ELSEVIER

Journal of Organometallic Chemistry 656 (2002) 217–227

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reactions of cobaloxime η^1-allyl complexes with electron deficient alkenes

Dean R. Lantero, Mark E. Welker *

Department of Chemistry, Wake Forest University, P.O. Box 7486, Winston-Salem, NC 27109, USA

Received 1 April 2002; received in revised form 20 May 2002; accepted 20 May 2002

Abstract

The preparation of several new η^1-allyl (dimethylglyoxime)$_2$ cobalt complexes (**7**–**12**) containing varied axial pyridine ligands is reported. These complexes are synthesized via three different methods: (1) in situ generation and allylation of [L(dmg)$_2$Co]$_2$ dimers (where L = various pyridines); (2) generation and allylation of L(dmg)$_2$Co anions; and (3) an apparent 1,4-hydrocobaltation of 1,3-dienes. Tetracyanoethylene addition to cobaloxime allyl complexes (**5**–**12**) yielded cyclized complexes (**17**–**23**) and insertion products (**24**–**27**). Yields of the cyclized and uncyclized complexes are influenced by the electronics of the axial pyridine ligand with the more electron withdrawing pyridine ligands favoring the formation of more cyclized product. Treatment of cobaloxime allyl complexes (**8**–**10**) with benzoquinone yielded rearranged cobaloxime allyl complexes (**30** and **31**) along with *para*-allyloxysubstituted phenols (**32**–**34**). The substituted phenols presumably arise from a Michael addition of the allyl fragment onto benzoquinone followed by a retro Claisen reaction.

Keywords: Cobaloxime η^1-allyl complexes; Electron deficient alkenes; Pyridine ligands

1. Introduction

Cobaloxime η^1-allyl complexes (such as **1**) (Cobaloxime = pyridine(dimethylglyoxime)$_2$Co) were first prepared in the early 1970s [1] and their reactions with tetracyanoethylene (TCNE) and sulfur dioxide were reported shortly thereafter [2]. The reactions of allyl cobaloximes with TCNE were reported to give 'a variety of products of different colors' from which 3+2 cycloaddition products could, in most cases, only be isolated in moderate yields. A two step cycloaddition mechanism involving a cationic cobaloxime alkene complex (**3**) as an intermediate was proposed based on the observation that the *trans* cinnamyl complex led to *trans* disubstituted cyclopentyl products [2a]. Conversely, reactions of cobaloxime allyls with SO_2 were reported to give only SO_2 insertion products and no 3+2 cycloaddition products [2b]. Branchaud [3] and Pattenden [4] then subsequently showed that the η^2-alkene cobaloxime complexes, proposed as intermediates in the allyl complex–SO_2 reactions and the allyl complex–TCNE cycloadditions, were unusual in structure and reactivity compared to many other alkenyl complexes. The cobaloxime alkenyl complexes contain alkenes which are invariably unsymmetrically bound and nucleophiles add to these cationic alkene complexes at the most substituted carbon. Most recently, Brown et al. have studied the thermal decomposition of allyl cobaloximes and find that the allyl and dimethyl glyoxime fragments react to produce pyridines [5]. We have had some success modulating Diels–Alder cycloaddition chemistry of cobaloxime dienyl complexes by changing the axial ligand *trans* to the dienyl component [6]. Here, we report a systematic study of the reactions of cobaloxime allyls with alkenyl electrophiles where the electron donating abilities of the ligands axial to the allyl fragment and the constitution of the allyl fragment have been systematically varied.

* Corresponding author. Tel.: +1-336-7585325/6139; fax: +1-336-7584321

E-mail address: welker@wfu.edu (M.E. Welker).

0022-328X/02/$ - see front matter
PII: S0022-328X(02)01596-6

2. Experimental

2.1. General

All reactions were performed under an atmosphere of N_2 or Ar unless specified otherwise. Chloro(pyridine)bis(dimethyglyoxime)cobalt(III) was synthesized according to the literature [7]. Chloro(4-dimethylaminopyridine)bis(dimethylglyoxime)cobalt(III) and chloro(4-^{t}butylpyridine)bis(dimethylglyoxime)cobalt(III) were synthesized via a procedure analogous to [7] using the appropriate pyridine ligand. (Pyridine)cobaloxime(2-butene) (**6**) (obtained in a 25:75 ratio of *cis–trans* isomers) and (pyridine)cobaloxime(allyl) (**5**) were prepared according to the literature method [8]. Compounds **17** and **18** had been characterized previously [2b]. TCNE (Aldrich) and benzoquinone (Fisher) were sublimed prior to use. Allyl bromide, 4-dimethylaminopyridine (DMAP), isoprene, 2-bromopropene, pyridine, 4-bromo-2-methyl-2-butene, potassium *tert*-butoxide (1.0 M in THF), sodium borohydride, sodium borodeuteride and AcOH-d_1 were purchased from Aldrich and used without further purification. Crotyl bromide was purchased from Fluka and used without further purification. Dimethylglyoxime (dmg) was purchased from Fisher Scientific and recrystallized from 95% EtOH prior to use. Cobalt chloride hexahydrate (Strem) was used as received.

^{1}H-NMR spectra were recorded on a Bruker Avance 300 DPX or Bruker Avance 500 DRX operating at 300.1 and 500.1 MHz, respectively, and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 DPX operating at 75.5 MHz or Bruker Avance 500 DRX operating at 125.5 MHz. ^{1}H-NMR spectra were referenced to the residual proton solvent signal and ^{13}C-NMR spectra were referenced to the ^{13}C-NMR resonance of the deuterated solvent. ^{2}H-NMR spectra were recorded on a Bruker Avance 500 DRX operating at 76.8 MHz and referenced to the residual deuterium signal of the protonated solvent. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. High resolution mass spectra (HRMS) were obtained at the mass spectrometry facility at Duke University, Durham, NC. M.p.s were determined on a Mel-Temp apparatus and are reported uncorrected.

2.2. Experimental procedures for the preparation of cobaloxime allyl complexes

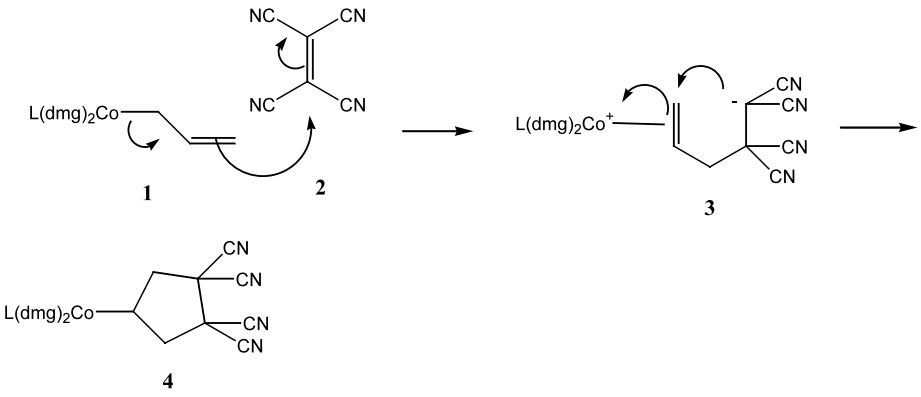
2.2.1. Pyridine(3-methyl-2-butene)bis(dimethylglyoxime)cobalt(III) (7)

2.2.1.1. Method 2. This compound was synthesized in a fashion similar to that found in the literature [8]. A slurry of $Cl(C_5H_5N)(dmg)_2Co$ (526 mg, 1.31 mmol) in MeOH (20 ml) was degassed. A NaOH solution (180 mg, 4.48 mmol in H_2O (1 ml)) was added causing the cobalt complex to dissolve and turning the reaction deep orange. After degassing, the solution was cooled to 0 °C. A $NaBH_4$ solution (90 mg, 2.38 mmol in H_2O (1 ml)) was then added turning the solution to deep blue. A MeOH solution (5 ml) of 4-bromo-2-methyl-2-butene (583 mg, 3.92 mmol) was added dropwise over 5 min. The reaction vessel was wrapped in Al foil and allowed to warm to room temperature (r.t.). After 3 h, a deep orange solid had precipitated from the red orange solution. Water (20 ml cooled to 0 °C) was added and the resulting slurry was further cooled in an ice H_2O bath and filtered. The collected orange solid was rinsed with ice H_2O and vacuum dried yielding **7** (295 mg, 0.68 mmol, 52%). M.p: 146–148 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.53 (d, $J = 4.9$ Hz, 2H), 7.66 (t, $J = 7.6$ Hz, 1H), 7.26 (m, 2H), 4.98 (t, $J = 9.4$ Hz, 1H), 2.41 (d, $J = 9.4$ Hz, 2H), 2.08 (s, 12H), 1.22 (s, 3H), 1.12 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 150.0, 149.0, 137.2, 131.4, 130.5, 125.1, 27.3, 18.2, 11.8. Anal. Calc. for $C_{18}H_{28}CoN_5O_4$: C, 49.44; H, 6.41; N, 16.02. Found: C, 49.30; H, 6.45; N, 15.86%.

2.2.1.2. Method 1. Cobalt (II) chloride hexahydrate (2.380 g, 10.00 mmol) was dissolved in a two-neck round bottom flask containing degassed MeOH (50 ml). DMG (2.320 g, 20.00 mmol) was added turning the solution pink. Sodium hydroxide (NaOH) (0.800 g in H_2O (5 ml)) was added followed by pyridine (0.790 g, 10.00 mmol). The deep orange solution was stirred at r.t. for 1 h. Another NaOH solution (0.800 g in H_2O (5 ml)) was added followed immediately by 4-bromo-2-methyl-2-butene (1.490 g, 10.00 mmol). The mixture was again stirred at r.t. for 1 h after which H_2O (40 ml) was added. The solution was then cooled in a ice–H_2O bath for 1 h prompting an orange solid to precipitate from solution. The solid was collected by filtration and washed with small quantities of cold H_2O until the filtrates were colorless. The collected solid was vacuum dried overnight yielding **7** (1.632 g, 3.70 mmol, 37%).

2.2.2. 4-Dimethylaminopyridine(allyl)bis-(dimethylglyoxime)cobalt(III) (8)

Cobalt(II) chloride hexahydrate (476 mg, 2.00 mmol) was dissolved in degassed MeOH (20 ml). DMG (464 mg, 4.00 mmol) was then added turning the solution pink. NaOH (160 mg), dissolved in H_2O (1 ml), was added turning the solution orange and then 4-dimethylaminopyridine (DMAP) (246 mg, 2.02 mmol) was added as a solid immediately thereafter. The reaction was stirred for 1 h at r.t. during which time dark rust–orange microcrystals were deposited. A NaOH solution (160 mg in H_2O (1 ml)) was then added followed immediately by allyl bromide (242 mg, 2.00 mmol). The reaction was stirred at r.t. covered in Al foil for another 1.5 h. The volatiles were removed by rotary



evaporation and H_2O (20 ml) was added to the orange solid. The reaction was vacuum filtered and the collected orange solid was washed with H_2O until the filtrates were colorless. The orange solid was dried on a vacuum pump yielding **8** (444 mg, 0.98 mmol, 49%). M.p: 187–190 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.01 (d, $J = 7.1$ Hz, 2H), 6.38 (d, $J = 7.1$ Hz, 2H), 5.65 (m, 1H), 4.87 (dd, $J = 9.8$ Hz, 2.8 Hz, 1H), 4.80 (dd, $J = 16.8$, 2.5 Hz, 1H), 2.95 (s, 6H), 2.17 (d, $J = 8.8$ Hz, 2H), 2.13 (s, 12H). ^{13}C-NMR ($C_6D_6^*$): δ 154.2, 149.6, 148.4, 146.2, 109.8, 107.6, 37.9, 12.1. *Prolonged exposure to chlorinated solvent resulted in gradual decomposition. Anal. Calc. for $C_{18}H_{29}CoN_6O_4$: C, 47.80; H, 6.42; N, 18.59. Found: C, 47.06; H, 6.18; N, 18.83%.

2.2.3. 4-Dimethylaminopyridine(E and Z-2-butene)bis(dimethylglyoxime)cobalt(III) (9)

This compound was synthesized in a similar fashion as that found in the literature [8]. To a degassed MeOH solution (50 ml) of cobalt(II) chloride hexahydrate (2.380 g, 10.00 mmol) was added dmg (2.320 g, 20.00 mmol). NaOH (0.800 g in H_2O (5 ml)) was added turning the pink solution to orange, then DMAP was added (1.230 g, 10.00 mmol). The mixture was stirred for 30 min at r.t. during which time dark rust–orange microcrystals were deposited. Crotyl bromide (1.350 g, 10.00 mmol) was added followed by NaOH (800 mg in H_2O (5 ml)). The solution was stirred at r.t. for another 1.5 h while covered with Al foil. An orange solid precipitated from solution. Water (50 ml) was added and the solution was stirred for an additional 20 min then vacuum filtered. The collected solid was washed with H_2O until the filtrates were colorless. The orange solid was vacuum dried overnight yielding **9** (2.104 g, 4.50 mmol, 45%). Two isomers were synthesized in a 71:29 ratio based on ^{1}H-NMR spectral integration. M.p. (combined isomeric mixture): 142–145 °C (dec). ^{1}H-NMR (major isomer) ($CDCl_3$): δ 8.01 (d, $J = 7.0$ Hz, 2H), 6.38 (d, $J = 7.0$ Hz, 2H), 5.26 (m, 2H), 2.93 (s, 6H), 2.17 (d, $J = 7.6$ Hz, 2H), 2.10 (s, 12H), 1.17 (d, $J = 5.6$ Hz, 3H). ^{1}H-NMR (minor isomer) ($CDCl_3$): δ 8.07 (d, $J = 6.3$ Hz, 2H), 6.27 (d, $J = 6.9$ Hz, 2H), 5.54 (m, 1H), 5.26 (m, 1H), 2.93 (s, 6H), 2.28 (d, $J = 9.6$ Hz, 2H), 2.10 (s, 12H), 1.12 (dd, $J = 7.0$, 1.2 Hz, 3H). ^{13}C-NMR (combined isomeric mixture) ($CDCl_3$): δ 154.2, 149.1, 149.0, 148.6, 148.4, 137.9, 137.0, 121.5, 120.8, 107.5, 39.0, 19.0, 13.0, 12.0, 11.9. Anal. Calc. for $C_{19}H_{31}CoN_6O_4$: C, 48.94; H, 6.65; N, 18.03. Found: C, 48.77; H, 6.63; N, 18.18%.

2.2.4. 4-Dimethylaminopyridine(3-methyl-2-butene)bis(dimethylglyoxime)cobalt(III) (10)

Chloro(DMAP)bis(dmg)cobalt (III) (1.458 g, 3.27 mmol) was dissolved in a basic EtOH solution (450 mg NaOH dissolved in 95% EtOH (50 ml)) and degassed. The reaction mixture was cooled in an ethylene glycol–dry ice bath after which $NaBH_4$ (225 mg, 5.91 mmol) was added. After 1 h, AcOH was added dropwise until the pH 7 at which point the color had turned to a deep blue–green. Isoprene (444 mg, 6.53 mmol) was added and the solution was allowed to warm to 25 °C. After 2 h, a rust orange solid appeared and after 4 h, the reaction was poured into ice H_2O (60 ml) and filtered. The deep orange solid was washed several times with 5 ml quantities of H_2O and vacuum dried yielding **10** (1.187 g, 2.47 mmol, 76%). M.p: 174–177 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.02 (d, $J = 6.9$ Hz, 2H), 6.38 (d, $J = 6.8$ Hz, 2H), 4.96 (t, $J = 9.5$ Hz, 1H), 2.94 (s, 6H), 2.29 (d, $J = 9.4$ Hz, 2H), 2.07 (s, 12H), 1.24 (s, 3H), 1.13 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 154.2, 149.0, 148.4, 131.4, 129.5, 107.5, 39.0, 27.2, 18.0, 11.7. Anal. Calc. for $C_{20}H_{33}CoN_6O_4$: C, 50.01; H, 6.88; N, 17.50. Found: C, 50.19; H, 6.85; N, 17.56%.

2.2.5. Deuterium labeling experiment. Preparation of deuterated complex 10

Sodium hydroxide (308 mg, 7.67 mmol) was dissolved in EtOD (25 ml). Chloro(DMAP)cobaloxime (1.000 g, 2.24 mmol) was added to the basic solution which was then cooled in a dry ice–ethylene glycol bath. Sodium

borodeuteride (170 mg, 4.05 mmol), dissolved in D_2O (1.5 ml), was added to the cold reaction. The solution was stirred for 1 h during which time the reaction turned to a dark color. Acetic acid-d_1 was added until the pH 7 and the color of the reaction turned to a deep red. Isoprene (305 mg, 4.48 mmol) was added and the reaction was allowed to warm to 25 °C. The reaction was stirred for 4 h and then H_2O (30 ml) was added. The mixture was cooled in an ice–H_2O bath for 20 min. A light orange solid was collected by filtration and washed several times with H_2O until the filtrates were colorless. The solid was then vacuum dried overnight yielding monodeuterated **10** (863 mg, 1.79 mmol, 80%) based on incorporation of 1 D. According to ^{1}H-NMR spectral analysis, deuterium incorporation was 71% of theoretical. ^{1}H-NMR ($CDCl_3$): δ 7.99 (d, $J = 7.0$ Hz, 2H), 6.36 (d, $J = 7.0$ Hz, 2H), 4.94 (t, $J = 9.4$ Hz, 1H), 2.92 (s, 6H), 2.26 (d, $J = 9.4$ Hz, 2H), 2.05 (s, 12H), isomer 1 [1.21 (s, CH_3), 1.08 (s, CH_2D)], isomer 2 [1.19 (s, CH_2D), 1.11 (s, CH_3)]. Total integral for these CH_3 and CH_2D resonances is 5H. ^{13}C-NMR ($CDCl_3$): δ 154.1, 148.9, 148.4, 131.3, 129.4, 107.4, 39.0, 27.21, 27.18, 26.9 (t, $J_{CD} = 19.2$ Hz, CH_2D (APT)), 25.8, 18.0, 17.7 (t, $J_{CD} = 19.3$ Hz, CH_2D (APT)), 11.6. ^{2}H{^{1}H}-NMR ($CHCl_3$): δ 1.24, 1.14. HRFABMS: *m/z* Calc. for $C_{25}H_{32}CoDN_6O_4$ [M^+]: 480.1895. Found: 480.1876.

2.2.6. 4-Cyanopyridine(*E* and *Z*-2-butene)bis(dimethylglyoxime)cobalt(III) (**11**)

Cobalt(II) chloride hexahydrate (952 mg, 4.00 mmol) was dissolved in degassed MeOH (40 ml). DMG (928 mg, 8.00 mmol) was added turning the solution pink. A NaOH solution (320 mg dissolved in H_2O (2 ml)) was added followed by 4-cyanopyridine (420 mg, 4.04 mmol). The deep orange solution was stirred at r.t. for 1 h and then another NaOH solution (320 mg dissolved in H_2O (2 ml)) was added. Crotyl bromide (540 mg, 4.00 mmol) was added and the resulting deep orange solution was stirred at r.t. for another hour. The volume of the reaction was cut in half by rotary evaporation and then H_2O (35 ml) was added. The resulting solution was stirred and cooled in an ice–H_2O bath for 30 min. A deep orange precipitate was collected by filtration. The micro crystals were washed with small portions (10 ml) of H_2O until the filtrates were colorless. The solid was vacuum dried overnight yielding **11** (in a *E*–*Z* ratio of 71:29) (540 mg, 1.20 mmol, 30%). M.p. (combined isomeric mixture): 126–128 °C (dec). ^{1}H-NMR (major isomer) ($CDCl_3$): δ 8.82 (d, $J = 6.4$ Hz, 2H), 7.56 (d, $J = 6.4$ Hz, 2H), 5.44 (m, 1H), 5.27 (m, 1H), 2.42 (d, $J = 8.7$ Hz, 2H), 2.14 (s, 12H), 1.18 (d, $J = 6.5$ Hz, 3H). ^{1}H-NMR (minor isomer) ($CDCl_3$): δ 8.82 (buried, 2H), 7.56 (buried, 2H), 5.71 (m, 1H), 5.27 (m, 1H), 2.53 (d, $J = 9.5$ Hz, 2H), 2.14 (buried, 12H), 1.13 (d, $J = 6.1$ Hz, 3H). ^{13}C-NMR (combined isomeric mixture) ($CDCl_3$): δ 151.4, 151.2, 149.8, 149.6, 137.5, 136.5, 126.9, 123.4, 122.6, 121.9, 115.5, 19.2, 12.3, 12.1. Anal. Calc. for $C_{18}H_{28}CoN_5O_4$: C, 48.22; H, 5.58; N, 18.75. Found: C, 47.59; H, 5.58; N, 18.59%.

2.2.7. 4-^{t}Butylpyridine(3-methyl-2-butene)bis(dimethylglyoxime)cobalt(III) (**12**)

Chloro(4-^{t}butylpyridine)bis(dmg)cobalt(III) (1.502 g, 3.27 mmol) was dissolved in basic EtOH (450 mg NaOH in 95% EtOH (50 ml)) and cooled in an ethylene glycol–dry ice bath. $NaBH_4$ (225 mg, 5.91 mmol) was added and after 1 h, AcOH was added until the pH 7 turning the color to a deep blue. Isoprene (444 mg, 6.53 mmol) was added and the reaction was allowed to warm to r.t. After 4 h, a bright orange solid had precipitated. Ice H_2O (60 ml) was then added and the reaction filtered. The orange solid was washed with 5 ml portions of ice H_2O until the filtrates were colorless and then vacuum dried yielding **12** (976 mg, 1.98 mmol, 61%). M.p.: 135–137 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.36 (d, $J = 6.6$ Hz, 2H), 7.21 (d, $J = 6.6$ Hz, 2H), 4.97 (t, $J = 9.4$ Hz, 1H), 2.37 (d, $J = 9.4$ Hz, 2H), 2.08 (s, 12H), 1.23 (s, 9H), 1.23 (s, 3H), 1.13 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 161.5, 149.5, 148.8, 131.4, 130.2, 122.3, 34.8, 30.2, 27.3, 18.1, 11.8. Anal. Calc. for $C_{22}H_{36}CoN_5O_4$: C, 53.56; H, 7.30; N, 14.20. Found: C, 53.50; H, 7.47; N, 14.21%.

2.3. Reactions of cobaloxime allyl complexes with carbon electrophiles

2.3.1. Reaction of (pyridine)cobaloxime(2-butene) (**6**) + tetracyanoethylene to produce (**18** and **24**)

Pyridine(2-butene)cobaloxime (**6**) (200 mg, 0.47 mmol) was dissolved in distilled, degassed CH_2Cl_2 (25 ml). The flask was covered with Al foil and then TCNE (120 mg, 0.95 mmol) was added as a solid under a flow of nitrogen. The mixture was stirred at r.t. for 2 h and then the volatiles were removed by blowing air over the solution. The dark residue was dissolved in EtOAc and chromatographed on a silica gel column using EtOAc as the eluent. The EtOAc from the early fraction was removed by reduced pressure yielding (146 mg, 0.26 mmol, 56%) of a yellow–orange solid **18**. Removal of the EtOAc from the later fraction by reduced pressure yielded (46 mg, 0.084 mmol, 18%) of a red solid **24**. Analytical data for **18**: M.p.: 184–186 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.43 (d, $J = 5.1$ Hz, 2H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.32 (apparent t, $J = 7.0$ Hz, 2H), 2.57 (dd, $J = 15.0$ Hz, 8.5 Hz, 1H), 2.20 (s, 6H), 2.19 (s, 6H), 2.10 (m, 2H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.33 (buried, 1H). ^{13}C-NMR ($CDCl_3$): δ 151.8, 151.7, 149.7, 138.3, 125.6, 112.1, 111.7, 111.3, 110.2, 51.0, 49.0, 44.3, 41.9, 19.2, 12.7. Analytical data for **24**: M.p.: 124–127 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.22 (d, $J = 5.4$ Hz, 2H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.27 (apparent t, $J = 6.8$ Hz, 2H), 5.76 (m, 1H), 5.34 (d, $J = 13.1$ Hz, 1H), 5.31 (d, $J = 6.4$ Hz, 1H), 2.64 (m, 1H), 2.38 (s, 12H), 1.26 (d, $J = 6.7$ Hz,

3H). ^{13}C-NMR ($CDCl_3$): δ 153.4, 151.0, 144.6, 139.4, 134.7, 126.0, 120.4, 119.1, 113.6, 113.2, 45.1, 15.4, 13.2. HRFABMS: *m/z* Calc. for $C_{23}H_{27}CoN_9O_4$ [M+H$^+$]: 552.1518. Found 552.1523.

2.3.2. Reaction of (pyridine)cobaloxime(3-methyl-2-butene) (7) +tetracyanoethylene to produce (19 and 25)

(Pyridine)(3-methyl-2-butene) cobaloxime (**7**) (206 mg, 0.472 mmol) was dissolved in distilled, degassed CH_2Cl_2 (25 ml). The flask was covered in Al foil and then TCNE (120 mg, 0.946 mmol) was added as a solid. The mixture was stirred at r.t. for 2 h and then the volatiles were removed by blowing air over the solution. The residue was dissolved in a 4:1 CH_2Cl_2–acetone solution and then chromatographed on silica gel using CH_2Cl_2–acetone as the eluent. The yellow fraction collected first yielded **19** (13 mg, 0.024 mmol, 5%), when the volatiles were removed by rotary evaporation. The red fraction collected second yielded **25** (103 mg, 0.11 mmol, 38%), when the volatiles were removed by reduced pressure. Analytical data for **19**: M.p.: 118–120 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.40 (d, $J=5.0$ Hz, 2H), 7.73 (t, $J=6.2$ Hz, 1H), 7.30 (apparent t, $J=$ 6.6 Hz, 2H), 2.95 (m, 1H), 2.30 (m, 1H), 2.19 (s, 6H), 2.18 (s, 6H), 1.45 (m, 1H), 1.42 (s, 3H), 0.99 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 152.24, 152.16, 149.3, 138.3, 125.6, 113.3, 113.2, 112.0, 110.2, 58.8, 55.1, 46.9, 39.1, 25.1, 18.5, 12.6, 12.5. HRFABMS: *m/z* Calc. for $C_{24}H_{28}CoN_9O_4$ [M$^+$]: 565.1596. Found: 565.1600%. Analytical data for **25**: M.p.: 104–106 °C (dec). ^{1}H =-NMR ($CDCl_3$): δ 8.19 (d, $J=5.4$ Hz, 2H), 7.74 (t, $J=$ 7.1 Hz, 1H), 7.27 (apparent t, $J=7.0$ Hz, 2H), 5.86 (dd, $J=17.2$ Hz, 10.7 Hz, 1H), 5.29 (d, $J=10.7$ Hz, 1H), 5.22 (d, $J=17.2$ Hz, 1H), 2.36 (s, 12H), 1.20 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ 153.7, 150.9, 142.0, 139.6, 139.4, 126.1, 117.7, 113.2, 47.3, 22.4, 13.2. HRFABMS: *m/z* Calc. for $C_{24}H_{29}CoN_9O_4$ [M+H$^+$]: 566.1674. Found: 566.1677.

2.3.3. Reaction of (DMAP)cobaloxime(allyl) (8) + tetracyanoethylene to produce (20)

(DMAP) cobaloxime(allyl) (**8**) (165 mg, 0.36 mmol) was added to a 100 ml two-neck round bottom flask and dissolved in distilled CH_2Cl_2 (25 ml). After degassing the orange solution, the flask was covered with Al foil and then 93 mg TCNE (0.73 mmol) was added as a solid. The mixture was stirred at r.t. for 2 h. The volatiles were removed from the golden solution by rotary evaporation. The resulting solid was dissolved in EtOAc and chromatographed on silica gel using EtOAc as the eluent. A golden yellow fraction was collected that yielded **20** (114 mg, 0.19 mmol, 54%) when the solvent was removed by reduced pressure. M.p.: 194–196 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 7.86 (d, $J=6.5$ Hz, 2H), 6.37 (d, $J=6.4$ Hz, 2H), 2.97 (s, 6H), 2.55 (dd, $J=14.6$, 8.6 Hz, 2H), 2.18 (s, 12H), 1.97 (m, 2H), 1.69 (m, 1H). ^{13}C-NMR ($CDCl_3$): Anal. Calc. for $C_{24}H_{29}CoN_{10}O_4$: C, 49.66; H, 5.00; N, 24.14. Found: C, 49.76; H, 5.11; N, 24.02%.

2.3.4. Reaction of (DMAP)cobaloxime(2-butene) (9) + tetracyanoethylene to produce (21 and 26)

2.3.4.1. Method A. DMAP(2-butene)bis(dmg)cobalt(III) (**9**) (110 mg, 0.24 mmol) and DMAP (29 mg, 0.24 mmol) were dissolved in distilled, degassed CH_2Cl_2 (5 ml) in a two-neck round bottom flask equipped with a dropping funnel. The resulting orange solution was cooled to −20 °C in an ethylene glycol–dry ice bath and covered with Al foil. Tetracyanoethylene (60 mg, 0.473 mmol) was dissolved in distilled, degassed CH_2Cl_2 (10 ml) and added dropwise over 5 min and once the addition was complete, the reaction was stirred for 1 h at −20 °C. The color gradually turned to yellow–orange during the reaction time. The volatiles were removed by rotary evaporation yielding a green–yellow solid. The solid was dissolved in 6:1 CH_2Cl_2–acetone and chromatographed on silica gel using the same solvent system. A yellow band was collected first yielding a yellow solid **21** (74 mg, 0.12 mmol, 53%) once the volatiles were removed by rotary evaporation. A ^{1}H-NMR spectrum confirmed the product to be **21** consisting of two isomers in a 90:10 ratio based on ^{1}H-NMR spectra integration. A second fraction was collected yielding a red solid **26** (14 mg, 0.024 mmol, 10%) upon solvent removal. Analytical data for **21**: M.p. (combined isomeric mixture): 164–167 °C (dec). ^{1}H-NMR (major isomer) ($CDCl_3$): δ 7.88 (d, $J=7.1$ Hz, 2H), 6.37 (d, $J=7.1$ Hz, 2H), 2.97 (s, 6H), 2.57 (dd, $J=14.9$, 8.4 Hz, 1H), 2.20 (s, 6H), 2.19 (s, 6H), 2.10 (m, 2H), 1.31 (d, $J=6.8$ Hz, 3H), 1.23 (m, 1H). ^{1}H-NMR (minor isomer) ($CDCl_3$): δ 7.85 (d, $J=7.2$ Hz, 2H), 6.37 (buried, 2H), 2.97 (buried, 6H), 2.83 (m, 1H), 2.76 (dd, $J=13.6$, 7.1 Hz, 1H), 2.19 (s, 6H), 2.16 (s, 6H), 2.10 (buried, 2H), 1.81 (m, 1H), 1.05 (d, $J=7.2$ Hz, 3H). ^{13}C-NMR (combined isomeric mixture) ($CDCl_3$): δ 154.4, 151.1, 151.0, 148.4, 112.2, 111.9, 111.5, 110.4, 107.7, 51.1, 49.2, 44.5, 42.1, 39.0, 19.3, 12.5. Anal. Calc. for $C_{25}H_{31}CoN_{10}O_4$: C, 50.51; H, 5.22; N, 23.57. Found: C, 50.47; H, 5.33; N, 23.56%. Analytical data for **26**: M.p.: 102–105 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 7.53 (d, $J=7.2$ Hz, 2H), 6.30 (d, $J=7.3$ Hz, 2H), 5.76 (m, 1H), 5.32 (d, $J=13.0$ Hz, 1H), 5.29 (d, $J=6.3$, 1H), 2.97 (s, 6H), 2.61 (m, 1H), 2.35 (s, 12H), 1.24 (d, $J=6.8$ Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ 154.7, 153.0, 148.9, 141.9, 134.9, 120.2, 113.9, 113.4, 108.4, 45.2, 42.3, 39.2, 15.4, 13.0. HRFABMS: *m/z* Calc. for $C_{25}H_{32}CoN_{10}O_4$ [M+H$^+$]: 595.1940. Found: 595.1919.

2.3.4.2. Method B. (DMAP)cobaloxime(2-butene) (**9**) (110 mg, 0.24 mmol) was dissolved in distilled CH_2Cl_2 (10 ml) and degassed. The flask was covered with Al foil

and then TCNE was added as a solid (60 mg, 0.47 mmol). The solution was allowed to stir at r.t. for 2 h. The volatiles were removed by blowing a stream of air over the solution. The tacky solid was dissolved in EtOAc and then chromatographed on silica gel using EtOAc as the eluent. A yellow fraction was collected first that yielded **21** (86 mg, 0.15 mmol, 61%) containing two isomers in a 5:1 ratio based on ^{1}H-NMR spectral data. The major isomer for this method is the also the major isomer that is described in Method A. A second fraction was collected yielding **26** (5 mg, 0.010 mmol, 4%) as a red solid. The NMR data for the two compounds from Method B are identical to that listed above for Method A.

NMR experiments (^{1}H, ^{13}C attached proton test, ^{13}C, ^{1}H correlation, g-COSY and g-NOESY) were undertaken to determine the stereochemical configuration of the major isomer **21** isolated in the above reaction. The ^{13}C, ^{1}H correlation spectra were used to determine the position of the proton resonances in the ^{1}H-NMR spectra. Two proton resonances (2.57 and 2.10 ppm) displayed cross peaks to one carbon resonance. A ^{13}C APT confirmed that carbon was a secondary carbon resonance. Another proton resonance at 2.10 ppm (two protons based on integration of the ^{1}H-NMR spectrum) was coupled to the methyl resonance at δ 1.31. The last proton resonance of the ring was centered at 1.23 ppm. NOESY data could be used to determine if the orientation of the methyl group of the cyclized ring and the cobaloxime cluster were *cis* or *trans* to one another. A large NOE cross peak between the methyl resonance at 1.31 ppm and the proton resonance at 1.23 ppm would help confirm the *trans* geometry while the absence of a NOE cross peak would indicate a *cis* geometry. NOESY data exhibited a large cross peak between these two resonances, therefore the *trans* geometry is proposed for the major isomer.

2.3.5. Reaction of (DMAP)cobaloxime(3-methyl-2-butene) (*10*) + tetracyanoethylene to produce (*22* and *27*)

Distilled CH_2Cl_2 (30 ml) was used to dissolve (DMAP)(3-methyl-2-butene)cobaloxime (**10**) (226 mg, 0.47 mmol) in a 100 ml two-neck round bottom flask. The flask was covered with Al foil and then TCNE (120 mg, 0.95 mmol) was added as a solid. The mixture was allowed to stir at r.t. for 2 h and then the volatiles were removed by blowing air over the solution. The dark residue was dissolved in EtOAc and chromatographed on silica gel using EtOAc as the eluent. The solvent was removed by reduced pressure from the yellow fraction collected first yielding **22** (26 mg, 0.042 mmol, 9%). The red fraction collected second yielded **27** (48 mg, 0.080 mmol, 17%). Analytical data for **22**: M.p.: 106–108 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 7.84 (d, $J = 6.2$ Hz, 2H), 6.36 (d, $J = 6.3$ Hz, 2H), 2.96 (s, 6H), 2.32 (m, 2H), 2.18 (s, 6H), 2.17 (s, 6H), 1.40 (s, 3H), 1.35 (dd, $J = 13.4$, 7.8 Hz, 1H), 0.97 (s, 3H). ^{13}C-NMR ($CDCl_3$): δ 154.3, 151.5, 151.4, 147.8, 113.5, 113.4, 112.1, 110.4, 107.7, 59.0, 47.1, 39.4, 39.0, 25.1, 18.5, 12.44, 12.40. Anal. Calc. for $C_{26}H_{33}CoN_{10}O_4$: C, 51.32; H, 5.43. Found: C, 51.15; H, 5.48%. Analytical data for **27**: M.p.: 100–103 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 7.49 (d, $J = 7.2$ Hz, 2H), 6.30 (d, $J = 7.2$ Hz, 2H), 5.85, (dd, $J = 17.2$, 10.7, 1H), 5.27 (d, $J = 10.7$ Hz, 1H), 5.20 (d, $J = 17.2$ Hz, 1H), 2.95 (s, 6H), 2.33 (s, 12H), 1.20 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ 154.7, 153.0, 148.5, 139.65, 139.58, 117.5, 113.4, 108.3, 47.4, 39.2, 22.3, 13.0. HRFABMS: *m/z* Calc. for $C_{26}H_{34}CoN_{10}O_4$ [M+H$^+$]: 609.2096. Found: 609.2095.

2.3.6. Reaction of (4-cyanopyridine)cobaloxime(2-butene) (*11*) + tetracyanoethylene to produce (*23*)

(4-cyanopyridine)cobaloxime(2-butene) (**11**) (114 mg, 0.25 mmol) was added to distilled CH_2Cl_2 (20 ml) and degassed. The flask was covered with Al foil and then TCNE (65 mg, 0.51 mmol) was added. The solution was stirred at r.t. for 2 h and then the volatiles were removed by rotary evaporation. The residue was dissolved in EtOAc and chromatographed on silica gel using EtOAc as the eluent. A yellow fraction was collected yielding a yellow solid **23** (29 mg, 0.050 mmol, 20%) when the solvent was removed by reduced pressure. Analytical data for **23**: M.p.: 166–169 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 8.68 (d, $J = 6.6$ Hz, 2H), 7.57 (d, $J = 6.6$ Hz, 2H), 2.55 (dd, $J = 15.2$, 8.6 Hz, 1H), 2.22 (s, 6H), 2.20 (s, 6H), 2.03 (m, 2H), 1.40 (m, 1H), 1.33 (d, $J = 6.9$ Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ 164.0, 152.1, 152.0, 150.6, 139.3, 124.9, 112.1, 111.7, 111.3, 110.1, 53.3, 48.9, 44.3, 41.9, 19.1, 12.7. Anal. Calc. for $C_{24}H_{25}CoN_{10}O_4$: C, 50.01; H, 4.34. Found: C, 49.30; H, 4.83%.

2.3.7. Reaction of (DMAP)cobaloxime(3-methyl-2-butene) (*10*) + benzoquinone to produce (*32*)

2.3.7.1. Method A. (DMAP)cobaloxime(3-methyl-2-butene) (**10**) (150 mg, 0.31 mmol) was dissolved in distilled THF (20 ml) and degassed. Benzoquinone (33 mg, 0.34 mmol) was then added as a solid and the resulting solution was heated to reflux. After 2 h, the solution was cooled to r.t. and filtered. The collected solid was washed with additional EtOAc until the filtrates were colorless. The solvent was removed from the dark red filtrate and the residue was dissolved in EtOAc and chromatographed on silica gel. A deep red fraction was collected and reduced to dryness by rotary evaporation yielding **32** (19 mg, 0.107 mmol, 35%). Analytical data for **32**: M.p.: 34–37 °C. ^{1}H-NMR ($CDCl_3$): δ 6.83 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 8.8$ Hz, 2H), 6.07, (dd, $J = 17.6$, 10.8 Hz, 1H), 5.09 (d, $J = 17.8$ Hz, 1H), 5.08 (d, $J = 10.3$ Hz, 1H), 4.88 (br, 1H), 1.36 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ 151.3, 148.9, 144.1, 124.2, 115.3, 113.5, 79.6,

26.6. HRFABMS: *m/z* Calc. for $C_{11}H_{14}O_2$ [M^+]: 178.0994. Found: 178.0996.

2.3.7.2. Method B. (DMAP)cobaloxime(3-methyl-2-butene) (**10**) (226 mg, 0.47 mmol) was dissolved in distilled THF (20 ml) and degassed. The solution was cooled to 0 °C. Potassium *tert*-butoxide (0.94 ml of a 1.0 M THF solution, 0.94 mmol) was added slowly by syringe. The color gradually turned from orange to deep red. After 15 min, benzoquinone (56 mg, 0.52 mmol) was added and the flask was covered with Al foil and stirred at 0 °C for 2 h. The color gradually turned to a deep green during the course of the reaction. Water (20 ml) was added to the solution and then saturated aq. NH_4Cl (20 ml) was added. Methylene chloride was used to extract the solution. The combined CH_2Cl_2 extractions were dried with $MgSO_4$, filtered and evaporated to dryness. The resulting solid was chromatographed on silica gel using EtOAc as the eluent. A bright yellow solid (26 mg, 0.042 mmol, 9%) was collect with data consistent with the formulation of (DMAP)cobaloxime(1,1-dimethyl-2-propene) (**30**). Analytical data for **30**: M.p.: 178–180 °C (dec). ^{1}H-NMR ($CDCl_3$): δ 7.71 (d, $J = 7.0$ Hz, 1H), 6.25 (d, $J = 7.0$ Hz, 1H), 5.82, (dd, $J = 17.7$, 10.9 Hz, 1H), 4.81 (d, $J = 17.7$ Hz, 1H), 4.76 (dd, $J = 10.9$, 1.0 Hz, 1H), 2.91 (s, 6H), 2.24 (s, 12H), 0.96 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ 154.3, 151.1, 149.4, 145.2, 110.9, 107.6, 39.0, 24.4, 12.4. HRFABMS: *m/z* Calc. for $C_{20}H_{33}CoN_6O_4$ [M^+]: 479.1817. Found: 479.1808.

*2.3.8. Reaction of (DMAP)cobaloxime(3-methyl-2-butene) (**10**) +potassium tert-butoxide to produce (**30**)*

(DMAP)cobaloxime(3-methyl-2-butene) (**10**) (226 mg, 0.47 mmol) was dissolved in distilled THF (30 ml) and degassed. The solution was cooled to 0 °C. The flask was covered with Al foil and then potassium *tert*-butoxide (0.94 ml of a 1.0 M THF solution, 0.94 mmol) was added slowly by syringe. The temperature was maintained at 0 °C for 6 h during which time the color gradually turned from orange to deep red and then onto a deep green. Water (30 ml), cooled to 0 °C, was added to the solution and then saturated aqueous NH_4Cl (30 ml) was added. Methylene chloride was used to extract the orange solution. The combined CH_2Cl_2 extractions were dried with $MgSO_4$, filtered and evaporated to dryness. The resulting solid was chromatographed on silica gel using EtOAc was the eluent. A yellow band was collected first and then the eluent was changed to 90:10 EtOAc–EtOH which allowed an orange band to be collected. The solvent was removed by rotary evaporation from the yellow solution, yielding a yellow–orange solid, and the ^{1}H-NMR spectrum of this solid was consistent with unreacted starting material **10** (13 mg, 0.027 mmol, 6%). The volatiles of the orange solution were removed by rotary evaporation yielding **30** (33 mg, 0.068 mmol, 15%) identical by spectroscopic comparison to the material reported above.

*2.3.9. Reaction of (DMAP)cobaloxime(2-butene) (**9**) + benzoquinone to produce (**33** and **34**)*

DMAP(2-butene)bis(dmg)cobalt(III) (**9**) (600 mg, 1.29 mmol) was added to a 100 ml two-neck round bottom equipped with a reflux condenser and dissolved in distilled CH_2Cl_2 (50 ml). After degassing the orange solution, benzoquinone (274 mg, 2.54 mmol) was added as a solid. The resulting solution was heated to a gentle reflux for 4 h and then the volatiles were removed by rotary evaporation. The resulting solid was slurried in CH_2Cl_2–C_3H_6O (19:1) and chromatographed on a silica gel column using the same CH_2Cl_2–C_3H_6O solution as the eluent. A pale red fraction was collected second that yielded a viscous red oil (18 mg, 0.11 mmol, 9%) upon evaporation of the solvent. ^{1}H-NMR spectra indicated the formation of two isomers (65% for the major isomer (**33**) and 35% for the minor isomer (**34**)) and a low resolution GC/MS confirmed equal masses for the two isomers. Analytical data for major isomer (**33**): ^{1}H-NMR ($CDCl_3$): δ 6.77 (m, 2H), 6.71 (m, 2H), 5.87 (m, 1H), 5.21 (dt, $J = 17.3$, 1.0 Hz, 1H), 5.13 (d, $J = 10.6$ Hz, 1H), 4.80 (br, 1H), 4.64 (p, $J = 6.3$ Hz, 1H), 1.38 (d, $J = 6.4$ Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ 152.0, 149.6, 139.4, 117.7, 115.9, 115.7, 75.9, 21.3. Analytical data for minor isomer (**34**): ^{1}H-NMR ($CDCl_3$): δ 6.77 (m, 2H), 6.71 (m, 2H), 5.80 (m, 1H), 5.70 (m, 1H), 4.80 (br, 1H), 4.37 (d, $J = 6.1$ Hz, 2H), 1.73 (dd, $J = 6.4$, 1.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$): δ 152.8, 149.5, 130.6, 126.2, 116.0, 115.8, 69.4, 17.9. HRFABMS (combined isomeric mixture): *m/z* Calc. for $C_{10}H_{12}O_2$ [M^+]: 164.0837. Found: 164.0839.

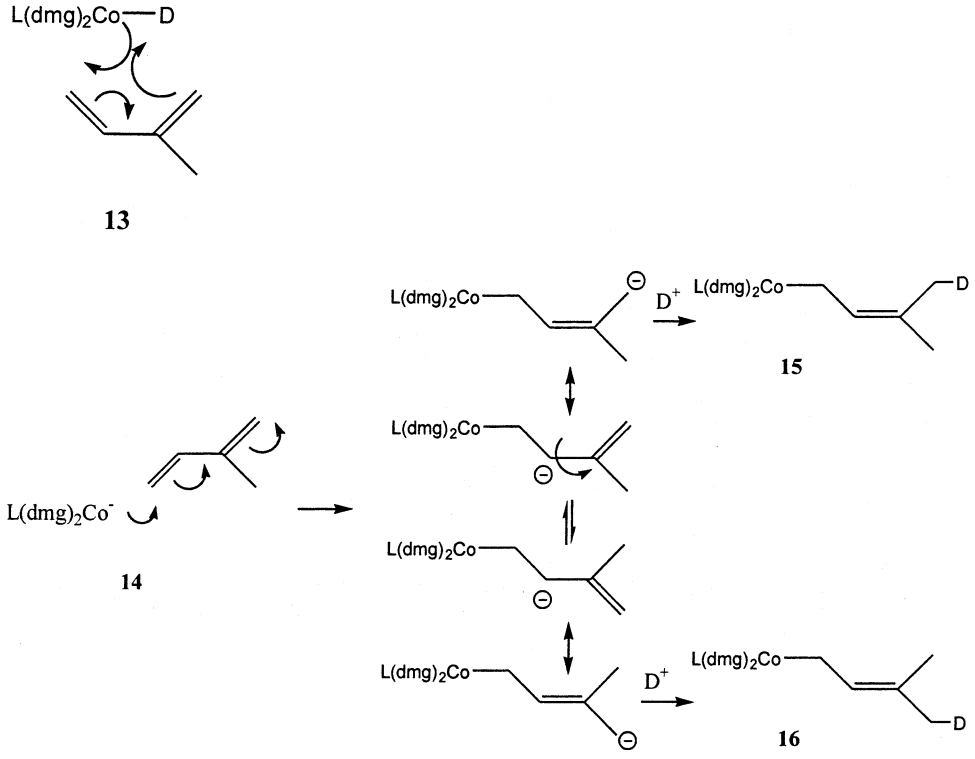
3. Results and discussion

3.1. Preparation of cobaloxime allyl complexes

Cobaloxime allyl complexes were prepared by one of four different methods: (1) in situ generation and allylation of $[L(dmg)_2Co]_2$ dimers; (2) generation and allylation of $L(dmg)_2Co$ anions prepared from $L(dmg)_2CoCl$ complexes; and (3) 1,4-hydrocobaltation of 1,3-dienes [9].

Generation and allylation of $[L(dmg)_2Co]_2$ dimers is simple to effect but this method suffers from the disadvantage of producing a mole of $L(dmg)_2Co$-halide for every mole of $L(dmg)_2Co$-allyl produced. When hydrometallation of a 1,3-diene could be used (Table 1, entries 7 and 9) yields were generally higher. This 1,4-hydrocobaltation is also an interesting reaction from a mechanistic standpoint. These cobaloxime reactions are known to contain mixtures of cobaloxime anions and hydrides in polar protic solvents [10]. To gain some

additional insight into this reaction, we prepared complex **10** using $NaBD_4$ as reductant in D_2O–EtOD and brought the pH of the solution back to 7 using CH_3CO_2D and then followed this by isoprene addition. The allyl complexes isolated (75% yield) consisted of a 1:1 mixture of **15**–**16**. This result is inconsistent with a concerted 1,4-hydrocobaltation of the diene (**13**) and is best explained by cobaloxime anion addition to the isoprene (**14**) followed by deuteration or addition of pyr(dmg)$_2$Co(II) to the diene to generate allyl radical analogs of the allyl anions shown, which are then quenched by deuterium atom abstraction.



3.2. Reactions of cobaloxime η^1-allyl complexes with TCNE

The first electrophile to be investigated was TCNE since some reactions of pyridine cobaloxime allyl complexes with this substrate had been reported in the 1970s [2]. As reported previously [2], the unsubstituted allyl complex (**5**) reacted with TCNE to produce cyclized product (**17**) with none of the uncyclized product (**24**, $R_1 = R_2 = H$) seen. The 2-butenyl complex (**6**) (3:1, *E*–*Z*) also provided cyclized product (**18**) (56%, 3:1, *trans*–*cis*) as the major product as reported previously [2] however, we also isolated a significant amount (18%) of the uncyclized isomer (**24**) which had not been reported previously. The 3-methyl-2-butenyl complex (**7**) reacted with TCNE to provide a small amount of the cyclized product (**19**) with the uncyclized isomer (**25**) being the major product in this case. If these reactions proceed through an alkene complex like **3**, then the alkene complex from **7** plus TCNE is presumably less stable due to methyl group steric group interactions, thereby facilitating alkene dissociation and leading to a preponderance of the uncyclized product. In cobaloxime Diels–Alder chemistry, we found DMAP dienyl complexes to be considerably more reactive than their pyridine complex counterparts so we looked at the corresponding DMAP cobaloxime allyl complex reactions with TCNE. The results obtained using DMAP allyl complexes (**8**–**10**) were almost identical to those obtained for the pyridine cobaloximes. The DMAP 2-butenyl complex (**9**) was found to cyclize with TCNE at −20 °C over 1 h, consistent with enhanced Diels–Alder reactivities we had noted for DMAP cobaloximes earlier [6]. The electron donating DMAP ligand did not, however, significantly alter the ratios of cyclized to uncyclized products seen. We also hypothesized that a

Table 1
Cobaloxime allyl complex preparation

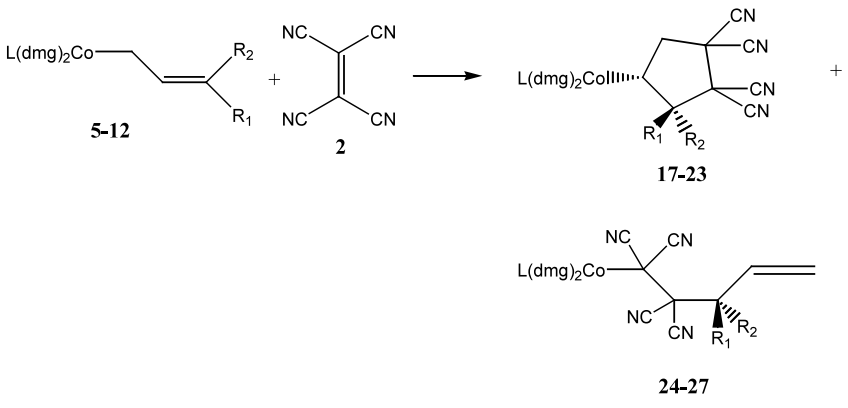
Entry no.	Compound	Preparation method	L	R_1	R_2	%Yield
(1)	**5**	1 [a]	Pyr	H	H	19
(2)	**6**	1 [a]	Pyr	Me	H	42 3:1 *E*:*Z*
(3)	**7**	2	Pyr	Me	Me	52
(4)	**7**	1 [a]	Pyr	Me	Me	37
(5)	**8**	1 [a]	DMAP	H	H	49
(6)	**9**	1 [a]	DMAP	Me	H	45 3:1 *E*:*Z*
(7)	**10**	3	DMAP	Me	Me	76
(8)	**11**	1 [a]	4-CNpyr	Me	H	30 3:1 *E*:*Z*
(9)	**12**	3	4-^{t}Bupyr	Me	Me	61

[a] The maximum possible yield of Co-allyl from this method is 50%.

more electron withdrawing pyridine ligand might lead to stronger alkene binding and increase the amount of cyclized products seen. We prepared the 4′-cyanopyridine 2-butenyl complex (**11**) and also treated it with TCNE under conditions identical to those used for the pyridine and DMAP allyl complexes. This more electron withdrawing ligand would be expected to slow initial allyl attack on TCNE but accelerate the subsequent cyclization. We isolated a reduced amount of the cyclized product (**23**) and see no evidence for production of the uncyclized complex, consistent with the hypothesis stated above (Table 2).

Table 2
Reactions of cobaloxime allyl complexes with TCNE

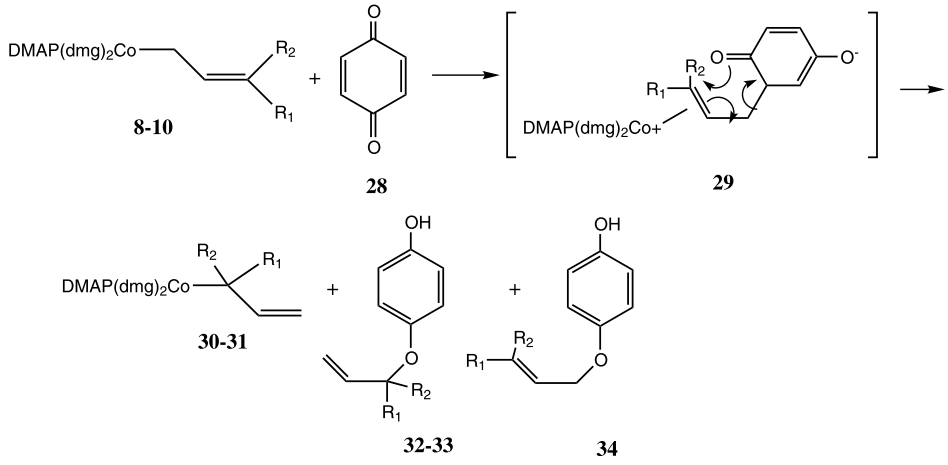
L	R_1	R_2	(#), % Cyclized	(#), % Uncyclized
Pyridine	H	H	(17) 64	Not detected
	H	Me	(18) 56	(24) 18
	Me	Me	(19) 5	(25) 38
DMAP	H	H	(20) 54	Not detected
	H	Me		(26) 10
	Me	Me		(27) 17
4-Cyanopyridine	H	Me	(23) 20	Not detected



3.3. Reaction of DMAP allyl cobaloximes with other carbon electrophiles

Having thoroughly investigated the reactions of cobaloxime allyls with TCNE, we proceeded to investigate other electrophiles. Treatment of the DMAP allyl complex (**8**) with diethylacetylenedicarboxylate in CH_2Cl_2 at 25 °C resulted in recovery of unreacted allyl complex starting material. Likewise, treatment of allyl complex (**9**) with diethylmethylenemalonate (25 °C) also resulted in recovery of unreacted allyl complex starting material. Heating allyl complex (**8**) with diethylmethylenemalonate just resulted in complex decomposition. Reaction of the DMAP allyl complex (**10**) with benzoquinone in refluxing THF produced a new organic compound (**32**, $R_1 = R_2 = Me$) in moderate yield (35%). The structure of this addition product was determined to be a *para* alkoxy substituted phenol (**32**). The

isolation of this unexpected compound is best rationalized by a Michael addition followed by a retro Claisen rearrangement [11]. Cobaloxime complexation to the alkene in (**29**) may accelerate the proposed retro Claisen. We suspected that the bridging glyoxime ligand OH protons were protonating proposed intermediate (**29**) thereby quenching the possibility of isolating a cobaloxime product. To try to avoid this proton transfer, cobaloxime allyl (**10**) was first treated with KO^tBu in THF followed by benzoquinone addition. However, rather than isolating any new addition compounds or complexes, we instead isolated a rearranged cobaloxime allyl complex (**30**, $R_1 = R_2 = Me$). Deprotonation/recombination of allyl complex (**10**) can be used to account for the production of this rearranged complex (**30**, $R_1 = R_2 = Me$). Treatment of 2-butenyl complex (**9**) with benzoquinone also resulted in the production of addition compounds (**33**, $R_1 = H$, $R_2 = Me$) and **34**, $R_1 = Me$, $R_2 = H$) in a ratio of 65:35 (9% isolated yield) as well as some recovered starting material (**9**) and rearranged allyl (**31**, $R_1 = H$, $R_2 = Me$). The unexpected alkoxy substituted phenols (**33** and **34**) also presumably arise from Michael addition/retro Claisen tandem reactions.



4. Summary

In summary, we have demonstrated that cobaloxime allyl complexes react with tetracyanoethylene to give mixtures of cyclized and uncyclized addition products. The ratio of cyclized to uncyclized products is influenced by allyl complex substitution pattern as well as the axial ligand present in the allyl complex. DMAP substituted allyl complexes will add to less reactive carbon electrophiles such as benzoquinone but in those cases the major products isolated are demetallated organic addition/rearrangement products rather than cobaloxime complex addition products.

Acknowledgements

We thank the National Science Foundation (CHE-0104083) for support of this work. Low resolution mass spectra were obtained on instruments purchased with the partial support of the North Carolina Biotechnology Center (Grant #2001 IDG 1004). The Duke University Center for Mass Spectrometry performed high resolution mass spectral analyses.

References

[1] C.J. Cooksey, D. Dodd, C. Gatford, M.D. Johnson, G.J. Lewis, D.M. Titchmarsh, J. Chem. Soc. Perkin Trans. II (1972) 655.
[2] (a) D. Dodd, M.D. Johnson, I.P. Steeples, E.D. McKenzie, J. Am. Chem. Soc. 98 (1976) 6399;
(b) C.J. Cooksey, D. Dodd, M.D. Johnson, B.L. Lockman, J. Chem. Soc. Dalton Trans. (1978) 1814.
[3] (a) J.L. Gage, B.P. Branchaud, J. Org. Chem. 61 (1996) 837;
(b) L.M. Grubb, B.P. Branchaud, J. Org. Chem. 62 (1997) 242;
(c) J.L. Gage, B.P. Branchaud, Tetrahedron Lett. 38 (1997) 7007;
(d) L.M. Grubb, K.A. Brown, B.P. Branchaud, Tetrahedron Lett. 39 (1998) 3447;
(e) Y. Nishikubo, B.P. Branchaud, J. Am. Chem. Soc. 121 (1999) 10924.
[4] (a) G.B. Gill, G. Pattenden, G.A. Roan, Tetrahedron Lett. 37 (1996) 9369;
(b) G. Kettschau, G. Pattenden, Tetrahedron Lett. 39 (1998) 2027;
(c) G. Kettschau, G. Pattenden, SynLett (1998) 783.
[5] T.M. Brown, C.J. Cooksey, A.T. Dronsfield, J.H. Fowler, Inorg. Chim. Acta 288 (1999) 112.

[6] For recent references to our Diels–Alder work see: (a) M.E. Welker, Curr. Org. Chem. 5 (2001) 89;
(b) J.J. Chapman, C.S. Day, M.E. Welker, Eur. J. Org. Chem. 12 (2001) 2273.
[7] D.L. Jameson, J.J. Grzybowski, D.E. Hammels, R.K. Castellano, M.E. Hoke, K. Freed, S. Basquill, A. Mendel, W.J. Shoemaker, J. Chem. Educ. 75 (1998) 447.
[8] G.N. Schrauzer, R.J. Windgassen, J. Am. Chem. Soc. 89 (1967) 1999.
[9] For a recent review which covers synthesis of alkyl cobaloximes, see: M. Tada, Rev. Heteroat. Chem. 20 (1999) 97.
[10] D. Dodd, M.D. Johnson, J. Organomet. Chem. 52 (1973) 1.
[11] For a review of the Claisen rearrangement, see: S.J. Rhoads, N.R. Raulins, Org. React. 22 (1975) 1.