chlorides, anhydrides, and imidazoles) with cobaloxime anions were performed in polar aprotic solvents.[3b] Generation of cobaloxime anion **1** in DMF followed by treatment with cinammoyl chloride (**17a**) produced acyl complex **18** in 39% yield. This complex could also be isolated when $pyr(dmg)_2CoCl$ was reduced with Na(Hg) in THF and treated with cinnamoyl chloride (**17a**), but the isolated yield was much lower. Using cinnamoylimidazole (**17b**)[12] rather than cinnamoyl chloride provided a complex mixture of products, possibly because the liberated imidazole undergoes ligand exchange with the pyridine. Reactions

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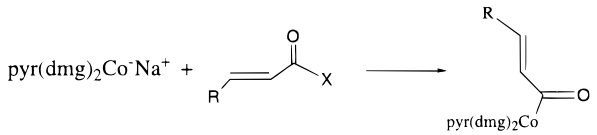


1 **17** **18**

17a R = Ph, X = Cl **18** R = Ph

17b R = Ph, X = imidazole

17c R = H, X = Cl

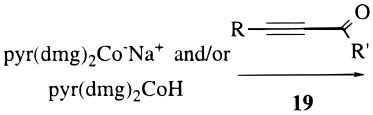
17d R = Me, X = Cl

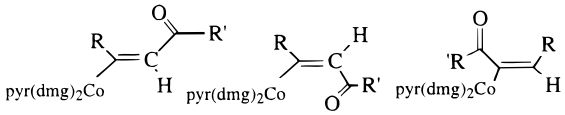
with acryloyl and crotonyl chlorides (**17c**,**d**) and crotonic anhydride yielded products that had extremely high water solubilities and could not be extracted by a variety of polar aprotic solvents. When the cobalt ligand set was changed from dimethylglyoxime (dmg) to diphenylglyoxime (dpg)[1] in an attempt to decrease water solubility following reaction with these electrophiles, we instead recovered the pyr(dpg)$_2$CoCl starting material.

Reactions of Ynones and Ynoates with Cobaloximes. Hydrometalation of a variety of ynones and ynoates was investigated in both polar protic and aprotic solvents. Three different types of hydrometalation protocols were used, and the results of these experiments are presented in Table 1. In method A, pyr(dmg)$_2$CoCl was dissolved in DMF, reduced with $LiBH_4$ or $NaBH_4$, and then treated with ynone or ynoate. Ethyl 2-butynoate (**19d**), ethyl 3-phenyl-2-propiolate (**19e**), and 4-phenyl-3-butyn-2-one (**19c**) all yielded β-cobaloxime α,β-unsaturated acyl complexes where cobalt and the α alkene hydrogen are *syn* (**20c**−**e**) (Table 1, entries 3−5). 3-Butyn-2-one (**19a**) (entry 1) reacted to produce a complex or mixture of complexes that could not be extracted by a variety of organic solvents and ethyl propiolate (**19b**) (entry 2) was the only substrate that produced an acyl complex (**21b**) where cobalt and the α alkene hydrogen were *anti* [^{1}H NMR alkene protons ($CDCl_3$) δ 6.61 (d), 5.71 (d, J = 10.5 Hz], as well as a small amount of α-cobaloxime substituted-complex **22b** (5:1 **21b**:**22b**). If we switched from DMF to 95% EtOH in this protocol for the problem substrate, 3-butyn-2-one mentioned above, we isolated a 4:1 mixture (44% total yield) of α (**22a**):cis-β (**21a**)-substituted acyl complexes.

The product of the ethyl 2-butynoate reaction (**20d**) had been prepared via reaction of cobaloxime anion **10** with *trans*-β-chloroethyl propenoate previously,[10] so we were fairly confident of the alkene stereochemistry. This alkene configuration was then subsequently confirmed by X-ray crystallography. The ORTEP drawing of this complex (**20d**) is provided in Figure 1, and the data collection and refinement parameters as well as selected bond lengths and angles are provided in Tables 2 and 3. The cobalt−sp^2 carbon (C(14)) bond length in this complex (1.976(4) Å) is within the range of cobalt−sp^2 carbon bond lengths we have observed previously in related dienyl complexes (1.954(15)−2.019(6) Å).[1b,c] The dihedral (torsion) angle in the α,β-unsaturated acyl portion of the molecule is the closest we have observed yet to an *s-cis* conformation for a transition-metal-substituted diene or heterodiene (C(14)−C(15)−C(16)−O(5), 9.3°), which bodes well for future possible hetero Diels−Alder reactions.

Table 1. Reactions of Ynones and Ynoates with Cobaloxime Anions and/or Hydrides





entry	method[a]	R	R′	compd no.	solvent	product no.	yield (%)
1	A	H	Me	**19a**	DMF		*b*
2	A	H	OEt	**19b**	DMF	**21b:22b**	25 (5:1)
3	A	Ph	Me	**19c**	DMF	**20c**	30
4	A	Me	OEt	**19d**	DMF	**20d**	47
5	A	Ph	OEt	**19e**	DMF	**20e**	39
6	B	H	Me	**19a**	MeOH	**21a**	74
7	B	H	OEt	**19b**	MeOH	**21b**	81
8	B	Ph	Me	**19c**	MeOH	**21c**	61
9	B	Me	OEt	**19d**	MeOH	**21d**	77
10	B	Ph	OEt	**19e**	MeOH	**21e**	53
11	C	H	Me	**19a**	95% EtOH		*b*
12	C	H	OEt	**19b**	95% EtOH	**22b**	17
13	C	Ph	Me	**19c**	95% EtOH	**20c**	16
14	C	Me	OEt	**19d**	95% EtOH	**21d**	42
15	C	Ph	OEt	**19e**	95% EtOH	**20e**	28

[a] A: (1) pyr(dmg)$_2$CoCl in DMF, (2) $LiBH_4$ or $NaBH_4$, (3) ynone or ynoate. B: (1) pyr(dmg)$_2$CoCl, NaOH and $NaBH_4$ in MeOH, (2) ynone or ynoate (ca. 5 min), (3) CH_3CO_2H. C: (1) [pyr(dmg)$_2$Co]$_2$, $NaBH_4$, (2) CH_3CO_2H to pH = 6−7, (3) ynone or ynoate. [b] No product could be isolated, presumably due to its high water solubility.

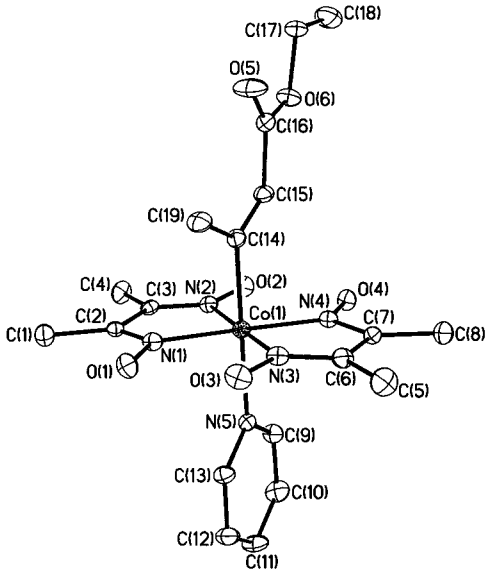


Figure 1. Molecular structure of complex **20d**.

All three of the hydrometalation products **20c**−**e** exhibited α alkene ^{1}H NMR resonances (in $CDCl_3$, δ 5.79 for **20d**, 5.41 for **20e**, and 5.60 for **20c**) downfield of those seen in their alkene isomer counterparts to be discussed below. This protocol, which contains no added external base to raise the pH and produce a preponderance of cobaloxime anions (**10**) over hydrides (**11**), would appear to be a good method for producing the alkene isomer expected of a hydrometalation. Exceptions to this generalization occur where the alkyne is terminal, in which case the Michael addition product **21b** was isolated for **19b**, and both α- and β-substituted products

Table 2. Crystal Data and Structure Refinement for 20d

identification code	welx
empirical formula	$C_{21}H_{32}Cl_2CoN_5O_6$
formula weight	580.35
temperature	218 (2) K
wavelength	0.710 73 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 8.2032(4)$ Å, $\alpha = 86.4120(10)°$ $b = 12.0116(6)$ Å, $\beta = 81.7030(10)°$ $c = 14.0365(7)$ Å, $\gamma = 74.4130(10)°$
volume, Z	1317.85(11) Å3, 2
density (calcd)	1.463 g/cm^3
absorption coefficient	0.899 mm^{-1}
$F(000)$	604
crystal size	0.25 mm × 0.15 mm × 0.04 mm
crystal color	yellow blade
θ range for data collection	1.76−28.28°
limiting indices	$-10 \le h \le 10$, $-15 \le k \le 15$, $-18 \le l \le 16$
reflections collected	7884
independent reflections	5655 ($R_{int} = 0.0414$)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5651/0/316
goodness-of-fit on F^2	1.141
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0692$, w$R_2 = 0.1317$
R indices (all data)	$R1 = 0.1265$, w$R_2 = 0.1564$
largest diff peak and hole	0.518 and -0.551 e Å^{-3}

were isolated for **19a** when the solvent was changed to 95% EtOH. Clearly, this reaction is much more complicated using this protocol in a polar protic versus aprotic solvent, and discussion of the production of an α-substituted product will be presented below, after discussion of the other data in Table 1. For terminal alkynes (**19a**,**b**), the rate of Michael addition would appear to be much faster than the rate of hydrometalation, since the Michael addition product **21b** is observed as the exclusive product, even under conditions where there is much more cobaloxime hydride (**11**) than anion (**10**) present. We suspect that this hydrometalation follows a mechanism like hydroboration or hydroalumination of an alkyne rather than alkyne insertion into a transition metal hydride, since the latter would require pyridine loss, equatorial ligand reorientation, alkyne complexation, insertion, and pyridine recoordination.

In method B, pyr(dmg)$_2$CoCl was treated with NaOH and $NaBH_4$ in the polar protic solvent, methanol. In this traditional method of cobaloxime anion generation, ynone or ynoate was quickly added, followed shortly thereafter (ca. 5 min) by acetic acid.[13] For all substrates tried (**19a**−**e**) (Table 1, entries 6−10), this method produced the alkene isomer where cobaloxime and the α alkene proton were *anti*. This alkene stereochemistry was easily distinguished for the ethyl propiolate and 3-butyn-2-one adducts (**21b**,**a**), which exhibited ^{1}H NMR alkene resonances at (in $CDCl_3$) δ 6.61 (d) and 5.71 (d, $J = 10.5$ Hz) for **21b** and δ 6.09 (d) and 5.97 (d, $J = 10.5$ Hz) for **21a**. The ethyl 2-butynoate, ethyl 3-phenyl-2-propiolate, and 4-phenyl-3-butyn-2-one adducts (**21c**−**e**) were all different from the products produced by method A, and all had ^{1}H NMR alkene proton resonances upfield from those of their alkene isomers (**20c**−**e**) (in $CDCl_3$, δ 5.36 for **21d**, 5.38 for **21e**, and 5.50 for **21c**), so all three of these complexes are also presumed to have the cobaloxime and α alkene proton *anti*. Yields were routinely good using method B, and these products (**21a**−**e**) are easily explained by Michael addition of the cobaloxime anion (**10**) at the β-carbon of the α,β-unsaturated ynone or ynoate followed by protonation of the resulting enolate upon acidification. This Michael addition is rapid even at very low temperatures. When ethyl propiolate (**19b**) was subjected to method B conditions, except that all additions and anion generation were perfomed at −78 °C, **21b** was again isolated in good yield (56%).

We[1c,d] and others[9] have noted some unexpected products from cobaloxime chemistry performed in polar protic solvents when initially formed cobaloxime complexes have been allowed to remain in these solvents for extended periods of time. In method C, we first prepared the cobaloxime dimer[7,8] and then added $NaBH_4$ followed by acetic acid to bring the pH down to the 6−7 range, where both cobaloxime anion **10** and hydride **11** are present. Ynone or ynoate was then added, and the mixtures were allowed to stir overnight at 25 °C, followed by product precipitation, which was induced by pouring these 95% EtOH solutions into ice water containing pyridine.

Table 3. Bond Lengths (Å) and Angles (deg) for 20d

Co(1)−N(1)	1.881(4)	Co(1)−N(2)	1.883(3)
Co(1)−N(3)	1.890(4)	Co(1)−N(4)	1.890(4)
Co(1)−C(14)	1.976(4)	Co(1)−N(5)	2.067(3)
O(1)−N(1)	1.354(4)	O(2)−N(2)	1.340(4)
O(3)−N(3)	1.345(4)	O(4)−N(4)	1.351(4)
O(5)−C(16)	1.200(5)	O(6)−C(16)	1.353(5)
O(6)−C(17)	1.450(5)	N(1)−C(2)	1.300(5)
N(2)−C(3)	1.306(5)	N(3)−C(6)	1.293(6)
N(4)−C(7)	1.301(5)	N(5)−C(9)	1.338(5)
N(5)−C(13)	1.355(5)	C(1)−C(2)	1.492(6)
C(2)−C(3)	1.461(6)	C(3)−C(4)	1.499(6)
C(5)−C(6)	1.489(6)	C(6)−C(7)	1.473(6)
C(7)−C(8)	1.483(6)	C(9)−C(10)	1.374(6)
C(10)−C(11)	1.382(6)	C(11)−C(12)	1.377(6)
C(12)−C(13)	1.380(6)	C(14)−C(15)	1.336(6)
C(14)−C(19)	1.498(6)	C(15)−C(16)	1.480(6)
C(17)−C(18)	1.497(7)	Cl(1)−C(102)	1.758(8)
Cl(2)−C(101)	1.789(8)	C(102)−C(101)	1.378(9)
N(1)−Co(1)−N(2)	81.4(2)	N(1)−Co(1)−N(3)	98.9(2)
N(2)−Co(1)−N(3)	179.4(2)	N(1)−Co(1)−N(4)	178.8(2)
N(2)−Co(1)−N(4)	98.4(2)	N(3)−Co(1)−N(4)	81.3(2)
N(1)−Co(1)−C(14)	90.4(2)	N(2)−Co(1)−C(14)	89.9(2)
N(3)−Co(1)−C(14)	89.5(2)	N(4)−Co(1)−C(14)	90.9(2)
N(1)−Co(1)−N(5)	90.1(2)	N(2)−Co(1)−N(5)	90.75(14)
N(3)−Co(1)−N(5)	89.79(14)	N(4)−Co(1)−N(5)	88.74(14)
C(14)−Co(1)−N(5)	179.2(2)	C(16)−O(6)−C(17)	116.0(4)
C(2)−N(1)−O(1)	120.1(4)	C(2)−N(1)−Co(1)	117.0(3)
O(1)−N(1)−Co(1)	122.8(3)	C(3)−N(2)−O(2)	120.7(3)
C(3)−N(2)−Co(1)	116.6(3)	O(2)−N(2)−Co(1)	122.7(3)
C(6)−N(3)−O(3)	120.8(4)	C(6)−N(3)−Co(1)	116.6(3)
O(3)−N(3)−Co(1)	122.5(3)	C(7)−N(4)−O(4)	119.4(4)
C(7)−N(4)−Co(1)	117.2(3)	O(4)−N(4)−Co(1)	123.4(3)
C(9)−N(5)−C(13)	117.4(4)	C(9)−N(5)−Co(1)	121.6(3)
C(13)−N(5)−Co(1)	121.0(3)	N(1)−C(2)−C(3)	112.4(4)
N(1)−C(2)−C(1)	124.0(4)	C(3)−C(2)−C(1)	123.6(4)
N(2)−C(3)−C(2)	112.5(4)	N(2)−C(3)−C(4)	122.9(4)
C(2)−C(3)−C(4)	124.7(4)	N(3)−C(6)−C(7)	113.2(4)
N(3)−C(6)−C(5)	122.7(4)	C(7)−C(6)−C(5)	124.2(4)
N(4)−C(7)−C(6)	111.6(4)	N(4)−C(7)−C(8)	123.2(4)
C(6)−C(7)−C(8)	125.1(4)	N(5)−C(9)−C(10)	123.3(4)
C(9)−C(10)−C(11)	119.1(4)	C(12)−C(11)−C(10)	118.3(4)
C(11)−C(12)−C(13)	119.8(4)	N(5)−C(13)−C(12)	122.1(4)
C(15)−C(14)−C(19)	123.6(4)	C(15)−C(14)−Co(1)	118.3(3)
C(19)−C(14)−Co(1)	118.1(3)	C(14)−C(15)−C(16)	126.7(4)
O(5)−C(16)−O(6)	122.3(4)	O(5)−C(16)−C(15)	129.4(5)
O(6)−C(16)−C(15)	108.3(4)	O(6)−C(17)−C(18)	106.0(4)
C(101)−C(102)−C1(1)	112.2(6)	C(102)−C(101)−Cl(2)	113.3(6)

(13) (a) Pasto, D. J.; Timmers, D. A. *Inorg. Chem.* **1984**, *23*, 4115. (b) Pasto, D. J.; Timmers, D. A.; Huang, N.-Z. *Inorg. Chem.* **1984**, *23*, 4117.

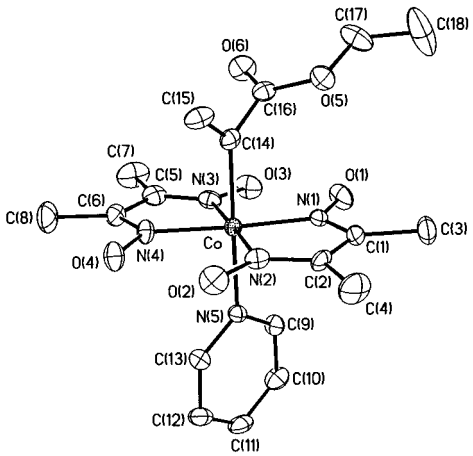


Figure 2. Molecular structure of complex **22b**.

Table 4. Crystal Data and Structure Refinement for 22b

identification code	welw
empirical formula	$C_{18}H_{26}CoN_5O_6$
formula weight	467.37
temperature	249(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	$P2_1$
unit cell dimensions	$a = 7.811(2)$ Å, $\alpha = 90°$ $b = 15.857(3)$ Å, $\beta = 90.04(1)°$ $c = 8.510(1)$ Å, $\gamma = 90°$
volume, Z	1054.0(4) Å^3, 2
density (calcd)	1.473 Mg/m^3
absorption coefficient	0.859 mm^{-1}
$F(000)$	488
crystal size	0.40 mm × 0.20 × 0.08 mm
crystal color	orange blade
θ range for data collection	2.39−25.00°
limiting indices	$-1 \le h \le 9$, $-1 \le k \le 18$, $-10 \le l \le 10$
reflections collected	2570
independent reflections	2084 ($R_{int} = 0.0315$)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2084/1/271
goodness-of-fit on F^2	1.106
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0396$, w$R^2 = 0.0871$
R indices (all data)	$R_1 = 0.0481$, w$R_2 = 0.0891$
absolute structure parameter	0.02(2)
largest diff peak and hole	0.413 and −0.283 e Å^{-3}

Again, 3-butyn-2-one (**19a**) (Table 1, entry 11) produced a product or product mixture that was too water soluble to be extracted with a variety of organic solvents. Ethyl propiolate (**19b**) (Table 1, entry 12) produced a new hydrometalation regioisomer (**22b**), which has been characterized by X-ray crystallography. The ORTEP drawing of this complex is provided in Figure 2, and the data collection and refinement parameters as well as selected bond lengths and angles are provided in Tables 4 and 5. The cobalt−sp^2 carbon (C(14)) bond length in this complex (1.977(6) Å) is within the range of cobalt−sp^2 carbon bond lengths we have observed previously in related dienyl complexes (1.954(15)−2.019(6) Å).[1b,c] The dihedral (torsion) angles in the α,β-unsaturated acyl portion of the molecule are the closest we have observed yet to what would be expected for a completely unconjugated system (90°) (C(15)−C(14)−C(16)−O(6), 94.6°; C(15)−C(14)−C(16)−O(5), 87.0°), and this geometry is presumably due to unfavorable glyoxime ligand/ethoxy substituent steric interactions.

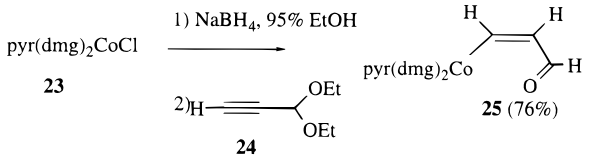
The phenyl-substituted alkynes **19c**,**e** (Table 2, entries 13 and 15) yielded hydrometalation products **20c**,**e** in low yields (16 and 28%, respectively) using method C, whereas ethyl 2-butynoate (Table 2, entry 14) produced the expected Michael addition product (**21d**) in 42% yield. Where does **22b** come from in this protocol? Complex **22b** apparently does not arise from a base-catalyzed isomerization of **21b**, since use of method C with ynoate **19b** without acetic acid acidification produced **21b**, not **22b**, in 43% isolated yield. Complex **22b** also does not appear to arise from a hydride- or acid-mediated isomerization of **21b** either, since subjecting **21b** to method C conditions without base (treatment with $NaBH_4$ followed by acetic acid at −20 °C and then warming to 25 °C overnight) resulted in recovery of **21b** intact in high mass balance (95%). We know from our prior dienyl work that these types of addition reactions are reversible.[1d,e] Perhaps under these method C conditions, the ortho ester of **19b** is slowly formed and hydrometalated as expected for a simple alkyne to produce **22b** following the aqueous workup.[7] Likewise, **21d** does not appear to arise from an isomerization of initially formed **20d**, since subjecting **20d** to $NaBH_4$ and NaOH sequentially followed by acetic acid in 95% EtOH over 3 h produced no **21d**, and **20d** was also recovered in high mass balance (90%). At this slightly acidic pH used in method C, where a significant amount of hydride **11** as well as anion **10** is present, we think that the amount of Michael addition decreases for the more hindered phenyl-substituted alkynes (**19c**,**e**), since there

Table 5. Bond Lengths (Å) and Angles (deg) for 22b

Co−N(3)	1.877(5)	Co−N(1)	1.882(4)
Co−N(4)	1.886(4)	Co−N(2)	1.891(5)
Co−C(14)	1.977(6)	Co−N(5)	2.047(4)
O(1)−N(1)	1.340(6)	O(2)−N(2)	1.314(6)
O(3)−N(3)	1.350(6)	O(4)−N(4)	1.355(6)
O(5)−C(16)	1.347(7)	O(5)−C(17)	1.445(8)
O(6)−C(16)	1.207(7)	N(1)−C(1)	1.294(7)
N(2)−C(2)	1.319(7)	N(3)−C(5)	1.296(8)
N(4)−C(6)	1.274(7)	N(5)−C(13)	1.337(7)
N(5)−C(9)	1.346(7)	C(1)−C(2)	1.464(9)
C(1)−C(3)	1.500(8)	C(2)−C(4)	1.490(9)
C(5)−C(6)	1.452(9)	C(5)−C(7)	1.491(9)
C(6)−C(8)	1.500(8)	C(9)−C(10)	1.361(9)
C(10)−C(11)	1.382(9)	C(11)−C(12)	1.375(9)
C(12)−C(13)	1.387(8)	C(14)−C(15)	1.293(9)
C(14)−C(16)	1.523(9)	C(17)−C(18)	1.444(11)
N(3)−Co−N(1)	98.8(2)	N(3)−Co−N(4)	80.6(2)
N(1)−Co−N(4)	177.0(3)	N(3)−Co−N(2)	178.6(2)
N(1)−Co−N(2)	82.6(2)	N(4)−Co−N(2)	98.1(2)
N(3)−Co−C(14)	90.1(2)	N(1)−Co−C(14)	88.3(2)
N(4)−Co−C(14)	88.7(3)	N(2)−Co−C(14)	90.2(2)
N(3)−Co−N(5)	89.3(2)	N(1)−Co−N(5)	90.9(2)
N(4)−Co−N(5)	92.1(2)	N(2)−Co−N(5)	90.4(2)
C(14)−Co−N(5)	178.9(3)	C(16)−O(5)−C(17)	116.1(5)
C(1)−N(1)−O(1)	121.1(5)	C(1)−N(1)−Co	116.0(4)
O(1)−N(1)−Co	122.8(4)	O(2)−N(2)−C(2)	121.1(5)
O(2)−N(2)−Co	123.7(4)	C(2)−N(2)−Co	115.2(4)
C(5)−N(3)−O(3)	119.9(5)	C(5)−N(3)−Co	117.3(4)
O(3)−N(3)−Co	122.8(4)	C(6)−N(4)−O(4)	120.7(4)
C(6)−N(4)−Co	117.1(4)	O(4)−N(4)−Co	122.1(3)
C(13)−N(5)−C(9)	117.1(5)	C(13)−N(5)−Co	121.2(4)
C(9)−N(5)−Co	121.6(4)	N(1)−C(1)−C(2)	113.5(5)
N(1)−C(1)−C(3)	122.9(6)	C(2)−C(1)−C(3)	123.6(6)
N(2)−C(2)−C(1)	112.7(5)	N(2)−C(2)−C(4)	122.5(6)
C(1)−C(2)−C(4)	124.8(6)	N(3)−C(5)−C(6)	111.8(5)
N(3)−C(5)−C(7)	123.6(7)	C(6)−C(5)−C(7)	124.7(6)
N(4)−C(6)−C(5)	113.2(5)	N(4)−C(6)−C(8)	122.7(6)
C(5)−C(6)−C(8)	124.1(5)	N(5)−C(9)−C(10)	123.1(6)
C(9)−C(10)−C(11)	119.2(6)	C(12)−C(11)−C(10)	119.1(6)
C(11)−C(12)−C(13)	118.0(6)	N(5)−C(13)−C(12)	123.4(6)
C(15)−C(14)−C(16)	118.0(7)	C(15)−C(14)−Co	125.1(6)
C(16)−C(14)−Co	116.9(4)	O(6)−C(16)−O(5)	122.2(6)
O(6)−C(16)−C(14)	125.1(6)	O(5)−C(16)−C(14)	112.7(5)
C(18)−C(17)−O(5)	110.9(7)		

is more hydride present (compared to method B) to compete (via hydrometalation) for these substrates.

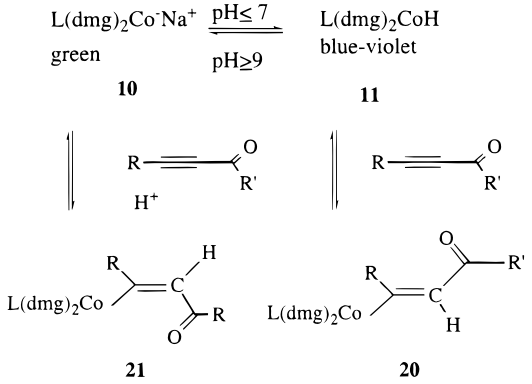
In chemistry somewhat related to that described above, we also found that propionaldehyde diethyl acetal (**24**) could also be hydrometalated and the acetal hydrolyzed to the aldehyde **25** in excellent yield by treatment with cobaloxime anion/hydride in 95% EtOH using the short reaction times of method B. We suspect,



based on the stereochemistry and regiochemistry of the product (**25**) isolated, that acetal hydrolysis has occurred prior to hydrocobaltation of the alkyne. When this reaction was attempted using method A in DMF, a 1:1.5 mixture of **25** and its *E* alkene isomer were isolated in very low yield (8%), demonstrating again that method A is a poor choice for terminal alkynes. Likewise, when **24** was treated with cobaloxime using method C, a 2:1 mixture of **25** and its *E* alkene isomer was isolated in 28% yield, which again demonstrates that minimizing exposure of these acyl complexes to the reaction conditions in polar protic solvents (method B) is highly desirable.

Summary and Conclusions

In summary, we have identified methods for producing either stereoisomer of a variety of β-cobaloxime-substituted α,β-unsaturated acyl complexes. Under conditions where the dominant cobaloxime species is hydride **11** (method A), we isolate *E* alkenes **20** for all internal alkynes surveyed. Under conditions where the cobaloxime anion **10** is the major cobaloxime species present (method B) and the cobalt product is prepared and removed rapidly from the polar protic solvent, we isolate *Z* alkenes **21** regardless of alkyne substitution pattern. Treatment of ynones and ynoates containing terminal alkynes with cobaloxime in a polar protic solvent over an extended period of time where both



cobalt hydrides (**11**) and cobaloxime anions (**10**) are present leads to α− and β-cobalt-substituted α,β-unsaturated acyl complexes, so this classical method of cobaloxime generation should be avoided with these substrates. *In general, exposure of cobaloxime acyls to polar protic solvents and anion or hydride producing conditions for extended periods of time is to be avoided regardless of alkyne substrate used.* We will report the use of these acyls and other dienyl complexes in hetero Diels−Alder reactions in due course.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters for **20d** and **22b** (6 pages). Ordering information is given on any current masthead page.

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