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Preliminary communication

PROTONATION AND METHYLATION OF η^4-2,3,5,6-TETRAMETHYL-1,4-BENZOQUINONE(η^5-PENTAMETHYLCYCLOPENTADIENYL)COBALT

GEOFFREY FAIRHURST and COLIN WHITE*
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)
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Summary

The preparation of the η^4-2,3,5,6-tetramethyl-1,4-benzoquinone complex $[Co(C_5Me_5)(C_{10}H_{12}O_2)]$ (I) is reported. Complex I undergoes reversible protonation to yield the 2—6-η-4-hydroxy-1-oxo-2,3,5,6-tetramethylcyclohexadienyl complex $[Co(C_5Me_5)(C_{10}H_{13}O_2)]BF_4$ (II) and diprotonation to yield the η^6-1,4-dihydroxy-2,3,5,6-tetramethylbenzene complex $[Co(C_5Me_5)(C_{10}H_{14}O_2)](BF_4)_2$ (III). Methylation of complex I with MeI/$AgPF_6$ gives the 2—6-η-4-methoxy-1-oxo-2,3,5,6-tetramethylcyclohexadienyl complex $[Co(C_5Me_5)(C_{11}H_{15}O_2)]PF_6$ (IV). In trifluoroacetic acid solution complex IV is protonated to form the η^6-1-hydroxy-4-methoxy-2,3,5,6-tetramethylbenzene cation $[Co(C_5Me_5)(C_{11}H_{16}O_2)]^{2+}$.

There have been several studies of protonation reactions of metal complexes containing the 2,3,5,6-tetramethyl-1,4-benzoquinone ligand (duroquinone, dq). The products of these reactions have either been the free reduced ligand, i.e. hydroduroquinone [1,2] or η^6-hydroduroquinone-metal complexes [3,4]; the latter have been inferred to be present in strongly acidic media from spectroscopic evidence and no η^6-hydroduroquinonemetal complexes or intermediate monoprotonated complexes have been isolated. In this communication we report the isolation of such complexes derived from mono- and di-protonation of $[Co(C_5Me_5)dq]$ (I) in addition to products derived from methylation of I. The reactions studied are summarised in Scheme 1.

The complex $[Co(C_5Me_5)dq]$ (I) was prepared in 75% yield by refluxing duroquinone and $[Co(C_5Me_5)(CO)_2]$ in petroleum ether (b.p. 120—150°C) for 60 h; this is similar to the procedure reported for the preparation of $[Co(C_5H_5)dq]$ [3]. Complex I was hygroscopic but prolonged pumping in vacuo at 82°C yielded the anhydrous product as an amorphous brown solid*.

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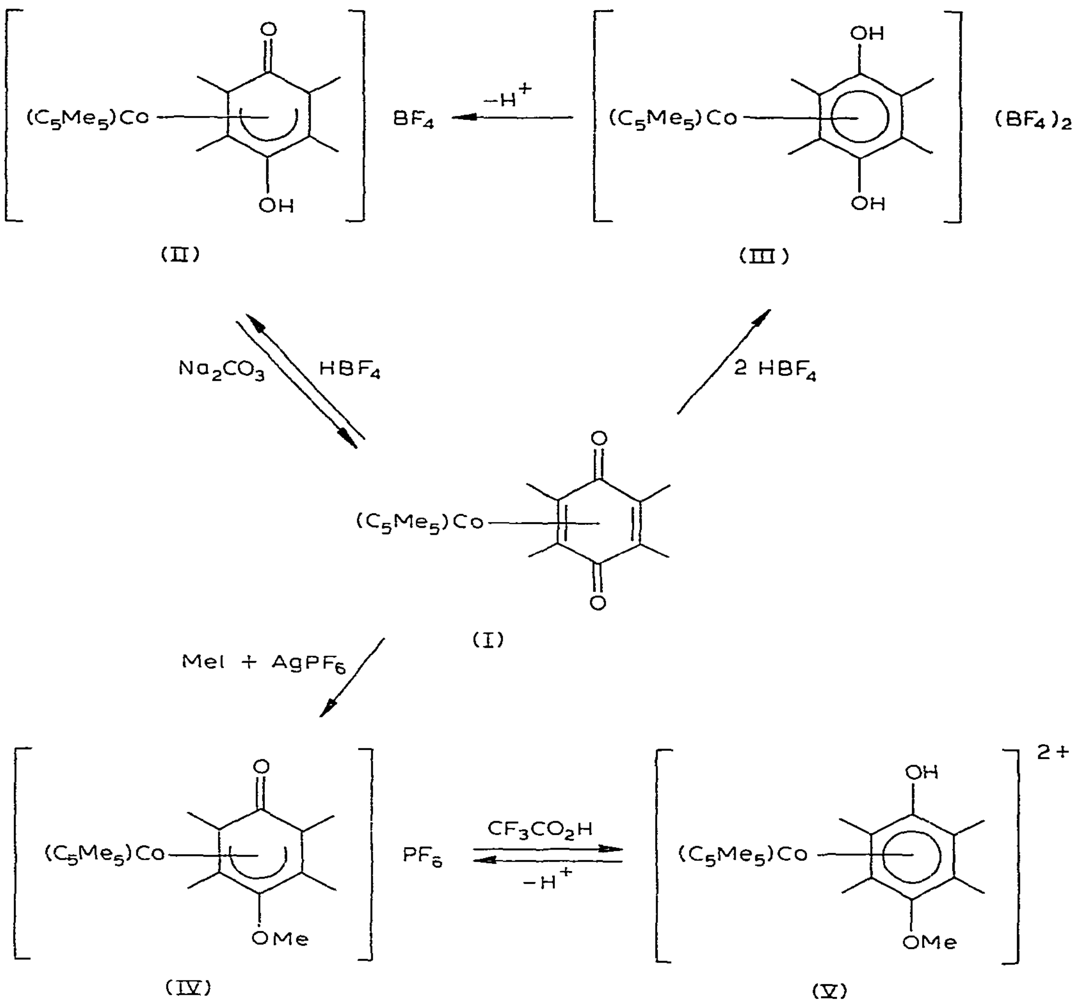
*Satisfactory analyses were obtained for all new compounds reported.



SCHEME 1. Reactions of η^4-duroquinone(η^5-pentamethylcyclopentadienyl)cobalt.

Two carbonyl bands at 1566 and 1545 cm^{-1} were observed in the IR spectrum (KBr) (cf. Co(C_5H_5)dq, 1563 and 1536 cm^{-1} [3]) and the NMR data (Table 1) are also consistent with the assigned duroquinone structure.

Addition of a few drops of aqueous HBF_4 (40%) to a suspension of complex I in acetone caused the solid to dissolve and addition of ether to the resultant orange solution precipitated orange crystals of the 2—6-η-4-hydroxy-1-oxo-2,3,5,6-tetramethylcyclohexadienyl complex, [Co(C_5Me_5)(dq.H)]BF_4 (II). The IR spectrum (KBr) showed only one carbonyl band (1556 cm^{-1}) and a band at 1331 cm^{-1} which was not present in the starting complex I and which is assigned to ν(C—OH). In addition, the spectrum contained a broad band (ca. 2400—2500 cm^{-1}) indicative of hydrogen bonding. It would appear therefore that intermolecular hydrogen bonding between the oxo and hydroxy groups occurs analogous to that observed in the dimeric phenol complexes [{M(η^5-C_5Me_5)}$_2${η^6-PhO—H···O(η^6-)Ph}][PF_6]$_3$ (M = Rh or Ir) [5]. No bands

TABLE 1

^{1}H AND $^{13}C\{^{1}H\}$ NMR DATA (δ (ppm) SCALE)

Assignment			Compound				
			I^{a}	II^{b}	III^{c}	IV^{b,d}	V^{c,e}
^{1}H	C_5-ring	Me_5	1.48	1.78	1.86	1.59	1.89
	C_6-ring	Me_4	1.79	2.27	2.46	1.89, 2.20	2.46, 2.54
		OR (R = H or Me)		6.5-7.5(br)	*f*	3.89	4.10^{f}
^{13}C	C_5-ring	C-*Me*	7.6	7.8	8.9	7.7	9.1
		C-Me	96.0^{g}	99.2^{h}	106.5^{i}	99.1	107.1
	C_6-ring	C-*Me*	12.1	11.9	12.4	11.5	12.6, 12.9
		C-Me	95.0^{g}	98.9^{h}	104.5^{i}	106.8, 107.1	106.2, 112.5
		OMe				61.1	63.6
		C-O	145.1 (CO)	139.4 (CO, COH)	133.5 (COH)	121.6(*C*OMe) 155.3(CO)	132.1(*C*OMe) 137.2(*C*OH)

[a] Spectra recorded in chloroform-*d*. [b] In acetone-d_6. [c] In CF_3CO_2H. [d] In chloroform-*d* (^{13}C NMR). [e] In CF_3CO_2H 10% chloroform-*d* (^{13}C NMR). [f] OH signal not observed. [g,h,i] These assignments may be interchanged.

were observed in the region 1700—2300 cm^{-1} clearly indicating that direct protonation of the metal to give the hydrido complex $[Co(C_5Me_5)(H)(dq)]BF_4$ had not occurred.

The ^{1}H and ^{13}C NMR spectra of II (Table 1) do not show the asymmetry of the monoprotonated duroquinone ligand; in particular only one signal was observed in the ^{13}C NMR spectrum for the carbons C(1) and (C4) instead of the expected two. This conflicts with the IR data and suggests that in solution a rapid process occurs which equilibrates the two ends of the protonated duroquinone ligand.

Deprotonation of complex II was readily achieved by treatment with a base (e.g. Na_2CO_3) to give $[Co(C_5Me_5)dq]$ almost quantitatively.

The diprotonated hydroduroquinone complex $[Co(C_5Me_5)(dq.H_2)](BF_4)_2$ (III) was prepared by treating $[Co(C_5Me_5)dq]$ with HBF_4 in a solution of trifluoroacetic acid and trifluoroacetic anhydride. The orange product proved to be extremely hygroscopic and although quite stable when stored in a desiccator it rapidly absorbed moisture when exposed to the atmosphere. This compound is formulated as the η^6-hydroduroquinone complex III on the basis of analysis, NMR and, in particular, IR spectroscopy. In contrast to the spectra of compounds I and II, the IR spectrum (KBr) of III showed no carbonyl bands in the region 1500—1600 cm^{-1} but it did contain bands at 1301 and 3300—3500 cm^{-1} which are assigned to ν(C—O) and ν(O—H), respectively.

Attempts to recrystallise III from a mixture of dry acetone and ether gave only the monoprotonated complex II. The ease of deprotonation of the hydroduroquinone complex III is not surprising in view of the fact that the related complex $[Ir(C_5Me_5)(C_6H_5OH)](PF_6)_2$ also deprotonates readily when warmed in vacuo [5].

The successful protonation of $[Co(C_5Me_5)dq]$ (I) led to attempts to alkylate this complex. Addition of a molar equivalent of $AgPF_6$ to a stirred acetone solution of I containing excess iodomethane gave the 2—6-η-4-methoxy-1-oxo-2,3,5,6-tetramethylcyclohexadienyl complex (IV) in 52% yield. The IR spectrum (KBr) of the product showed a single carbonyl band (1575 cm^{-1}) and bands at 1185 and 2855 cm^{-1} which are assigned to ν(C—OMe) and ν(OC—H), respectively. As expected, the carbonyl C(1), and the carbon bonded to the methoxy group C(4), are readily distinguished in the ^{13}C NMR spectrum (Table 1).

When recorded in trifluoroacetic acid solution, the ^{13}C NMR spectrum of compound IV was significantly different to that recorded in acetone. In particular, acidification of IV resulted in a large upfield shift of the carbonyl, C(1), resonance. We observed similar upfield shifts upon protonation of the carbonyl groups of complexes I and II; other workers have reported similar results when the complexes [M(C_5H_5)(dq)] (M = Co, Rh or Ir) are protonated to give solutions of the corresponding hydroduroquinone complexes [4]. We therefore propose that the species formed when IV is dissolved in trifluoroacetic acid is the η^6-1-hydroxy-4-methoxy-2,3,5,6-tetramethylbenzene complex (V). Unfortunately we have not yet succeeded in isolating this complex. Similarly, attempts to prepare a dimethylated complex by reaction of [Co(C_5Me_5)dq] with iodomethane and two molar equivalents of $AgPF_6$ have been unsuccessful.

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