Oxidative Addition Reactions of *trans*-Halogenodicarbonyl(triphenylphosphine)rhodium Complexes

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The new complex *trans*-[RhCl(CO)$_2$(PPh$_3$)] (I), obtained by chlorine-bridge splitting of [Rh(CO)$_2$Cl]$_2$ with PPh$_3$, undergoes a series of oxidative additions with such molecules X–Y as halogens, Ph–I, and Cl–CO$_2$Et to give adducts of the type [RhXYCl(CO)$_2$(PPh$_3$)]. The addition of hydrogen chloride in dichloromethane affords [RhCl$_3$(CO)$_2$(PPh$_3$)]. Acetyl chloride in the same solvent adds on (I) to give [RhCl$_2$(CO)(COMe)(PPh$_3$).0·5CH$_2$Cl$_2$]. Addition of methyl iodide involves rearrangement of the methyl-rhodium(III) adduct to the acetyl-rhodium complex [RhClI(CO)(COMe)(PPh$_3$)], which is presumably five-co-ordinate. The product of the addition of ethyl chloroformate to (I), [RhCl$_2$(CO)$_2$(CO$_2$Et)(PPh$_3$)], reacts with dry HCl in chloroform to give the labile cation [RhCl$_2$(CO)$_3$-(PPh$_3$)]$^+$ which is converted into the neutral [RhCl$_3$(CO)$_2$(PPh$_3$)] on standing in solution with evolution of carbon monoxide. Complex (I) undergoes metathesis of the halogen to give *trans*-[RhX(CO)$_2$(PPh$_3$)](X = Br and I). The latter reacts with bromine or iodine to give [RhX$_3$(CO)$_2$(PPh$_3$)] (X = Br and I). Near- and far-i.r. data are discussed.

WE described[1] the preparation of the new complex *trans*-[RhCl(CO)$_2$(PPh$_3$)] (I) and its reactions with electronegatively substituted olefins. Its high reactivity prompted us to study its chemical versatility (oxidative additions, activation of small molecules, *etc.*) to compare it with similar complexes of Rh^I and Ir^I.

The halogen bridge in rhodium carbonyl chloride dimer, [Rh(CO)$_2$Cl]$_2$, is readily split by amines to give mononuclear amine complexes of the type *cis*-[RhCl(CO)$_2$(amine)].[2] Analogous complexes have been

carbonyl stretching band at 1980 cm.$^{-1}$ (Table 2), consistent with the presence of *trans*-terminal carbonyl groups. Its far-i.r. spectrum shows ν(Rh–Cl) at 298 cm.$^{-1}$, in agreement with a chloride *trans* to a tertiary arylphosphine in a Rh^I complex.[7]

We now find that when the reaction leading to (I) is carried out at −10° in low-boiling light petroleum, a red solid is deposited at first. On standing at room temperature for a few minutes this turns to an orange-yellow product which is identified as (I). The i.r. spectrum of the red, labile product shows two equally

TABLE 1

Analyses and physical properties of complexes

Complex	Colour	Recrystn. solvent	Found (%)					Calc. (%)				
			C	H	Cl	Br	I	C	H	Cl	Br	I
trans-{RhCl(CO)$_2$[P(C$_6$H$_5$)$_3$]}	Orange-yellow	CHCl$_3$–pentane	52·8	3·1	7·6	—	—	52·6	3·3	7·8	—	—
trans-{RhBr(CO)$_2$[P(C$_6$H$_5$)$_3$]}	Orange	CH$_2$Cl$_2$–ether	47·6	2·8	—	16·2	—	47·9	3·0	—	15·9	—
trans-{RhI(CO)$_2$[P(C$_6$H$_5$)$_3$]}	Brown	CH$_2$Cl$_2$–pentane	43·1	2·2	—	—	23·7	43·8	2·8	—	—	23·2
RhCl$_3$(CO)$_2$[P(C$_6$H$_5$)$_3$]	Orange-yellow	CH$_2$Cl$_2$–pentane	45·1	3·1	20·6	—	—	45·5	2·9	20·2	—	—
RhBr$_3$(CO)$_2$[P(C$_6$H$_5$)$_3$]	Orange	CH$_2$Cl$_2$–CCl$_4$	36·5	2·6	—	35·9	—	36·3	2·3	—	36·3	—
RhI$_3$(CO)$_2$[P(C$_6$H$_5$)$_3$]	Dark-brown	CH$_2$Cl$_2$–CCl$_4$	29·3	1·7	—	—	48·0	29·9	1·9	—	—	47·5
RhClBr$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]	Orange	CH$_2$Cl$_2$–CCl$_4$	39·1	2·2	5·5	26·9	—	39·6	2·5	5·8	26·3	—
RhClI$_2$(CO)$_2$[P(C$_6$H$_5$)$_3$]	Brown	CH$_2$Cl$_2$–CCl$_4$	33·5	1·9	5·0	—	36·0	33·8	2·1	5·0	—	35·7
RhClI(CO)(COCH$_3$)[P(C$_6$H$_5$)$_3$]	Brown	CH$_2$Cl$_2$–pentane	42·0	3·1	6·0	—	20·9	42·1	3·0	5·9	—	21·2
RhCl$_2$(CO)(COCH$_3$)[P(C$_6$H$_5$)$_3$],0·5CH$_2$Cl$_2$	Pale yellow	CH$_2$Cl$_2$	46·6	3·4	19·6	—	—	46·9	3·5	19·4	—	—
RhClI(CO)$_2$(C$_6$H$_5$)[P(C$_6$H$_5$)$_3$]	Buff	CH$_2$Cl$_2$–ether	47·0	3·1	5·3	—	19·5	47·2	3·0	5·4	—	19·2
RhCl$_2$(CO)$_2$(CO$_2$C$_2$H$_5$)[P(C$_6$H$_5$)$_3$]	Pale yellow	CH$_2$Cl$_2$–C$_6$H$_6$	48·7	3·8	12·9	—	—	48·8	3·6	12·6	—	—

obtained by bridge splitting with enimines.[3] By contrast, four moles of tertiary phosphines, arsines, or stibines react easily with one mole of rhodium carbonyl chloride to give mononuclear complexes of type *trans*-[RhCl(CO)L$_2$].[4–6] We found[1] that the reaction of two moles of triphenylphosphine and one mole of [Rh(CO)$_2$Cl]$_2$ in benzene or dichloromethane at room temperature gives unexpectedly the orange-yellow *trans*-[RhCl(CO)$_2$(PPh$_3$)]. Analyses and physical properties for this and other complexes are reported in Table 1. The i.r. spectrum of (I) shows a single terminal

intense, strong terminal carbonyl stretching bands (2082, 2019 cm.$^{-1}$) and ν(Rh–Cl) at 308 cm.$^{-1}$, suggesting that it may be the *cis*-[RhCl(CO)$_2$(PPh$_3$)] formed by direct halogen-bridge splitting of [Rh(CO)$_2$Cl]$_2$. The conditions required for carrying out the reaction leading to (I) are critical since even a small excess of PPh$_3$ reacts further with this complex to give [RhCl(CO)-(PPh$_3$)$_2$]. It appears, therefore, that the *trans*-dicarbonyl configuration is rather labile, though thermodynamically more stable than the *cis*-configuration.

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The chloride in (I) is easily replaced by bromide or iodide in acetone, the *trans*-configuration being retained. The resulting deeply coloured complexes *trans*-[RhX(CO)₂(PPh₃)], (II) (X = Br, I) have ν(CO) fairly close to that of (I). The iodide complex has a poorly resolved far-i.r. spectrum and ν(Rh–I) can only tentatively be located at 152 cm.⁻¹ (Table 2).

room temperature causes dissolution of the solid to give a solution from which [RhCl₃(CO)₂(PPh₃)] can be isolated quantitatively. An i.r. study of the reaction course shows that this is the only product formed at any stage of the addition, since the disappearance of the peak at 1980 cm.⁻¹ [ν(CO) of (I)] is accompanied by the concomitant appearance of only one peak at 2111 cm.⁻¹

TABLE 2

Selected i.r. bands (cm.⁻¹) of rhodium complexes [a]

Complex	$\nu(C{\equiv}O)$	$\nu(C{=}O)$	$\nu(Rh{-}Cl)$	$\nu(Rh{-}Br)$	$\nu(Rh{-}I)$	Other bands
trans-[RhCl(CO)₂(PPh₃)]	1980vs	—	298ms	—	—	266w, 255m, 234w, 227w, 212w
trans-[RhBr(CO)₂(PPh₃)]	1984vs	—	—	230m	—	262w, 257w, 205w, 170w
trans-[RhI(CO)₂(PPh₃)]	1970vs	—	—	—	152w [c]	260mbr, 250mbr
RhCl₃(CO)₂(PPh₃)	2111vs	—	354vs, 339s	—	—	300m, 280w, 256s, 244sh, 226s, 205w, 133m, 115w
RhBr₃(CO)₂(PPh₃)	2100vs	—	—	280 [c]	—	260mbr, 230mbr, 218mbr, 202sh
RhI₃(CO)₂(PPh₃)	2085vs	—	—	—	205m, 190sh	260wbr, 218m, 136mbr
RhClBr₂(CO)₂(PPh₃)	2105vs	—	334m	280m [c]	—	310w, 255mbr, 232w, 218m, 170w, 122w
RhClI₂(CO)₂(PPh₃)	2090vs	—	320m	—	[d]	
RhClI(CO)(COMe)(PPh₃)	2065vs	1710vs	326m [c]	—	[d]	260wbr, 232wbr, 210sh
RhCl₂(CO)(COMe)(PPh₃)],0·5CH₂Cl₂	2082vs	1706vs	344ms, 264s	—	—	318w, 258sh, 240w, 199mbr
RhClI(CO)(Ph)(PPh₃)	2063vs	—	325m	—	[d]	—
RhCl₂(CO)₂(CO₂Et)(PPh₃)	2102vs	1705vs	334s, 276s	—	—	360m, 284sh, 260sh, 219m, 197w, 149w, 139m
[RhCl₂(CO)₃(PPh₃)]Cl [b]	2110vs; 2093vs; 2012s	—	—	—	—	—

[a] As Nujol mulls; abbreviations used to describe i.r. band intensities are: vs, very strong; s, strong; ms, medium strong; m medium; w, weak (br = broad; sh = shoulder). [b] In CH₂Cl₂, not isolated. [c] Tentative assignment. Poorly resolved spectrum. [d] Could not be located with certainty.

The complexes (I) and (II) undergo rapid and quantitative oxidative additions with halogens to give the Rhᴵᴵᴵ adducts [RhXY₂(CO)₂(PPh₃)] (III). These adducts show one single strong band due to ν(CO), indicating that the original *trans*-dicarbonyl configuration of the parent compounds is maintained during the reactions. This is reminiscent of the fact that the *trans*-disposition of the two phosphines is retained during various oxidative additions of *trans*-[IrCl(CO)(PPh₂Me)₂].[8] The CO stretching frequencies in (III) are about 100—130 cm.⁻¹ higher than in the parent complexes (I) and (II). This increasing frequency on going from Rhᴵ to Rhᴵᴵᴵ complexes is attributable to a reduced back-donation of electrons from the metal to the carbon monoxide in the higher oxidation state.[6,9] The far-i.r. spectra of (III) show ν(Rh–Cl) in the range 320—355 cm.⁻¹, ν(Rh–Br) at *ca.* 280 cm.⁻¹, and ν(Rh–I) in the range 190—205 cm.⁻¹. Although isomers are possible we have no evidence to suggest the formation of more than one species. The *trans*-addition of the halogen was chosen in line with the findings of Collman *et al.*[8,10] concerning the stereochemical course of oxidative additions on four co-ordinate transition-metal complexes.

The action of gaseous hydrogen chloride on *trans*-[RhCl(CO)₂(PPh₃)] suspended in dichloromethane at

[ν(CO) of RhCl₃(CO)₂(PPh₃)]. This indicates that a likely intermediate for this reaction, *i.e.*, [RhHCl₂-(CO)₂(PPh₃)] (IV) is too unstable to be isolated. Attempts to trap this intermediate at low temperatures were unsuccessful. Examples of cleavage of a transition-metal–hydride bond by acids with evolution of molecular hydrogen such as the above are quite common.[6,11,12]

The reaction of (I) with methyl iodide is intriguing in that it affords the acetyl complex [RhClI(CO)(COMe)-(PPh₃)] (V) whose i.r. spectrum shows a strong band at 2065 cm.⁻¹ (metal carbonyl stretch) and a strong band at 1710 cm.⁻¹ (acyl carbonyl stretch). We cannot say whether this reaction proceeds *via* prior formation of a methyl–rhodium(III) complex. Kinetic work is in progress to determine the mechanism.[13] Since no other product appears to be formed, however, it is likely that (V) is produced by intramolecular rearrangement of a labile rhodium–methyl σ-bonded intermediate. Elemental analysis shows that (V) is isolated without incorporation of molecules of reaction solvent, (CH₂Cl₂), indicating that, at least in the solid, it is a five-co-ordinate monomer or a halide-bridged six-co-ordinate dimer. The difficulty in establishing whether a five-co-ordinate species will become six-co-ordinate in solution through solvation is widely recognized. On the other hand five-co-ordination in rhodium(III) complexes

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is becoming quite common.[11,14] The far-i.r. spectrum of (V) was poorly resolved and was of no help in deducing the configuration of the complex. [RhClI(CO)(COMe)(PPh₃)] is stable indefinitely in the solid but decomposes rapidly in solution to give unknown, brown materials. This prevented a molecular-weight determination. The interconversion of alkyl- and acyl-carbonyl complexes of rhodium and iridium has been extensively studied;[15-20] the stability of alkyl-Rh^{III} complexes appears to be related to the promotional energy for the process M$^{I} \longrightarrow$ M^{III}, and hence to the electronic properties (polarisability, π-acidity) of the ligands in the complex. Thus, [RhClIMe(CO)(PBu^{n}₃)₂] is stable,[16] but [RhCl₂Me(CO)(PPh₃)₂] isomerizes in solution to give the acyl complex [RhCl₂(COMe)(PPh₃)₂];[15] consistently, our [RhCl(CO)₂(PPh₃)], wherein one PPh₃ has been replaced by the strong π-acid CO, gives only the acyl complex [RhClI(CO)(COMe)(PPh₃)] even when reacting with MeI. On a different approach, it is noteworthy that phenyl iodide adds at room temperature on [RhCl(CO)₂(PPh₃)] to give the phenyl-rhodium(III) complex [RhClI(CO)₂(Ph)(PPh₃)] (VI). Its i.r. spectrum shows one single strong terminal carbonyl stretching at 2063 cm.$^{-1}$, indicating again a *trans*-dicarbonyl configuration; below 400 cm.$^{-1}$, a medium band at 325 cm.$^{-1}$ can be assigned to ν(Rh–Cl) whereas ν(Rh–I) cannot be located with certainty. The exact configurations of (V) and (VI) are unknown. The divergent course taken by the reactions with MeI and PhI points to a higher stability of aryl-rhodium(III) complexes than of alkyl complexes, a trend which has already been observed for both non-transitional[21] and transitional metal–carbon σ-bonded derivatives.[22] Analogous results were obtained by Wilkinson *et al.*[15] for the reversible system [RhXCl(COR)(PPh₃)₂] $\rightleftharpoons$ [RhXCl(R)(CO)(PPh₃)₂], for which the equilibrium constant increased in the order of R = Et < Me < Ph.

As regards the influence of the halide X on the ease of addition of RX to [RhCl(CO)₂(PPh₃)] we find that alkyl and aryl chlorides or bromides are unreactive even after prolonged heating. This can be accounted for in terms of the lower carbon–iodine dissociation energy, a factor which probably plays an important role in oxidative additions of this type.[23] On the other hand [IrCl(CO)(Ph₂PMe)₂] does react easily also with alkyl chlorides and bromides.[8] All these findings emphasize how strictly the tendency of d^{8} complexes to undergo oxidative addition depends on the nature of the transition metal and of the ligands attached to it as well as on the addendum.

When [RhCl(CO)₂(PPh₃)] is treated at room tem-

perature with acetyl chloride in dichloromethane, a pale yellow solid precipitates immediately. This has the stoicheiometry [RhCl₂(CO)(COMe)(PPh₃)],0·5CH₂Cl₂ (VII) and the solvent is probably incorporated in the lattice. Its i.r. spectrum shows one strong band at 2082 cm.$^{-1}$ (terminal carbonyl stretch) and one other at 1706 cm.$^{-1}$ (acetyl carbonyl stretch; acyl carbonyl stretching frequencies in acyl metal complexes have been found to fall in the range 1590—1730 cm.$^{-1}$ [6,8,15-20,22]). In the far-i.r. region two medium strong bands at 344 and 264 cm.$^{-1}$ can be assigned to ν(Rh–Cl) *trans* to triphenylphosphine and acetyl, respectively [*cf.* ν(Rh–Cl) in RhCl₂(CO)(COMe)(PMe₂Ph)₂].[24] Apparently, the expected product of this reaction, *viz.*, [RhCl₂(CO)₂(COMe)(PPh₃)] is unstable toward loss of CO and the co-ordination site that is thereby made available is occupied by a solvent molecule. Such instability may be due to the presence of strongly π-acidic ligands, *i.e.*, CO and COR, competing with one another for electron density on the central metal through π-back-donation.

When a suspension of [RhCl(CO)₂(PPh₃)] in benzene is refluxed with ethyl chloroformate the solid dissolves gradually. From the hot solution the pale yellow ethoxy-carbonylrhodium(III) complex [RhCl₂(CO₂Et)(CO)₂(PPh₃)] (VIII) is isolated. Its i.r. spectrum shows two strong bands, at 2102 and 1705 cm.$^{-1}$, due to metal carbonyl and ethoxycarbonyl stretchings respectively. In the far-i.r. spectrum two intense bands, at 334 and 276 cm.$^{-1}$, could be assigned to ν(Rh–Cl) *trans* to PPh₃ and to CO₂Et respectively. However, we cannot definitely rule out a *trans*-dichloro-isomer. While this work was in progress, a series of similar alkoxycarbonyl-iridium(III) complexes of the formula [IrCl₂(CO)(CO₂R)L₂] prepared by oxidative addition of alkyl chloroformates to *trans*-[IrCl(CO)L₂] were reported.[25] When dry HCl is bubbled through a suspension of (VIII) in dichloromethane the solid dissolves rapidly to give a yellow solution. The i.r. spectrum of this in the carbonyl stretching region shows that the original bands of the starting complex have been replaced by three strong, sharp bands at 2110, 2093, and 2012 cm.$^{-1}$. This suggests that the complex present in solution is the tricarbonylrhodium(III) cation [RhCl₂(CO)₃(PPh₃)]$^{+}$ (IX) formed by attack of HCl on the CO₂Et group of (VIII).

The complexes [IrCl₂(CO₂R)(CO)L₂] also were found to undergo attack of HCl at the CO₂R groups to give cationic dicarbonyl species [IrCl₂(CO)₂L₂]$^{+}$.[25] Attempts to isolate the cation (IX) by precipitation with bulky anions such as BPh₄$^{-}$ or PF₆$^{-}$ were unsuccessful. Re-

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moval of the solvent under reduced pressure leaves the orange-yellow [RhCl₃(CO)₂(PPh₃)], indicating that the tricarbonyl species (IX) is unstable toward replacement of one carbon monoxide by the counter-anion Cl⁻. The cation (IX) is converted into [RhCl₃(CO)₂(PPh₃)] also upon standing in solution for *ca.* 0·5 hr. The instability of the complex prevented a complete characterization. The cation (IX) is one of the very few examples of cationic carbonylrhodium(III) complexes yet reported. By contrast, cationic carbonylrhodium(I) complexes are rather common and display various degrees of stability.[1,26-28] The positive charge combined with the high oxidation state of the central metal in the former probably reduce back-donation to such an extent that one carbon monoxide ligand can be easily removed. Thus, for instance, oxidative addition of halogens or hydrogen halides (XY) to [Rh(CO)(dmpe)₂]⁺ (dmpe = Me₂P·C₂H₄·PMe₂) results in loss of CO to give [RhXY(dmpe)₂]⁺ instead of the expected [RhX(CO)(dmpe)₂]²⁺.[26]

From the results described it appears that *trans*-[RhX(CO)₂(PPh₃)] is a versatile complex for various oxidative additions. We are investigating its properties toward activation of small covalent molecules such as hydrogen, oxygen, sulphur dioxide, carbon monoxide, ethylene, and substituted olefins.

EXPERIMENTAL

Materials.—[Rh(CO)₂Cl]₂ was prepared by the method of Powell and Shaw.[29] All other chemicals were reagent grade materials. All reactions were carried out at room temperature (unless otherwise stated) under nitrogen but work-up of reaction mixtures was usually done in the open atmosphere.

trans-Chlorodicarbonyl(triphenylphosphine)rhodium(I), [RhCl(CO)₂(PPh₃)].—[Rh(CO)₂Cl]₂ (0·39 g., 1 mmole) in 20 ml. of benzene was treated slowly dropwise with triphenylphosphine (0·524 g., 2 mmoles) in 20 ml. of benzene with vigorous stirring. The resulting orange solution was concentrated to a small volume on a rotating evaporator. Addition of pentane gave the orange-yellow *product* which was filtered off, washed with pentane, and dried *in vacuo*. *trans-Bromodicarbonyl(triphenylphosphine)rhodium(I)* and *trans-iododicarbonyl(triphenylphosphine)rhodium(I)* were prepared by metathetical reactions with the appropriate lithium halides in acetone.

Addition of Halogens to trans-[RhX(CO)₂(PPh₃)].—(a) *Addition of chlorine to* trans-[RhCl(CO)₂(PPh₃)]. Dry chlorine was bubbled through a suspension of *trans*-[RhCl(CO)₂(PPh₃)] in dichloromethane for 2 min., whereupon the solid dissolved completely to give an orange-yellow solution.

Concentration to a small volume and addition of pentane gave the *product* [RhCl₃(CO)₂(PPh₃)] as an orange-yellow powder.

(b) *Addition of bromine to* trans-[RhX(CO)₂(PPh₃)] (X = Cl, Br). A solution of bromine in carbon tetrachloride (excess) was added to a suspension of *trans*-[RhX(CO)₂(PPh₃)] in the same solvent with stirring. After 1 hr., the *products* [RhXBr₂(CO)₂(PPh₃)] (X = Cl, Br) were filtered off, washed with carbon tetrachloride, and pentane, and dried.

(c) *Addition of iodine to* trans-[RhX(CO)₂(PPh₃)] (X = Cl, I). These reactions were carried out similarly to (b) with iodine in place of bromine and gave [RhXI₂(CO)₂(PPh₃)] (X = Cl, I).

Action of Dry Hydrogen Chloride on trans-[RhCl(CO)₂(PPh₃)].—Hydrogen chloride was bubbled through a suspension of *trans*-[RhCl(CO)₂(PPh₃)] in dichloromethane for 5 min., whereupon the solid dissolved to give an orange-yellow solution. This was concentrated to a small volume and pentane was added. The orange-yellow solid that precipitated was filtered off, dried *in vacuo*, and identified as [RhCl₃(CO)₂(PPh₃)] by its analysis and i.r. spectrum (see text).

Reactions of trans-[RhCl(CO)₂(PPh₃)].—(a) *With methyl iodide.* trans-[RhCl(CO)₂(PPh₃)] was treated with excess of methyl iodide in the dark. During 2 hr. the solid dissolved to give a red-brown solution. This was dried under reduced pressure and the residue taken up with dichloromethane. Addition of pentane gave [RhClI(CO)(COMe)(PPh₃)] as a brown powder.

Similarly, iodobenzene and acetyl chloride gave the complexes [RhClI(CO)₂(Ph)(PPh₃)] and [RhCl₂(CO)(COMe)(PPh₃)],0·5CH₂Cl₂.

(b) *With ethyl chloroformate.* A suspension of *trans*-[RhCl(CO)₂(PPh₃)] in anhydrous benzene containing an excess of ethyl chloroformate was heated at reflux for 0·5 hr. From the resultant hot solution a pale yellow solid separated slowly. This was filtered off, washed with benzene, and pentane, and identified as [RhCl₂(CO)₂(CO₂Et)(PPh₃)].

A suspension of [RhCl₂(CO)₂(CO₂Et)(PPh₃)] in dichloromethane was treated for 1 min. with dry hydrogen chloride. The resulting yellow solution was proved to contain [RhCl₂(CO)₃(PPh₃)]Cl from its i.r. spectrum (see text). This solution, upon evaporation to dryness, left an orange-yellow solid identified as [RhCl₃(CO)₂(PPh₃)].

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