

Structure of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and $(\text{RhBr}_2\text{allyl})_n$ and Their Application in Homogeneous Hydrogenation

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The $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and $(\text{RhBr}_2\text{allyl})_n$ complexes were found to yield the catalysts for homogeneous hydrogenation of olefins from their reaction with phosphines, amines and sulphides in alcoholic solutions in hydrogen. The NMR spectrum of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ was examined, the X-ray crystallographic structure of this compound was determined and the IR spectra of both these compounds were measured over the 60–450 cm^{-1} range.

Introduction

In our earlier works dichloro(2-methylallyl)rhodium (III) was found to yield complex compounds which catalyze the hydrogenation reactions of unsaturated hydrocarbons by reacting with phosphines, sulphides and amines in alcoholic solutions in hydrogen 1–3. Therefore, we have decided to examine the catalytic properties of the compounds obtained from the above mentioned ligands and other allyl complexes of rhodium.

In the present work the structure and the catalytic properties of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and $(\text{RhBr}_2\text{allyl})_n$ are discussed.

Results and Discussion

Spectroscopic measurements indicate that the bridging group in $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ has a symmetrical structure. In order to confirm it, the X-ray structure of this compound was determined. $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ crystallizes in the monoclinic system and is most probably isostructural with a similar chloride compound examined by McPartlin and Mason⁵; it is not, however, certain since these authors provide neither the unit cell parameters nor the space group. Measurements of the unit cell parameters and reflection intensities were carried out in a Synthex P2₁, four-circle diffractometer using the $\text{CuK}\alpha$ radiation and a graphite monochromator. 1130 independent reflections were measured up to the 2θ 110 angle using a θ – 2θ scan technique. Intensities were corrected by the Lorentz and polarizing factor.

Crystallographic data. Compound: $\text{Rh}_2\text{Br}_2(\text{allyl})_4$. $a = 6.774(3)\text{Å}$, $b = 7.387(3)\text{Å}$, $c = 15.494(6)\text{Å}$;

$\beta = 102.87(8)^\circ$; $v = 755.8\text{Å}^3$, $z = 2$, $D_x = 2.33$, $D_m = 2.33\text{ g cm}^{-3}$. $\mu(\text{CuK}\alpha) = 248.3\text{ cm}^{-1}$. Space group P2₁/c.

The structure was solved by means of three-dimensional Patterson and Fourier maps. After refining the structural parameters by means of the FMLS method, use was made of intensities of 964 reflections for which $F > 3.96\sigma(F)$.

As a result of refinement of atomic coordinates and anisotropic structural factors for non-hydrogen atoms, the following values for R-indices were determined: $R = 0.050$, $R_w = 0.061$; $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_w = (\Sigma_w (|F_o| - |F_c|)^2 / \Sigma_w (|F_o|)^2)^{1/2}$.

All structural calculations were carried out in a Nova 1200 computer using the "Syntex XTL Structure Determination System" from the Syntex programme library.

The centrosymmetric complex configuration, interatomic distances and angles are given in Fig. 1 and Table III.

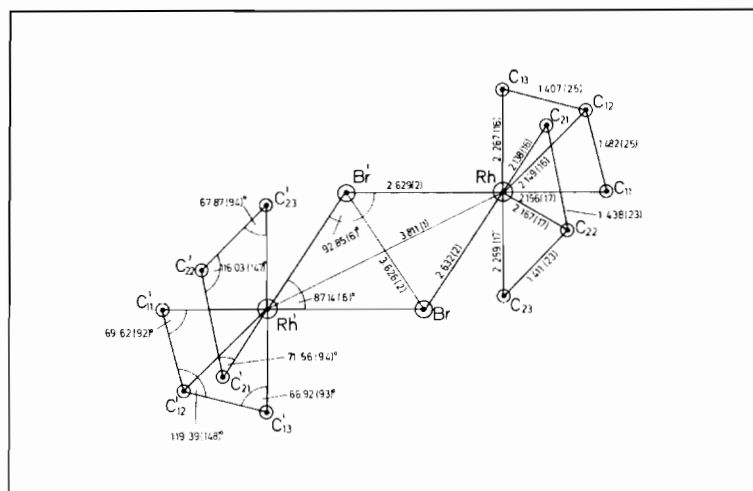
The X-ray structure of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ indicates that the Rh–Br bond lengths are identical within experimental error. For this reason the difference in frequencies between $\nu_s(\text{Rh–Br})$ and $\nu_{as}(\text{Rh–Br})$ (13 cm^{-1}) is considerably smaller than that for the respective frequencies of $(\text{Rh}_2\text{Cl}_2(\text{allyl})_4)^{(4)}$ (for this compound Rh–Cl distances are equal: 2.511 and 2.469 Å).

A smaller difference in the $\nu(\text{Pd–Cl})$ frequencies was found also for the $\text{Pd}_2\text{Cl}_2(\text{allyl})_2$ complexes^{6–8} where the Pd–Cl bond lengths are identical.

The differences between the $\nu_s(\text{Rh–X})$ and $\nu_{as}(\text{Rh–X})$ frequencies in the $\text{Rh}_2\text{X}_2(\text{allyl})_4$ compounds decrease on passing from the chloride (28 cm^{-1}) to bromide (13 cm^{-1}) and iodide (5 cm^{-1}) complexes⁽⁹⁾.

TABLE I. Fractional Atomic Coordinates.

	x	y	z
Rh ₁	0.0587(2)	0.1621(2)	0.0981(1)
Br	0.1551(3)	0.1354(2)	–0.0567(1)
C ₁₁	0.3101(23)	0.3401(24)	0.1484(11)
C ₁₂	0.3317(22)	0.1696(26)	0.2001(10)
C ₁₃	0.3439(21)	0.0040(24)	0.1567(11)
C ₂₁	0.8823(24)	0.2319(24)	0.1917(10)
C ₂₂	0.8606(24)	0.3733(22)	0.1265(11)
C ₂₃	0.7766(26)	0.3214(22)	0.0383(11)

Figure 1. Molecular structure of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$.TABLE II. Thermal Parameters (\AA^2).

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh ₁	1.95(5)	2.27(5)	1.50(5)	-0.11(5)	-0.06(4)	-0.12(4)
Br	3.53(8)	2.99(8)	2.49(7)	-0.52(7)	0.57(6)	0.03(6)
C ₁₁	2.11(72)	4.20(88)	3.78(81)	-1.34(72)	-0.85(63)	-1.12(73)
C ₁₂	1.37(66)	5.93(107)	3.11(77)	-0.65(75)	-0.50(58)	-0.03(77)
C ₁₃	0.91(62)	4.89(99)	3.87(86)	0.10(66)	-1.13(58)	-0.84(75)
C ₂₁	3.31(82)	4.52(90)	2.54(68)	0.83(74)	0.63(63)	-1.15(67)
C ₂₂	2.87(77)	3.53(83)	3.31(77)	1.32(66)	0.40(64)	-0.75(64)
C ₂₃	3.67(84)	3.25(83)	4.40(88)	1.98(75)	1.17(72)	0.49(69)

TABLE III. The Angles for the $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ Molecule.

Atoms	Angle (deg)
C ₁₃ -Rh-Br	87.95(41)
C ₂₃ -Rh-Br	88.03(43)
C ₁₃ -Rh-Br'	92.35(41)
C ₂₃ -Rh-Br'	91.42(43)
C ₁₃ -Rh-Rh	90.21(41)
C ₂₃ -Rh-Rh	89.62(43)
C ₁₁ -Rh-C ₂₁	97.06(63)
C ₁₂ -Rh-C ₂₂	107.60(63)
C ₁₃ -Rh-C ₂₃	179.24(60)
C ₁₃ -Rh-C ₁₁	68.61(60)
C ₁₃ -Rh-C ₂₁	114.03(60)
C ₁₃ -Rh-C ₂₂	143.19(59)
C ₂₂ -Rh-C ₁₂	143.00(63)
C ₂₃ -Rh-C ₁₁	111.00(62)
C ₂₃ -Rh-C ₂₁	66.62(62)

The $\nu(\text{Rh-allyl})$ frequency for the bromide complex is only slightly lower (about 5 cm^{-1}) than that for the chloride complex. This indicates that the Rh-allyl force constants are practically identical in both these compounds.

The $(\text{RhBr}_2\text{allyl})_n$ complex contains both the bridging and terminal bromine atoms (like in $(\text{RhCl}_2\text{allyl})_n$ where allyl = C_3H_5 and $\text{CH}_2-\text{C}(\text{CH}_3)-\text{CH}_2$). This is indicative of the presence of strong and broad $\nu(\text{Rh-Br})$ bands at 260, 185 and 174 cm^{-1} .

It is quite probable that this compound, apart from the bromide bridges, contains also some allyl bridges as indicated by changes in the IR spectrum of this compound in comparison to $\text{Rh}_2\text{X}_2(\text{allyl})_4$ (Table IV).

The ^1H NMR spectrum of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ in CDCl_3 at 24°C is similar to that of $\text{Rh}_2\text{Cl}_2(\text{allyl})_4$ ¹⁰ and consists of four doublets and one multiplet of identical relative intensities. This is a AGMPX type spectrum where the four allyl groups are equivalent and the terminal atoms of each group are unequivalent. The asymmetry of the allyl group appears also in the solid state: the C₁₁-C₁₂ and C₁₂-C₁₃ distances are 1.482 Å and 1.407 Å, respectively. However, this does not result in

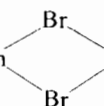
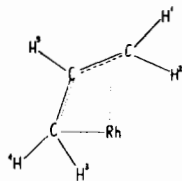
any changes of the bridging Rh  Rh group symmetry.

TABLE IV. IR Spectra (450–60 cm^{-1}) of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and $(\text{RhBr}_2\text{allyl})_n$.

$\text{Rh}_2\text{Br}_2(\text{allyl})_4$		$(\text{RhBr}_2\text{allyl})_n$	
Frequencies (cm^{-1})	Assignments	Frequencies (cm^{-1})	Assignments
439(s)		410(vw)	
406(s)	$\nu_{\text{as}}(\text{Rh-allyl})$	370(vw)	
400(s)	$\nu_{\text{s}}(\text{Rh-allyl})$	347(vw)	
286(s)		258(s)	$\nu(\text{Rh-Br})$ terminal
221(w)		186(s)	$\nu(\text{Rh-Br})$ bridging
197(w)		174(s)	$\nu(\text{Rh-Br})$ bridging
193(w)		103(m)	
163(vs)	$\nu_{\text{as}}(\text{Rh-Br})$ bridging		
150(sh)	$\nu_{\text{s}}(\text{Rh-Br})$ bridging		
113(sh)			
109(vs)			

The values of chemical shifts for the protons are as follows: $\tau_4 = 4.7$, $\tau_2 = 5.65$, $\tau_3 = 7.95$, $\tau_4 = 7.38$, $\tau_5 = 5.2$.



Catalytic Activity

The catalytic activities of the compounds obtained from $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and $(\text{RhBr}_2\text{allyl})_n$ in reactions with amines, phosphines and sulphides in ethanol solutions saturated with hydrogen were examined in the hydrogenation reactions of olefins.

Hydrogenation of cyclohexene to cyclohexane is catalyzed by the complexes formed *in situ* from an allyl compound of rhodium and the respective ligand.

In general, it should be noted that the sulphides yield poor catalysts under the same conditions. On the other hand, the complexes obtained from the amines and phosphines are much more active (Table V). The activities of the complexes formed depend also on the number of mol of the ligand used per Rh atom. For PPh_3 , at a molar ratio $\text{PPh}_3/\text{Rh} = 3$, the hydrogenation rate of cyclohexene is very high (1860 mol H_2 /hour mol Rh).

In hydrogen the allyl groups become hydrogenated to form propane and their sites are substituted with phosphines yielding Wilkinson's catalysts. This is similar to the case of an allyl chloride complex Rh_2Cl_2

TABLE V. Maximum Hydrogenation Rate of Cyclohexene (mol H_2 /hour mol Rh) Using the Rhodium Complexes. Temp. 30°C, solvent = EtOH, hydrogen pressure = atmospheric pressure–vapour pressure, cyclohexene concentration 0.9M.^a

Ligand	$(\text{RhBr}_2\text{allyl})_n$	$\text{Rh}_2\text{Br}_2(\text{allyl})_4$
PPh_3	290(2)	110(2)
PPh_3		1860(3)
$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$	140(1)	180(1)
$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$		110(1.5)
$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$		70(2)
$\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}_3$		430(2)
$\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}_3$		1650(3)
$\text{P}(\text{OEt})_3$	650(2)	470(2)
$\text{P}(\text{OEt})_3$		250(2)
1,10-phenanthroline	40(1)	650(1)
2-aminopyridine	1090(1)	320(1)
1,8-diaminonaphthalene	570(1)	1430(1)
1,8-diaminonaphthalene		40(1.5)
Et_2S		40(2)
Bu_2S		40(3)
Bu_2S		7(4)

^a The molar ratio L : Rh is given in brackets. Maximum hydrogenation rate of cyclohexene using $\text{RhCl}(\text{PPh}_3)_3 = 2800$.

(allyl)₄ from which $\text{RhCl}(\text{PPh}_3)_3$ may be obtained by using excess PPh_3 ⁴.

For the reaction between $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and PPh_3 where the reactant ratio $\text{PPh}_3/\text{Rh} = 2$, the hydrogenation rate is much lower (110 mol H_2 /hour mol Rh).

Some stable allyl compounds of Rh(III) whose catalytic activity is considerably lower as compared to $\text{RhBr}(\text{PPh}_3)_3$ are most probably formed. Similar reactions take place in the case of tolylphosphine and $\text{Rh}_2\text{Br}_2(\text{allyl})_4$.

A change in the molar ratio $\text{PPh}_2\text{C}_6\text{H}_4\text{CH}_3/\text{Rh}$ from 3 to 2 results in a considerable decrease of the hydrogen absorption rate by the catalytic system from 1650 mol H_2 /hour mol Rh down to 430 mol H_2 /hour mol Rh.

The gas–liquid chromatography of the products formed by the reaction between $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and 1,8-diaminonaphthalene in ethanol in hydrogen has shown the presence of propane. One may believe that during the course of reaction the allyl groups become hydrogenated to form propane and simultaneously become coordinated with the formation of a complex rhodium compound with 1,8-diaminonaphthalene which is an active catalyst for hydrogenation of cyclohexene.

The catalytic systems prepared from 1,8-diaminonaphthalene or 2-aminopyridine and $(\text{RhBr}_2\text{allyl})_n$ are relatively active; however, a certain amount of a brown–black compound is formed during the reaction. No reduction to metallic rhodium takes place here, however, since the precipitate is soluble in highly polar solvents such as formamide and DMSO. Similar precipitates are formed also in the catalytic systems prepared

from $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and 1,10-phenanthroline or 1,8-diaminonaphthalene.

The hydrogenation reaction of allyl groups proceeds relatively slowly since the catalytic activity during the second hydrogenation was higher in many cases (see Experimental). An increase in the hydrogenation rate, sometimes very considerable, was found after careful oxidation of the catalyst with air. By storing the catalyst for several minutes in the air the hydrogenation rate was increased.

An increase in the hydrogenation rate was also found on oxidizing the catalysts prepared from $\text{Rh}_2\text{Cl}_2(\text{allyl})_4$ and $(\text{RhCl}_2\text{allyl})_n$ and the same ligands with air.

These studies show that the amines may form with rhodium certain complex compounds which catalyze very efficiently the hydrogenation reactions of olefins.

Experimental

Infrared spectra were measured on a Perkin-Elmer 180 spectrophotometer while the ^1H NMR spectrum was measured in a JNMPS-100 spectrophotometer.

Preparation of the Compounds

Rhodium trichloride used was supplied by FLUKA. $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ was prepared according to a method provided in ref. 11. $\text{RhBr}_3(\text{H}_2\text{O})_x$ was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ by precipitating the hydroxide $\text{Rh}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ which was then dissolved in HBr.

$\text{Rh}_2\text{Br}_2(\text{CO})_4$ was prepared in a similar way as $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ by passing CO through the solid rhodium tribromide at 100°C . Both these carbonyl compounds were purified by sublimation. $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ was not prepared by the Powell and Shaw method⁴ by exchanging chlorine for bromine in $\text{Rh}_2\text{Cl}_2(\text{allyl})_4$ but a method employed by these authors for the preparation of $\text{Rh}_2\text{Cl}_2(\text{allyl})_4$ was used which enabled us to reach higher yields.

Preparation of $\text{Rh}_2\text{Br}_2(\text{allyl})_4$

(i) A solution containing 0.1 g $\text{Rh}_2\text{Br}_2(\text{CO})_4$ and 0.4 ml allyl bromide in 0.75 ml methyl alcohol was treated with 0.25 ml water. The mixture was kept for 4 hours at room temperature. The yellow precipitate was filtered off, washed and then recrystallized from a mixture of methylene chloride and methanol. Yield: 35%.

(ii) A solution containing 0.4 g $\text{Rh}_2\text{Br}_2(\text{CO})_4$ and 1.6 ml allyl bromide in 3 ml methanol was treated dropwise with 5N KOH in such quantities to achieve a neutral reaction.

The mixture was concentrated to about $2/3$ of the original volume. The residue was treated with 4 ml water and left for 2 hours. The precipitate was filtered off, washed with water and recrystallized from a mixture of methylene chloride and methanol. Yield: 70%. The compounds prepared by various methods had the

same IR spectra and the same compositions. *Anal.* Found % C 27.5, % H 4.1; calcd. for $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{Rh}_2$: % C 27.2, % H 3.8.

(iii) A synthesis similar to the preceding one was attempted with $\text{Rh}_2\text{Br}_2(\text{CO})_4$ instead of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. Yield: 70%.

Crystals for structural determinations were prepared by slow crystallization from a mixture of methylene chloride and methanol.

Preparation of $\text{RhBr}_2\text{allyl}$

A suspension of 0.1 g $\text{Rh}_2\text{Br}_2(\text{allyl})_4$ and 0.148 g $\text{RhBr}_3 \cdot 3\text{H}_2\text{O}$ in 2.4 ml methanol was heated under reflux for about one hour. A brown compound was formed. Yield 60%. *Anal.* Found: % C 11.6, % H 1.54; calcd. for $\text{C}_3\text{H}_5\text{Br}_2\text{Rh}$: % C 11.86, % H 1.66.

Hydrogenation Reactions

Absolute ethanol (99.8%) employed as solvent was supplied by POCH and was used without additional purification. Cyclohexene was distilled before use under argon over sodium.

Hydrogenation reactions were carried out in a constant volume reactor provided with a heating jacket, sampling valve for chromatographic measurements and connected to a dropping funnel and cooler. A mercury pressure gauge was connected to the equipment through the cooler. A magnetic stirrer was employed. Electrolytic hydrogen was used without additional purification. A suitable amount of the rhodium complex was placed in the reactor, the equipment was filled with hydrogen and then 20 ml alcohol was added through the dropping funnel. The solution was stirred for 1 hour under hydrogen and then 2 ml cyclohexene was added. The rate of hydrogenation was determined from pressure changes. In certain cases, after the pressure dropped by about 30 cm Hg, stirring was interrupted and hydrogen was refilled without refilling the olefins.

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