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# Simple preparation of cobaloxime dienyl complexes and their *exo* selective Diels–Alder cycloadducts

## Progress toward transition metal-mediated Diels–Alder reactions which are catalytic in metal dienyl complex

Kerry A. Pickin, Jennifer M. Kindy, Cynthia S. Day, Mark E. Welker\*

Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109-7486, USA

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### Abstract

A new method for the synthesis of cobaloxime dienyl complexes (cobaloxime = pyridine(dimethylglyoxime)<sub>2</sub>Co) which involves a zinc-mediated hydrocobaltation of enynes is reported. Use of this dienyl complex synthesis method allows subsequent Diels–Alder reactions of these complexes to be accomplished without isolation of the dienyl complexes. A new silane-based cobaloxime-substituted cycloadduct demetallation protocol is then reported which provides Diels–Alder cycloadducts and cobalt complexes which have been recycled into the zinc-mediated dienyl complex synthesis.

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**Keywords:** Diels–Alder; Dienyl complexes; [4+2] Cycloaddition; Demetallation

### 1. Introduction

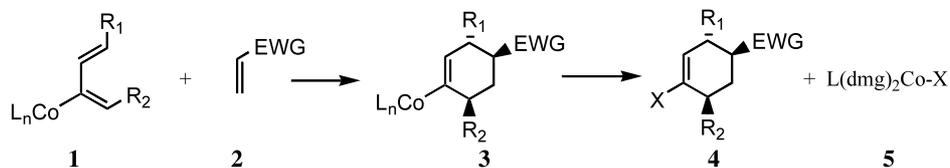
The use of cobalt complexes to mediate or catalyze organic reactions has grown tremendously in the last few years and there are now many reported examples of cobalt-mediated cycloaddition or cyclization reactions [1]. Of these cycloaddition reaction types, the Diels–Alder reaction is the most thoroughly studied in all of organic chemistry. ISI's citation database contains almost 1000 publications per year for each of the last 4 years that deal with some aspects of Diels–Alder chemistry.

About 10 years ago, we first became interested in preparing 2-transition metal-substituted 1,3-butadienes

(**1**) for use in 4+2 cycloadditions [2]. We initially prepared a number of cobaloxime- and cosalen-substituted 1,3-dienes (**1**) and found them to be air-stable solids of high thermal stability that could be prepared on a multi-gram scale from inexpensive starting materials [3]. The cobalt dienyl complexes (**1**) reacted with a variety of dienophiles (**2**) both regioselectively and stereoselectively (with high *exo* diastereoselectivity and enantioselectivity [4]) to produce air-stable cobalt-substituted cyclohexenes (**3**) in high yield. We also developed a number of methods for cleavage of the cobalt–carbon bonds in the cycloadducts which would yield organic products (**4**) as well as a cobalt complex (**5**) which could be recycled into the synthesis of the starting dienyl complexes (**1**). The *exo* diastereoselectivity of these cycloaddition reactions provides access to cyclohexene stereochemistries which are complimentary to those obtained from traditional *endo* selective Diels–Alder reactions.

\* Corresponding author. Tel.: +1-336-758-5758; fax: +1-336-758-4321.

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



This chemistry would be more useful to the organic community if the stoichiometric reaction sequence described above could be affected without isolation and purification of **1** and **3** or, even better, through a series of reactions which were catalytic rather than stoichiometric in metal complex. In theory, a catalytic cycle for the reaction sequence can be drawn (Fig. 1) and all the individual steps involved in the cycle (cobalt hydride (**6**) generation, enyne (**7**) hydrometallation, Diels–Alder reactions of cobalt dienyl complexes (**8**) with dienophiles (**9**) to generate metal-substituted cycloadducts (**10**), and reductive demetallation of cycloadducts (**10**) to produce compounds like **11**) have been reported previously by our group [3]. In practice, there are numerous challenges to be overcome to effect the cycle shown and our progress toward that goal is presented here.

## 2. Results and discussion

### 2.1. Control experiments to test the viability of the cycle in Fig. 1

We will first discuss some of the potential problems in the proposed cycle and what control experiments we ran

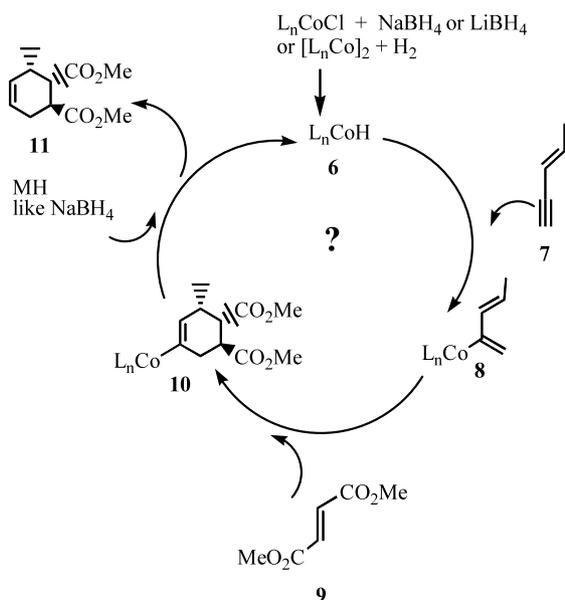


Fig. 1. A possible catalytic cycle for effecting transition metal-mediated Diels–Alder reactions.

to address them. We wondered if we used boron hydride for catalyst generation and reductant whether our enynes (such as **7**) would be stable in the presence of these reagents. We thought that even if enynes were hydroborated [5] faster than hydrocobaltation occurred those species must be transmetallating to cobalt or else we would never have been able to isolate good yields of cobaloxime dienes from our hydrometallation experiments [6]. However, since the proposed cycle would require enynes to be unreactive, relative to Co(II) toward mild reducing agents, and the order of addition of reagents was different from our earlier work [6], we ran the control experiment. *trans*-Pentenyne (**7**) in methanol was treated with NaBH<sub>4</sub> first, followed by addition of (pyr)(dmg)<sub>2</sub>CoCl and then dropwise addition of acetic acid to bring the pH back to 8. Quenching of this reaction with ice water containing a few drops of pyridine produced dienyl complex (**8**) in the same purity (by <sup>1</sup>H-NMR comparison) and in the same isolated yield as that observed from our typical order of addition [6]. Even if boron-substituted dienes were made as transient intermediates, they are unlikely to compete with transition metal-substituted dienes in Diels–Alder reactions. (This observation may prove useful in that we may be able to make transition metal dienyl complexes by transmetalation rather than hydrometallation in the future.) 1,3-Dienes substituted with main group elements in the 2 position are much less reactive than cobalt-substituted dienes [7]. For instance, 2-stannyl or seleno-substituted dienes require 2–3 days at 25 °C to react with maleic anhydride whereas similar cobalt-substituted diene reactions are complete in 15–30 min [8].

The catalytic cycle proposed in Fig. 1 also requires that dienophiles such as dimethyl fumarate (**9**) be stable in the presence of cobalt anions and hydrides (**6**) and we were concerned that these species might react faster with dienophiles than the enynes [9]. The cobaloxime anion/hydride mixture generated by the addition of NaBH<sub>4</sub> to (pyr)(dmg)<sub>2</sub>CoCl was treated with a 1:1 mixture of *trans*-2-pentenyne (**7**) and dimethyl fumarate (**9**) at 0 °C. We isolated only cobaloxime diene (**8**, L<sub>n</sub> = (dmg)<sub>2</sub>pyr) and cobaloxime-substituted cycloadduct (**10**) (60% mass balance, 1:2 diene:cycloadduct). Cobaloximes have reasonable water solubility and so when we have to do an extraction to isolate complexes our mass balances for cobalt are usually in the 60–70% range. No product of addition of cobaloxime to dimethyl fumarate was

isolated. This competition experiment was also encouraging in that two of the three cycle steps, enyne hydrometallation and Diels–Alder reaction, have occurred in the desired sequence under very mild conditions (0 °C). We also ran the control of treating dimethyl fumarate with NaBH<sub>4</sub> in methanol to make sure the dienophile was not reduced by our reaction conditions.

## 2.2. Demetallation questions/controls

An absolutely critical chemical requirement for the cycle in Fig. 1 is that the metal sp<sup>2</sup>–carbon bond in the diene (**8**) be more stable than the cobalt sp<sup>2</sup>–carbon bond in the cycloadduct (**10**). We had noticed this to be true on many occasions when we ran demetallations [8], i.e. cobalt-substituted cycloadducts (such as **10**) containing small amounts of unreacted cobalt diene (**8**) could be treated with reductants and the demetallated cycloadduct (**11**) isolated along with unreacted cobalt-substituted diene (**8**) but we had never run a formal competition experiment. A 1:1 mixture of dienyl complex (**8**) to cycloadduct (**10**) was treated with an equimolar amount of NaBH<sub>4</sub> in methanol to produce demetallated cycloadduct (**11**) and recovered unreacted diene (**8**). We also found that we could treat cobalt-substituted cycloadduct (**10**) with 1:1 mixture of NaBH<sub>4</sub> and the enyne (**7**) and produce a 1:1 mixture of demetallated cycloadduct (**11**) (27% isolated yield) to cobaloxime dienyl complex (**8**) (29%). The isolated yields here were not great but it did show that the demetallation and hydrometallation steps of the cycle could also be performed in the same pot.

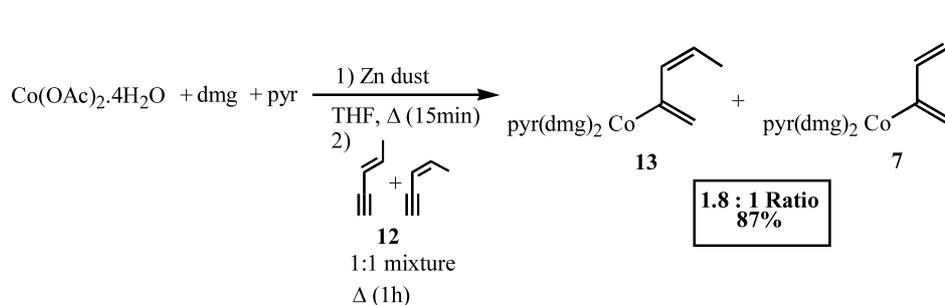
Once the control experiments were completed, we were ready to test the cycle outlined in Fig. 1 as a one-pot reaction. Cobaloxime chloride [pyr(dm<sub>g</sub>)<sub>2</sub>CoCl] was treated with NaBH<sub>4</sub> at 0 °C to generate cobaloxime hydride (**6**). This solution was then warmed to 25 °C after enyne (**7**) was added. Dimethyl fumarate (**9**) was then added and the solution was refluxed for 1 h. Additional NaBH<sub>4</sub> was added to effect demetallation and the crude product was analyzed by <sup>1</sup>H-NMR. Compounds **11**, **10** and **8** were present in a 1.6:1:1 ratio. Considerable effort to optimize conditions for each of

these individual steps led us to the conclusion that, while the cycloaddition and demetallation steps could be performed in >90% yield, we were going to be limited by the hydrometallation used since chemical yields for this step are routinely in the 50–60% range. This limitation is presumably due to the thermal sensitivity of the cobalt hydride (**6**) [9] and we viewed the temperature cycling that this reaction sequence required as a significant disadvantage. A metal dienyl complex generation procedure which could be performed at elevated temperatures in high yield was first needed.

## 2.3. Development of a new method for cobaloxime dienyl complex preparation

We first screened a number of possible reductants for the enyne hydrocobaltation step. In general, we found that aluminum hydrides were too reactive, whereas silanes were generally unreactive as possible reductants. A cobaloxime reduction/electrophile trapping method which used zinc as a reductant had been developed previously by Roussi and Widdowson [10]. We had used a modification of this method previously to prepare sp<sup>2</sup> carbon–cobalt bonds from vinyl triflates [11] and alkynes [12].

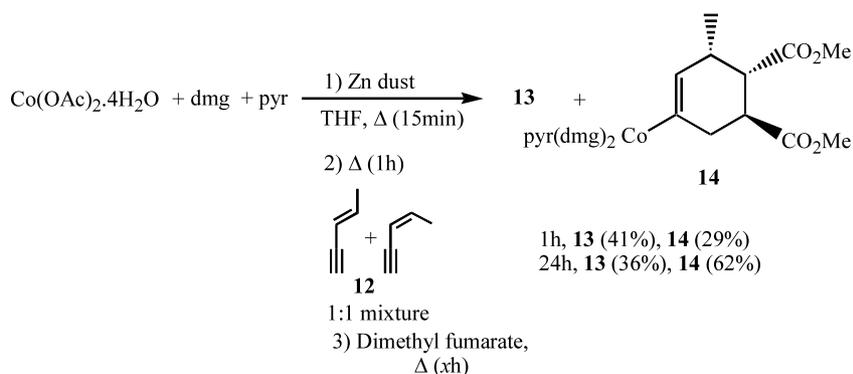
The successful metallation of the alkyne of alkynes led us to consider the enyne as a substrate for the modified Widdowson protocol. By substituting the alkyne with (*E*)- and (*Z*)-3-pentene-1-yne (**12**), we were able to produce the 2-substituted dienyl complexes, **13** and **7**, in excellent yield. The zinc-assisted metallation of the enyne provides a replacement method for the synthesis of the initial cobalt dienyl complex in the cycle and can be performed at elevated temperatures where cycloaddition reactions should also be rapid. The ratio of *E* to *Z* isomers produced by this method is similar to the ratio we had noted previously when the (*Z*)-pentenyne was hydrometallated using a borohydride-based procedure [6]. We had previously demonstrated that (*E*)-cobaloxime dienyl complex (**7**) participated in Diels–Alder reactions much faster than (*Z*)-dienyl complex (**13**) and that *Z*:*E* isomerization was much faster than cycloaddition [13]. These observations per-



mitted us to use the more readily available *E:Z* mixture of enynes (**12**) [14] in the complex preparation.

#### 2.4. One-pot dienyl complex synthesis/Diels–Alder reactions

Once this initial dienyl complex preparation step proved successful, the reaction was taken to the next step of the cycle in the same reaction flask. Upon completion of the initial 1-h reflux, dienophile dimethyl fumarate was added to the reaction and the mixture was refluxed for an additional 1 or 24 h.



The results for the one-pot reaction showed that synthesis of the dienyl complex and cycloaddition could occur in the same reaction vessel. However, the presence of a significant amount of unreacted (*Z*)-dienyl complex (**13**) in the 24-h reaction suggested possible interference from one of the other reactants during the cycloaddition reaction. When the purified *E/Z* mixture of dienyl complexes (**13** and **7**) was heated to reflux in THF with five equivalents of dimethyl fumarate overnight, cycloadduct **14** was isolated in 90–98% yield. Likewise, additional control cycloadditions run using **13** and **7** with dimethyl fumarate plus 20 mol%  $\text{pyr(dmg)}_2\text{CoCl}$  or 20 mol%  $\text{pyrHCl}$  (compounds likely to be in the one-pot cycloaddition) produced **14** only again in near-quantitative yield. However, a control cycloaddition run with 20 mol% zinc and 20 mol%  $\text{Zn(OAc)}_2$  present produced cycloadduct **14** in only 55% isolated yield. Competing zinc metal reduction of a significant portion of the dienophile [15] prior to cycloaddition appeared to be one possible cause for the reduced yields of cycloadduct seen in the one-pot reaction. Another possibility might be that  $\text{Zn(OAc)}_2$  exchanges with the bridging OH in the dmg ligands and that complex is significantly less reactive in Diels–Alder reactions [13]. Such a dienyl complex would be hydrolyzed back to the protonated ligand form upon work up or chromatography [13].

#### 2.5. Tandem dienyl complex synthesis/Diels–Alder reactions

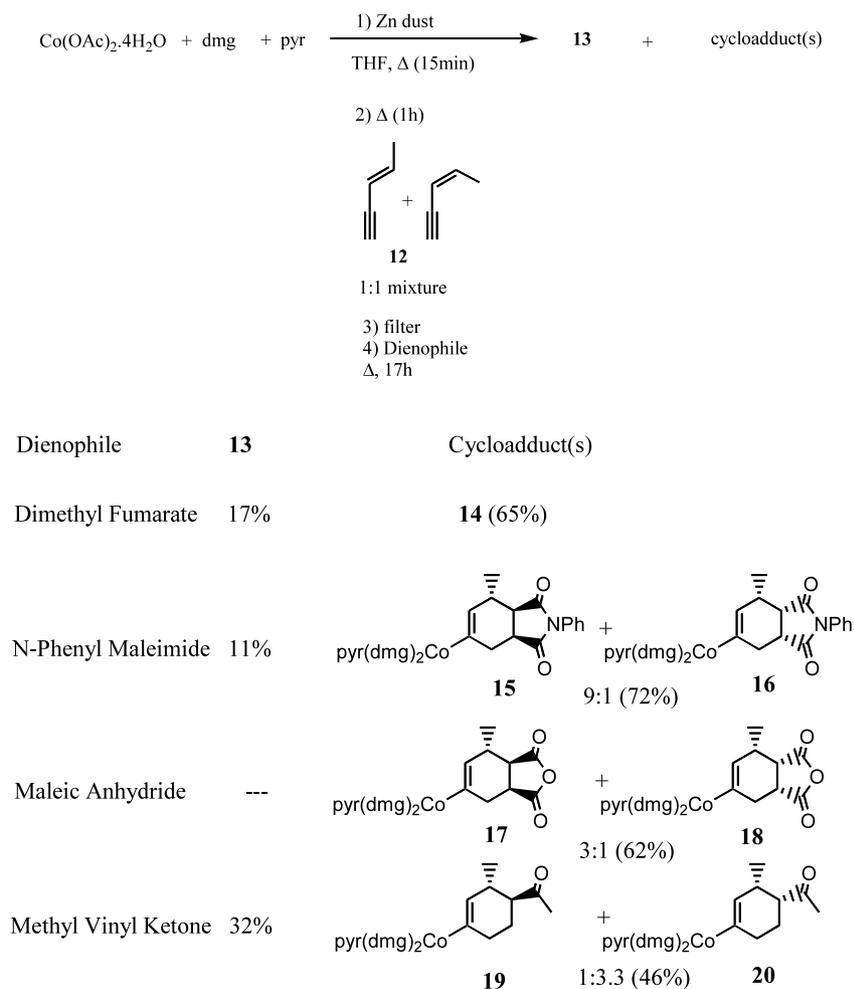
Mindful of the fact that we were trying to simplify preparation of organic cycloadducts from cobalt-mediated Diels–Alder reactions, we decided that removal of zinc dust, prior to the cycloaddition, could probably be accomplished without chromatography but removal of  $\text{Zn(OAc)}_2$  (which has reasonable THF solubility) would be more problematic. Removal of most zinc dust from the reaction pot was accomplished using a specially adapted double-ended needle where

one side of the needle was fitted with a glass frit. The reaction solution was then transferred through the filter fitted needle into a clean reaction vessel.

Once the zinc removal system had been successfully developed, the scope of the dienyl complex synthesis/cycloaddition sequence was determined using a number of dienophiles. When dimethyl fumarate was used again as the dienophile, the amount of unreacted dienyl complex (**13**) dropped to 17% and the isolated yield of the one diastereomer produced (**14**) improved to 65%. *N*-Phenyl maleimide cyclized to produce a 9:1 mixture of diastereomers. The major diastereomer is assigned as the *anti* diastereomer (**15**) and the minor diastereomer was assigned the *syn* stereochemistry (**16**). We had earlier noted that  $^1\text{H-NMR}$  *anti* cycloadduct methyl resonances in maleic anhydride cycloadducts ( $\delta$  0.99 ppm,  $\text{CDCl}_3$ ) were considerably upfield of the corresponding *syn* adducts ( $\delta$  1.37 ppm,  $\text{CDCl}_3$ ) [8,16]. We see the same trend for the major and minor diastereomers (**15** and **16**) here (major diastereomer methyl doublet:  $\delta$  1.04 ppm,  $\text{CDCl}_3$ ; minor diastereomer methyl doublet:  $\delta$  1.35 ppm,  $\text{CDCl}_3$ ). Maleic anhydride cyclized to produce a 3:1 mixture of *anti:syn* diastereomers (**17:18**) as we had seen in our earlier work [8]. A Diels–Alder reaction which proceeds through predominantly an *exo* rather than *endo* transition state rationalizes **15** and **17** as the major products and the larger size

of *N*-phenyl maleimide would account for the larger proportion of *anti* adduct for that dienophile. The small dienophile, methyl vinyl ketone, which also contains only one electron-withdrawing group, cyclizes in lower yield and has a preference for the product predicted from an *endo* (**20**) rather than *exo* (**19**) transition state [8]. It should be noted that the yields reported for cycloadduct below are the cumulative isolated yields for two chemical steps, dienyl complex synthesis and Diels–Alder reaction.

mediated reactions typically favor products which have arisen from *exo* rather than *endo* transition states when di-, tri- or tetra-substituted dienophiles are used [3]. Dimethyl fumarate is unusual among the dienophiles in this series because it does not have different possible regiochemical outcomes and *endo* or *exo* selectivity requires clarification due to the opposing, symmetrical substitution pattern of the methyl esters. In any approach pattern of the dienophile to the diene, one of the methyl esters will be *endo* and one will be *exo* (**21**

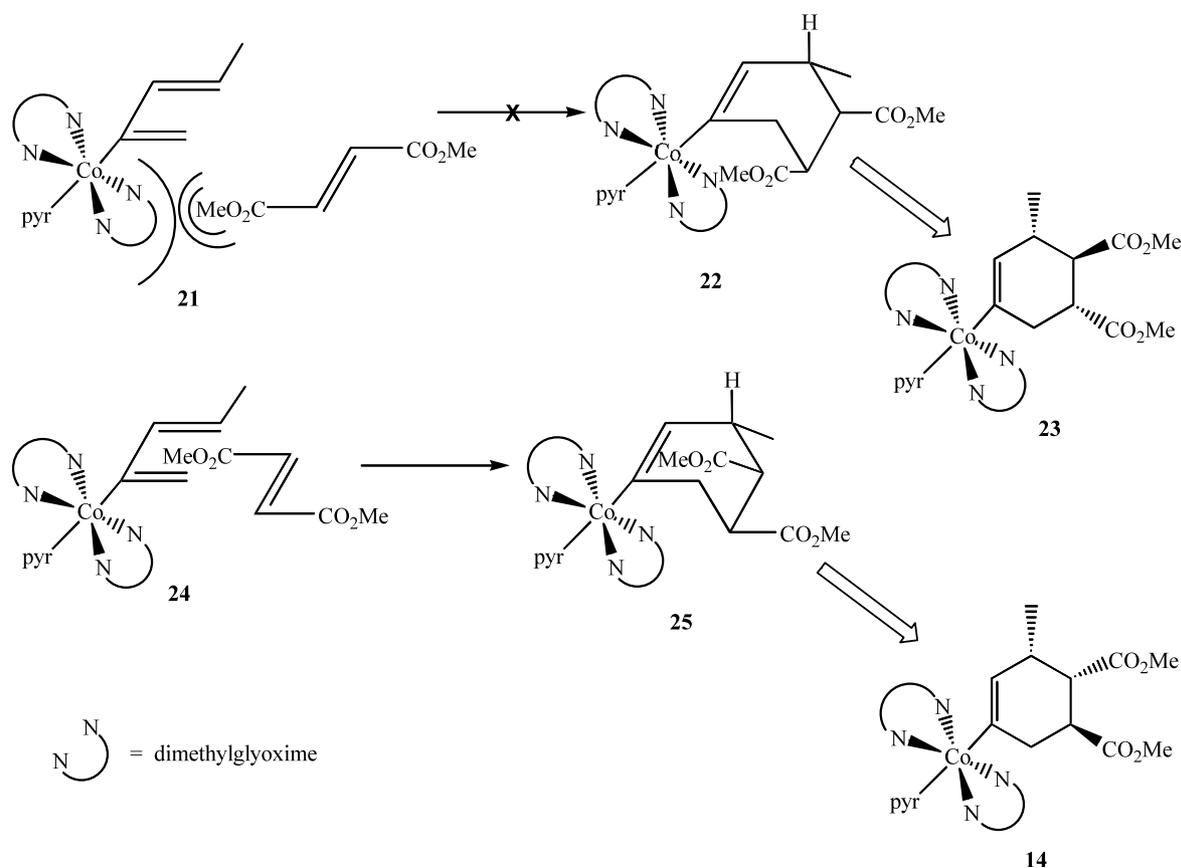


The stereochemical outcome of the cycloaddition with dimethyl fumarate deserves additional comment. The stereochemical outcome of cobalt-mediated cycloaddition reactions is many times unique. These cobalt-

and **24**). However, the reaction did produce a single, unique stereochemical outcome in the cycloadduct. Steric arguments would predict that the dienophile would favor an approach that places the methyl ester

that is *endo* away from the cobaloxime moiety (**24**). The relative stereochemistry of **14**, which would arise from the diene-dienophile approach shown in **24**, was con-

moity must be cleaved from the cycloadduct and a viable metal species needed to be regenerated for reuse in the cycle.



firmed by X-ray crystallography (see Fig. 2). Table 1 contains details of the structure determination. A partial list of bond lengths and angles for **14** appears in Table 2.

### 2.6. Demetallation reactions

Many of the demetallation reactions we reported in our earlier work were performed in protic solvents (where transesterification or hydrolysis of some substrates could be a problem) or at low temperatures [3]. Since the diene complex synthesis and cycloadditions reported for the first two steps of the cycle were now being performed in THF at 25 °C or above, ideally we would develop a demetallation which could be effected under these same conditions. In order to complete the reaction cycle initially proposed (Fig. 1), the metal

Chlorosilane-mediated demetallations met the requirements outlined above in that they could be performed in THF at 25 °C or above. The results of treatment of the cobaloxime cycloadduct (**14**) with various silanes under both thermodynamic and photochemical conditions are presented in Table 3. The best cleavage reaction combined six equivalents of dichloromethyl silane with reflux for 1 h to produce the desired cycloadduct (**26**) in high yield. During this reaction, the solution changed color from yellow to bright green and a fine teal solid precipitated out of solution. Analysis of the precipitate by MS showed it to be a mixture of cobalt salts including  $[\text{pyrCoCl}_3]^- (\text{pyrH})^+$  and  $(\text{pyr})_2\text{CoCl}_2$ . The exact composition of this salt mixture was not determined since what we were really interested in was a demetallation which could result in the

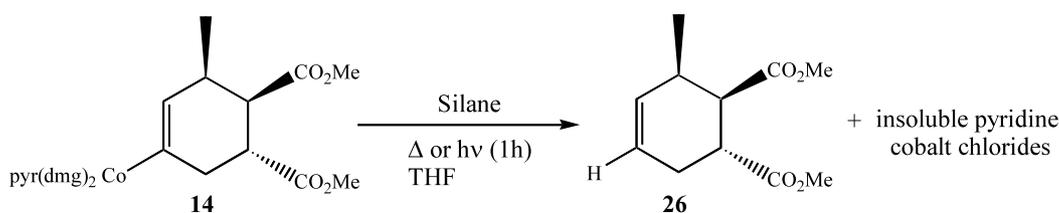
Table 1

Crystal data and structure refinement for (1,2-dicarboxylic acid dimethyl ester-3-methyl-4-cyclohexen-5-yl)pyridinebis(dimethylglyoximate)cobalt

Empirical formula	Co(NC <sub>5</sub> H <sub>5</sub> )(N <sub>2</sub> C <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> H) <sub>2</sub> (C <sub>6</sub> (CH <sub>3</sub> )H <sub>6</sub> (CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> )·1.5Cl <sub>2</sub> C <sub>2</sub> H <sub>4</sub>
Formula weight	727.92
Temperature (K)	228(2)
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, <i>C2/c</i> - <i>C</i> <sub>2h</sub> <sup>6</sup> (no. 15)
Unit cell dimensions	
<i>a</i> (Å)	35.207(5)
<i>b</i> (Å)	9.163(1)
<i>c</i> (Å)	23.743(3)
β (°)	114.19(1)
<i>V</i> (Å <sup>3</sup> )	6987(2)
<i>Z</i> , calculated density (g cm <sup>-3</sup> )	8, 1.384
Absorption coefficient (mm <sup>-1</sup> )	0.771
<i>F</i> (0 0 0)	3032
Crystal size (mm <sup>3</sup> )	0.09 × 0.44 × 0.50
Theta range for data collection (°)	2.31–24.15
Limiting indices	−1 ≤ <i>h</i> ≤ 40, −1 ≤ <i>k</i> ≤ 10, −27 ≤ <i>l</i> ≤ 25
Reflections collected/unique	6061/5111 [ <i>R</i> <sub>int</sub> = 0.048]
Absorption correction	empirical
Max. and min. transmission factors	0.978 and 0.643
Absolute structure parameter	0.09(2)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/parameters	5111/451
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.020
Final <i>R</i> indices	
[2896 <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> ) data]	<i>R</i> <sub>1</sub> = 0.063, <i>wR</i> <sub>2</sub> = 0.128
[all 5111 data]	<i>R</i> <sub>1</sub> = 0.050, <i>wR</i> <sub>2</sub> = 0.106
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.463 and −0.304

regeneration of the cobaloxime dienyl complexes (**13** and **7**) needed for cycloaddition. The cobalt salt mixture was suspended in a solution of THF and followed by the

dienyl complexes (**13** and **7**) followed by filtration of the solution to remove excess of Zn dust. Dienophile was added and the reaction mixture was refluxed for 17 h.



addition of dmg, pyridine, enyne and Zn dust in that order. The reaction mixture was refluxed for 1 h to regenerate the dienyl cobaloxime complexes (**13** and **7**) in 99% yield.

### 2.7. Completion of Fig. 1 reaction cycle

Once the individual steps of the alternative reaction cycle had been optimized, a complete cycle with no intermediate purifications or isolations was attempted. The cycle began with the synthesis of the cobaloxime

Silane was then added to the reaction pot to cleave the cobalt moiety from the cycloadduct. The solution was filtered to remove the green precipitate and the cleaved cycloadduct (**26**) was isolated by pentane extractions and radial chromatography. The green precipitate was regenerated into cobaloxime dienyl complexes (**13** and **7**). The complete cycle was attempted with dimethyl fumarate producing 23% (62% average yield for each of the three steps with no intermediate isolation) of the cleaved cycloadduct (**26**) and 28% of the regenerated dienyl complexes (**13** and **7**). (The original cobalt used

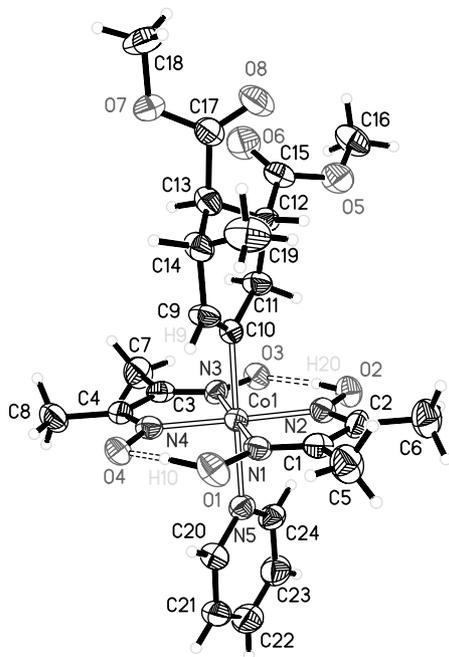


Fig. 2. Perspective drawing of the solid-state structure for  $\text{Co}(\text{N}-\text{C}_3\text{H}_5)(\text{N}_2\text{C}_2(\text{CH}_3)_2\text{O}_2\text{H})_2(\text{C}_6(\text{CH}_3)\text{H}_6(\text{CO}_2\text{CH}_3)_2)$  (**14**). All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion. Hydrogen-bonding interactions are represented with dashed open bonds.

has gone through four reaction steps: initial dienyl complex synthesis, Diels–Alder reaction, demetallation and dienyl complex regeneration to get to this point.)

### 3. Summary

In conclusion, we report here a new method for cobaloxime dienyl complex generation and Diels–Alder cycloadditions which does not require the isolation and purification of the cobalt dienyl complexes. We also report a new silane-mediated cobalt  $\text{sp}^2$ –carbon bond cleavage which yields Diels–Alder cycloadducts and cobalt salts which have been converted back into dienyl complexes in high yield. Both these observations are significant advances over our previously reported procedures [3]. While all three steps of the cycle proposed in Fig. 1 can be performed without intermediate characterization and purification, in practice, the chemical yields are higher if just the first two steps of the cycle are run in this manner. Using our optimized protocol, cobaloxime-substituted Diels–Alder cycloadducts are now isolated and purified prior to performing the silane-mediated demetallation reaction. We are directing current efforts toward development of a cycle which uses transmetallation rather than hydrometallation for initial dienyl complex synthesis.

### 4. Experimental

#### 4.1. General

Proton nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance 300 MHz spectrometer operating at 300.1 MHz or a Bruker 500 MHz spectrometer operating at 500.1 MHz.  $^{13}\text{C}$ -NMR spectra were obtained using a Bruker 300 MHz spectrometer

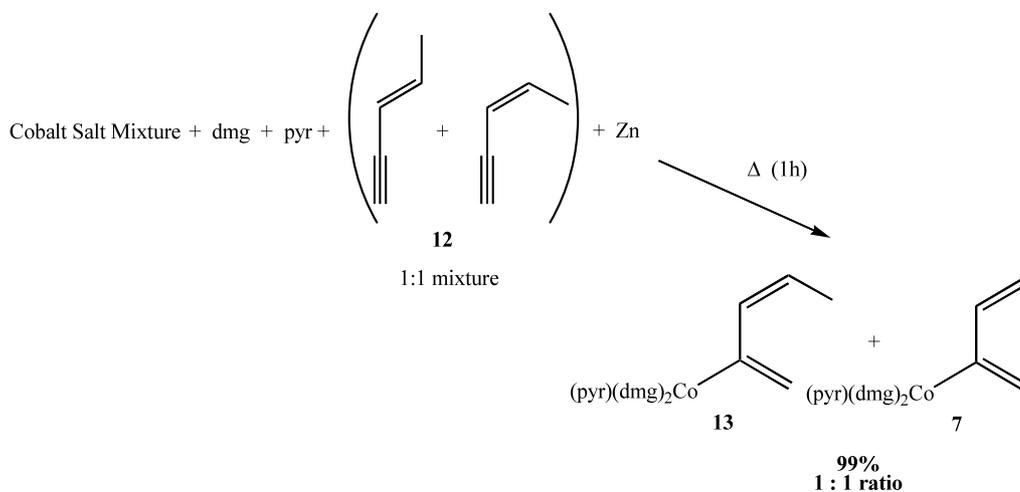


Table 2  
Selected bond lengths and angles in crystalline (1,2-dicarboxylic acid dimethyl ester-3-methyl-4-cyclohexen-5-yl)pyridinebis(dimethylglyoximate)cobalt<sup>a</sup>

Bond length (Å)	
Co <sub>1</sub> –N <sub>1</sub>	1.894(5)
Co <sub>1</sub> –N <sub>2</sub>	1.894(5)
Co <sub>1</sub> –C <sub>10</sub>	2.001(6)
O <sub>5</sub> –C <sub>15</sub>	1.344(7)
O <sub>5</sub> –C <sub>16</sub>	1.453(7)
O <sub>6</sub> –C <sub>15</sub>	1.193(7)
C <sub>9</sub> –C <sub>10</sub>	1.323(8)
C <sub>9</sub> –C <sub>14</sub>	1.519(8)
C <sub>10</sub> –C <sub>11</sub>	1.514(7)
C <sub>11</sub> –C <sub>12</sub>	1.531(7)
C <sub>13</sub> –C <sub>14</sub>	1.540(8)
Co <sub>1</sub> –N <sub>3</sub>	1.895(4)
Co <sub>1</sub> –N <sub>4</sub>	1.896(5)
Co <sub>1</sub> –N <sub>5</sub>	2.079(5)
O <sub>7</sub> –C <sub>17</sub>	1.347(7)
O <sub>7</sub> –C <sub>18</sub>	1.433(7)
O <sub>8</sub> –C <sub>17</sub>	1.194(7)
C <sub>9</sub> –H <sub>9</sub>	0.99(4)
C <sub>12</sub> –C <sub>15</sub>	1.494(8)
C <sub>13</sub> –C <sub>17</sub>	1.502(8)
C <sub>12</sub> –C <sub>13</sub>	1.525(8)
C <sub>14</sub> –C <sub>19</sub>	1.523(9)
Bond angle (°)	
N <sub>2</sub> –Co <sub>1</sub> –N <sub>1</sub>	81.6(2)
N <sub>2</sub> –Co <sub>1</sub> –N <sub>3</sub>	98.5(2)
N <sub>1</sub> –Co <sub>1</sub> –N <sub>4</sub>	97.7(2)
N <sub>3</sub> –Co <sub>1</sub> –N <sub>4</sub>	82.2(2)
N <sub>2</sub> –Co <sub>1</sub> –C <sub>10</sub>	88.3(2)
N <sub>1</sub> –Co <sub>1</sub> –C <sub>10</sub>	90.0(2)
N <sub>3</sub> –Co <sub>1</sub> –C <sub>10</sub>	89.1(2)
N <sub>4</sub> –Co <sub>1</sub> –C <sub>10</sub>	90.3(2)
C <sub>17</sub> –O <sub>7</sub> –C <sub>18</sub>	115.8(5)
C <sub>9</sub> –C <sub>10</sub> –C <sub>11</sub>	121.6(5)
C <sub>9</sub> –C <sub>10</sub> –Co <sub>1</sub>	120.9(4)
C <sub>11</sub> –C <sub>10</sub> –Co <sub>1</sub>	117.4(4)
C <sub>17</sub> –C <sub>13</sub> –C <sub>14</sub>	111.9(5)
N <sub>2</sub> –Co <sub>1</sub> –N <sub>5</sub>	90.9(2)
N <sub>1</sub> –Co <sub>1</sub> –N <sub>5</sub>	92.03(19)
N <sub>3</sub> –Co <sub>1</sub> –N <sub>5</sub>	88.95(19)
N <sub>4</sub> –Co <sub>1</sub> –N <sub>5</sub>	90.4(2)
N <sub>1</sub> –Co <sub>1</sub> –N <sub>3</sub>	179.0(2)
N <sub>2</sub> –Co <sub>1</sub> –N <sub>4</sub>	178.5(2)
C <sub>10</sub> –Co <sub>1</sub> –N <sub>5</sub>	177.8(2)
C <sub>15</sub> –O <sub>5</sub> –C <sub>16</sub>	116.2(5)
C <sub>10</sub> –C <sub>9</sub> –C <sub>14</sub>	124.8(5)
C <sub>10</sub> –C <sub>9</sub> –H <sub>9</sub>	124(3)
C <sub>14</sub> –C <sub>9</sub> –H <sub>9</sub>	111(3)
C <sub>10</sub> –C <sub>11</sub> –C <sub>12</sub>	113.1(5)
C <sub>15</sub> –C <sub>12</sub> –C <sub>13</sub>	112.0(5)

Atoms are labeled in agreement with Fig. 1.

<sup>a</sup> The numbers in parentheses are the estimated standard deviations in the last significant digit.

operating at 75.48 MHz. All spectra were referenced to the residual proton or carbon signals of the respective deuterated solvents. Infrared (IR) spectra were obtained on a Mattson Genesis II FTIR or Perkin–Elmer 1600 Series FTIR. All elemental analyses were performed by

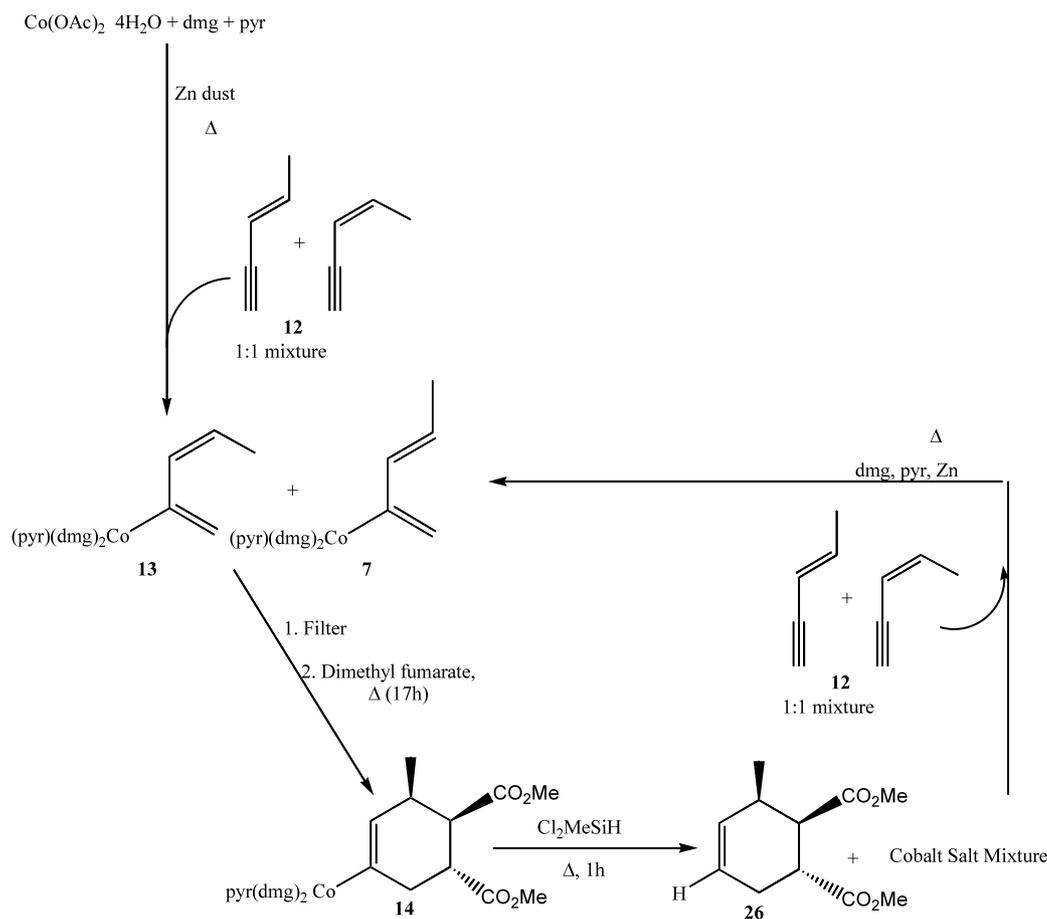
Atlantic Microlabs, Inc., Norcross, GA. High-resolution mass spectrometry was performed at the Duke Mass Spectrometry Facility, Duke University in Durham, NC. Melting points were recorded using a Mel-temp apparatus and are reported uncorrected. Thin-layer chromatography was carried out on 0.25 mm pre-coated Polygram SIL G/UV plates purchased from Bodman. Silica gel 60 purchased from Natland International Corporation was used for standard column chromatography. Silica gel 60/UV 254 purchased from EM Science was used for radial chromatography.

All reactions were carried out under a dry nitrogen atmosphere in flame-dried glassware unless otherwise specified. Tetrahydrofuran and diethyl ether were distilled under nitrogen from sodium/benzophenone immediately prior to use. Dichloromethane, pentane, toluene and benzene were distilled under nitrogen from calcium hydride immediately prior to use. Dimethyl fumarate, maleic anhydride, methyl vinyl ketone, *N*-phenyl maleimide, dichloromethylsilane, dimethylchlorosilane, diphenylsilane and triethylsilane were purchased from Aldrich and used as received. Dimethylglyoxime was purchased from Aldrich and recrystallized from 95% EtOH (12 ml g<sup>-1</sup>) prior to use. Pyridine was purchased from either Aldrich or Acros and use as received. Zinc dust and cobalt acetate hexahydrate were purchased from Strem and used as received. 3-Penten-1-yne was prepared according to a known literature procedure [14]. Control experiments where NaBH<sub>4</sub> was used for reduction or demetallation were performed using procedures we have previously reported [8].

#### 4.2. Synthesis of (3*E*)- and (3*Z*)-1,3-pentadien-2-ylpyridinebis(dimethylglyoximate)cobalt(III) (7 and 13) using Zn as reductant

Cobalt(II) acetate hexahydrate (0.489 g, 2.0 mmol) and dimethylglyoxime (0.464 g, 4.0 mmol) were dissolved in degassed THF (50 ml). Pyridine (0.475 g, 6.0 mmol) was added followed by Zn dust (0.654 g, 10.0 mmol). This mixture was refluxed for 15 min. The solution was cooled briefly to stop the reflux and 3-penten-1-yne (0.200 g, 3.0 mmol) was added. Reflux was resumed for 1 h. The reaction was cooled to 25 °C and the solution was filtered through a pad of celite (10 mm) to remove the excess Zn dust. The celite was washed with THF (3 × 15 ml). THF was removed from the combined extracts by rotary evaporation. The crude product was recrystallized from a minimum amount of hot methanol to yield **13** and **7** (0.754 g, 1.73 mmol, 87%, 1.8:1 *Z* to *E* ratio). These compounds were determined to be identical to previously reported material by <sup>1</sup>H-NMR comparison [8,13].

Table 3  
Results from silane cleavage reactions



Silane	Equivalents of silane	Heat source	Yield (cycloadduct, %)
$\text{Cl}_2\text{MeSiH}$	Four equivalents	$h\nu$	19
	Four equivalents	$\Delta$	44
	Six equivalents	$h\nu$	62
	Six equivalents	$\Delta$	85
$\text{ClMe}_2\text{SiH}$	Six equivalents	$\Delta$	22
$\text{Ph}_2\text{SiH}_2$	Six equivalents	$\Delta$	14
$\text{Et}_3\text{SiH}$	Six equivalents	$\Delta$	No Cleavage

#### 4.3. General procedure for synthesis of Diels–Alder adducts

Cobalt(II) acetate hexahydrate (0.489 g, 2.0 mmol) and dimethylglyoxime (0.464 g, 4.0 mmol) were dissolved in degassed THF (50 ml). Pyridine (0.475 g, 6.0 mmol) was added followed by Zn dust (0.654 g, 10.0 mmol). This mixture was refluxed for 15 min. The solution was cooled briefly to stop the reflux and 3-penten-1-yne (0.200 g, 3.0 mmol) was added. Reflux was resumed for 1 h. The reaction pot was cooled to stop the reflux and the warm solution was transferred to another flask via cannula fitted with a glass/fiberglass filter apparatus (on

the transferring end) to remove excess Zn dust. The Zn residue was washed with additional THF (15 ml) and the washings were transferred through the cannula. Five equivalents of the dienophile were added and the solution was refluxed for the specified amount of time. The solution was cooled to 25 °C and the solvent was removed by rotary evaporation. The residue was chromatographed on silica using EtOAc. In every case except one, the cobalt diene and the cobalt cycloadduct came off as a single band. All attempts to separate the two compounds are failed. All reported yields where residual dienyl complex (**13**) was present are percentages of the isolated products based on the NMR ratio of the

methyl doublets for the cobalt diene and the cobalt cycloadduct.

*4.3.1. Synthesis of (1,2-dicarboxylic acid dimethyl ester-3-methyl-4-cyclohexen-5-yl)pyridinebis(dimethylglyoximate)cobalt(III) (14)*

This complex was synthesized using three different methods.

*4.3.1.1. Method A (Zn was removed by chromatographic purification of 13 and 7 prior to cycloaddition).* Co diene mixture, **13** and **7** (1.010 g, 2.32 mmol) and dimethyl fumarate (0.670 g, 4.645 mmol) were dissolved in degassed THF (50 ml) and the solution was refluxed for 17 h. The solvent was removed by rotary evaporation. The residue was chromatographed on silica gel (EtOAc). The product was collected as a yellow solid (**14**) (1.195 g, 2.064 mmol, 90%). m.p.: 195–197 °C dec. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.58 (dd, *J* = 5.6, 1.3 Hz, 2H), 7.69 (tt, *J* = 7.0, 1.2 Hz, 1H), 7.28 (d, *J* = 6.5 Hz, 2H), 5.14 (dd, *J* = 5.0, 1.9 Hz, 1H), 3.64 (s, 3H), 3.59 (s, 3H), 2.83 (dd, *J* = 12.1, 6.0 Hz, 1H), 2.70 (dd, *J* = 11.5, 4.9 Hz, 1H), 2.64–2.58 (m, 1H), 2.48 (dd, *J* = 17.2, 4.9 Hz, 1H), 2.08 (s, 6H), 2.05 (s, 6H), 1.87–1.78 (m, 1H), 0.64 (d, *J* = 6.9 Hz, 3H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 176.2, 174.7, 150.1, 150.0, 149.6, 137.5, 129.4, 125.1, 51.7, 51.3, 46.0, 39.4, 35.4, 32.8, 17.8, 12.1 ppm. IR (NaCl): 2946, 1733, 1559, 1442, 1232, 1166, 1086 cm<sup>-1</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>35</sub>CoN<sub>5</sub>O<sub>5</sub>: C, 49.66; H, 6.08. Found: C, 49.57; H, 6.05%.

*4.3.1.2. Method B (no chromatographic purification of 13 and 7 and no Zn removal prior to cycloaddition).* Initial optimization of the general procedure outlined above was completed using dimethyl fumarate. The variations were as follows: the above procedure was used without removal of the Zn from the reaction flask prior to the addition of the dimethyl fumarate (0.432 g, 3.0 mmol). This reaction pot was then refluxed for 1 or 24 h. The reaction was cooled to 25 °C and the solution was filtered through a pad of celite (10 mm) to remove the excess Zn dust. The celite was washed with THF (3 × 15 ml). The THF washings were combined and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (EtOAc) to produce **13** (0.357 g, 0.820 mmol, 41%) and **14** (0.336 g, 0.581 mmol, 29%) as a yellow solid from the 1-h reaction and **13** (0.311 g, 0.715 mmol, 36%) and **14** (0.717 g, 1.24 mmol, 62%) as a yellow solid from the 24-h reaction. The product (**14**) was identical by <sup>1</sup>H-NMR spectroscopic comparison to the material isolated in method A.

*4.3.1.3. Method C (Zn removal by double-ended needle filtration prior to cycloaddition).* The general procedure outlined above using Zn removal by glass frit double-

ended needle filtration prior to the addition of dimethyl fumarate (1.441 g, 10.0 mmol) and 17-h reflux produced **13** (0.147 g, 0.339 mmol, 17%) and **14** (0.752 g, 1.30 mmol, 65%). The product (**14**) was identical by <sup>1</sup>H-NMR spectroscopic comparison to the material isolated in method A.

*4.3.2. Synthesis of trans- and cis-4-methyl-2-phenyl-3a,4,7,7a-tetrahydro-1,3-dioxoisindol-4-ylpyridinebis(dimethylglyoximate)cobalt(III) (15 and 16)*

This complex, like **14**, was synthesized with and without dienyl complex purification prior to the Diels–Alder.

*4.3.2.1. Method A (Zn removal prior to Diels–Alder by chromatographic purification of 13 and 7).* Purified cobalt dienes, **13** and **7** (0.211 g, 0.485 mmol) and *N*-phenyl maleimide (0.125 g, 0.725 mmol) were dissolved in degassed THF (15 ml) in a sealed tube. The tube was sealed under N<sub>2</sub> and heated to 100 °C for 24 h. The tube was cooled to 25 °C and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (1.5 column volumes of 1:1 pent: Et<sub>2</sub>O followed by 1.5 column volumes of EtOAc). The products (**15** and **16**, 9:1) were collected as a yellow powder (0.248 g, 0.407 mmol, 89%) after solvent removal under vacuum. m.p.: 185–187 °C dec. NMR data for major diastereomer (**15**): <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 8.60 (dd, *J* = 6.8, 1.4 Hz, 2H), 7.69 (tt, *J* = 7.6, 1.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 5.49 (dd, *J* = 6.5, 2.4 Hz, 1H), 3.04–3.02 (m, 1H), 2.80 (dt, *J* = 8.9, 2.5 Hz, 1H), 2.73 (dd, *J* = 8.9, 2.5 Hz, 1H), 2.65 (dd, *J* = 16.7, 3.3 Hz, 1H), 2.34 (ddd, *J* = 16.7, 6.8, 2.4 Hz, 1H), 1.98 (s, 12H), 1.04 (d, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 179.7, 178.9, 150.3, 150.1, 149.8, 137.6, 132.4, 131.7, 128.8, 128.4, 126.4, 125.2, 46.4, 42.2, 33.8, 29.7, 20.5, 12.0 ppm. The minor diastereomer (**16**) exhibited a methyl doublet, *J* = 7.1 Hz, at δ 1.35 ppm. IR (CDCl<sub>3</sub>): 3152, 2260, 1705, 947 cm<sup>-1</sup>. Anal. Calcd. for C<sub>28</sub>H<sub>33</sub>CoN<sub>6</sub>O<sub>6</sub>: C, 55.26; H, 5.47. Found: C, 54.79; H, 5.59%.

*4.3.2.2. Method B (Zn removed using a filter fitted double-ended needle).* The general procedure using Zn removal, *N*-phenyl maleimide (1.732 g, 10.0 mmol) and 17-h reflux produced **13** (0.0992 g, 0.228 mmol, 11%) and **15:16** (9:1) (0.880 g, 1.45 mmol, 72%). The product was identical by <sup>1</sup>H-NMR spectroscopic comparison to the material isolated and characterized in method A.

#### 4.3.3. Synthesis of *trans*- and *cis*-1,3,3a,4,7,7a-hexahydro-7-methyl-1,3-dioxo-isobenzofuran-5-ylpyridinebis(dimethylglyoximate)cobalt(III) (**17** and **18**)

The general procedure using zinc filtration, maleic anhydride (0.981 g, 10.0 mmol) and 17-h reflux produced only **17** and **18** (3:1) (0.656 g, 1.23 mmol, 62%) identical to previously reported material by <sup>1</sup>H-NMR comparison [8].

#### 4.3.4. Synthesis of *cis*- and *trans*-1-acetyl-2-methyl-3-cyclohexene-4-ylpyridinebis(dimethylglyoximate)cobalt(III) (**20** and **19**)

The general procedure using zinc filtration, methyl vinyl ketone (810  $\mu$ l, 0.700 g, 10.0 mmol) and 17-h reflux produced **13** (0.279 g, 0.640 mmol, 32%) and **20** and **19** (3.3:1) (0.462 g, 0.913 mmol, 46%). Compounds **20** and **19** were determined to be identical to previously reported material by <sup>1</sup>H-NMR comparison [8].

#### 4.4. General procedure for the cleavage of cobalt–carbon bonds with silanes

A typical procedure for the cleavage of **14** with a silane is as follows: complex **14** (0.150 g, 0.258 mmol) was dissolved in degassed THF (12 ml) and six equivalents of silane were added. The solution was refluxed under N<sub>2</sub> for 1 h. During this time, the solution turned from yellow to bluish-green due to the formation of a bluish-green precipitate. The reaction pot was cooled to 25 °C and the solvent was evaporated under a stream of N<sub>2</sub>. The residue was extracted with 3  $\times$  3 ml of pentane to isolate the cleaved cycloadduct (**26**) as a clear, pale yellow oil. The isolated product was determined to be identical to previously reported material by <sup>1</sup>H-NMR comparison [17]. The remaining solid was washed with CHCl<sub>3</sub> leaving a bluish-green precipitate. The solid was analyzed by MS and determined to be a mixture of salts consisting primarily of [(pyrCoCl<sub>3</sub>)]<sup>-</sup>(pyrH<sup>+</sup>) and (pyr)<sub>2</sub>CoCl<sub>2</sub>. The exact composition of the salt was not able to be determined.

##### 4.4.1. Cleavage of **14** with Cl<sub>2</sub>MeSiH and regeneration of **13** and **7**

Initial optimization of the general procedure above was performed using Cl<sub>2</sub>MeSiH. Variations were as follows: (i) Cl<sub>2</sub>MeSiH (165  $\mu$ l, 121.6 mg, 1.58 mmol) and 1-h irradiation with light (flood lamp) produced **26** (10.4 mg, 0.049 mmol, 19%); (ii) Cl<sub>2</sub>MeSiH (110  $\mu$ l, 121.6 mg, 1.06 mmol) and 1-h reflux produced **26** (24.0 mg, 0.113 mmol, 44%); (iii) Cl<sub>2</sub>MeSiH (165  $\mu$ l, 182.3 mg, 1.58 mmol) and 1-h irradiation with light (flood lamp) produced **26** (33.9 mg, 0.160 mmol, 62%); (iv) Cl<sub>2</sub>MeSiH (165  $\mu$ l, 182.3 mg, 1.58 mmol) and 1-h reflux produced **26** (46.8 mg, 0.221 mmol, 86%); (v) in a separate

experiment, the cleavage reaction described in part (iv) was coupled with the cobalt regeneration procedure described below using 0.195 g (0.336 mmol) of **14** as starting material. The desired cycloadduct, **26**, was isolated in 75% yield (53.6 mg, 0.253 mmol) and 99% of cobalt was regenerated as **13** and **7** (144 mg, 0.331 mmol).

##### 4.4.2. Regeneration of cobalt salt mixture to **13** and **7**

The bluish-green solid (0.226 g) obtained from the optimized Cl<sub>2</sub>MeSiH cleavage of **14** (0.336 mmol) described above was suspended in degassed THF (15 ml). Dimethylglyoxime (0.080 g, 0.69 mmol), pyridine (0.082 g, 1.03 mmol), 3-penten-1-yne (0.046 g, 0.69 mmol) and Zn dust (0.113 g, 1.73 mmol) were added in this order. The order of addition for these reactants is important. The suspension was refluxed for 1 h. During this time, the reaction pot turned from a bluish-green suspension to a yellow solution. The solution was cooled to 25 °C and filtered through a pad of celite (10 mm) to remove the excess Zn dust. The celite was washed with THF (3  $\times$  15 ml). The THF washings were combined with the filtered reaction mixture and the solvent was removed by rotary evaporation. The residue was dissolved in CHCl<sub>3</sub> and washed with 2  $\times$  10 ml distilled water, 2  $\times$  10 ml 1.2-M HCl, 1  $\times$  10 ml NaHCO<sub>3</sub> and 2  $\times$  10 ml 1-M NaOH. The aqueous extracts were combined and back-extracted with 2  $\times$  20 ml CHCl<sub>3</sub>. All CHCl<sub>3</sub> extracts were combined and dried with MgSO<sub>4</sub>. MgSO<sub>4</sub> was removed by filtration and the solvent was removed by rotary evaporation. The product was dried in vacuo to produce **13** and **7** as a yellow powder (1:1 *E* to *Z* ratio) (0.144 g, 0.331 mmol, 99%). The product was determined to be identical to previously reported **13** and **7** by <sup>1</sup>H-NMR comparison [8].

##### 4.4.3. Cleavage of **14** with ClMe<sub>2</sub>SiH

The cleavage procedure outlined above but using ClMe<sub>2</sub>SiH (180  $\mu$ l, 153.4 mg, 1.62 mmol) produced **26** (12.0 mg, 0.057 mmol, 22%).

##### 4.4.4. Cleavage of **14** with Ph<sub>2</sub>SiH

The cleavage procedure outlined above but using Ph<sub>2</sub>SiH<sub>2</sub> (300  $\mu$ l, 297.9 mg, 1.62 mmol) produced **26** (7.8 mg, 0.037 mmol, 14%).

#### 4.5. Reaction cycle procedure

Cobalt(II) acetate hexahydrate (0.489 g, 2.0 mmol) and dimethylglyoxime (0.464 g, 4.0 mmol) were dissolved in degassed THF (50 ml). Pyridine (0.475 g, 6.0 mmol) was added followed by Zn dust (0.654 g, 10.0 mmol). This mixture was refluxed for 15 min. The solution was cooled briefly to stop the reflux and 3-penten-1-yne (0.200 g, 3.0 mmol) was added. Reflux was resumed for 1 h. The reaction pot was cooled to stop reflux and the

warm solution was transferred via cannula fitted with a glass/fiberglass filter apparatus (on the transferring end) to remove excess Zn dust. The Zn residue was washed with additional THF (15 ml) and transferred through the cannula. Five equivalents of dienophile were added and refluxed for 17 h. The solution was cooled to 25 °C and Cl<sub>2</sub>MeSiH (1.38 g, 12.0 mmol) was added. The reaction pot was refluxed for 1 h. During this time, the solution turned from yellow to green due to the formation of a bluish-green precipitate. The reaction pot was cooled to 25 °C and the solid precipitate was filtered out and washed with a minimum amount of pentane (10 ml). The precipitate was set aside for dienyl complex (**13** and **7**) regeneration. The reaction pot solution and the pentane wash were combined and the solvent was removed by rotary evaporation. The residue was extracted with 3 × 5 ml of pentane. The residue is extracted to remove the cleaved cycloadduct from the large excess of dimethyl fumarate which has a limited solubility in pentane. The pentane extracts were filtered through a cotton plug and evaporated under a stream of N<sub>2</sub>. The residue from the pentane washes was chromatographed using radial chromatography on a silica gel plate eluted with 8:1 pentane:Et<sub>2</sub>O. The solvent was removed under a stream of N<sub>2</sub> and the cleaved cycloadduct was isolated. The bluish-green precipitate was washed with 2 × 20 ml of CHCl<sub>3</sub> to remove any excess of dienophile and then regenerated into **13** and **7** using the method previously discussed. The optimized reaction cycle using dimethyl fumarate (1.44 g, 10.0 mmol) produced the cleaved cycloadduct **26** (96 mg, 0.453 mmol, 23%) and recovered the cobalt as the diene **13** and **7** (1:1 *E* to *Z* ratio) (0.246 g, 0.565 mmol, 28%) identical by <sup>1</sup>H-NMR spectroscopic comparison to material reported above.

#### 4.6. X-ray crystallographic characterization of Co(NC<sub>5</sub>H<sub>5</sub>)(N<sub>2</sub>C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>O<sub>2</sub>H)<sub>2</sub>(C<sub>6</sub>(CH<sub>3</sub>)H<sub>6</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)·1.5Cl<sub>2</sub>C<sub>2</sub>H<sub>4</sub> (**14**)

Single crystals of Co(NC<sub>5</sub>H<sub>5</sub>)(N<sub>2</sub>C<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>O<sub>2</sub>H)<sub>2</sub>(C<sub>6</sub>(CH<sub>3</sub>)H<sub>6</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)·1.5 Cl<sub>2</sub>C<sub>2</sub>H<sub>4</sub> are, at 218(2) K, monoclinic, space group *C2/c-C*<sub>2h</sub><sup>6</sup> (No. 15) with *a* = 35.207(5) Å, *b* = 9.163(1) Å, *c* = 23.743(3) Å, β = 114.19(1)°, *V* = 6987(2) Å<sup>3</sup> and *Z* = 8 {*d*<sub>calcd</sub> = 1.384 g cm<sup>-3</sup>, μ<sub>a</sub>(Mo–K<sub>α</sub>) = 0.771 mm<sup>-1</sup>}. A total of 6061 independent absorption-corrected reflections having 2*T*(Mo–K<sub>α</sub>) < 48.3° (the equivalent of 0.7 limiting Cu–K<sub>α</sub> spheres) were collected on a computer-controlled Bruker-AXS P4 autodiffractometer using ω scans and graphite-monochromated Mo–K<sub>α</sub> radiation. Of these, 5111 were unique and gave *R*<sub>int</sub> = 0.048. The structure was solved using “Direct Methods” techniques with the Bruker AXS SHELXTL-PC (Version 6.12) software package. The resulting structural parameters have been refined to convergence {*R*<sub>1</sub>(unweighted, based on

*F*) = 0.063 for 2896 independent reflections having 2*T*(Mo–K<sub>α</sub>) < 48.3° and *F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)} {*R*<sub>1</sub>(unweighted, based on *F*) = 0.131 and *wR*<sub>2</sub>(weighted, based on *F*<sup>2</sup>) = 0.157 for all 5111 reflections} using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms (except disordered solvent atoms C<sub>27</sub>–C<sub>37</sub> which were refined as isotropic atoms). Hydrogen atoms H<sub>3O</sub>, H<sub>4O</sub>, H<sub>9</sub>, H<sub>25A</sub> and H<sub>25B</sub> were located from a difference Fourier map and refined as independent isotropic atoms. The methyl groups (C<sub>5</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>19</sub> and their hydrogen atoms) were refined as rigid rotors with idealized sp<sup>3</sup>-hybridized geometry and a C–H bond length of 0.97 Å. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp<sup>2</sup>- or sp<sup>3</sup>-hybridization of the carbon atoms and C–H bond lengths of 0.94–0.98 Å) “riding” on their respective carbon atoms. The isotropic thermal parameters for H<sub>3O</sub>, H<sub>4O</sub> and H<sub>9</sub> refined to final *U*<sub>iso</sub> values of 0.10(3), 0.10(3) and 0.01(1) Å<sup>2</sup>, respectively. The isotropic thermal parameters of the remaining hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded.

The crystal lattice contains three regions occupied by dichloroethane or pentane solvent molecules of crystallization. The first (half) dichloroethane molecule is ordered and sits on a crystallographic inversion center at (0, –1/2, 1/2) in the unit cell; it is specified by atoms Cl<sub>1</sub>, C<sub>25</sub>, H<sub>25A</sub> and H<sub>25B</sub>. The second dichloroethane molecule is disordered about the twofold axis at (0, *y*, 1/4) in the unit cell and specified by half-occupancy chlorine and carbon atoms designated as Cl<sub>2</sub>, Cl<sub>3</sub>, C<sub>26</sub> and C<sub>27</sub> (C<sub>27</sub> lies on the twofold axis). Hydrogen atoms were not included in the structural model for this or the third solvent molecule. The identity of the third disordered solvent molecule could not be unambiguously established as dichloroethane or pentane. A difference Fourier map of this area contained several peaks of electron density above the background level without meaningful chemical connectivity. Half-occupancy carbon atoms were placed at 10 of these sites and refined as isotropic atoms.

All calculations were performed using the SHELXTL-PC (Version 6.12) interactive software package (G. Sheldrick, Bruker AXS, Madison, WI).

## 5. Supplementary material

Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and angles and anisotropic displacement parameters for **14** have been deposited at the Cambridge Crystallographic Data Centre (CCDC

No. 212517). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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