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THE CHEMISTRY OF η^5-CpCo(CO)(maleoyl) AND η^5-CpCo(CO)(phthaloyl) COMPLEXES

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Summary

Insertion of η^5-CpCo(CO)$_2$ into dimethylcyclobutenedione and benzocyclobutenedione gave high yields of η^5-CpCo(CO)(dimethylmaleoyl) and η^5-CpCo(CO)(phthaloyl); respectively. Replacement of the carbon monoxide ligand in these complexes with thermally labile ligands (CH_3CN, PhCN, C_5H_5N, $(C_2H_5)_2S$) allowed a facile reaction with alkynes to occur. The maleoyl cobalt complex gave very high yields of stable η^5-CpCo(benzoquinone) complexes which cleaved to the free quinones on treatment with cerium(IV). The phthaloylcobalt complex reacted to form unstable η^5-CpCo(naphthoquinone) complexes and free naphthoquinones.

Introduction

In 1974 Dickson and Kirsch reported the isolation of maleoylcobalt complex **1** and duroquinone complex **2**, as well as free duroquinone, in low yields from the thermal reaction of 2-butyne with η^5-CpCo(CO)$_2$ [1]. Because of our interest in maleoylmetal and phthaloylmetal complexes as synthetically viable precursors to benzoquinones and naphthoquinones; respectively [2–9], we were intrigued by the simultaneous formation of **1** and **2** in the same reaction mixture. Although Dickson and Kirsch reported that treatment of **1** with excess 2-butyne at 120°C did not produce any duroquinone complex **2** (**1** was quantitatively recovered after 20 h at 120°C) [1], we decided to search for a practical synthesis of η^5-CpCo complexes such as **1** and explore their reactions with alkynes as a possible route to quinones and/or their cobalt complexes. We now report a simple, high-yield synthesis of maleoylcobalt complex **1** and phthaloylcobalt complex **3** and the facile reaction of these compounds with alkynes to form quinones when the carbon monoxide ligand is replaced with a readily dissociable ligand.

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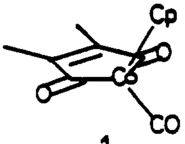

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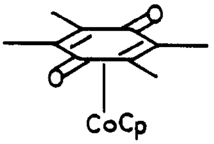

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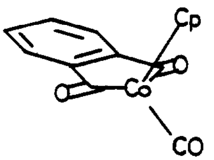


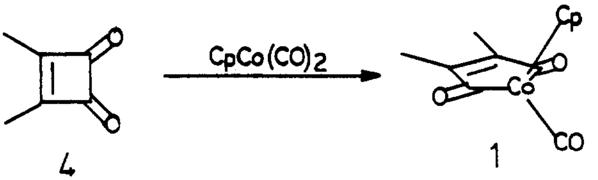
3

Results

Synthesis of the cobalt complexes

Based on our previous successful insertions of low-valent transition metal complexes into benzocyclobutenediones [2,4,5,7,9] and cyclobutenediones [6,8,9] we anticipated that maleoylcobalt complex **1** and phthaloylcobalt complex **3** should be preparable according to equations 1 and 2. According to plan, reaction of 3,4-dimethylcyclobut-3-ene-1,2-dione (**4**) [6] and benzocyclobutenedione (**5**) [5] with η^5-CpCo(CO)$_2$ under argon in refluxing xylene gave dimethylmaleoylcobalt complex **1** (80%) and phthaloylcobalt complex **3** (98%); respectively, after chromatography.

As previously described [1], complex **1** was an air-stable, yellow crystalline solid soluble in a variety of solvents. The orange-yellow phthaloylcobalt complex **3**, m.p. 132–133°C (Et$_2$O), showed solubility properties and air stability similar to **1**.



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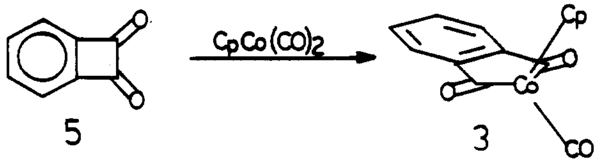

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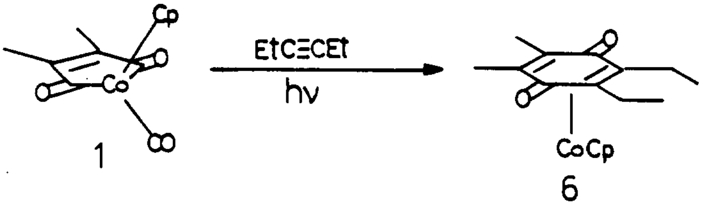
Reactivity studies of maleoylcobalt complex 1

In contrast to the observation of Dickson and Kirsch, [1] we found a very slow reaction of **1** with 3-hexyne at 120°C in xylene (a trace of quinone complex was observed by TLC after 5 h; after 16 h at 120°C and 24 h at 140°C η^5-CpCo(2,3-diethyl-5,6-dimethylbenzoquinone) was isolated in 24% yield along with 76% of recovered **1**). Since no precautions were taken to protect the thermal reaction from light, we cannot discount the slow formation of the quinone complex by a photochemical pathway (vida infra). Given the reasonable thermal stability of **1** (note the conditions of its synthesis), it was not surprising to us that this coordinatively saturated, 18-electron complex was poorly reactive with alkynes, and we presumed that a reasonable prerequisite for reaction was formation of a 16-electron complex by loss of the carbon monoxide ligand. In accord with this postulate, photochemically induced loss of CO from **1** in the presence of 3-hexyne gave the quinone complex **6** in 94% yield after photolysis for 24 h in benzene (eq. 3).



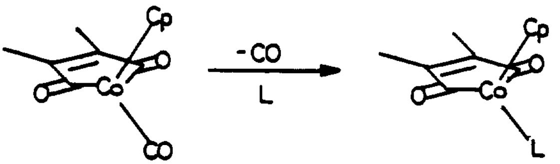
(3)

Having established CO loss as the mechanistic link from maleoylcobalt complex **1** to quinone complex **2**, we turned our attention to the synthesis of related maleoylcobalt complexes in which the carbon monoxide ligand was replaced by a thermally labile ligand. Our goal was to synthesize a maleoylcobalt complex related to **1** that could be stored in a bottle and would rapidly react with alkynes on moderate warming to give benzoquinone complexes. Using photochemical and oxidative ($Me_3N \rightarrow O$) [10–12] techniques for removing the carbon monoxide ligand from **1**, we were able to synthesize stable, crystalline complexes **7**–**9** in very good yields (Table 1). The $Me_3N \rightarrow O$ technique was attempted in all three cases shown in Table 1, but only gave good yields in the replacement of CO by pyridine.

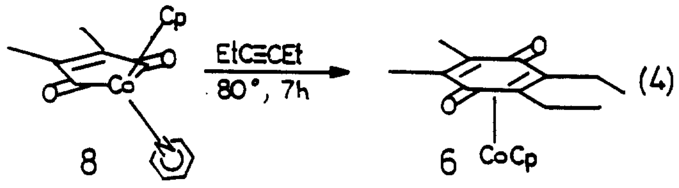
The PPh_3 complex, **7**, showed no evidence of reaction with 3-hexyne after 15 h at 100°C in CH_2Cl_2 (sealed tube). However, when pyridine was the auxiliary ligand (**8**), reaction with 3-hexyne (1.5 equiv.) proceeded smoothly in a number of solvents at 80°C to give good yields of benzoquinone complex **6** within 7 h (eq. 4). Even though unreacted **8** remained in each reaction, longer reaction times did not significantly increase the yield of **6**. We attributed this phenomenon to a decrease in the concentration of the reactive, 16-electron maleoylcobalt complex caused by the increasing concentration of free pyridine in solution as the reaction proceeded.

The diethylsulfide complex **9** proved even more to be reactive than its pyridine counterpart, **8**. Reaction of **9** with a variety of alkynes (1.5 equiv.) occurred within a few hours at 80°C in dichloroethane to give very good yields of stable, η^5-CpCo(benzoquinone) complexes. Excellent isolated yields could be achieved in less than 2 h simply by increasing the equivalents of alkyne used (Table 2). Although various

TABLE 1



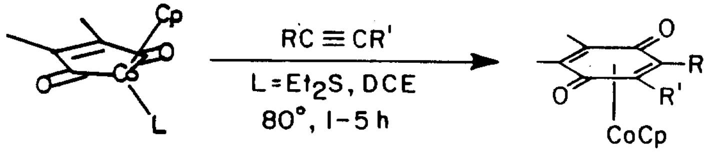
Reaction conditions	Complex	Yield(%)
$h\nu$, PPh_3, PhH	**7**, L = PPh_3	72
Me_3NO, C_5H_5N	**8**, L = C_5H_5N	75
$h\nu$, Et_2S, CH_2Cl_2	**9**, L = Et_2S	88



Solvent	%6	%8
C_6H_6	58	33
DME	68	26
DCE	86	13

benzoquinone complexes have been reported previously [1,13–26], the method described in this manuscript represents the first general and high yield approach to such highly functionalized quinone complexes. Consistent with the previously described properties of the duroquinone complex **2**, all of our quinone complexes were very polar, deeply colored materials which showed good solubility in H_2O and alcohol solvents and variable solubility in CH_2Cl_2 and THF. The more lipophilic the quinone substituents were, the better the observed solubility in the latter solvents. All of the quinone complexes were hygroscopic to varying degrees, but otherwise they were very air-stable.

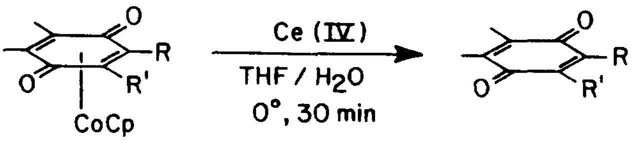
TABLE 2



R	R'	yield (%) complex
Et	Et	90
H	Bu	96
OEt	Et	97
Et	$COCH_3$	90
Me	$C(Me)=CH_2$	91
H	CH_2Cl	97
H	CH_2NHBz	61
Me	CH_2OEt	80
H	CH_2OH	82

The free benzoquinones could be liberated from the cobalt in high yield on treatment with ceric ammonium nitrate in THF/H_2O. Five representative examples are shown in Table 3. The high yields associated with the overall transformation from cyclobutenedione **4** to the substituted benzoquinones could make this procedure competitive with our previously described benzoquinone synthesis [8] if the preparation of maleoylcobalt complexes such as **1** proves to be general.

TABLE 3

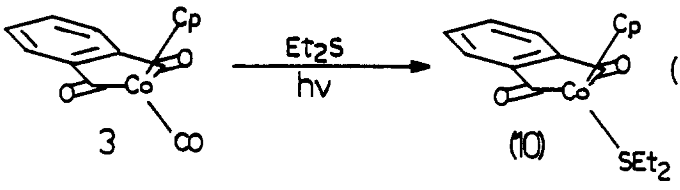


R	R'	yield (%) quinone
Et	Et	87
H	Bu	85
OEt	Et	91
Et	$COCH_3$	84
Me	$C(Me)=CH_2$	84

Reactivity studies of phthaloylcobalt complex 3

Phthaloylcobalt complex **3** was inert to reaction with 3-hexyne at 120°C after 12 h in toluene, CH_2Cl_2 or CH_3CN (sealed tube). However, photolysis of a benzene solution of **3** for 24 h in the presence of 3-hexyne gave 2,3-diethyl-1,4-naphthoquinone in 91% isolated yield. Photolysis of **3** in the presence of 1-hexyne was less efficient and gave 2-n-butyl-1,4-naphthoquinone in 40% yield. In contrast to the formation of very stable η^5-CpCo(benzoquinone) complexes in the maleoyl series, the direct formation of the free naphthoquinones in this reaction was consistent with the expected lower stability of a η^5-CpCo(naphthoquinone) complex. For the naphthoquinone to function as a four electron donor, aromaticity would have to be broken.

Following the leads we established in the maleoyl series, we next replaced the photo-labile CO of **3** with a number of thermally labile ligands in order to explore the practical preparation of naphthoquinones. Replacement of CO by Et_2S, the most reactive ligand in the maleoyl system, was accomplished in 81% yield by photolysis of complex **3** in the presence of 10 equivalents of Et_2S (eq. 5). However, the new compound **10**, proved too stable to react with 3-hexyne at 80°C in dichloroethane within 6 h. In an attempt to increase the reactivity of the diethylsulfide complex **10**, we theorized that oxidation of the coordinated diethylsulfide to a sulfoxide would labilize the ligand and allow reaction with the alkyne to occur. In the event, treatment of **10** with 1.1 equivalents of *m*-chloroperbenzoic acid at $-78°C$ in CH_2Cl_2 followed by addition of 3-hexyne and warming to room temperature led to the isolation of η^5-CpCo(2,3-diethyl-1,4-naphthoquinone) (**11**) in 42% yield (eq. 6). Although the yield of naphthoquinone complex **11** was not spectacular in this case, the novel and mild conditions of its synthesis are worth emphasizing – oxidative labilization of organic sulfide ligands may prove to be a mild means of generating coordinatively unsaturated metal complexes.



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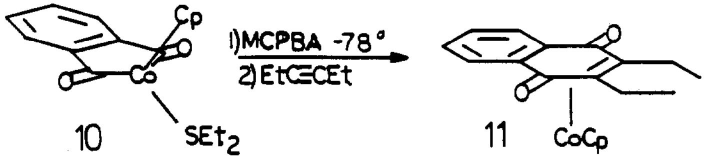
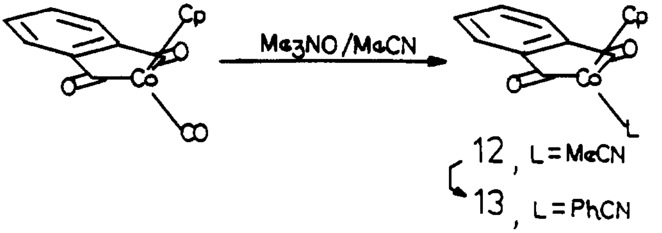


(6)

The successful oxidative activation of the diethylsulfide complex led us to attempt direct reaction of the parent CO system, **3**, with alkynes in the presence of an amine *N*-oxide. At 0°C in CH_2Cl_2, addition of $Me_3N \rightarrow O$ to a solution of **3** and 3-hexyne caused the formation of naphthoquinone complex **11** in 39% yield. A similar reaction in acetone gave **11** in 24% yield. Use of the terminal alkyne, 1-hexyne, in place of 3-hexyne led directly to the free naphthoquinone, 2-n-butyl-1,4-naphthoquinone, in 30–40% isolated yield. In some cases, the naphthoquinone complex could be observed by TLC, but the η^5-CpCo complex of the monosubstituted naphthoquinone appeared much less stable than the disubstituted system, **11**.

In a search for a phthaloylcobalt complex with a ligand more labile than diethylsulfide, we prepared the acetonitrile and benzonitrile complexes, **12** and **13**



(7)

(eq. 7). Both of these new complexes showed reasonable reactivity with 3-hexyne. Heating 3-hexyne with the acetonitrile complex **12** in dichloroethane at 80°C for 3 h gave **11** in 28% yield along with 55% of free, 2,3-diethyl-1,4-naphthoquinone. The more reactive benzonitrile system **13** produced the quinone complex in 62% yield in 1 h at 80°C in dichloroethane. Presumably, the difference in yields of the moderately unstable naphthoquinone complex **11** can be attributed to the shorter reaction time required for the benzonitrile reaction to reach completion. Consistent with this notion, reaction of **12** with 3-hexyne in CH_2Cl_2 at 40°C (sealed tube) after 14 h gave **11** in 62% yield with 27% of the starting material **12** remaining unreacted.

Good yields of 2,3-diethyl-1,4-naphthoquinone could be obtained directly by performing the reaction under conditions that led to clean decomplexation of the cobalt. For example, reaction of 3-hexyne and **12** in dichloroethane at 80°C in the presence of 1,5-cyclooctadiene gave 2,3-diethylnaphthoquinone in 73% yield. A similar reaction with duroquinone as the additive produced a 72% yield of the free naphthoquinone.

Unfortunately, naphthoquinone formation from other alkynes did not proceed in good yield. Under a variety of conditions, 1-hexyne showed, at most, a trace of the suspected cobalt complex of 2-n-butyl-1,4-naphthoquinone. The free naphthoquinone was obtained in 44% yield after treating the benzonitrile complex **13** with 1-hexyne in dichloroethane at 80°C for 40 minutes. Propargyl chloride and 3-hexyn-2-one failed to give any useful results.

Conclusions

The chemistry described in this manuscript complements our other studies of phthaloyl- and maleoylmetal complexes as precursors to naphthoquinones and benzoquinones, respectively. [2–9]. Furthermore, it underscores the generality of the formation of quinones from organometallic intermediates since we now know that a variety of transition metal and ligand combinations can be used in this chemistry.

It is instructive to compare the differences between the benzoquinone and naphthoquinone systems. An incredible variety of reactive alkynes participate in the reaction with maleoylcobalt complex **9** and give uniformly high yields of benzoquinone complexes. We attribute the success of this chemistry to the fact that the η^5-CpCo unit ends up firmly complexed to the benzoquinone and is not free to participate in side reactions such as alkyne cyclotrimerization or quinone destruction. In contrast, the naphthoquinones do not form very stable complexes with η^5-CpCo and accordingly it is difficult to achieve high yields of naphthoquinones. Additives which coordinate well with η^5-CpCo(1,5-cyclooctadiene or duroquinone) did show some beneficial influence in the naphthoquinone system and it is likely that the synthesis of naphthoquinones can be improved by the proper choice of a η^5-CpCo trap.

Experimental

General

Microanalyses were carried out by Gailbraith Laboratories, Knoxville, Tennessee. ^{1}H NMR spectra were recorded on IBM 200 and 270 MHz spectrometers using tetramethylsilane as an internal standard; chemical shifts were expressed in parts per million using the δ scale. Infrared spectra were recorded on a Perkin–Elmer model 1320 spectrometer. Low-resolution electron-impact mass spectra were obtained on a Finnigan 4510 GC/MS system by a direct insertion probe. High-resolution electron impact mass spectra were obtained on an A.E.I. MS-902 instrument. All melting points were performed in open capillary tubes and are uncorrected. Analytical thin-layer chromatography was done with E. Merck silica gel 60F-254 glass-backed plates of 0.25 mm thickness and were visualized with appropriate combinations of UV light, phosphomolybdic acid stain, and $KMnO_4$ stain. Preparative scale separations were effected with "Flash grade" silica gel available from Aldrich Chemical Co. Solvents were dried by passing through activated alumina (CH_2Cl_2, $C_2H_4Cl_2$, C_6H_6) or by distillation off of benzophenone ketyl under argon (dimethoxyethane) or were used as received from freshly opened bottles of reagent grade quality (hexanes, petroleum ether, diethyl ether, CH_3CN, pyridine, CH_3OH, acetone). Alkynes were purchased from Farchan Laboratories and Aldrich Chemical Co. and were used as received with the exception of propargyl chloride which was distilled prior to use. $CpCo(CO)_2$ was purchased from Strem Chemical Co. and used as received. Unless otherwise noted, all other chemicals and reagents were used as received.

Synthesis of η^5-$CpCo(C_6H_6O_2)(CO)$ (1)

$CpCo(CO)_2$ (3.6 ml, 27.3 mmol) was added by syringe to a nitrogen-saturated solution of 3,4-dimethylcyclobut-3-ene-1,2-dione [6] (2.0 g, 18.2 mmol) in o-xylene (20 ml) in a 50 ml round-bottomed flask fitted with a cold water reflux condenser. The top of the condenser was fitted with a rubber septum through which a syringe needle attached to a balloon filled with argon was passed. The flask was immersed in an oil-bath held at 160°C and the reaction was monitored for disappearance of starting material by TLC (SiO_2, 50% Et_2O/hexane, $KMnO_4$ stain). After 5.5 h the reaction mixture was allowed to cool room temperature and the entire contents of the flask were loaded onto a silica gel column (100 g, "flash grade", petroleum ether). After a non-polar reddish-brown band was eluted off with petroleum ether, use of 5% Et_2O/petroleum ether caused a yellow band to separate on the column and flushing with Et_2O then allowed the yellow compound to be collected. Evaporation of solvent gave 3.92 g of crude product that on recrystallization from hot hexanes gave 3.81 g (80%) of maleoylcobalt complex **1**, m.p. 80–81°C (lit. [1] 86–87°C); IR (CH_2Cl_2, cm^{-1}): 2025(s), 1725(w), 1683(m), 1650(s); ^1H NMR (200 MHz, $CDCl_3$): δ 5.09(s,5H), 1.96(s,6H) ppm.

Synthesis of η^5-$CpCo(C_8H_4O_2)(CO)$ (3)

$CpCo(CO)_2$ (3.04 ml, 23.1 mmol) was added by syringe to a nitrogen-saturated *o*-xylene (18.5 ml) solution of benzocyclobutenedione [5] (2.43g, 18.4 mmol) in a 100 ml round-bottomed flask fitted with a reflux condenser and an argon balloon as described in the preceding procedure. The flask was immersed in an oil bath held at 160°C and the reaction was monitored by TLC (SiO_2, 50% Et_2O/hexanes, $KMnO_4$ stain) for loss of starting material. After 3.25 h the reaction mixture was allowed to cool to room temperature and the entire contents of the flask were loaded onto a silica gel column (100 g, "flash grade", petroleum ether). The column was eluted with petroleum ether to remove non-polar materials and then with CH_2Cl_2 to collect the desired orange-yellow band. Evaporation of the solvent gave an orange-yellow solid which was recrystallized from Et_2O/ petroleum ether to give 5.14 g (98%) of phthaloylcobalt complex **3**, m.p. 132–133°C; IR (CH_2Cl_2, cm^{-1}): 2023(s), 1715(m), 1655(s); ^1H NMR (270 MHz, $CDCl_3$) δ 7.77(dd, *J* 3 Hz, *J* 5.5 Hz, 2H), 7.50(dd, *J* 3, 5.5 Hz, 2H), 5.19 (s, 5H) ppm. Anal. Found: C, 58.99; H, 3.24. $C_{14}H_9O_3Co$ calcd.: C, 59.17; H, 3.19%.

*Reaction of **1** with 3-hexyne (thermal)*

Complex **1** (50 mg, 0.19 mmol), 3-hexyne (107 μl, 0.95 mmol) and *o*-xylene (0.19 ml) were added to a 5 ml heavy-walled resealable reaction tube (purchased from Regis Chemical Co.). After sealing with a teflon sealing disc and a two-piece threaded aluminum coupling, the reaction vessel was placed in an oil bath held at 120°C for 16.5 h and then at 140°C for 24 h. After this time the reaction mixture had turned from yellow to red. The cooled reaction tube was opened and the contents were chromatographed on SiO_2 (10 g, "flash grade", 10% $MeOH/CH_2Cl_2$). After separation of a yellow band of starting material, **1** (38 mg, 76% recovered), a reddish-brown band was eluted that proved to be the desired quinone complex **6**, 14 mg (23%); m.p. 265–267°C; IR (CH_2Cl_2, cm^{-1}): 1567 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 4.74 (s, 5H), 3.00 (m, 2H), 2.19 (m, 2H), 2.08 (s, 6H), 1.30 (t, J 7 Hz, 6H). Anal. Found: 64.28; H, 6.83. $C_{17}H_{21}O_2Co$ calcd.: C, 64.56; H, 6.69%.

*Reaction of **1** with 3-hexyne (photolysis)*

Cobalt complex **1** (50 mg, 0.19 mmol), 3-hexyne (42 μl, 0.38 mmol) and benzene (3 ml) were added to the 5 ml resealable tube described in the previous procedure. Photolysis was accomplished with a G.E. 150 W Flood lamp placed about 10 cm from the tube. Within an hour the solution had changed from bright yellow to red and a dark red solid formed as the reaction progressed. After 24 h, the solvent was evaporated and the red residue was chromatographed on 10 g of SiO_2 ("flash grade", 10% $MeOH/CH_2Cl_2$) to give 57 mg (95%) of quinone complex **6**.

*Synthesis of η^5-$CpCo(C_6H_6O_2)(L)$ from **1***

*(a) $L = PPh_3$ (**7**).* Carbon monoxide complex **1** (250 mg, 0.95 mmol), triphenylphosphine (256 mg, 0.97 mmol) and benzene (9 ml) were added to a 25 ml round-bottomed flask fitted with a reflux condenser. The reaction mixture was placed under a nitrogen atmosphere and was irradiated with a GE 150 W Flood Lamp from a distance of 10 cm. Ater 27 h, TLC (SiO_2, 50% Et_2O/hexanes, 2% $KMnO_4$ stain) showed that most of the starting material was gone. The reaction mixture was concentrated on a rotary evaporator and chromatographed (50 g "flash grade" SiO_2, 25% Et_2O/hexanes) to give 354 mg (72%) of the triphenylphosphine complex **7** as a red-orange solid, m.p. 219°C (Et_2O/hexanes); IR (CH_2Cl_2, cm^{-1}): 1602 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 7.41 (m, 18H), 4.73 (s, 5H), 1.42 (s, 6H); Anal. Found: C, 70.07; H, 5.45. $C_{29}H_{26}O_2CoP$ calcd.: C, 70.16; H, 5.28%.

*b. $L = C_5H_5N$ (**8**).* To a solution of cobalt complex **1** (931 mg, 3.55 mmol) in N_2-saturated pyridine (35.5 ml) in a 100 ml round-bottomed flask equipped with an argon balloon and cooled in an ice-water bath, was added 1 eq. of freshly sublimed Me_3NO (267 mg, 3.55 mmol) in one portion. After 10 min an additional portion of Me_3NO (140 mg, 1.87 mmol) was added and after an additional 15 min TLC (SiO_2, 75% Et_2O/hexane) showed no starting material remained. The reaction mixture was concentrated on a rotary evaporator and the residue was chromatographed (50 g SiO_2, "flash grade", 2% C_5H_5N/CH_2Cl_2) to give 836 mg (75%) of pyridine complex **8** as shiny red-black crystals, m.p. 170–180°C (decomp); IR (CH_2Cl_2, cm^{-1}): 1660 (w), 1603 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 8.92 (d, J 7 Hz, 2 H), 7.54 (t, J 7 Hz, 1 H), 7.05 (t, J 7 Hz, 2 H), 4.70 (s, 5 H), 1.90 (s, 6 H). Anal. Found: C, 61.57; H, 5.05. $C_{16}H_{16}NO_2Co$ calcd.: C, 61.35; H, 5.15%.

*c. $L = Et_2S$ (**9**).* Cobalt complex **1** (2.00 g, 7.64 mmol), Et_2S (8.23 ml, 76.4 mmol) and CH_2Cl_2 (1.6 l) were added to a 3 l round-bottomed flask fitted with an efficient reflux condensor. After the reaction mixture was brought under a nitrogen atmosphere, the reaction apparatus was clamped above a G.E. 150 W Flood lamp and the top and sides of the flask were shrouded with aluminum foil. During the photolysis the reaction turned from yellow to red-orange and the solvent slowly refluxed. After 34 h the light was turned off, the solvent was evaporated and the residue was chromatographed (30 g "flash grade" SiO_2, 2% Et_2S in 20% Et_2O/CH_2Cl_2) to give a red-brown residue that was dissolved in a minimum amount of CH_2Cl_2 and filtered through a small plug of celite. After removal of solvent the material was pumped to dryness to yield 2.17 g (88%) of deep red **9**, m.p.

99–103°C; IR (CH_2Cl_2, cm^{-1}) 1661 (w), 1605 (s); ^1H NMR (200 MHz, $CDCl_3$) δ 4.80 (s, 5H), 2.40 (q, J 5.8 Hz, 4H), 1.88 (s, 6H), 1.2 (t, J 5.8 Hz, 6H). Anal. Found: C, 55.61; H, 6.48. $C_{15}H_{21}O_2SCo$ calcd.: C, 55.55; H, 6.53%.

Reactions of η^5-$CpCo(C_6H_6O_2)(L)$ with alkynes. General Procedure

The complex, alkyne, and solvent were added to a 5 ml heavy-walled resealable pressure tube (Regis) containing a small magnetic stirring bar. After sealing the reaction vessels were immersed in an oil bath at the indicated temperature and were stirred with heating. To monitor for completion of the reaction, the vessel was cooled to room temperature opened, and checked by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$) for disappearance of starting material. If the reaction was not complete, the tube was immediately resealed and placed back in the oil bath. Work-up of the reactions was accomplished by evaporation of solvent and chromatography (10 g "flash grade" SiO_2, 10% $MeOH/CH_2Cl_2$). All of the quinone complexes were red-brown solids.

a. Reaction of η^5-$CpCo(C_6H_6O_2)(PPh_3)$ (7) with 3-hexyne. Complex **7** (50 mg, 0.10 mmol), 3-hexyne (17 μl, 0.15 mmol) and CH_2Cl_2 (1 ml) gave no quinone product after 15 h at 100°C. Only unreacted **7** was observed by TLC.

b. Reaction of η^5-$CpCo(C_6H_6O_2)(C_5H_5N)$ (8) with 3-hexyne. Complex **8** (100 mg, 0.32 mmol), and 3-hexyne (54 μl, 0.48 mmol) in benzene (3 ml) gave 58 mg (58% yield) of quinone complex **6** and 33 mg (33%) of unreacted **8** after 7 h at 80°C. In dimethoxyethane the yields of **6** and **8** were 68 and 26%, respectively, while in dichloroethane the yield improved to 86% **6** and 13% recovered **8**.

c. Reaction of η^5-$CpCo(C_6H_6O_2)(Et_2S)$ (9) with various alkynes at 80°C in dichloroethane. Cobalt complex **9** (100 mg, 0.31 mmol) and 3-hexyne (52 μl, 0.46 mmol, 1.5 equiv.) in dichloroethane (3 ml) for 1.5 h gave 88 mg (90%) of quinone complex **6**. Alternatively, complex **9** (250 mg, 0.77 mmol) and 3-hexyne (438 μl, 3.86 mmol, 5 equiv.) in 7.7 ml dichloroethane after 1 h gave 220 mg (90%) of **6**.

Cobalt complex **9** (100 mg, 0.31 mmol) and 1-hexyne (53 μl, 0.46 mmol, 1.5 equiv.) in 3 ml dichloroethane for 1 h gave 88 mg (90%) of η^5-CpCo(2,3-dimethyl-5-n-butyl-1,4-benzoquinone), m.p. 145–147°C; IR (CH_2Cl_2, cm^{-1}): 1580 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 5.38 (s,1 H), 4.91 (s, 5H), 2.94 (m, 1 H), 2.11 (s, 3H), 2.10 (m, 1H), 2.05 (s, 3H), 1.74 (m, 2H), 1.40 (m, 2H), 0.93 ppm (t, J 7 Hz, 3H). Anal. Found: C, 64.26; H, 6.47. $C_{17}H_{21}O_2Co$ calcd.: C, 64.56; H, 6.69%. Alternatively, complex **9** (250 mg, 0.77 mmol) and 1-hexyne (442 μl, 3.86 mmol, 5 equiv.) in 7.7 ml dichloroethane for 1 h gave 235 mg (96%) of the quinone complex.

Cobalt complex **9** (100 mg, 0.31 mmol) and ethyl-1-butynyl ether (50 μl, 0.46 mmol, 1.5 equiv.) in 3 ml dichloroethane for 1.5 h gave 92 mg (90%) of η^5-CpCo(2,3-dimethyl-5-ethoxy-6-ethyl-1,4-benzoquinone), m.p. 158–160°C; IR (CH_2Cl_2, cm^{-1}): 1576 (s); ^1H NMR(200 MHz, $CDCl_3$): δ 5.09 (m, 1H), 4.83 (s, 5H), 4.13 (m, 1H), 2.85 (m, 1H), 2.32 (m, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 1.43 (t, J 7.8 Hz, 3H), 1.17 ppm (t, J 7.8 Hz, 3H). Anal. Found: C, 61.20; H, 6.45. $C_{17}H_{21}O_3Co$ calcd.: C, 61.45; H, 6.37%. Alternatively, complex **9** (250 mg, 0.77 mmol) and ethyl-1-butynyl ether (417 μl, 3.86 mmol, 5 equiv.) in 7.7 ml dichloroethane for 1 h gave 248 mg (97%) of the quinone complex.

Cobalt complex **9** (100 mg, 0.31 mmol) and 3-hexyne-2-one (43 μl, 0.46 mmol, 1.5 equiv.) in 3 ml of dichloroethane for 5 h gave 91 mg (90%) of η^5-CpCo(2,3-dimethyl-5-acetyl-6-ethyl-1,4-benzoquinone), m.p. ≥ 208°C (with decomp); IR (CH_2Cl_2, cm^{-1}): 1705 (s), 1678 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 5.02 (s, 5H), 2.90 (m, 1H), 2.66 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (m, 1H), 1.17 ppm (t, *J* 7.8 Hz, 3H); Anal. Found: C, 61.50; H, 5.78. $C_{17}H_{19}O_3Co$ calcd.: C, 61.83; H, 5.80%. Alternatively, complex **9** (250 mg, 0.77 mmol) and 3-hexyne-2-one (361 μl, 3.86 mmol, 5 equiv.) in 7.7 ml dichloroethane for 1.75 h gave 225 mg (89%) of the quinone complex.

Complex **9** (100 mg, 0.31 mmol) and *N*-benzylpropargylamine (69 μl, 0.46 mmol, 1.5 equiv.) in 3 ml of dichloroethane for 2 h gave 71 mg (61%) of η^5-CpCo(2,3-dimethyl-5-(*N*-benzylamino)methyl-1,4-benzoquinone), m.p. 127–131°C (decomp.); IR (CH_2Cl_2, cm^{-1}): 3045 (w), 1582 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 7.34 (m, 5H), 5.39 (s, 1H), 4.93 (s, 5H), 3.86 (br s, 2H), 3.60 (d, *J* 13 Hz, 1H), 3.27 (d, *J* 13 Hz, 1H), 2.09 (s, 3H), 2.4–1.5 (br s, 1H) 2.06 (s, 3H) ppm. Anal. Found: C, 66.43; H, 5.95. $C_{21}H_{22}NO_2Co$ calcd.: C, 66.49; H, 5.85%.

Cobalt complex **9** (100 mg, 0.31 mmol) and ethyl-2-propynyl ether (47 μl, 0.46 mmol, 1.5 equiv.) in 3 ml of dichloroethane for 2 h gave 82 mg (80%) of η^5-CpCo(2,3,5-trimethyl-6-ethoxymethyl-1,4-benzoquinone), m.p. 193–196°C (decomp); IR (CH_2Cl_2, cm^{-1}): 1578 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 4.86 (s, 5H), 4.54 (d, *J* 10.4 Hz, 1H), 4.33 (d, *J* 10.4 Hz, 1H), 3.66 (q, *J* 7.8 Hz, 2H), 2.13 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 1.24 ppm (t, *J* 7.8 Hz, 3H). Anal. Found: C, 61.20; H, 6.35 $C_{17}H_{21}O_3Co$ calcd.: C, 61.45; H, 6.37%.

Cobalt complex **9** (100 mg, 0.31 mmol) and 2-methyl-1-penten-3-yne (46 μl, 0.46 mmol, 1.5 equiv.) in 3 ml of dichloroethane for 1.25 h gave 82 mg (84%) of η^5-CpCo(2,3,5-trimethyl-6-(2-propenyl)-1,4-benzoquinone), m.p. 213–216°C (decomp); IR (CH_2Cl_2, cm^{-1}): 1580 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 5.50 (br s, 1H), 5.04 (br s, 1H), 4.88 (s, 5H), 2.13 (s, 6H), 2.07 (s, 3H), 2.05 (s, 3H) ppm. Anal. Found: C, 64.88; H, 6.04. $C_{17}H_{19}O_2Co$ calcd.: C, 64.97; H, 6.09%. Alternatively, complex **9** (250 mg, 0.77 mmol) and 2-methyl-1-penten-3-yne (386 μl, 3.86 mmol, 5 equiv.) in 7.7 ml dichloroethane for 1 h gave 220 mg (91% of the quinone complex.

Cobalt complex **9** (100 mg, 0.31 mmol) and propargyl chloride (33 μl, 0.46 mmol, 1.5 equiv.) in 3 ml of dichloroethane for 2.5 h gave 79 mg (83%) of η^5-CpCo(2,3-dimethyl-5-chloromethyl-1,4-naphthoquinone); m.p. 141–142°C (violent decomp); IR (CH_2Cl_2, cm^{-1}): 1590 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 5.63 (s, 1H), 5.02 (s, 5H), 4.57 (d, *J* 13.6 Hz, 1H), 4.40 (d, *J* 13.6 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H) ppm. Anal. Found: C, 54.19; H, 4.80. $C_{14}H_{14}ClO_2Co$ calcd.: C, 54.48; H, 4.57. Alternatively, complex **9** (500 mg, 1.54 mmol) and propargyl chloride (558 μl, 7.71 mmol, 5 equiv.) in 16 ml dichloroethane for 1 h gave 459 mg (96%) of the quinone complex.

Cobalt complex **9** (100 mg, 0.31 mmol) and propargyl alcohol (90 μl, 1.54 mmol, 5 equiv.) in 3 ml of dichloroethane for 1.25 h gave 74 mg (82%) of η^5-CpCo(2,3-dimethyl-5-hydroxymethyl-1,4-benzoquinone), m.p. 170–180°C (decomp) as a dihydrate; IR (CH_2Cl_2, cm^{-1}): 3350 (br), 1602 (s), 1565 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 5.41 (s, 1H), 5.10 (s, 5H), 4.68 (d, *J* 14 Hz, 1H), 3.95 (d, *J* 14 Hz, 1H), 1.12 (s, 3H), 1.09 (s, 3H) ppm. Anal. Found: C, 51.40; H, 5.90. $C_{14}H_{15}O_3Co \cdot 2H_2O$ calcd.: C, 51.54; H, 5.87%.

Synthesis of the free quinones. General Procedure

The quinone complex, THF (12 ml) and H_2O (4 ml) were added to a 100 ml round-bottomed flask and the mixture was cooled in an ice-bath to 0°C with stirring. Then $Ce(NH_4)_2(NO_3)_6$ (2 equiv.) was added as a solid and the reaction was stirred at 0°C for 30 min. After 30 min the light orange reaction mixture was poured into 70 ml of H_2O and the mixture was extracted with 3 × 50 ml portions of Et_2O. The Et_2O layers were combined, dried over $MgSO_4$, filtered, and evaporated on a rotary evaporator to leave a red oil that was chromatographed (13 g "flash grade" SiO_2, 50% Et_2O/petroleum ether) to yield the pure benzoquinone.

a. η^5-CpCo(2,3-dimethyl-5,6-diethyl-1,4-benzoquinone) (210 mg, 0.66 mmol) and $Ce(NH_4)_2(NO_3)_6$ (728 mg, 1.33 mmol) gave 112 mg (87%) of 2,3-dimethyl-5,6-diethyl-1,4-benzoquinone as a yellow oil (m.p. 26–27°C); IR (CH_2Cl_2, cm^{-1}): 1632 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 2.5 (q, J 8 Hz, 4H), 2.02 (s, 6H), 1.08 ppm (t, J 8 Hz, 6H). High resolution MS Found: 192.1127. $C_{12}H_{16}O_2$ calcd.: 192.1149.

b. η^5-CpCo(2,3-dimethyl-5-n-butyl-1,4-benzoquinone) (235 mg, 0.74 mmol) and $Ce(NH_4)_2(NO_3)_6$ (815 mg, 1.49 mmol) gave 121 mg (85%) of 2,3-dimethyl-5-n-butyl-1,4-benzoquinone as a yellow oil IR (CH_2Cl_2, cm^{-1}): 1640 (s), 1614 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 6.50 (t, $J < 1$ Hz, 1H), 2.42 (dt, J 7.6 Hz, $J < 1$ Hz, 2H), 2.00 (m, 6H), 1.42 (m, 4H), 0.95 ppm (t, J 6 Hz, 3H); High resolution MS Found: 192.1120. $C_{12}H_{16}O_2$ calcd.: 192.1150.

c. η^5-CpCo(2,3-dimethyl-5-ethoxy-6-ethyl-1,4-benzoquinone) (248 mg, 0.75 mmol) and $Ce(NH_4)_2(NO_3)_6$ (820 mg, 1.50 mmol) gave 141 mg (91%) of 2,3-dimethyl-5-ethoxy-6-ethyl-1,4-benzoquinone as a yellow oil; IR (CH_2Cl_2, cm^{-1}): 1640 (s), 1610 (s): ^1H NMR (200 MHz, $CDCl_3$): δ 4.24 (q, J 7.4 Hz, 2H), 2.47 (q, J 8 Hz, 2H), 2.01 (s, 6H), 1.36 (t, J 7.4 Hz, 3H), 1.04 ppm (t, J 8 Hz, 3H); High resolution MS Found: 208.1093. $C_{12}H_{16}O_3$ calcd.: 208.1099.

d. η^5-CpCo(2,3-dimethyl-5-acetyl-6-ethyl-1,4-benzoquinone) (225 mg, 0.68 mmol) and $Ce(NH_4)_2(NO)_3)_6$ (748 mg, 1.37 mmol) gave 118 mg (84%) of 2,3-dimethyl-5-acetyl-6-ethyl-1,4-benzoquinone as a yellow solid, m.p. 33–34°C; IR (CH_2Cl_2, cm^{-1}): 1703 (s); 1640 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 2.42 (s, 3H), 2.37 (q, J 7.7 Hz, 2H), 2.04 (m, 3H), 2.02 (m, 3H), 1.1 ppm (t, J 7.7 Hz, 3H); High resolution MS Found: 206.0931. $C_{12}H_{14}O_3$ calcd.: 206.0942.

e. η^5-CpCo(2,3,5-trimethyl-6-(2-propenyl)-1,4-benzoquinone) (220 mg, 0.70 mmol) and $Ce(NH_4)_2(NO_3)_6$ (767 mg, 1.40 mmol) gave 112 mg (84%) of 2,3,5-trimethyl-6-(2-propenyl)-1,4-benzoquinone as a yellow oil; IR(CH_2Cl_2, cm^{-1}) 1637 (s), 1611 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 5.29 (br q, $J < 1$ Hz, 1H), 4.79 (br s, 1H), 2.022, 2.019, 2.005 (all s, 3H each), 1.92 (br s, 3H) ppm; High resolution MS Found: 190.0977. $C_{12}H_{14}O_2$ calcd.: 190.0993.

Synthesis of η^5-CpCo($C_8H_4O_2$)(L) from 3

a. $L = Et_2S$ (10). Phthaloylcobalt complex **3** (284 mg, 1.0 mmol), Et_2S (1.08 ml, 10 mmol) and N_2-saturated CH_2Cl_2 (200 ml) were added to a 500 ml round-bottomed flask equipped with a reflux condensor. The reaction mixture was brought under N_2 and irradiated from below with a GE 150 W Flood lamp for 15.5 h at which time the red-orange solution contained very little starting material (TLC, SiO_2, 50% Et_2O/hexanes). The reaction mixture was concentrated on a rotary evaporator and chromatographed (17 g "flash grade" SiO_2, CH_2Cl_2 to remove unreacted **3** then 10% Et_2O/CH_2Cl_2 to elute the product) to give 279 mg (80%) of **10** as a red solid, m.p. 94–95°C; IR (CH_2Cl_2, cm^{-1}): 1623 (s) 1575 (s); ^1H NMR (270 MHz, $CDCl_3$): δ 7.60 (dd, J 5 Hz, 3 Hz, 2H), 7.39 (dd, J 5 Hz, 3Hz, 2H), 4.89 (s, 5H), 2.37 (q, J 6.5 Hz, 4H), 1.18 ppm (t, J 6.5 Hz, 6H). Anal. Found: C, 59.00; H, 5.66. $C_{17}H_{19}O_2SCo$ calcd.: C, 58.96; H, 5.53%.

b. $L = CH_3CN$ (**12**). Cobalt complex **3** (1.00 g, 3.52 mmol) and CH_3CN (35.2 ml) were added to a 50 ml round-bottomed flask and the contents were brought under an Ar atmosphere. $Me_3NO \cdot 2H_2O$ (391 mg, 3.52 mmol) was added as a solid in portions over a 5 min period. The solution turned from yellow to deep red-brown. After 15 min TLC (SiO_2, 5% CH_3CN/CH_2Cl_2) indicated the disappearance of starting material and the reaction mixture was concentrated on a rotary evaporator and the residue was chromatographed (20 g "flash grade" SiO_2, 5% CH_3CN/CH_2Cl_2) to yield 979 mg (94%) of **12** as a red-brown solid, m.p. 156–159°C (decomp); IR (CH_2Cl_2, cm^{-1}): 2290 (w), 1725 (w), 1630 (s), 1578 (s); ^1H NMR (200 MHz, $CDCl_3$): δ 7.68 (dd, J 5 Hz, 3 Hz, 2H), 7.42 (dd, J 5 Hz, 3 Hz, 2H), 4.95 (s, 5H), 2.01 (s, 3H) ppm. Anal. Found: C, 60.51; H, 4.20. $C_{15}H_{12}NO_2Co$ calcd.: C, 60.62; H, 4.07.

c. $L = C_6H_5CN$ (13). Acetonitrile complex **12** (305 mg, 1.03 mmol) and C_6H_5CN (524 μl, 5.13 mmol) in 10.2 ml of dichloroethane were heated at 80°C for 1 h in a round-bottomed flask under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator and the residue was chromatographed (10 g "flash grade" SiO_2, 50% Et_2O/hexanes) to give a red oil that was titurated with petroleum ether and gave 323 mg (88%) of the benzonitrile complex **13** as a red solid, m.p. 148–151°C (decomp); IR (CH_2Cl_2, cm^{-1}): 2258 (w), 1715 (w), 1633 (s), 1580 (m), ^1H NMR (90 MHz, $CDCl_3$): δ 7.72 (dd, J 5 Hz, 3 Hz, 2H) 7.38 (m, 7H), 4.83 (s, 5H) ppm. Anal. Found: C, 66.70; H, 4.05. $C_{20}H_{14}NO_2Co$ calcd.: C, 66.86; H, 3.93.

Reactions of η^5-$CpCo(C_8H_4O_2)(L)$ with alkynes

a. L = CO (3). Phthaloylcobalt complex **3** (142 mg, 0.50 mmol), 3-hexyne (85 μl, 0.75 mmol) and CH_2Cl_2 (5 ml) were added to a 10 ml round-bottomed flask. The reaction mixture was placed under an argon atmosphere, cooled in a −10°C cold bath, and $Me_3NO \cdot 2H_2O$ was added as a solid in portions until **3** was consumed as judged by TLC (SiO_2, 10% MeOH/acetone). About 3–4 equiv. of $Me_3NO \cdot 2H_2O$ were required. Chromatography (20 g "flash grade SiO_2, 10% MeOH/acetone) gave 67 mg (39%) of η^5-CpCo(2,3-diethyl-1,4-naphthoquinone) (**11**) as a green solid; m.p. $\geqslant$ 132°C (decomp); IR (CH_2Cl_2, cm^{-1}); 1570 (s); ^1H NMR (200 MHz, $CDCl_3$); δ 8.45 (m, 2H), 7.59 (m, 2H), 4.36 (s, 5H), 3.32 (dq, J 14 Hz, 7 Hz, 2H), 2.31 (dq, J 14 Hz, 7 Hz, 2H), 1.37 ppm (t, J 7 Hz, 6H); Anal. Found: C, 67.46; H, 5.78. $C_{19}H_{19}O_2Co$ calcd.: C, 67.75; H, 5.66. The reaction of **3** with 3-hexyne in acetone with Me_3NO or N-methylmorpholine N-oxide gave similar yields of the naphthoquinone complex.

N-Methylmorpholine N-oxide (62 mg, 0.53 mmol), 1-hexyne (303 μl, 2.64 mmol) and acetone (5.2 ml) were added to a round-bottomed flask. The reaction mixture was brought under N_2 and complex **3** (100 mg, 0.35 mmol) in 1 ml of acetone was added slowly by syringe. After 10 min, TLC analysis (SiO_2, 50% Et_2O/hexanes) revealed a trace of starting material remained in the green solution so an additional small portion of the N-oxide was added. The green color of the solution was attributed to the formation of η^5-CpCo(2-n-butyl-1,4-naphthoquinone) that could be observed by TLC (SiO_2, 10% MeOH/acetone). However, any attempt to isolate this naphthoquinone complex led to facile decomplexation, so the reaction mixture was subjected to an oxidative work-up to provide the free quinone. An 0.1 M aqueous solution of $Ce(NH_4)_2(NO_3)_6$ was added until the reaction mixture turned yellow. The resulting solution was poured into 3 volumes of saturated NaCl and the solution was extracted 3 times with Et_2O. The combined Et_2O layers were dried ($MgSO_4$), filtered, concentrated, and chromatographed (10 g of "flash grade" SiO_2, 50% CH_2Cl_2/hexanes) to give 30 mg (40%) of 2-n-butyl-1,4-naphthoquinone as a yellow oil identical with a previously prepared sample [3].

b. $L = Et_2S$ *(10).* Phthaloylcobalt complex **10** (50 mg, 0.14 mmol) and 3 ml CH_2Cl_2 were added to a 10 ml round-bottomed flask. The contents were brought under an Ar atmosphere and the flask was cooled to −78°C. With stirring, *m*-chloroperbenzoic acid (27 mg, 0.16 mmol) was added as a solid in one portion. After 1 h, 3-hexyne (25 μl, 0.22 mmol) was added and the reaction mixture was allowed to warm to room temperature. Chromatography (10 g "flash grade" SiO_2, 10% MeOH/acetone) gave 20 mg (42%) of η^5-CpCo(2,3-diethyl-1,4-naphthoquinone), **11**, as a green solid.

c. $L = CH_3CN$ *(12).* Cobalt complex **12** (148 mg, 0.5 mmol), 3-hexyne (85 μl, 0.75 mmol) and 2.5 ml of dichloroethane were heated at 80°C in a sealed tube for 3 h. Evaporation of solvent followed by chromatography (15 g "flash grade" SiO_2, 10% MeOH/acetone) gave a fast moving yellow band and then a green band containing 47 mg (28%) of **11** as a green solid. The less polar yellow material was chromatographed (10 g "flash grade SiO_2, 50% hexanes/CH_2Cl_2) and gave 59 mg (55%) of 2,3-diethyl-1,4-naphthoquinone as a yellow oil identical with a previously prepared sample [3].

Cobalt complex **12** (100 mg, 0.34 mmol), 3-hexyne (57 μl, 0.50 mmol) and 3.4 ml CH_2Cl_2 were heated at 40°C in a sealed tube for 14 h. The reaction mixture was directly loaded onto an SiO_2 column and chromatographed (10 g "flash grade" SiO_2, 89/10/1 acetone/CH_3OH/CH_3CN) to give 27 mg (27%) unreacted **12** and 62 mg (55%) of naphthoquinone complex **11**.

Cobalt complex **12** (139 mg, 0.47 mmol), 3-hexyne (79 μl, 0.70 mmol), 1,5-cyclooctadiene (57 μl 0.47 mmol), and 2.3 ml dichloroethane were heated at 80°C in a sealed tube for 9 h. Analysis by TLC (SiO_2, 10% CH_3OH/acetone) showed disappearance of **12**, a trace of the quinone complex **11**, and a significant amount of free naphthoquinone. The reaction mixture was diluted with CH_2Cl_2, washed with distilled H_2O containing 100 mg of $Ce(NH_4)_2(NO_3)_6$, dried (Na_2SO_4), filtered, and condensed on a rotary evaporator to give a yellow-green oil that was chromatographed (10 g "flash grade" SiO_2, 50% CH_2Cl_2/hexanes) and gave 73 mg (73%) of 2,3-diethyl-1,4-naphthoquinone. A similar reaction with added duroquinone in place of the 1,5-cyclooctadiene gave the naphthoquinone in 74% yield.

d. $L = C_6H_5CN$ *(13).* Phthaloylcobalt complex **13** (60 mg, 0.17 mmol), 3-hexyne (38 μl, 0.33 mmol) and 1.7 ml dichloroethane were heated at 80°C in a sealed tube for 1 h. Evaporation of solvent and chromatography (10 g "flash grade" SiO_2, 10% CH_3OH/acetone) gave 35 mg (62%) of the green naphthoquinone complex **11**.

Cobalt complex **13** (54 mg, 0.15 mmol), 1-hexyne (35 μl, 0.30 mmol) and 1.5 ml dichloroethane were heated in a sealed tube for 40 min. Evaporation of solvent and chromatography (10 g "flash grade" SiO_2, CH_2Cl_2) gave 14 mg (44%) of 2-n-butyl-1,4-naphthoquinone.

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