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Synthesis of (η^4-1,4-Naphthoquinone)(η^5-pentamethylcyclopentadienyl)cobalt Complexes†

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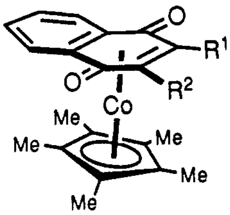
Benzocyclobutenedione reacts with (η^5-C_5Me_5)Co(CO)$_2$ (generated in situ from $Co_2(CO)_8$ and pentamethylcyclopentadiene) in toluene at 160 °C to give the very stable (η^5-C_5Me_5)(phthaloyl)Co(CO)$_2$ in 70% yield. Gentle oxidative removal of a coordinated CO with *N*-methylmorpholine *N*-oxide in 1,2-dichloroethane in the presence of an alkyne produces good yields of the very polar (η^5-pentamethylcyclopentadienyl)(η^4-1,4-naphthoquinone)cobalt complexes. An X-ray crystallographic study of (η^5-pentamethylcyclopentadienyl)(η^4-2,3-dimethyl-1,4-naphthoquinone)cobalt confirmed the η^4 bonding of the naphthoquinone ligand to the cobalt.

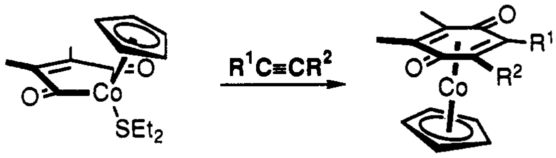
Since the first isolation and characterization of (η^4-duroquinone)Fe(CO)$_3$ dating back to the late 1950s,[2,3] there have been many η^4-1,4-benzoquinone complexes of various metal–ligand systems described.[4-19] A few η^4-coordinated 1,4-benzoquinones have been prepared by the direct reaction of a 1,4-benzoquinone with an appropriate transition-metal reagent; however, most of the characterized η^4-1,4-benzoquinone complexes were formed in low yield on reaction of an alkyne with a transition-metal carbonyl species. No general and high yielding synthesis of (η^4-1,4-benzoquinone)metal complexes was available until the discovery of the reaction of (η^5-cyclopentadienyl)maleoylcobalt complexes with alkynes.[18,19]

Much less common are η^2-1,4-benzoquinones and η^2-1,4-naphthoquinones coordinated to a transition metal,[5,13,14,20] and η^4-1,4-naphthoquinone complexes appear to be unknown. A η^4 structure has been suggested for the nickel(0)–anthraquinone complex, [(c-C_6H_{11})$_3$P]Ni(anthraquinone).[17] An interest in the synthesis and chemistry of (η^5-cyclopentadienyl)- and (η^5-pentamethylcyclopentadienyl)cobalt complexes of 1,4-benzoquinones[18,19] led to the exploration of similar chemistry in the naphthoquinone series. Herein is reported a general synthetic method for the synthesis of (η^5-pentamethylcyclopentadienyl)(η^4-1,4-naphthoquinone)cobalt complexes 1 and an X-ray crystal structure analysis of the compound having the molecular structure 1, $R^1 = R^2 =$ Me.

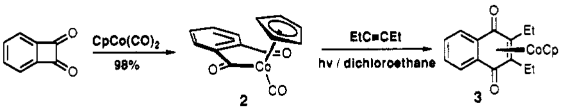


1

During an earlier study of the formation of η^5-cyclopentadienyl-η^4-benzoquinones by reaction of alkynes with (η^5-cyclopentadienyl)maleoylcobalt complexes (eq 1), a brief investigation of the naphthoquinone series was undertaken.[19] (η^5-Cyclopentadienyl)phthaloylcobalt carbonyl 2 was prepared in 98% yield by reaction of CpCo(CO)$_2$ with benzocyclobutenedione at 160 °C in *o*-xylene (eq 2).



(1)



(2)

The remarkable thermal stability of the 18-electron species 2 (note the conditions of its formation) precluded its direct reaction with alkynes under conditions of thermal activation, but reaction did ensue when solutions of 2 and an alkyne were photolyzed with a GE 150-W flood lamp or treated with Me_3NO or when the CO ligand of 2 was replaced with a thermally labile ligand such as MeCN or PhCN prior to reaction with an alkyne. These operations

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† Dedicated to the memory of John Stille.

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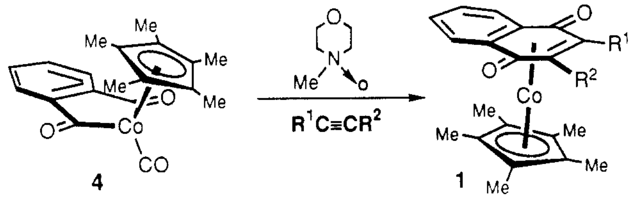
Table I. Synthesis of (η^4-Naphthoquinone)(η^5-pentamethylcyclopentadienyl)cobalt Complexes from Alkynes and Phthaloylcobalt Complex 4

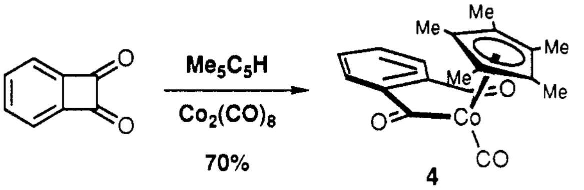


entry	R^1	R^2	compd	yield, %
1	Me	Me	**1a**	83
2	Et	Et	**1b**	61
3	H	n-C_4H_9	**1c**	61
4	H	c-C_6H_{11}	**1d**	58
5	Me	CO_2Et	**1e**	86
6	Me	OEt	**1f**	40
7	H	OEt	**1g**	82
8	Me	CH_2OEt	**1h**	70
9	H	CH_2OH	**1i**	75
10	H	Ph	**1j**	58

were necessary in order to generate a coordinatively unsaturated species. The reaction of **2** and its CO-substituted variants was explored with a number of alkynes, but a reasonably stable, dark green 1,4-naphthoquinone complex was formed only with 3-hexyne (**3**); other alkynes (1-hexyne) led to very unstable 1,4-naphthoquinone complexes that decomposed to the free naphthoquinone or to complex mixtures of products (3-hexyn-2-one and propargyl chloride).

It was reasonable to assume that the sensitivity of the naphthoquinone complexes compared to the benzoquinone derivatives could be attributed to the diminished ability of the naphthoquinone to function as a η^4 ligand when compared to a benzoquinone. On the presumption that decomposition of the weakly ligated naphthoquinone complexes was initiated by intermolecular attack of various ligands at the cobalt atom, we theorized that more stable naphthoquinone complexes should result when coordinated to a sterically more encumbered (η^5-pentamethylcyclopentadienyl)cobalt unit. This proved to be true.

Treatment of benzocyclobutenedione with pentamethylcyclopentadiene and $Co_2(CO)_8$ at 160 °C in *o*-xylene for 25 h gave (η^5-pentamethylcyclopentadienyl)phthaloylcobalt carbonyl **4** in 70% yield (eq 3). Oxidative decarbonylation of **4** with *N*-methylmorpholine *N*-oxide (NMMNO) in dichloroethane at room temperature in the presence of a variety of alkynes produced good yields of stable, chromatographable, dark green (η^4-naphthoquinone)(η^5-pentamethylcyclopentadienyl)cobalt complexes **1** (Table I). The formation of 1,4-naphthoquinone complexes was quite general, encompassing reactions of terminal, internal, electron-rich, electron-deficient, and propargylic alkynes. All of the 1,4-naphthoquinone complexes were dark green to dark brown in color, were air-stable, were very polar (elution on SiO_2 with 10% $MeOH/CH_2Cl_2$), and decomposed without melting at high temperature. The naphthoquinone complexes showed a significant tendency to hydrate, making accurate combustion analysis difficult. Infrared spectra of the complexes showed two carbonyl bands near 1575 and 1550 cm^{-1}. In contrast to the numerous unsuccessful attempts to prepare 1,4-naphthoquinone complexes with the (η^5-cyclopentadienyl)cobalt fragment, it is clear that the use of the pentamethylcyclopentadienyl ligant imparts significant stability to the η^4-coordinated 1,4-naphthoquinone complexes.



(3)

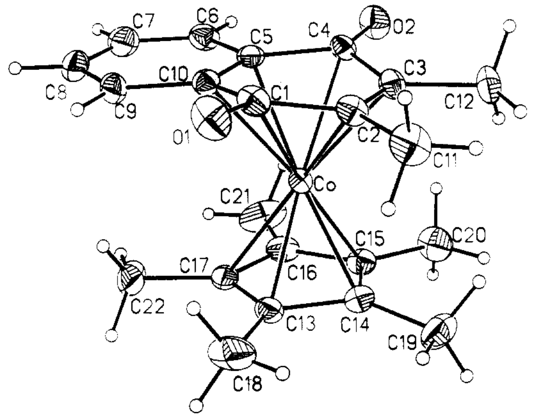


Figure 1. ORTEP diagram of (η^5-C_5Me_5)Co(η^4-2,3-dimethyl-1,4-naphthoquinone), **1a**.

Table II. Bond Lengths of (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), 1a

bond	length, Å	bond	length, Å	bond	length, Å
Co–C1	2.284 (4)	C8–C9	1.365 (7)	C1–O1	1.257 (5)
Co–C3	2.089 (4)	C13–C14	1.434 (5)	C2–C11	1.512 (6)
Co–C5	2.176 (3)	C13–C18	1.506 (7)	C3–C12	1.509 (5)
Co–C13	2.069 (3)	C14–C19	1.492 (6)	C4–O2	1.247 (4)
Co–C15	2.059 (4)	C15–C20	1.508 (6)	C5–C10	1.426 (5)
Co–C17	2.063 (4)	C16–C21	1.533 (6)	C7–C8	1.408 (6)
C1–C10	1.463 (5)	Co–C2	2.081 (4)	C9–C10	1.432 (5)
C2–C3	1.412 (5)	Co–C4	2.281 (3)	C13–C17	1.392 (6)
C3–C4	1.460 (5)	Co–C10	2.158 (3)	C14–C15	1.439 (5)
C4–C5	1.476 (5)	Co–C14	2.043 (3)	C15–C16	1.385 (5)
C5–C6	1.417 (5)	Co–C16	2.063 (4)	C16–C17	1.444 (6)
C6–C7	1.355 (6)	C1–C2	1.452 (5)	C17–C22	1.506 (7)

The hapticity of the 1,4-naphthoquinone ligand was confirmed by an X-ray structure determination on a suitable single crystal of **1a**, $R^1 = R^2 =$ Me. The ORTEP diagram of **1a** is shown in Figure 1, and bond lengths and bond angles are given in Tables II and III. The data clearly demonstrate the η^4 nature of the bonding of the naphthoquinone ligand to the cobalt, bond lengths from Co to the aromatic ring carbons C5 and C10 being only slightly longer (2.176, 2.158) than those from Co to C2 and C3 (2.081, 2.089). The dissymmetry in some of the bond lengths can be attributed to crystal packing forces. An interesting structural feature **1a** shares in common with related η^4-benzoquinone complexes[4,13] is the bending of the C═O groups away from the metal (Figure 2). This structural effect can be seen most readily by the side view of the line drawing of **1a** shown in Figure 2.

In summary, a synthesis of η^4-2,3-substituted 1,4-naphthoquinone complexes coordinated to (η^5-C_5Me_5)Co has been achieved by reaction of (η^5-C_5Me_5)(phthaloyl)-Co(CO) with *N*-methylmorpholine *N*-oxide (to remove the coordinated CO) and alkyne. The reaction proceeds with a complete range of alkynes (internal, terminal, electron deficient, and electron rich), and the naphthoquinone complexes are stable and easily characterized.

Experimental Section

General Methods. All melting points were obtained in open capillary tubes by using a Thomas-Hoover melting point apparatus

Table III. Bond Angles of (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), 1a

angle	deg	angle	deg
C1–CO–C2	38.5 (1)	C1–CO–C3	70.0 (1)
C2–CO–C3	39.6 (1)	C1–CO–C4	81.1 (1)
C2–CO–C4	70.1 (1)	C3–CO–C4	38.7 (1)
C1–CO–C5	69.0 (1)	C2–CO–C5	83.7 (1)
C3–CO–C5	70.9 (1)	C4–CO–C5	38.6 (1)
C1–CO–C10	38.3 (1)	C2–CO–C10	70.7 (1)
C3–CO–C10	84.0 (1)	C4–CO–C10	69.4 (1)
C5–CO–C10	38.4 (1)	C1–CO–C13	103.9 (1)
C2–CO–C13	112.4 (1)	C3–CO–C13	140.7 (1)
C4–CO–C13	174.5 (1)	C5–CO–C13	145.2 (1)
C10–CO–C13	115.9 (1)	C1–CO–C14	122.6 (1)
C2–CO–C14	103.4 (1)	C3–CO–C14	108.3 (1)
C4–CO–C14	134.4 (1)	C5–CO–C14	167.9 (1)
C10–CO–C14	153.3 (1)	C13–CO–C14	40.8 (1)
C1–CO–C15	162.0 (1)	C2–CO–C15	127.8 (1)
C3–CO–C15	105.2 (1)	C4–CO–C15	106.3 (1)
C5–CO–C15	126.9 (1)	C10–CO–C15	159.6 (2)
C13–CO–C15	68.3 (1)	C14–CO–C15	41.1 (1)
C1–CO–C16	154.4 (1)	C2–CO–C16	166.9 (1)
C3–CO–C16	132.2 (2)	C4–CO–C16	108.8 (1)
C5–CO–C16	103.6 (1)	C10–CO–C16	121.7 (2)
C13–CO–C16	67.6 (2)	C14–CO–C16	67.6 (2)
C15–CO–C16	39.3 (2)	C1–CO–C17	117.3 (1)
C2–CO–C17	146.1 (1)	C3–CO–C17	172.6 (1)
C4–CO–C17	140.1 (2)	C5–CO–C17	111.8 (1)
C10–CO–C17	102.3 (1)	C13–CO–C17	39.4 (2)
C14–CO–C17	67.6 (1)	C15–CO–C17	67.6 (1)
C16–CO–C17	41.0 (2)	CO–C1–C2	63.2 (2)
CO–C1–C10	66.2 (2)	C2–C1–C10	114.5 (3)
CO–C1–O1	136.2 (3)	C2–C1–O1	122.7 (3)
C10–C1–O1	122.4 (3)	CO–C2–C1	78.3 (2)
CO–C2–C3	70.5 (2)	C1–C2–C3	122.7 (3)
CO–C2–C11	130.4 (3)	C1–C2–C11	114.8 (3)
C3–C2–C11	122.1 (3)	CO–C3–C2	69.9 (2)
CO–C3–C4	77.8 (2)	C2–C3–C4	121.9 (3)
CO–C3–C12	130.0 (3)	C2–C3–C12	121.8 (3)
C4–C3–C12	116.0 (3)	CO–C4–C3	63.5 (2)
CO–C4–C5	66.8 (2)	C3–C4–C5	114.8 (3)
CO–C4–O2	135.5 (3)	C3–C4–O2	123.4 (3)
C5–C4–O2	121.5 (3)	CO–C5–C4	74.6 (2)
CO–C5–C6	130.2 (3)	C4–C5–C6	119.7 (3)
CO–C5–C10	70.1 (2)	C4–C5–C10	121.4 (3)
C6–C5–C10	118.9 (3)	C5–C6–C7	121.0 (4)
C6–C7–C8	120.7 (4)	C7–C8–C9	120.5 (4)
C8–C9–C10	120.4 (4)	CO–C10–C1	75.5 (2)
CO–C10–C5	71.5 (2)	C1–C10–C5	121.9 (3)
CO–C10–C9	128.9 (3)	C1–C10–C9	119.5 (3)
C5–C10–C9	118.5 (3)	CO–C13–C14	68.6 (2)
CO–C13–C17	70.1 (2)	C14–C13–C17	107.8 (3)
CO–C13–C18	125.7 (3)	C14–C13–C18	124.8 (4)
C17–C13–C18	127.5 (4)	CO–C14–C13	70.6 (2)
CO–C14–C15	70.1 (2)	C13–C14–C15	107.6 (3)
CO–C14–C19	129.1 (3)	C13–C14–C19	127.1 (4)
C15–C14–C19	125.1 (3)	CO–C15–C14	68.9 (2)
CO–C15–C16	70.5 (2)	C14–C15–C16	108.0 (3)
CO–C15–C20	127.4 (3)	C14–C15–C20	125.7 (4)
C16–C15–C20	126.3 (4)	CO–C16–C15	70.2 (2)
CO–C16–C17	69.5 (2)	C15–C16–C17	108.4 (3)
CO–C16–C21	127.0 (3)	C15–C16–C21	125.1 (4)
C17–C16–C21	126.5 (4)	CO–C17–C13	70.5 (2)
CO–C17–C16	69.5 (2)	C13–C17–C16	108.3 (3)
CO–C17–C22	128.2 (3)	C13–C17–C22	126.0 (4)
C16–C17–C22	125.6 (4)		

and are uncorrected. Analytical thin-layer chromatography (TLC) was performed with E. Merck silica gel 60F-254 glass-backed plates of 0.25 mm thickness that were visualized with appropriate combinations of UV light, phosphomolybdic acid stain, $KMnO_4$ (5% in water), and vanillin stain. Preparative-scale separations were effected with "flash grade" silica gel available from Aldrich Chemical Company and by radial chromatography using a Model 7924T Chromatotron purchased from Harrison Research on rotors coated with Merck PF254 silica gel.

Table IV. Summary of X-ray Crystallography for $C_{22}H_{25}O_2Co$

Crystal Data	
MW	380.38
dimens, mm	0.1 × 0.1 × 0.4
space group	$P2_1/c$
cell const	
a, Å	6.9274 (27)[a]
b, Å	28.9403 (180)
c, Å	9.0732 (44)
α, deg	90.000 (0)
β, deg	103.973 (37)
γ, deg	90.000 (0)
Z	1
V, Å^3	1765.18
μ_{calcd}, cm^{-1}	9.80
no. of rflns used to determine cell consts	25
Data Collection and Refinement Details	
diffractometer	Syntex $P2_1$ (Nicolet P3/F program)
monochromator	graphite, Bragg $2\theta_m$ angle = 12.2 deg (perpendicular mode, assumed 50% perfect)
radiation	Mo Kα (λ = 0.71073 Å)
temp of data collc, °C	20
scan method	Wyckoff ω
scan speed (min/max), deg·min^{-1}	4.00/29.30
bkgd/scan time (TR)	1.00
no. of stds (monitoring freq/no. rflns)	81 (3/97)
2θ range, deg	4–45
check rflns (*hkl*)	(004), (0,10,0), (200)
hkl octants	–8,0,0 to 8,32,10
attenuation	26.843
mean abs coeff $(mr)_{est}$	0.50
no. of rflns collected	2631
no. of indep rflns used in final refinement	2314 ($F_o > 3\sigma F_o$)
R_{merg}	0.0487
R_σ	0.0363

[a] The estimated standard deviations of all parameters are given in parentheses for the least significant digit(s) given.

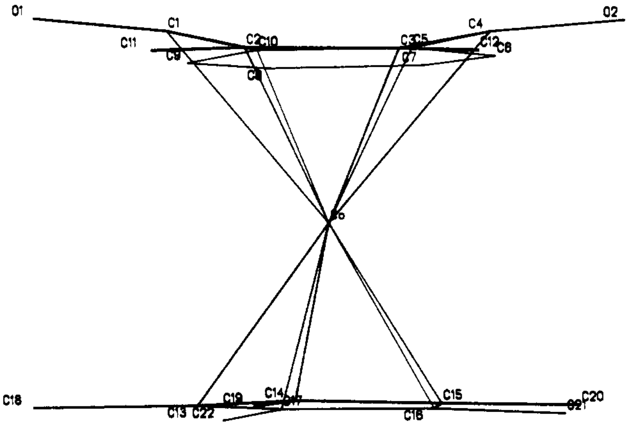


Figure 2. Side view line drawing of (η^5-C_5Me_5)Co(η^4-2,3-dimethyl-1,4-naphthoquinone), **1a**.

1,2-Dichloroethane was purified for use by washing with H_2SO_4 and water and then distilling from KOH. Methylene chloride was purified for use by distillation over CaH_2 under a nitrogen atmosphere. All other solvents were reagent-grade quality and used as received. Alkynes were purchased from Farchan Laboratories and Aldrich and were used as received. $Co_2(CO)_8$ was purchased from Alfa Chemical Company. (η^5-Cp)Co(CO)$_2$ was purchased from Strem Chemical Company and was used as received. Pentamethylcyclopentadiene, *N*-methylmorpholine *N*-oxide, and trimethylamine *N*-oxide were obtained from Aldrich. The *N*-methylmorpholine *N*-oxide was used as received and was stored under argon between uses. Trimethylamine *N*-oxide was dried by using the method of Soderquist.[21] Benzocyclo-

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Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) of (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), 1a

	x	*y*	*z*	U^a
Co	879 (1)	6312 (1)	8854 (1)	28 (1)
C1	−1331 (5)	5893 (1)	9813 (4)	40 (1)
C2	−1080 (5)	6376 (1)	10259 (4)	39 (1)
C3	−1401 (5)	6741 (1)	9195 (4)	37 (1)
C4	−1996 (5)	6656 (1)	7561 (4)	37 (1)
C5	−1817 (5)	6171 (1)	7109 (4)	33 (1)
C6	−2070 (5)	6060 (1)	5554 (4)	47 (1)
C7	−1985 (6)	5615 (2)	5101 (5)	60 (2)
C8	−1619 (6)	5253 (2)	6169 (5)	56 (2)
C9	−1353 (5)	5344 (1)	7682 (5)	48 (2)
C10	−1466 (5)	5808 (1)	8202 (4)	34 (1)
C11	−679 (7)	6460 (2)	11949 (5)	62 (2)
C12	−1339 (7)	7240 (1)	9683 (5)	55 (2)
C13	3624 (5)	6058 (1)	9996 (4)	39 (1)
C14	3510 (5)	6549 (1)	10177 (4)	39 (1)
C15	3151 (5)	6753 (1)	8690 (4)	38 (1)
C16	3016 (5)	6400 (1)	7641 (4)	46 (1)
C17	3301 (5)	5966 (1)	8449 (5)	43 (1)
C18	3985 (7)	5713 (2)	11278 (6)	74 (2)
C19	3887 (7)	6811 (2)	11634 (5)	64 (2)
C20	3006 (7)	7264 (2)	8349 (7)	70 (2)
C21	2668 (8)	6466 (2)	5920 (5)	80 (2)
C22	3353 (7)	5496 (2)	7742 (8)	86 (3)
O1	−1231 (4)	5571 (1)	10758 (3)	59 (1)
O2	−2433 (4)	6971 (1)	6599 (3)	59 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Hydrogen Atom Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) of (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), 1a

	x	*y*	*z*	*U*
H6	−2318	6302	4809	49 (11)
H7	−2162	5547	4041	63 (12)
H8	−1560	4941	5830	61 (12)
H9	−1086	5094	8400	46 (11)
H11A	−541	6786	12146	92 (18)
H11B	524	6306	12456	104 (20)
H11C	−1770	6343	12319	144 (26)
H12A	−929	7257	10771	157 (28)
H12B	−2638	7374	9341	129 (22)
H12C	−410	7406	9251	160 (27)
H18A	4141	5877	12220	134 (26)
H18B	5169	5539	11296	173 (28)
H18C	2870	5507	11145	177 (29)
H19A	4082	6599	12471	113 (21)
H19B	2760	7004	11631	151 (26)
H19C	5052	6999	11733	125 (21)
H20A	3143	7433	9278	158 (29)
H20B	1735	7329	7681	127 (22)
H20C	4043	7353	7871	105 (18)
H21A	2641	6170	5440	163 (31)
H21B	3728	6648	5710	189 (32)
H21C	1424	6621	5533	203 (35)
H22A	3089	5528	6658	191 (36)
H22B	2360	5302	7998	218 (37)
H22C	4642	5361	8118	167 (27)

Table VII. Anisotropic Thermal Parameters ($Å^2 \times 10^3$) of (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), 1a[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	30 (1)	29 (1)	27 (1)	1 (1)	9 (1)	2 (1)
C1	35 (2)	44 (2)	43 (2)	7 (2)	16 (2)	3 (2)
C2	42 (2)	48 (2)	29 (2)	2 (2)	14 (2)	8 (2)
C3	41 (2)	38 (2)	34 (2)	−2 (2)	15 (2)	5 (2)
C4	34 (2)	33 (2)	41 (2)	6 (2)	7 (2)	6 (1)
C5	25 (2)	40 (2)	33 (2)	−1 (2)	4 (1)	0 (1)
C6	39 (2)	60 (3)	38 (2)	−2 (2)	3 (2)	5 (2)
C7	51 (3)	74 (3)	50 (3)	−24 (3)	4 (2)	4 (2)
C8	47 (2)	51 (3)	70 (3)	−26 (2)	11 (2)	−4 (2)
C9	38 (2)	35 (2)	71 (3)	2 (2)	15 (2)	−4 (2)
C10	30 (2)	30 (2)	43 (2)	0 (2)	10 (2)	−1 (1)
C11	72 (3)	83 (4)	37 (2)	−1 (2)	23 (2)	13 (3)
C12	65 (3)	42 (2)	61 (3)	−11 (2)	20 (2)	10 (2)
C13	31 (2)	33 (2)	50 (2)	10 (2)	5 (2)	1 (2)
C14	36 (2)	42 (2)	38 (2)	0 (2)	6 (2)	−5 (2)
C15	33 (2)	36 (2)	47 (2)	9 (2)	12 (2)	−5 (2)
C16	34 (2)	69 (3)	37 (2)	2 (2)	14 (2)	−1 (2)
C17	26 (2)	40 (2)	64 (3)	−14 (2)	14 (2)	−1 (2)
C18	56 (3)	65 (3)	89 (4)	47 (3)	−4 (3)	0 (2)
C19	57 (3)	79 (3)	51 (3)	−20 (3)	4 (2)	−16 (3)
C20	66 (3)	50 (3)	96 (4)	31 (3)	24 (3)	−3 (2)
C21	61 (3)	149 (5)	34 (2)	2 (3)	20 (2)	−18 (3)
C22	42 (3)	68 (3)	150 (6)	−57 (3)	30 (3)	0 (2)
O1	76 (2)	51 (2)	58 (2)	26 (1)	30 (2)	8 (1)
O2	70 (2)	44 (2)	46 (2)	14 (1)	6 (1)	11 (1)

[a] The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2(a^*)^2U_{11} + ... + 2hka^*b^*U_{12})$.

butenedione was prepared according to the published procedure.[22]

The resolution of the NMR spectra of the cobalt complexes was enhanced by filtering the NMR sample through a small plug of Florisil.

Preparation of (η^5-C_5Me_5)Co(phthaloyl)(CO), 4. Into a 40-mL heavy-walled resealable reaction tube (purchased from Ace Glass Company) were added benzocyclobutenedione[22] (414 mg, 3.1 mmol), $Co_2(CO)_8$ (644 mg, 1.9 mmol), pentamethylcyclopentadiene (470 mg, 3.4 mmol), nitrogen-saturated xylene (20 mL), and a small magnetic stirring bar. After sealing with a Teflon cap, the reaction vessel was immersed up to the cap in an oil bath held at 160 °C. After the contents were stirred for 25 h, the reaction tube was cooled, opened, and the contents were directly loaded onto a silica gel column (18 g, Aldrich flash grade). Elution with hexane removed a red–brown forerun that was discarded, and 35% EtOAc/hexanes brought a bright orange band off the column. Removal of solvent on a rotary evaporator and then on a vacuum pump left 773 mg, 70%, of 4 as a bright yellow–orange solid, mp 142–143 °C. IR (CH_2Cl_2, cm^{-1}): 2004, 1640. ^1H NMR (360 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 5.6, *J* = 3.1 Hz, 2 H), 7.46 (dd, *J* = 5.6, *J* = 3.1 Hz, 2 H), 1.70 (s, 15 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 251.6, 152.8 (C=O), 132.1 (HC=C—), 119.8 (HC=C—), 8.9 (CH_3). Anal. Calcd for $C_{19}H_{19}O_3Co$: C, 64.41; H, 5.37. Found: C, 64.35; H, 5.42.

Preparation of (η^5-C_5Me_5)Co(η^4-2,3-dimethyl-1,4-naphthoquinone), 1. Phthaloylcobalt complex 4 (75 mg, 0.2 mmol), 2-butyne (45 μL, 0.5 mmol), and 1,2-dichloroethane (5 mL) were added to a 10-mL round-bottomed flask containing a small magnetic stirring bar. The reaction was placed under a nitrogen atmosphere and cooled to 0 °C in an ice bath. *N*-Methylmorpholine *N*-oxide was added as a solid (100 mg, 0.7 mmol), and the reaction was monitored by TLC (SiO_2, 10% MeOH/CH_2Cl_2) until starting material 4 was consumed. The reaction mixture was allowed to warm to ambient temperature, and after 1 h, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (15 g, Aldrich flash grade). Elution with 10% MeOH/CH_2Cl_2 removed a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 67 mg, 83%, of naphthoquinone complex 1a as a green–black solid, mp 280 °C dec. IR (CH_2Cl_2, cm^{-1}): 1575, 1538. ^1H NMR (360 MHz, $CDCl_3$): δ 8.18 (m, 2 H), 7.66 (m, 2 H), 1.93 (s, 6 H), 1.19 (s, 15 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 146.1, 130.9, 126.3, 96.1, 91.7, 90.4, 11.6, 6.6. Exact mass (*m/e*): calcd for $C_{22}H_{25}O_2Co$, 380.1186; found, 380.1191.

Preparation of (η^5-C_5Me_5)Co(η^4-2,3-diethyl-1,4-naphthoquinone), 1b. Phthaloylcobalt complex 4 (50 mg, 0.14 mmol), 3-hexyne (35 μL, 0.3 mmol), and 1,2-dichloroethane (3 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, and NMMNO (23 mg, 0.17 mmol) was added as a solid. TLC monitoring (SiO_2, 10% MeOH/CH_2Cl_2) showed the reaction to be incomplete, so another equivalent of NMMNO was added, and the reaction mixture was stirred at room temperature for 1 h. The contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% MeOH/

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(22) South, M. S.; Liebeskind, L. S. *J. Org. Chem.* **1982**, *47*, 3815.

CH_2Cl_2 removed a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 36 mg, 61%, of naphthoquinone complex **1b** as a green–black solid, mp 234–236 °C dec. IR (CH_2Cl_2, cm^{-1}): 3040 w, 1573, 1546. ^1H NMR (360 MHz, $CDCl_3$): δ 8.18 (m, 2 H), 7.67 (m, 2 H), 3.01 (m, 2 H), 1.96 (m, 2 H), 1.26 (t, J = 7.2 Hz, 6 H), 1.18 (s, 15 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.6, 131.1, 126.3, 97.2, 95.2, 91.9, 20.3, 13.1, 6.9. Exact mass (*m/e*): calcd for $C_{24}H_{29}O_2Co$, 408.1499; found, 408.1500.

Preparation of (η^5-C_5Me_5)Co(η^4-2-*n*-butyl-1,4-naphthoquinone), 1c. Phthaloylcobalt complex **4** (100 mg, 0.28 mmol), 1-hexyne (100 μL, 0.84 mmol), and 1,2-dichloroethane (4 mL) were added to a 25-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (46 mg, 0.34 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). An additional equivalent of NMMNO was added, and the reaction mixture was stirred at room temperature for 4 h. The contents of the reaction vessel were filtered through Celite with 10% $MeOH/CH_2Cl_2$, and the resulting solution was condensed on a rotary evaporator to give a greenish-black sludge that was purified by radial chromatography on a silica gel rotor, eluting with 10% $MeOH/CH_2Cl_2$ to provide a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 69.7 mg, 61%, of naphthoquinone complex **1c** as a green–black solid, mp 180–182 °C dec. IR (CH_2Cl_2, cm^{-1}): 1580, 1548. ^1H NMR (360 MHz, $CDCl_3$): δ 8.24 (d, J = 8 Hz, 1 H), 8.08 (d, J = Hz, 1 H), 7.70 (m, 2 H), 4.82 (s, 1 H), 3.05 (s, 1 H), 1.72 (m, 1 H), 1.40 (m, 2 H), 1.28 (s, 15 H), 1.24 (m, 2 H), 0.92 (t, J = 7 Hz, 3 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 146.3 (C=O), 146.1 (C=O), 131.6 (C=C—H), 130.9 (C=C—H), 126.6 (C=C—H), 125.2 (C=C—H), 97.9 (C=C), 97.2 (C=C), 95.6 (C=C), 92.7 (C=C), 81.5 (C=C—H), 31.4 (—CH_2—), 28.9 (—CH_2—), 22.5 (—CH_2—), 13.8 (—CH_3), 7.2 (—CH_3). Exact mass (*m/e*): calcd for $C_{24}H_{29}O_2Co$, 408.1499; found, 408.1477.

Preparation of (η^5-C_5Me_5)Co(η^4-2-cyclohexyl-1,4-naphthoquinone), 1d. Phthaloylcobalt complex **4** (50 mg, 0.14 mmol), cyclohexylacetylene (36 μL, 0.3 mmol), and 1,2-dichloroethane (1.5 mL) were added to a 5-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (57 mg, 0.42 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). After 8 h at room temperature, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% $MeOH/CH_2Cl_2$ removed a brown band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump, leaving 35 mg, 58%, of naphthoquinone complex **1d** as a dark brown solid, mp >230 °C. IR (CH_2Cl_2, cm^{-1}): 1575, 1535. ^1H NMR (360 MHz, $CDCl_3$): δ 8.26 (br d with fine splitting, J = 8 Hz, 1 H), 8.05 (br d with fine splitting, J = 8 Hz, 1 H), 7.64 (m, 2 H), 4.99 (s, 1 H), 2.83, (m, 1 H), 2.47 (m, 1 H), 1.88 (m, 2 H), 1.77 (m, 2 H), 1.57 (m, 2 H), 1.31 (m, 2 H), 1.25 (s, 15 H), 0.84 (m, 1 H), 0.84 (m, 1 H). Exact mass (*m/e*): calcd for $C_{26}H_{31}O_2Co$, 434.1656; found, 434.1626.

Preparation of (η^5-C_5Me_5)Co(η^4-2-carboethoxy-3-methyl-1,4-naphthoquinone), 1e. Phthaloylcobalt complex **4** (50 mg, 0.14 mmol), ethyl butynoate (33 μL, 0.3 mmol), and 1,2-dichloroethane (3 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (57 mg, 0.42 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). At completion, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% $MeOH/CH_2Cl_2$ removed a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 53 mg, 86%, of naphthoquinone complex **1e** as a green–black solid, mp 157 °C dec. IR (CH_2Cl_2, cm^{-1}): 1730, 1580, 1554. ^1H NMR (360 MHz, $CDCl_3$): δ 8.18 (m, 2 H), 7.73 (m, 2 H), 4.39 (q, J = 7 Hz, 2 H), 1.75 (s, 3 H), 1.37 (t, J = 7 Hz, 3 H), 1.27 (s, 15 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 173.21, 145.6, 130.9, 130.3, 126.3, 125.6, 118.8, 95.9, 94.5, 92.4, 85.8, 66.9, 29.6, 15.7, 8.9, 6.5. Exact mass (*m/e*): calcd for $C_{24}H_{27}O_4Co$, 438.1241; found, 438.1268.

Preparation of (η^5-C_5Me_5)Co(η^4-2-ethoxy-3-methyl-1,4-naphthoquinone), 1f. Phthaloylcobalt complex **4** (55 mg, 0.15 mmol), ethyl propynyl ether (40 μL, 0.4 mmol), and 1,2-dichloroethane (1.5 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (40 mg, 0.3 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). After 0.5 h at room temperature, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% $MeOH/CH_2Cl_2$ removed a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 27 mg, 40%, of naphthoquinone complex **1f** as a green–black solid, mp >240 °C dec. IR (CH_2Cl_2, cm^{-1}): 3040, 1575, 1560, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 8.12 (m, 2 H), 7.63 (m, 2 H), 4.66 (m, 1 H), 4.24 (m, 2 H), 1.92 (s, 3 H), 1.36 (t, J = 7 Hz, 3 H), 1.21 (s, 15 H). Exact mass (*m/e*): calcd for $C_{23}H_{27}O_3Co$, 424.1449; found, 424.1464.

Preparation of (η^5-C_5Me_5)Co(η^4-2-ethoxy-1,4-naphthoquinone), 1g. Phthaloylcobalt complex **4** (49 mg, 0.14 mmol), ethyl ethynyl ether (40 μL, 0.4 mmol), and 1,2-dichloroethane (1.5 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (38 mg, 0.28 mmol) was added as a solid followed by an additional equivalent of NMMNO, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). After 1.5 h at room temperature, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 mg, Aldrich flash grade). Elution with 10% $MeOH/CH_2Cl_2$ removed a green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 46 mg, 82%, of naphthoquinone complex **1g** as a green–black solid, mp >225 °C dec. IR (CH_2Cl_2, cm^{-1}): 1575, 1560, 1440, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 8.26 (br d with fine splitting, J = 7 Hz, 1 H), 8.01 (br d with fine splitting, J = 7 Hz, 1 H), 7.62 (m, 2 H), 4.93 (s, 1 H), 4.03 (q, J = 7 Hz, 2 H), 1.43 (t, J = 7 Hz, 3 H), 1.28 (s, 15 H). Exact mass (*m/e*): calcd for $C_{22}H_{25}O_3Co$, 396.1136; found, 396.1134.

Preparation of (η^5-C_5Me_5)Co(η^4-2-(ethoxymethyl)-3-methyl-1,4-naphthoquinone), 1h. Phthaloylcobalt complex **4** (49 mg, 0.14 mmol), ethoxy-2-butyne (43 μL, 0.4 mmol), and 1,2-dichloroethane (1.5 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (23 mg, 0.17 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). Additional NMMNO was added as a solid (4–5 equiv) until starting material had disappeared. When the reaction was completed, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% $MeOH/CH_2Cl_2$ removed a dark brown band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 41 mg, 70%, of naphthoquinone complex **1h** as a dark brown solid, mp >235 °C dec. IR (CH_2Cl_2, cm^{-1}): 3040, 1570, 1545, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 8.19 (m, 2 H), 7.7 (m, 2 H), 5.04 (d, J = Hz, 1 H), 4.03 (d, J = 10 Hz, 1 H), 3.57 (m, 2 H), 2.02 (s, 3 H), 1.21 (s, 15 H), 1.16 (t, J = 7 Hz, 3 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 146.5, 146.4, 131.6, 131.2, 126.5, 126.1, 98.3, 92.2, 91.8, 86.7, 65.8, 63.7, 29.6, 15.2, 11.4, 7.0. Exact mass (*m/e*): calcd for $C_{24}H_{29}O_3Co$, 424.1449; found, 424.1464.

Preparation of (η^5-C_5Me_5)Co(η^4-2-(hydroxyethyl)-1,4-naphthoquinone), 1i. Phthaloylcobalt complex **4** (58 mg, 0.16 mmol), propyn-3-ol (20 μL, 0.3 mmol), and 1,2-dichloroethane (1.5 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (65 mg, 0.48 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% $MeOH/CH_2Cl_2$). After 6 h at room temperature, the contents of the reaction vessel were condensed on a rotary evaporator and loaded onto a silica gel column (10 g, Aldrich flash grade). Elution with 10% MeOH/CH_2Cl_2 removed a dark green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 40 mg, 75%, of naphthoquinone complex **1i** as a green–black solid, mp >230 °C dec. IR (CH_2Cl_2, cm^{-1}): 3300 (br, w), 1585, 1545. ^1H NMR (360 MHz, $CDCl_3$): δ 8.15 (m, 2 H), 7.72 (m, 2 H), 5.67 (br s, 1 H), 4.76 (s, 1 H), 4.63 (d, J = 14 Hz, 1 H), 4.06 (d, J = Hz, 1 H), 1.35 (s, 15 H). Exact mass (m/e): calcd for $C_{21}H_{23}O_3Co$, 382.0979; found, 382.0981.

Preparation of (η^5-C_5Me_5)Co(η^4-2-(hydroxyethyl)-1,4-naphthoquinone), 1j. Phthaloylcobalt complex 4 (100 mg, 0.28 mmol), phenylacetylene (92 μL, 85.8 mg, 0.84 mmol), and 1,2-dichloroethane (4 mL) were added to a 10-mL round-bottomed flask equipped with a small magnetic stirring bar. The reaction mixture was placed under a nitrogen atmosphere, NMMNO (76 mg, 0.56 mmol) was added as a solid, and the reaction mixture was monitored for disappearance of starting material by TLC (SiO_2, 10% MeOH/CH_2Cl_2). An additional equivalent of NMMNO was added, and the reaction mixture was stirred at room temperature for 8 h. The contents of the reaction vessel were filtered through a short plug of SiO_2 with 15% MeOH/CH_2Cl_2, and the filtrate was condensed on a rotary evaporator and loaded onto a 1-mm SiO_2 rotor. The starting material was eluted with CH_2Cl_2, and 10% MeOH/CH_2Cl_2 removed a dark green–black band that was collected and evaporated on a rotary evaporator and dried on a vacuum pump to leave 69 mg, 58%, of naphthoquinone complex **1j** as a green–black solid, mp >245 °C dec. IR (CH_2Cl_2, cm^{-1}): 3040, 1580, 1550, 1490, 1440, 1380. ^1H NMR (360 MHz, $CDCl_3$): δ 8.34 (m, 1 H), 8.27 (m, 2 H), 8.13 (m, 1 H), 7.74 (m, 2 H), 7.44 (m, 3 H), 5.44 (s, 1 H), 1.11 (s, 15 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 148.2, 132.9, 131.7, 131.2, 129.7, 128.9, 128.1, 127.5, 124.9, 92.9, 90.9, 7.0. Exact mass (m/e): calcd for $C_{26}H_{25}O_2Co$, 428.1186; found, 428.1192.

X-ray Crystallographic Data for (η^5-C_5Me_5)Co(η^4-2,3-dimethyl-1,4-naphthoquinone), 1a. Data Collection. A representative single crystal of $C_{22}H_{25}O_2Co$, recrystallized from methylene chloride/hexane, was attached to the end of a glass fiber with epoxy cement and mounted on the goniometer head of a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromater and scintillation counter with pulse height discrimination. Accurate cell dimensions were obtained by least-squares refinement of 25 centered reflections (2θ = 7.39–24.93). The $\theta - 2\theta$ scan method was used with a variable scan rate of 4.00–29.30°/min (scan time/background = 1). Intensity measurements of 3 standards every 97 reflections showed no evidence of crystal deterioration.

Structure Solution and Refinement. The structure was solved on a Data General Eclipse S-140 computer using Nicolet SHELXTL software (Rev. 4.1). Analysis of systematic absences indicated absences at hkl ($h + 1 = 2n + 1$), hkl ($l = 2n + 1$), and hkl ($k = 2n + 1$), suggesting the space group $P2_1/c$. The position of the Co atom was determined by using the Patterson synthesis, and the carbons and oxygens were located in subsequent difference Fourier synthesis. The hydrogens were allowed to "ride" on their parent carbons (C–H = 0.96 Å, $U_{iso}(H) = 1.2[U_{ij}(C)]$). Block-cascade-matrix least-squares refinement of 251 variables gave final agreement factors of $R = 0.0490$ and $R_w = 0.0645$, where $R = S||F_o| - |F_c||/|F_o|$ and R_w $[Sw(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$. The GOF value was 0.577; GOF = $[Sw(|F_o| - |F_c|)^2/n_o - n_v]^{1/2}$. On the last cycle of the least-squares refinement, the overall ratio of maximum shift to the estimated standard deviation was 0.117. The weighting scheme, utilizing weights of the form $w = [s^2|F_o| + |g|F_o^2]^{-1}$ (where $g = -0.019\,173$), was implemented as a result of the analysis of the data set as a function of F_o, $2q$, and hkl. Scattering factors were those for neutral atoms.

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Supplementary Material Available: A table of observed and calculated structure factors for (η^5-C_5Me_5)Co(η^5-2,3-dimethyl-1,4-naphthoquinone), **1a** (11 pages). Ordering information is given on any current masthead page.