Preparation and Reactivity of Iodomethyl Complexes of Rhodium(III); Crystal and Molecular Structure of Carbonylchloroiodo(iodomethyl)bis(triethylphosphine)rhodium(III)†

Rosslyn C. Gash,[a] David J. Cole-Hamilton,*[,a] Robin Whyman,[b] John C. Barnes[c] and (in part) Michael C. Simpson[a]
[a] *School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK*
[b] *Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK*
[c] *Department of Chemistry, University of Dundee, Dundee, Tayside DD1 4HN, UK*

Diiodomethane oxidatively added to $[RhCl(CO)(PR_3)_2]$ formed $[RhCl(I)(CH_2I)(CO)(PR_3)_2]$ for R_3 = Me_3, Et_3 or Et_2Ph but not for R_3 = $EtPh_2$, Ph_3, $(C_6H_{11})_3$ or $(OMe)_3$; CH_2Br_2 gave a mixture of bromo- and chloromethyl complexes whilst CH_2ICl gave two isomers of $[RhCl(I)(CH_2Cl)(CO)(PEt_3)_2]$ with I or Cl *trans* to CH_2Cl. In polar solvents or on treatment with water or MeOH, $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ underwent a halide-scrambling reaction to give several compounds containing CH_2I or CH_2Cl ligands which have been identified spectroscopically. The same scrambling occurs under high pressures of CO, although IR, NMR and model studies suggest the $Rh{-}C(O)CH_2X$ species are also formed by insertion of CO into the $Rh{-}CH_2X$ bond. Most of the acyl products are unstable to loss of ketene, but one may be stable [ν(C=O) 1665 cm^{-1}]. The complex $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ has been characterised crystallographically: triclinic, space group $P\bar{1}$, a = 12.343(3), b = 14.327(2), c = 15.426(2) Å, α = 113.78(1), β = 67.25(1), γ = 90.20(1)°, Z = 4, R = 0.0453. Each unit cell contains two pairs of molecules differing in the relative orientations of one PEt_3 ligand. In both cases, Rh–C [2.080(6), 2.063(9) Å], C–I [2.151(9), 2.121(10) Å] and Rh–C–I [119.9(5), 120.3(4)°] are similar to those reported for related compounds. Both molecules have mutually *trans* phosphines and CH_2I *trans* to I.

During the course of extensive studies of the use of rhodium complexes containing trialkylphosphines as catalysts for a variety of carbonylation reactions,[1–6] we have shown that diiodomethane can be doubly carbonylated to *e.g.* diethyl propanedioate (diethyl malonate) using $[Rh_2(O_2CMe)_4]$ in the presence or absence of PEt_3 in ethanol.[6] In the presence of PEt_3 the active species is believed to be $[Rh(O_2CMe)(CO)(PEt_3)_2]$[7] and it is plausible to assume that oxidative addition of diiodomethane occurs across the rhodium centre to give an iodomethyl complex. Further steps may include insertion of CO into the $M{-}CH_2I$ bond or further oxidative addition to give a bridging carbene. In this paper we report studies aimed at investigating the plausibility of oxidative addition of dihalogenoalkanes across a related rhodium(I) centre and investigations of the reactivity of the products towards CO and nucleophiles.

In addition, it has been reported that iodide promotes the formation of C_2 products, especially ethane-1,2-diol, during carbon monoxide hydrogenation reactions catalysed by ruthenium complexes[8] or mixed ruthenium–rhodium complexes.[9,10] The classical mechanism for C–C bond formation in both of these reactions involves insertion of CO into an $M{-}CH_2OH$ bond, but attempts to model this insertion using isolated complexes containing CO and hydroxymethyl ligands have not been successful, presumably because the electron-withdrawing OH group makes the C atom too δ^+.[11,12] Since it is known that hydroxymethyl complexes can react with I^- to give $M{-}CH_2I$,[13] it is possible that the role of the iodide promoter is to convert the hydroxymethyl intermediate into iodomethyl and that insertion of CO into the $M{-}CH_2I$ bond occurs more readily, iodide being less electron withdrawing than is OH.

No studies of insertion of CO into an $M{-}CH_2I$ bond appear to have been reported although bis(dibenzylideneacetone)palladium reacts with $P(C_6H_{11})_3$ followed by CH_2I_2 and CO to give ketene derivatives[14] and CO inserts into the $Co{-}CH_2Cl$ bond of $[Co(CH_2Cl)(CO)_3(PPh_3)]$ to give $[Co(COCH_2Cl)(CO)_3(PPh_3)]$.[15] The preparation and reactivity of halogenomethyl complexes of transition elements have recently been reviewed.[16]

Results

Reactions of trans-$[RhCl(CO)(PR_3)_2]$ *with Dihalogenoalkanes.*—(*i*) CH_2I_2. The complexes $[RhCl(CO)(PR_3)_2]$ react with CH_2I_2 in diethyl ether to give orange solutions from which orange crystalline products analysing as $[RhCl(I)(CH_2I)(CO)(PR_3)_2]$ can be isolated for R = Me or Et. For R_3 = Et_2Ph the oxidative-addition product was obtained after long reaction times as indicated by ^{31}P and ^1H NMR studies, but it could not be separated from small amounts of unidentified decomposition products. For R_3 = Ph_2Et or Ph_3, no reaction was observed with an excess of CH_2I_2 even after prolonged stirring with a large excess of CH_2I_2.

The observed trend in reactivity could arise either from steric factors or because the larger number of phenyl rings on the phosphine renders the rhodium centre less electron rich and hence less reactive towards oxidative addition. To test this the reaction of $[RhCl(CO)\{P(OMe)_3\}_2]$ with CH_2I_2 was examined since $P(OMe)_3$ is known to be more electron withdrawing than is PPh_3, but has a smaller cone angle than that of PEt_3.[17] No reaction was observed, confirming that the oxidative-addition reaction is largely controlled by electronic factors. Steric

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: atm = 101 325 Pa.

Table 1 Spectroscopic parameters for new rhodium complexes at 298 K[a]

	^{31}P		^{1}H						
Complex	δ	J(P–H)	δ[b]	J(H–Ph)	J(H–P)	δ[c]	δ[d]	J(H–H)	$\tilde{\nu}$(C≡O)/cm^{-1}
$[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$[e]	9.8	80	3.3	2.2	4.3	2.1	0.9	9	2053
$[RhCl(I)(CH_2I)(CO)(PEt_2Ph)_2]$[e]	12.5	86	2.58	2.2	7.4	2.4, 2.8	0.9, 1.3	9	2087
$[RhCl(I)(CH_2I)(CO)(PMe_3)_2]$[e]	11.1	85	2.99	2.2	4.8		1.6[f]	4	2050
$[RhI_2(CH_2Cl)(CO)(PEt_3)_2]$ **A**[g]	2.7	80	4.35	2.7	6.4	2.3	1.1	9	2055
$[RhCl(I)(CH_2Cl)(CO)(PEt_3)_2]$ **B**[g]	11.3	82	4.32	2.9	6.0	2.3	1.3	9	
$[RhCl(I)(CH_2Cl)(CO)(PEt_3)_2]$ **C**[h]	17.2	80	4.05	2.8	6.1	2.2	1.3	9	
$[RhCl_2(CH_2Cl)(CO)(PEt_3)_2]$ **D**[h]	15.9	85	4.02	2.6	6.0	2.3	1.1	9	
$[RhClI_2(CO)(PEt_3)_2]$[h]	6.2	73	—			2.4	1.2	8	2057
$[RhI_3(CO)(PEt_3)_2]$[h]	−3.8	73	—			2.4	1.0	8	

[a] δ in ppm to high frequency of $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P), J in Hz. [b] CH_2X ligand, all resonances are dt. [c] PCH_2, complex multiplet. [d] PCH_2CH_3 (t). [e] In C_6D_6. [f] PCH_3. [g] In thf. [h] In CD_2Cl_2.

reactions can be important since CH_2I_2 is unreactive towards $[RhCl(CO)\{P(C_6H_{11})_3\}_2]$. Related studies have been carried out using $[IrCl(CO)(PR_3)_2]$ but interestingly, in this case, oxidative addition is observed for $R_3 = Me_3$, Me_2Ph or $MePh_2$.[18,19]

The complexes $[RhCl(I)(CH_2I)(CO)(PR_3)_2]$ all give a single doublet in the ^{31}P NMR spectrum indicating equivalent phosphines and a doublet of triplets near δ 3 in the ^1H NMR spectrum from the CH_2I group. In common with other iodomethyl complexes,[16] a characteristic resonance is observed from the CH_2I group at δ −7.4 (dt) in the ^{13}C NMR spectrum. The crystal structure of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ (see below) confirms that the phosphines are mutually *trans* and that the CH_2I group is *trans* to I, *i.e.* the *trans* addition product is obtained. Such *trans* additions are well established for oxidative additions of a variety of alkyl halides across rhodium(I) centres.[20]

(*ii*) *Other dihalogenoalkanes.* Despite the fact[21] that CH_2Cl_2 reacts readily with *e.g.* $[RhCl(PMe_3)_3]$ to give $[RhCl_2(CH_2Cl)(PMe_3)_3]$, we find that $[RhCl(CO)(PEt_3)_2]$ is unreactive towards CH_2Cl_2 under all conditions examined. Once again we attribute the lower reactivity of the carbonyl complex to electronic effects since CO, being a good π acceptor, will reduce the electron density on the metal and make it less reactive towards oxidative-addition reactions.

The complex $[RhCl(CO)(PEt_3)_2]$ does react with neat CH_2Br_2 but the mixture of products cannot be separated. Phosphorus-31 NMR studies on the mixture showed eight doublets and ^1H NMR studies showed four doublets of triplets at δ 4.47, 4.42, 4.17 and 4.13. It appears that a variety of different complexes has been formed by halide-scrambling reactions (see below). The resonances near δ 4.4 are attributed to chloromethyl complexes whilst those near δ 4.1 are attributed to bromomethyl complexes.

The complex $[RhCl(CO)(PEt_3)_2]$ also reacts with CH_2ICl to give a mixture of two complexes in low yield which could not be separated from unreacted starting material but could be spectroscopically characterised. As expected, both the products arise from activation of the C–I (not C–Cl) bond, as indicated by the appearance of doublets of triplets at δ 4.35 and 4.47 in the ^1H NMR spectrum. These arise from complexes with CH_2Cl *trans* to Cl and I respectively, the assignment being made on the basis that the compound with the resonance at δ 4.47 (4.05 in CD_2Cl_2) is also obtained from a halogen-scrambling reaction (see below). From the relative intensities of the CH_2 resonances in the ^1H NMR spectrum it is then possible to assign the doublets in the ^{31}P NMR spectrum as shown in Table 1. It seems that the relative stabilities of the *cis* and *trans* addition products are determined by steric factors; the bulky CH_2I group favours having the bulky I ligand *trans* whilst the less bulky CH_2Cl can accommodate the I ligand *cis* or *trans*. Curiously, for the related iridium complexes $[IrCl(I)(CH_2X)(CO)(PR_3)_2]$, *trans* products are always obtained except when $R_3 = Ph_2Me$, the most bulky ligand studied when both *cis* and *trans* products were obtained for X = Cl or I.[19]

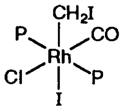
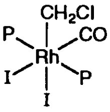
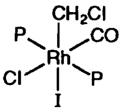
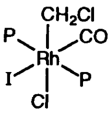
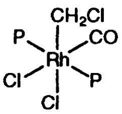
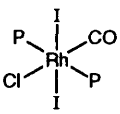
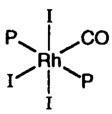
Reactions of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ *with Nucleophiles.*—As indicated above, we were interested in the relative reactivities of Rh–CH_2I or Rh–CH_2OR (R = H or Me) towards insertion of CO. Since it is known that M–CH_2I can react with water or alcohols to give M–CH_2OR,[16] we attempted these reactions.

On addition of water or methanol to solutions of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ in tetrahydrofuran (thf) or benzene the resonances from the CH_2I group were reduced in intensity and a new resonance appeared in the ^1H NMR spectrum at δ 4.35 (dt) (values quoted are for thf as solvent; small solvent shifts are observed). In addition, a new doublet resonance appeared in the ^{31}P NMR spectrum at δ 2.7 and a new doublet of triplets in the ^{13}C NMR at δ 35.2. The positions of these signals (compound **A**) were identical whether the reagent was water or methanol, although only partial conversion into **A** was observed. Fractional crystallisation of these solutions, or, more cleanly, recrystallisation of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ from methanol which gives **A** in higher yields, gave pure compound **A**. The NMR studies showed that, even if the reagent was methanol, there was no signal attributable to Rh–CH_2OMe and the compound had the same empirical formula as that of the starting material. These results together with other reactions described below allowed us to identify **A** as $[RhI_2(CH_2Cl)(CO)(PEt_3)_2]$, formed by exchange of halogens between the metal and the CH_2I ligand.

Allowing the solutions containing water or methanol to stand for longer periods results in higher conversion of the starting material and, in addition to **A**, a new compound **B** is formed with resonances at δ 11.3 (^{31}P), 4.32 (dt, ^1H) and 40.5 (dt, ^{13}C). This compound is identical to one of the products obtained from $[RhCl(CO)(PEt_3)_2]$ and CH_2ClI and we assign it to $[RhCl(I)(CH_2Cl)(CO)(PEt_3)_2]$ with I *trans* to CH_2Cl since this product would arise from direct attack of Cl^- on $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ without rearrangement of the halogen atoms around rhodium. Prolonged stirring in water leads to new ^{31}P NMR resonances at δ 6.2 and −3.8 which can be attributed (see later) to $[RhClI_2(CO)(PEt_3)_2]$ and $[RhI_3(CO)(PEt_3)_2]$ respectively.

Other studies also confirm that halide scrambling is facile in this system. Thus, although $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ is stable in C_6D_6 for up to 2 weeks, solutions in thf under nitrogen change over a period of 7 d to give **A** and **B** in approximately equal amounts. Dissolving $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ in CH_2Cl_2 also gives **A**. Adding an excess of $[NEt_3Ph]Cl$ to $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ in CH_2Cl_2 alters the products so that **A** is not observed but the major products are **B**–**D** with the NMR parameters shown in Table 1.

Table 2 Structures and amounts (%) of products obtained from various reactions of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$]

Solvent	t/d	Additive		 A	 B	 C	 D		
thf[a]	0.75	CH$_2$ICl			5	15			
[^{2}H$_8$]thf	0.04	Water	44	56					
C$_6$D$_6$	1	Water	6	52	27	5		8	2
[^{2}H$_8$]thf	0.04	MeOH	50	50					
[^{2}H$_8$]thf	b	MeOH	11	67	22				
[^{2}H$_8$]thf[c]	14	—	33	33	33				
MeOH	1	—		100					
MeOH	34	—	4	46	4			36	10
CD$_2$Cl$_2$	1	—	56	44					
CD$_2$Cl$_2$	1	[NEt$_3$Ph]Cl	35		15	31	19		
CD$_2$Cl$_2$[d]	0.01	CO[e]	5	32	33	3		12	10
CD$_2$Cl$_2$[f]	0.04	CO[e]		2	13	6		64	9
CD$_2$Cl$_2$[g]	0.01	ICH$_2$COCl						67	21

[a] Starting material: [RhCl(CO)(PEt$_3$)$_2$]. [b] Solid isolated by crystallisation after several days. [c] Small amounts of other products not containing CH$_2$X are observed and may help to explain the halide mass imbalance. [d] Other ^{31}P NMR resonances observed at δ 8.8 (3) and 1.0 (2%). [e] 70 atm, times are heating times (100 °C); spectra were recorded at ambient temperature. [f] Other ^{31}P NMR resonances observed at δ 14.63(3), 8.8 (1) and 2.6 (3%). [g] Starting material: [RhI(CO)(PEt$_3$)$_2$]. Other ^{31}P NMR resonances observed at δ 14.6 (5), 10.7 (4), 2.6 (2) and 1.8 (1%).

Compound **C** is identical to the second isomer obtained from the reaction of [RhCl(CO)(PEt$_3$)$_2$] with CH$_2$ICl so we assign it as [RhCl(I)(CH$_2$Cl)(CO)(PEt$_3$)$_2$] with Cl *trans* to CH$_2$Cl and, since compound **D** is also a chloromethyl complex (^{1}H δ 4.02) and is only formed if an excess of Cl$^-$ is present, we assign it as [RhCl$_2$(CH$_2$Cl)(CO)(PEt$_3$)$_2$]. Consistently, the amounts of **B**–**D**, all of which contain more Cl$^-$ and less I$^-$ than in the starting material, are increased if the reaction is carried out in the presence of an excess of Cl$^-$. The NMR parameters for **A**–**D** are collected in Table 1, whilst their assignments and the amounts produced from various reactions are collected in Table 2.

Halide scrambling has been observed by others, *e.g.* in the oxidative addition of CH$_2$ICl to [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] which gives all possible isomers of [PdY(CH$_2$X)(PPh$_3$)$_2$] (X, Y = Cl, I),[22] but the mechanism is not known. In our case, the fact that the reaction occurs much more readily in polar solvents or if polar solvents are added and that an excess of chloride can participate in the reaction suggests an ionic mechanism, although whether the CH$_2$I or the Rh–Cl bond breaks first cannot be determined directly.

Reactions of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$] *with* CO.—No reaction is observed between [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$] and CO at 1 atm in thf, C$_6$H$_6$ or CH$_2$Cl$_2$. Accordingly, we have studied this reaction under high pressures in a high-pressure infrared cell.

The IR spectrum (2500–1500 cm^{-1}) of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$] at room temperature in CH$_2$Cl$_2$ showed a single ν(C≡O) at 2057 cm^{-1} [Fig. 1(*a*)]. Under CO (70 atm) no change was observed until the sample was heated. At 80 °C new weak bands appeared at 2081, 2002 and 1665 cm^{-1} whilst the peak at 2057 shifted to 2060 cm^{-1}. Further heating to 100 °C resulted in an increase in intensity of the new bands, the major peak was apparent as a doublet at 2057 and 2060 cm^{-1} and there were further new weak peaks at 2100, 1943, 1802 and 1706 cm^{-1} [Fig. 1(*b*)]. All of the new peaks except that at 1665 cm^{-1} increased in intensity on further standing at 100 °C for 1 h. When the solution was cooled to ambient temperature and flushed with N$_2$ the peak at 1665 cm^{-1} disappeared whilst the others remained. Very similar results were obtained in thf although other irreversible peaks at 1779 and 1772 cm^{-1} were also observed.

The peak at 1665 cm^{-1} is in the region expected for ν(C=O) of a Rh–C(O)CH$_2$I complex, *cf.* 1702 cm^{-1} for [Co{C(O)CH$_2$Cl}(CO)$_3$(PEt$_3$)].[15] The less electron-withdrawing nature of the rhodium centre is likely to lead to a lower ν(C=O) for [RhCl(I){C(O)CH$_2$I}(CO)(PEt$_3$)$_2$]. The removal of this absorption when the solution was flushed with nitrogen at room temperature is also consistent with its arising from an acyl species. The intensity of the absorption at 1665 cm^{-1} was lower than would be expected if all of the iodomethyl complex had been converted into acyl. We, therefore, studied the same system under CO in a high-pressure NMR cell (sapphire tube).

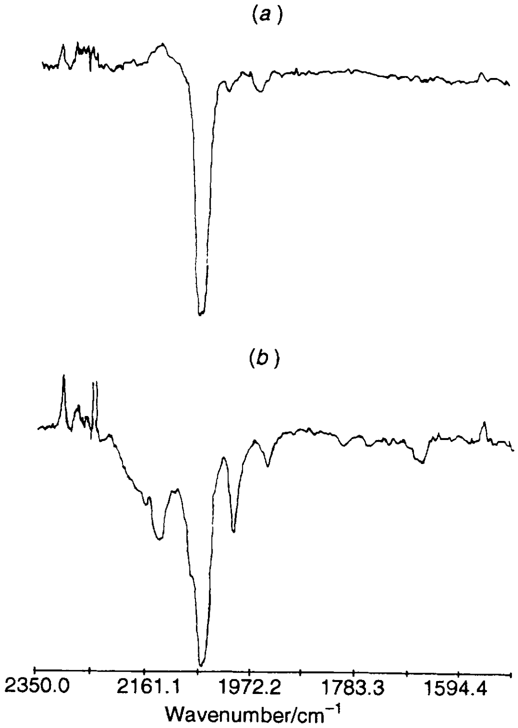


Fig. 1 The IR spectra of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$] in CH$_2$Cl$_2$ under CO (70 atm), (*a*) before heating, (*b*) after heating at 100 °C for 1 h

The ^{31}P NMR studies of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$] under CO (70 atm) after heating in CD$_2$Cl$_2$ to 100 °C show several resonances, most of which can be attributed to the products arising from halide scrambling (Table 2), as described above. These decrease in intensity and are replaced by resonances at δ 6.3 and −3.8, which we have shown in separate reactions can be attributed to $[RhClI_2(CO)(PEt_3)_2]$ and $[RhI_3(CO)(PEt_3)_2]$ respectively. In addition, there are small doublet resonances at δ 14.5, 8.8, 2.6 and near 32 (each 2–3%) which may possibly be attributable to $Rh(COCH_2I)$ complexes and new singlets in the ^1H NMR spectrum at δ 5.37, 5.0, 4.65 (CH_2ICl) and 3.0.

In order to gain more information on the possible formation of complexes containing $Rh(COCH_2I)$, we have carried out the reaction between $[RhI(CO)(PEt_3)_2]$ and ICH_2COCl, which should give a complex analogous to that which would be obtained from insertion of CO into the Rh–CH_2I bond of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$. In practice, the ^{31}P NMR spectrum obtained is similar to that obtained from the high-pressure NMR experiment, with the major products being $[RhClI_2(CO)(PEt_3)_2]$ and $[RhI_3(CO)(PEt_3)_2]$ (Table 2). A weak doublet is also observed at δ 14.6. In addition, resonances at δ 4.83 (dt), 4.49 (dt) and 3.9 (dt) attributable[23] to diketene are also observed in the ^1H NMR spectrum. This shows that complexes containing $RhC(O)CH_2I$ are unstable with respect to loss of ketene. The intensities of the diketene resonances are only about 20% of those that would be expected for 0.5 mol per mol of Rh present suggesting that other decomposition pathways or fates for the ketene formed must also be available. New singlets at δ 4.95, 3.6, 4.57, 3.82, 2.67, 2.20 and 2.10 are also observed in the ^1H NMR spectrum. These are all unidentified, although the peak at δ 3.82 may arise from cyclobutane-1,3-dione (lit.,[24] δ 3.86), which can also be a product from dimerisation of ketene.[25] In the studies of the reaction of CO with $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ we do not observe diketene or cyclobutane-1,3-dione as a product, either by IR or by ^1H NMR spectroscopy.[24,26] This may be because the reaction is carried out under high pressure of CO and at 100 °C, conditions where ketene may undergo reactions other than dimerisation. The only resonance that is present in the ^1H NMR spectrum of both the product from this reaction and that from the reaction of $[RhI(CO)(PEt_3)_2]$ with ICH_2COCl is at δ 4.95. It is possible that this arises from the $RhCOCH_2X$ group, but the small amount of this material present means that any assignment must be extremely tentative.

We conclude that under CO the first reaction of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ is scrambling of the halides to give Rh–CH_2Cl complexes; CO then inserts into the Rh–CH_2X bonds to give $Rh(CO)CH_2X$ which are unstable with respect to loss of ketene so that $[RhX_3(CO)(PEt_3)_2]$ are the major observed products. The ketene undergoes a variety of side reactions. It is possible that one isomer of $[RhX(X')(COCH_2X'')(CO)(PEt_3)_2]$ (X, X′, X″ = Cl or I) is stable [ν(C=O) at 1665 cm^{-1}, ^{31}P NMR doublet at δ 14.6 and ^1H NMR singlet at δ 4.95], but we are not able on the evidence available to identify which one this might be.

Crystal and Molecular Structure of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$.—The two symmetry-independent molecules, atoms Rh(1)–C(21) and Rh(31)–C(51) respectively, are almost identical in the first co-ordination sphere, with mutually *trans* phosphine ligands and CH_2I *trans* to I (Fig. 2). Atoms Rh(1), Cl(2), I(3), C(4), O(5) and C(6) are coplanar within 0.05 Å with I(7) 0.60 Å out of the plane; Rh(31), Cl(32), I(33), C(34), O(35) and C(36) are coplanar within 0.02 Å with I(37) 0.63 Å out of the plane.

The phosphine ligands are close to being mutually eclipsed when viewed down the P–Rh–P axis. In each ligand the three CH_2 groups form a plane parallel (6°) to the Rh(1), Cl(2), I(3), C(4), O(5), C(6) plane. Two CH_3 groups lie in this plane with the third perpendicular and away from the Rh atom. The major difference between the two independent molecules is in the arrangement of these CH_3 groups. In molecule 1 the perpendicular CH_3 group of each phosphine [C(10), C(19)] is attached to the CH_2 group which is closest to Cl(2) but in molecule 2 the perpendicular CH_3 groups [C(44), C(51)] are attached to those CH_2 groups close to I(33). Three of the phosphine ligands are arranged as clockwise propellers when viewed down the P–Rh axis, but the P(38) phosphine has C(39) anticlockwise and C(41) clockwise. Torsion angles about the P–C bonds are given in Table 4. The consequence of these conformational differences is that in molecule 1 Cl(2) and I(7) have no short intramolecular contacts but in molecule 2, Cl(32) is approached by C(47) (3.7 Å) and I(37) by C(49) (3.9 Å). This is associated with the change in the I(3)–Rh(1)–Cl(2) angle from 98.3(1)° in molecule 1 to 92.9(0)° in molecule 2.

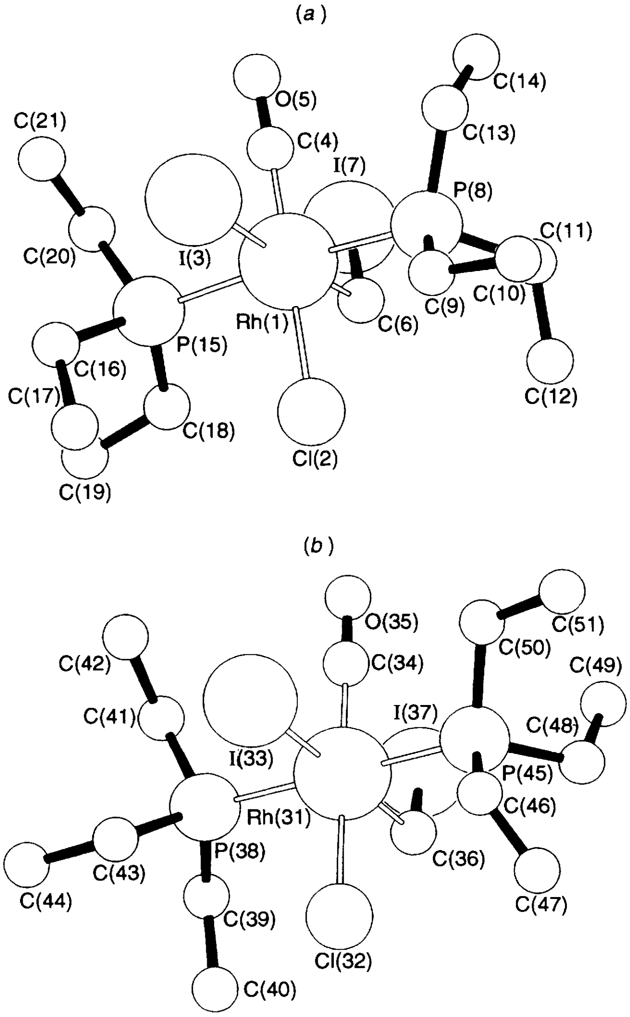


Fig. 2 Molecular structure and numbering scheme for two unrelated molecules in the crystal of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$

The C–I bond lengths are not significantly different [2.151(9) and 2.121(10) Å] and are similar to those observed for other iodomethyl complexes [2.10(3)–2.21(2) Å].[27–30] Other differences in bond lengths and angles are not significant and they are all in the ranges observed for other iodomethyl complexes. Examples are the Rh–C–I angles of 119.9(5) and 120.3(4)° and the Rh–C bond lengths of 2.080(6) and 2.063(9) Å, close to the sum of the covalent radii for Rh and sp^3-hybridised C (2.022 Å) but rather shorter than the Rh–C bond in $[RhCl(CH_2Cl)(Me_2PCH_2CH_2PMe_2)_2]Cl$ [2.161(2) Å].[21] The rather shorter Rh–C bond in $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ perhaps suggests a greater contribution from the carbenic resonance form **b** and may in part be responsible for the ready halogen exchange observed in this complex.

Table 3 Bond lengths (Å) and angles (°) for both crystallographic forms of [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$]

Cl(2)–Rh(1)	2.374(2)	I(3)–Rh(1)	2.803(1)	Cl(32)–Rh(31)	2.381(3)	I(33)–Rh(31)	2.765(1)
C(4)–Rh(1)	1.827(9)	C(6)–Rh(1)	2.063(9)	C(34)–Rh(31)	1.849(11)	C(36)–Rh(31)	2.080(6)
P(8)–Rh(1)	2.386(3)	P(15)–Rh(1)	2.393(3)	P(38)–Rh(31)	2.378(2)	P(45)–Rh(31)	2.398(2)
O(5)–C(4)	1.140(11)	I(7)–C(6)	2.121(10)	O(35)–C(34)	1.099(14)	I(37)–C(36)	2.151(9)
C(9)–P(8)	1.834(10)	C(11)–P(8)	1.824(8)	C(39)–P(38)	1.842(8)	C(41)–P(38)	1.828(14)
C(13)–P(8)	1.827(8)	C(10)–C(9)	1.502(18)	C(43)–P(38)	1.817(8)	C(40)–C(39)	1.498(20)
C(12)–C(11)	1.508(14)	C(14)–C(13)	1.493(12)	C(42)–C(41)	1.546(15)	C(44)–C(43)	1.528(14)
C(16)–P(15)	1.829(6)	C(18)–P(15)	1.829(10)	C(46)–P(45)	1.827(12)	C(48)–P(45)	1.795(7)
C(20)–P(15)	1.849(12)	C(17)–C(16)	1.535(14)	C(50)–P(45)	1.815(12)	C(47)–C(46)	1.464(22)
C(19)–C(18)	1.494(16)	C(21)–C(20)	1.494(17)	C(49)–C(48)	1.567(16)	C(51)–C(50)	1.526(14)
I(3)–Rh(1)–Cl(2)	98.3(1)	C(4)–Rh(1)–Cl(2)	179.4(3)	C(34)–Rh(31)–Cl(32)	178.6(2)	C(34)–Rh(31)–I(33)	88.5(2)
C(4)–Rh(1)–I(3)	82.2(3)	C(6)–Rh(1)–Cl(2)	84.5(2)	C(36)–Rh(31)–Cl(32)	84.5(3)	C(36)–Rh(31)–I(33)	177.2(3)
C(6)–Rh(1)–I(3)	176.7(2)	C(6)–Rh(1)–C(4)	95.0(4)	C(36)–Rh(31)–C(34)	94.1(3)	P(38)–Rh(31)–Cl(32)	88.1(1)
P(8)–Rh(1)–Cl(2)	87.4(1)	P(8)–Rh(1)–I(3)	87.7(1)	P(38)–Rh(31)–I(33)	91.0(0)	P(38)–Rh(31)–C(34)	92.0(3)
P(8)–Rh(1)–C(4)	92.9(3)	P(8)–Rh(1)–C(6)	90.7(3)	P(38)–Rh(31)–C(36)	90.1(2)	P(45)–Rh(31)–Cl(32)	90.5(1)
P(15)–Rh(1)–Cl(2)	87.3(1)	P(15)–Rh(1)–I(3)	91.4(1)	P(45)–Rh(31)–I(33)	85.3(0)	P(45)–Rh(31)–C(34)	89.5(3)
P(15)–Rh(1)–C(4)	92.5(3)	P(15)–Rh(1)–C(6)	90.5(3)	P(45)–Rh(31)–C(36)	93.6(2)	P(45)–Rh(31)–P(38)	176.0(1)
P(15)–Rh(1)–P(8)	174.4(1)	O(5)–C(4)–Rh(1)	177.8(7)	O(35)–C(34)–Rh(31)	179.6(5)	I(37)–C(36)–Rh(31)	119.9(5)
I(7)–C(6)–Rh(1)	120.3(4)	C(9)–P(8)–Rh(1)	112.4(3)	C(39)–P(38)–Rh(31)	117.5(3)	C(41)–P(38)–Rh(31)	113.1(4)
C(11)–P(8)–Rh(1)	117.5(4)	C(11)–P(8)–C(9)	103.9(5)	C(41)–P(38)–C(39)	100.6(5)	C(43)–P(38)–Rh(31)	113.8(3)
C(13)–P(8)–Rh(1)	113.8(4)	C(13)–P(8)–C(9)	105.7(5)	C(43)–P(38)–C(39)	103.2(5)	C(43)–P(38)–C(41)	107.2(4)
C(13)–P(8)–C(11)	102.2(4)	C(10)–C(9)–P(8)	117.2(5)	C(40)–C(39)–P(38)	117.5(7)	C(42)–C(41)–P(38)	115.6(8)
C(12)–C(11)–P(8)	114.7(5)	C(14)–C(13)–P(8)	116.8(7)	C(44)–C(43)–P(38)	115.2(6)	C(46)–P(45)–Rh(31)	113.2(4)
C(16)–P(15)–Rh(1)	117.5(4)	C(18)–P(15)–Rh(1)	112.2(3)	C(48)–P(45)–Rh(31)	118.0(3)	C(48)–P(45)–C(46)	104.4(5)
C(18)–P(15)–C(16)	105.2(4)	C(20)–P(15)–Rh(1)	115.5(3)	C(50)–P(45)–Rh(31)	112.0(3)	C(50)–P(45)–C(46)	104.8(5)
C(20)–P(15)–C(16)	102.3(4)	C(20)–P(15)–C(18)	102.5(5)	C(50)–P(45)–C(48)	103.0(5)	C(47)–C(46)–P(45)	115.7(7)
C(17)–C(16)–P(15)	116.1(6)	C(19)–C(18)–P(15)	118.4(7)	C(49)–C(48)–P(45)	113.8(7)	C(51)–C(50)–P(45)	117.6(8)
C(21)–C(20)–P(15)	113.3(10)	I(33)–Rh(31)–Cl(32)	92.9(0)				

Table 4 Selected torsion angles (°) for [RhCl(I)(CH$_2$I)(CO)(PEt$_3$)$_2$]

Rh(1)–P(8)–C(9)–C(10)	176.2
Rh(1)–P(8)–C(11)–C(12)	−70.6
Rh(1)–P(8)–C(13)–C(14)	−76.6
Rh(1)–P(15)–C(16)–C(17)	−63.2
Rh(1)–P(15)–C(18)–C(19)	168.9
Rh(1)–P(15)–C(20)–C(21)	−76.3
Rh(31)–P(38)–C(39)–C(40)	72.4
Rh(31)–P(38)–C(41)–C(42)	−70.3
Rh(31)–P(38)–C(43)–C(44)	−178.0
Rh(31)–P(45)–C(46)–C(47)	101.2
Rh(31)–P(45)–C(48)–C(49)	68.1
Rh(31)–P(45)–C(50)–C(51)	170.4

Conclusion

We conclude that CH$_2$I$_2$ (or CH$_2$ICl) can readily be oxidatively added to electron-deficient rhodium centres to give iodomethyl (or chloromethyl) complexes. In polar solvents the iodomethyl complexes exchange iodide with chloride co-ordinated to the metal to give various different chloromethyl complexes *via* an ionic mechanism. Under CO the major reaction is halide scrambling but there is some evidence for insertion of CO into the M–CH$_2$X (X = Cl or I) bond to give products which are unstable with respect to the formation of [RhXI$_2$(CO)(PEt$_3$)$_2$] (X = Cl or I).

Experimental

Microanalyses were by the University of St. Andrews Materials Analysis service. The NMR spectra were recorded on a Brüker Associates AM300 spectrometer operating in the Fourier-transform mode with, for ^{13}C and ^{31}P, noise proton decoupling, IR spectra on a Perkin-Elmer 1710 FTIR spectrometer (4000–400 cm^{-1}) as Nujol mulls between CsI plates unless otherwise stated.

All solvents were thoroughly dried by distillation from sodium diphenylketyl [thf, Et$_2$O, toluene, light petroleum (b.p. 40–60 °C)], magnesium methoxide (methanol) or CaH$_2$ (CH$_2$Cl$_2$). All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-line and catheter-tubing techniques. The compounds RhCl$_3$·3H$_2$O (Johnson Matthey), CH$_2$I$_2$, CH$_2$Br$_2$, PMe$_3$ (Aldrich), CH$_2$ICl (Fluka), ICH$_2$COCl (Aldrich), PEt$_3$ and P(C$_6$H$_{11}$)$_3$ (Strem) were reagent grade and were used as supplied; [RhCl(CO)(PPh$_3$)$_2$][31] and [{RhCl(C$_8$H$_{14}$)$_2$}$_2$][32] were prepared by published methods.

The complexes [RhCl(CO)(PR$_3$)$_2$] [R$_3$ = Me$_3$, Et$_3$, Et$_2$Ph, EtPh$_2$, (C$_6$H$_{11}$)$_3$ or (OMe)$_3$] were prepared as follows: [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] (2.0 g) was stirred in light petroleum (30 cm^3) with PR$_3$ (1.7 cm^3) under argon for 20 h. The solvent was removed *in vacuo* and the product dissolved in diethyl ether (20 cm^3). Carbon monoxide was bubbled through the solution for 5 min during which time it changed from orange-red to pale yellow. The solution was reduced in volume to 4 cm^3 and then held at −30 °C for 18 h. The product was filtered off cold (−50 °C), washed with cold diethyl ether (2 cm^3) and dried *in vacuo*. Yields were of the order of 85% and the compounds were characterised by comparison of their IR, ^{1}H and ^{31}P NMR data with literature values.[33–35]

Carbonylchloroiodo(iodomethyl)bis(triethylphosphine)rhodium(III).—Diiodomethane (1.0 g, 3.8 mmol) in diethyl ether (5 cm^3) was added to a solution of [RhCl(CO)(PEt$_3$)$_2$] (0.75 g, 1.9 mmol) in diethyl ether (30 cm^3). After stirring in the dark for 18 h at room temperature the solvent was evaporated under vacuum to 5 cm^3 and light petroleum (5 cm^3) added with vigorous stirring. After cooling to −20 °C for 48 h orange crystals separated. These were filtered off, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield 0.84 g, 67% (Found: C, 25.4; H, 5.2. C$_{14}$H$_{32}$ClI$_2$OP$_2$Rh requires C, 25.1; H, 4.8%). ^{13}C NMR: δ 187.1 [dt, *J*(C–Rh) = 64, *J*(C–P) = 10.0, RhCO], 17.1 (m, RhP*C*H$_2$CH$_3$), 8.3 (s, RhPCH$_2$*C*H$_3$) and −7.2 [dt, *J*(C–Rh) = 27.6, *J*(C–P) = 5.0 Hz, RhCH$_2$I]. Similarly prepared were: *carbonylchloroiodo(iodomethyl)bis(trimethylphosphine)rhodium*(II) from [RhCl(CO)(PMe$_3$)$_2$] (0.2 g, 0.6 mmol) in thf (30 cm^3) and CH$_2$I$_2$ (0.33 g, 1.2 mmol) in thf (10 cm^3), yield 0.2 g (57%) (Found: C, 16.7; H, 3.5. C$_8$H$_{20}$ClI$_2$OP$_2$Rh requires C, 16.4; H, 3.4%) and *carbonylchlorobis(diethylphenylphosphine)iodo(iodomethyl)rhodium*(III) from [RhCl(CO)(PEt$_2$Ph)$_2$] (1 g, 2.1 mmol) in thf (30 cm^3)

and CH_2I_2 (1.1 g, 4.2 mmol) in thf ($10\ cm^3$) over 72 h, yield 0.8 g (50%). The latter complex could not be separated from small amounts of starting material and decomposition products but accounted for 70% of the product (^{31}P NMR data).

Similar reactions using $[RhCl(CO)(PR_3)_2]$ [$R_3 = EtPh_2$, Ph_3, $(C_6H_{11})_3$ or $P(OMe)_3$] were unsuccessful with only starting materials being recovered.

Reactions of $[RhCl(CO)(PEt_3)_2]$.—*With* CH_2Br_2. The complex $[RhCl(CO)(PEt_3)_2]$ (0.2 g, 0.5 mmol) was dissolved in CH_2Br_2 ($5\ cm^3$) and the resulting solution stirred at room temperature for 18 h. Diethyl ether ($20\ cm^3$) was added with vigorous stirring and the resulting yellow precipitate was collected, washed with diethyl ether ($2 \times 10\ cm^3$) and dried *in vacuo*. It was identified as a mixture of chloromethyl and bromomethyl species (see text).

With CH_2ICl. Chloroiodomethane (0.18 g, 1.0 mmol) in thf ($10\ cm^3$) was added to $[RhCl(CO)(PEt_3)_2]$ (0.2 g, 0.5 mmol) in thf ($10\ cm^3$). After stirring at room temperature for 18 h the solvent was removed *in vacuo* to yield a yellow oil. This was shown by ^{31}P and ^1H NMR spectroscopy (see text) to consist of $[RhCl(CO)(PEt_3)_2]$ (75%), $[RhI(CO)(PEt_3)_2]$ (5%) and $[RhCl(I)(CH_2Cl)(CO)(PEt_3)_2]$ [CH_2Cl *trans* to I (5%) and *trans* to Cl (15%)].

Carbonylchlorodiiodobis(triethylphosphine)rhodium(III).—The complex $[RhCl(CO)(PEt_3)_2]$ (0.25 g, 0.62 mmol) and iodine (0.016 g, 0.062 mmol) were stirred in CH_2Cl_2 ($40\ cm^3$) for 2 h. The solution was evaporated to $5\ cm^3$ and allowed to stand at −20 °C for 2 weeks. The brown crystals were collected and any excess of iodine and residual solvents were sublimed from them *in vacuo* (Found: C, 22.9; H, 4.1. $C_{13}H_{30}ClI_2OP_2Rh$ requires C, 23.8; H, 4.6%).

Reactions of $[RhI(CO)(PEt_3)_2]$.—*With* I_2. The complex $[RhI(CO)(PEt_3)_2]$ (0.11 g) was treated with an excess of I_2 (0.15 g) in CD_2Cl_2 ($0.9\ cm^3$). The ^{31}P NMR studies showed partial conversion into a product giving a doublet at δ −3.8 [J(P–Rh) = 73 Hz]. This was identified as a rhodium(III) complex from the low value of J(P–Rh) and as $[RhI_3(CO)(PEt_3)_2]$ on the basis of its synthetic method.

With ICH_2COCl. The complex $[RhI(CO)(PEt_3)_2]$ (0.10 g) in CD_2Cl_2 ($0.7\ cm^3$) was treated with ICH_2COCl ($0.1\ cm^3$) at room temperature or −60 °C. The ^{31}P NMR studies at the appropriate temperature showed the major products to be $[RhClI_2(CO)(PEt_3)_2]$ and $[RhI_3(CO)(PEt_3)_2]$ (see Table 2). In addition there were small amounts of other products (Table 2). Proton NMR studies showed the presence of diketene and several other resonances (see text). At −60 °C, the relative intensity of the ^{31}P NMR signals at δ 14.6 was greater than at room temperature.

Reactions of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ *with Nucleophiles.*—A saturated solution of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ was prepared in an appropriate solvent (C_6D_6, CD_2Cl_2 or $[^2H_8]$thf, $1\ cm^3$). It was placed in an NMR tube and its ^1H NMR spectrum recorded. The appropriate reagent, MeOH, water (50 μl), $[NEt_3Ph]Cl$ (0.01 g), NaOMe (0.015 g) in methanol (50 μl), NaOEt (0.01 g) in ethanol (50 μl) or NaOH ($1\ mol\ dm^{-3}$) in water (50 μl), was added under N_2 and the solutions left to stand in the dark. The NMR spectra (^1H, ^{13}C and ^{31}P) were recorded after 4 and 24 h and after a variety of time intervals subsequently. Precipitation with an excess of diethyl ether of solutions in $[^2H_8]$thf after reaction with water or methanol produced pure *carbonyl(chloromethyl)diiodobis(triethylphosphine)rhodium*(III) (isomer **A**) [Found: (from MeOH) C, 25.5; H, 4.6. (from water) C, 26.3; H, 5.1. $C_{14}H_{32}ClI_2OP_2Rh$ requires C, 25.1; H, 4.8%]. This compound was prepared more cleanly as follows: $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ (0.1 g) was stirred in methanol ($20\ cm^3$) in the dark for 4 h. The methanol was removed in the dark and the resulting orange solid was dried *in vacuo*. The NMR studies showed it to be the complex in an essentially pure state: ^{13}C, δ 181.8 [dt, J(C–Rh) = 90, J(C–P) = 13.4, RhCO], 21.3 (m, $RhPCH_2CH_3$), 10.7 (s, $RhPCH_2CH_3$) and 35.2 [dt, J(C–Rh) = 25.5, J(C–P) = 4.7 Hz, $RhCH_2Cl$]. For isomer **B**; δ 40.5 [dt, J(C–Rh) = 28, J(C–P) = 5 Hz, $RhCH_2Cl$].

High-pressure Infrared Studies.—The cell used has been previously described.[36] The complex $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ (0.3 g) in CH_2Cl_2 or thf ($15\ cm^3$) was injected into the cell which had previously been flushed with N_2. The cell was sealed and an IR spectrum recorded; N_2 was replaced with CO (70 atm). The cell was then heated to 100 °C and the IR spectrum recorded after various time intervals. When the high-temperature experiments were concluded the cell was cooled to room temperature, the IR spectrum measured, the CO vented and the cell flushed with N_2 before the final IR spectrum was recorded.

High-pressure NMR Studies.—A sapphire NMR tube (5 mm outside diameter) connected to a suitable adaptor was flushed with N_2 and charged with a saturated solution of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ in CH_2Cl_2 ($1.0\ cm^3$). The ^{31}P and ^1H NMR spectra were recorded. The tube was then charged with CO (70 atm) and heated to 100 °C (water-bath) for 15 min. It was then cooled and the ^{31}P NMR spectrum recorded. Further ^{31}P, ^1H and ^{13}C NMR spectra were recorded after heating for 30 min. The results are collected in Table 2.

Crystallography.—Orange crystals of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ were obtained by recrystallisation of the complex from diethyl ether–light petroleum. The solution was kept at room temperature (and in the dark) during dissolution and filtration, then cooled to −20 °C for 48 h. The crystals were filtered whilst cold, then washed with light petroleum at −78 °C and dried *in vacuo*. They were stable indefinitely under N_2, and it was possible to handle them briefly in air without apparent decomposition.

A crystal measuring 0.92 × 0.2 × 0.32 mm was sealed in a Lindemann glass capillary. Cell dimensions were refined from 25 carefully centred reflections ($8 < \theta < 13°$) using an Enraf–Nonius CAD4 diffractometer (SERC service at Cardiff). 8666 Measured reflections yielded 7897 unique data, of which 6547 with $F > 3\sigma_F$ were used in the refinement.

Data were collected in the range $1.5 < \theta < 25°$ for index limits $0 < h < 14$, $-17 < k < 17$, $-18 < l < 18$, and corrected for absorption by ψ scans on the diffractometer (maximum and minimum transmission factors 0.92, 0.74).

Crystal data. $C_{14}H_{32}ClI_2OP_2Rh$, $M = 670.52$, triclinic, space group $P\bar{1}$, $a = 12.343(3)$, $b = 14.327(2)$, $c = 15.426(2)$ Å, $\alpha = 113.78(1)$, $\beta = 67.25(1)$, $\gamma = 90.20(1)°$, $U = 2264.2$ Å^3, $Z = 4$, $D_c = 1.967\ Mg\ m^{-3}$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 8.37\ cm^{-1}$, $F(000) = 897.95$, $T = 293$ K.

The structure was solved by the use of direct methods, employing the SHELXS 86 program.[37] Density calculation indicated two independent molecules in the asymmetric unit. This was confirmed by the E map. Refinement by least-squares and Fourier-difference map techniques used the SHELX 76 program.[38] Molecular geometry calculations used XANADU,[39] and drawings were prepared with PLUTON.[40] Hydrogen atoms were placed on calculated positions with isotropic thermal parameters refined in batches.

Final refinement. Function minimised $\Sigma w(|F_o| - |F_c|)^2$, 386 refined parameters, $R = 0.0453$, $R' = 0.0668$, $w = 2.1508/[\sigma^2(F) + 0.000\,497F^2]$, mean shift/e.s.d. = 0.0005, maximum shift/e.s.d. = +0.0104. Maximum peaks on final difference map = 0.30 and −0.12 e Å^{-3}.

Full bond lengths and angles are collected in Table 3, torsion angles about the P–C bonds in Table 4 and atomic coordinates in Table 5.

Table 5 Coordinates (× 10^4) for non-hydrogen atoms of both forms of $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	1 037(1)	1 521(1)	2 303(1)	Rh(31)	3 824(1)	3 429(1)	7 338(1)
Cl(2)	493(2)	65(1)	1 222(2)	Cl(32)	3 127(2)	3 999(2)	6 363(2)
I(3)	2 858(1)	1 846(1)	727(1)	I(33)	5 685(1)	1 986(1)	5 564(1)
C(4)	1 449(7)	2 639(6)	3 145(7)	C(34)	4 338(7)	3 011(5)	8 125(6)
O(5)	1 743(6)	3 326(5)	3 645(5)	O(35)	4 644(6)	2 757(5)	8 589(5)
C(6)	−324(7)	1 373(7)	3 515(6)	C(36)	2 424(7)	4 554(6)	8 632(6)
I(7)	−372(1)	2 034(1)	5 035(1)	I(37)	1 747(1)	4 464(1)	10 102(1)
P(8)	−341(2)	2 584(1)	2 193(1)	P(38)	2 524(2)	2 200(1)	7 226(1)
C(9)	−169(8)	2 171(6)	849(6)	C(39)	907(7)	2 705(7)	7 868(7)
C(10)	−1 039(9)	2 742(7)	690(8)	C(40)	411(9)	3 191(8)	7 370(9)
C(11)	−1 929(7)	2 654(6)	2 924(7)	C(41)	2 605(9)	1 389(7)	7 867(8)
C(12)	−2 397(9)	1 675(8)	2 499(9)	C(42)	3 772(11)	590(7)	7 319(10)
C(13)	−200(8)	3 950(5)	2 667(7)	C(43)	2 777(8)	1 334(6)	5 896(6)
C(14)	−709(9)	4 579(7)	3 824(7)	C(44)	1 930(9)	557(6)	5 795(7)
P(15)	2 414(2)	320(1)	2 267(1)	P(45)	5 220(2)	4 597(1)	7 323(1)
C(16)	3 710(7)	−417(7)	1 029(6)	C(46)	5 779(9)	4 799(8)	6 140(7)
C(17)	3 441(9)	−1 154(7)	119(7)	C(47)	5 230(16)	5 763(10)	6 242(11)
C(18)	1 694(7)	−654(6)	2 653(7)	C(48)	4 738(8)	5 883(6)	8 372(7)
C(19)	2 468(10)	−1 566(8)	2 486(9)	C(49)	4 522(11)	5 919(8)	9 456(7)
C(20)	3 111(8)	886(7)	3 185(8)	C(50)	6 545(8)	4 116(6)	7 369(8)
C(21)	4 077(10)	1 455(10)	2 832(11)	C(51)	7 530(8)	4 766(7)	7 324(9)

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom coordinates and thermal parameters.

Acknowledgements

We thank Dr. B. E. Mann (Sheffield) for the loan of the high-pressure NMR tube, Professor M. B. Hursthouse (Cardiff) for the crystallographic data set under the auspices of the SERC service, the SERC, Royal Society and ICI for an Industrial Fellowship (to R. W.), BP Chemicals, BP Research International and the SERC for studentships (to R. C. G. and M. C. S.) and Johnson Matthey plc for generous loans of rhodium salts.

References

1 J. K. MacDougall and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1990, 165.
2 J. K. MacDougall and D. J. Cole-Hamilton, *Polyhedron*, 1990, **9**, 1235.
3 J. K. MacDougall, M. C. Simpson and D. J. Cole-Hamilton, *Polyhedron*, 1993, **12**, 2877.
4 M. C. Simpson, K. Porteous, J. K. MacDougall and D. J. Cole-Hamilton, *Polyhedron*, 1993, **12**, 2883.
5 J. K. MacDougall, M. C. Simpson and D. J. Cole-Hamilton, unpublished work.
6 W. S. Weston, R. C. Gash and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1994, 745.
7 W. Weston and D. J. Cole-Hamilton, unpublished work.
8 B. D. Dombek, *J. Organomet. Chem.*, 1983, **250**, 467.
9 B. D. Dombek, *Organometallics*, 1985, **4**, 1707.
10 J. K. Knifton, *J. Chem. Soc., Chem. Commun.*, 1983, 729.
11 Y. C. Lin, D. Milstein and S. S. Wreford, *Organometallics*, 1983, **2**, 1461.
12 G. O. Nelson, *Organometallics*, 1983, **2**, 1474.
13 A. Stasunik, D. R. Wilson and W. Malisch, *J. Organomet. Chem.*, 1986, **306**, C41.
14 M. Huser, M.-T. Youinou and J. A. Osborn, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1386.
15 V. Galamb, G. Palyi, R. Boese and G. Schmid, *Organometallics*, 1987, **6**, 861.
16 H. B. Friedrich and J. R. Moss, *Adv. Organomet. Chem.*, 1991, **33**, 235.
17 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
18 J. A. Labinger, J. A. Osborn and N. J. Colville, *Inorg. Chem.*, 1980, **19**, 3236.
19 M. A. Bennett and G. T. Crisp, *Aust. J. Chem.*, 1986, **39**, 1363.
20 R. S. Dickson, *Organometallic Chemistry of Rhodium and Iridium*, Academic Press, London, 1983 and refs. therein.
21 T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.
22 Z. Y. Yang and G. B. Young, *J. Chem. Soc., Dalton Trans.*, 1984, 2019.
23 C. J. Pouchert and J. Behnke, Aldrich Library of ^{13}C and ^1H FT NMR spectra, Aldrich Chemical Co., 1993, vol. 1, 1124C.
24 H. H. Wasserman, J. U. Piper and E. V. Dehmlow, *J. Org. Chem.*, 1973, **38**, 1451.
25 *Dictionary of Organic Compounds*, 5th edn., Chapman and Hall, New York, 1982, p. 3508.
26 F. A. Miller and S. D. Koch, *J. Am. Chem. Soc.*, 1948, **70**, 1890.
27 H. Berke, R. Birk, G. Huttner and L. Zsolnai, *Z. Naturforsch., Teil B*, 1984, **39**, 1380.
28 J. L. Hubbard and W. K. McVicar, *Organometallics*, 1990, **9**, 2683.
29 M. A. Ciriano, F. Viguri, L. A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 444.
30 N. J. Kermode, M. F. Lappert, D. W. Skelton, A. H. White and J. Holton, *J. Chem. Soc., Chem. Commun.*, 1981, 698.
31 D. F. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.
32 A. van der Ent and A. L. Onderderlinden, *Inorg. Synth.*, 1973, **14**, 92.
33 B. E. Mann, C. Masters and B. L. Shaw, *J. Chem. Soc. A*, 1971, 1104.
34 T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada and M. Tanaka, *J. Am. Chem. Soc.*, 1990, **112**, 7221.
35 F. G. Moers, *J. Inorg. Nucl. Chem.*, 1973, **35**, 1915.
36 R. Whyman, K. A. Hunt, R. W. Page and S. Rigby, *J. Phys. E, Sci. Instrum.*, 1984, **17**, 559.
37 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
38 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
39 P. Roberts and G. M. Sheldrick, XANADU, University of Cambridge, 1975.
40 A. L. Spek, PLUTON 92, University of Utrecht, 1992.

Received 7th February 1994; *Paper* 4/00727A