

PREPARATION AND REACTIVITY OF SOME HALOGEN BRIDGED COMPLEXES OF RHODIUM(I)

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(Received April 24th, 1972)

SUMMARY

Hydrogen chloride or bromide reacts with the square-planar rhodium(I) complexes, $\text{Rh}(\text{Acac})(\text{CO})\text{L}$, ($\text{L} = \text{PPh}_3$ or AsPh_3) to give the halogen bridged dimers, $[\text{RhX}(\text{CO})\text{L}]_2$, ($\text{X} = \text{Cl}$ or Br) which are cleaved by donor ligands, L' , to give the mixed ligand complexes, $\text{RhX}(\text{CO})\text{LL}'$, [$\text{L} = \text{PPh}_3$; $\text{L}' = \text{AsPh}_3$, SbPh_3 or $\text{P}(\text{OPh})_3$; $\text{L} = \text{AsPh}_3$, $\text{L}' = \text{SbPh}_3$ or $\text{P}(\text{OPh})_3$]. Reactions of the complexes, $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ and $\text{Rh}(\text{Acac})(1,5\text{-cyclooctadiene})$ with carbon monoxide, tetrafluoroethylene and methyl iodide are also reported.

INTRODUCTION

Although the reaction of triphenylphosphine with $[\text{RhCl}(\text{CO})_2]_2$ was thought to initially involve halogen bridge cleavage¹, further studies^{2,3} have shown that the first step in the reaction involves carbonyl displacement to give the halogen bridged dimer, $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$. We have found that the action of hydrogen chloride or bromide on the square planar rhodium(I) complexes $\text{Rh}(\text{Acac})(\text{CO})\text{L}$, ($\text{L} = \text{PPh}_3$ or AsPh_3), also leads to halogen bridged dimers, and we now describe our studies on these complexes together with related work on the complexes $\text{Rh}(\text{Acac})(1,5\text{-COD})$ and $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$.

RESULTS AND DISCUSSION

The halogen bridged dimers, $[\text{RhX}(\text{CO})\text{L}]_2$, ($\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{PPh}_3$ or AsPh_3), which readily result from the action of the appropriate hydrogen halide on $\text{Rh}(\text{Acac})(\text{CO})\text{L}$ exhibit one strong carbonyl stretching frequency (Table 1) but in the absence of dipole moment data it is not possible to assign either *cis*- or *trans*-structures to these complexes. In the region $400\text{--}200\text{ cm}^{-1}$ the chloro complexes show two strong bands in the range $260\text{--}300\text{ cm}^{-1}$ (Table 1) which are absent from the spectra of the corresponding bromides and hence can be assigned to rhodium-chlorine stretching frequencies. The dimeric halogen bridged complexes, $[\text{RhCl}(\text{CO})_2]_2$ ⁴, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ⁵ and $(1,5\text{-COD})\text{RhCl}_2\text{Rh}[(\text{P}(\text{OPh})_3)]_2$ ⁶ have been shown by X-rays studies to contain

* COS = Cyclooctadiene

TABLE 1 CARBONYL STRETCHING FREQUENCIES AND INFRARED SPECTRA OF THE COMPLEXES (400–200 cm^{-1})

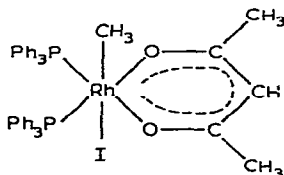
Compound	$\nu(\text{CO})^a$ (cm^{-1})	$\nu(\text{CO})^b$ (cm^{-1})	400–200 cm^{-1} ^c		
				Half band width	Rel. intensity
$[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]^d$	1975	1983(31)	348	(23)	(0.23)
	1984		<u>293</u>	(15)	(1.00)
			<u>262</u>	(5)	(0.16)
			250.5	(9)	(0.65)
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2^e$ $\text{RhCl}(\text{CO})(\text{AsPh}_3)(\text{PPh}_3)$	1960	1977(36)	<u>311.5</u>	(12)	
	1962	1976(30)	330	(15)	(1.00)
			325	(15)	(0.85)
			<u>311.5</u>	(14)	(0.78)
$\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{SbPh}_3)$	1962	1975(40)	<u>308</u>	(13)	(0.73)
			304		(0.57)
			277.5	(14)	(0.98)
			267.5	(16)	(1.00)
			250		(0.29)
			225	(13)	(0.18)
$\text{RhCl}(\text{CO})(\text{PPh}_3)[\text{P}(\text{OPh})_3]$ $[\text{RhCl}(\text{CO})(\text{AsPh}_3)]_2$	1967	1978(28)	<u>310</u>	(12)	
	1977	1980(37)	344.5	(8)	(0.82)
	1972		329	(13)	(1.00)
			<u>295</u>	(14)	(1.00)
			<u>261</u>	(7)	(0.75)
			255		(0.82)
$\text{RhCl}(\text{CO})(\text{AsPh}_3)(\text{SbPh}_3)$	1953	1972(34)	327	(25)	(1.00)
			<u>309.5</u>	(15)	(0.73)
			277	(8)	(0.78)
			268	(10)	(0.82)
$\text{RhCl}(\text{CO})(\text{AsPh}_3)[\text{P}(\text{OPh})_3]$	1956	1971(29)	325	(28)	(1.00)
			<u>310</u>	(15)	(0.71)
$\text{RhCl}(\text{CO})(\text{AsPh}_3)_2^e$	1963	1974(30)	329	(31)	(1.00)
			<u>311</u>	(15)	(0.87)
			305		(0.71)
$[\text{RhBr}(\text{CO})(\text{PPh}_3)]_2$	1980	1987(35)	239.5	(8)	(0.24)
	1970		225.5	(7)	(0.36)
			215	(9)	(1.00)
$\text{RhBr}(\text{CO})(\text{PPh}_3)_2$ $\text{RhBr}(\text{CO})(\text{AsPh}_3)(\text{PPh}_3)$	1968	1978(30)			
	1964	1977(37)	331	(14)	(1.00)
$\text{RhBr}(\text{CO})(\text{PPh}_3)[\text{P}(\text{OPh})_3]$	1965	2000(35)	321.5	(10)	(0.87)
	1984				
$\text{RhBr}(\text{CO})(\text{PPh}_3)(\text{SbPh}_3)$	1957	1976(34)	277.5	(18)	(1.00)
	1984		269	(13)	(1.00)
$[\text{RhBr}(\text{CO})(\text{AsPh}_3)]_2$	1978	1980(41)	347	(15)	(0.85)
	1968		329	(22)	(1.00)
			236		(0.21)
			228.5	(7)	(0.62)
$\text{RhBr}(\text{CO})(\text{AsPh}_3)(\text{SbPh}_3)$	1962	1973(27)	215.5	(6)	(0.19)
			328	(24)	(1.00)
			278	(7)	(0.38)
			268	(11)	(0.38)
$\text{RhBr}(\text{CO})(\text{AsPh}_3)[\text{P}(\text{OPh})_3]$ $\text{RhBr}(\text{CO})(\text{AsPh}_3)_2$	1960	1973(32)	327	(20)	
	1965	1976(33)	353	(12)	(0.97)
			344.5	(15)	(1.00)

^a Nujol mull. ^b In CHCl_3 solution, half band width in parentheses. ^c Rhodium-halogen stretching frequencies are underlined. ^d See ref. 3. ^e See ref. 8.

bent RhCl_2Rh unit (C_{2v} symmetry) whereas in $[\text{RhCl}(1,5\text{-COD})]_2$ a planar RhCl_2Rh unit (D_{2h} symmetry) is present. Infrared studies on these types of complexes have shown that the spectra obtained do not always distinguish a bent RhCl_2Rh unit from a planar arrangement⁸. Consequently although only two rhodium-chlorine stretching frequencies are observed for the complexes $[\text{RhCl}(\text{CO})\text{L}]_2$, ($\text{L} = \text{PPh}_3$ or AsPh_3), which would be consistent with a planar arrangement, the present data do not preclude a bent RhCl_2Rh unit.

The halogen bridges in the complexes $[\text{RhX}(\text{CO})\text{L}]_2$ are readily cleaved by donor ligands to give monomeric square planar compounds, *trans*- $\text{RhX}(\text{CO})(\text{L})(\text{L}')$, where $\text{L}' = \text{AsPh}_3$, SbPh_3 and $\text{P}(\text{OPh})_3$. These mixed ligand compounds are formulated with a *trans*-configuration since their carbonyl and metal-halogen stretching frequencies (Table 1) are very similar to those found in the adducts, *trans*- $\text{RhX}(\text{CO})(\text{PPh}_3)_2$ ^{8,9}. In a recent preliminary note it has also been independently reported that the chloride bridges in $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ are cleaved by donor ligands³.

The precursors for the halogen bridged complexes, $\text{Rh}(\text{Acac})(\text{CO})\text{L}$ have previously been prepared by the action of the ligand L on $\text{Rh}(\text{Acac})(\text{CO})_2$ ¹⁰. However, during the course of our studies, we have found that the phosphine complex, $\text{Rh}(\text{Acac})(\text{CO})(\text{PPh}_3)$, can also be prepared by the action of carbon monoxide upon $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$. Further indication of the reactivity of $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ is provided by its reaction with tetrafluoroethylene at 50° which gives $\text{Rh}(\text{Acac})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$. This complex has previously been obtained from $\text{Rh}(\text{Acac})(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$ and triphenylphosphine¹¹. Recently it has been shown that pentafluorobenzenesulphonyl chloride, hexafluoroacetone and hexafluoroisopropylidene react with and displace one molecule of triphenylphosphine from $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ ¹². However, we find that methyl iodide gives an octahedral complex (I), without loss of triphenylphosphine. The IR spectrum of (I) shows bands of the acetylacetonate ligand at 1581, 1572 and 1512 cm^{-1} which indicate that it is still oxygen-bonded to the rhodium and the presence of only one methyl resonance for the acetylacetonate ligand in the ^1H NMR spectrum suggests that (I) may have a symmetrical structure.



(I)

Although $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ readily undergoes oxidation reactions we have not been able to isolate similar products using $\text{Rh}(\text{Acac})(1,5\text{-COD})$. Thus methyl iodide has no action upon $\text{Rh}(\text{Acac})(1,5\text{-COD})$, (II), in refluxing diethyl ether or petroleum spirit. However, in refluxing methanol the iodo-bridged complex, $[\text{RhI}(1,5\text{-COD})]_2$, is precipitated. Presumably in methanol there is some solvolysis of the methyl iodide to generate hydroiodic acid which can then attack (II). The reluctance of (II) to oxidatively add methyl iodide is in agreement with previous studies which have shown that coordinated dienes tend to inhibit oxidative addition to rhodium(I)¹³. Similarly, attempts to oxidatively add mercury(II) chloride to $\text{Rh}(\text{Acac})(1,5\text{-COD})$ results in cleavage of the acetylacetonate ligand to give the adduct $[\text{RhCl}(1,5\text{-COD})]_2$.

2HgCl_2 which has previously been obtained from $[\text{RhCl}(\text{1,5-COD})]_2$ ¹⁴.

Although tetrafluoroethylene will displace a molecule of ethylene from $\text{Rh}(\text{Acac})(\text{C}_2\text{H}_4)_2$ this olefin has no action upon $\text{Rh}(\text{Acac})(\text{1,5-COD})$ in diethyl ether at room temperature. However, at 100° a reaction does take place to give a product for which consistent analytical data could not be obtained. The IR spectrum of the product contains a strong absorption at 2100 cm^{-1} typical of a metal-carbonyl stretching frequency and since under these reaction conditions tetrafluoroethylene is known to undergo hydrolytic degradation to carbon monoxide¹⁵⁻¹⁷ it seems likely that the reaction does involve the formation of an intermediate tetrafluoroethylene complex. In this context it is noteworthy that the reaction of tetrafluoroethylene with $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ at 100° also gives a carbonyl complex, $\text{Rh}(\text{Acac})(\text{CO})(\text{PPh}_3)$, which is presumably formed via hydrolysis of $\text{Rh}(\text{Acac})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$.

EXPERIMENTAL

Analytical data, yields and melting points for all new complexes are given in Table 2. IR spectra (Table 1) were recorded on a Perkin-Elmer model 225 spectrophotometer. Proton NMR spectra were obtained in deuteriochloroform as solvent using a Varian Associates T60 spectrometer.

The complexes $\text{Rh}(\text{Acac})(\text{1,5-COD})$,^{10,18} $\text{Rh}(\text{Acac})(\text{CO})(\text{PPh}_3)$ ¹⁰ and $\text{Rh}(\text{Acac})(\text{CO})(\text{AsPh}_3)$ ¹⁰ were prepared as described in the literature.

Preparation of the complexes $[\text{RhX}(\text{CO})\text{L}]_2$

A freshly standardised (ca. 0.01 M) methanolic solution of the hydrogen halide (1.0 mmol) was added dropwise to a vigorously stirred suspension of $\text{Rh}(\text{Acac})(\text{CO})(\text{L})$ (1.0 mmol) in diethyl ether (30 ml). The resulting bright orange solid $[\text{RhX}(\text{CO})\text{L}]_2$ was washed with ether and dried *in vacuo* at 56° .

Preparation of the complexes $\text{RhX}(\text{CO})\text{LL}$

A solution of the phosphine, phosphite, stibine or arsine (ca. 2 mmol) in ether (10 ml) was added to a solution of the halogen bridged dimer, $[\text{RhX}(\text{CO})\text{L}]_2$ (1 mmol) in warm benzene (30 ml). The solution was allowed to stand for 15 h at room temperature to afford bright yellow crystals of the complexes $\text{RhX}(\text{CO})\text{LL}$.

Reactions of $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$.

(a). *With carbon monoxide.* Passage of carbon monoxide gas through a stirred suspension of $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ (0.5 g) in diethyl ether (30 ml) for 10 min gave yellow crystals of $\text{Rh}(\text{Acac})(\text{CO})(\text{PPh}_3)$ (0.3 g, 100%) identified by its m.p. and IR spectrum¹⁰.

(b). *With tetrafluoroethylene.* Tetrafluoroethylene (2 ml) was condensed onto a suspension of $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ (0.5 g) in diethyl ether (20 ml) contained in a thick-walled glass tube cooled in liquid nitrogen. The tube was sealed and heated at 100° for 15 h. Evaporation of the solvent gave yellow crystals of $\text{Rh}(\text{Acac})(\text{CO})(\text{PPh}_3)$ (0.3 g, 90%) identified by its m.p. and IR spectrum¹⁰.

(c). *With methyl iodide.* A suspension of $\text{Rh}(\text{Acac})(\text{PPh}_3)_2$ (0.5 g) in diethyl ether (30 ml) and methyl iodide (1 ml) were refluxed together for 3 h under a nitrogen atmosphere. The brick-red crystalline precipitate which formed was washed with diethyl ether and recrystallised from methylene chloride/diethyl ether to give $\text{Rh}(\text{Acac})(\text{I})(\text{Me})(\text{PPh}_3)_2$ (0.6 g, 100%). The ¹H NMR spectrum (CDCl_3) showed peaks at τ 2.0-2.9 (30 H, m, $\text{C}_6\text{H}_5\text{P}$), 5.74(1H,s), 8.52(6H,s) and 9.13(3H,s).

TABLE 2
ANALYTICAL DATA FOR COMPLEXES

Compound	Colour	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)			Mol. wt found ^a (calcd.)
				C	H	Hal	
Rh(Acac)IME(PPh ₃) ₂ ^b	Brick red	100	165 (dec.)	57.93 (58.90)	4.61 (4.71)		854 (856)
Rh(Acac)(PPh ₃) ₂ ^c	Orange	100	135 (dec.)	67.77 (67.77)	5.23 (4.86)		
[RhCl(CO)(PPh ₃) ₂]	Orange	90	200–204 (dec.)	53.05 (53.24)	3.41 (3.53)	8.40 (8.27)	801 ± 20 (857)
RhCl(CO)(AsPh ₃)(PPh ₃)	Yellow	92	209–212	60.70 (60.47)	4.28 (4.11)	5.09 (4.82)	716 ± 10 (735)
RhCl(CO)(PPh ₃)(SbPh ₃)	Yellow	80	160 (dec.) ^d	57.88 (56.85)	4.16 (3.87)	4.80 (4.54)	746 ± 12 (782)
RhCl(CO)(PPh ₃)[P(OPh) ₃]	Yellow	77	176–179	60.77 (60.14)	4.03 (4.09)	4.80 (4.80)	746 ± 11 (739)
[RhCl(CO)(AsPh ₃) ₂]	Rust-orange	89	180 (dec.) ^d	48.47 (48.29)	3.38 (3.20)	7.40 (7.50)	960 ± 30 (945)
RhCl(CO)(AsPh ₃)(SbPh ₃)	Yellow	73	220 (dec.) ^d	55.29 (53.82)	3.93 (3.66)	4.50 (4.29)	797 ± 27 (826)
RhCl(CO)(AsPh ₃)[P(OPh) ₃]	Yellow	70	181–185	55.10 (56.77)	3.71 (3.86)	4.70 (4.53)	756 ± 27 (783)
[RhBr(CO)(PPh ₃) ₂]	Rust-orange	93	185 (dec.) ^d	48.30 (48.28)	3.35 (3.20)	16.65 (16.89)	900 ± 40 (946)
RhBr(CO)(AsPh ₃)(PPh ₃)	Yellow	87	193–195 (dec.)	57.63 (57.02)	4.02 (3.88)	9.61 (10.25)	747 ± 22 (779)
RhBr(CO)(PPh ₃)[P(OPh) ₃]	Pale yellow	73	162–163	57.46 (56.73)	3.85 (3.86)	10.20 (10.20)	756 ± 18 (783)
RhBr(CO)(PPh ₃)(SbPh ₃)	Deep yellow	71	180 (dec.) ^d	53.61 (53.79)	3.82 (3.66)	9.18 (9.67)	786 ± 19 (826)
[RhBr(CO)(AsPh ₃) ₂]	Rust-orange	89	160 (dec.) ^d	46.48 (44.14)	3.08 (2.92)	14.20 (15.45)	1002 ± 35 (1034)
RhBr(CO)(AsPh ₃)(SbPh ₃)	Yellow	68	174–175	51.20 (51.07)	3.37 (3.48)	8.90 (9.18)	850 ± 17 (870)
RhBr(CO)(AsPh ₃)[P(OPh) ₃]	Yellow	65	175 (dec.) ^d	52.31 (53.71)	3.47 (3.66)	9.02 (9.66)	790 ± 24 (827)
RhBr(CO)(AsPh ₃) ₂	Yellow	89	228–230	54.21 (53.98)	3.78 (3.67)	9.33 (9.71)	789 ± 20 (823)

^a Molecular weights were determined osmometrically in chloroform. ^b Found: P, 7.1; Rh, 11.7. Calcd.: P, 7.2; Rh, 12.0%.

^c Found: P, 8.2; Rh, 14.2. Calcd.: P, 8.5; Rh, 14.2%. ^d Decomposes without melting.

Reactions of Rh(Acac)(1,5-COD).

(a). *With triphenylphosphine.* Triphenylphosphine (0.85 g) was added to a solution of Rh(Acac)(1,5-COD) (0.5 g) in diethyl ether (20 ml) under nitrogen. The yellow solution became dark red and after refluxing the solution for 10 min bright orange crystals of acetylacetonatobis(triphenylphosphine)rhodium(I) (1.17 g, 100%) were deposited. M.p. 135° (dec.) (Found: C, 67.8; H, 5.2; P, 8.2; Rh, 14.2. C₄₁H₃₇O₂P₂Rh calcd: C, 67.8; H, 5.1; P, 8.5; Rh, 14.2%). This complex has previously been obtained from Rh(Acac)(C₂H₄)₂^{1,2}.

(b). *With carbon monoxide.* Carbon monoxide was bubbled through a solution

of Rh(Acac)(1,5-COD) (0.2 g) in petroleum spirit (b.p. 40–60°) for 5 min. The yellow solution darkened slightly and evaporation to a small volume under reduced pressure and cooling to 0° gave crystals of acetylacetonatodicarbonylrhodium(I) (0.16 g, 95%) identified by its m.p. and IR spectrum¹⁰.

(c). *With tetrafluoroethylene*. Tetrafluoroethylene (ca. 2 ml) was condensed onto a solution of Rh(Acac)(1,5-COD) (0.5 g) in diethyl ether contained in a thick-walled glass tube cooled in liquid nitrogen. The tube was sealed, allowed to warm to room temperature and heated at 100° for 3 h. The tube was opened and the brown precipitate was filtered off, washed with light petroleum (b.p. 40–60°) and dried *in vacuo*. The brown solid (0.25 g) was hygroscopic and no consistent analytical data could be obtained. It exhibited a strong absorption at 2100 cm⁻¹ in its IR spectrum.

(d). *With methyl iodide*. Rh(Acac)(1,5-COD) (0.2 g) in diethyl ether (30 ml), or petroleum spirit (b.p. 40–60°), and methyl iodide (1 ml) were refluxed together for 15 h. The solution was evaporated to dryness to give unchanged Rh(Acac)(1,5-COD).

On repeating the above experiment but using methanol (30 ml) as solvent and keeping the reaction mixture at 40° for 2 h, a brown deposit and a red brown solution was obtained. The brown solid was recrystallised from benzene to give brick red crystals of [RhI(1,5-COD)]₂ (0.1 g, 46%) identified by its m.p. and IR spectrum¹⁸.

(e). *With mercury(II) chloride*. A solution of Rh(Acac)(1,5-COD) (0.4 g) in chloroform (20 ml) was added dropwise to a stirred solution of mercury(II) chloride (5 g) in acetone (20 ml). The red crystalline precipitate which formed was identified as [RhCl(1,5-COD)]₂·2HgCl₂ by its m.p. and IR spectrum¹⁴.

ACKNOWLEDGEMENTS

We thank Johnson, Matthey & Company Limited for the loan of rhodium and the S.R.C. for maintenance grants (to D.M.B. and M.J.H.).

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