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METAL COMPLEXES OF FLUOROPHOSPHINES
III. SOME OXIDATIVE ADDITION REACTIONS OF A RHODIUM–TRIFLUOROPHOSPHINE COMPLEX*

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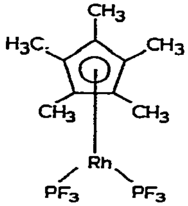
SUMMARY

Some oxidative addition reactions of $(CH_3)_5C_5Rh(PF_3)_2$ with various iodine compounds are described. Iodine reacts with $(CH_3)_5C_5Rh(PF_3)_2$ in benzene at room temperature to give the deep red crystalline diiodide $(CH_3)_5C_5Rh(PF_3)I_2$. The perfluoroalkyl iodides R_fI ($R_f = CF_3$, C_2F_5, n-C_3F_7, and n-C_7F_{15}) react with $(CH_3)_5C_5Rh(PF_3)_2$ in benzene at room temperature to give the orange to deep red $(CH_3)_5C_5Rh(PF_3)(R_f)I$ ($R_f = CF_3$, C_2F_5, n-C_3F_7, and n-C_7F_{15}). The IR and proton and fluorine NMR spectra of these new (pentamethylcyclopentadienyl)rhodium-trifluorophosphine complexes are discussed.

INTRODUCTION

The reaction between the readily available[3] (pentamethylcyclopentadienyl)rhodium derivative $[(CH_3)_5C_5RhCl_2]_2$ and the commercially available $Ni(PF_3)_4$ provides a facile synthesis of the rhodium–trifluorophosphine derivative $(CH_3)_5C_5Rh(PF_3)_2$(I)[1,2]. The analogy between metal–trifluorophosphine derivatives and metal carbonyl derivatives suggested that $(CH_3)_5C_5Rh(PF_3)_2$ might undergo oxidative addition reactions similar to those reported for the carbonyl analogues $R_5C_5M(CO)_2$



(I)

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* (*a*) For Part II see ref. 1; (*b*). For a preliminary communication of some of this work see ref. 2; (*c*). Portions of this work were presented to the Division of Fluorine Chemistry at the 162nd National American Chemical Society Meeting, Washington, D.C., September, 1971.

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(R = H, M = Co[4-6] and Rh[5,7]; R = CH_3, M = Rh[8] and Ir[8,9]). This paper reports several such oxidative addition reactions of $(CH_3)_5C_5Rh(PF_3)_2$ (I). These reactions are apparently the first reported examples of oxidative addition reactions of a metal–trifluorophosphine complex.

EXPERIMENTAL

Materials

The $(CH_3)_5C_5Rh(PF_3)_2$ used in this work was prepared by the previously described[1,2] procedure using as raw materials commercial samples of rhodium trichloride trihydrate (Englehard Industries, Newark, New Jersey; 39.9% rhodium), hexamethylbicyclo[2.2.0]hexadiene ("hexamethyl-Dewar-benzene", Henley and Company New York, New York), and tetrakis(trifluorophosphine)nickel (Ozark Mahoning Company, Tulsa, Oklahoma). The iodine compounds used in this work all were commercial samples.

Reaction of $(CH_3)_5C_5Rh(PF_3)_2$ with iodine

A mixture of 0.5 g (1.21 mmoles) of $(CH_3)_5C_5Rh(PF_3)_2$, 0.3 g (1.18 mmoles of I_2) of iodine, and 20 ml of benzene was stirred for 21 h at room temperature. The resulting precipitate of $(CH_3)_5C_5Rh(PF_3)I_2$ was removed by filtration and washed with three 5 ml portions of benzene. Additional product was isolated by evaporation of the benzene filtrate.

Reactions of $(CH_3)_5C_5Rh(PF_3)_2$ with perfluoroalkyl halides

A mixture of 0.5 g (1.21 mmoles) of $(CH_3)_5C_5Rh(PF_3)_2$ and excess (5 to 15 g) of the perfluoroalkyl iodide in 5 to 10 ml of benzene was kept at 25° for 37 to 120 h. All volatile materials were then removed in vacuum at room temperature. The solid residue was crystallized from the solvent system indicated in Table 1 to give the $(CH_3)_5C_5Rh(PF_3)R_fI$ derivative in the indicated yield.

TABLE 1

(PENTAMETHYLCYCLOPENTADIENYL)RHODIUM–TRIFLUOROPHOSPHINE DERIVATIVES PREPARED IN THIS WORK

Compound	Color	M.p.[a] (°C)	Crystallization solvent	Yield (%)	Analyses found[b] (calcd.) (%)				
					C	H	F	I	P
$Me_5C_5Rh(PF_3)I_2$	Deep red	>275°		95	21.0 (20.7)	2.6 (2.6)	10.3 (9.8)	43.4 (43.8)	5.6 (5.3)
$Me_5C_5Rh(PF_3)(CF_3)I$	Orange-brown	dec. >200°	Benzene/heptane	72	25.1 (25.2)	3.0 (2.9)	21.0 (21.9)	24.7 (24.3)	5.6 (5.9)
$Me_5C_5Rh(PF_3)(C_2F_5)I$	Red	230–231°	CH_2Cl_2/hexane	76	25.1 (25.2)	2.6 (2.6)	26.7 (26.6)	22.1 (22.1)	5.6 (5.4)
$Me_5C_5Rh(PF_3)(n\text{-}C_3F_7)I$	Deep red	147–149°	Benzene/heptane	77	25.3 (25.1)	2.4 (2.4)	31.3 (30.5)	20.3 (20.5)	5.1 (5.0)
$Me_5C_5Rh(PF_3)(n\text{-}C_7F_{15})I$	Orange	86–88°	Hexane	62	25.0 (24.8)	2.0 (1.8)	41.4 (41.7)	15.4 (15.4)	

[a] Melting points were taken in capillaries and are uncorrected. [b] Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Reactions of $(CH_3)_5C_5Rh(PF_3)_2$ *with other halogen derivatives*

(*a*). *1,2-Diiodotetrafluoroethane.* Reaction of $(CH_3)_5Rh(PF_3)_2$ with excess 1,2-diiodotetrafluoroethane in benzene at room temperature gave an 88% yield of $(CH_3)_5C_5Rh(PF_3)I_2$ identified by its IR spectrum and by elemental analyses. (Found: C, 21.0; H, 2.4; I, 42.1; P, 5.7%. Calcd. see Table 1.)

(*b*). *Allyl iodide.* Reaction of $(CH_3)_5C_5Rh(PF_3)_2$ with excess allyl iodide in benzene at room temperature gave a 77% yield of $(CH_3)_5C_5Rh(PF_3)I_2$ identified by its IR spectrum and by elemental analyses. (Found: C, 21.7; H, 2.6; P, 6.5%. Calcd. see Table 1.)

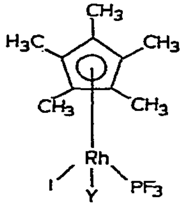
(*c*). *Bromine.* Reaction of $(CH_3)_5C_5Rh(PF_3)_2$ with excess bromine in benzene at room temperature for 32 h gave an 87% yield of the known[3] compound $[(CH_3)_5C_5RhBr_2]_2$ identified by comparison of its IR spectrum with that of an authentic sample. In particular, the strong ν(PF) frequencies in the 800–900 cm^{-1} range arising from coordinated PF_3 were absent.

DISCUSSION

The rhodium compound $(CH_3)_5C_5Rh(PF_3)_2$ (I) reacted with elemental iodine and with the perfluoroalkyl iodides with expulsion of one PF_3 ligand according to the following equation:

$$\underset{(I)}{(CH_3)_5C_5Rh(PF_3)_2} + YI \rightarrow \underset{(II)}{(CH_3)_5C_5Rh(PF_3)YI} + PF_3$$

Where Y = I, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}. This reaction is thus completely analogous to the corresponding reactions of iodine and the perfluoroalkyl iodides with the related carbonyl derivatives $R_5C_5M(CO)_2$ (R = H, M = Co[4-6] and Rh[5,7]; R = CH_3, M = Rh[8] and Ir[8,9]). No evidence for any ionic intermediates of the type $[(CH_3)_5C_5Rh(PF_3)_2Y]^+$ was observed in this reaction.



(II)

The spectroscopic properties of these new $(CH_3)_5C_5Rh(PF_3)YI$ derivatives (II) were in accord with the proposed structures. Their IR spectra (Table 2) exhibited two relatively strong bands at 891±8 and 873±3 cm^{-1} corresponding to the expected two ν(PF) frequencies of the coordinated trifluorophosphine. In addition, the IR spectra of the perfluoroalkyl derivatives of the type $(CH_3)_5C_5Rh(PF_3)R_fI$ [(II), Y = CF_3, C_2F_5, n-C_3F_7 and n-C_7F_{15}] exhibited bands in the 1300–900 cm^{-1} ν(CF) region similar to those found[9] for the corresponding $(CH_3)_5C_5Ir(CO)R_fI$ derivatives. The proton NMR spectra of the $(CH_3)_5C_5Rh(PF_3)YI$ derivatives [(II), Y = I, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}] exhibited a doublet around τ 8 corresponding to the fifteen

TABLE 2

IR SPECTRA OF (PENTAMETHYLCYCLOPENTADIENYL)RHODIUM–TRIFLUOROPHOSPHINE DERIVATIVES[a] (cm^{-1})

Compound	ν(PF)	ν(CF)	Other bands, 1300–700 cm^{-1}
$Me_5C_5Rh(PF_3)_2$	905 s, 836 s		
$Me_5C_5Rh(PF_3)I_2$	899m, 876 s		1026w, 1018w
$Me_5C_5Rh(PF_3)(CF_3)I$	883s, 870s	1069s, 1008s	1040w, 1022w
$Me_5C_5Rh(PF_3)(C_2F_5)I$	886s, 875s	1298m, 1192m, 1170m, 1052m, 1017m, 915s	900m, 734m, 725w
$Me_5C_5Rh(PF_3)(n\text{-}C_3F_7)I$	888s, 871s	1325m, 1215s, 1191s, 1164m, 1086m, 1041m, 1014m	908m, 805m, 723m
$Me_5C_5Rh(PF_3)(n\text{-}C_7F_{15})I$	883m, 870m	1235m, 1200m, 1185vw, 1150m, 1125vw, 1085vw, 1045w, 1022w	723w

[a] These IR spectra (1300–700 cm^{-1}) were taken in Nujol mulls and recorded on a Perkin–Elmer Model 621 spectrometer with grating optics.

TABLE 3

NMR SPECTRA OF (PENTAMETHYLCYCLOPENTADIENYL)RHODIUM–TRIFLUOROPHOSPHINE DERIVATIVES

Compound	Proton NMR[a]		Fluorine NMR[b]			
	τ (CH_3)	^4J (PH)	Φ(PF_3)	^1J(PF)	^2J(RhF)	Other[c]
$Me_5C_5Rh(PF_3)_2$	7.97	4.5	+10.8	1330	30	
$Me_5C_5Rh(PF_3)I_2$	7.82	8	+20.8	1374	17	
$Me_5C_5Rh(PF_3)(CF_3)I$	7.97	7	+24.7	1392	25	CF_3: Φ 1.6t (J 10 Hz.)
$Me_5C_5Rh(PF_3)(C_2F_5)I$	7.98	7	+22.5	1383	25	CF_2: AB pattern centered at Φ 68.8 [^2J(FF) 253 Hz, δ 11.6 ppm] CF_3: Φ 82.2
$Me_5C_5Rh(PF_3)(C_3F_7)I$	7.98	7	+21.7	1389	25	α-CF_2: $\Phi \sim 60$ β-CF_2: Φ 114.8d ($\sim$94 Hz separation) CF_3: Φ 79.3t (J 12 Hz)
$Me_5C_5Rh(PF_3)(C_7F_{15})I$	7.97	7	+22.2	1379	20	α-CF_2: $\Phi \sim 59$ β-CF_2: $\Phi \sim$ 111d ($\sim$120 Hz separation) γ-CF_2 and δ-CF_2: $\Phi \sim 122$ ε-CF_2: Φ 122.9 m ζ-CF_2: Φ 126.4 m CF_3: Φ 81.3t (J 10 Hz)

[a] Proton NMR spectra were taken at 100 MHz in CH_2Cl_2 solution and recorded on a Varian HA-100 spectrometer. Tetramethylsilane was used as an internal standard. [b] Fluorine NMR spectra were taken at 56.456 MHz in CH_2Cl_2 solution and recorded on a Perkin–Elmer Hitachi R-20 spectrometer. 1,2-Difluoro-1,1,2,2-tetrachloroethane (Φ 67.8) was used as an internal standard. [c] The following abbreviations were used: d = doublet, t = triplet, m = multiplet. Coupling constants are given in Hz.

equivalent protons of the pentamethylcyclopentadienyl ring. The splitting of this proton NMR resonance into a doublet (J 7 to 8 Hz) is assigned to the ^4J(PH) coupling rather than the apparently slightly less remote ^3J(RhH) coupling for the following reasons: (*a*) The compound $(CH_3)_5C_5Rh(PF_3)_2$ exhibits a triplet in accord with the presence of two phosphorus atoms for splitting; (*b*) The ^3J(RhH) coupling measured[8] in $(CH_3)_5C_5Rh(CO)_2$ is only 0.4 Hz. The fluorine NMR spectra of the $(CH_3)_5C_5Rh(PF_3)YI$ derivatives [(II), Y = I, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}] all exhibit a double doublet centered around Φ 20 to 25. The large splitting (1370 to 1390 Hz) of this double doublet arises from the ^1J(PF) coupling characteristic of phosphorus–fluorine compounds. The small splitting (~20 Hz) of this double doublet arises from the ^2J(RhF) coupling. In addition, the fluorine NMR spectra of the perfluoroalkyl derivatives $(CH_3)_5C_5Rh(PF_3)R_fI$ [(II), Y = CF_3, C_2F_5, and n-C_3F_7] exhibited resonances corresponding to the fluorine atoms of the perfluoroalkyl groups which had similar chemical shifts and fine structures to the fluorine NMR resonances observed[9] in the analogous perfluoroalkyl iridium derivatives of the type $(CH_3)_5C_5Ir(CO)R_fI$.

Reactions of the iridium compound $(CH_3)_5C_5Ir(CO)_2$ with allyl iodide and with 1,2-diiodotetrafluoroethane were found[9] to give ionic compounds containing the cations $[(CH_3)_5C_5Ir(CO)_2R]^+$ (R = CH_2=$CHCH_2$ or ICF_2CF_2). In attempts to prepare similar cationic derivatives of the type $[(CH_3)_5C_5Rh(PF_3)_2R]^+$ the corresponding reactions of $(CH_3)_5C_5Rh(PF_3)_2$ (I) with these halides were investigated. However, the reaction of $(CH_3)_5C_5Rh(PF_3)_2$ with an excess of either allyl iodide or 1,2-diiodotetrafluoroethane gave only the diiodide $(CH_3)_5C_5Rh(PF_3)I_2$. Thus in both of these cases the organic iodide acted only as an iodinating agent with complete release of the organic group attached to the iodine.

The mass spectra of several of the new compounds prepared in this work of the type $(CH_3)_5C_5Rh(PF_3)YI$ [(II), Y = I, C_2F_5, n-C_3F_7, etc.] were investigated using the normal conditions (chamber temperature 220°), However, in no cases were the molecular ions observed. Thus the three highest m/e ions in the mass spectrum of $(CH_3)_5C_5Rh(PF_3)I_2$ were $(CH_3)_5C_5RhI_2^+$, $(CH_3)_5C_5Rh(PF_3)I^+$, and $(CH_3)_5C_5RhI^+$. The mass spectra of the fluorocarbon derivatives $(CH_3)_5C_5Rh(PF_3)R_fI$ were considerably more complex. Ions clearly not derivable by fragmentation from the molecular ion were observed suggesting that pyrolytic decomposition was taking place in the mass spectrometer. A detailed study of the dependence of the mass spectra of these compounds on the sample and chamber temperatures is needed before their interpretation can be discussed in detail. The relative complexity of the mass spectra of the $(CH_3)_5C_5Rh(PF_3)YI$ derivatives prepared in this work contrasts with the relative simplicity of the mass spectra of the $(CH_3)_5C_5Ir(CO)YI$ compounds, at least in the higher *m/e* region[9].

In an attempt to prepare a dibromide $(CH_3)_5C_5Rh(PF_3)Br_2$ the reaction between $(CH_3)_5C_5Rh(PF_3)_2$ and bromine was investigated. However, this reaction led to the complete loss of the coordinated trifluorophosphine from the starting material resulting in the ultimate formation of the known $[(CH_3)_5C_5RhBr_2]_2$.

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