Complexes of the Platinum Metals. Part 30.[1] Fragmentation Reactions of Rhodium and Iridium Trichloro- and Tribromo-acetates

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The nitrosyl complexes $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) react readily with trichloroacetic acid in acetone solution at ambient temperature to afford the dichloro-complexes $[MCl_2(NO)(PPh_3)_2]$ in excellent yield. The rhodium-based reaction performed at *ca.* 0 °C and quickly worked-up affords the carboxylate complex $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ which is stable in pure acetone, but rapidly converts to the dichloride $[RhCl_2(NO)(PPh_3)_2]$ when free trichloroacetic acid *and* triphenylphosphine are introduced to the solution. The complexes $[MCl(CO)(PPh_3)_2]$, $[MH(CO)(PPh_3)_3]$, *mer*-$[IrH_3(PPh_3)_3]$, and $[RhCl(PPh_3)_3]$ also react with trichloroacetic acid to form trichloroacetates which undergo similar ligand fragmentation reactions. Reaction pathways involving formation of CCl_3^-, Cl^-, $:CCl_2$, and CO_2 fragments are outlined; hydrolysis of dichlorocarbene affords carbonyl ligands. Similar reactions have been observed with tribromoacetic acid.

The decarboxylation of carboxylic acids, an important procedure in synthetic organic chemistry[2] and a key step in many biochemical processes,[3] has been the subject of numerous kinetic and mechanistic studies in the past 100 years.[4] The closely related process of carbon dioxide extrusion from metal carboxylate complexes, first observed by Pesci[5] in 1901 while attempting to mercurate phthalic acid, has subsequently developed into a powerful method for the synthesis of organometallic derivatives of the *p*-block elements,[6] notably Hg^{II},[6,7,8] Tl^{III},[6] Sn^{IV},[7] and Pb^{IV}.[7] More recently the same technique has been applied to convert carboxylate complexes of the d^{10} coinage metal ions Cu^{I},[9–11] Ag^{I},[12] and Au^{I}[13] into the corresponding organometallic derivatives. Finally, certain polyhalobenzoate complexes containing the d^8 transition metal ions Rh^{I},[14,15] Ni^{II},[16] Pd^{II},[17] and Pt^{II}[15,18] undergo carbon dioxide extrusion in organic media, notably pyridine, to yield polyhalophenyl derivatives. Fragmentation of trihaloacetic acids CX_3CO_2H (X = Cl or Br), a reaction of particular interest in the present context, was first reported by Silberstein[19] in 1884. The reaction is highly solvent dependent, proceeding particularly readily in the presence of dimethyl sulphoxide,[20,21] and is generally accepted to involve decomposition of $CX_3CO_2^-$ anions to yield CO_2 and CX_3^- anions. The latter products can then abstract a proton to yield 'haloforms', CHX_3, or lose halide anions to generate dihalocarbenes. These reactions have found application in organic chemistry as routes to highly reactive trihalomethyl and dihalocarbene intermediates.[2] Fragmentation reactions of trihaloacetate ligands in transition metal complexes have attracted relatively little attention to date. However, two pioneering studies clearly indicate scope for work in this area. In the first of these the treatment of $[IrCl(CO)(PPh_3)_2]$ with NaO_2CCClF_2 afforded $[IrCl(CO)(CHF_2)(O_2CCClF_2)(PPh_3)_2]$ which, on thermal decomposition, gave $[IrCl_2(CO)(CHF_2)(PPh_3)_2]$ in quantitative yield.[22–24] In the second, $[WH_2(\eta\text{-}C_5H_5)_2]$ was found to react with NaO_2CCCl_3 in glyme ($MeOCH_2CH_2OMe$) to form $[WH(CHCl_2)(\eta\text{-}C_5H_5)_2]$.[25] Moreover, in a recent study[26,27] trichloromethyl ligands, generated from $Hg(CCl_3)_2$, have been shown to fragment into Cl^- and $:CCl_2$ moieties, and to serve as precursors for a range of platinum metal dichlorocarbene complexes.

Encouraged by these reports, we have extended our earlier work on platinum metal carboxylate[28] and perfluorocarboxylate[29] complexes to include trichloro- and tribromo-acetates and, in so doing, have uncovered an extensive range of very facile carboxylate fragmentation reactions. In this paper we describe results obtained with some rhodium and iridium trihaloacetate systems. A preliminary report on this work has been published elsewhere.[30]

Experimental

Triphenylphosphine complexes of rhodium and iridium were prepared by standard literature methods.[31] Perhalocarboxylic

Table 1. Melting points, analytical,[a] and spectroscopic[b] data

Complex	M.p.(°C)	Analysis (%) C	H	N	ν(NO)/ cm^{-1}	$\nu(OCO)_{asym}$/ cm^{-1}	δ(P)/p.p.m.	$^1J(RhP)$/ Hz
$[Rh(O_2CCH_2Cl)_2(NO)(PPh_3)_2]$	205	57.3 (56.9)	4.0 (4.0)	1.6 (1.7)	1 620	1 630	22.49 (d)	123.5
$[Rh(O_2CCHCl_2)_2(NO)(PPh_3)_2]$	194—195	52.9 (52.6)	3.5 (3.5)	1.6 (1.5)	1 655	1 630	21.81 (d)	119.6
$[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$	—	—	—	—	1 667	1 620	20.25 (d)	119.1
$[Rh(O_2CCClF_2)_2(NO)(PPh_3)_2]$	196—197	51.8 (52.4)	3.5 (3.3)	1.6 (1.5)	1 665	1 682	21.04 (d)	117.2
$[Rh(O_2CC_6H_4NO_2)_2(NO)(PPh_3)_2]$	176 (decomp.)	60.3 (60.8)	3.8 (3.8)	4.2 (4.3)	1 630	1 710	23.19 (d)	122.1
$[Rh\{O_2CC_6H_3(NO_2)_2\}_2(NO)(PPh_3)_2]$	231	54.7 (55.7)	3.4 (3.3)	6.3 (6.5)	1 635	1 532	23.96 (d)	122.0
$[Rh(O_2CC_6H_4Cl)_2(NO)(PPh_3)_2]$	178	61.6 (62.1)	4.0 (3.9)	1.6 (1.5)	1 625	1 585	22.55 (d)	125.0
$[Rh(CCl_3)(HgCCl_3)(NO)(PPh_3)_2]$	229 (decomp.)	40.3 (40.5)	2.8 (2.7)	1.0 (1.2)	1 612, 1 602	—	29.99 (d)	126.5

[a] Calculated values are given in parentheses. [b] ν(NO) and $\nu(OCO)_{asym}$ values may be transposed in some instances.

acids were purchased from Aldrich and dried *in vacuo* prior to use. Reagent grade solvents were dried over sodium (benzene) or molecular sieves. All reactions were performed under a nitrogen atmosphere but products were worked-up in air unless otherwise indicated. Analyses were performed by the Microanalytical Laboratory, University College, London. I.r. spectra were obtained as Nujol mulls using a Perkin-Elmer grating spectrometer. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded in $CDCl_3$ solution on a Bruker HFX 90 spectrometer operating at 90 and 36.44 MHz respectively; spectra are referenced against internal $SiMe_4$ (^1H) and external 85% H_3PO_4 (^{31}P). Data are collected in Table 1. Known products, particularly when obtained as mixtures and therefore not amenable to elemental analysis, were identified by spectroscopic comparison with authentic samples prepared by literature methods.

Dichloro(nitrosyl)bis(triphenylphosphine)rhodium.—Trichloroacetic acid (0.10 g, 0.61 mmol) was added to a solution of $[Rh(NO)(PPh_3)_3]$ (0.20 g, 0.218 mmol) in acetone (5 cm^3). The mixture was allowed to react for 20 min at ambient temperature; the resulting brown solution was diluted with light petroleum (b.p. 60—80 °C, 10 cm^3) and then allowed to evaporate slowly in a stream of nitrogen. The light brown solid which separated was washed with light petroleum and dried *in vacuo* to yield the product (0.13 g, 82%) as fine brown microcrystals [ν(NO) = 1 630 cm^{-1}].

Nitrosylbis(trichloroacetato)bis(triphenylphosphine)rhodium.—Trichloroacetic acid (0.10 g, 0.61 mmol) was added to a cooled solution (0 °C, ice–water bath) of $[Rh(NO)(PPh_3)_3]$ (0.20 g, 0.218 mmol) in acetone (5 cm^3). The cooled mixture was stirred in an open flask for 10 min during which time the colour changed from red through brown to green and a green precipitate separated. The green solid was filtered off, washed successively with cold acetone and light petroleum (b.p. 60—80 °C), then dried *in vacuo* to yield a mixture of $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ [70%; ν(NO) = 1 667 cm^{-1}; ^{31}P n.m.r., δ 20.25 p.p.m. (d), ^1J(RhP) = 119.1 Hz] and $[RhCl_2(NO)(PPh_3)_2]$ [30%; ν(NO) = 1 630 cm^{-1}; ^{31}P n.m.r., δ 28.89 p.p.m. (d), ^1J(RhP) = 113 Hz].

Conversion of Nitrosylbis(trichloroacetato)bis(triphenylphosphine)rhodium to Dichloro(nitrosyl)bis(triphenylphosphine)rhodium.—(*a*) $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ (0.10 g, 0.102 mmol) was suspended in acetone (10 cm^3). Triphenylphosphine (0.06 g, 0.204 mmol) and trichloroacetic acid (excess) were added to the suspension which was then stirred for 10 min in an open flask. The green solution turned brown and, on addition of light petroleum (b.p. 60—80 °C, 10 cm^3) followed by slow evaporation, the product $[RhCl_2(NO)(PPh_3)_2]$ [ν(NO) = 1 630 cm^{-1}] deposited as a brown powder (90%).

The same procedure, performed in the absence of added triphenylphosphine *or* trichloroacetic acid gave unchanged $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ even after 48 h.

(*b*) $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ (0.10 g, 0.102 mmol) was dissolved in dimethyl sulphoxide (7 cm^3) at ambient temperature to afford a green solution which turned brown over a period of 3 h. Evaporation under reduced pressure followed by crystallisation of the brown residue from acetone–light petroleum (b.p. 60—80 °C) gave a brown powder which, after washing with light petroleum and drying *in vacuo*, was identified as $[RhCl_2(NO)(PPh_3)_2]$ [0.045 g, 61%; ν(NO) = 1 630 cm^{-1}].

Dibromo(nitrosyl)bis(triphenylphosphine)rhodium.—This was prepared from nitrosyltris(triphenylphosphine)rhodium (0.20 g, 0.218 mmol) and tribromoacetic acid (0.13 g, 0.436 mmol) in acetone solution, and was isolated in the same way as the corresponding dichloro-complex (see above). It formed brown microcrystals [0.16 g, 89%; ν(NO) = 1 630 cm^{-1}].

Reactions of Nitrosyltris(triphenylphosphine)rhodium with other Carboxylic Acids.—*Bis(chloroacetato)nitrosylbis(triphenylphosphine)rhodium.* A suspension of $[Rh(NO)(PPh_3)_3]$ (0.20 g, 0.22 mmol) in acetone (10 cm^3) was treated with chloroacetic acid (0.04 g, 0.44 mmol). The mixture was stirred at ambient temperature for 30 min. The green precipitate which formed was filtered off, and washed with acetone and light petroleum (b.p. 60—80 °C) to yield green microcrystals (0.12 g, 67%).

The following were similarly prepared using the appropriate carboxylic acids: bis(dichloroacetato)nitrosylbis(triphenylphosphine)rhodium as green microcrystals (60%); bis(chlorodifluoroacetato)nitrosylbis(triphenylphosphine)rhodium as green microcrystals (56%); bis(3,5-dinitrobenzoato)nitrosylbis(triphenylphosphine)rhodium as pale green microcrystals (51%); bis(2-nitrobenzoato)nitrosylbis(triphenylphosphine)rhodium as green microcrystals (84%); bis(2-chlorobenzoato)nitrosylbis(triphenylphosphine)rhodium as green microcrystals (48%).

Reactions of Nitrosyltris(triphenylphosphine)rhodium with Bis(trichloromethyl)mercury(II).—(*a*) *In refluxing toluene.* A solution of $[Rh(NO)(PPh_3)_3]$ (0.10 g, 0.109 mmol) and $Hg(CCl_3)_2$ (0.10 g, 0.22 mmol) in sodium-dried toluene (10 cm^3) was heated under reflux for 15 min. Evaporation of the orange solution and crystallisation of the residue from dichloromethane–methanol gave a brown solid (0.07 g, 88%) which was identified as $[RhCl_2(NO)(PPh_3)_2]$ [ν(NO) = 1 630 cm^{-1}].

(*b*) *In cold toluene.* When the above mixture was allowed to react at 0 °C (ice–water bath) for 30 min, nitrosyl(trichloromethyl)(trichloromethylmercurio)bis(triphenylphosphine)rhodium (0.07 g) was precipitated as a stable bright yellow solid.

Reactions of Carbonyl(hydrido)tris(triphenylphosphine)rhodium(I) *with Trichloroacetic Acid.*—A mixture of $[RhH(CO)(PPh_3)_3]$ (0.10 g, 0.109 mmol) and trichloroacetic acid (0.02 g, 0.109 mmol) was stirred in benzene (10 cm^3) at ambient temperature for 30 min. The solution was evaporated to near dryness and the residue treated with methanol to yield a yellow powder which, after washing successively with methanol and hexane, was dried *in vacuo* and identified as carbonyl(chloro)bis(triphenylphosphine)rhodium(I) [0.072 g, 95%; ν(CO) = 1 960 cm^{-1}; ^{31}P n.m.r., δ 29.05 p.p.m. (d), ^1J(RhP) = 128 Hz].

The above procedure, when repeated with a longer reaction time (2 h) and excess acid yielded a yellow precipitate which was identified as (carbonyl)trichlorobis(triphenylphosphine)rhodium(III) [0.06 g, 72%; ν(CO) = 2 100 cm^{-1}; ^{31}P n.m.r., δ 13.00 p.p.m. (d), ^1J(RhP) = 78.1 Hz].

When the above reaction was followed by ^{31}P-{^1H} n.m.r., using solutions in C_6D_6, doublet signals at δ 29.80 p.p.m., ^1J(RhP) = 132 Hz, and δ 29.05 p.p.m., ^1J(RhP) = 128 Hz, attributable to $[Rh(O_2CCCl_3)(CO)(PPh_3)_2]$ and $[RhCl(CO)(PPh_3)_2]$ respectively, were observed.

Carbonyl(trichloroacetato)bis(triphenylphosphine)rhodium(I).—Trichloroacetic acid (0.1 g, 0.55 mmol) was added to a solution of $[Rh(O_2CCF_3)(CO)(PPh_3)_2]$ (0.1 g, 0.13 mmol) in benzene (10 cm^3). After stirring the solution at ambient temperature for 1.5 h the solvent was removed under reduced pressure and the residue was treated with methanol to yield a yellow solid (0.08 g, 75%). This was shown by i.r. and ^{31}P n.m.r. to be the required product [ν(CO) = 1 990, ν(OCO) = 1 680, 1 670 cm^{-1}; ^{31}P n.m.r., δ 29.80 p.p.m. (d), ^1J(RhP) = 132 Hz] contaminated by a trace of [$RhCl(CO)(PPh_3)_2$] [δ 29.05 p.p.m. (d), ${}^1J$(RhP) = 128 Hz].

Conversion of Carbonyl(trichloroacetato)bis(triphenylphosphine)rhodium(I) *to Carbonyl(chloro)bis(triphenylphosphine)rhodium*(I).—Trichloroacetic acid (0.05 g, 0.31 mmol) and triphenylphosphine (0.08 g, 0.31 mmol) were added to a solution of [$Rh(O_2CCCl_3)(CO)(PPh_3)_2$] (0.08 g, 0.098 mmol) in acetone (10 cm^3). The mixture was stirred at ambient temperature for 10 min then evaporated to dryness under reduced pressure. The residue, crystallised from dichloromethane–hexane, afforded the product [ν(CO) = 1 960 cm^{-1}; ${}^{31}P$ n.m.r., δ 29.05 p.p.m. (d), ${}^1J$(RhP) = 128 Hz] as yellow crystals (0.04 g, 57%).

Reactions of Carbonyl(chloro)bis(triphenylphosphine)rhodium(I) *with Trichloroacetic Acid.*—(*a*) *In refluxing benzene.* [$RhCl(CO)(PPh_3)_2$] (0.10 g, 0.145 mmol) suspended in benzene (7 cm^3) was treated with a solution of trichloroacetic acid (0.04 g, 0.29 mmol) in benzene (5 cm^3) and the mixture heated under reflux for 3 h. The dark yellow solid which precipitated from the cooled solution was collected, washed with methanol and hexane then dried *in vacuo* to afford (carbonyl)trichlorobis(triphenylphosphine)rhodium [ν(CO) = 2 100 cm^{-1}; ${}^{31}P$ n.m.r., δ 13.0 p.p.m. (d), ${}^1J$(RhP) = 78.1 Hz] as a yellow powder (0.060 g, 54%).

(*b*) *In cold benzene.* The same mixture reacted at ambient temperature over a period of 3 h to afford a solid product which was identified by i.r. spectroscopy as a mixture of [$RhCl(CO)(PPh_3)_2$] [ν(CO) = 1 960 cm^{-1}] and [$RhCl_3(CO)(PPh_3)_2$] [ν(CO) = 2 100 cm^{-1}].

A similar reaction mixture in deuteriobenzene showed no evidence of high-field (hydride) resonances when examined by ${}^1H$ n.m.r.

Reactions of Chlorotris(triphenylphosphine)rhodium(I) *with Trichloroacetic acid.*—(*a*) *Molar ratio* 1:1. Chlorotris(triphenylphosphine)rhodium (0.10 g, 0.109 mmol) was added to a degassed solution of trichloroacetic acid (0.02 g, 0.109 mmol) in benzene (15 cm^3). The solution was stirred at ambient temperature for 3 h, then evaporated to dryness under reduced pressure. The residue was triturated with diethyl ether to yield [$RhCl(CO)(PPh_3)_2$] [ν(CO) = 1 960 cm^{-1}] as a yellow powder (0.05 g, 67%).

(*b*) *Molar ratio* 1:3. Chlorotris(triphenylphosphine)rhodium (0.10 g, 0.108 mmol) was added to a degassed solution of trichloroacetic acid (0.054 g, 0.324 mmol) in benzene (10 cm^3) and the mixture was stirred at ambient temperature for 8 h. From this solution [$RhCl_3(CO)(PPh_3)_2$] [ν(CO) = 2 100 cm^{-1}] spontaneously deposited as a deep yellow solid (0.08 g, 97%).

Reaction of Chlorotris(triphenylphosphine)rhodium(I) *with Bis(trichloromethyl)mercury*(II).—Chlorotris(triphenylphosphine)rhodium(I) (0.1 g, 0.109 mmol) and bis(trichloromethyl)mercury(II) (0.1 g, 0.228 mmol) were added to sodium-dried toluene (10 cm^3) and the mixture was heated under reflux for 25 min. The orange solution was evaporated to dryness under reduced pressure, and the residue was crystallised from dichloromethane–methanol to yield impure [$RhCl_3(CO)(PPh_3)_2$] [ν(CO) = 2 100 cm^{-1}] as a light brown solid (0.08 g, 61%).

Dichloro(nitrosyl)bis(triphenylphosphine)iridium.—A solution of trichloroacetic acid (0.05 g, 0.298 mmol) in benzene (5 cm^3) was added to [$Ir(NO)(PPh_3)_3$] (0.015 g, 0.149 mmol) and the mixture was heated under reflux for 5 min. The clear solution was evaporated under reduced pressure and the residue triturated with ethanol to afford an orange solid which was washed successively with ethanol and hexane then dried *in vacuo*. The product (0.009 g, 74%) was identified as [$IrCl_2(NO)(PPh_3)_2$] [ν(NO) = 1 559 cm^{-1}].

Reactions of Carbonyl(hydrido)tris(triphenylphosphine)iridium(I) *with Trichloroacetic Acid.*—(*a*) *Formation of* [$IrH_2(CO)(PPh_3)_3$][$H(O_2CCCl_3)_2$]. A suspension of [$IrH(CO)(PPh_3)_3$] (0.10 g, 0.099 mmol) in acetone (10 cm^3) was added to a solution of trichloroacetic acid (0.032 g, 0.20 mmol) in acetone (5 cm^3) and the mixture was stirred at room temperature for 10 min. The colourless solution was evaporated to dryness and the residue was triturated then washed with hexane to afford a white powder (0.10 g, 76%). This product was identified as [$IrH_2(CO)(PPh_3)_3$][$H(O_2CCCl_3)_2$] by spectroscopic methods [ν(CO) = 2 000, ν(IrH) = 2 100, ν(OCO) = 1 750, 1 430 cm^{-1}; ${}^1H$ n.m.r., δ(IrH) −9.37 p.p.m. (d of t of d), ${}^2J$(HP) = 13.4 and 18.0, ${}^2J$(HH′) 4.9 Hz; δ(IrH) −11.23 p.p.m. (d of t of d), ${}^2J$(HP) 114.8 and 18.3 Hz].

(*b*) *Decomposition of* CCl_3CO_2H. The above reaction was allowed to proceed for 1 h at room temperature whereupon carbonyl(hydrido)tris(triphenylphosphine)iridium(I) precipitated from the mixture in 80% yield. The carbon dioxide evolved in this reaction, swept from the vessel in a stream of nitrogen and determined gravimetrically as barium carbonate, was found to be equal to *ca.* 2 mol per mol of iridium complex.

A similar reaction performed in C_6D_6 solution was shown by g.l.c. (squalene column, 180 °C) and ${}^1H$ n.m.r. (δ 8.03 p.p.m.) to yield chloroform.

(*c*) *Formation of (carbonyl)trichlorobis(triphenylphosphine)iridium*(III). Trichloroacetic acid (0.06 g, 0.4 mmol) was added to a suspension of carbonyl(hydrido)tris(triphenylphosphine)iridium(I) (0.10 g, 0.099 mmol) in toluene (10 cm^3) and the mixture was heated under reflux for 1 h. The precipitate which formed was collected and washed with light petroleum (b.p. 60—80 °C) to afford [$IrCl_3(CO)(PPh_3)_2$] [ν(CO) = 2 080 cm^{-1}] as a pale yellow solid (0.06 g, 71%).

Reactions of [$IrX(CO)(PPh_3)_2$] (X = Cl *or* Br) *with Perhalocarboxylic Acids.*—(*a*) *Formation of carbonyldichlorohydridobis(triphenylphosphine)iridium*(III) *and carbonyltrichlorobis(triphenylphosphine)iridium*(III). Trichloroacetic acid (0.06 g, 0.38 mmol) in benzene (5 cm^3) and [$IrCl(CO)(PPh_3)_2$] (0.15 g, 0.19 mmol) in benzene (10 cm^3) were mixed and heated under reflux for 1 h. The yellow solution was evaporated to dryness and the residue crystallised from methanol then washed with methanol and hexane to afford a rather insoluble pale yellow solid (0.07 g) which was identified by i.r. spectroscopy as a mixture of [$IrHCl_2(CO)(PPh_3)_2$] [ν(IrH) = 2 240, ν(CO) = 2 010 cm^{-1}] and [$IrCl_3(CO)(PPh_3)_2$] [ν(CO) = 2 080 cm^{-1}].

(*b*) ${}^1H$ *N.m.r. study.* A suspension of [$IrCl(CO)(PPh_3)_2$] (*ca.* 0.05 mmol) in C_6D_6 (1 cm^3) was treated with an equimolar quantity of the appropriate perhalocarboxylic acid. After *ca.* 10 min the solution was filtered if necessary, then n.m.r. (${}^1H$) spectra were recorded. Data are collected in Table 2. The product from the [$IrCl(CO)(PPh_3)_2$]/CCl_3CO_2H system was isolated as an off-white solid.

Reactions of mer-*Trihydridotris(triphenylphosphine)iridium*(III) *with Trichloroacetic Acid.*—(*a*) *In benzene.* A mixture of trichloroacetic acid (0.04 g, 0.306 mmol) and *mer*-[$IrH_3(PPh_3)_3$] (0.10 g, 0.102 mmol) in benzene (10 cm^3) was heated under reflux for 30 min to give chloro(dihydrido)tris(triphenylphosphine)iridium(III) as a white powder (0.085 g, 82%).

(*b*) *In ethanol.* A mixture of trichloroacetic acid (0.04 g, 0.306 mmol) and *mer*-[$IrH_3(PPh_3)_3$] (0.10 g, 0.102 mmol) in ethanol (15 cm^3) was heated under reflux for 30 min. The off-white solid (0.11 g) which precipitated was identified by ${}^1H$ n.m.r. (see Discussion section) as a 2:1 mixture of [$IrH_2(O_2$-

Table 2. High-field proton n.m.r. data for $[IrCl(CO)(PPh_3)_2]$—CX_3CO_2H systems

	(III)		(IV)		(V)		(VI)	
Stereochemistry	δ(H)/p.p.m.	^2J(PH)/Hz	δ(H)/p.p.m.	^2J(PH)/Hz	δ(H)/p.p.m.	^2J(PH)/Hz	δ(H)/p.p.m.	^2J(PH)/Hz
CCl_3CO_2H	−12.6 (t)	11.0	−18.8 (t)	12.2	−17.1 (t)	11.6	−14.6 (t)	11.0
$CClF_2CO_2H$	−12.7 (t)	11.0	−18.8 (t)	11.6	−17.1 (t)	11.0	−14.7 (t)	11.6
CF_3CO_2H	−12.9 (t)	10.5	−18.8 (t)	11.5	−17.2 (t)	10.5	−14.8 (t)	10.5

$CCCl_3)(PPh_3)_3]$ and $[IrH_2Cl(PPh_3)_3]{\cdot}EtOH$ contaminated with a trace of $[IrH(CO)(PPh_3)_3]$.

When the reaction was repeated with a reflux time of 2 h, $[IrH_2Cl(PPh_3)_3]{\cdot}EtOH$ was obtained in 87% yield.

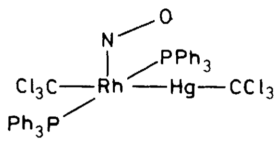
Results and Discussion

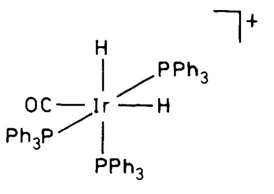
Reactions involving Rhodium and Iridium Nitrosyls $[M(NO)(PPh_3)_3]$.—The rhodium nitrosyl $[Rh(NO)(PPh_3)_3]$ reacts with excess trichloroacetic acid in acetone or benzene solution under very mild conditions (25 °C, *ca.* 5—10 min) to afford the known dichloride $[RhCl_2(NO)(PPh_3)_2]$ in essentially quantitative yield. The product is frequently contaminated with small amounts of $[RhCl(CO)(PPh_3)_2]$ [ν(CO) = 1 960 cm^{-1}] and $[RhCl_3(CO)(PPh_3)_2]$ [ν(CO) = 2 100 cm^{-1}]. With tribromoacetic acid the corresponding bromo-products are obtained. The reactions have been found to involve liberation of carbon dioxide {2 mol per mol of $[Rh(NO)(PPh_3)_3]$ used} and formation of phosphorus-containing species [^{31}P-{^1H} n.m.r. singlet at δ 33.44 (chloride) or 30.76 p.p.m. (bromide)] which are believed to be hydrolysis products of the (dihalomethylene)triphenylphosphoranes $Ph_3P{=}CX_2$ (X = Cl or Br).[32]

The green carboxylate complex $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ can be isolated when the reaction with trichloroacetic acid is performed at 0 °C and the mixture worked-up within 10 min. This product is thermally stable when heated to reflux for several hours in fresh solvent but rapidly fragments to form $[RhCl_2(NO)(PPh_3)_2]$ even in cold solvent when free triphenylphosphine *and* trichloroacetic acid are added to the solution.

In marked contrast other halocarboxylic and substituted benzoic acids RCO_2H [R = CF_3, CF_2Cl, $CHCl_2$, CH_2Cl, 2-ClC_6H_4, 2-$NO_2C_6H_4$, and 3,5-$(NO_2)_2C_6H_3$], several of which are known to decarboxylate readily under other conditions,[2] afford carboxylate complexes $[Rh(O_2CR)_2(NO)(PPh_3)_2]$ which show little or no tendency to undergo fragmentation even when heated to reflux in toluene for 1 h in the presence of excess phosphine and free acid.

In view of the facile decarboxylation of trichloroacetic acid in dimethyl sulphoxide (dmso) solution, recently reported by Gold and co-workers,[20,21] the rates of fragmentation of the complexes $[Rh(O_2CR')_2(NO)(PPh_3)_2]$ [R′ = CCl_3, $CHCl_2$, CH_2Cl, or $CClF_2$] in dmso, acetone, and acetone with added acid and PPh_3 were qualitatively compared. For the trichloroacetate, conversion to $[RhCl_2(NO)(PPh_3)_2]$ in dmso solution took *ca.* 3 h whereas in acetone with added acid and PPh_3 the same reaction was complete in 2—3 min; in neat acetone there was no evidence of conversion even after several days. The dichloroacetate complex $[Rh(O_2CCHCl_2)_2(NO)(PPh_3)_2]$ fragmented over a period of *ca.* 48 h in acetone solution with added acid and PPh_3 to afford the dichloride but the complexes $[Rh(O_2CCH_2Cl)_2(NO)(PPh_3)_2]$ and $[Rh(O_2CCCl_2F)_2(NO)(PPh_3)_2]$ were recovered unchanged from similar solutions after one week. It is apparent from these observations that the acetone–acid–PPh_3 mixture is much more efficient than dmso in causing decarboxylation of the rhodium complex, and that the reaction is effectively limited to the trichloro- and tribromoacetates.


(I)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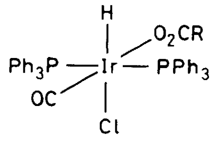
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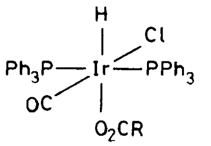
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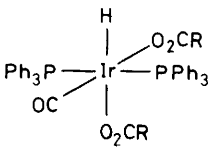
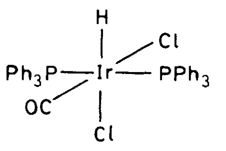
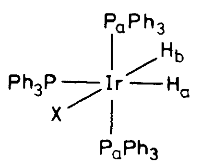
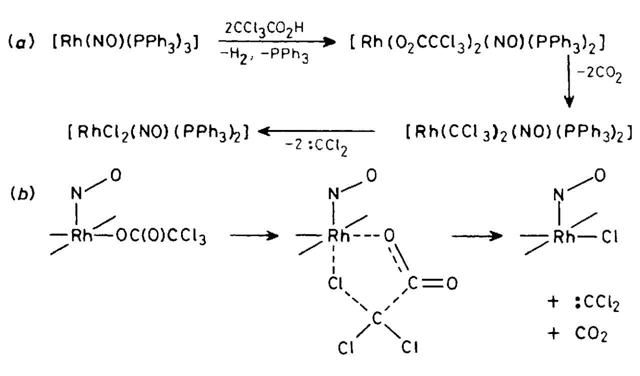

(V)


(VI)


(VII)

The trichloroacetate complex $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ displays a ν(NO) vibration at *ca.* 1 667 cm^{-1} and appears to be directly analogous to the corresponding trifluoroacetate complex [ν(NO) = 1 671 cm^{-1}] which has been shown by *X*-ray diffraction methods to possess a tetragonal pyramidal structure with an apical angular RhNO arrangement.[33]

Although the detailed mechanism for the conversion of $[Rh(NO)(PPh_3)_3]$ to $[RhCl_2(NO)(PPh_3)_2]$ in the presence of CCl_3CO_2H has still to be investigated, information already available enables some general conclusions to be reached with reasonable confidence. The detection of a transient emerald green colouration during the reaction, and the isolation of $[Rh(O_2CCCl_3)_2(NO)(PPh_3)_2]$ from reaction mixtures at low temperatures strongly suggest that the carboxylate complex is an intermediate. We have already shown that formation of the corresponding trifluoroacetate from $[Rh(NO)(PPh_3)_3]$ and CF_3CO_2H occurs primarily by a mechanism involving dioxygen,[34] and it seems likely that a similar mechanism is operative in the formation of the trichloroacetate complex. However, this point has yet to be confirmed. Conversion of the trichloroacetate to the chloride $[RhCl_2(NO)(PPh_3)_2]$ probably involves carbon dioxide extrusion to generate trichloromethyl intermediates which subsequently lose dichlorocarbene to afford the final product. Decarboxylation of free and co-ordinated carboxylate anions is well established; previous work in this area is summarised in the introduction to this paper. Moreover, observation of carbon dioxide evolution from the $[Rh(NO)(PPh_3)_3]$–CCl_3CO_2H system points to the occurrence of a similar process in the present instance. The tendency of trichloromethyl ligands to generate dichlorocarbene moieties is also well known and has been employed by Roper and co-workers [26,27] to synthesise CCl_2 complexes of several platinum group metals. Evidence confirming the feasibility of a mechanism involving formation and fragmentation of rhodium–trichloromethyl intermediates in the present instance was provided by the reaction of $[Rh(NO)(PPh_3)_3]$ with $Hg(CCl_3)_2$ in boiling toluene which gave $[RhCl_2(NO)(PPh_3)_2]$ in good yield. The same mixture in cold toluene (30 min, ice–water bath) yielded a yellow product which analysed correctly for $[Rh(CCl_3)(HgCCl_3)(NO)(PPh_3)_2]$, structure (I) and displayed a $^{31}P\text{-}\{^1H\}$ n.m.r. pattern [δ 29.99 (d), $^1J(RhP)$ = 126.5 Hz] consistent with this formulation. These results support the view that the reaction of $[Rh(NO)(PPh_3)_3]$ with trichloroacetic acid proceeds by the generation of a trichloroacetate complex which, like the trichloroacetate anion, decomposes by a stepwise process involving trichloromethyl intermediates [Scheme 1(*a*)]. However, they do not exclude an alternative 'concerted' mechanism for the carboxylate fragmentation step involving collapse of a cyclic intermediate with concomitant liberation of CO_2 and $:CCl_2$ [Scheme 1(*b*)]. A mechanism of this type has previously been advanced to account for the fragmentation of the carboxylate ligands in the $[IrCl(CO)(PPh_3)_2]$–$CClF_2CO_2H$ system.[22–24] Moreover it would offer an explanation of the role of triphenylphosphine in the fragmentation process since the 'concerted' decomposition of $CClF_2CO_2^-$ anions into CO_2, $:CF_2$, and Cl^- is known to be promoted by free triphenylphosphine which scavenges the carbene to form $Ph_3P{=}CF_2$.[35] However the free $CClF_2CO_2^-$ anion, unlike its trichloroacetate analogue, decomposes by a concerted mechanism;[36] therefore our observation that the closely related complex, $[Rh(O_2CCClF_2)_2(NO)(PPh_3)_2]$, does not fragment even in the presence of excess phosphine strongly suggests that the 'concerted' mechanism is not operative in these reactions. Consequently in the following discussion of related reactions involving other rhodium and iridium substrates we have made the assumption that a stepwise rather than a concerted fragmentation of CCl_3CO_2 ligands occurs. This assumption will be tested in future work.

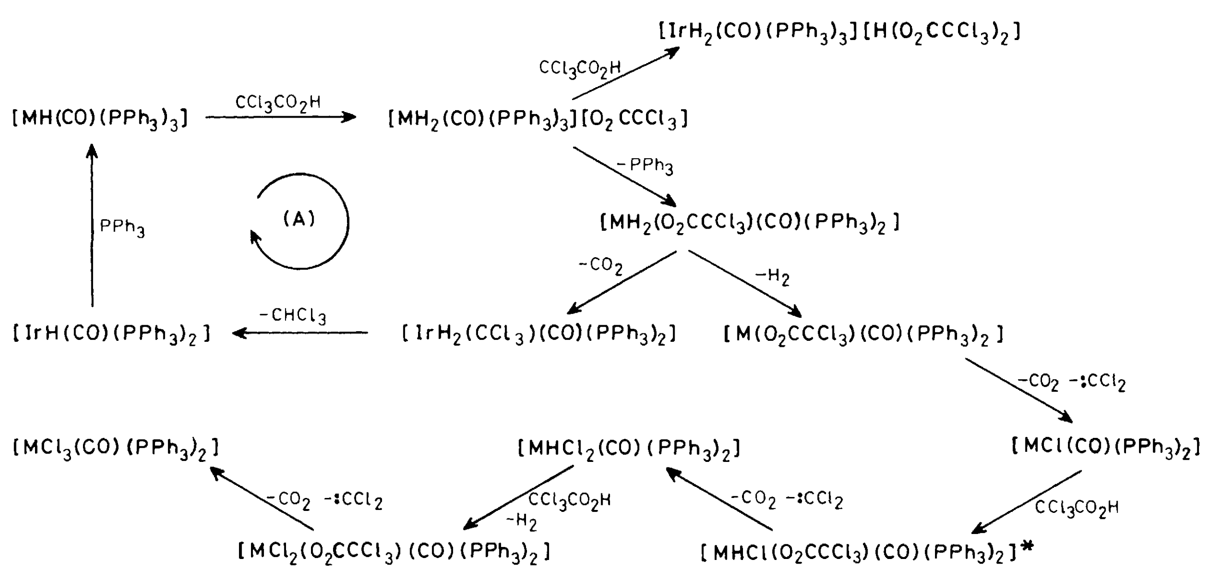


Scheme 1.

Formation of the minor products $[RhCl(CO)(PPh_3)_2]$ and $[RhCl_3(CO)(PPh_3)_2]$, albeit in small yield, was rather unexpected since nitrosyl ligands are known strongly to resist displacement.[37] However, generation of the CO ligand can readily be ascribed to hydrolysis of dichlorocarbene intermediates by adventitious water. Reactions of this type are well known and several examples are discussed below. Likewise the conversion of $[RhCl(CO)(PPh_3)_2]$ to $[RhCl_3(CO)(PPh_3)_2]$ by excess trichloroacetic acid has been demonstrated in the present work and is reported later in this paper.

The iridium complex $[Ir(NO)(PPh_3)_3]$ reacts with trichloroacetic acid even more readily than its rhodium analogue. The dichloro-complex $[IrCl_2(NO)(PPh_3)_2]$ forms after 1—2 min at ambient temperature in acetone and, since no visible colour change accompanies this reaction, it has not proved possible to isolate a carboxylate intermediate. However, a reaction sequence similar to that observed for the corresponding rhodium system seems probable.

Reactions involving Rhodium and Iridium Carbonyl Hydrides $[MH(CO)(PPh_3)_3]$.—In cold or refluxing benzene, $[RhH(CO)(PPh_3)_3]$ reacts with one mol of CCl_3CO_2H to liberate carbon dioxide (1 mol) and form $[RhCl(CO)(PPh_3)_2]$. The



Scheme 2. M = Rh or Ir (steps which are significant only for Ir are indicated). * Plus isomers and disproportionation products (see Discussion)

^{31}P-{^{1}H} n.m.r. spectrum of the solution obtained when this reaction was performed in cold benzene showed a doublet [δ 29.05 p.p.m., $^{1}J(RhP) = 128$ Hz] attributable to $[RhCl(CO)(PPh_3)_2]$ and a second weaker doublet [δ 29.80 p.p.m., $^{1}J(RhP) = 132$ Hz] which we assign to $[Rh(O_2CCCl_3)(CO)(PPh_3)_2]$. This assignment was confirmed by comparison with an authentic sample of the trichloroacetate complex prepared by treating $[Rh(O_2CCF_3)(CO)(PPh_3)_2]$ with excess trichloroacetic acid in benzene solution for 1.5 h at ambient temperature. Formation of the observed products can be explained in terms of the reaction sequence shown in Scheme 2 (M = Rh). However, the lability of the Rh^{I}/Rh^{III} system defeated all attempts to detect the postulated hydridic intermediates by high-field ^{1}H n.m.r. spectroscopy. As reported below, the product $[RhCl(CO)(PPh_3)_2]$ reacts further with excess trichloroacetic acid to yield $[RhCl_3(CO)(PPh_3)_2]$ (Scheme 2).

The corresponding iridium complex, $[IrH(CO)(PPh_3)_3]$, reacts in a rather different manner (Scheme 2, M = Ir) presumably because the iridium dihydride cation $[IrH_2(CO)(PPh_3)_3]^+$ is much more reluctant than its rhodium analogue to undergo reductive elimination of dihydrogen. For reaction mixtures containing less than *ca.* 2 mol of trichloroacetic acid per mol of iridium complex, formation of chloroform and liberation of carbon dioxide have been detected by ^{1}H n.m.r./g.l.c. and gravimetric methods respectively. Formation of $[IrH_2(CO)(PPh_3)_3]^+$ and subsequent regeneration of $[IrH(CO)(PPh_3)_3]$ has been established by high-field ^{1}H n.m.r. These observations point to a closed cycle [Scheme 2, cycle (A)] for the decomposition of CCl_3CO_2H to CO_2 and $CHCl_3$. However the reaction is not easily rendered catalytic, since the introduction of excess CCl_3CO_2H leads to stabilisation of the intermediate cation $[IrH_2(CO)(PPh_3)_2]^+$, by formation of a salt containing the H-bonded counter anion $[H(O_2CCCl_3)_2]^-$, and thus breaks the catalytic cycle. The quantitative formation of the cation $[IrH_2(CO)(PPh_3)_3]^+$, structure (**II**), in the presence of excess trichloroacetic acid has been confirmed by high-field ^{1}H n.m.r.; the spectra of the solutions obtained were essentially identical with that previously reported for the closely related salt $[IrH_2(CO)(PPh_3)_3][H(O_2CCF_3)_2]$.[38,39]

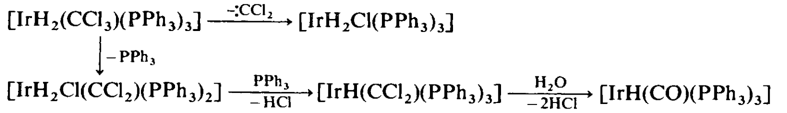
The temperature of the reaction was raised (boiling toluene) in an attempt to break up the complex salt and render the cyclic reaction truly catalytic. However, this treatment precipitated a complex series of reactions (Scheme 2) leading to formation of $[IrCl_3(CO)(PPh_3)_2]$ [ν(CO) = 2 080 cm^{-1}] as the major product.

Reactions involving Rhodium and Iridium Carbonyls $[MX(CO)(PPh_3)_2]$.—Treatment of $[RhCl(CO)(PPh_3)_2]$ with excess trichloroacetic acid in cold or boiling benzene affords $[RhCl_3(CO)(PPh_3)_2]$ together with 2 mol of carbon dioxide. This system, in common with many others involving rhodium(I), is very labile and all attempts to detect hydridic intermediates by high-field ^{1}H n.m.r. monitoring of $[RhCl(CO)(PPh_3)_2]$–trichloroacetic acid solutions in cold benzene were unsuccessful. However, it seems probable that the reaction follows a course essentially identical with that set out in the latter part of Scheme 2 (M = Rh). The corresponding iridium system is somewhat less labile and therefore rather more informative. Treatment of $[IrCl(CO)(PPh_3)_2]$ with one mol of trichloroacetic acid in deuteriobenzene at ambient temperature affords a solution which was shown by high-field ^{1}H n.m.r. to contain four hydridic species. Similar ^{1}H n.m.r. patterns were observed when CF_3CO_2H and $CClF_2CO_2H$ were used in place of CCl_3CO_2H (see Table 2). These results parallel those observed for various $[IrCl(CO)(PR_3)_2]$–$R'CO_2H$ systems by Singer and Wilkinson[40] and, more recently, by van Doorn *et al.*[41] The latter workers concluded that four hydride signals arose from *cis* and *trans* adducts (**III**) and (**IV**), respectively, together with the disproportionation products (**V**) and (**VI**). The assignments give in Table 2 follow those of van Doorn *et al.*[41] Prolonged treatment of $[IrCl(CO)(PPh_3)_2]$ with excess trichloroacetic acid in boiling benzene induces formation of $[IrHCl_2(CO)(PPh_3)_2]$ [ν(IrH) = 2 240, ν(CO) = 2 010 cm^{-1}] and $[IrCl_3(CO)(PPh_3)_2]$ [ν(CO) = 2 080 cm^{-1}]. A feasible reaction sequence leading to formation of these products is shown in the lower half of Scheme 2 (M = Ir).

Reactions involving mer-$[IrH_3(PPh_3)_3]$.—The interaction of *mer*-$[IrH_3(PPh_3)_3]$ with trichloroacetic acid in refluxing ethanol for 30 min produced a mixture, the components of which were identified by spectroscopic methods as $[IrH_2(O_2CCCl_3)(PPh_3)_3]$ (**VII**, X = O_2CCCl_3), $[IrH_2Cl(PPh_3)_3]$ (**VII**, X = Cl), and a trace of $[IrH(CO)(PPh_3)_3]$. A longer reaction time (2 h reflux) led to the isolation of pure $[IrH_2Cl(PPh_3)_3]$.

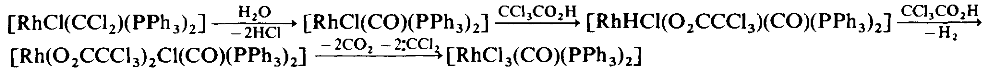
Pure $[IrH_2Cl(PPh_3)_3]$ was also obtained when *mer*-$[IrH_3(PPh_3)_3]$ was refluxed with CCl_3CO_2H in benzene for 30 min. Small differences in spectroscopic data recorded for samples of $[IrH_2Cl(PPh_3)_3]$ extracted from reactions in benzene [ν(IrH) = 2 190, 2 105 cm^{-1}; δ(IrH) = −10.68 and −20.51 p.p.m.] (Table 3) and ethanol [ν(IrH) = 2 180, 2 122 cm^{-1}; δ(IrH) = −11.6 and −21.5 p.p.m.] were attributed to formation of an ethanol solvate in the latter case. The ethanol, the presence of which was indicated by ^{1}H n.m.r. [δ 0.9 (t) and 3.3 (q), $^{3}J(HH') = 6.7$ Hz] was lost when the solvate was crystallised from CH_2Cl_2 solution.

Formation of small amounts of $[IrH(CO)(PPh_3)_3]$, noted above, is attributed to a side reaction involving formation of a dichlorocarbene intermediate $[IrH(CCl_2)(PPh_3)_3]$ which sub-



$$\begin{tikzcd}
mer\text{-}[IrH_3(PPh_3)_3] \arrow[r, "CCl_3CO_2H", "-H_2"'] & {[IrH_2(O_2CCCl_3)(PPh_3)_3]} \arrow[r, "-CO_2"] & {[IrH_2(CCl_3)(PPh_3)_3]} \\
{[IrH_2(CCl_3)(PPh_3)_3]} \arrow[r, "-:CCl_2"] \arrow[d, "-PPh_3"] & {[IrH_2Cl(PPh_3)_3]} & \\
{[IrH_2Cl(CCl_2)(PPh_3)_2]} \arrow[r, "PPh_3", "-HCl"'] & {[IrH(CCl_2)(PPh_3)_3]} \arrow[r, "H_2O", "-2HCl"'] & {[IrH(CO)(PPh_3)_3]}
\end{tikzcd}$$

Scheme 3.



$$[RhCl(PPh_3)_3] \xrightarrow{CCl_3CO_2H} [RhHCl(O_2CCCl_3)(PPh_3)_3] \xrightarrow{-HCl} [Rh(O_2CCCl_3)(PPh_3)_3] \xrightarrow{-CO_2} [Rh(CCl_3)(PPh_3)_3] \xrightarrow{-PPh_3}$$
$$[RhCl(CCl_2)(PPh_3)_2] \xrightarrow[-2HCl]{H_2O} [RhCl(CO)(PPh_3)_2] \xrightarrow{CCl_3CO_2H} [RhHCl(O_2CCCl_3)(CO)(PPh_3)_2] \xrightarrow[-H_2]{CCl_3CO_2H}$$
$$[Rh(O_2CCCl_3)_2Cl(CO)(PPh_3)_2] \xrightarrow{-2CO_2\ -2{:}CCl_2} [RhCl_3(CO)(PPh_3)_2]$$

Scheme 4.

Table 3. Hydrogen-1 n.m.r. data (δ/p.p.m., J/Hz) for **(VII)**

	$X = CCl_3CO_2$	$X = Cl$
$\delta(H_a)$	−10.31	−10.68
$\delta(H_b)$	−24.61	−20.51
$^2J(P_aH_a)$	19.5	21.0
$^2J(P_bH_a)$	99.0	132.0
$^2J(H_aH_b)$	6.0	4.5
$^2J(P_aH_b)$	17.5	15.0
$^2J(P_bH_b)$	14.0	15.0

sequently undergoes hydrolysis by adventitious traces of moisture present in the ethanol or the acid used (Scheme 3).

Reactions involving $[RhCl(PPh_3)_3]$.—Treatment of $[RhCl(PPh_3)_3]$ with trichloroacetic acid (molar ratio 1:1) in cold benzene afforded a *ca.* 67% yield of $[RhCl(CO)(PPh_3)_2]$. The same reaction repeated using excess trichloroacetic acid and a longer reaction time gave $[RhCl_3(CO)(PPh_3)_2]$ in almost quantitative yield. Again we attribute formation of the carbonyl ligands to the generation and subsequent hydrolysis of a co-ordinated dichlorocarbene moiety (Scheme 4).

It appears clear from the foregoing discussion that the dichlorocarbene intermediates postulated in this work are readily hydrolysed with concomitant formation of carbonyl ligands, and that the routine drying of solvents undertaken was insufficient to prevent this reaction occurring. A further set of experiments, involving scrupulously dried reagents and aimed at isolating and characterising these intermediates is planned as part of a more detailed investigation into the mechanisms of the fragmentation reactions.

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