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REACTIONS INVOLVING TRANSITION METALS

XVII *. REACTION OF ORGANIC HALOGEN COMPOUNDS WITH $[Rh(CO)_2(PPh_3)_2]_2$ AND $[Rh(CO)(PPh_3)_2S]_2$ ($S = CH_2Cl_2$, THF)

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Summary

The complexes $[Rh(CO)_2(PPh_3)_2]_2$ and $[Rh(CO)(PPh_3)_2S]_2$ ($S = CH_2Cl_2$, THF) have been shown to react with $CXCl_3$ (X = Cl, H) to form $[RhCl(CO)(PPh_3)_2]$ with generation of both dichlorocarbene and trichloromethyl radical. Reaction of $[Rh(CO)(PPh_3)_2(THF)]_2$ with CF_3I, allyl- and benzyl-halides takes a different course giving organic coupling products and $[RhX(CO)(PPh_3)_2]$. The THF solvate complex also causes coupling of *gem*-dihalides, and dehalogenation of *vic*-dihalides to produce alkenes. Possible mechanisms for these reactions are discussed.

Introduction

Polyhalogenomethanes [1] and $PhHgCCl_3$ [2] have been shown to react with $[Co_2(CO)_8]$ in non-polar solvents to form $[ClCCo_3(CO)_9]$ in high yield. A key intermediate in these reactions appears to be the complex $[CCl_3Co(CO)_4]$, which can decompose either by a 1,2-chlorine shift generating dichlorocarbene and $[ClCo(CO)_4]$, or by homolysis of the carbon—cobalt bond giving $\dot{C}Cl_3$ radical. A similar breakdown of an intermediate $[CX_3Rh(CO)_2(PPh_3)_2]$ (X = Cl, Br) has also been proposed to explain the formation of carbene and radical species during the reactions of $Na[Rh(CO)_2(PPh_3)_2]$ with CX_4 and CCl_3COCl [3]. We now report some reactions of the dimer $[Rh(CO)_2(PPh_3)_2]_2$ and the solvates $[Rh(CO)(PPh_3)_2(S)]_2$ ($S = CH_2Cl_2$, THF) with polyhalogenomethanes, halogenoalkanes, *gem*- and *vic*-dihalogen compounds which appear to be related mechanistically to these other reactions of cobalt(I) and rhodium(I) complexes.

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[*] For part XVI see ref. 16.

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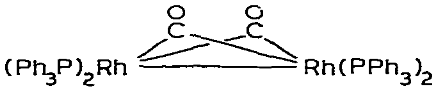
Results and discussion

A suspension of $[Rh(CO)_2(PPh_3)_2]_2$ [4,5] in tetrahydrofuran (THF) reacted with an excess of CCl_4 at room temperature under an atmosphere of CO to give $[RhCl(CO)(PPh_3)_2]$ in 67% yield. When this reaction was repeated in the presence of the carbene trap, cyclohexene, GLC analysis (3 m TXP column, 140°C) of the reaction mixture showed the presence of 7,7-dichloronorcarane, and the yield of $[RhCl(CO)(PPh_3)_2]$ was unaffected. A similar reaction carried out in the presence of a 1 : 1 mole mixture of methyl methacrylate and styrene gave a 1 : 1 copolymer resulting from free radical polymerisation [1—3,6] in addition to $[RhCl(CO)(PPh_3)_2]$ (49%). Polymer formation was completely inhibited by the presence of the radical scavenger, 1,1-diphenyl-2-picrylhydrazyl, but formation of $[RhCl(CO)(PPh_3)_2]$ was not prevented although the yield was reduced to 34%. Both $CHCl_3$ and CF_3CCl_3 reacted with a suspension of $[Rh(CO)_2(PPh_3)_2]_2$ in THF under similar conditions to give $[RhCl(CO)(PPh_3)_2]$ in 63% and 66% yields, respectively, but no reaction occurred with n-C_3F_7I even on refluxing for 2 days in light petroleum (b.p. 60—80°C).

A suspension of $[Rh(CO)_2(PPh_3)_2]_2$ in THF stirred under nitrogen at room temperature for 15 h gave an orange-red suspension of the solvate $[Rh(CO)(PPh_3)_2THF]_2$. The IR spectrum (mull, Nujol) showed bridging rhodium-carbonyl absorptions at 1768m and 1740vs cm^{-1}, which compare favourably with the bands at 1765w and 1739s cm^{-1} observed in the solid state spectrum of $[Rh(CO)(PPh_3)_2(CH_2Cl_2)]_2$ [7]. The presence of THF has been confirmed by elemental analysis, IR bands at 2850vw [ν(C—H)], 1060m, 596m [$\nu(CH_2—O—CH_2)$] and 906m [ν(C—C)] cm^{-1}, and signals in the ^1H NMR spectrum (CS_2 solution) at δ 2.64 (m, 2, β-CH_2) and 4.47 ppm (m, 2, α-CH_2). It is assumed that this compound has a similar structure (I) to that found for the solvates $[Rh(CO)(PPh_3)_2(S)]_2$ (S = CH_2Cl_2, EtOH) [8]. In these complexes it has been shown that there is no interaction between the solvent molecules and the rhodium atom, and each metal atom may be considered to be coordinatively unsaturated.



(I)

When a solution of $[Rh(CO)(PPh_3)_2(THF)]_2$ in benzene was stirred for 6 h at room temperature under nitrogen the IR spectrum changed until there was only a single strong band at 1965 cm^{-1} in the metal carbonyl region. This is presumably due to the formation of the solvent-free species $[Rh(CO)(PPh_3)_2]_2$, previously observed by Wilkinson [9], and thought to have only terminal carbonyl ligands and a rhodium—rhodium bond. Attempts to isolate this product by concentrating the solution and adding n-hexane gave an orange-red solid [ν(CO) 1960s cm^{-1}], but analysis indicated that it was slightly impure.

Both $[Rh(CO)(PPh_3)_2(CH_2Cl_2)]_2$ and $[Rh(CO)(PPh_3)_2(THF)]_2$ react with an equimolar amount of CCl_4 at room temperature under nitrogen to give $[RhCl(CO)(PPh_3)_2]$ in 52 and 64% yield, respectively [Table 1]. No rhodium starting material was recovered from these reactions, and the yield of [RhCl(CO)-

TABLE 1

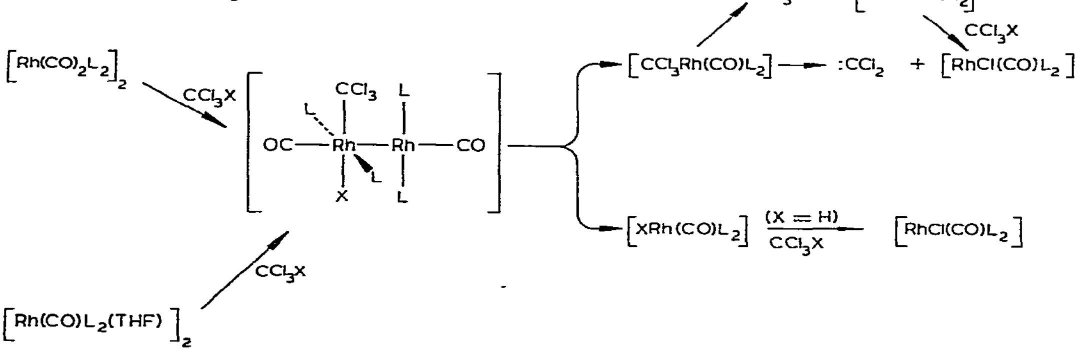
REACTIONS OF $[Rh(CO)(PPh_3)_2(THF)]_2$ WITH ORGANIC HALOGEN COMPOUNDS [a]

Reactant	Mole ratio	Time (h)	Products (Yield, %)
CCl_4	1 : 1	100	$RhCl(CO)(PPh_3)_2$ (64)
CCl_4	$\geqslant$1 : 2 [b]	4	$RhCl(CO)(PPh_3)_2$ (61)
$CHCl_3$	1 : 1	100	$RhCl(CO)(PPh_3)_2$ (29) [c]
$CHCl_3$	1 : 2 [b]	100	$RhCl(CO)(PPh_3)_2$ (67)
$CHCl_3$	$\geqslant$1 : 2 [b]	16	$RhCl(CO)(PPh_3)_2$ (64)
CF_3I	1 : 1	50	$RhI(CO)(PPh_3)_2$ (26), C_2F_6 (46) [d]
CF_3I	1 : 2 [b]	4	$RhI(CO)(PPh_3)_2$ (44), C_2F_6 (79)
$PhCH_2Br$	1 : 2 [b]	4	$RhBr(CO)(PPh_3)_2$ (40), $PhCH_2CH_2Ph$ (11)
$CH_2{=}CHCH_2I$	1 : 2 [b]	0.5	$RhI(CO)(PPh_3)_2$ (47), $CH_2{=}CHCH_2CH_2CH{=}CH_2$ (33)
$CH_2{=}CHCH_2Br$	1 : 2 [b]	1.0	$RhBr(CO)(PPh_3)_2$ (38), $CH_2{=}CHCH_2CH_2CH{=}CH_2$ (25)
$MeCH{=}CHCH_2Br$	1 : 2 [b]	1.0	$RhBr(CO)(PPh_3)_2$ (48), $MeCH{=}CHCH_2CH_2CH{=}CHMe$ (13)

[a] All reactions at 20°C. [b] 1 mole rhodium complex: 2 mole organic halogen compound. [c] $[Rh(CO)(PPh_3)_2(THF)]_2$ (38%) recovered. [d] $[Rh(CO)(PPh_3)_2(THF)]_2$ (43%) recovered.

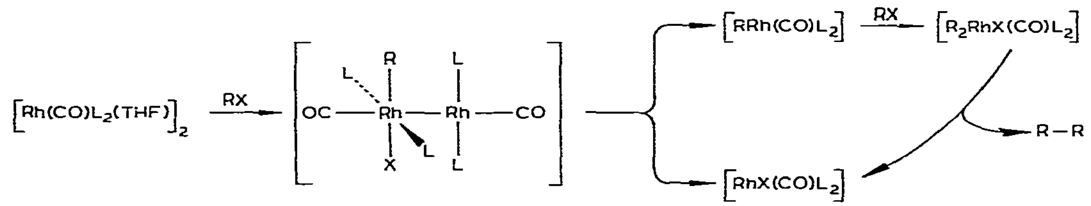
$(PPh_3)_2]$ was not improved by employing $\geqslant$2 molar excess of CCl_4 in the reaction with the THF solvate. Mechanistically, the reaction of $[Rh(CO)(PPh_3)_2(THF)]_2$ with CCl_4 is very similar to that of a suspension of $[Rh(CO)_2(PPh_3)_2]_2$ in THF, and probably involves the same intermediates. When the reaction with an excess of CCl_4 was carried out in the presence of cyclohexene the yield of $[RhCl(CO)(PPh_3)_2]$ (59%) was unaffected and 7,7-dichloronorcarane was detected among the reaction products. The use of a 1 : 1 mixture of methyl methacrylate and styrene in this reaction gave a 36% yield of a 1 : 1 copolymer together with $[RhCl(CO)(PPh_3)_2]$ (55%); this polymerisation reaction was completely inhibited by 1,1-diphenyl-2-picrylhydrazyl. Slightly different behaviour was observed with chloroform under similar conditions. Using a 1 : 1 mole ratio of rhodium complex : chloroform the yield of $[RhCl(CO)(PPh_3)_2]$ was only 29%, and unchanged starting material was recovered. The maximum yield of $[RhCl(CO)(PPh_3)_2]$ was obtained using a 2 : 1 mole excess of chloroform, and there was no significant improvement in the yield on further increasing the amount of chloroform. These observations can be rationalised by the reaction sequence outlined in Scheme 1. The first step is suggested to be oxidative addi-

SCHEME 1
(X = Cl or H; L = PPh₃)



tion of the halogenoalkane to one of the rhodium atoms of $[Rh(CO)_2(PPh_3)_2]_2$ or $[Rh(CO)(PPh_3)_2(THF)]_2$ with cleavage of the metal carbonyl bridges. This is followed by reductive elimination of $[RhY(CO)(PPh_3)_2]$ (Y = Cl, H) with formation of $[CCl_3Rh(CO)L_2]$, which can breakdown by homolysis of the carbon—rhodium bond to give $\dot{C}Cl_3$, and by a 1,2-chlorine shift to give CCl_2. When the substrate is CCl_4 one mole will convert both rhodium atoms of $[Rh(CO)(PPh_3)_2(THF)]_2$ into $[RhCl(CO)(PPh_3)_2]$. In contrast, the reactions of $CHCl_3$ require two moles for maximum conversion to $[RhCl(CO)(PPh_3)_2]$. The formation of dichlorocarbene in this reaction implies that one of the rhodium atoms of $[Rh(CO)(PPh_3)_2(THF)]_2$ is converted into the hydride $[RhH(CO)(PPh_3)_2]$ at some stage in the reaction sequence, but not necessarily as shown in the scheme if oxidative addition takes place in the sense Cl—$CHCl_2$. The extra mole of $CHCl_3$ is required to convert this hydride into $[RhCl(CO)(PPh_3)_2]$; a reaction which has been reported previously by Wilkinson [5]. The major organic products with CF_3I, benzylic- and allylic-halogen compounds arise by carbon—carbon coupling (Table 1), implying a change of mechanism. The isolation of octa-2,6-diene as the only organic product from 1-bromobut-2-ene is more consistent with coupling via a reductive-elimination reaction rather than radical combination (Scheme 2). When the reaction between allyl bromide and $[Rh(CO)(PPh_3)_2(THF)]$ was monitored by IR spectroscopy the spectra showed the rapid formation of $[RhBr(CO)(PPh_3)_2]$ [ν(CO) 1975 cm^{-1}] which remained throughout the reaction, and an absorption at 2036 cm^{-1} which increased in intensity with time and then decayed. This is consistent with the transitory formation of a rhodium(III) carbonyl intermediate as proposed in Scheme 2. A possible alternative pathway is a double oxidative addition of RX to $[Rh(CO)(PPh_3)_2(THF)]_2$ giving an intermediate $[(Ph_3P)_2(CO)RXRh]_2$, but this seems less likely and it is difficult to see how such an intermediate could break down to the observed products except by a complex homolytic route.

SCHEME 2
($L = PPh_3$)



At moderate temperatures a number of *gem*-dihalides, R_2CX_2, react with $[Rh(CO)(PPh_3)_2(THF)]_2$ to form the alkenes, $R_2C{=}CR_2$ (Table 2). A related reaction is known for $[Co_2(CO)_8]$, and Seyferth [10] has demonstrated the involvement of *vic*-dihalides, R_2CXCXR_2, probably produced by a radical coupling reaction. The possible intermediacy of carbenes, suggested by Coffey [11], was also considered, but rejected in favour of the radical mechanism. In the reactions with $[Rh(CO)(PPh_3)_2(THF)]_2$ both carbene and *vic*-dihalide intermediates appear to be involved in alkene formation.

When the reaction between $[Rh(CO)(PPh_3)_2(THF)]_2$ and Ph_2CCl_2 was conducted in the presence of an excess of 1,1-diphenylethene the product mixture was found to contain tetraphenylethene (26%), $[RhCl(CO)(PPh_3)_2]$ (63%), and

TABLE 2

REACTIONS OF $[Rh(CO)(PPh_3)_2(THF)]_2$ WITH *gem*- AND *vic*-DIHALIDES

Reactant	Mole Ratio	Time (h)	Temp. (°C)	Products (Yield, %)
Ph_2CCl_2	1 : 1	3.5	50	$RhCl(CO)(PPh_3)_2$ (70), $Ph_2C{=}CPh_2$ (54)
Ph_2CCl_2	1 : 2 [a]	3.5	60	$RhCl(CO)(PPh_3)_2$ (34), $RhCl_3(CO)(PPh_3)_2$ (13), $Ph_2C{=}CPh_2$ (36)
9,9-dichlorofluorene	1 : 1	3.5	55	$RhCl(CO)(PPh_3)_2$ (53), bisfluorenylidene (18)
9,9-dichlorofluorene	1 : 2 [a]	3.5	55	$RhCl(CO)(PPh_3)_2$ (32), $RhCl_3(CO)(PPh_3)_2$ (19), bisfluorenylidene (40)
$Br_2C(CO_2Me)_2$	1 : 1	2.3	50	$RhBr(CO)(PPh_3)_2$ (66), $(MeO_2C)_2C{=}C(CO_2Me)_2$ (19)
$Br_2C(CO_2Me)$	1 : 2 [a]	3.3	50	$RhBr(CO)(PPh_3)_2$ (20), $RhBr_3(CO)(PPh_3)_2$ (33), $(MeO_2C)_2C{=}C(CO_2Me)_2$ (63)
$Ph_2CClCClPh_2$	1 : 1	3.5	50	$RhCl(CO)(PPh_3)_2$ (68), $RhCl_3(CO)(PPh_3)_2$ (19), $Ph_2C{=}CPh_2$ (54)
9,9′-dichlorobisfluorenyl	1 : 1	3.5	50	$RhCl(CO)(PPh_3)_2$ (48), $RhCl_3(CO)(PPh_3)_2$ (15), bisfluorenylidene (24)

[a] 1 mole rhodium complex: 2 mole organic halogen compound.

1,1,2,2-tetraphenylcyclopropane (17%), presumably formed by trapping of diphenylcarbene. In a separate experiment the reaction between $[Rh(CO)(PPh_3)_2(THF)]_2$ and Ph_2CCl_2 (1 : 1 mole ratio) in THF at room temperature was quenched after 15 min by cooling to −78°C. Analysis of the product mixture by HPLC showed the presence of $Ph_2CClCClPh_2$, $Ph_2C{=}CPh_2$ and unchanged Ph_2CCl_2. It has also been shown that the *vic*-dihalides, $Ph_2CClCClPh_2$ and 9,9′-dichlorobisfluorenyl react with $[Rh(CO)(PPh_3)_2(THF)]_2$ (1 : 1 mole ratio) to give the corresponding alkenes under conditions comparable to those used for the *gem*-dihalides (Table 2). A noticeable feature of these reactions is that the *vic*-dihalides (1 : 1 mole ratio) and *gem*-dihalides (≥2 : 1 mole ratio) always produce $[RhCl_3(CO)(PPh_3)_2]$ in addition to $[RhCl(CO)(PPh_3)_2]$, but this rhodium(III) complex is never obtained when equimolar amounts of *gem*-dihalide and $[Rh(CO)(PPh_3)_2(THF)]_2$ are used. These observations can be accounted for by the reaction sequence outlined in Scheme 3. The essential reactions in this proposed scheme are the same as those postulated for the polyhalogenomethanes (Scheme 1), but with the added complication that the rhodium(I) complexes $[RhX(CO)(PPh_3)_2]$ can also react with the *gem*- and *vic*-dihalides to give alkene and $[RhX_3(CO)(PPh_3)_2]$. That this is feasible has been demonstrated by the separate set of experiments involving $[RhX(CO)(PPh_3)_2]$ (X = Cl, Br) and *gem*- and *vic*-dihalides listed in Table 3. Several of the intermediates proposed in this scheme could also decompose homolytically to give $R_2\dot{C}X$ radicals (and hence *vic*-dihalides). While we do not exclude this possibility, we do not believe that a radical pathway is of major importance in these reactions.

SCHEME 3
(L = PPh_3)

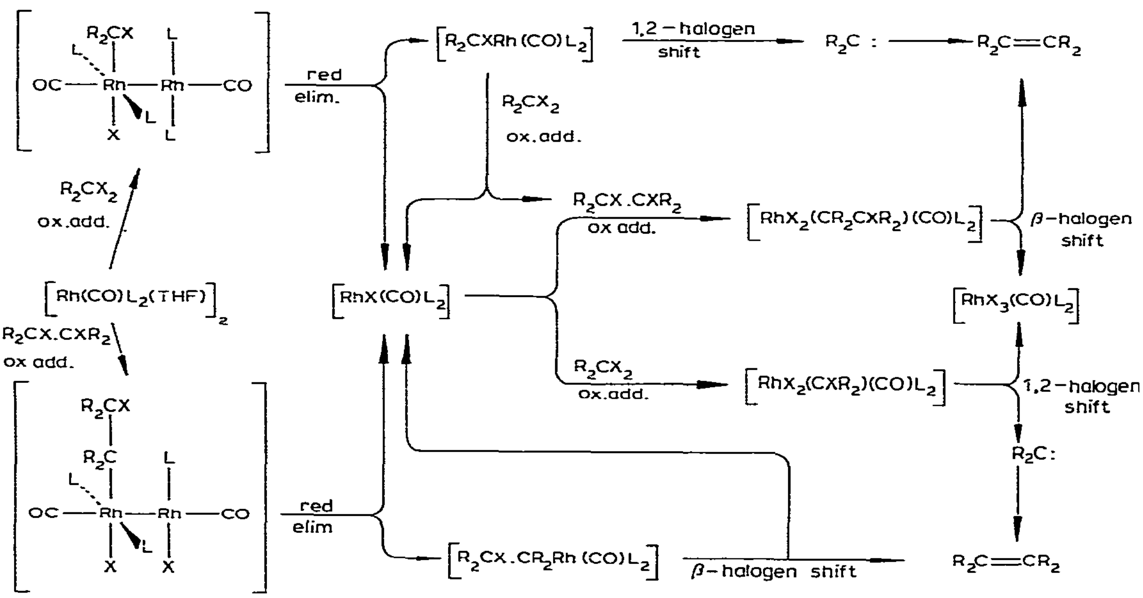


TABLE 3

REACTIONS OF [RhCl(CO)(PPh$_3$)$_2$] WITH *gem*- AND *vic*-DIHALIDES

Reactant	Mole ratio	Time (h)	Temp. (°C)	Products (Yield, %)
Ph$_2$CCl$_2$	1 : 1	4	55	RhCl$_3$(CO)(PPh$_3$)$_2$ (63), Ph$_2$C=CPh$_2$ (66)
Ph$_2$CClCClPh$_2$	1 : 1	20	60	RhCl$_3$(CO)(PPh$_3$)$_2$ (22), Ph$_2$C=CPh$_2$ (25)
9,9-dichlorofluorene	1 : 1	5	55	RhCl$_3$(CO)(PPh$_3$)$_2$ (42), bisfluorenylidene (17)
9,9'-dichlorobisfluorenyl	1 : 1	4.5	50	RhCl$_3$(CO)(PPh$_3$)$_2$ (58), bisfluorenylidene (42)
Br$_2$C(CO$_2$Me)$_2$ [a]	1 : 1	5.0	50	RhBr$_3$(CO)(PPh$_3$)$_2$ (39), (MeO$_2$C)$_2$C=C(CO$_2$Me (23)

[a] With [RhBr(CO)(PPh$_3$)$_2$].

Experimental

IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and ^{1}H NMR were determined on a Perkin-Elmer R32 instrument using tetramethylsilane as internal reference. GLC analyses were carried out on a Pye 104 gas chromatograph. The complexes [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ [4] and [Rh(CO)(PPh$_3$)$_2$-(CH$_2$Cl$_2$)]$_2$ [5] were prepared by previously reported procedures, and all other reagents were commercial samples. Except where stated all reactions were carried out under an atmosphere of dry nitrogen, and all solvents were thoroughly dried and purified by standard procedures.

Preparation of [Rh(CO)(PPh$_3$)$_2$(THF)]$_2$

A yellow suspension of [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ (1.80 g, 1.32 mmol) in THF (60 cm^3) stirred for 15 h at room temperature gave a red suspension. The volume of solvent was reduced to 10 cm^3 in a fast stream of nitrogen, and the product was filtered, washed with THF (3 × 30 cm^3) and dried in vacuo to give [Rh(CO)-(PPh$_3$)$_2$(THF)]$_2$ (1.46 g, 0.74 mmol, 56%) m.p. 110—114°C with decomp. Anal. Found: C, 67.2; H, 5.2. $C_{82}H_{76}O_4P_4Rh_2$ calcd.: C, 67.6; H, 5.2%.

Attempted preparation of [Rh(CO)(PPh$_3$)$_2$]$_2$

A solution of [Rh(CO)(PPh$_3$)$_2$(THF)]$_2$ (0.55 g, 0.38 mmol) in benzene (60 cm^3) was stirred for 6 h at room temperature, and the solution was then concentrated to give a red oil from which a red solid was obtained on addition of n-hexane. Attempts to recrystallize the solid or purify it by chromatography were unsuccessful. Anal. Found: C, 66.2; H, 4.6. $C_{37}H_{30}OP_2Rh$ calcd.: C, 67.8; H, 4.6%.

Reactions of [Rh(CO)$_2$(PPh$_3$)$_2$]$_2$ with halogenoalkanes

(a) Chloroform. A suspension of the rhodium complex (1.80 g, 1.32 mmol) in THF (60 cm^3) and chloroform (2.60 g, 20.0 mmol) was stirred at room temperature under an atmosphere of carbon monoxide for 23 h. Chromatography (Florisil, CHCl$_3$ eluent) of the product mixture gave [RhCl(CO)(PPh$_3$)$_2$] (1.15 g, 1.66 mmol, 63%).

(b) Carbon tetrachloride. Under similar conditions the rhodium complex (1.80 g, 1.32 mmol) and carbon tetrachloride (8.14 g, 52.8 mmol) after 5 h at

room temperature gave [$RhCl(CO)(PPh_3)_2$] (1.23 g, 1.78 mmol, 67%).

(c) 1,1,1-Trichloro-2,2,2-trifluoroethane. A suspension of the rhodium complex (0.90 g, 0.66 mmol) in THF (40 cm^3) and 1,1,1-trichloro-2,2,2-trifluoroethane (1.58 g, 8.40 mmol) was stirred at room temperature under carbon monoxide for 16 h. Chromatography of the product gave [$RhCl(CO)(PPh_3)_2$] (0.60 g, 0.87 mmol, 66%).

Reactions of [$Rh(CO)(PPh_3)_2(THF)]_2$ with organic halogen compounds

In a typical experiment a suspension of the rhodium complex (0.96 g, 0.66 mmol) in THF (30 cm^3) and the organic halogen compound (0.66 mmol or 1.32 mmol) sealed in vacuo in a Pyrex reaction tube (70 cm^3 capacity) was either stirred or shaken for several hours at room temperature. The solvent and any volatile products were removed under vacuum and collected in a trap cooled at —196°C; this was then analysed by GLC. The residue was chromatographed using hexane eluent to elute any hydrocarbon products, and then either benzene or chloroform eluent to elute the halogenocarbonyl-bis(triphenylphosphine)rhodium(I) complex, which was usually recrystallised from a mixture of either chloroform and ethanol or benzene and methanol. The results of individual experiments are given in Table 1.

Reactions of [$Rh(CO)(PPh_3)_2(THF)]_2$ with gem- and vic-dihalides

Typical procedures only are given for each of the halogen compounds.

(a) Dichlorodiphenylmethane. A solution of dichlorodiphenylmethane (0.63 g, 2.65 mmol) in THF (10 cm^3) was added to a suspension of the rhodium complex (1.92 g, 1.32 mmol) in the same solvent and the mixture was stirred at 60°C for 3 h to give a yellow precipitate. The solvent was removed and the residue was chromatographed (alumina-grade III, hexane eluent) to give triphenylphosphine (0.19 g), followed by 1,1,2,2-tetraphenylethene (0.16 g, 0.48 mmol, 36%) m.p. 223—224°C (lit. [12] m.p. 223—224°C). Anal. Found: C, 94.3; H, 6.3. $C_{26}H_{20}$ calcd.: C, 94.0; H, 6.0%. Final elution with chloroform gave [$RhCl(CO)(PPh_3)_2$] (0.62 g, 0.90 mmol, 34%).

(b) 1,2-Dichloro-1,1,2,2-tetraphenylethane. Reaction between the rhodium complex (0.98 g, 0.67 mmol), and 1,1-dichloro-1,1,2,2-tetraphenylethane (0.27 g, 0.67 mmol) in THF (50 cm^3) at 50°C for 9 h, followed by removal of the solvent, gave an orange-yellow solid. This was extracted with ethanol (5 × 50 cm^3) to give an extract containing 1,1,2,2-tetraphenylethene (0.12 g, 0.36 mmol, 54%). The yellow solid residue, which was insoluble in ethanol, was extracted with THF (5 × 20 cm^3) to give a yellow solid extract, which was recrystallised from a chloroform/hexane mixture to give [$RhCl_3(CO)(PPh_3)$] (0.19 g, 0.25 mmol, 19%), m.p. 189—193°C decomp. (lit. [13] 190—195°C decomp.) which was filtered off. The filtrate was concentrated to give a yellow solid which was fractionally recrystallized from a benzene/methanol mixture to give [$RhCl(CO)(PPh_3)_2$] (0.63 g, 0.91 mmol, 68%).

(c) 9,9,-Dichlorofluorene. A suspension of the rhodium complex (1.92 g, 1.32 mmol) and 9,9-dichlorofluorene (0.31 g, 1.32 mmol) in THF (50 cm^3) heated at 55°C for 3.5 h gave an orange solution. Removal of the solvent and extraction with light petroleum (b.p. 40—60°C) gave orange crystals of bisfluorenylidene (40 mg, 0.12 mmol, 18%) m.p. 188—190°C (lit. [14] m.p.

186—187°C). Anal. Found: C, 95.1; H, 4.7. $C_{26}H_{16}$ calcd.: C, 95.2; H, 4.8%. The extraction residue was [$RhCl(CO)(PPh_3)_2$] (0.96 g, 1.39 mmol, 53%).

(d) 9,9′-Dichlorobisfluorenyl. Concentration of the reaction mixture produced on heating the rhodium complex (1.13 g, 0.78 mmol) and 9,9′-dichlorobisfluorenyl (0.31 g, 0.78 mmol) in THF for 8 h at 50°C gave an orange-yellow solid. This was extracted with hexane (5 × 50 cm^3) to give bisfluorenylidene (62 mg, 0.19 mmol, 24%), and the yellow solid residue was extracted with benzene to give [$RhCl(CO)(PPh_3)_2$] (0.52 g, 0.75 mmol, 48%). The benzene-insoluble residue was chromatographed (alumina-grade III, $CHCl_3$ eluent) to give [$RhCl_3(CO)(PPh_3)_2$] (0.18 g, 0.24 mmol, 15%).

(e) Dimethyl dibromomalonate. The rhodium complex (0.87 g, 0.60 mmol) and dimethyl dibromomalonate (0.18 g, 0.62 mmol) in THF (50 cm^3) was heated at 50°C for 2.25 h, and gave a brown-yellow semi-solid after removal of the solvent. Extraction with hexane gave colourless crystals of tetracarbomethoxyethene (15 mg, 0.06 mmol, 19%) m.p. 118—120°C (lit. [15] m.p. 119—120°C), which were recrystallised from a mixture of dichloromethane/ethanol. The extraction residue was chromatographed (chloroform eluent) to give [$RhBr(CO)(PPh_3)_2$] (0.58 g, 0.79 mmol, 66%).

Reactions of [$RhCl(CO)(PPh_3)_2$] with geminal- and vicinal-dihalides

These reactions and the work-up procedures were carried out in a similar manner to those described for [$Rh(CO)(PPh_3)_2(THF)$]$_2$. The conditions employed and results of individual experiments are given in Table 3.

Acknowledgement

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References

1 B.L. Booth, G.C. Casey and R.N. Haszeldine, J. Chem. Soc. Dalton, (1975) 1850.
2 B.L. Booth, G.C. Casey and R.N. Haszeldine, J. Chem. Soc. Dalton, (1980) 403.
3 B.L. Booth, G.C. Casey and R.N. Haszeldine, J. Organometal. Chem., 219 (1981) 401.
4 B.L. Booth, M.J. Else, R. Fields and R.N. Haszeldine, J. Organometal. Chem., 27 (1971) 119.
5 D. Evans, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1968) 2660.
6 G. Henrici-Olivé and S. Olivé, J. Organometal. Chem., 52 (1973) C49; C. Walling, E.R. Brigg, W. Cummings, and F.R. Mayo, J. Amer. Chem. Soc., 72 (1950) 48.
7 G. Yagupsky, C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 1392.
8 P. Singh, C.B. Dammann and D.J. Hodgson, Inorg. Chem., 12 (1973) 1335.
9 M. Yagupsky, C.K. Brown, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1970) 937.
10 M.D. Miller and D. Seyferth, J. Organometal. Chem., 38 (1972) 373.
11 C.E. Coffey, J. Amer. Chem. Soc., 83 (1961) 1623.
12 R.E. Buckles and G.M. Matlack, Org. Synth., 31 (1951) 104.
13 L. Vallerino, J. Inorg. Nucl. Chem., 8 (1958) 288.
14 J. Schmidt and H. Wagner, Ber., 43 (1910) 1796.
15 B.B. Corson, R.K. Hazen and J.S. Thomas, J. Amer. Chem. Soc., 50 (1928) 913.
16 B.L. Booth, R.N. Haszeldine, and R.G.G. Holmes, J. Chem. Soc., Dalton, submitted for publication.