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PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM COMPLEXES

VIII*. DI-μ-HYDRIDOBIS[CHLORO(PENTAMETHYLCYCLOPENTADIENYL)IRIDIUM] AND RELATED COMPOUNDS

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Summary

The synthesis of the novel di-μ-hydridoiridium complexes $[H_2(IrC_5Me_5)_2X_2]$ (X = Br, Cl) is described. These complexes react with butadiene, but only in very polar solvents, to give η-1-methylallyl complexes, with phosphines to give $[HIrC_5Me_5(X)(R_3P)]$, and with AgOCOR to give $[H_2(IrC_5Me_5)_2OCOR]^+$. The preparation and some properties of $[MC_5Me_5Br_2]_2$ (M = Ir or Rh), $[IrC_5Me_5I_2]_2$, $[(RhC_5Me_5)(PMe_2Ph)_2X]^+$, $[(RhC_5Me_5)(NO_3)_2]_n$, $[H(MC_5Me_5)_2Br_3]$, and $[H(IrC_5Me_5)_2I_3]$ are also reported.

The synthesis of a range of hydride-bridged binuclear pentamethylcyclopentadienyl-rhodium and -iridium complexes, including $[H(MC_5Me_5)_2Cl_3]$, $[H(MC_5Me_5)_2Y_2]^+$, $[H_2(MC_5Me_5)_2Y]^+$ (Y = OCOMe, OCOCF$_3$)**, and $[H_3(IrC_5Me_5)_2]^+$, has recently been reported [1]. The structures proposed for these complexes have been confirmed by an X-ray structure determination of $[H(RhC_5Me_5)_2Cl_3]$ [2].

In the course of studies on the homogeneous hydrogenation of olefins using $[IrC_5Me_5Cl_2]_2$ (Ib), or $[H(IrC_5Me_5)_2Cl_3]$ (IIb), as catalysts a new hydrido complex was detected by NMR spectroscopy after hydrogenation was complete [3].

This new complex IIIa was obtained on a preparative scale by treating either Ib or IIb in benzene with isopropanol and triethylamine. The deuterido

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[*] For Part VII see Ref. 1.

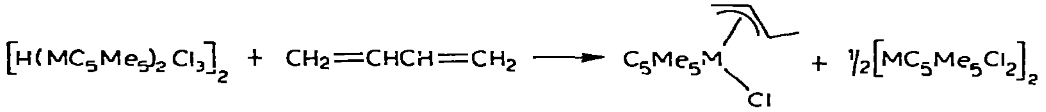
[**] Throughout, M = Ir or Rh.

complex IIIb was obtained by extended reaction of Ib with deuterium in benzene in the presence of base. Both methods have been used to prepare II and their deuterido analogues, except that shorter reaction times were needed. The bromohydrido complex IIIc was similarly prepared, but it was not possible to obtain a chlorohydridorhodium analogue, nor could any such species, apart from $[H(RhC_5Me_5)_2Cl_3]$ be detected during hydrogenation studies.

The complex IIIa was fully characterised by analysis, molecular weight measurements and spectroscopy. The ^{1}H NMR spectrum showed singlets at τ 8.32 and 23.94, with intensity ratio 15/1; the former resonance is due to the equivalent C_5Me_5 protons and the high field resonance arises from an Ir—H group. In common with the other binuclear hydrides we examined, IIIa showed no band in the 1800-2100 cm^{-1} region of the infrared normally associated with a terminal ν(Ir—H). However, a band at 1162 cm^{-1} in IIIa, which is moved to 830 cm^{-1} in the deuterido complex IIIb, may be assigned to ν(Ir—H) bridging. The complex also showed a strong band at 276 cm^{-1}, owing to ν(Ir—Cl) terminal; the corresponding band in the bromo complex (IIIc), ν(Ir—Br) terminal, was at 183 cm^{-1}. We may therefore conclude that the complexes contain bridging hydrides and terminal halides and we propose the structure shown. It also appears likely that the complexes have a *trans*-configuration.

The complex IIIa reacted with triphenylphosphine to give only the known monomeric V [4], and both IIIa and IIIc reacted with 1,2-bis(diphenylphosphino)ethane to give VI, which showed terminal ν(Ir—H) bands at 2090 (X = Cl) and 2091 (X = Br) cm^{-1}. The complexes were also converted to the known di-μ-hydrido-μ-acetato or μ-trifluoroacetato complexes (VII) [1] on reaction with the appropriate silver carboxylate, followed by addition of ammonium hexafluorophosphate.

The mono-μ-hydrido complexes IIa and IIb (X = Cl) react readily with a wide variety of dienes in dichloromethane at 20-30° to give the η-allylic complexes (e.g. VIII, from butadiene) and (I) [5]:



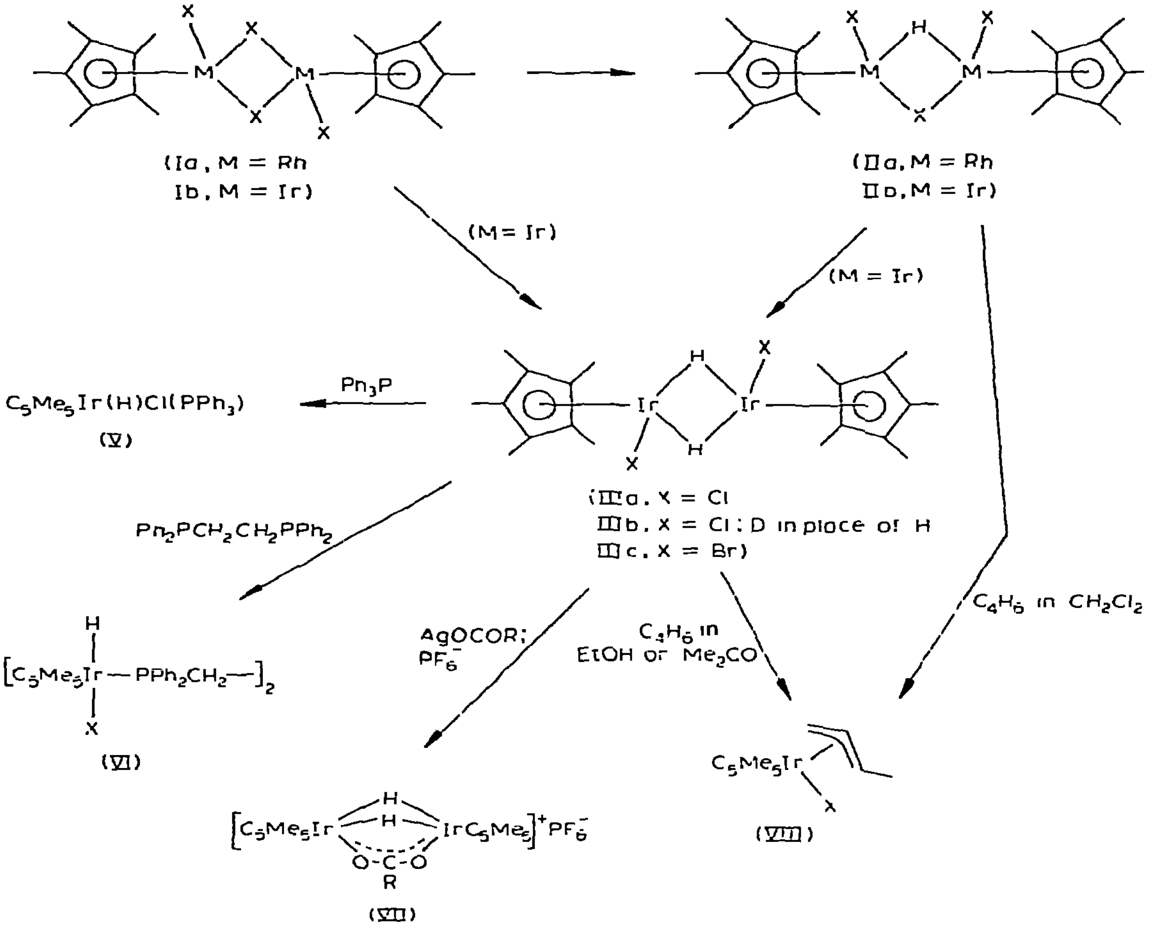
$$[H(MC_5Me_5)_2Cl_3]_2 + CH_2{=}CHCH{=}CH_2 \longrightarrow C_5Me_5M(\eta\text{-}C_4H_7)Cl + \tfrac{1}{2}[MC_5Me_5Cl_2]_2$$

By contrast, neither IIIa nor IIIc reacts with dienes in dichloromethane, though reaction to give the η-allylic complexes in high yield does occur in more polar solvents (ethanol or acetone).

This result is in accord with the deductions from kinetic data that the rate-determining step in the reaction of IIa and IIb (X = Cl) in dichloromethane is not the opening of the M—H—M bridge [5]. The reaction of III with dienes in alcohol or acetone can be accounted for since these will solvate the intermediates better. A vacant site, at which coordination of the diene and reaction can occur, can be created either by opening the Ir—H—Ir bridge or by ionising a halide; either of these processes would be aided by good solvation.

The complex IIIa is a very effective olefin hydrogenation catalyst at 25° and 1 atm. H_2, particularly in a very polar solvent such as isopropanol; addition of base (triethylamine) causes a small increase in rate. The complex also isomerises olefins, for example, 4-methylcyclohexene to 1-methylcyclohexene [3].

SCHEME 1



Details are also given in the Experimental section of the synthesis and spectroscopic properties of pentamethylcyclopentadienyl-rhodium and -iridium complexes that have not previously been reported. These include $[MC_5Me_5Br_2]_2$, $[IrC_5Me_5I_2]_2$, $[(RhC_5Me_5)(PMe_2Ph)_2X]^+$ (X = Cl, I), $[(RhC_5Me_5)(NO_3)_2]_n$, $[H(MC_5Me_5)_2Br_3]$ and $[H(IrC_5Me_5)_2I_3]$. It was not possible to obtain $[H(RhC_5Me_5)_2I_3]$ by these methods.

Experimental

All reactions were carried out under nitrogen except where stated.

Di-μ-hydridobis[chloro(pentamethylcyclopentadienyl)iridium] (IIIa)

Method A. A suspension of $[IrC_5Me_5Cl_2]_2$ (0.2 g), in benzene (4 ml), isopropanol (1 ml) and triethylamine (0.3 ml) was stirred (24 h/20°). All volatile materials were removed on a rotary evaporator to leave a dark solid; this was extracted with benzene, the solvent removed in vacuo, and the residue crystallised from benzene/light petroleum to give dark blue crystals of IIIa

(0.18g, 95%), m.p. 210° (dec.). [Found: C, 33.2; H, 4.3; Cl, 9.6%; mol. wt., 709. $C_{20}H_{32}Cl_2Ir_2$ calcd.: C 33.1; H, 4.4; Cl, 9.1%; mol. wt. 727.]

Method B The complex IIIa was also obtained (95% yield) by the above reaction, using [H(IrC$_5$Me$_5$)Cl$_3$] as starting material.

Di-μ-deuteridobis[chloro(pentamethylcyclopentadienyl)iridium] (IIIb)

A suspension of [IrC$_5$Me$_5$Cl$_2$]$_2$ (0.1g) in benzene (10 ml) containing triethylamine (0.2 ml) was stirred under deuterium (C.P. grade 99.5% D_2) at 20° for 36 h. The product was then worked up as described above to yield IIIb (0.08 g, 85%).

Di-μ-bromobis[bromo(pentamethylcyclopentadienyl)-rhodium and -iridium]

A suspension of [RhC$_5$Me$_5$Cl$_2$]$_2$ (0.4g) and lithium bromide in methanol (20 ml) was stirred at 60° for 6h. The reaction mixture was cooled, and filtered; the precipitate was then recrystallised from chloroform/benzene to give [Rh(C$_5$Me$_5$)Br$_2$]$_2$ (0.47g, 90%) as dark brown crystals, m.p. > 260°; NMR ($CDCl_3$) singlet at τ 8.28. [Found: C, 30.4; H, 3.7; Br, 40.4%. $C_{20}H_{30}Br_4Rh_2$ calcd.: C, 30.2; H, 3.8; Br, 40.2%.]

The iridium complex [Ir(C$_5$Me$_5$)Br$_2$]$_2$ was prepared analogously (90%); NMR ($CDCl_3$) singlet at τ 8.35. [Found: C, 22.5; H, 3.0; Br, 32.9%; $C_{20}H_{30}Br_4Ir_2$ calcd.: C, 22.6; H, 3.1; Br, 32.8%.]

Di-μ-hydridobis[bromo(pentamethylcyclopentadienyl)iridium] (IIIc)

This was obtained as dark green crystals in 92% yield from [Ir(C$_5$Me$_5$)Br$_2$]$_2$ by method A above; m.p. 226° (dec.), NMR (CH_2Cl_2) τ 8.27 (s, 30H, C$_5$Me$_5$) and 24.97 (s, 2H). [Found: C, 29.8; H, 4.0%. $C_{20}H_{32}Br_2Ir_2$ calcd.: C, 29.4; H, 4.0%.]

Di-μ-hydrido-μ-acetato- and trifluoroacetato-bis(pentamethylcyclopentadienyliridium) hexafluorophosphate (VII)

A mixture of [H$_2$(IrC$_5$Me$_5$)$_2$Cl$_2$] (0.09 g) and silver acetate (0.04 g) was stirred in methanol for 5 min at 25°. The solution was filtered and 2 ml of a saturated solution of ammonium hexafluorophosphate in acetone was added to the filtrate. The precipitate was filtered off and crystallised from dichloromethane/light petroleum to give [H$_2$(IrC$_5$Me$_5$)$_2$OAc]PF$_6$ (0.1g, 95%); NMR (CH_2Cl_2) τ 7.47 (s, 3H, OAc), 8.08 (s, 30H, C$_5$Me$_5$) and 22.57 (s, 2H). [Found: C, 30.7; H, 4.02%. $C_{22}H_{35}F_6Ir_2O_2P$ calcd.: C, 30.6; H 4.2%.] An analogous reaction with silver trifluoroacetate gave [H$_2$(IrC$_5$Me$_5$)$_2$OCOCF$_3$]PF$_6$ (95%) [1].

Chlorohydrido(triphenylphosphine)pentamethylcyclopentadienyliridium (V)

[H$_2$(IrC$_5$Me$_5$)$_2$Cl$_2$] (0.05g) was added to a solution of triphenylphosphine (0.05g) in benzene (5 ml) and the solution was stirred for 20 min at 25°. This gave a yield of 80% of V, identified by NMR [4].

μ-1,2-Bis(diphenylphosphino)ethanebis[chloro(hydrido)(pentamethylcyclopentadienyl)iridium] (VI)

1,2-Bis(diphenylphosphino)ethane (0.1 g) was added to a solution of [H$_2$(IrC$_5$Me$_5$)$_2$Cl$_2$] (0.05g) in benzene (10 ml). The solution was stirred (0.5 h/

25°), the solvent was then removed in vacuo and the residue was crystallised from ether to give the yellow (VI, X = Cl) (0.05 g, 70%), m.p. 130° (dec.); infrared ν(Ir—H) 2090 cm^{-1}; ^{1}H NMR (CH_2Cl_2) τ 2.63 (m, 20H, phenyl), 8.22 (m, 4H, CH_2), 8.50 [dd, 30H, C_5Me_5, J(Me—P) = 2; J(Me—H) = 1Hz], 23.87 [d, broad, 2H, J(H—P) = 36 Hz]. [Found: C, 49.6; H, 4.8; Cl, 6.2%. $C_{46}H_{56}Cl_2Ir_2P_2$ calcd.: C, 49.7; H, 5.0; Cl, 6.3%.]

$[H(IrC_5Me_5)(Br)Ph_2PCH_2—]_2$ (VI, X = Br) was prepared analogously (70% yield), m.p. 122° (dec.), infrared ν(Ir—H) 2091 cm^{-1}; ^{1}H NMR (CH_2Cl_2) τ 2.68 (m, 20H, phenyl), 8.17 (m, 4H, CH_2), 8.48 [dd, 30H, C_5Me_5, J(Me—P) = 2, J(Me—H) = 1 Hz], 24.27 [d, broad, 2H, J(H—P) = 36 Hz]. [Found: C, 50.5; H, 5.0%. $C_{46}H_{56}Br_2Ir_2P_2$ calcd.: C 50.6; H, 5.1%.]

Reaction of $[H_2(IrC_5Me_5)_2Br_2]$ (IIIc) with butadiene to give VIII

Butadiene was passed in a slow stream for 3 h through a suspension of $[H_2(IrC_5Me_5)_2Br_2]$ (0.1g) in acetone (20 ml) at 25°. The solvent was removed in vacuo and the residue crystallised from benzene/light petroleum to give bromo(η-1-methylallyl)pentamethylcyclopentadienyliridium (VIII, X = Br) (0.1 g, 85%). NMR ($CDCl_3$) τ 6.10 (m, 1H), 6.47 (m, 1H), 6.77 (dd, 1H, J = 2 Hz), 7.17 (dd, 1H), 8.17 (s, 15H), 8.35 (d, 3H, J = 6 Hz). [Found: C, 36.8; H, 5.0; Br, 17.4%. $C_{14}H_{22}BrIr$ calcd.: C, 36.7; H, 4.8; Br, 17.3%.]

An analogous reaction with butadiene and IIIa gave the known chloro(η-1-methylallyl)pentamethylcyclopentadienyliridium (VIII, X = Cl) (90%) [4].

Neither IIIa nor IIIc underwent any reaction with a variety of dienes in dichloromethane at 25° during 10h (by NMR) even in the presence of triethylamine [5].

Di-μ-iodobis[iodo(pentamethylcyclopentadienyl)iridium] (I, X = I)

This was obtained as brown crystals [90%, m.p. > 250°, NMR ($CDCl_3$), τ 8.17 (s)] in the same manner as the rhodium analogue [6]. [Found: C, 20.5; H, 2.6; I, 43.8%. $C_{20}H_{30}I_4Ir_2$ calcd.: C, 20.7; H, 2.6; I, 43.7%.]

μ-Bromo-μ-hydridobis[bromo(pentamethylcyclopentadienyl)-rhodium and -iridium] (II, X = Br)

$[H(RhC_5Me_5)_2Br_3]$ (IIa, X = Br) was prepared from $[RhC_5Me_5Br_2]_2$ in 65-88% yield by the methods described for the synthesis of $[H(RhC_5Me_5)_2Cl_3]$ [1]. The best yield was obtained by borohydride reduction (method ii). NMR (CH_2Cl_2) τ 8.38 (s, 30H) and 22.61 (t, 1H, J(H—Rh) = 23 Hz); IR ν(Rh—H) 1153 cm^{-1}. [Found: C, 33.5; H, 4.3; Br, 33.3%. $C_{20}H_{31}Br_3Rh_2$ calcd.: C, 33.5; H, 4.4; Br, 33.4%.] The orange $[H(IrC_5Me_5)_2Br_3]$ (IIb, X = Br) was obtained in 92% yield by borohydride reduction of $[IrC_5Me_5Br_2]_2$. NMR (CH_2Cl_2) τ 8.32 (s, 30H) and 24.87 (s, 1H); IR ν(Ir—H) 1156 cm^{-1}. [Found: C, 26.7; H, 3.6; Br, 26.7%; $C_{20}H_{31}Br_3Ir_2$ calcd.: C, 26.8; H, 3.5; Br, 26.8%.]

μ-Iodo-μ-hydridobis[iodo(pentamethylcyclopentadienyl)iridium] (IIb, X = I)

$[H(IrC_5Me_5)I_3]$ was obtained as purple crystals in 90% yield by the borohydride reduction of $[IrC_5Me_5I_2]_2$. It was also obtained in the same yield by bubbling a slow stream of hydrogen through a benzene solution of $[IrC_5Me_5I_2]_2$

(0.1 g in 40 ml) at 20° for 48 h. Removal of the solvent followed by crystallisation from benzene/light petroleum afforded the complex. NMR (CH_2Cl_2) τ 8.22 (s, 30H) and 27.17 (s, 1H); IR, ν(Ir—H) 1158 cm^{-1}. [Found: C, 23.5; H, 2.8; I, 37.3%. $C_{20}H_{31}I_3Ir$ calcd.: C, 23.2; H, 3.0; I, 36.7%.]

Chlorobis(dimethylphenylphosphine)pentamethylcyclopentadienylrhodium chloride and tetraphenylborate

A mixture of $[RhC_5Me_5Cl_2]_2$ (0.2 g) and dimethylphenylphosphine (0.2g) in ethanol (20 ml) was refluxed (5 h). The solvent was removed in vacuo and the solid remaining was crystallised from dichloromethane/light petroleum to yield orange crystals of $[Rh(C_5Me_5)Cl(PMe_2Ph)_2]Cl$ (0.3 g, 90%), NMR ($CDCl_3$) τ 2.23 and 2.52 (m, broad, 10H, phenyl), 7.97 [dd, 6H, *J*(Me—P) = 4 and 8 Hz], 8.20 [dd, 6H, *J*(Me—P) = 4 and 8Hz] and 8.64 [t, 15H, *J*(Me—P) = 4Hz]. [Found: C, 52.6; H, 6.5%. $C_{26}H_{37}Cl_2P_2Rh$ calcd.: C, 53.3; H, 6.3%.] This was also converted into the tetraphenylborate, $[Rh(C_5Me_5)Cl(PMe_2Ph)_2]BPh_4$. [Found: C, 69.6; H, 6.6%. $C_{50}H_{57}BClP_2Rh$ calcd.: C, 69.1; H, 6.6%.]

Iodobis(dimethylphenylphosphine)(pentamethylcyclopentadienyl)rhodium iodide and tetraphenylborate

These were prepared from $[Rh(C_5Me_5)I_2]_2$ in the same manner as above. $[Rh(C_5Me_5)I(PMe_2Ph)_2]I$, NMR ($CDCl_3$) τ 2.1 and 2.4 (m, broad, 10H, phenyl), 7.87 [dd, 6H, *J*(Me—P) = 4 and 8 Hz], 7.97 [dd, 6H, *J*(Me—P) = 4 and 8 Hz], 8.27 [t, 15H, *J*(Me—P) = 4 Hz]. [Found: C, 40.8, H, 5.1; I, 33.6%. $C_{26}H_{37}I_2P_2Rh$ calcd.: C, 40.6; H, 4.8; I, 33.3%.] $[Rh(C_5Me_5)I(PMe_2Ph)_2]BPh_4$, found: C, 65.5; H, 5.9; I, 13.1%. $C_{50}H_{57}BIP_2Rh$ calcd.: C, 65.6; H, 5.9; I, 13.2%.

Dinitrato(pentamethylcyclopentadienyl)rhodium

A mixture of $[RhC_5Me_5Cl_2]_2$ (0.2 g) and silver nitrate (0.4 g) was stirred in methanol (40 ml) at 25° for 1 h. The solution was filtered and the solvent removed in vacuo leaving yellow-orange crystals which were recrystallised from chloroform/ether giving the pure nitrato complex (0.22g, 92%), NMR ($CDCl_3$) 8.30 (s). [Found: C, 34.7; H, 4.3; N, 8.1%. $C_{10}H_{15}N_2O_6Rh$ calcd.: C, 34.1; H, 4.2; N, 8.1%.]

Acknowledgement

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