Notes

Reactions of Cobaloximes with Alkenyl Triflates and Halides as a New Method for the Preparation of Cobalt−sp^2 Carbon Bonds

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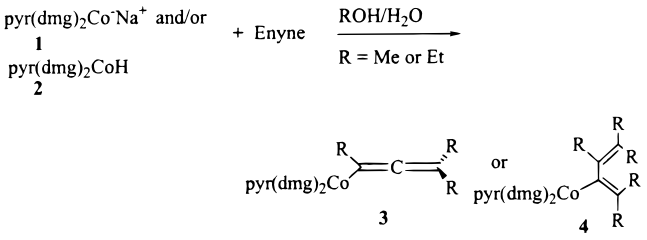
Summary: Cobaloxime complex [(pyridine)$_2$(dimethylglyoxime)$_2$Co(II)] (generated in situ) reacts with a number of alkenyl triflates and halides in the presence of zinc, providing a new, simple route to alkenyl cobaloxime compounds.

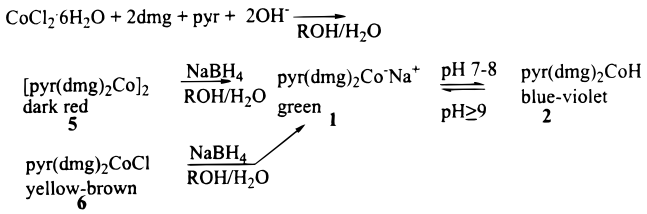
Introduction

Hydrometalation of alkynes as a route to new transition metal alkenyl complexes has been studied for over 20 years.[1] Hydrometalation of both alkenes and alkynes involving cobaloxime chemistry has also been reported, and the product outcomes of these experiments were heavily pH dependent.[2] In 1996, we reported that hydrometalation of the alkyne portion of readily available enynes could prove a mild, general alternative to our previously reported allenic electrophile route to 2-cobaloxime-substituted 1,3-dienyl complexes (**4**).[3] However, some enynes hydrometalate to give mixtures of allenes (**3**) and dienes (**4**) or hydrometalate exclusively to allenes (**3**). We have been utilizing cobaloxime- (**4**) and Co(salen)-1,3-dienyl complexes in *exo* selective and enantioselective Diels−Alder reactions;[4] therefore we have continued to search for mild methods of making cobalt−sp^2 carbon bonds. Reaction of in situ generated (pyr)$_2$(dmg)$_2$Co(II) with alkenyl triflates and halides has proven to be such a method and is described here.

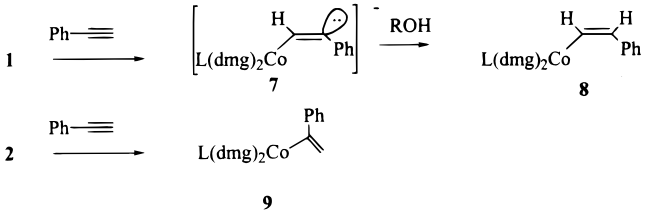


Results and Discussion

Cobaloxime anions (**1**) are typically generated by one of two methods: (i) in situ by way of reduction of the dark red cobalt(II) dimer (**5**) or (ii) via reduction of the yellow-brown preformed cobalt(III) chloride (**6**).[5] At pH ≥ 9, these aqueous alcohol solutions contain predominantly the deep green cobaloxime anion (**1**), but as the pH of the solution is lowered to 7−8, the deep blue-violet cobalt hydrides (**2**) are formed.[2,5]



Hydrometalation of alkynes via cobaloxime chemistry has also been reported.[6] Anionic complex **1** is reported to react with phenyl acetylene to yield the *β*-styryl complex **8** at pH ≥ 9, whereas **2** is reported to react with phenyl acetylene to yield the α-styryl complex **9** at pH = 7. At pH's between 7 and 9, a mixture of **8** and **9** was isolated.[6] The formation of the *cis*-alkene isomer **8** was postulated to arise from a short-lived vinyl anion intermediate (**7**).[6a,b]



In the 1970s, Gaudemer and Johnson et al. independently reported that the reaction of cobaloxime anion

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(1) For a review see: Labinger, J. A. In *Comprehensive Organic Syntheses*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 3, pp 667−702.

(2) For a review see: Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.

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

(4) Chapman, J. J.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, *19*, 1615, and references therein.

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

(6) (a) Naumberg, M.; Van Duong, K. N.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *25*, 231. (b) Van Duong, K. N.; Gaudemer, A. *J. Organomet. Chem.* **1970**, *22*, 473. (c) Johnson, M. D.; Meeks, B. S. *J. Chem. Soc. (B)* **1971**, 185. (d) Dodd, D.; Johnson, M. D.; Van Duong, K. N.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1261.

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(**1**) with *cis*- and *trans* β-bromostyrene produced *cis*-**8** and *trans*-styryl cobaloxime complexes in 30−60% isolated yields.[6] These reactions were also postulated to proceed through addition−elimination mechanisms with short-lived anionic intermediates.

We were also intrigued by a cobaloxime reduction/electrophile trapping procedure originally reported by Widdowson[7] in 1982 for making cobaloxime complexes from base and polar protic solvent sensitive α-halocarbonyl compounds. The zinc-assisted Widdowson cobaloxime preparation is reported to initially generate $Co(II)(Pyr)_2(dmg)_2$ (**10**), which then reacts with electrophiles by electron transfer chemistry rather than via cobaloxime anion **1** nucleophilic addition or cobaloxime hydride **2** hydrometalation. Widdowson et al. performed a number of control experiments to elucidate the role of the zinc in this reaction. They originally thought the zinc reacted with their α-halocarbonyl compounds to form a Reformatsky reagent. However, when the Reformatsky reagents were preformed and treated with cobaloxime(III) chloride (**6**), no alkyl cobaloximes were produced. They also performed control experiments to test for the presence of cobaloxime(I) species and found no evidence for their zinc-mediated generation in this preparation. They concluded that the function of the zinc was to regenerate cobalt(II) (**10**) from the cobalt(III) halide (**12**) that would otherwise consume half of the cobalt used in the reaction. The mechanistic scheme Widdowson proposed for α-halocarbonyl compounds is shown below and presumably also operable in the chemistry we describe here.

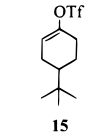
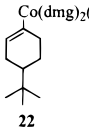
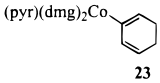
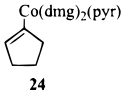
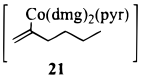
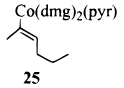
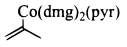
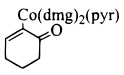
$$\underset{\textbf{10}}{(py)_2(dmgH)_2Co(II)} + \underset{\textbf{11}}{RX} \longrightarrow \underset{\textbf{12}}{py(dmgH)_2Co(III)X} + R\cdot + py$$

$$R\cdot + (py)_2(dmgH)_2Co(II) \longrightarrow \underset{\textbf{13}}{py(dmgH)_2Co(III)R} + py$$

$$2\ py(dmgH)_2Co(III)X + Zn + 2\ py \longrightarrow 2\ (py)_2(dmgH)_2Co(II) + ZnX_2$$

Since vinyl triflates are now readily available from ketones and aldehydes,[8] we decided to explore the possibility of using these substrates to make cobaloxime alkenyl complexes via Widdowson's protocol. We find that the Widdowson method of cobaloxime generation yields a cobalt species that reacts with a number of alkenyl triflates and halides to cleanly generate cobalt-substituted alkenes in high yield and stereoisomeric purity. The reaction works equally well for cyclic and acylic alkenyl triflates (entries 1, 3, 4 below), although the initially isolated cobaloxime complex **21**, containing a terminal alkene (entry 4), quickly isomerized to an internal alkene (**25**). The dienyl triflate **16** also worked but with a significantly reduced isolated yield. Alkenyl and aromatic halides proved to be poorer substrates. 2-Bromopropene (entry 5) worked reasonably well, but 2-bromo-2-cyclohexen-1-one[9] (entry 6) was a poor substrate, and 4-iodoanisole as well as 2-bromofuran failed to participate in the reaction. We also tried using Pd(0) in conjunction with cobaloxime anion **1** and triflates instead of zinc(0) and cobalt(II). We found that this presumed transmetalation/coupling scheme worked for triflate **15** (56% isolated yield of **22**) but not triflate **16** (only a 3% isolated yield of **23**). This palladium preparation is referred to as method B in the Experimental Section and involved in situ preparation of Pd(0), addition of the triflate followed by addition of cobaloxime anion **1**, and workup.

Table 1. Reactions of Alkenyl Triflates or Halides with Cobaloximes

	Alkenyl Triflate or Halide	Product	% Yield
1)	 **15**	 **22**	52
2)	 **16**	 **23**	34
3)	 **17**	 **24**	64
4)	 **18** ⇒ [ **21**] ⇒	 **25**	70
5)	 **19**	 **26**	49
6)	 **20**	 **27**	4

In summary, the ready availability of alkenyl triflates coupled with the ease of this preparative method should make this zinc-mediated cobaloxime reduction the method of choice for preparing most simple cobaloxime-substituted alkenes (Table 1).

$$\underset{\textbf{14}}{Co(OAc)_2\cdot 4H_2O} \xrightarrow{DMG,\ pyridine} \underset{\textbf{10}}{(DMG)_2(pyr)_2Co(II)} \xrightarrow[\text{or halide}\ Zn\ dust,\ THF]{\text{alkenyl triflate}} (DMG)_2(pyr)Co(III)(\eta^1\text{-alkene})$$

Experimental Section

General Procedures. All nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVANCE 300 FT NMR. All absorptions were expressed in parts per million relative to residual protonated solvent. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR. All elemental analyses were performed by Atlantic Microlab, Inc. of Norcross, GA. High-resolution mass spectral analyses were performed by the Duke University Mass Spectrometry Facility. Melting points were determined on a Mel-Temp apparatus and are reported uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen immediately prior to use. Dichloromethane was distilled from calcium hydride immediately prior to use. All reactions were carried out under an atmosphere of dry nitrogen. Cobalt acetate tetrahydrate was purchased from Strem Chemicals and used

(7) Roussi, P. F.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1025.
(8) (a) Scott, W. J.; Crisp, G. T.; Stille, J. K. *Org. Synth.* **1989**, *68*, 116. (b) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500. (c) Karlstrom, A. S. E.; Ronn, M.; Thorarensen, A.; Backvall, J. E. *J. Org. Chem.* **1998**, *63*, 2517.
(9) Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *J. Org. Chem.* **1968**, *33*, 1454.

as received. Dimethylglyoxime was purchased from Fischer Scientific and recrystallized from 95% EtOH (12 mL/g) prior to use. All alkenyl triflates used have been reported previously: **15**,[8a] **16**[8b,c] **17**,[10] **18**.[11] 2-Bromo-2-cyclohexen-1-one (**20**) was also prepared according to a literature procedure.[9] 2-Bromopropene, zinc dust, and pyridine were purchased from Aldrich and used as received. All reactions were performed under an atmosphere of nitrogen unless specified otherwise.

4-*tert*-Butyl-1-cyclohexen-1-ylpyridinebis(dimethylglyoximato)cobalt(III) (22). This complex was synthesized using two different procedures. **Method A**: Cobalt(II) acetate tetrahydrate (0.501 g, 2.01 mmol), dimethylglyoxime (0.466 g, 4.01 mmol), and pyridine (0.485 mL, 6.00 mmol) were combined in a flame-dried flask and dissolved in dry, degassed THF (50 mL). Zinc dust (0.660 g, 10.1 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 4-*tert*-butylcyclohexen-1-yl triflate (**15**) (0.859 g, 3.00 mmol) was added. The reaction mixture was reheated and refluxed for 1 h. The mixture was cooled to 25 °C and filtered through a Celite pad to remove excess zinc dust. The solvent was removed under reduced pressure, and the residue was dissolved in $CHCl_3$ (50 mL). The $CHCl_3$ was washed with H_2O (2 × 10 mL), and the H_2O layers were combined and back extracted with addition $CHCl_3$ (5 × 10 mL). All the $CHCl_3$ extracts were combined and dried with $MgSO_4$. The $MgSO_4$ was removed by filtration, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using EtOAc to yield the product (**22**) as a bright yellow solid (0.521 g, 1.03 mmol, 52%). Mp: 162−164°C dec. ^{1}H NMR ($CDCl_3$): 8.57 (dd, J = 6.3, 1.4 Hz, 2H), 7.62 (tt, J = 7.6, 1.4 Hz, 1H), 7.22 (t, J = 6.3 Hz, 2H), 4.96 (m,1H), 2.13−1.97 (m, 3H), 2.03 (s, 12H), 1.86−1.78 (m, 2H), 1.06−1.02 (m, 2H), 0.71 (s, 9H). ^{13}C NMR ($CDCl_3$): 150.40, 150.02, 149.77, 137.69, 125.41, 124.85, 44.92, 35.18, 32.37, 30.44, 27.96, 27.64, 12.48. IR (NaCl): 2957, 1559, 1448, 1232, 1088, 1070, 1037 cm^{-1}. Anal. Calcd for $C_{23}H_{35}CoN_5O_4$: C, 54.76; H, 6.99. Found: C, 54.43; H, 7.25. **Method B**: Pd(Ph_3P)$_2Cl_2$ (5 mg, 0.007 mmol) and CuI (3 mg, 0.03 mmol) were combined in a flame-dried flask under N_2 and dissolved in dry, degassed THF (5 mL). Diisobutylaluminum hydride (13 μL of a 1 M solution in THF, 0.014 mmol) was added, and the solution was stirred for 15 min at 25 °C. 4-*tert*-Butylcyclohexen-1-yl triflate (**15**) (209 mg, 0.731 mmol) was then added, and the solution was stirred at 25 °C for 30 min. The reaction mixture was cooled to 0 °C and stirred for 10 min. The cobaloxime anion (**1**) was then generated by adding (pyr)(dmg)$_2$Co−I[5] (308 mg, 0.624 mmol) followed by lithium borohydride (350 μL of a 2 M solution in THF, 0.70 mmol). The reaction was stirred at 0° C for 5 h and then quenched by pouring the mixture into a solution of ice water (50 mL) containing 5 drops of pyridine. The reaction mixture was extracted with CH_2Cl_2 (5 × 50 mL). The CH_2Cl_2 layers were combined and dried with $MgSO_4$. The $MgSO_4$ was removed by filtration, and the solvent was evaporated under reduced pressure. The crude product was purified using column chromatography on silica gel (EtOAc) to yield the product (**22**) as a bright yellow solid (180 mg, 0.357 mmol, 56%). The product was identical by spectroscopic comparison to the material isolated using method A reported above.

1,3-Cyclohexadien-2-ylpyridinebis(dimethylglyoximato)cobalt(III) (23). This complex was also synthesized using these two different procedures. **Method A**: Cobalt(II) acetate tetrahydrate (0.240 g, 0.964 mmol), dimethylglyoxime (0.222 g, 1.92 mmol), and pyridine (0.24 mL, 2.88 mmol) were combined in a flame-dried flask and dissolved in freshly distilled, degassed THF (40 mL). Zinc dust (0.332 g, 5.07 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 1,3-cyclohexadiene-2-yl triflate (**16**) (0.859 g, 3.00 mmol) was added. The reaction was then continued as described under method A above. The crude product was purified by column chromatography on silica gel (EtOAc) to yield the product (**23**) as a bright yellow solid (0.145 g, 0.324 mmol, 34%). Mp: 135−137 °C dec. ^{1}H NMR ($CDCl_3$): 8.66 (dd, J = 5.6, 1.7 Hz, 2H), 7.71 (tt, J = 7.1, 1.4 Hz, 1H), 7.31 (t, J = 6.7 Hz, 2H), 5.95 (dd, J = 10.3, 1.2 Hz, 1H), 5.40 (dt, J = 9.5, 3.9 Hz, 1H), 5.32 (t, J = 3.9 Hz, 1H), 2.18−2.03 (m, 2H), 2.11 (s, 12H), 1.84−1.77 (m, 2H). ^{13}C NMR ($CDCl_3$): 150.52, 150.25, 137.89, 131.56, 126.99, 125.52, 123.00, 26.10, 23.16, 12.54. IR (NaCl): 2926, 1603, 1561, 1448, 1234, 1154, 1089 cm^{-1}. Anal. Calcd for $C_{19}H_{26}CoN_5O_4$: C, 51.01; H, 5.86. Found: C, 52.12; H, 6.70. FAB HRMS (*m*/*e*) calcd for $C_{19}H_{27}O_4N_5Co$: 448.1395. Found: 448.1400. **Method B**: Pd(Ph_3P)$_2Cl_2$ (8 mg, 0.01 mmol) and CuI (3 mg, 0.03 mmol) were combined in a flame-dried flask under N_2 and dissolved in dry, degassed THF (5 mL). Diisobutylaluminum hydride (22 μL of a 1 M solution in THF, 0.022 mmol) was added and stirred for 15 min at 25 °C. The 1,3-cyclohexadien-2-yl triflate (**16**) was prepared and used without purification and cooled to 0 °C, and the reduced Pd/Cu solution was added to the triflate via cannula and stirred at 0 °C for 30 min. The cobaloxime anion (**1**) was then generated in a separate flask by combining (pyr)(dmg)$_2$Co−I[5] (0.534 mg, 1.08 mmol) and lithium borohydride (600 μL of a 2 M solution in THF, 1.20 mmol) in THF at 0 °C and stirring for 30 min. The cobaloxime anion (**1**) was added via a double-ended needle into the reaction vessel containing the triflate and stirred at 0 °C for 5 h. The reaction was warmed slowly to 25 °C overnight and quenched after 20 h by pouring the mixture into a solution of ice water (50 mL) containing 5 drops of pyridine. The remainder of the workup was as described for method B above. The crude product was purified using column chromatography on silica gel (EtOAc) to yield the product (**23**) as a bright yellow solid (16.1 mg, 0.036 mmol, 3%). The product was identical by spectroscopic comparison to the material prepared using method A.

1-Cyclopenten-1-ylpyridinebis(dimethylglyoximato)cobalt(III) (24). Cobalt(II) acetate tetrahydrate (0.500 g, 2.01 mmol), dimethylglyoxime (0.465 g, 4.01 mmol), and pyridine (0.490 mL, 6.06 mmol) were combined in a flame-dried flask and dissolved in freshly distilled, degassed THF (50 mL). Zinc dust (0.670 g, 10.2 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 1-cyclopenten-1-yl triflate (**17**) (0.679 g, 3.14 mmol) was added. The reaction mixture was reheated and refluxed for 1 h. The mixture was then cooled to 25 °C and quenched by pouring into a solution of ice water (50 mL) containing 5 drops of pyridine. The remainder of the workup was performed as described above except no chromatography was required. The product (**24**) was a bright yellow solid (0.556 g, 1.28 mmol, 64%). Mp: 202−203.5 °C dec. ^{1}H NMR ($CDCl_3$): 8.64 (dd, J = 6.3, 1.3 Hz, 2H), 7.71 (tt, J = 7.6, 1.5 Hz, 1H), 7.31 (t, J = 6.6 Hz, 2H), 5.11 (m, 1H), 2.26−2.16 (m, 4H), 2.08 (s, 12H), 1.63 (pentet, J = 3.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): 150.34, 149.81. 137.91, 127.34, 125.52, 38.36, 32.24, 23.14, 12.39. IR ($CDCl_3$): 3690, 2927, 2845, 2337, 2275, 1605, 1563, 1449, 1232, 1088, 1071 cm^{-1}. Anal. Calcd for $C_{18}H_{26}CoN_5O_4$: C, 49.66; H, 6.02. Found: C, 49.67; H, 5.99.

(*E*)-2-Hexen-2-ylpyridinebis(dimethylglyoximato)cobalt(III) (25). Cobalt(II) acetate tetrahydrate (0.999 g, 4.01 mmol), dimethylglyoxime (0.929 g, 8.01 mmol), and pyridine (0.980 mL, 12.1 mmol) were combined in a flame-dried flask and dissolved in freshly distilled, degassed THF (50 mL). Zinc dust (1.362 g, 20.8 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 1-hexen-2-yl triflate (**18**) (1.406 g, 6.05 mmol) was added. The reaction mixture was reheated and refluxed for 1 h. The mixture was then cooled to 25 °C and quenched by pouring into a solution of ice water (50 mL) containing 5 drops of pyridine. The remainder of the workup was performed as

(10) Dueber, T. E. *Angew. Chem., Intl. Ed. Engl.* **1970**, *9*, 521
(11) Sumerville, R. H.; Senkler, C. A.; Von Schleyer, P.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 1100.

described above. By ^{1}H NMR, the crude product, prior to chromatography, had spectroscopic data consistent with structure **21**. ^{1}H NMR ($CDCl_3$) (**21**): 8.64 (dd, J = 6.3, 1.5 Hz, 2H), 7.68 (tt, J = 7.6, 1.5 Hz, 1H), 7.28 (t, J = 6.3 Hz, 2H), 4.70 (d, J = 1.9 Hz, 1H), 4.17 (d, J = 2.0 Hz, 1H), 2.07 (s, 12H), 2.01 (m, 2H), 1.26 (m, 4H), 0.80 (t, J = 7.4 Hz, 3H). The crude product was purified by column chromatography on silica gel (EtOAc) to yield the product (**25**) as a bright yellow solid (1.268 g, 2.81 mmol, 70%). Mp: 188.5−190 °C dec. ^{1}H NMR ($CDCl_3$): 8.64 (dd, J = 6.3, 1.5 Hz, 2H), 7.68 (tt, J = 7.6, 1.5 Hz, 1H), 7.28 (t, J = 6.3 Hz, 2H), 4.88 (t, J = 7.1 Hz, 1H), 2.07 (s, 12H), 2.01 (m, 2H), 1.44 (s, 3H), 1.26 (sextet, J = 7.2 Hz, 2H), 0.73 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): 150.48, 149.90, 137.67, 128.62, 125.42, 31.02, 23.01, 20.12, 13.51, 12.39. IR (NaCl): 2924, 2854, 1603, 1448, 1227, 1078, 1035 cm^{-1}. Anal. Calcd for $C_{19}H_{30}CoN_5O_4$: C, 50.55; H, 6.70. Found: C, 50.90; H, 6.69.

1-Propen-2-ylpyridinebis(dimethylglyoximato)cobalt-(III) (26). Cobalt(II) acetate tetrahydrate (0.966 g, 3.88 mmol), dimethylglyoxime (0.930 g, 8.02 mmol), and pyridine (0.980 mL, 12.1 mmol) were combined in a flame-dried flask and dissolved in freshly distilled, degassed THF (50 mL). Zinc dust (1.545 g, 23.6 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 2-bromopropene (**19**) (0.540 mL, 6.08 mmol) was added. The reaction mixture was reheated and refluxed for 1 h. The mixture was then cooled to 25 °C and quenched by pouring into a solution of ice water (50 mL) containing 5 drops of pyridine. The remainder of the workup was performed as described above. The crude product was purified by column chromatography on silica gel (EtOAc) to yield the product (**26**) as a bright yellow solid (0.807 g, 1.967 mmol, 49%). Mp: 165.0−166.5 °C dec. ^{1}H NMR ($CDCl_3$): 8.67 (dd, J = 6.4, 1.5 Hz, 2H), 7.73 (tt, J = 7.6, 1.5 Hz, 1H), 7.33 (t, J = 5.6 Hz, 2H), 4.64 (s, 1H), 4.30 (s, 1H), 2.11(s, 12H), 1.64, (d, J = 1.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): 150.40, 150.10, 137.88, 125.53, 114.68, 28.49, 12.46. IR (NaCl): 2930, 1591, 1558, 1448, 1232, 1086, 1074, 1036. Anal. Calcd for $C_{16}H_{24}CoN_5O_4$: C, 46.83; H, 6.14. Found: C, 46.57; H, 5.87. FAB HRMS (*m*/*e*) calcd for $C_{16}H_{25}CoN_5O_4$: 409.1160. Found: 409.1158.

2-Cyclohexen-1-on-2-ylpyridinebis(dimethylglyoximato)cobalt(III) (27). Cobalt(II) acetate tetrahydrate (0.500 g, 2.01 mmol), dimethylglyoxime (0.465 g, 4.01 mmol), and pyridine (0.490 mL, 6.06 mmol) were combined in a flame-dried flask and dissolved in freshly distilled, degassed THF (50 mL). Zinc dust (0.713 g, 10.9 mmol) was added, and the solution was refluxed for 15 min. The solution was cooled to 25 °C, and 2-bromo-2-cyclohexen-1-one (**20**) (0.522 g, 3.00 mmol) was added.[5] The reaction mixture was reheated and refluxed for 1 h. The mixture was then cooled to 25 °C and filtered through a Celite pad to remove excess zinc dust. The solvent was evaporated under reduced pressure. The residue was dissolved in a minimal amount of $CHCl_3$ and purified by column chromatography on silica gel (EtOAc) to yield the product as a bright yellow solid (**27**) (0.038 g, 0.082 mmol, 4%). Mp: 177−179 °C dec. ^{1}H NMR ($CDCl_3$): 8.65 (dd, J = 6.3, 1.4 Hz, 2H), 7.69 (tt, J = 7.6, 1.4 Hz, 1H), 7.28 (t, J = 7.0, 2H), 6.47 (t, J = 4.3 Hz, 1H), 2.33−2.28 (m, 4H), 2.10 (s, 12H), 1.74 (pentet, J = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): 201.03, 152.07, 150.54, 150.31, 137.96, 125.46, 42.07, 29.77, 24.05, 12.65. IR (NaCl): 2924, 1670, 1653, 1540, 1087, 1072 cm^{-1}. Anal. Calcd for $C_{19}H_{26}CoN_5O_5$: C, 49.25; H, 5.66. Found: C, 50.30; H, 6.03. FAB HRMS (*m*/*e*) calcd for $C_{19}H_{27}O_5N_5Co$: 463.1266. Found: 463.1264.

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