

(PENTAMETHYLCYCLOPENTADIENYL)RHODIUM AND -IRIDIUM COMPLEXES

IV*. OXIDATIVE ADDITION REACTIONS TO DICARBONYL(PENTAMETHYLCYCLOPENTADIENYL)RHODIUM AND -IRIDIUM

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SUMMARY

The reactions of $C_5Me_5M(CO)_2$ [(Ia), $M=Rh$; (Ib), $M=Ir$] with methyl iodide are described. (Ia) gave the acetyl complex $C_5Me_5Rh(COMe)(CO)I$, while (Ib) gave the ionic methyl complex $[C_5Me_5Ir(CO)_2Me]^+I^-$. The latter complex decomposed to (Ib) and methyl iodide in the solid and to (Ib) and $C_5Me_5Ir(CO)I_2$ in solution. $C_5Me_5Ir(CO)I_2$ was also prepared by carbonylation of $[C_5Me_5IrI_2]_2$. The iridium complex (Ib) oxidatively added sulfonyl chlorides to give $C_5Me_5IrCO(SO_2R)Cl$ ($R=Me, C_6H_5, p-MeC_6H_4, p-BrC_6H_4$); on heating, the complexes with $R=aryl$ decomposed smoothly with loss of SO_2 to give the aryl-iridium complexes, $C_5Me_5IrCO(R)Cl$.

INTRODUCTION

We have recently reported in detail on the (pentamethylcyclopentadienyl)-rhodium and -iridium halides¹, and a number of their reactions, particularly with olefins²⁻⁶. In the course of our work we have now also prepared and investigated some reactions of the dicarbonyls (I). As these are typical d^8 complexes with the metal [Rh^I, Ir^I] having pseudo-five coordination, they may be expected to undergo similar reactions to other five-coordinate d^8 complexes, such as oxidative addition accompanied by loss of a neutral ligand (CO)⁷. In particular, the complexes (I) are expected to behave similarly to the unsubstituted dicarbonylcyclopentadienylcobalt, -rhodium and -iridium complexes. The first two of these have received some attention⁸⁻¹³, but very little, other than the preparation¹⁴, has been published on $C_5H_5Ir(CO)_2$.

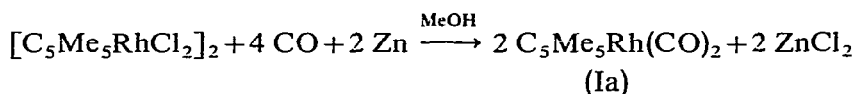
RESULTS AND DISCUSSION

The preparation of the iridium complex (Ib) has already been described¹. We

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have now also been able to prepare (Ia) by a number of routes. The most convenient, described here, is by reaction of carbon monoxide at one atmosphere with $[C_5Me_5-RhCl_2]_2$ in methanol in the presence of zinc,



The complex (Ia) showed two $\nu(CO)$ in the IR, at 1950 and 2000 cm^{-1} , close to the values reported¹ for (Ib). It was also more reactive than (Ib) and decomposed slowly in the solid in air or, faster, in solution under nitrogen, either on heating or irradiation.

The iridium complex (Ib) underwent reaction rapidly with methyl iodide either in ether or in the absence of solvent to give high yields of a new complex, $C_5Me_5Ir(CO)_2MeI$, (II). This still retained both terminal carbonyls, but the $\nu(CO)$ observed (Table I) were at higher frequency than for (Ib). This suggested that oxidative addition

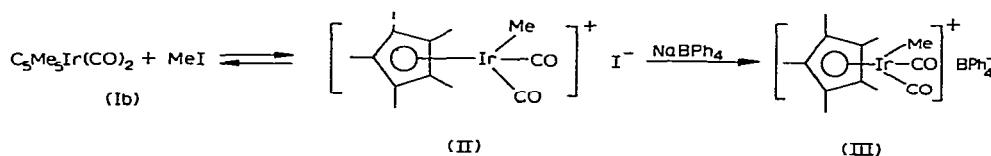
TABLE I

INFRARED SPECTRA^{a,b} (cm^{-1})

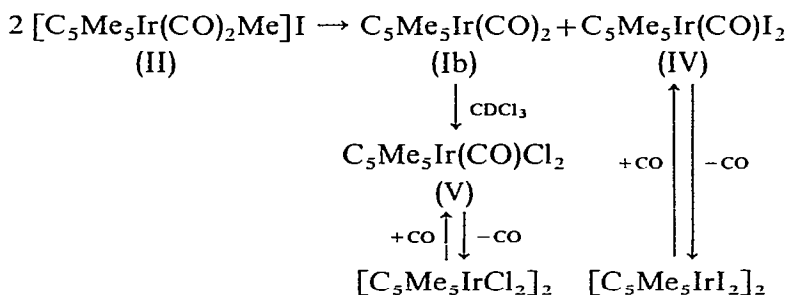
Compound	$\nu(CO)$	$\nu_{sym}(SO_2)$	$\nu_{asym}(SO_2)$
$C_5Me_5Rh(CO)_2$ (Ia)	1950, 2000		
$C_5Me_5Ir(CO)_2$ (Ib)	1925, 2000		
$[C_5Me_5Ir(CO)_2Me]Ir^+$ (II)	2050, 2100		
$[C_5Me_5Ir(CO)_2Me]BPh_4^-$ (III)	2050, 2095		
$C_5Me_5Ir(CO)I_2$ (IV)	2040		
$C_5Me_5Ir(CO)Cl_2$ (V)	2035		
$C_5Me_5RhCO(COMe)I$ (VI)	1675 ^d , 2050		
$C_5Me_5IrCl(CO)SO_2Me$ (VII)	2030	1065	1225
$C_5Me_5IrCl(CO)SO_2C_6H_5$ (VII)	2050	1055	1218
$C_5Me_5IrCl(CO)SO_2C_6H_4Br-p$ (VII)	2040	1050	1225
$C_5Me_5IrCl(CO)SO_2C_6H_4Me-p$ (VII)	2050	1050	1223
$C_5Me_5IrCl(CO)C_6H_5$ (VIII)	2025		
$C_5Me_5IrCl(CO)C_6H_4Br-p$ (VIII)	2020		
$C_5Me_5IrCl(CO)C_6H_4Me-p$ (VIII)	2010		

^a Except where indicated all measurements were carried out on KBr discs. ^b Only the strongest bands are listed. ^c Nujol mull. ^d $\nu(CO)$ for $IrCOMe$.

had occurred to give an Ir^{III} complex. The presence of ionic I^- was shown by its conversion to (III) on reaction with sodium tetrphenylborate. The complexes (II) and (III) exhibited very similar values of $\nu(CO)$ and both showed NMR resonances for the C_5Me_5 and methyl groups in similar positions; we therefore propose the structures shown for them. Neither contained an iridium-acetyl bond nor were we able to convert them into acetyl complexes, for example, $C_5Me_5IrCO(COMe)I$, on heating.

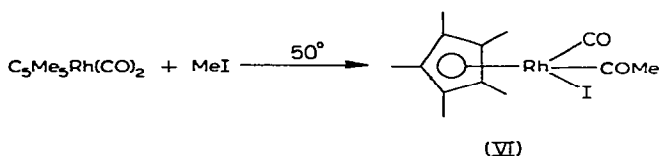


On standing in air, solid (II) slowly lost methyl iodide and regenerated (Ib). In acetone- d_6 a fairly rapid reaction was observed by NMR to give two complexes. One was identified as $C_5Me_5Ir(CO)_2$, (Ib), the other as $C_5Me_5Ir(CO)I_2$, (IV), and they were formed in an approximately 1/1 molar ratio. The complex (II) also decomposed in chloroform- d at 30° to give a 1/1 mixture of (IV) and $C_5Me_5Ir(CO)Cl_2$ (V). Since (Ib) also reacted with chloroform to give (V), we presume the overall reactions which occur to be,

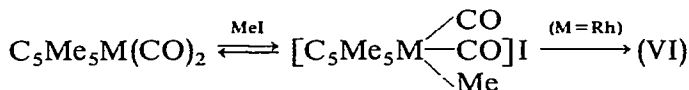


Both the carbonyl halides (IV) and (V) slowly lost carbon monoxide to form the dihalide dimers; this reaction was reversible and the carbonyl dihalides were formed in high yields on passing CO into suspensions of the dihalide dimers in benzene.

The rhodium carbonyl complex (Ia) reacted more slowly with methyl iodide at 25° and gave products which could not be characterised. On the other hand, at 50° in benzene, the acetyl complex (VI) was formed in high yield. This was identified largely by its characteristic IR spectrum which showed the presence of only one terminal $\nu(CO)$ at 2050 and an acetyl $\nu(CO)$ at 1675 cm^{-1} .



We therefore suggest that oxidative addition to (I) occurs first to form an ionic adduct such as (II), which in the case of the rhodium complex undergoes a methyl migration reaction^{15,16} accompanied by nucleophilic attack of iodide at the metal to give (VI)¹⁷.



The reversible formation of (II) presumably occurs by a nucleophilic attack by the metal on the methyl of CH_3I , as has been suggested for other systems by several authors^{16,18}. In the iridium complex, however, nucleophilic attack by I^- must be quite difficult and an ionic product results. Somewhat similar reactions have recently been shown to occur with $C_5H_5RhCO(PPhMe_2)$ and methyl iodide, and also involve an ionic intermediate¹⁹.

A number of other organic halides were reacted with the iridium carbonyl (Ib). Reactions were much slower for ethyl and propyl iodides; in each case at 80°

in benzene the only product isolated was the carbonyl diiodide, (IV). In contrast to $C_5H_5Rh(CO)_2^{20}$, (Ib) did not react with triphenylphosphine in benzene at 80° .

Another typical oxidative addition reaction undergone by d^8 metal complexes is with sulfonyl chlorides²¹. The iridium dicarbonyl (Ib) reacted easily with methyl and aryl sulfonyl chlorides in ether to give products identified as (VII).

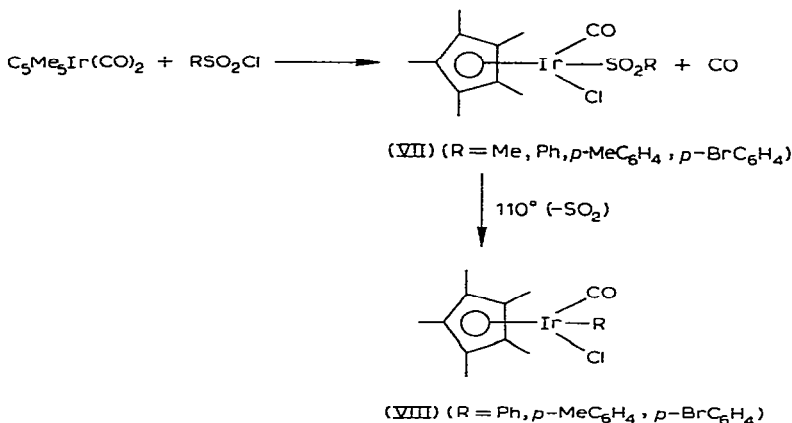


TABLE 2

¹H NMR SPECTRA IN CDCl₃ (τ) (ppm)

Compound	τ(C ₅ Me ₅)	τ(Me)	Other
C ₅ Me ₅ Rh(CO) ₂ ^a (Ia)	7.95(d)		
C ₅ Me ₅ Ir(CO) ₂ (Ib)	7.81(s)		
C ₅ Me ₅ Ir(CO)I ₂ (IV)	8.00(s)		
C ₅ Me ₅ Ir(CO)Cl ₂ (V)	8.09(s)		
[C ₅ Me ₅ Ir(CO) ₂ Me]I (II)	7.70(s)	8.94(s)	
[C ₅ Me ₅ Ir(CO) ₂ Me]BPh ₄ ^b (III)	7.76(s)	8.84(s)	2.65 + 3.12 (m. C ₆ H ₅)
C ₅ Me ₅ RhI(CO)COMe (VI)	8.05(s)	7.21(s)	
C ₅ Me ₅ IrCl(CO)SO ₂ Me (VII)	8.03(s)	6.76(s)	
C ₅ Me ₅ IrCl(CO)SO ₂ C ₆ H ₅	8.07(s)		2.33(m, C ₆ H ₅)
C ₅ Me ₅ IrCl(CO)SO ₂ C ₆ H ₄ Br- <i>p</i>	8.05(s)		2.39(d, C ₆ H ₄)
C ₅ Me ₅ IrCl(CO)SO ₂ C ₆ H ₄ Me- <i>p</i>	8.07(s)	7.60(s)	2.55(q, C ₆ H ₄)
C ₅ Me ₅ IrCl(CO)C ₆ H ₅ (VIII)	8.27(s)		2.90(m, C ₆ H ₅)
C ₅ Me ₅ IrCl(CO)C ₆ H ₄ Br- <i>p</i>	8.23(s)		2.80(bs)
C ₅ Me ₅ IrCl(CO)C ₆ H ₄ Me- <i>p</i>	8.23(s)	7.71(s)	2.95(q, C ₆ H ₄)

^a $J(\text{Rh-H}) = 0.4 \text{ Hz}$. ^b In acetone-*d*₆.

The structure (VII) was based on analysis (Table 3), NMR (Table 2), and particularly on the IR spectrum (Table 1) which showed the presence only one terminal $\nu(\text{CO})$ [between 2030 and 2050 cm^{-1} , in agreement with an Ir^{III} complex] and strong bands at around 1070 and 1225 cm^{-1} , ascribed to an S-bonded sulfinate²¹. By contrast to the reactions with methyl iodide, nucleophilic attack by chloride at the metal with replacement of one CO, has occurred here.

Other authors^{21,22} have shown that such complexes extrude sulfur dioxide irreversibly on heating, and indeed the rhodium complex, $(\text{Ph}_3\text{P})_3\text{RhCl}$, has been suggested as a catalyst for the catalytic desulfonylation of aryl sulfonyl halides²³. On heating the *aryl* sulfinates (VII) ($\text{R} = \text{phenyl}$, etc.) in benzene or toluene, a smooth desulfonylation occurred to give the aryliridium complex (VIII) ($\text{R} = \text{phenyl}$, etc.) in high yields. The methylsulfinato complex, $\text{C}_5\text{Me}_5\text{IrCO}(\text{SO}_2\text{Me})\text{Cl}$, also decomposed under these conditions, but did *not* give (VIII) ($\text{R} = \text{Me}$). The complex (VIII) ($\text{R} = p\text{-tolyl}$) did not react with sulfur dioxide in benzene at 80° .

TABLE 3

YIELDS, ANALYTICAL DATA AND DECOMPOSITION TEMPERATURES

Compound	Yield (%)	Color	Decompn. temp. ($^\circ\text{C}$)	Analysis found (calcd.) (%)				
				C	H	Cl	I	S
$\text{C}_5\text{Me}_5\text{Rh}(\text{CO})_2$ (Ia) ^a	56	Orange	101–107	48.79 (48.98)	5.16 (5.10)			
$\text{C}_5\text{Me}_5\text{RhI}(\text{CO})\text{COCH}_3$ (VI)	74	Brown	147–150	35.52 (35.78)	4.15 (4.13)		28.72 (29.13)	
$\text{C}_5\text{Me}_5\text{Ir}(\text{CO})\text{Cl}_2$ (V)	95	Yellow	^b	30.80 (30.98)	3.86 (3.52)	16.48 (16.69)		
$\text{C}_5\text{Me}_5\text{Ir}(\text{CO})\text{I}_2$ (IV)	92	Red	^b	21.75 (21.67)	2.31 (2.46)		42.20 (41.71)	
$[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2\text{Me}]\text{I}$ (II)	87	Pale yellow	^c	29.98 (29.71)	3.67 (3.43)		24.02 (24.19)	
$[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2\text{Me}]\text{BPh}_4$ (III)	85	White	155–158	61.54 (61.94)	5.06 (5.29)			
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{SO}_2\text{Me}$ (VII)	94	Yellow	183–186	30.77 (30.64)	3.90 (3.83)	7.06 (7.66)		6.37 (6.81)
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{SO}_2\text{C}_6\text{H}_5$ (VII)	91	Yellow	146–152	38.29 (38.35)	3.61 (3.86)			5.43 (6.01)
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{SO}_2\text{C}_6\text{H}_4\text{Br-}p$ (VII)	96	Orange	159–163	33.24 (33.39)	3.24 (3.11)			4.91 (5.24)
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{SO}_2\text{C}_6\text{H}_4\text{Me-}p$ (VII)	94	Orange-yellow	161–163	39.51 (39.56)	4.01 (4.03)	6.07 (6.59)		5.50 (5.86)
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{C}_6\text{H}_5$ (VIII)	87	Yellow	150–153	43.35 (43.59)	3.98 (4.27)			
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{C}_6\text{H}_4\text{Br-}p$ (VIII)	65	Pale yellow	160–165	37.02 (37.48)	3.72 (3.48)			
$\text{C}_5\text{Me}_5\text{IrCl}(\text{CO})\text{C}_6\text{H}_4\text{Me-}p$ (VIII)	81	Pale yellow	175–178	44.82 (44.81)	4.86 (4.56)			

^a Mass-spectroscopic mol. wt., 294; calcd.: mol. wt. 294. ^b Decomposed to $[\text{C}_5\text{Me}_5\text{IrX}_2]$. ^c Decomposed to (Ib).

EXPERIMENTAL

The (pentamethylcyclopentadienyl)metal dihalides and (Ib) were prepared as already described¹. For the new compounds described herein yields, analytical data, melting points, NMR resonances and the most important bands in the IR spectra have been tabulated (Tables 1–3). Experimental details for typical reactions are given below. All reactions were carried out under nitrogen.

Dicarbonyl(pentamethylcyclopentadienyl)rhodium, (Ia)

Carbon monoxide was bubbled into a well-stirred suspension of $[\text{C}_5\text{Me}_5\text{-RhCl}_2]_2$ (300 mg) and zinc metal (100 mg) in 30 ml of methanol at 65° for 3 h. The mixture was filtered and the residue was washed with a small amount of methanol. The combined filtrate and washings were evaporated at 25° under reduced pressure and the residue was sublimed at $30\text{--}40^\circ$ (10^{-3} mm); yield 160 mg (56%) of $\text{C}_5\text{Me}_5\text{Rh}(\text{CO})_2$ as orange-red crystals.

Dicarbonylmethyl(pentamethylcyclopentadienyl)iridium(III) iodide, (II)

(i). Methyl iodide (100 mg, 0.70 mmole) was added to a solution of $\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2$ (Ib) (100 mg, 0.26 mmole) in 20 ml of ether. The solution was warmed briefly and then allowed to crystallise at 0° for 18 h. The pale yellow crystals deposited were collected on a filter, washed with cold ether and dried in air to give 110 mg (80%) of pure (II).

(ii). A mixture of $\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2$ (100 mg) and 3 ml of methyl iodide was stirred at 25° under nitrogen for 1 h. The solid product was collected on a filter, washed with cold ether and dried in air to give 120 mg (87%) of analytically pure (II).

On standing at room temperature the crystals of (II) slowly lost methyl iodide and reformed (Ib). They could, however, be stored at -5° under nitrogen.

Dicarbonylmethyl(pentamethylcyclopentadienyl)iridium(III) tetraphenylborate, (III)

A solution of sodium tetraphenylborate (100 mg, 0.29 mmole) in 5 ml of methanol was quickly added to one of $[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2\text{Me}]_2\text{I}$ (II) (100 mg, 0.19 mmole) in 3 ml of methanol. After stirring at 25° for 1 h the white crystals which had been deposited were collected on a filter, washed with a small amount of cold methanol and dried in air. Yield, 115 mg (85%) of analytically pure (III).

Acetylcarbonyliodo(pentamethylcyclopentadienyl)rhodium(III), (VI)

A solution of $\text{C}_5\text{Me}_5\text{Rh}(\text{CO})_2$ (Ia) (200 mg, 0.68 mmole) and methyl iodide (500 mg, 3.5 mmole) in 5 ml of benzene was heated at 50° with stirring for 1 h. The solvent was removed under reduced pressure at 40° and the residue was recrystallized from benzene/hexane to give 220 mg (74%) of pure (VI) as dark red crystals.

Carbonyldichloro(pentamethylcyclopentadienyl)iridium(III), (V)

Carbon monoxide was passed through a stirred suspension of $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ (300 mg) in 20 ml of benzene at 25° for 1 h. The yellow solution was evaporated under reduced pressure. Recrystallization of the crude product from benzene/hexane afforded 305 mg (95%) of the complex (V) as yellow crystals. On heating, the complex (V) decomposed to $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ without melting. A similar decomposition was observed to occur when the solid was allowed to stand at 25° for prolonged periods.

Carbonylchloro(p-toluenesulfonato)(pentamethylcyclopentadienyl)iridium(III), (VII)

A solution of $\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2$ (100 mg, 0.26 mmole) and *p*-toluenesulfonyl chloride (80 mg, 0.42 mmole) in 20 ml of ether was refluxed for 10 min. The yellow solution was allowed to stand at room temperature and the orange yellow needles deposited were collected on a filter, washed with cold ether and dried in air to give 135 mg (94%) of pure complex (VII) (R = *p*-tolyl).

Carbonylchloro-p-tolyl(pentamethylcyclopentadienyl)iridium(III), (VIII)

A solution of (VII) (R = *p*-tolyl) (200 mg) in 20 ml of toluene was refluxed with stirring for 24 h. Removal of the solvent under reduced pressure gave a pale yellow solid which, on recrystallization from ether/hexane afforded, 155 mg (81 %) of pure (VIII) (R = *p*-tolyl).

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