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METAL TO LIGAND GROUP TRANSFER REACTIONS

II* REACTIONS OF SOME π-ALLYLRHODIUM(I) COMPLEXES WITH TRIFLUOROACETIC ACID AND ALKYL, ACYL AND TRIMETHYLTIN HALIDES

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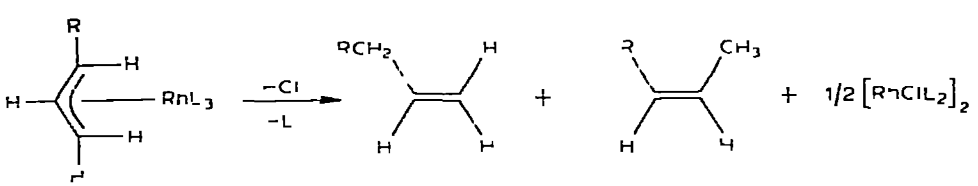
Summary

$Rh(\pi\text{-}C_3H_5)(PF_3)_3$ (I), reacts with trifluoroacetic acid to form propene and $[Rh(CF_3COO)(PF_3)_2]_2$ (II) I reacts with t-butyl bromide to give $[RhBr(PF_3)_2]_2$ and a mixture of propene and 2-methyl 1-propene and with n propyl bromide to give propene and $[RhBr(PF_3)_2]_2$ $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ (III), and t-butyl bromide yield propene and 2 methyl-1 propene In these reactions a mechanism involving β-hydrogen abstraction and hydrogen migration via the metal to carbon is proposed When III reacts with Me_3SnCl the Me_3Sn— moiety migrates intact to the π-allyl group I reacts with acetyl chloride to give propene, $[RhCl(PF_3)_2]_2$ and the carbonyl rhodium complex $Rh_2Cl_2(PF_3)_3(CO)$ II does not apparently undergo phosphine ligand exchange unlike the analogous halogeno bridged dimers

Introduction

We have recently discussed the factors affecting olefin formation in reactions of hydrogen halides with various π-allylic complexes of cobalt(I) and rhodium(I) [1,2], e g ,



(L = PF_3)

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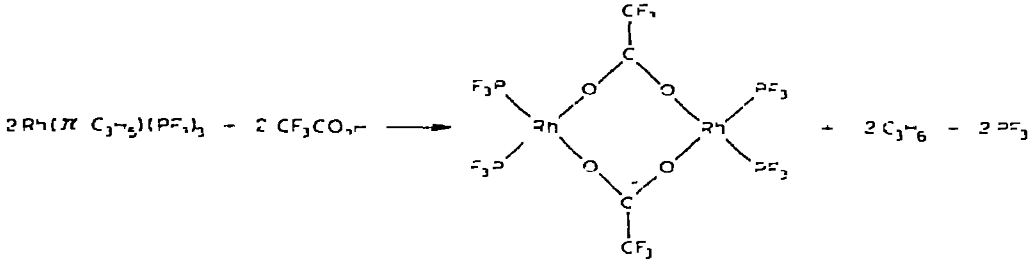
* For Part I see ref. 1

In one case an intermediate π allylic rhodium(III) hydride [formed by an initial oxidative addition of the HCl to the rhodium(I) complex] was characterised at low temperature by NMR spectroscopy [1]

We have now extended this work to the study of reactions of some π allylrhodium(I) complexes with trifluoroacetic acid and some alkyl, acyl and trimethyl-tin halides

Results and discussion

Rh(π C_3H_5)$(PF_3)_3$ (I) readily reacts with trifluoroacetic acid at 60 °C producing propene, trifluorophosphine and the new dimeric complex, di μ-(trifluoroacetato)tetrakis(trifluorophosphine)dirhodium, $[Rh(CF_3COO)(PF_3)_2]_2$ (II) This magenta crystalline sublimable complex was also made from the chloro-dimer $[RhCl(PF_3)_2]_2$ [3,4], by treatment with silver trifluoroacetate



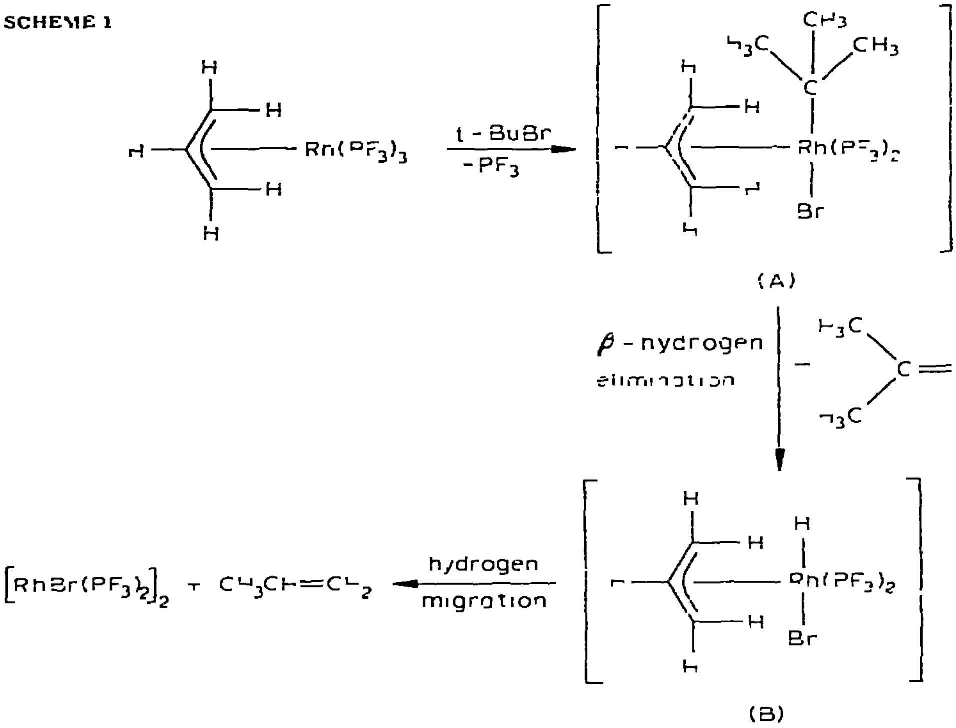
(II)

I reacts with t-butyl bromide at room temperature to give $[RhBr(PF_3)_2]_2$, trifluorophosphine and roughly equimolar amounts of propene and 2 methyl 1-propene As the reaction proceeds $(CH_3)_2CHBr$ is formed by addition of HBr to propene A similar mixture of propene and 2 methyl 1 propene is also obtained when Rh(π C_3H_5)$(PPh_3)_2$ (III), and t-butyl bromide are heated at 110 °C Although I does not react with n propyl bromide at room temperature, the reaction at 120 °C gives propene as the only olefinic product, together with $[RhBr(PF_3)_2]_2$ and free PF_3

In the above reactions the first step probably involves an oxidative addition reaction analogous to that suggested previously for the hydrogen halide reactions to give an alkyl π-allylhalogenorhodium(III) intermediate (A) which then could undergo β-hydrogen elimination to form B and an olefin Subsequent proton migration from the metal atom of the π-allylhydridorhodium complex (B) to the coordinated π-allylic group would then lead to the formation of the second olefin molecule These steps are summarised in Scheme 1 for the reaction of I with t BuBr

I also reacts with acetyl chloride to give propene and a mixture of $[RhCl(PF_3)_2]_2$ and $[Rh_2Cl_2(PF_3)_3(CO)]$ [3] Acyl halides are known to add oxidatively to d^8 transition metal complexes and the products are susceptible to decarbonylation [5], [e g, $IrCl(PPh_3)_3$ has been shown to react with acyl chlorides to give products containing alkyl and carbon monoxide ligands] [6] It would appear that the observation of propene in the reaction of I with CH_3COCl might possibly arise by hydrogen migration from some intermediate methyl—rhodium spe-

SCHEME 1



cies formed from the intermediate acylrhodium complex. Elimination of α-hydrogen is not as yet a well established process in transition metal—alkyl systems, but recently Green et al. [7] have presented evidence for the reversible α elimination of hydrogen from a tungsten—methyl compound. So far we have not been able to identify the other hydrocarbon products resulting from the possible α elimination process and further studies are in progress.

It is interesting to note in connection with these results that the thermal decomposition of the methyl iodide adduct of an alkenylrhodium(I) complex has been reported to lead to a specific methyl group migration from the metal to the organic moiety affording an isomeric mixture of olefins [8].

Complex III only reacts slowly with Me_3SnCl, but in this case the trimethylstannyl group migrates intact from the metal to the alkyl group, the presence of the tin atom as expected suppressing β-hydrogen elimination.

$$Rh(\pi\text{-}C_3H_5)(PPh_3)_2 + Me_3SnCl \rightarrow \tfrac{1}{2}\,[RhCl(PPh_3)_2]_2 + Me_3SnC_3H_5$$

Interestingly Abel et al. [9] have used the reverse of the above type of reaction to synthesise π-allyldicarbonylrhodium(I) complexes from trimethylallyltin and $[RhCl(CO)_2]_2$.

Finally we note an interesting difference in the intermolecular trifluorophosphine ligand exchange behaviour for both the acetato-bridged dimers $[Rh(RCOO)(PF_3)_2]_2$ (II) ($R = CH_3, CF_3$)*, compared to that previously re-

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* The acetato-complex was made from $[RhCl(PF_3)_2]_2$ and silver acetate (see Experimental).

TABLE 1

NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SOME DIMERIC TRIFLUOROPHOSPHINE RHODIUM(I) COMPLEXES

Complex	$\phi(PF_3)^a$	$^1J(PF)$ + $^3J(PF)^{b\ c}$	$^2J(PP)^c$	$^2J(RhF)^c$	$^1J(RhP)^c$	Solvent	Reference
$[Rh(CF_3COO)(PF_3)_2]_2{}^d$	18 1	1306	100 0	31 0	350 ± 5	CCl_3F	This work
$[Rh(CH_3COO)(PF_3)_3]_2{}^e$	17 2	1308	103 0	31 0		CCl_3F	This work
$[RhCl(PF_3)_2]_2$	17 0	1309	63 5	31 5		C_6H_6	4 11
$[RhBr(PF_3)_2]_2$	15 9	1309		31 5		C_6H_6	11
$[RhI(PF_3)_2]_2$	14 2	1316		31 5		C_6H_6	11
$[RhCl(PF_3)_2]$ + PF_3	18 8 - 0 9	1354 24				C_6H_6	4 11

^{a}In ppm relative to CCl_3F ^{b} $^1J(PF)$ and $^3J(PF)$ are of opposite sign ^{c}Coupling constants are in Hz $^d\phi(CF_3)$ = 74 5 ppm (singlet) relative to CCl_3F $^e CH_3 = \tau$ 8 0 (singlet)

ported [3,4] for the halogeno-complexes $[RhX(PF_3)_2]_2$ (X = Cl, Br, I)

The ^{19}F NMR spectrum of II shows the expected mirror image pattern of lines expected for the X part of an $[X_3A]_2$ nuclear spin system [10] (A = phosphorus, X = fluorine) with further doubling due to the presence of the ^{103}Rh nucleus (I = ½, 100% abundant) In the trifluoromethyl complex the CF_3 resonance occurs as a sharp singlet Chemical shift and coupling constants are listed in Table 1, together with related data for $[RhX(PF_3)_2]_2$ (X = Cl, Br, I) The values of $^2J(PRhP')$ for both acetato-complexes are larger than the value previously reported for X = Cl, which presumably is related to the greater electronegativity of the oxygen atoms in the acetato bridges

When a small amount of PF_3 is sealed off with the acetato bridged dimers no collapse of the pattern of lines in the ^{19}F NMR spectrum is observed This contrasts with the behaviour of the analogous halogeno-bridged dimers $[RhX(PF_3)_2]_2$ which undergo a rapid intermolecular ligand exchange process with free PF_3 causing immediate loss of coupling between the rhodium and fluorine nuclei [3,4]

The difference in the intermolecular phosphine ligand exchange may possibly be due to blocking of the vacant coordination site in these roughly square planar rhodium(I) systems by the larger bridging acetato ligands It is interesting to note that the related chloro and acetato-palladium complexes, $[PdX(\pi\ C_3H_5)]_2$, (X = Cl, CH_3COO) have markedly different structures [12]

Experimental

Reactions were carried out and complexes handled in vacuo or under an atmosphere of dry nitrogen gas Solvents were dried and freshly distilled before use $Rh(\pi\ C_3H_5)(PF_3)_3$ was made either from $Rh(\pi\ C_3H_5)_3$, $RhH(PF_3)_4$, or $KRh(PF_3)_4$ as described elsewhere [13] $Rh(\pi\text{-}C_3H_5)(PPh_3)_2$ was made from $Rh(\pi\text{-}C_3H_5)_3$ by the method of Powell and Shaw [14]

^1H NMR spectra were recorded on either a Varian HA100 spectrometer operating at 100 MHz, or a Varian T60 at 60 MHz and ^{19}F NMR spectra recorded at 94 1 MHz Elemental analyses were carried out by Mrs A E Olney of this department

Reaction between $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ (I) and trifluoroacetic acid

A mixture of $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ (0 384 g, 0 941 mmol) and trifluoroacetic acid (0 108 g, 0 938 mmol) in hexane (4 ml) was heated in vacuo at 60 °C for 2 h Fractionation of the volatile products in the vacuum line afforded PF_3 and propene The dark red solid residue was extracted under dinitrogen with n-pentane (4 × 10 ml) and after concentration cooling the solution to —78 °C gave magenta crystals of di μ (trifluoroacetato)tetrakis(trifluorophosphine)dirhodium(I), $[Rh(CF_3COO)(PF_3)_2]_2$, (0 180 g, 0 228 mmol, 48%) which was identical to a sample made from $[RhCl(PF_3)_2]_2$ with silver trifluoroacetate (see below)

Preparation of di-μ-acetatotetrakis(trifluorophosphine)dirhodium(I)

A large excess of silver acetate was added to a solution of $[RhCl(PF_3)_2]_2$ (0 110 g, 0 175 mmol) in ether (5 ml) under nitrogen gas and the mixture stirred at room temperature for 1 h After removal of the ether under reduced pressure sublimation of the brown solid residue in vacuo at 80 °C gave red-brown crystals of $[Rh(CH_3COO)(PF_3)_2]_2$ (0 098 g, 0 145 mmol) 82 9%, m p 126 128 °C (Found C, 7 1, H, 0 9, F, 33 5, P, 18 1 $C_2H_3F_6O_2P_2Rh$ calcd C, 7 11, H, 0 89, F, 33 73, P, 18 33%) Infrared spectrum 2950(sh), 2920w, 2850vw, 1710w, 1550s, 1425m, 1351m, 1050w 1030w, 948s, 925(sh), 915s, 910(sh), 890(sh), 875vs, 678w, 555s, 545s, 530s cm^{-1} (hexachlorobutadiene and Nujol mulls and pentane solution) The mass spectrum showed peaks assignable to both the parent dimeric ion $Rh_2(CH_3COO)_2(PF_3)_4$ and to the ions $Rh_2(CH_3COO)_2(PF_3)_x^+$ (x = 0, 1, 2, 3) indicating a stepwise loss of trifluorophosphine

Preparation of di μ (trifluoroacetato)tetrakis(trifluorophosphine)dirhodium(I)

In a similar way to the above a large excess of silver trifluoroacetate reacted with $[RhCl(PF_3)_2]_2$ (0 100 g, 0 159 mmol) in ether to give after sublimation magenta crystals of $[Rh(CF_3COO)(PF_3)_2]_2$ (0 097 g, 0 123 mmol), 77 4%, m p 123 125 °C (Found C, 6 2, H, 0 0, F, 43 3, P, 16 0 $C_2F_9O_2P_2Rh$ calcd C, 6 09, H, 0 00, F, 43 41, P, 15 72%) Infrared spectrum 1670s, 1640s, 1200s, 1175(sh), 1135s, 940s, 920(sh), 912vs, 905(sh), 870vs, 803w, 730m, 720m, 555m, 548s, 530(sh), 522 cm^{-1} (Nujol mull) The parent ion for the *dimer* was observed in the mass spectrum

Reaction between I and t butyl bromide

A mixture of complex I (0 075 g, 0 183 mmol) and t-butyl bromide (0 033 g, 0 241 mmol) in CCl_3F were sealed off in vacuo and the reaction which was monitored by ^{19}F and ^{1}H NMR spectroscopy was complete after 7 days The ^{1}H NMR spectrum showed resonances assignable to roughly equimolar amounts of propene and 2-methyl-1-propene while the ^{19}F NMR spectrum consisted of a widely spaced sharp doublet (ϕ_F = 17 0 ppm, $^{1}J(PF)$ = 1367 Hz) characteristic of $[RhBr(PF_3)_2]_2$ undergoing intermolecular exchange with trifluorophosphine

In a separate experiment a mixture of I (0 150 g, 0 368 mmol) and an excess of t butyl bromide kept at room temperature for 13 days gave the volatile, red-brown solid $[RhBr(PF_3)_2]_2$ (0 090 g, 0 125 mmol), 68%, m p 60 62 °C, whose infrared spectrum was identical with that previously reported [3]

Reaction between I and n propyl bromide

Complex I (0 069 g, 0 169 mmol) and n propyl bromide (0 018 g, 0 146 mmol) were sealed with CCl_3F in vacuo in an NMR tube On heating the mixture at 120 °C a slow reaction took place as evidenced by the appearance of propene (identified by its ^1H NMR spectrum) and $[RhBr(PF_3)_2]_2$ (^{19}F NMR spectrum δ_F = 18 8 ppm, $^1J(PF)$ = 1357 Hz expected for the bromo-dimer undergoing intermolecular ligand exchange with PF_3)

Reaction between I and acetyl chloride

A mixture of complex I (0 122 g, 0 299 mmol) and acetyl chloride (carefully fractionated to remove traces of HCl) (0 023 g, 0 293 mmol) in CCl_3F was heated at 100 °C The reaction was complete after 25 h and the ^{19}F NMR spectrum of the products consisted of a sharp doublet (δ_F = 19 3 ppm, $^1J(PF)$ = 1347 Hz) The ^1H NMR spectrum showed resonances assignable to propene together with a broad unassigned resonance at τ = 7 7 ppm Removal of the volatiles under reduced pressure gave a red crystalline solid, m p 60 °C, whose infrared spectrum showed bands at 2060s, 935(sh), 918(sh), 902(sh), 870s, 830m cm^{-1} which are similar to those reported for a mixture of $[RhCl(PF_3)_2]_2$ and $Rh_2Cl_2(CO)(PF_3)_3$ [3]

Reactions of II with t-BuBr and Me_3SnCl

These reactions were carried out on samples in sealed NMR tubes and the course of the reaction monitored by ^1H NMR spectroscopy

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