

ORGANIC REACTIONS INVOLVING TRANSITION METALS II*. REACTION OF IRIIDIUM TRICHLORIDE TETRAHYDRATE WITH HEXAMETHYLBICYCLO[2.2.0]HEXA-2,5-DIENE

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SUMMARY

The *para*-bonded isomer of hexamethylbenzene, hexamethylbicyclo[2.2.0]hexa-2,5-diene, reacts with iridium trichloride tetrahydrate to give di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium, $(C_5Me_5IrCl_2)_2$, and hexamethylbenzene. The same compound has also been obtained from the reaction of 1-(1-methoxyethyl)pentamethyl-2,4-cyclopentadiene with $IrCl_3 \cdot 4 H_2O$ under similar conditions. Reaction of the compound $(C_5Me_5IrCl_2)_2$ with sodium iodide gives the corresponding iodo-complex, and reaction with pyridine, *p*-toluidine, triphenylphosphine or 1,5-cyclooctadiene gives the compounds $C_5Me_5IrCl_2L$ (where $L = PPh_3$, C_5H_5N or *p*- $CH_3C_6H_4NH_2$) and $C_5Me_5IrC_8H_{12}$ respectively.

INTRODUCTION

There has been considerable recent interest in the preparation and reactions of transition metal complexes of *para*-bonded benzene derivatives². A recent investigation^{1,3} of the reaction of hexamethylbicyclo[2.2.0]hexa-2,5-diene (I) with rhodium trichloride trihydrate in methanol has shown that ring contraction of the diene occurs to give di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium [(IIb), $X = Cl$] in high yield. The reaction of the diene (I) with iridium trichloride tetrahydrate briefly mentioned previously¹, and independently reported in a note by Maitlis, Kang and Mosley⁴, is now reported in detail, together with some new reactions of the complex.

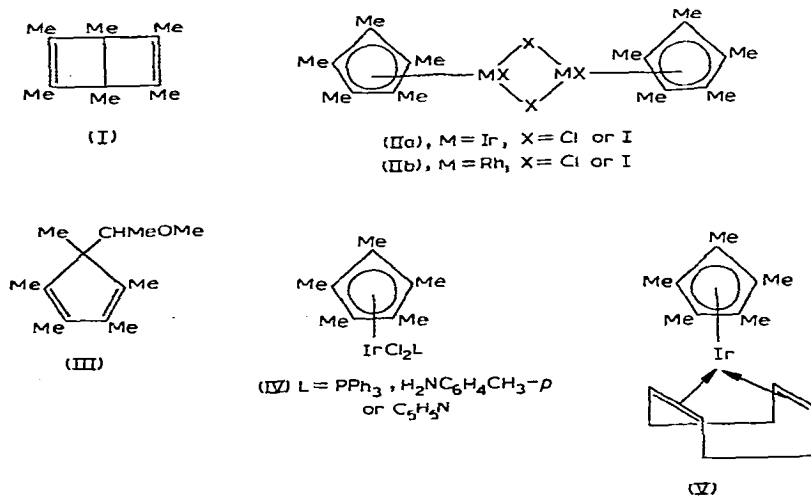
RESULTS AND DISCUSSION

When the compound (I) and iridium trichloride tetrahydrate are heated at 60° for 24 h in dry methanol, di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium [(IIa), $X = Cl$] is obtained in 19% yield (based on iridium) as a peach solid, together with hexamethylbenzene (59%). The same compound [(IIa), $X = Cl$] is also

* For Part I see ref. 1.

obtained in 11% yield from the reaction of 1-(1-methoxyethyl)pentamethyl-2,4-cyclopentadiene (III) with $\text{IrCl}_3 \cdot 4 \text{H}_2\text{O}$ in methanol at 60° for 7 h. The product has been characterised by elemental analysis (C and H), molecular weight determination and IR spectroscopy. Its ^1H NMR spectrum (Table 1) shows only a singlet absorption indicating the equivalence of the methyl protons.

The compound (IIa) ($\text{X}=\text{Cl}$) reacts with sodium iodide in acetone at room temperature over 3 days to give the corresponding iodo complex [(IIa), $\text{X}=\text{I}$] in 72% yield as a red solid, which has a similar IR spectrum and ^1H NMR spectrum (Table 1) to that of the chloro-compound. The chloro-compound (IIa) ($\text{X}=\text{Cl}$) also reacts readily with triphenylphosphine, *p*-toluidine, or pyridine at room temperature in chloroform to give the compounds $\text{C}_5\text{Me}_5\text{IrCl}(\text{L})$ [(IV), where $\text{L}=\text{PPh}_3$, $\text{H}_2\text{N}-\text{C}_6\text{H}_4\text{CH}_3$ -*p*, or $\text{C}_5\text{H}_5\text{N}$] in high yields (>75%) as stable, yellow solids. The ^1H NMR spectra of these compounds are given (Table 1). The spectrum of the compound (IV) ($\text{L}=\text{PPh}_3$) shows a doublet τ 8.66 ($|J|2$ Hz) for the methyl protons due to coupling with the phosphorus atom of the phosphine ligand.



When an ethanolic solution of compound (IIa) ($\text{X}=\text{Cl}$) is heated under reflux with *cis*, *cis*-1,5-cyclooctadiene in the presence of sodium carbonate for 2 h the compound (V) is obtained in 63% yield as a white solid m.p. 170 – 171° . Its ^1H NMR spectrum (Table 1) shows a band at τ 8.20 (singlet; methyl protons) and broad bands at *ca.* τ 7.30 (olefinic protons) and *ca.* τ 8.17 (methylene protons) for the 1,5-cyclooctadiene ligand in the intensity ratio $^1\text{H}(\text{C}_8\text{H}_{12})/^1\text{H}(\text{C}_5\text{Me}_5)$ of 12/15 in agreement with the structure assigned. The bands for the 1,5-cyclooctadiene ligand in this iridium complex are shifted to high field compared to those in the analogous rhodium complex [*cf.* τ 7.05 (olefinic protons), τ 7.94 (methylene protons)] indicating the higher shielding effect of Ir^I compared to Rh^I . Confirmation of the structure of compound (V) is given by its mass spectrum (Table 2), which shows a very strong molecular ion $(\text{C}_5\text{Me}_5^{193}\text{IrC}_8\text{H}_{12})^+$ at m/e 436, in addition to peaks at m/e 328 $(\text{C}_5\text{Me}_5^{193}\text{Ir})^+$ and m/e 135, 134, 133, 121, 119, 105 and 91 for the ion $(\text{C}_5\text{Me}_5)^+$ and its fragmentation products. Peaks at m/e 162 $(\text{C}_6\text{Me}_6)^+$ and m/e 147 $(\text{C}_6\text{Me}_5)^+$ expected for a hexa-

TABLE 1

¹H NMR SPECTRA OF PENTAMETHYLCYCLOPENTADIENYL-IRIDIUM COMPLEXES

Compound	Chemical shift ^a (τ) (intensity)	
	C ₅ Me ₅ protons	Other protons
(C ₅ Me ₅ IrCl ₂) ₂	8.40 s	
(C ₅ Me ₅ IrI ₂) ₂	8.19 s	
C ₅ Me ₅ IrCl ₂ PPh ₃	8.66 d (15)	2.65 m, 2.26 m (15)
	[J(P-H) 2.0 Hz]	(C ₆ H ₅ protons)
C ₅ Me ₅ IrCl ₂ C ₇ H ₉ N	8.62 s (15)	7.69 s [(3), methyl protons]
		2.86 d [(4), aromatic protons]
C ₅ Me ₅ IrCl ₂ C ₅ H ₅ N ^b	8.54 s (15)	2.72 m, 2.35 m, 1.12 m
		[(5), pyridine protons]
C ₅ Me ₅ IrC ₈ H ₁₂	8.20 s (15)	ca. 8.17 b [(8), methylene protons]
		ca. 7.30 b [(4), olefinic protons]

^a Except where stated otherwise spectra were recorded at 60 MHz in CDCl₃ with TMS as internal reference; s = singlet; d = doublet; m = multiplet; b = broad. ^b Spectrum recorded at 100 MHz in CDCl₃ with TMS as internal reference.

TABLE 2

MASS SPECTRUM OF THE COMPOUND C₅Me₅IrC₈H₁₂

Ion	Mass (m/e)	Relative intensity
(C ₅ Me ₅ ¹⁹³ IrC ₈ H ₁₂) ⁺ (P)	436	100
(C ₅ Me ₅ ¹⁹¹ IrC ₈ H ₁₂) ⁺ (P')		
+ (P-H ₂) ⁺	434	67.5
(P'-H ₂) ⁺ + (P-2 H ₂) ⁺	432	7.4
(P'-2 H ₂) ⁺	430	8.8
(P-CH ₃) ⁺	421	17.7
(P'-CH ₃) ⁺ + (P-CH ₃ -H ₂) ⁺	419	33.9
(P'-CH ₃ -H ₂) ⁺	417	19.1
(P-C ₂ H ₆) ⁺	407	11.3
(P-C ₂ H ₆) ⁺	406	12.3
(P'-C ₂ H ₆) ⁺	405	7.9
(P'-C ₂ H ₆) ⁺	404	7.4
(P-C ₃ H ₇) ⁺	393	8.4
(P'-C ₃ H ₇) ⁺	391	4.9
(C ₅ Me ₅ ¹⁹³ Ir) ⁺	328	0.6
(C ₅ Me ₄ CH ₂ ¹⁹³ Ir) ⁺	327	0.5
(C ₅ Me ₅ ¹⁹¹ Ir) ⁺	326	2.0
(C ₅ Me ₄ CH ₂ ¹⁹¹ Ir) ⁺	325	6.4
(¹⁹³ Ir) ⁺	193	0.3
(¹⁹¹ Ir) ⁺	191	0.2

methylbenzene ligand are absent from the spectrum. A study of the metastable peaks (Table 3) shows that the major initial fragmentation processes are by loss of H₂, C₂H₆ or CH₃ from the parent ion.

It has previously been shown¹ that the reaction of the diene (I) or the methoxy compound (III) with RhCl₃ · 3 H₂O occurs by an initial acid-catalysed carbonium ion rearrangement to pentamethylcyclopentadiene, which has been shown in a

TABLE 3

METASTABLE TRANSITIONS OBSERVED IN THE MASS SPECTRUM OF $C_5Me_5IrC_8H_{12}$

$(P)^+$	\rightarrow	$(P-H_2)^+ + H_2$	$m^* = 432$
$(P')^+$	\rightarrow	$(P'-H_2)^+ + H_2$	$m^* = 430$
$(P'-H_2)^+$	\rightarrow	$(P'-2H_2)^+ + H_2$	$m^* = 428$
$(P)^+$	\rightarrow	$(P-CH_3)^+ + CH_3$	$m^* = 406.4$
$(P')^+$	\rightarrow	$(P'-CH_3)^+ + CH_3$	$m^* = 404.6$
$(P)^+$	\rightarrow	$(P-C_2H_6)^+ + C_2H_6$	$m^* = 377.9$
$(P')^+$	\rightarrow	$(P'-C_2H_6)^+ + C_2H_6$	$m^* = 376$
$(P-CH_3)^+$	\rightarrow	$(P-CH_3-H_2)^+ + H_2$	$m^* = 417$
$(P'-CH_3)^+$	\rightarrow	$(P'-CH_3-H_2)^+ + H_2$	$m^* = 415$

separate experiment to react almost quantitatively with further $RhCl_3 \cdot 3H_2O$ to give the isolated complex (IIb) ($X=Cl$). Although the reactions with $IrCl_3 \cdot 4H_2O$ have not been studied in the same detail, it is considered that they occur by a similar mechanism, although it is apparent from the results presented that the reaction to form the iridium complex is much slower and leads to appreciable isomerisation of the diene (I) to hexamethylbenzene. This path seems just as reasonable as the one recently suggested⁴, whereby the compounds (IIa) or (IIb) ($X=Cl$) arise via the intermediate formation of a methoxycyclopentadienyl- Rh^{III} or $-Ir^{III}$ complex which then undergoes decomposition.

EXPERIMENTAL

IR spectra were recorded as hexachlorobutadiene and Nujol mulls on a Perkin-Elmer 257 grating instrument. UV spectra were recorded on a Hilger and Watts "Ultrascan" spectrometer on dilute solutions in ethanol and hexane. 1H NMR spectra were recorded either on a Perkin-Elmer R10 instrument at 60 MHz or on a Varian HA 100 at 100 MHz in $CDCl_3$ using tetramethylsilane as an internal reference. Mass spectra were recorded on an A.E.I. MS 9 double-focussing mass spectrometer operating at 70 eV ionising energy, and molecular weight determinations were carried out using a "Mechrolab" osmometer.

1-(1-Methoxyethyl)pentamethyl-2,4-cyclopentadiene was prepared by the perchloric acid catalysed reaction of hexamethylbicyclo[2.2.0]hexa-2,5-diene and methanol⁵, and identified by NMR, IR, UV and mass spectroscopy. Iridium trichloride tetrahydrate, hexamethylbicyclo[2.2.0]hexa-2,5-diene, triphenylphosphine, pyridine, *p*-toluidine and *cis,cis*-1,5-cyclooctadiene were commercial samples used without further purification. Methanol and ethanol were dried by treatment with quicklime, followed by treatment with magnesium activated by iodine. Except where stated otherwise all reactions were in an atmosphere of dry nitrogen.

Preparation of di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium

(a). From hexamethylbicyclo[2.2.0]hexa-2,5-diene. Iridium trichloride tetrahydrate (10.1 g, 27.1 mmole) and the diene (17.9 g, 110 mmole) in dry methanol (20 ml) were heated at 60° for 24 h to give a peach solid which precipitated after about 9 h. The solid was filtered through a sintered glass crucible (porosity 4), washed with methanol and very thoroughly with ether, and dried *in vacuo*, before recrystallising

from a dichloromethane/hexane mixture to give di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (2.1 g, 2.62 mmole, 19%) as a crystalline peach solid which did not melt below 300°. [Found: C, 30.4; H, 3.8; mol. wt., 766 (dichloroethane). $C_{20}H_{30}Cl_4Ir_2$ calcd.: C, 30.1; H, 3.8%; mol. wt., 796.] Its IR spectrum showed bands at 2990 m, 2970 m, 2920 m, 1475 (sh), 1470 (sh), 1460 (sh), 1450 s, 1388 s, 1378 s, 1360 w (sh), 1160 m, 1082 (sh), 1075 m, 1034 s, 975 vw, 955 vw, 795 vw, 738 m, 723 m cm^{-1} . Evaporation of the filtrate, *in vacuo*, gave hexamethylbenzene (10.6 g, 65.4 mmole, 59%, based on the diene taken) m.p. 165° (lit.⁶ m.p. 164°). The separation of hexamethylbenzene was quite rapid initially but became slower as the reaction proceeded.

(b). From 1-(1-methoxyethyl)pentamethyl-2,4-cyclopentadiene. Iridium trichloride tetrahydrate (0.52 g, 1.4 mmole) and the diene (1.0 g, 5.15 mmole) in dry methanol (10 ml) were heated at 60° for 7 h to give di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.06 g, 0.075 mmole, 11%). The analysis and IR and NMR spectra of this product were identical with those obtained for the product from the reaction described above.

Preparation of di- μ -iodo-diiodobis(pentamethylcyclopentadienyl)diiridium

Di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.20 g, 0.25 mmole) was shaken with sodium iodide (0.93 g, 6.2 mmole) in acetone (50 ml) for 3 days. The red solution was filtered and evaporated to dryness *in vacuo* to give a red solid which was washed with water and dried (P_2O_5) in a vacuum desiccator. Recrystallisation from chloroform gave red crystals of di- μ -iodo-diiodobis(pentamethylcyclopentadienyl)diiridium (0.21 g, 0.18 mmole, 72%). [Found: C, 20.8; H, 2.4; mol. wt., 1106 (dichloroethane). $C_{20}H_{30}I_4Ir_2$ calcd.: C, 20.7; H, 2.6%; mol. wt., 1162.] Its IR spectrum showed bands at 2985 m, 2962 m, 2910 m, 2730 vw, 1478 (sh), 1460 s, 1450 s, 1420 m, 1408 w, 1385 (sh), 1380 s, 1375 (sh), 1360 w, 1308 vw, 1170 w, 1158 m, 1078 m, 1030 s, 1022 s, 975 vw, 950 vw, 720 m cm^{-1} .

Reaction of di- μ -chlorodichlorobis(pentamethylcyclopentadienyl)diiridium with ligands

(a). *p*-Toluidine. Di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.20 g, 0.25 mmole), *p*-toluidine (0.23 g, 2.15 mmole) in chloroform (8 ml) were kept at room temperature for 1 h. The solvent was evaporated *in vacuo* to half bulk and ether was added to precipitate a yellow solid which was filtered, washed with ether and dried *in vacuo*. The solid was purified by reprecipitation from chloroform with ether to give dichloro(*p*-toluidine)(pentamethylcyclopentadienyl)iridium (0.25 g, 0.50 mmole, 99%). [Found: C, 40.7; H, 4.9; N, 2.8; mol. wt., 564 (dichloroethane). $C_{17}H_{24}Cl_2IrN$ calcd.: C, 40.4; H, 4.7; N, 2.8%; mol. wt., 505.] Its IR spectrum showed bands at 3280 s, 3200 (sh), 3190 s, 3160 s, 3108 s, 3060 vw, 3040 vw, 3020 vw, 2980 s, 2920 s, 2875 s, 2810 vw, 2780 vw, 2730 vw, 1613 w, 1600 w, 1570 m, 1560 (sh), 1515 s, 1470 (sh), 1460 (sh), 1455 s, 1415 w, 1380 s, 1360 vw, 1352 vw, 1308 w, 1220 m, 1180 w, 1155 m, 1120 m, 1080 m, 1030 s, 970 w, 935 vw, 920 vw, 845 w, 830 (sh), 820 s, 735 (sh), 715 s, 695 w cm .

(b). Triphenylphosphine. Under similar conditions to those described above di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.20 g, 0.25 mmole) and triphenylphosphine (0.23 g, 0.88 mmole) gave dichloro(triphenylphosphine)(pentamethylcyclopentadienyl)iridium as a yellow-orange solid (0.25 g, 0.38 mmole, 76%).

[Found: C, 51.1; H, 4.8; mol.wt., 636 (dichloroethane). $C_{28}H_{30}Cl_2IrP$ calcd.: C, 50.9; H, 4.5%; mol.wt., 660.] Its IR spectrum had bands at 3075 w, 3060 m, 3050 m, 2980 m, 2920 w, 2860 w, 1590 w, 1574 w, 1505 vw, 1485 s, 1452 m, 1446 s, 1435 s, 1402 vw, 1380 m, 1362 w, 1310 w, 1185 m, 1170 vw, 1158 w, 1115 w, 1097 s, 1090 s(sh), 1080 w, 1070 w, 1030 s, 1000 w, 975 w, 850 w, 760 s, 750 s, 744 s, 725 w, 704 s, 700 s, 690 s cm^{-1} .

(c). *Pyridine*. Di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.20 g, 0.25 mmole) and pyridine (3 ml) gave dichloropyridine(pentamethylcyclopentadienyl)iridium as a yellow solid (0.22 g, 0.46 mmole, 92%). [Found: C, 37.6; H, 4.9; N, 2.9; mol.wt., 471 (dichloroethane). $C_{15}H_{20}Cl_2IrN$ calcd.: C, 37.7; H, 4.2; N, 2.9%; mol.wt., 477.] Its IR spectrum had bands at 3130 vw, 3100 vw, 3050 m, 2995 m, 2970 m, 2925 m, 2860 vw, 2785 vw, 2720 vw, 1602 m, 1488 w, 1470 m, 1445 s, 1418 m, 1380 s, 1360 vw, 1340 vw, 1235 m, 1210 m, 1160 m, 1080 w, 1065 w, 1060 m, 1045 m, 1030 m, 990 vw, 960 vw, 770 vs, 740 m, 700 vs, 640 m cm^{-1} .

(d). *1,5-Cyclooctadiene*. Di- μ -chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium (0.30 g, 0.38 mmole), *cis, cis*-1,5-cyclooctadiene (7 ml), sodium carbonate (0.5 g) in dry ethanol (20 ml) were heated under reflux for 2 h. The solution was allowed to cool, filtered and the filtrate evaporated *in vacuo* to leave a white solid. Chromatography on an alumina column (6% w/w water) and elution with light petroleum (b.r. 40–60°) gave a first fraction of a white solid, which was recrystallised from light petroleum to give 1,5-cyclooctadiene(pentamethylcyclopentadienyl)iridium (0.21 g, 0.48 mmole, 63%) m.p. 170–171°. [Found: C, 49.8; H, 6.5; mol.wt., 431 (dichloroethane). $C_{18}H_{27}Ir$ calcd.: C, 49.6; H, 6.2%; mol.wt., 435.] Its UV spectrum in ethanol and hexane had λ_{max} 213–214 m μ (ϵ 22,000) and its IR spectrum had bands at 2960 vs, 2920 vs, 2875 vs, 2825 vs, 2720 vw, 1488 w, 1470 (sh), 1460 (sh), 1455 s, 1440 s, 1385 s, 1378 (sh), 1350 w, 1315 s, 1295 w, 1235 m, 1198 m, 1170 vw, 1160 w, 1150 m, 1070 m, 1030 m, 1005 m, 998 (sh), 980 m, 905 vs, 870 w, 838 m, 805 m, 780 m, 720 m, 705 vw cm^{-1} .

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