The Cyclometallation of Benzoic Acid to give Rhodium, Iridium, and Osmium *C,O*-Benzoates. *X*-Ray Structure Determination of the Dibenzoate $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$†

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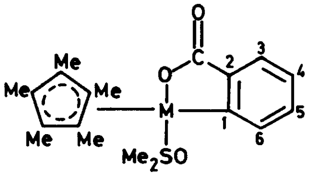
The cyclometallated benzoate complexes $[(C_5Me_5)M(OOCC_6H_4)(Me_2SO)]$ [M = Rh (**1a**) or Ir (**1b**)] and $[(p\text{-}MeC_6H_4CHMe_2)Os(OOCC_6H_4)(Me_2SO)]$ were prepared by reaction of $[(C_5Me_5)MMe_2(Me_2SO)]$ or $[(p\text{-}MeC_6H_4CHMe_2)OsMe(Cl)(Me_2SO)]$ with benzoic acid or silver benzoate respectively. Methane was formed in these reactions. Complex (**1b**) was also prepared from $[(C_5Me_5)IrCl_2(Me_2SO)]$ with silver benzoate. Complex (**1a**) reacted with water to give $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][OOCPh]$ and the dibenzoate hydrate $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$ (**5a**). Complex (**5a**) was also formed when (**1a**) was reacted with benzoic acid or when $[(C_5Me_5)RhCl_2(Me_2SO)]$ reacted with two equivalents of silver benzoate. The structure of (**5a**) was determined by an *X*-ray study which showed two benzoates attached in a monodentate manner to the $(C_5Me_5)Rh$ moiety; the rhodium also bore a co-ordinated water, which was also hydrogen-bonded to the two benzoate carbonyl oxygens. Both the rhodium and the iridium complexes (**1a**) and (**1b**) reacted with methyl iodide to give the cyclometallated methyl benzoate complexes $[(C_5Me_5)M\{OC(OMe)C_6H_4\}(I)]$. They also underwent carbonylation to give phthalic anhydride and $[(C_5Me_5)Rh(CO)_2]$ from (**1a**), and $[(C_5Me_5)Ir(OOCC_6H_4)(CO)]$ from (**1b**). Mechanisms of the various transformations are discussed.

Many cyclometallation reactions have been described in which an aromatic ring, bearing a functional group bonded to a metal, is attacked by the metal *ortho* to the functional group to give a four-, five-, or six-membered chelate ring.[1] Related reactions have also been used for organic synthesis; for example the orthothallation of benzoic acid, followed by transmetallation with Pd^{II}, offers useful synthetic routes to phthalic anhydride or isocoumarins.[2,3]

However the cyclometallation of benzoic acid itself, a very attractive starting material for many reactions, did not appear to have been described prior to our work. We here give details of the synthesis of complexes of rhodium, iridium, and osmium containing cyclometallated benzoic acid (and substituted benzoic acids) and on some reactions of the resultant complexes. A preliminary account of part of this work, together with an *X*-ray structure determination of the iridium complex $[(C_5Me_5)Ir(OOCC_6H_4)(Me_2SO)]$ (**1b**), which confirmed that the bonding had been correctly deduced from the spectroscopic data, has been published.[4]

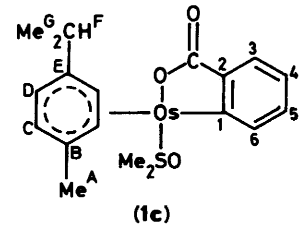
Results and Discussion

Syntheses of the Cyclometallated Complexes derived from Benzoic Acid.—The complexes (**1a**) and (**1b**) were originally prepared by reaction of the dimethyl complexes (**2a**) and (**2b**) with benzoic acid, the other product being methane [equation (1), C_5Me_5 = η^5-pentamethylcyclopentadienyl]. This is a viable and useful route to (**1a**) or (**1b**), but other routes [equations (2) or (3)] were then developed which have their own advantages. The most convenient preparation depends on the metal.



(**1a**); M = Rh

(**1b**); M = Ir



(**1c**)

$$[\mathrm{LMMe_2(Me_2SO)}] + \mathrm{PhCOOH} \longrightarrow$$

(**2a**); LM = $(C_5Me_5)Rh$

(**2b**); LM = $(C_5Me_5)Ir$

$$[\mathrm{LM(OOCC_6H_4)(Me_2SO)}] + 2\mathrm{CH_4} \qquad (1)$$

(**1a**) or (**1b**)

$$[\mathrm{LMMe(Cl)(Me_2SO)}] + \mathrm{PhCOOAg} \longrightarrow$$

(**3a**); LM = $(C_5Me_5)Rh$

(**3b**); LM = $(C_5Me_5)Ir$

(**3c**); LM = $(p\text{-}MeC_6H_4CHMe_2)Os$

$$[\mathrm{LM(OOCC_6H_4)(Me_2SO)}] + \mathrm{AgCl} + \mathrm{CH_4} \qquad (2)$$

(**1a**), (**1b**), or (**1c**)

$$[\mathrm{LIrCl_2(Me_2SO)}] + 2\mathrm{PhCOOAg} \longrightarrow$$

(**4b**)

$$[\mathrm{LIr(OOCC_6H_4)(Me_2SO)}] + 2\mathrm{AgCl} + \mathrm{PhCOOH} \qquad (3)$$

(**1b**)

Equation (2) gives the most general route; the chloromethyl-rhodium, -iridium, and -osmium complexes (**3a**), (**3b**), and (**3c**)[5–7] reacted with one equivalent of silver benzoate to give the cyclometallated complexes (**1a**), (**1b**), and (**1c**) respectively.

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† Aquabis(benzoato-*O*)(η^5-pentamethylcyclopentadienyl)rhodium(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 N m^{-2}.

Table 1. ^{1}H N.m.r. spectroscopic data* (δ/p.p.m.)

Complex	C_5Me_5 (or *p*-cymene)	Me_2SO	Benzoate	Other
(1a)	1.69	2.19 2.96	H(3) 7.56 (dd; *J* 7.5, 1.5) H(4) 7.10 (td; *J* 7.5, 1) H(5) 7.26 (td; *J* 7.5, 1.5) H(6) 7.52 (dd; *J* 7.5, 1)	
(1b)	1.78	2.49 2.90	H(3) 7.56(m) H(4) 7.08 (td; *J* 7.5, 1) H(5) 7.21 (td; *J* 7.5, 1) H(6) 7.51(m)	
(1c)	A 2.28 C + D 5.64(m) F 2.74 (sp; *J* 7) G 1.19 (d; *J* 7) 1.07 (d; *J* 7)	2.71 2.49	H(3) 7.35 (ddd; *J* 7.5, 2, 1) H(4) 6.96 (td; *J* 7.5, 1.5) H(5) 7.15 (td; *J* 7.5, 2) H(6) 7.78 (ddd; *J* 7.5, 1.5, 1)	
(5a)	1.71		H(2, 6) 8.00(m) H(3, 4, 5) 7.33(m)	H_2O 4.06 br
(5c)	A 2.36 C + D 6.72 (d; *J* 6) 6.42 (d; *J* 6) F 2.79 (sp; *J* 7) G 1.37 (d; *J* 7)		H(2, 6) 7.82 (dd; *J* 7, 1) H(4) 7.44 (tt; *J* 7, 1) H(3, 5) 7.32 (dd; *J* 7, 7)	
(5d)	A 2.31 C + D 5.95 (d; *J* 5.5) 5.72 (d; *J* 5.5) F 2.97 (sp; *J* 7) G 1.36 (d; *J* 7)		H(2, 6) 7.86 (dd; *J* 7, 1) H(4) 7.36 (tt; *J* 7, 1) H(3, 5) 7.28 (dd; *J* 7, 7)	
(6a)	1.71	2.20 2.94	H(3) 7.40 (d; *J* 2) H(5) 7.09 (dd; *J* 8, 2) H(6) 7.39 (d; *J* 8)	*p*-Me 2.28
(6b)	1.76	2.50 2.95	H(3) 7.43 (d; *J* 2) H(5) 7.07 (dd; *J* 7.5, 2) H(6) 7.40 (d; *J* 7.5)	*p*-Me 2.30
(7a)	1.70	2.20 3.02	H(3) 8.36 (d; *J* 2.5) H(5) 8.12 (dd; *J* 8, 2.5) H(6) 7.76 (d; *J* 8)	
(7b)	1.78	2.50 3.05	H(3) 8.40 (d; *J* 2.5) H(5) 8.10 (dd; *J* 8, 2.5) H(6) 7.76 (d; *J* 8)	
(8a)	1.71	2.20 2.96	H(3) 7.21 (d; *J* 3) H(5) 6.95 (dd; *J* 8, 3) H(6) 7.40 (d; *J* 8)	*p*-MeO 3.80
(8b)	1.86	2.48 2.96	H(3) 7.21 (d; *J* 2.5) H(5) 6.92 (dd; *J* 8, 2.5) H(6) 7.39 (d; *J* 8)	*p*-MeO 3.79
(9a)	1.71	2.32 2.84	H(3) 7.31 (dd; *J* 8, 1) H(4) 7.10 (t; *J* 8) H(5) 6.81 (dd; *J* 8, 1)	*o*-MeO 3.85
(9b)	1.86	2.55 2.89	H(3) 7.30 (dd; *J* 7.5, 1) H(4) 7.10 (t, *J* 7.5) H(5) 6.79 (dd; *J* 7.5, 1)	*o*-MeO 3.83
(11a)	1.82		H(3) 7.62(m) H(4) 7.17(m) H(5) 7.30(m) H(6) 7.35(m)	
(11b)	1.92		H(3) 7.61 (dd; *J* 7.5, 1.5) H(4) 7.15 (td; *J* 7.5, 1) H(5) 7.25 (td; *J* 7.5, 1.5) H(6) 7.38 (dd; *J* 7.5, 1)	
(13a)	1.72		H(3) 7.48(m) H(4) 6.93(m) H(5) 7.32(m) H(6) 7.61(m)	OMe 3.99
(13b)	1.78		H(3) 7.55 (ddd; *J* 7.5, 1.5, 0.5) H(4) 6.89 (td; *J* 7.5, 1) H(5) 7.30 (td; *J* 7.5, 1.5) H(6) 7.62 (ddd; *J* 7.5, 1.5, 0.5)	OMe 4.08

* All spectra measured in $CDCl_3$ except (**1c**) and (**5c**) which were measured in $(CD_3)_2CO$; $SiMe_4$ as internal reference. Coupling constants in Hz to the nearest 0.5 Hz. All spectra measured at 250 MHz except (**1a**), (**1b**), (**11b**) and (**13b**) which were measured at 400 MHz.

Methane was again produced. This is also the only route to the osmium complex (**1c**); thus, for example, reaction of [(*p*-$MeC_6H_4CHMe_2$)$OsCl_2(Me_2SO)$] (**4c**) with silver benzoate gave only the osmium dibenzoate complex (**5c**). The ruthenium dibenzoate complex (**5d**) was also the sole product from the reaction of the dichlororuthenium complex (**4d**) with silver benzoate [equation (4)].

$[LMCl_2(Me_2SO)] + 2PhCOOAg \longrightarrow$
(**4a**); LM = $(C_5Me_5)Rh$
(**4c**); LM = (*p*-$MeC_6H_4CHMe_2$)Os
(**4d**); LM = (*p*-$MeC_6H_4CHMe_2$)Ru
$LM(OOCPh)_2 + 2AgCl + Me_2SO$ (4)
(**5a**), (**5c**), or (**5d**)

The complexes were structurally characterised by careful analysis of their ^{1}H and ^{13}C n.m.r. spectra (Tables 1 and 2), including studies at 400 MHz (for ^{1}H) which assigned the benzenoid hydrogens. For complexes of benzoic acid itself the highest field aromatic resonance is assigned to H(4) since it is the one expected to be least influenced by the deshielding –COO– substituent (to which it is *meta*) and the metal (to which it is *para*). Using this as a base, the observed multiplicities of the other signals and their coupling constants, together with decoupling experiments, H(3) and H(5, 6) can be unambiguously assigned (Table 1). Interestingly, the chemical shifts observed for the benzenoid hydrogens in all the pairs of rhodium and iridium complexes described here are very similar indeed and usually differ by less than 0.02 p.p.m. This suggests that the metal has no great influence at all on those hydrogens, a situation which contrasts quite sharply with other organic ligands attached to these metals where the rhodium and iridium complexes show rather different hydrogen chemical shifts. That can even be seen for example, in the chemical shifts of the C_5Me_5 hydrogens; thus, for the rhodium complex (**1a**) they appear at δ 1.69, while for the iridium complex (**1b**) at 1.78.

The structures were confirmed by an *X*-ray determination of the iridium complex (**1b**).[4]

All attempts to prepare the ruthenium analogue (**1d**) have so far failed; even reaction of [(*p*-$MeC_6H_4CHMe_2$)RuMe(Cl)-(Me_2SO)] (**3d**) (*p*-$MeC_6H_4CHMe_2$ = *p*-cymene) with silver benzoate gave only a very dark air-sensitive solid which readily decomposed. The osmium complex (**1c**) was also very air- and moisture-sensitive; in contrast the rhodium and iridium complexes (**1a**) and (**1b**) were rather stable.

The most straightforward route to the iridium complex (**1b**) was by reaction of the dichloride (**4b**) with silver benzoate [equation (3)]. The tendency to form the iridium cyclometallate was so strong that even on reaction of (**4b**) with only one equivalent of silver benzoate, half of the (**4b**) was converted into (**1b**); no monobenzoate such as [$(C_5Me_5)IrCl(OOCPh)(Me_2SO)$] could be detected.

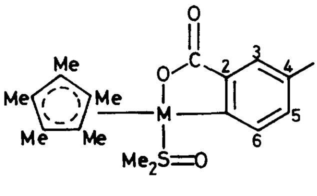
By contrast, this route gave the dibenzoate (**5a**) when the

Table 2. $^{13}C-\{^1H\}$ N.m.r. spectroscopic data[a] (δ/p.p.m.)

Complex	C_5Me_5	Me_2SO	C(1)	C(2)/C(6)	C(3)/C(5)	C(4)	CO_2	Other
(1a)	8.9	43.8	168.0(d)	140.7	131.8	124.4	179.9	
	99.8(d) [6]	43.2	[29]	134.7	129.9			
(1b)	8.7	42.5	150.1	138.5	131.9	123.9	183.3	
	94.0	43.8		134.8	130.1			
(5a)	8.8		135.7(d)	129.4	127.6	130.8	176.6	
	91.2(d) [8]		[6]					
(6a)	8.8	43.2	163.3(d)	140.3	130.5[b]	133.7	180.0	*p*-Me
	99.6(d) [8]	43.6	[29]	134.3[b]	132.7[b]			20.6
(6b)	8.7	42.4	145.9	138.3	133.1[b]	133.4	183.8	*p*-Me
	94.0	43.9		134.5[b]	130.8[b]			20.6
(7a)	8.9	43.3	180.4(d)	142.1	123.5[b]	146.1	177.7	
	100.4(d) [6]	44.0	[31]	135.5	125.0[b]			
(7b)	8.7	44.0	162.6	140.1	124.2[b]	145.6	181.1	
	95.0	42.9		135.6	125.5[b]			
(11a)[c]	9.3		158.7(d)	140.1	132.2[b]	125.1	178.9	CO
	117.0(d) [3]		[23]	134.7[b]	130.6[b]			186.7(d) [78]
(11b)	9.1		138.1	140.0	134.7[b]	125.0	183.1	CO
	99.8			132.3[b]	130.6[b]			183.1
(13a)	9.9		180.6(d)	133.5	128.5[b]	122.4	178.2	OMe
	95.3(d) [7]		[32]	137.7	125.0[b]			53.7
(13b)	9.7		169.0	133.1	134.3[b]	121.7	184.3	OMe
	87.5			136.6	129.2[b]			54.2

	p-Cymene											
	A	B + E	C + D	F	G	Me_2SO	C(1)	C(2)/C(6)	C(3)/C(5)	C(4)	CO_2	Other
(1c)	18.3	107.7	82.0	31.1	22.8	41.9	156.1	138.9	131.8	123.7	183.3	
		98.6	80.3		22.2	45.6		139.5	128.9			
			80.2									
			79.0									
(5c)	19.8	88.5	71.3	33.3	23.1		135.2	129.6	128.7	132.4	180.3	
		84.1	69.0									
(5d)	18.6	98.3	78.9	31.5	22.5		133.6	128.9	127.6	131.2	178.9	
		93.1	77.7									

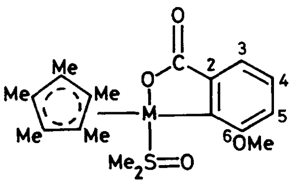
[a] All spectra measured in $CDCl_3$ except **(1c)** and **(5c)** which were measured in $(CD_3)_2CO$; all peaks singlets unless otherwise indicated. [ ] = *J*(Rh–C) in Hz to the nearest 1 Hz. Spectra measured on Bruker AB250, except **(11a)** which was measured on a Bruker WH400. Solvent as internal standard. [b] Arbitrary assignments. [c] Complex **(11a)** decomposed slowly during overnight accumulation of data; the original yellow solution turned orange-brown in this period.



(6); R = Me

(7); R = NO_2

(8); R = OMe



(9)

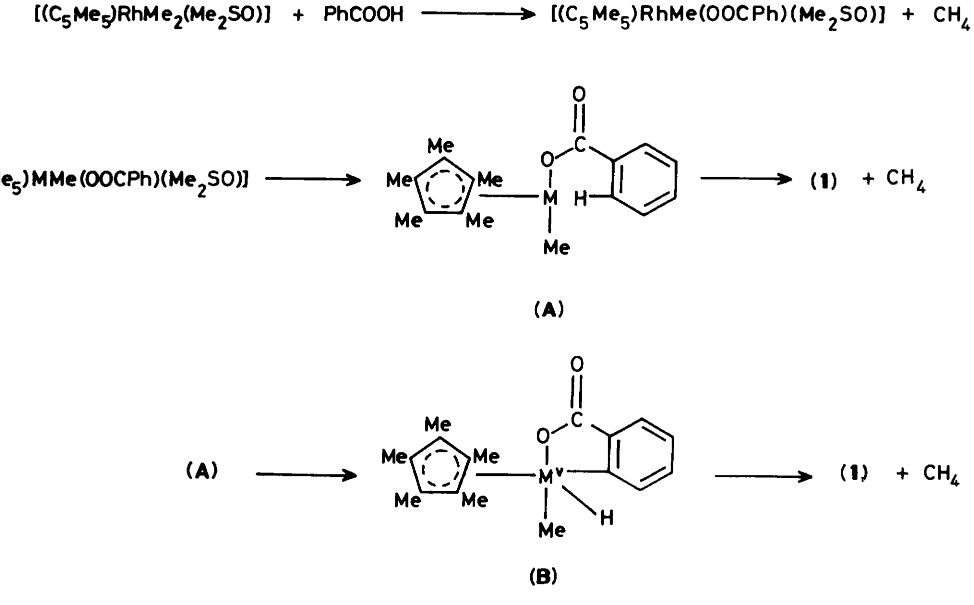
(a, M = Rh; b, M = Ir)

rhodium dichloride (**4a**) was treated with silver benzoate [equation (4)]. Some light is shed on these points by the observation that reaction of the cyclometallated rhodium complex (**1a**) with benzoic acid for more extended periods gave the dibenzoate hydrate (**5a**). In complete contrast, the cyclometallated iridium complex (**1b**) did not react with benzoic acid; indeed all attempts to prepare the dibenzoate (**5b**) have so far led to (**1b**).

Synthesis of Cyclometallated Complexes from Substituted Benzoic Acids.—The 3-methyl, 3-nitro-, and 3-methoxy-benzoic acids also reacted with the dimethyl complexes (**3a**) and (**3b**). Except for the last, 3-methoxybenzoic acid, they all gave only the expected isomers, (**6**) and (**7**). The isomers were readily identified from their ^1H n.m.r. spectra (Table 1). These showed a narrow doublet, with *J*(H–H) 2—2.5 Hz, usually at lowest field, which is ascribed to H(3), as that hydrogen is adjacent to the –COO group which is expected to be strongly deshielding. This doublet is coupled to H(5), a double-doublet with *J*(H–H) *ca.* 2 and 8 Hz, arising from coupling to H(3) and H(6) respectively. The remaining aromatic proton H(6) is a doublet, with *J* 8 Hz.

The product from reaction with 3-methoxybenzoic acid was found to be a mixture of the two isomers (**8**) and (**9**) in the ratio 35:65 for M = Rh and 44:56 for M = Ir. The isomer (**9**) was immediately identified by the characteristic pattern in the aromatic region of the ^1H n.m.r. spectrum: a triplet (*J* 8 Hz) at δ 7.1, ascribed to H(4), and two double-doublets (*J* 8 and 1 Hz), at 7.3 and 6.8, arising from H(3) and H(5) respectively. Isomer (**8**) had two doublets with *J* 8 Hz [H(5) at δ 6.9, H(6) 7.4] and one doublet with the long-range coupling *J* 3 Hz, which is assigned to H(3), at δ 7.2.

The absence of the isomers corresponding to (**9**) for the others indicates that steric hindrance makes attack at the 2-position in the 3-substituted benzoic acids normally unfavourable. The formation of (**9**) thus indicates the existence of a steering effect, presumably the methoxy oxygen can co-ordinate to the metal, bringing the hindered site between the methoxy and the carboxyl closer to the metal and favouring attack there in the transition state.



Scheme.

Mechanism of the Cyclometallation Reactions.—Since the cyclometallation products are achievable by three routes [equations (1)—(3)] we favour reactions proceeding in two steps. The first involves replacement of one σ-bonded ligand by an *O*-bonded benzoate, while the next is presumably the loss of dimethyl sulphoxide, creating a vacant site [as for example in (**A**)] at which the orthometallation can then occur (Scheme).

Some evidence comes from reaction of the chloromethylrhodium complex (**3a**) with silver benzoate. When the reaction was stopped after 35 min, cooled to −10 °C, and examined by ^1H n.m.r. spectroscopy a new doublet at δ 0.96 (Rh–Me), and a new singlet at δ 1.60 (C_5Me_5) were observed. We ascribe these to an intermediate, probably $[(C_5Me_5)RhMe(OOCPh)]$, corresponding to (**A**). When the solution was further warmed the reaction completed to give (**1a**).

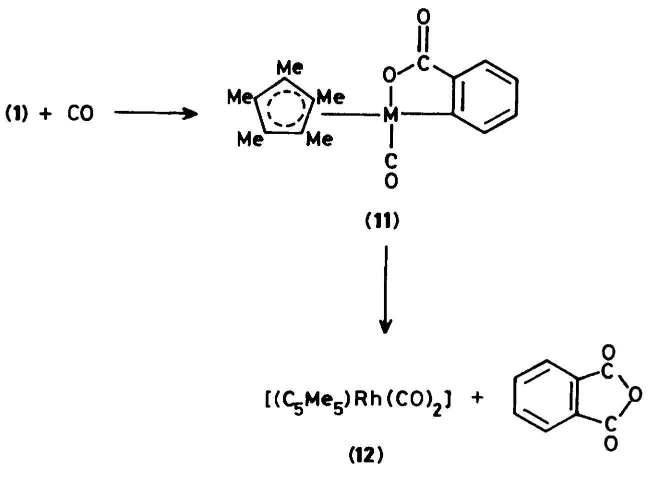
The nature of the process leading from (**A**) to (**1**) and methane is intriguing. Based upon the extensive organometallic chemistry now uncovered of rhodium(v) and iridium(v)[8–10] and the fact that such oxidation states are implicated as intermediates in a number of reactions,[11] we favour a transition state of type (**B**) (Scheme), formally in the +5 oxidation state, arising by an oxidative addition of C–H to the metal centre.

Cyclometallation reactions are also possible for d^0 systems where oxidative addition steps are unlikely. Those have been postulated to proceed by a concerted mechanism, *via* a multicentre transition state.[12] However it is not obvious that a concerted route would give a lower energy path for the system we are considering here.

An exactly analogous argument can be applied to formation of the osmium complex (**1c**); a transition state formally Os^{IV} would be implicated here, which is not unreasonable for this metal. This might also serve to explain why the ruthenium analogue of (**1c**) has not been made; Ru^{IV} could be significantly less accessible.

Although the cyclometallation of benzoic acid does not appear to have been described before, a complex with a closely related structure has been reported and characterised from the reaction[13] shown by equation (5).

$$[(C_5H_5)_2TiPh_2] + CO_2 \xrightarrow{80\text{—}90\,^\circ C} [(C_5H_5)_2Ti(OOCC_6H_4)] + C_6H_6 \quad (5)$$



Reactions of the Cyclometallated Complexes (**1a**) *and* (**1b**).—(a) *Reaction with water.* The iridium cyclometallate (**1b**) slowly dissolved in water, but without change, as indicated by the n.m.r. spectrum in D_2O. The rhodium complex (**1a**) was more easily soluble in water, but it underwent a reaction on doing so. Two products were isolated from the aqueous solution. One, the solid which precipitated, was identified as the dibenzoate hydrate (**5a**). The other, isolated from the solution after addition of sodium tetraphenylborate, was identified as the known tri-μ-hydroxodirhodium cation (**10**).[14] The overall reaction is given by equation (6).

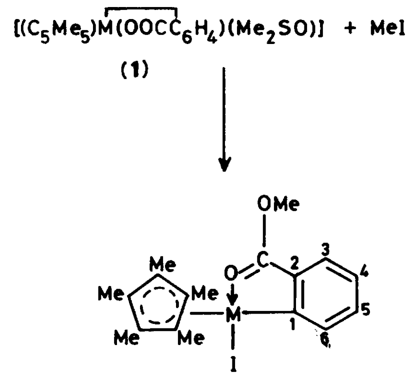
$$3\underset{(\mathbf{1a})}{[(C_5Me_5)Rh(OOCC_6H_4)(Me_2SO)]} + 4H_2O \longrightarrow \underset{(\mathbf{10})}{[(C_5Me_5)Rh(\mu\text{-}OH)_3Rh(C_5Me_5)][OOCPh]} + \underset{(\mathbf{5a})}{[(C_5Me_5)Rh(OOCPh)_2(H_2O)]} + Me_2SO \quad (6)$$

The dibenzoate hydrate (**5a**) was crystallised and a crystal was selected for an *X*-ray structure determination; this showed the structure discussed below.

Table 3. I.r. spectroscopic data (cm^{-1})[a]

Complex	Medium	ν(C=O)	ν(C–O)	ν(SO)	Other
(**1a**)	Nujol	1 641 1 625	1 315	1 109 1 013	
(**1b**)	Nujol	1 645 1 630	1 310	1 117 1 013	
(**1c**)	KBr disc	1 620	1 318	1 105	
(**5a**)	Nujol	1 550	1 390		H_2O 2 600—3 500
(**5c**)	KBr disc	Many strong bands in 1 650—1 350 region			
(**5d**)	KBr disc	Many strong bands in 1 650—1 350 region			
(**6a**)	CH_2Cl_2	1 628	1 308	1 109 1 014	
(**6b**)	Nujol	1 628br	1 310	1 117 1 018	
(**7a**)	Nujol	1 630	obsc.	1 110 1 020	NO_2 1 500 1 340
(**7b**)	Nujol	1 642br	obsc.	1 110 1 021	NO_2 1 503 1 332
(**8a**) (**9a**) [b]	Nujol	1 620br	1 322 1 311	1 109 1 098 (sh) 1 030 1 022 (sh)	
(**8b**) (**9b**) [b]	Nujol	1 630br	1 320 (sh) 1 308	1 115 1 097 1 023 1 118 (sh)	
(**11a**)	Toluene	1 657	1 298		CO 2 047
(**11b**)	Nujol	1 648	1 293		CO 1 996
(**13a**)	CH_2Cl_2	1 611	1 457 1 344		
(**13b**)	CH_2Cl_2	1 600	1 459 1 353		

[a] obsc. = Obscured. [b] Complexes (**8a**)/(**9a**) and (**8b**)/(**9b**) were mixtures of two isomers.


$[(C_5Me_5)M(OOCC_6H_4)(Me_2SO)]$ + MeI

(**1**)

(**13**)

(b) *Reactions with carbon monoxide.* Carbonylation of the cyclometallated iridium complex (**1b**) (1—5 atm, 20 °C) caused replacement of the co-ordinated dimethyl sulphoxide by CO to give $[(C_5Me_5)Ir(OOCC_6H_4)(CO)]$ (**11b**) [ν(CO) at 1 996 cm^{-1}]; no further reaction occurred even on heating under pressure.

By contrast, the rhodium complex (**1a**) underwent carbonylation (85 °C, 5 atm, 18 h) to give a mixture of phthalic anhydride (95%) and the dicarbonyl complex $[(C_5Me_5)Rh(CO)_2]$ (**12**).[15] However, under milder conditions carbonylation of (**1a**) (20 °C, 2.5 atm, 2 h) gave a yellow solid which was identified as (**11a**). This was quite unstable under vacuum or in the presence of halogenated solvents.

Table 4. Selected bond lengths (Å) and angles (°) for (**5a**)

Rh–O(1)	2.12(1)	Rh–C(1)	2.10(2)
Rh–O(2)	2.06(1)	Rh–C(2)	2.07(2)
Rh–O(4)	2.13(1)	Rh–C(3)	2.13(2)
C(11)–O(2)	1.25(2)	Rh–C(4)	2.12(2)
C(11)–O(3)	1.22(2)	Rh–C(5)	2.08(2)
C(18)–O(4)	1.27(3)	Rh–C mean	2.10
C(18)–O(5)	1.23(3)		
O(1)–Rh–O(2)	89.2(5)	Rh–O(2)–C(11)	131(1)
O(1)–Rh–O(4)	88.2(5)	Rh–O(4)–C(18)	126(2)
O(2)–Rh–O(4)	84.3(6)		

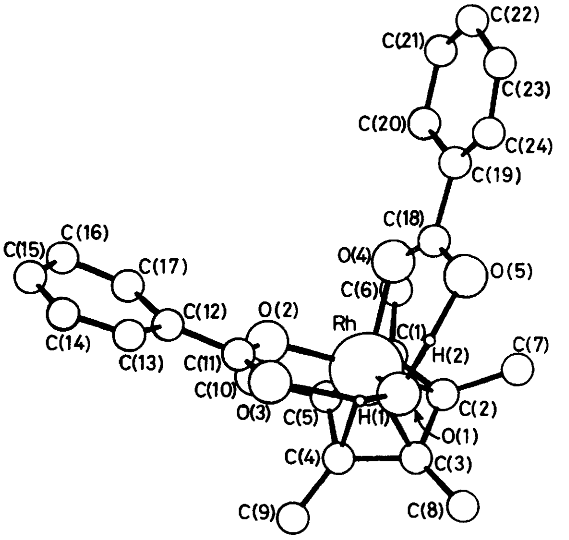


Figure. Molecular structure of complex $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$ (**5a**) [hydrogens omitted for clarity except for those linking O(1) to O(3) and O(5)]

We conclude that both the rhodium and the iridium complexes (**1a**) and (**1b**) react similarly, but that the rhodium carbonyl complex (**11a**) is very labile and, conversely, that the iridium complex (**11b**) is too inert to react further. This result is in agreement with the general principle that rhodium complexes are more reactive than their iridium analogues.

(c) *Reaction with methyl iodide.* Both the rhodium and the iridium complexes (**1a**) and (**1b**) readily underwent a facile reaction with methyl iodide to give adducts, identified as $[(C_5Me_5)M\{OC(OMe)C_6H_4\}(I)]$ (**13**).

The complexes were identified by their microanalyses and spectroscopically. Thus for example, the Me resonances appeared near δ 4 in the ^1H n.m.r. spectrum and near δ 54 in the ^{13}C n.m.r. spectrum; both are strongly indicative of a methoxy group and quite different from a methyl bonded either to metal (usually at or below δ 0) or carbon (typically δ 1—3). The complexes (**13a**) and (**13b**) still show co-ordinated carboxy peaks in the i.r. spectra, but >C=O appears at 1 611 cm^{-1} [(**13a**)] or 1 600 cm^{-1} [(**13b**)], well below the range (1 620—1 660 cm^{-1}) we find for the other orthometallated benzoates (**1**) and (**6**)—(**11**) (Table 3). These data rule out structures such as $[(C_5Me_5)MMe(OOCC_6H_4)(I)]$. A distantly related reaction has been reported for a cyclometallated nickel complex,[16]

Table 5. Microanalytical data

Complex	Found (calc.) (%) C	H	S	Other
(**1a**)	52.4	5.9	7.2	
	(52.3)	(5.8)	(7.4)	
(**1b**)	43.8	5.1	6.0	
	(43.4)	(4.8)	(6.1)	
(**1c**)[a]	43.3	5.0	5.1	
	(43.7)	(4.6)	(6.1)	
(**5a**)	58.1	5.7		
	(57.8)	(5.5)		
(**5c**)	50.6	4.5		
	(50.9)	(4.3)		
(**5d**)	60.5	5.2		
	(60.4)	(5.1)		
(**6a**)	53.1	5.9	6.6	
	(53.3)	(6.0)	(7.1)	
(**6b**)	44.2	5.5	5.6	
	(44.5)	(5.0)	(5.9)	
(**7a**)	48.2	5.5	7.4	N 2.4
	(47.4)	(5.0)	(6.7)	(2.9)
(**7b**)	40.4	4.2	5.8	N 2.5
	(40.0)	(4.2)	(5.6)	(2.5)
(**8a**) (**9a**) [b]	51.3	6.0	7.2	
	(51.5)	(5.8)	(6.9)	
(**8b**) (**9b**) [b]	43.1	5.1	5.9	
	(43.2)	(4.9)	(5.8)	
(**11a**)	55.7	5.1		
	(56.0)	(5.0)		
(**11b**)	45.8	4.1		
	(45.5)	(4.0)		
(**13a**)	42.8	4.6		I 24.8
	(43.2)	(4.4)		(25.4)
(**13b**)	37.5	4.2		I 20.6
	(36.7)	(3.8)		(21.5)

[a] Complex (**1c**) was very air sensitive and hygroscopic. [b] Complexes (**8a**)/(**9a**) and (**8b**)/(**9b**) were mixtures of two isomers.

equation (7). However, in this case the alkyl (R) adds to the

$$[(Me_2NCH_2CH_2NMe_2)\overline{Ni(OOCCMe{=}C}Me)] \xrightarrow{RX,\,H^+} Z\text{-}R(Me)C{=}C(Me)COOH \quad (7)$$

carbon and the halide (X) (presumably) to the metal. In the case of the reactions we describe the methyl attacks at oxygen; it is not clear what the reason is for this difference, but it may be due to the different stabilities of the two products.

X-Ray Structure Determination of the Rhodium Dibenzoate Hydrate (**5a**).—An *X*-ray structure determination was carried out on crystals of $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$ (**5a**) (Figure and Table 4). It was found that the molecule was a hydrate with a rather unusual feature. The pentamethylcyclopentadienyl was, as normal, η^5-bonded to rhodium (Rh–C av. 2.10 Å). The benzoates are monodentate to the metal [Rh–O(2), 2.06(1); Rh–O(4), 2.13(1) Å] and occupy two of the remaining three sites on the metal. The last site is occupied by a water molecule [Rh–O(1), 2.12(1) Å]; approximate positions for the water hydrogens were obtained from a low-angle difference map, which were, as expected, between the water oxygen and the benzoates, thus: $>C{=}O\cdots H\cdots O\cdots H\cdots O{=}C<$. The ORhO angles were quite close to right angles [O(1)–Rh–O(2) 89.2(5), O(1)–Rh–O(4) 88.2(5), and O(2)–Rh–O(4) 84.3(6)°].

Experimental

Reactions were generally carried out in Schlenk tubes under nitrogen; reactions involving silver salts were wrapped in metal foil. The final products (**1**)—(**13**) were generally not sensitive to air. Typical preparations are described. N.m.r. spectra are collected in Tables 1 and 2, i.r. spectra in Table 3, and microanalyses (carried out by the University of Sheffield Microanalytical Service) in Table 5. N.m.r. spectra were measured on Bruker WH80, AM250, and WH400 spectrometers; and i.r. spectra on a Perkin-Elmer 1710 Fourier-transform spectrometer.

$[(C_5Me_5)\overline{Rh(OOCC}_6H_4)(Me_2SO)]$ (**1a**).—Benzoic acid (0.11 g, 0.9 mmol) was added to a solution of $[(C_5Me_5)RhMe_2(Me_2SO)]$ (**2a**) (0.32 g, 0.9 mmol) in dichloromethane and stirred (48 h, 20 °C). The resultant orange-yellow solution was filtered and the solvent removed *in vacuo* to leave an oil which was triturated in diethyl ether to give complex (**1a**) (0.25 g, 62%).

$[(C_5Me_5)\overline{Ir(OOCC}_6H_4)(Me_2SO)]$ (**1b**).—Silver benzoate (0.3 g, 1.3 mmol) was added to a solution of $[(C_5Me_5)IrCl_2(Me_2SO)]$ (**4b**) (0.31 g, 0.65 mmol) in dichloromethane (25 cm^3). The mixture was stirred (2 h, 20 °C); the precipitated silver chloride was then filtered off, and the filtrate washed with sodium bicarbonate solution (to remove benzoic acid) and dried over sodium sulphate. Removal of the solvents and crystallisation of the yellow residue from dichloromethane yielded complex (**1b**) (0.31 g, 91%).

When the rhodium complex (**4a**) was reacted with silver benzoate in the same manner mixtures of (**1a**) and the dibenzoate (**5a**) were obtained; the amount of (**5a**) increased with the time of reaction thus, after stirring for 2 d in dichloromethane, a quantitative yield of (**5a**) was obtained.

$(p\text{-}MeC_6H_4CHMe_2)\overline{Os(OOCC}_6H_4)(Me_2SO)]$ (**1c**).—Silver benzoate (0.08 g, 0.35 mmol) was added to a solution of $[(p\text{-}MeC_6H_4CHMe_2)OsMe(Cl)(Me_2SO)]$[7](**3c**)(0.15g,0.33mmol)in tetrahydrofuran (10 cm^3) under argon. The brown suspension was filtered to give a yellow solution. After removal of the solvent *in vacuo* an oil remained which was triturated with diethyl ether to give an air-sensitive and hygroscopic greenish yellow powder (0.12 g, 70%) which was shown to be (**1c**). Attempts to prepare this complex directly from $[(p\text{-}MeC_6H_4CHMe_2)OsCl_2(Me_2SO)]$ and silver benzoate gave only the dibenzoate (**5c**). Attempts to prepare the ruthenium analogue (**1d**) gave either the dibenzoate (**5d**) [from (**4d**) and silver benzoate] or intractable and decomposed mixtures [from (**3d**) and silver benzoate].

Hydrolysis of $[(C_5Me_5)\overline{Rh(OOCC}_6H_4)(Me_2SO)]$ (**1a**) *to* $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$ (**5a**) *and* $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][OOCPh]$ (**10**).—Complex (**1a**) (0.3 g, 0.7 mmol) was stirred in water (20 cm^3, 12 d, 50 °C); the yellow solid was filtered from the yellow solution, washed, dried and crystallised from dichloromethane and hexane to give (**5a**) (0.1 g, 0.2 mmol). The yellow aqueous solution was treated with sodium tetraphenylborate (0.2 g, 0.6 mmol) to yield the known cation $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3]^+$ as the tetraphenylborate salt (0.24 g, 0.28 mmol).

X-Ray Structure Determination of $[(C_5Me_5)Rh(OOCPh)_2(H_2O)]$ (**5a**).—A crystal was selected from the batch prepared above.

Crystal data. $C_{24}H_{27}O_5Rh$, $M = 498$, orthorhombic, $a = 10.381(12)$, $b = 14.128(12)$, $c = 15.527(12)$ Å, $U = 2\,277$ Å^3, $Z = 4$, $D_c = 1.10$ g cm^{-3}, $D_m = 1.16$ g cm^{-3}, $F(000) = 1\,023.9$, space group $P2_12_12_1$ from systematic absences, Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu = 7.66$ cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit of the setting angles of 25 accurately centred reflections. *X*-Ray reflection data in the range $3.5 \leqslant 2\theta \leqslant 45°$ were collected on a Nicolet *R3M* four-circle diffractometer from a prismatic crystal measuring approximately 0.07 × 0.07 × 0.2 mm. 915 Independent reflections with $I \geqslant 4\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ψ-scans of nine reflections (325 measurements) was also applied. The maximum transmission factors obtained were 0.937 and 0.910.

The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.000\,04F_i^2]$ to a final R value of 0.0622 ($R' = 0.0470$). All the non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters.

Sufficient hydrogen atoms were located from a low-angle difference Fourier synthesis to define approximate torsion angles for all the methyl groups. The methyl and benzene hydrogen atoms were constrained to ride on the adjacent heavy atom with calculated bond lengths and angles; all the hydrogen (isotropic) vibration parameters were fixed at 1.2 times the U_{eq} values for their respective neighbours. Approximate positions for the water hydrogens were obtained from a further low-angle difference map. These positions were not constrained or refined. The parameter shifts obtained on the final cycle of refinement were in all cases less than 0.1 of the corresponding e.s.d.s. A final difference Fourier synthesis showed no peak higher than 0.7 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against sin θ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL suite of crystallographic programs was used throughout.[17] Selected bond lengths and angles are given in Table 4 and atomic co-ordinates in Table 6.

Carbonylation of Complex (**1a**).—(a) *To phthalic anhydride.* A solution of complex (**1a**) in tetrahydrofuran (10 cm^3) was stirred under an atmosphere of carbon monoxide (Fisher-Porter glass pressure vessel, 5 atm, 85 °C, 18 h). The solution was cooled and the pressure released; cyclohexanone (10 μl) was added as a gas chromatographic (g.c.) standard and the g.c. (OV17 column) and the g.c.-mass spectrum were run. The products were identified as phthalic anhydride (95%), benzoic acid (5%), $[(C_5Me_5)Rh(CO)_2]$, and dimethyl sulphoxide, by their g.c.-mass spectrum molecular ions and by comparison with authentic samples.

(b) *To complex* (**11a**). A solution of complex (**1a**) (0.15 g, 0.34 mmol) in toluene (10 cm^3) was carbonylated (2.5 atm, 20 °C, 2 h). The solid dissolved and the solution then precipitated a yellow solid; pentane (50 cm^3) was added to precipitate the remaining material which was filtered off and washed with pentane to yield $[(C_5Me_5)\overline{Rh(OOCC}_6H_4)(CO)]$ (**11a**) (0.1 g, 72%).

$[(C_5Me_5)\overline{Ir\{OC(OMe)C}_6H_4\}(I)]$ (**13b**).—Methyl iodide (1 cm^3, 16 mmol) was added to a solution of the iridium complex (**1b**) (0.31 g, 0.58 mmol) in benzene (20 cm^3). The Schlenk tube was then partially evacuated and warmed (70 °C, 18 h). The solvent was removed *in vacuo* to leave an oil which was dissolved in dichloromethane; the dichloromethane solution was washed with water, dried and evaporated to yield solid complex (**13b**) (0.29 g, 85%).

Table 6. Atom co-ordinates (× 10^4) for (**5a**)

Atom	*x*	*y*	*z*
Rh	1 689(2)	200(1)	2 280(1)
O(1)	2 694(12)	1 003(8)	3 222(8)
O(2)	−25(11)	723(8)	2 754(8)
O(3)	562(13)	1 386(10)	3 952(10)
O(4)	1 658(18)	1 430(9)	1 489(8)
O(5)	3 246(16)	2 237(11)	2 069(9)
C(1)	1 687(26)	−683(12)	1 191(12)
C(2)	2 875(19)	−687(14)	1 580(16)
C(3)	2 842(23)	−1 040(14)	2 425(16)
C(4)	1 469(19)	−1 237(12)	2 636(15)
C(5)	843(23)	−1 052(13)	1 854(15)
C(6)	1 315(23)	−460(15)	312(10)
C(7)	4 031(20)	−336(16)	1 118(15)
C(8)	3 992(20)	−1 066(15)	2 964(18)
C(9)	1 060(25)	−1 653(14)	3 447(12)
C(10)	−618(20)	−1 216(15)	1 781(17)
C(11)	−273(16)	1 136(13)	3 448(11)
C(12)	−1 575(23)	1 458(11)	3 577(11)
C(13)	−2 017(18)	1 891(13)	4 302(13)
C(14)	−3 228(25)	2 130(11)	4 464(11)
C(15)	−4 116(19)	1 948(14)	3 886(13)
C(16)	−3 863(17)	1 561(13)	3 095(16)
C(17)	−2 629(19)	1 264(13)	2 972(11)
C(18)	2 384(20)	2 104(17)	1 542(15)
C(19)	2 353(18)	2 828(15)	804(17)
C(20)	1 450(20)	2 664(13)	167(14)
C(21)	1 394(37)	3 394(16)	−449(13)
C(22)	1 931(41)	4 161(20)	−422(20)
C(23)	2 775(25)	4 291(22)	243(24)
C(24)	2 937(22)	3 652(16)	861(16)

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