Cyclopentadienyl- or Pentamethylcyclopentadienyl-(arene)cobalt(III) Complexes: Arene = Indole, Benzene, Mesitylene, Hexamethylbenzene, 1,4-Dihydroxy- and 1-Hydroxy-4-methoxytetramethylbenzene

By **Geoffrey Fairhurst** and **Colin White,*** Department of Chemistry, The University, Sheffield S3 7HF

Indole displaces acetone from the complex $[Co(C_5Me_5)(OCMe_2)_3][PF_6]_2$ to give indole(pentamethylcyclopentadienyl)cobalt(III) hexafluorophosphate in which the cobalt is complexed to the six-membered ring of the indole; attempts to prepare other arene complexes by this procedure have failed. The benzene complex $[Co(C_5Me_5)(\eta\text{-}C_6H_6)][BF_4]_2$ has been prepared by treatment of $[Co(C_5Me_5)(\eta^4\text{-}C_6H_8)]$ with $[CPh_3][BF_4]$. The related complex $[Co(C_5H_5)(\eta\text{-}C_6H_6)][BF_4]_2$ undergoes arene exchange with mesitylene and hexamethylbenzene to give $[Co(C_5H_5)(\eta\text{-}C_6Me_nH_{6-n})][BF_4]_2$ (n = 3 or 6) and with suitable donors (*e.g.* methyl-substituted benzenes) forms charge-transfer complexes in solution. 2,3,5,6-Tetramethyl-1,4-benzoquinone, $C_6Me_4O_2$, reacts with $[Co(C_5Me_4R)(CO)_2]$ to give $[Co(C_5Me_4R)(\eta^4\text{-}C_6Me_4O_2)]$ (R = Me or Et). Protonation and methylation of the pentamethylcyclopentadienyl complex gives the 4-hydroxy- and 4-methoxy-2,3,5,6-tetramethyl-1-oxocyclohexadienyl complexes $[Co(C_5Me_5)\{\eta^5\text{-}C_6Me_4(OR)O\}][BF_4]$ (R = H or Me). The latter are converted into the corresponding substituted-benzene complexes $[Co(C_5Me_5)\{\eta^6\text{-}C_6Me_4(OR)(OH)\}]^{2+}$ by acid. Infrared and ^1H and ^{13}C n.m.r. spectra are reported and the relative stabilities of the complexes are discussed.

IN recent years complexes of the type $[M(C_5Me_5)(arene)][PF_6]_2$ have been prepared with a wide range of arenes (*e.g.* M = Rh or Ir, arene = substituted benzenes,[1,2] phenanthrene, or indole;[2] M = Ir, arene = indene[2] or phenol[3]). Considering that they contain a six-membered aromatic hydrocarbon ring π-bonded to a metal in a +III oxidation state, the general stability of these complexes is really rather remarkable and has been attributed in part to the steric bulk and electron-donating properties of the C_5Me_5 ligand. It has also been noted that methyl substituents on the arene stabilise the complex and that the iridium complexes are significantly more stable than their rhodium analogues.[1,2] In view of these observations it is intriguing that, apart from a brief reference to the compounds $[Rh(C_5H_5)(C_6H_6)]X_2$ (X = BF_4 or PF_6),[4] the only well documented complex containing a η^6-arene co-ordinated to M^{III} is $[Co(C_5H_5)(C_6H_6)][BF_4]_2$[5] (1) which is not stabilised by methyl substituents and which contains a first-row transition metal.†

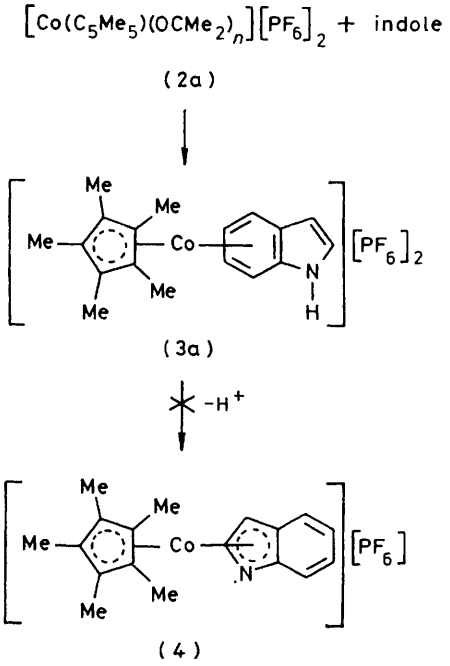
N.m.r. studies have shown that a related species $[Co(C_5H_5)\{C_6Me_4(OH)_2\}]^{2+}$ containing a 1—6-η-1,4-dihydroxy-2,3,5,6-tetramethylbenzene (*i.e.* hydroduroquinone) ligand is formed by diprotonating the duroquinone complex $[Co(C_5H_5)(\eta^4\text{-}C_6Me_4O_2)]$ with strong acids.[6,7] However, neither this nor any other η^6-hydroduroquinone complex has been isolated.

We describe herein the results of our investigations into the preparation and properties of arene complexes of cobalt(III) including the preparation of pentamethylcyclopentadienylcobalt(III) complexes containing η^6-hydroduroquinone and related ligands. A preliminary communication on part of this work has been published.[8]

RESULTS AND DISCUSSION

$[Co(C_5Me_5)(\eta^6\text{-arene})]$ *Complexes* (*arene = indole or benzene*).— Arenepentamethylcyclopentadienyl-rhodium(III) and -iridium(III) complexes are conveniently prepared by the reaction of the appropriate arene with the solvent complexes $[M(C_5Me_5)(solvent)_n][PF_6]_2$ (M = Rh or Ir, solvent = $OCMe_2$ or CH_2Cl_2, n believed to be 3).[2] Indole reacted similarly with the corresponding cobalt acetone complex (2a)[9] to give (3a—7a-η-indole)-(pentamethylcyclopentadienyl)cobalt(III) (3a).

The formulation of (3a) with the cobalt atom bound to the six-membered ring of the indole is supported by analysis and i.r. and n.m.r. spectroscopy (Tables 1 and 2). In particular, the ^{13}C n.m.r. spectrum closely resembles that of its rhodium analogue $[Rh(C_5Me_5)(C_8H_7N)][PF_6]_2$ (3b) and in the latter compound the mode of bonding is unambiguous since all the resonances of the six-membered ring exhibit coupling to ^{103}Rh.



Upon treatment with base the η^6-indoleiridium complex $[Ir(C_5Me_5)(C_8H_7N)][PF_6]_2$ reversibly deprotonates to give an η^5-indolyl complex. However, attempts to

---

† *Note added in proof*: M. L. H. Green and R. B. A. Pardy (*J.C.S. Dalton*, **1979**, 355) have recently prepared $[Co(\eta\text{-}C_5Me_4Et)(arene)][PF_6]_2$ (arene = benzene or toluene).

prepare a η^5-indolyl cobalt analogue (4) by deprotonation of (3a) with base {$Na_2[CO_3]$, NEt_3, or $K(OBu^t)$} failed; a rapid irreversible reaction occurred, similar to that reported for the rhodium indole complex (3b),[2] and no products could be characterised. In nitromethane solution, indene displaces indole from the complexes $[M(C_5Me_5)(\eta^6\text{-indole})][PF_6]_2$ (M = Rh or Ir) to give η^5-indenyl complexes.[2] Treatment of the cobalt indole complex (3a) with indene, however, merely resulted in a slow decomposition of the indole complex.

Attempts to prepare other cobalt arene complexes from the acetone complexes $[Co(C_5Me_5)(OCMe_2)_n]X_2$ [X = PF_6 (2a) or BF_4 (2b)] also failed. Electron-donating substituents in the arene ring are known to stabilise the complexes $[M(C_5Me_5)(\text{arene})][PF_6]_2$ (M = Rh or Ir) and consequently the complexes (2a) and (2b) were treated with 1,3,5-trimethoxybenzene and various methyl-substituted benzenes but no reaction was observed. Attempts to use solvent complexes containing other weakly co-ordinated solvents [*e.g.* tetrahydrofuran (thf), CH_3NO_2, and CH_2Cl_2] or to cause $Ag[PF_6]$ to react with either $[Co(C_5Me_5)I_2(CO)]$ or $[\{Co(C_5Me_5)I_2\}_n]$ in the presence of an arene (benzene or mesitylene) as the solvent also failed to give any characterisable products.

TABLE 1

Microanalytical and infrared data

	Complex	Analysis (%) [a]		I.r. (KBr) (cm^{-1})
		C	H	
(3a)	$[Co(C_5Me_5)(\eta^6\text{-indole})][PF_6]_2$ [b]	36.0 (36.0)	3.7 (3.7)	ν(NH) 3 380s,br [c]
(6)	$[Co(C_5Me_5)(\eta\text{-}C_6H_6)][BF_4]_2$	43.3 (43.1)	4.9 (4.7)	
(7)	$[Co(C_5H_5)(\eta\text{-}C_6H_3Me_3)][BF_4]_2$	40.2 (40.2)	4.1 (4.1)	
(8)	$[Co(C_5H_5)(\eta\text{-}C_6Me_6)][BF_4]_2$	44.3 (44.3)	5.0 (4.8)	
(9a)	$[Co(C_5Me_5)(\eta^4\text{-}C_6Me_4O_2)]$	67.0 (67.0)	7.6 (7.5)	ν(CO) 1 566 (sh), 1 548s
(9b)	$[Co(C_5Me_4Et)(\eta^4\text{-}C_6Me_4O_2)]$	67.5 (67.7)	7.8 (7.8)	ν(CO) 1 576s, 1 552s
(10)	$[Co(C_5Me_5)\{\eta^5\text{-}C_6Me_4(OH)O\}][BF_4]$	53.7 (53.8)	6.2 (6.3)	ν(C=O) 1 556s; ν(C–O) 1 331m ν(OH) 3 150—3 300s,br
(11)	$[Co(C_5Me_5)\{\eta^6\text{-}C_6Me_4(OH)_2\}][BF_4]_2$	45.0 (45.0)	5.7 (5.5)	ν(C–O) 1 298m ν(OH) 3 200—3 350m,br
(12)	$[Co(C_5Me_5)\{\eta^5\text{-}C_6Me_4(OMe)O\}][PF_6]$	48.7 (48.7)	5.8 (5.8)	ν(C=O) 1 575s; ν(C–O) 1 185m ν(OC–H) 2 855m

[a] Calculated values are given in parentheses. [b] N, 2.2 (2.3%). [c] In Nujol.

In the course of these experiments we did observe a very curious reaction. The complex $[Co(C_5Me_5)I_2(CO)]$ reacted with $Ag[PF_6]$ in indene as the solvent to give a purple oil of variable composition but which consistently contained nitrogen (1.8—3.1%). The reactions were carried out under dinitrogen and this appears to be the only source of nitrogen in the products since elemental analyses indicated that all starting materials were nitrogen-free. Further, the i.r. spectrum of the product contained a broad band at 840 cm^{-1} characteristic of the PF_6 anion and either one or two bands in the region 2 230—2 278 cm^{-1}; isocyanates, nitriles, and isocyanides typically absorb in the latter region of the spectrum.[10] Although the reaction occurred only in neat indene, the ^1H n.m.r. spectra of the purple oils indicated that indene was not always present in the product; these spectra did, however, all contain a singlet at *ca.* δ 0.9 in $CDCl_3$ which we assign to the C_5Me_5 ligand. Despite several attempts, no products could be characterised and we merely report these intriguing observations.

In view of the limited success in using the solvent complexes (2) to prepare cobalt arene complexes, an attempt was made to prepare (η-benzene)pentamethylcyclopentadienylcobalt(III) tetrafluoroborate (6) by a modification of the procedure reported for the corresponding cyclopentadienyl complex,[5] *i.e.*:

$$[Co(C_5Me_5)(CO)_2] \xrightarrow[h\nu]{C_6H_6} \underset{(5)}{[Co(C_5Me_5)(\eta^4\text{-}C_6H_6)]} \xrightarrow{2[CPh_3][BF_4]} \underset{(6)}{[Co(C_5Me_5)(\eta\text{-}C_6H_6)][BF_4]_2}$$

Although successful, the preparation suffered from the disadvantage that the formation of the initial hexa-1,3-diene complex (5) proceeded in low yield, the major product being an extremely air-sensitive, dark green oil which gave a complex i.r. spectrum with major bands at *ca.* 1 758, 1 948, and 2 005 cm^{-1}. We were unable to characterise this oil but note that u.v. irradiation of $[Co(C_5H_5)(CO)_2]$ gives a mixture of unstable polynuclear cobalt carbonyl complexes, *e.g.* $[\{Co(C_5H_5)(CO)\}_2CO]$ and $[Co_4(C_5H_5)_4(CO)_2]$.[11] It seems likely that similar products are formed from $[Co(C_5Me_5)(CO)_2]$ at the expense of the hexa-1,3-diene complex (5).

$[Co(C_5H_5)(\eta^6\text{-arene})][BF_4]_2$ (*arene = benzene, mesitylene, or hexamethylbenzene*).—(η-Benzene)cyclopentadienyl cobalt(III) tetrafluoroborate (1) was prepared from $[Co(C_5H_5)(CO)_2]$ by the procedure reported by Fischer and Brunner.[5] A cheaper alternative synthesis is described (see Experimental section) which starts from cobalt(II) chloride and involves the preparation of the cyclohexadienyl complex $[Co(C_5H_5)(C_6H_7)]I$ by reaction of cobaltacene with di-iodomethane.[12-14]

The corresponding mesitylene and hexamethylbenzene complexes $[Co(C_5H_5)(C_6H_nMe_{6-n})][BF_4]_2$ [n = 3 (7) or 0 (8)] were prepared from the benzene complex (1) by arene-exchange reactions:

$$[Co(C_5H_5)(C_6H_6)][BF_4]_2 + CH_nMe_{6-n} \longrightarrow [Co(C_5H_5)(C_6H_nMe_{6-n})][BF_4]_2 + C_6H_6$$

Thus refluxing solutions of $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ in trifluoroacetic acid containing *ca.* 2—5 mol equivalents

TABLE 2

Hydrogen-1 and ^{13}C-{^{1}H} n.m.r. spectroscopic data

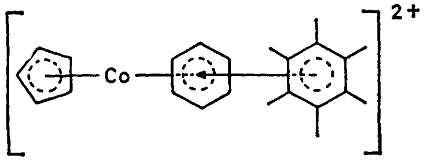
		^{1}H N.m.r.		^{13}C N.m.r.	
	Complex	Assignment	δ	Assignment	δ
(3a)	[Co(C$_5$Me$_5$)(η^6-indole)][PF$_6$]$_2$	C$_5$Me$_5$	1.94 (s) [a]	C$_5$Me$_5$	8.7, 105.5 [a]
		H(4), H(6)	7.03 (m)	C(7)	90.3
		H(3)	7.21 [d, J(H^{1}H^2) = 3 Hz]	C(4)	95.6
		H(5), H(7)	7.87 (m)	C(5)	96.2
		H(2)	8.33 [dd, J(H^{2}H^3) = 3.5 Hz]	C(6)	97.6
		H(1)	11.88 (br)	C(3)	103.1
				C(7a)	107.1
				C(3a)	114.8
				C(2)	145.9
(6)	[Co(C$_5$Me$_5$)(η-C$_6$H$_6$)][BF$_4$]$_2$	C$_5$Me$_5$	2.28 (s) [b]	C$_5$Me$_5$	11.5, 112.8 [b]
		C$_6$H$_6$	7.45 (s)	C$_6$H$_6$	107.6
(1)	[Co(C$_5$H$_5$)(η-C$_6$H$_6$)][BF$_4$]$_2$	C$_5$H$_5$	7.01 (s)	C$_5$H$_5$	97.4 [b]
		C$_6$H$_6$	7.86 (s)	C$_6$H$_6$	107.6
(7)	[Co(C$_5$H$_5$)(η-C$_6$H$_3$Me$_3$)][BF$_4$]$_2$	C$_5$H$_5$	6.76 (s) [b]	C$_5$H$_5$	97.1 [b]
		$\mathrm{C}_6H_3\mathrm{Me}_3$	7.50 (s, 3 H)	CH	103.2
		$\mathrm{C}_6\mathrm{H}_3Me_3$	2.82 (s, 9 H)	CMe	126.5
				Me	21.7
(8)	[Co(C$_5$H$_5$)(η-C$_6$Me$_6$)][BF$_4$]$_2$	C$_5$H$_5$	6.43 (s) [b]	C$_5$H$_5$	96.8 [b]
		C$_6$Me$_6$	2.89 (s)	CMe	119.2
(9a)	[Co(C$_5$Me$_5$)(η^4-C$_6$Me$_4$O$_2$)]	C$_5$Me$_5$	1.48 (s) [c]	C$_5$Me$_5$	7.6, 96.0, [*, c]
		C$_6$Me$_4$O$_2$	1.79 (s)	CMe	95.0 [*]
				Me	12.1
				CO	145.1
(9b)	[Co(C$_5$Me$_4$Et)(η^4-C$_6$Me$_4$O$_2$)]	C$_5$Me$_4$	1.52 (s), 1.55 (s) [d]	CEt	98.3 [e]
		CH_2Me	1.98 (q)	CMe	94.6, 92.6
		CH$_2$$Me$	0.94 (t, J = 6.5 Hz)	C$_5$ ring CH$_2$Me	16.4
		C$_6$Me$_4$O$_2$	1.84 (s)	CH$_2$$Me$	13.0
				CMe	7.6, 7.2
				CMe	94.1
				Me	12.3
				CO	149.5
(9c)	[Co(C$_5$H$_5$)(η^4-C$_6$Me$_4$O$_2$)]	C$_5$H$_5$	4.86 (s) [c, f]	C$_5$H$_5$	85.4 [c, g]
		C$_6$Me$_4$O$_2$	2.20 (s)	CMe	91.3
				Me	14.5
				CO	157.2
(10)	[Co(C$_5$Me$_5$){η^5-C$_6$Me$_4$(OH)O}][BF$_4$]	C$_5$Me$_5$	1.78 (s) [a]	C$_5$Me$_5$	7.8, [*] 99.2, [†, a]
		Me$_4$	2.27 (s)	CMe	98.9 [†]
		OH	6.5—7.5 (br)	Me	11.9 [*]
				CO, COH	139.4
(11)	[Co(C$_5$Me$_5$){η^6-C$_6$Me$_4$(OH)$_2$}][BF$_4$]$_2$	C$_5$Me$_5$	1.86 (s) [b]	C$_5$Me$_5$	12.4, 106.5, [*, b]
		Me$_4$	2.46 (s)	CMe	104.5
		OH	not observed	Me	8.9
				COH	133.5
	[Co(C$_5$H$_5$){η^6-C$_6$Me$_4$(OH)$_2$}]$^{2+}$	C$_5$H$_5$	6.02 (s) [f, h]	C$_5$H$_5$	89.7 [g, h]
		Me$_4$	2.72 (s)	CMe	98.0
		OH	not observed	Me	9.8
				COH	131.8
(12)	[Co(C$_5$Me$_5$){η^5-C$_6$Me$_4$(OMe)O}][PF$_6$]	C$_5$Me$_5$	1.59 (s) [a]	C$_5$Me$_5$	7.7, 99.1 [e]
		Me$_4$	1.89 (s), 2.20 (s)	CMe	106.8, 107.1
		OMe	3.89 (s)	Me$_4$	11.5
				COMe	121.6
				CO	155.3
				OMe	61.1
(13)	[Co(C$_5$Me$_5$){η^6-C$_6$Me$_4$(OMe)(OH)}]$^{2+}$	C$_5$Me$_5$	1.89 (s) [i]	C$_5$Me$_5$	9.1, 107.1 [b]
		Me$_4$	2.46 (s), 2.54 (s)	CMe	106.2, 112.5
		OMe	4.10 (s)	Me$_4$	12.6, 12.9
		OH	not observed	COMe	132.1
				COH	137.2
				OMe	63.6

[a] In [^{2}H$_6$]acetone. [b] In CF$_3$CO$_2$H. [c] In [^{2}H]chloroform. [d] In [^{2}H$_2$]water. [e] In CH$_2$Cl$_2$. [f] Ref. 6. [g] Ref. 7. [h] In H$_2$SO$_4$. [i] In CF$_3$CO$_2$H + 10% [^{2}H]chloroform. [*, †] These assignments may be interchanged.

of mesitylene or hexamethylbenzene effected complete arene exchange within 16 h. The choice of trifluoroacetic acid as solvent was dictated by the fact that in other solvents [*e.g.* dimethyl sulphoxide (dmso), water, methanol, acetonitrile, and acetone] rapid displacement of the arene ligands by solvent occurred at the temperatures necessary to effect exchange. Unfortunately, therefore, this procedure is unsuitable for the preparation of complexes of acid-sensitive arenes (*e.g.* indole or indene).

In the ^{1}H n.m.r. spectra of the cobalt arene complexes (Table 2) the resonances of the co-ordinated arenes are moved downfield with respect to the free arene. The upfield shift normally associated with complexation of an arene to a metal atom[15] is clearly more than counterbalanced by the downfield shift due to the dipositive charge on the cation. Similar shifts were observed for the complexes $[M(C_5Me_5)(arene)][PF_6]_2$ (M = Rh or Ir).[2] As other workers have noted,[16] in this type of sandwich compound the electron-releasing effect of the methyl substituents in either the arene or the cyclopentadienyl ring is reflected in the observed chemical shifts, *i.e.* methyl substitution of the arene ring in the complexes $[Co(C_5H_5)(C_6H_nMe_{6-n})][BF_4]_2$ ($n = 0, 3,$ or 6) causes an upfield shift of the cyclopentadienyl signal; similarly, methyl substituents on the cyclopentadienyl ring cause an upfield shift of the resonance of co-ordinated benzene. In contrast, in the ^{13}C n.m.r. spectra the upfield shift observed upon complexation of benzene is similar in both $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ and $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ (*i.e.* 22.0 and 22.3 p.p.m. respectively).

Charge-transfer Complexes.—During the investigations into arene-exchange reactions, it was observed that addition of mesitylene or hexamethylbenzene to a trifluoroacetic acid solution of $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ (1) caused immediate colour changes from pale yellow to deep red and purple respectively. It was confirmed that the intense colours did not arise from solvent interactions with either the arene or the complex (1) and it was also shown that no change in the chemical shifts of the two components occurred upon mixing together trifluoroacetic acid solutions of each. No colour change was observed upon adding an arene with electron-withdrawing groups (*e.g.* hexafluorobenzene) to a trifluoroacetic acid solution of complex (1) and it was concluded that the intense colours originate from the formation of charge-transfer complexes of the type:



This type of interaction was only found in trifluoroacetic acid solution, presumably because the interaction is very weak and is broken down in more strongly co-ordinating solvents. The complexes could not be isolated; attempts to precipitate them with diethyl ether caused an immediate discharge of the colour and the original complex was recovered. It was found, however, that careful addition of a large volume of mesitylene (*ca.* 100 cm^3) to a concentrated solution of complex (1) in trifluoroacetic acid (*ca.* 10 cm^3) followed by cooling at −25 °C caused a red-brown oil to separate. This was washed with pentane to leave a brown oily solid, but this was unstable and spontaneously regenerated the original complex within *ca.* 10 min.

Similar charge-transfer complexes have been reported by Braitsch,[17] who found that addition of arenes or other suitable donors such as ferrocene to concentrated acetone solutions of bis(hexamethylbenzene)iron(II) hexafluorophosphate complexes precipitated out 1 : 1 adducts. In view of our failure to isolate the cobalt charge-transfer complexes it is significant to note that although the iron complexes were stable in the solid state they decomposed rapidly in solution.

The Relative Stabilities of Cobalt(III) *Arene Complexes.*—The four complexes $[Co(C_5R_5)(arene)][BF_4]_2$ (arene = benzene, R = H or Me; arene = mesitylene or hexamethylbenzene, R = H) were all isolated as pale yellow crystalline solids. When stored for *ca.* 3 months at ambient temperatures noticeable decomposition occurred with all the complexes, particularly $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ which showed extensive decomposition even when stored at −25 °C.

In dmso solution complete displacement of both the cyclopentadienyl ring and the arene occurs very rapidly to give $[Co(OSMe_2)_6][BF_4]_2$ (see previous paper), but in acetonitrile or nitromethane only the arene ligand is displaced and the reactions could be monitored by ^{1}H n.m.r. spectroscopy.

$$[Co(C_5R_5)(arene)][BF_4]_2 \xrightarrow{\text{solvent}} [Co(C_5R_5)(solvent)_3][BF_4]_2 + \text{arene}$$
$$\text{solvent} = MeCN \text{ or } MeNO_2$$

In [^{2}H$_3$]acetonitrile, complete displacement of benzene from $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ occurred in *ca.* 2 h at 35 °C, whereas displacement of benzene from $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ took *ca.* 3 months at 20 °C. The approximate time required for the complete displacement of a complexed arene by [^{2}H$_3$]nitromethane at 20 °C is given in Table 3.

It is apparent that methyl substituents on either the cyclopentadienyl ligand or the arene stabilise the complex towards attack by the solvent. Thus $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ is significantly more stable than $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ in both acetonitrile and nitromethane. Similarly, upon changing from benzene to mesitylene to hexamethylbenzene the cyclopentadienylcobalt complexes become progressively more stable in nitromethane. It has been noted previously that methyl substituents stabilise the complexes $[Co(CO)_3(arene)]$[18] and $[Rh(C_5Me_5)(arene)][PF_6]_2$.[1,2] Methyl substituents on the arene would be expected to increase the donor ability of the arene whilst methyl substituents on the cyclopentadienyl ligand would also increase the electron density on the metal, which in turn could lead to increased back-donation to the arene; both effects would enhance the strength of the metal–arene bond. Combined with this is a steric effect of the methyl substituents which hinders nucleophilic attack upon the complex.

Also included in Table 2 are data for the complexes $[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$ [19] and $[Ir(C_5Me_5)(C_6H_6)][PF_6]_2$. It is interesting to note that displacement of the benzene ligand from the rhodium complex occurred within 6 weeks in nitromethane, whereas the pentamethylcyclopentadienyl-cobalt and -iridium benzene complexes were found to be quite stable in this solvent. It is extremely unlikely that replacement of the η-C_5Me_5 ligand with the η-C_5Me_4Et ligand would significantly affect the lability of co-ordinated benzene and hence the difference in the stabilities of these benzene complexes in nitromethane must arise from the difference in the nature of the metals. Thus, of the triad, the rhodium–benzene bond is the most labile. In this respect the complexes resemble $[M(CO)_6]$ (M = Cr, Mo, or W) [20] and $[M(C_5H_5)(CO)_2]$ (M = Co, Rh, or Ir) [21] in that the complex of the second-row metal is the most labile.

TABLE 3

Rate of displacement of complexed arene by $[^2H_3]$ nitromethane at 20 °C

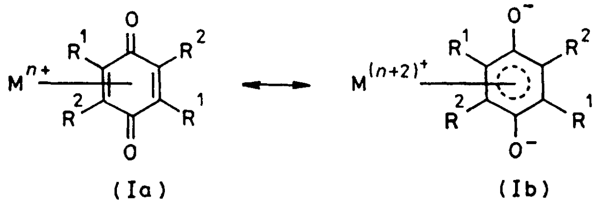
Complex	Time
$[Co(C_5H_5)(C_6Me_6)][BF_4]_2$	Stable *
$[Co(C_5H_5)(C_6H_3Me_3)][BF_4]_2$	12 weeks
$[Co(C_5H_5)(C_6H_6)][BF_4]_2$	3 d
$[Co(C_5Me_5)(C_6H_6)][BF_4]_2$	Stable *
$[Rh(C_5Me_4Et)(C_6H_6)][PF_6]_2$	6 weeks
$[Ir(C_5Me_5)(C_6H_6)][PF_6]_2$	Stable *

* *No free arene detected after 12 weeks in solution.*

Arene Complexes derived from Methylation and/or Protonation of $[Co(C_5Me_5)(\eta^4\text{-}C_6Me_4O_2)]$.—Refluxing duroquinone with $[Co(C_5Me_5)(CO)_2]$ in light petroleum (b.p. 120—150 °C) for 60 h gave the duroquinone complex $[Co(C_5Me_5)(C_6Me_4O_2)]$ (9a); similar treatment of $[Co(C_5Me_4Et)(CO)_2]$ yielded the corresponding ethyltetramethylcyclopentadienyl complex $[Co(C_5Me_4Et)(C_6Me_4O_2)]$ (9b). Both products were hygroscopic and the anhydrous complexes were obtained only after prolonged pumping *in vacuo* at 82 °C. Each complex exhibited two carbonyl bands [*i.e.* 1 566 and 1 548 cm^{-1} (C_5Me_5); 1 576 and 1 552 cm^{-1} (C_5Me_4Et)] similar to those reported for $[Co(C_5H_5)(C_6Me_4O_2)]$ (9c) (*i.e.* 1 563 and 1 536 cm^{-1}).[6] It was noted, however, that in the hydrated complexes the carbonyl bands occurred at significantly lower wavenumbers (up to 30 cm^{-1}) presumably due to hydrogen bonding between the water molecules and the carbonyl groups of the duroquinone ligands.

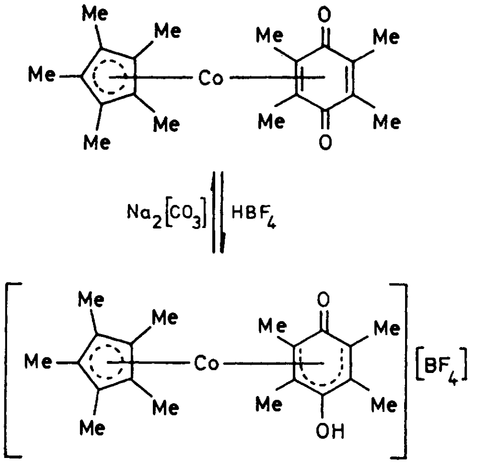
There has been considerable interest in the mode of bonding of duroquinone, or related ligands, to transition metals. For example duroquinone has been shown to act as a four-electron η-diene ligand [*i.e.* (Ia; $R^1 = R^2 =$ Me)] in the complexes $[Co(C_5H_5)(C_6Me_4O_2)]\cdot 2H_2O$ [22] and $[\{RhL(C_6Me_4O_2)\}_n]$ [$n = 1$, L = C_5H_5, C_9H_7, or pentane-2,4-dionate (acac); [23] $n = 2$, L = Cl [24]] whilst in the complex $[\{Pt(PPh_3)_2\}_2(C_6Me_4O_2)]$ the bridging duroquinone ligand functions as a two-electron η-ene ligand to each platinum atom.[25] In contrast, in the paramagnetic 2,5-dimethyl-1,4-benzoquinone complex $[Ni(C_8H_{12})(C_6H_2Me_2O_2)]$ the quinone is formally a hydroquinone dianion ligand [*i.e.* (Ib; R^1 = H, R^2 = Me)].[26]

Acidic media would be expected to stabilise the canonical form (Ib) and Bodner and Englemann have investigated this by examining the solvent dependence of the ^{13}C n.m.r. spectra of compounds containing complexed duroquinone.[7] They concluded that conversion of a duroquinone ligand into a η^6-hydroduroquinone form (Ib) is characterised by an upfield shift of the C(1,4) carbon signals and a large decrease in the value of δ', the difference in chemical shifts of the carbons C(1,4) and C(2,3,5,6). It is interesting, therefore, to compare the ^{13}C n.m.r. spectra of $[Co(C_5R^1_4R^2)(C_6Me_4O_2)]$ [$R^1 = R^2 =$ Me (9a); R^1 = Me, R^2 = Et (9b); and $R^1 = R^2 =$ H (9c)] (Table 2). The resonances due to C(1,4) occur at significantly higher fields in the peralkylated complexes whilst the values of δ' are smaller, *i.e.* $\delta' < 50.1$ for (9a), δ 55.4 for (9b), and 65.9 for (9c). This may be interpreted as evidence that the canonical form (Ib) is more significant in the structure of the peralkylated complexes than in the C_5H_5 complex. Certainly one could rationalise such a proposal in that the powerful electron-donating properties of the peralkylated cyclopentadienyl ligand should stabilise (Ib). Further, it would suggest that the peralkylated complexes, especially (9a), should protonate more readily than the cyclopentadienyl complex (9c). The results described below indicate that this indeed may be the case.



(Ia) (Ib)

Monoprotonation of complex (9a) was achieved by addition of a few drops of aqueous HBF_4 to a suspension of (9a) in acetone. The i.r. spectrum of the product contained no ν(M–H) bands in the region 1 700—2 300 cm^{-1}, clearly indicating that direct protonation of the metal to give the hydrido-complex $[Co(C_5Me_5)H(C_6Me_4O_2)][BF_4]$ had not occurred. In contrast, the i.r. spectrum corresponds exactly to that expected for the 2-6-η-4-hydroxy-2,3,5,6-tetramethyl-1-oxocyclohexadienyl complex (10) with one carbonyl band at 1 556 cm^{-1} {*cf.* $[RuH(\eta^5\text{-}PhO)(PPh_3)_2]\cdot MeOH$, ν(CO) at 1 550 cm^{-1}},[27] a broad band at *ca.* 3 300—3 400 cm^{-1} [ν(OH)], and a band at 1 331 cm^{-1} which is not present in the starting complex and which is assigned to ν(C–OH). In addition, the spectrum contained a weak broad band at *ca.* 2 400—2 500 cm^{-1}; such bands are typical of hydrogen bonding [28] indicating that intermolecular hydrogen bonding occurs between the oxo- and hydroxy-



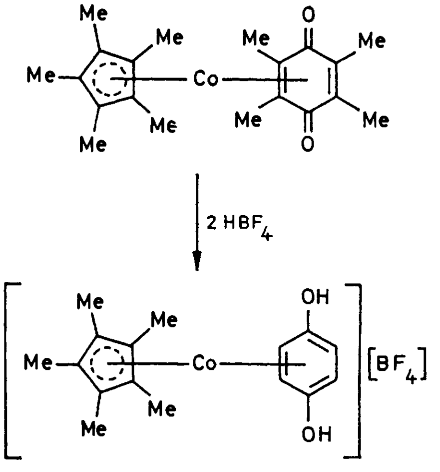
(10)

group. The dimeric phenol complexes $[\{M(C_5Me_5)\}_2\{\eta^6\text{-PhOH} \cdots O(\eta^5\text{-Ph})\}][PF_6]_3$ (M = Rh or Ir) also contain this type of hydrogen bonding.[3]

It is interesting that the asymmetry of the monoprotonated duroquinone ligand is not reflected in the ^1H or ^{13}C n.m.r. spectra. In particular, the ^{13}C n.m.r. spectrum contains only one signal for the carbons C(1) and C(4) instead of the expected two and suggests that in solution the two ends of the protonated duroquinone ligand rapidly equilibrate. The intermolecular hydrogen bonding present between the oxo- and hydroxy-groups should certainly facilitate such a proton-transfer process which must be extremely rapid since cooling the sample to −90 °C produced no change in the ^{13}C n.m.r. spectrum.

With base (Na$_2$[CO$_3$]), deprotonation of complex (10) occurred to regenerate the duroquinone complex $[Co(C_5Me_5)(C_6Me_4O_2)]$.

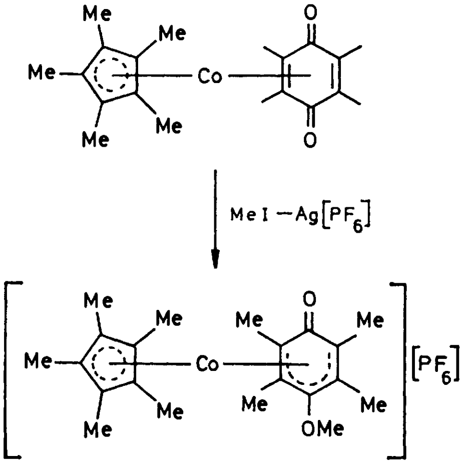
Diprotonation of $[Co(C_5Me_5)(C_6Me_4O_2)]$ was achieved by treatment with HBF$_4$ in a solution of trifluoroacetic acid and trifluoroacetic anhydride. These anhydrous conditions were necessary because the hydroduroquinone product $[Co(C_5Me_5)\{C_6Me_4(OH)_2\}][BF_4]_2$ (11) proved to be extremely hygroscopic. It also deprotonated readily and attempts to recrystallise the complex from dry acetone and dry diethyl ether gave only the monoprotonated complex (10). We have previously reported that the related phenol complex $[Ir(C_5Me_5)(PhOH)][PF_6]_2$ also readily deprotonates.[3]



(11)

To our knowledge complex (11) is the first 1—6-η-1,4-dihydroxy-2,3,5,6-tetramethylbenzene complex to be isolated and this lends some support to the proposal that the pentamethylcyclopentadienyl ligand helps to stabilise the hydroduroquinone ligand. Consistent with the proposed structure, the i.r. spectrum contained bands at 1 301 and 3 300—3 500 cm^{-1} which are assigned to ν(C–OH) and ν(O–H) respectively aud no ν(CO) bands in the region 1 500—1 600 cm^{-1}. The n.m.r. data (Table 2) are comparable to those attributed to $[Co(C_5H_5)\{C_6Me_4(OH)_2\}]^{2+}$ which is believed to be generated when $[Co(C_5H_5)(C_6Me_4O_2)]$ is dissolved in acidic media.[6,7]

In addition to protonation reactions, the duroquinone complex (9a) undergoes methylation. Thus reaction with iodomethane and 1 mol equivalent of Ag[PF$_6$] yielded the 2—6-η-4-methoxy-2,3,5,6-tetramethyl-1-oxocyclohexadienyl complex (12):

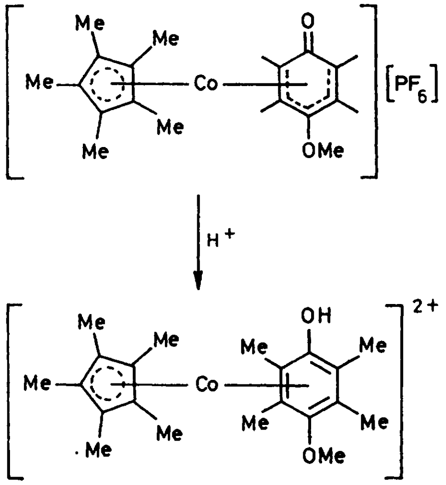


(12)

The presence of the methoxy group is clearly evident in the i.r. and n.m.r. spectra (Tables 1 and 2). Consistent with the proposed structure, the carbonyl carbon, C(1), and the carbon bonded to the methoxy group, C(4), are readily distinguished in the ^{13}C n.m.r. spectrum.

Attempts made to prepare a dimethylated complex by reaction of $[Co(C_5Me_5)(C_6Me_4O_2)]$ with iodomethane and 2 mol equivalents of Ag[PF$_6$] were unsuccessful. In trifluoroacetic acid, protonation of the monomethoxy-complex (12) occurred to form the 1—6-η-hydroxy-4-methoxy-2,3,5,6-tetramethylbenzene complex (13).

The ^{13}C n.m.r. spectrum of (13), recorded in trifluoroacetic acid, clearly indicated that protonation had occurred; in particular, the low-field carbonyl resonance (δ 155.3) which characterised the oxomethoxytetramethylcyclohexadienyl complex (12) was replaced by a signal at higher field (*i.e.* δ 137.2). Complex (13), like the corresponding hydroduroquinone complex, appears to deprotonate readily and all attempts to isolate it in the solid state failed.



(13)

EXPERIMENTAL

General experimental procedures and the preparation of the complexes $[Co(C_5Me_5)(CO)_2]$ and $[Co(C_5Me_5)I_2(CO)]$ have been described in the previous paper. The complex $[Co(C_5Me_4Et)(CO)_2]$ was prepared by the published procedure.[29]

(3a—7a-η-*Indole*)(η-*pentamethylcyclopentadienyl*)*cobalt*(III) *Hexafluorophosphate*, (3a).—A solution of $[Co(C_5Me_5)(OCMe_2)_n][PF_6]_2$ was prepared by addition of $Ag[PF_6]$ (210 mg, 0.84 mmol) to a stirred solution of $[Co(C_5Me_5)I_2(CO)]$ (200 mg, 0.42 mmol) in acetone (10 cm^3). After stirring for 2 min, the mixture was filtered through a cellulose column (1 × 3 cm) to remove the fine precipitate of AgI. The residue and column were washed with acetone (10 cm^3) and indole (300 mg, 2.6 mmol) was added to the combined filtrate and washings. The mixture was immediately concentrated (*ca.* 2 cm^3) and addition of diethyl ether precipitated a brown oily solid. Recrystallisation from acetone and ether gave orange crystals of $[Co(C_5Me_5)(\eta^6\text{-indole})][PF_6]_2$ (209 mg, 83%).

(η-*Benzene*)(η-*pentamethylcyclopentadienyl*)*cobalt*(III) *Tetrafluoroborate*, (6).—The complex $[Co(C_5Me_5)(CO)_2]$ (4.5 g, 18 mmol) and cyclohexa-1,3-diene (12 g, 150 mmol) were dissolved in light petroleum (75 cm^3, b.p. 60—80 °C) and the solution was irradiated in a silica flask for 30 d with u.v. radiation (3-kW Englehard–Hanovia lamp). After cooling, the solution was filtered and chromatographed on an alumina column (3 × 60 cm), eluting with light petroleum (b.p. 40—60 °C). Two components were separated: the first band (orange) contained the desired product, $[Co(C_5Me_5)(C_6H_8)]$, whilst the second band (green) contained a very air-sensitive material. Removal of the volatile materials *in vacuo* yielded red and green oils, respectively, from the two fractions. Attempts to purify the green material resulted in its rapid decomposition.

The red oil was converted, without further purification, into $[Co(C_5Me_5)(C_6H_6)][BF_4]_2$ by treatment with $[CPh_3][BF_4]$ (0.8 g, 2.4 mmol) in dichloromethane (10 cm^3). The resulting brown precipitate was filtered off and recrystallised from nitromethane and diethyl ether to give the product as pale yellow crystals (790 mg, 10%).

(η-*Benzene*)(η-*cyclopentadienyl*)*cobalt*(III) *Tetrafluoroborate*, (1).—This compound was prepared in 51% yield from $[Co(C_5H_5)(CO)_2]$ by the published procedure.[5] An alternative synthesis which has the advantage of starting from cobalt(II) chloride is described below.

Anhydrous $CoCl_2$ (5.0 g, 38.5 mmol) and $Tl(C_5H_5)$ (23.2 g, 86 mmol) were suspended in benzene (350 cm^3) and boiled under reflux for 1 h. The resulting $[Co(C_5H_5)_2]$ solution was cooled and filtered and CH_2I_2 (8.0 g, 30 mmol) was added. The mixture was stirred for 2 h at 20 °C and the yellow precipitate, $[Co(C_5H_5)_2]I$, which had formed was filtered off. The red filtrate, containing $[Co(C_5H_5)(C_5H_5CH_2I)]$, was reduced to a red oil *in vacuo* (4 h at 20 °C). The oily insoluble material which formed was filtered off and concentration of the filtrate followed by addition of diethyl ether precipitated an orange solid (1.50 g), shown by ^1H n.m.r. spectroscopy to be $[Co(C_5H_5)(C_6H_7)]I$ containing a small amount of $[Co(C_5H_5)_2]I$. The orange solid was dissolved in dichloromethane (10 cm^3) and the solution filtered and treated with a solution of $[CPh_3][BF_4]$ (4.0 g, 12 mmol) in dichloromethane (15 cm^3). The green precipitate which formed was collected by filtration and recrystallised from nitromethane and ether to give pale yellow crystals of $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ (1.45 g, 20%).

(η-*Cyclopentadienyl*)(1—6-η-1,3,5-*trimethylbenzene*)-*cobalt*(III) *Tetrafluoroborate* (7).—The complex $[Co(C_5H_5)(C_6H_6)][BF_4]_2$ (200 mg, 0.53 mmol) and mesitylene (1.8 g, 15 mmol) were refluxed in trifluoroacetic acid (8 cm^3) for 14 h. The deep red solution was cooled and filtered; addition of diethyl ether precipitated a pale yellow solid, which was recrystallised from nitromethane and ether to give $[Co(C_5Me_5)(C_6H_3Me_3)][BF_4]_2$ (130 mg, 60%). (η-*Cyclopentadienyl*)(1—6-η-*hexamethylbenzene*)*cobalt*(III) *tetrafluoroborate*, $[Co(C_5H_5)(C_6Me_6)][BF_4]_2$ (8), was prepared similarly as a yellow crystalline solid in 75% yield.

(η-*Pentamethylcyclopentadienyl*)(2—3:5—6-η-2,3,5,6-*tetramethyl*-1,4-*dioxocyclohexa*-2,5-*diene*)*cobalt*(I), (9a).—The complex $[Co(C_5Me_5)(CO)_2]$ (1.35 g, 5.4 mmol) and duroquinone (1.70 g, 10.4 mmol) were boiled under reflux in light petroleum (175 cm^3, b.p. 120—150 °C) for 60 h, until the i.r. spectrum of the reaction mixture no longer showed bands at 2 010 and 1 950 cm^{-1}, characteristic of $[Co(C_5Me_5)(CO)_2]$. The mixture was reduced in volume to *ca.* 30 cm^3 under reduced pressure at 70 °C and the black solid was filtered off. The product was extracted from the black solid in dichloromethane until the washings were colourless and the dichloromethane solution was reduced to a red oil *in vacuo*. Recrystallisation of the red oil from chloroform and hexane gave orange crystals of the hydrated product $[Co(C_5Me_5)(C_6Me_4O_2)]\cdot nH_2O$. Heating the hydrated product *in vacuo* at 85 °C for 16 h yielded the anhydrous product $[Co(C_5Me_5)(C_6Me_4O_2)]$ as a brown powder (1.45 g, 75%).

The composition of the hydrated material varied with each recrystallisation, but generally the product contained between 0.5 and 1.0 molecules of water per molecule of $[Co(C_5Me_5)(C_6Me_4O_2)]$. Recrystallisation from water, however, gave light brown plate-like crystals of approximate composition $Co(C_5Me_5)(C_6Me_4O_2)\cdot 1.5H_2O$.

(η-*Ethyltetramethylcyclopentadienyl*)(2—3:5—6-η-2,3,5,6-*tetramethyl*-1,4-*dioxocyclohexa*-2,5-*diene*)*cobalt*(I) (9b), was prepared similarly as red crystals (yield 14%) from $[Co(C_5Me_4Et)(CO)_2]$.

2—6-η-4-*Hydroxy*-2,3,5,6-*tetramethyl*-1-*oxocyclohexadienyl*)(η-*pentamethylcyclopentadienyl*)*cobalt*(III) *Tetrafluoro-*

borate, (10).—Tetrafluoroboric acid (0.5 cm^3 of a 40% aqueous solution) was added to a stirred suspension of [Co(C_5Me_5)($C_6Me_4O_2$)] (200 mg, 0.56 mmol) in acetone (5 cm^3). The resulting orange solution was filtered and reduced to a red oil *in vacuo*. Recrystallisation of the red oil from acetone and diethyl ether gave orange crystals of [Co(C_5Me_5){C_6Me_4(OH)O}][BF_4] (230 mg, 92%). The product in dichloromethane was quantitatively converted back into the starting material, [Co(C_5Me_5)($C_6Me_4O_2$)], by stirring with excess of anhydrous sodium carbonate.

(1—6-η-1,4-*Dihydroxy*-2,3,5,6-*tetramethylbenzene*)(η-*pentamethylcyclopentadienyl*)*cobalt*(III) *Tetrafluoroborate*, (11).—The product was extremely moisture sensitive and consequently this reaction was carried out under a dry nitrogen atmosphere. The complex [Co(C_5Me_5)($C_6Me_4O_2$)] (100 mg, 0.28 mmol) was dissolved in a mixture of trifluoroacetic acid (5 cm^3) and tetrafluoroboric acid (2 cm^3 of a 40% aqueous solution) and trifluoroacetic anhydride (8 cm^3) was cautiously added. After cooling, anhydrous diethyl ether (10 cm^3) was added dropwise and a yellow precipitate formed. The supernatant was decanted off and the yellow solid was washed with a mixture of 20% (v/v) trifluoroacetic anhydride in ether (2 × 15 cm^3). Pumping under vacuum at 82 °C for 6 h removed all traces of solvent and yielded the product as an orange powder. Since the product was extremely hygroscopic, its i.r. spectrum and microanalysis were obtained immediately and no value for the yield was recorded.

(2—6-η-4-*Methoxy*-2,3,5,6-*tetramethyl*-1-*oxocyclohexadienyl*)(η-*pentamethylcyclopentadienyl*)*cobalt*(III) *Hexafluorophosphate*, (12).—The salt Ag[PF_6] (140 mg, 0.56 mmol) was added to a stirred suspension of [Co(C_5Me_5)($C_6Me_4O_2$)] (200 mg, 0.56 mmol) in acetone (50 cm^3) containing iodomethane (2.5 g, 17.6 mmol). After stirring for 30 min, the insoluble material was filtered off and washed with acetone (20 cm^3). The combined filtrate and washings were reduced to an oil *in vacuo*. The product was extracted into chloroform and the solution was filtered. Careful addition of diethyl ether precipitated orange crystals of [Co(C_5Me_5){C_6Me_4(OMe)O}][PF_6] (150 mg, 52%).

We thank the S.R.C. for a studentship (to G. F.) and are grateful to Mr. A. Yates and Mrs. C. D. Chalk for their skilful assistance with some of the experimental work.

[8/1702 *Received*, 26*th September*, 1978]

REFERENCES

[1] C. White and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1971, 3322.

[2] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.

[3] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **127**, 415.

[4] H. B. Fritz and J. Manchot, *J. Organometallic Chem.*, 1964, **2**, 8.

[5] E. O. Fischer and H. Brunner, *Chem. Ber.*, 1965, **98**, 175.

[6] G. N. Schrauzer and H. Thyret, *Angew. Chem. Internat. Edn.*, 1963, **2**, 478.

[7] G. M. Bodner and T. R. Englemann, *J. Organometallic Chem.*, 1975, **88**, 391.

[8] G. Fairhurst and C. White, *J. Organometallic Chem.*, 1978, **160**, C17.

[9] G. Fairhurst and C. White, preceding paper.

[10] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley–Interscience, New York, 1969.

[11] K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organometallic Chem.*, 1975, **97**, 283.

[12] G. E. Herberich, E. Bauer, and J. Schwarzer, *J. Organometallic Chem.*, 1969, **17**, 445.

[13] G. E. Herberich and J. Schwarzer, *Chem. Ber.*, 1970, **103**, 2016.

[14] G. E. Herberich, G. Greiss, and H. F. Heil, *J. Organometallic Chem.*, 1970, **22**, 723.

[15] W. McFarlane and S. O. Grim, *J. Organometallic Chem.*, 1966, **5**, 147; D. A. Brown and J. R. Raju, *J. Chem. Soc.* (*A*), 1966, 1617.

[16] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1968, 2257.

[17] D. M. Braitsch, *J.C.S. Chem. Comm.*, 1974, 460.

[18] E. O. Fischer, K. Ofele, H. Essler, W. Frohlich, J. P. Martensen, and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763.

[19] G. Fairhurst and C. White, unpublished work.

[20] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, 1967, **6**, 2082; H. Werner and R. Prinz, *Chem. Ber.*, 1966, **99**, 3582.

[21] H. G. Shuchster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 1657.

[22] V. A. Uchtmann and L. F. Dahl, *J. Organometallic Chem.*, 1972, **40**, 403.

[23] G. G. Alexandrov, Yu. T. Schtruchkov, V. S. Khandkorova, and S. P. Gubin, *J. Organometallic Chem.*, 1970, **25**, 243.

[24] S. McVey and P. M. Maitlis, *Canad. J. Chem.*, 1966, **44**, 2429.

[25] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 416.

[26] G. N. Schrauzer and H. Thyret, *Chem. Ber.*, 1963, **96**, 1755.

[27] D. J. Cole-Hamilton, R. J. Young, and G. Wilkinson, *J.C.S. Dalton*, 1976, 1995.

[28] H. Ratajczak and W. J. Orville-Thomas, *J. Mol. Structure*, 1967–1968, **1**, 449; J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

[29] T. Dooley, G. Fairhurst, C. D. Chalk, K. Tabatabaian, and C. White, *Transition Metal Chem.*, 1978, **3**, 299.