

## Rhodium(I) complexes with 1,*n*-bis(diphenylphosphino)alkane ligands

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### Abstract

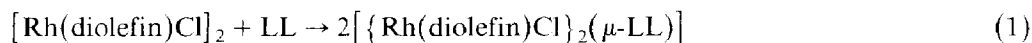
The reaction of  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  and 1,*n*-bis(diphenylphosphino)alkanes ( $n = 3-6$ ) (LL) in 2/1 ratio, gave dinuclear  $[\{\text{Rh}(\text{diolefin})\text{Cl}\}_2(\mu\text{-LL})]$  complexes with only one diphosphine group, bridging the two metal atoms, irrespective of the aliphatic chain length in the ligand. When the reactions were performed in solutions saturated with CO, only dinuclear  $[\text{Rh}(\text{Cl})(\text{CO})(\mu\text{-LL})]_2$  carbonylated complexes containing one molecule of diphosphine per rhodium atom were obtained. Addition of  $\text{SnCl}_2$  to  $[\text{Rh}(\text{diolefin})\text{Cl}]_2/\text{LL}$  (2/1) solutions gave only  $\text{Rh}(\text{SnCl}_3)(\text{diolefin})(\text{LL})$  complexes.

### Introduction

The chemistry of rhodium(I) complexes containing bis(phosphine) ligands has attracted much attention during the last years mainly owing to their possible catalytic activity [1]. Although compounds with bis(diphenylphosphino)methane and related ligands have been studied fairly extensively, less attention has been given to complexes containing  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ligand with,  $n > 2$ , and the isolated species contain at least one diphosphine group per rhodium atom [2-5]. Our previous observations, indicating that the reactions of  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  with bidentate N-donor ligands ( $\text{Rh}/\text{NN} = 2/1$ ) may give different types of products depending on electronic or steric factors in the ligands [6,7] prompted us to study such reactions with  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  species with  $n = 3-6$  in order to determine the influence of the chain length on the products formed when using  $\text{Rh}/\text{PP} = 2/1$  stoichiometric ratios, and on the reactivity of the complexes thus formed. The obtained results reveal the formation, irrespective of the ligand used, of dinuclear complexes  $[\{\text{Rh}(\text{diolefin})\text{Cl}\}_2(\mu\text{-LL})]$ , which contain only one diphosphine group, apparently bridging the two metal atoms.

## Results and discussion

The reaction between  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  dimers and diphosphine ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 3$ : dppp;  $n = 4$ : dppb;  $n = 5$ : dpppen;  $n = 6$ : dpph) in the stoichiometric ratio  $\text{Rh}/(\text{LL}) = 2/1$ , leads to neutral  $[\{\text{Rh}(\text{diolefin})\text{Cl}\}_2(\mu\text{-LL})]$  species.



The isolated complexes ( $n = 3, 4, 6$ ) are yellow, and reasonably stable in the solid state, and their analytical and IR data and yields are listed in Table 1. The compounds with dpppen, though formed as indicated by the  $^{31}\text{P}$  NMR spectra (Table 2), could not be isolated pure.

These compounds behave as non-electrolytes in acetone solution, and their IR spectra show one band around  $300\text{ cm}^{-1}$  due to  $\nu(\text{Rh}-\text{Cl})$ , confirming that the chlorine is bonded to the rhodium atom in the solid state. Vapor pressure osmometry in the case of the compounds containing dppb confirmed the dimeric nature of  $[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dppb})$  MW = 952 (calc. 919) and of  $[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppb})$  MW = 882 (calc. 887). (COD = cyclooctadiene, NBD = norbornadiene) The insolubility of dpph compounds and the instability of the dppp complexes solutions precluded molecular weight measurement.

Table 2 shows the  $^{31}\text{P}$  NMR data for the isolated complexes as well as those for equimolar mixtures of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and dpppen or of  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  and dpppen in  $\text{CDCl}_3$  at  $16^\circ\text{C}$ . All these compounds show only simple doublet patterns due to  $^{103}\text{Rh}$  splitting. The absence of any signal due to free phosphine confirms that both phosphorus atoms in the ligand are bonded to rhodium and equivalent. The spectra are unchanged when the temperature is lowered to  $-40^\circ\text{C}$ .

Table 1  
Analytical and IR data and yield for diphosphine complexes

Complex	Analysis (Found. (calc.)(%)		$\nu(\text{M}-\text{Cl})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}\equiv\text{O})$ ( $\text{cm}^{-1}$ )	Yield (%)
	C	H			
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dppp})$	56.13 (57.03)	5.76 (5.52)	258(w)		37
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppp})$	55.37 (56.36)	4.74 (4.81)	288(w)		40
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dppb})$	58.23 (57.47)	6.16 (5.70)	290(m)		73
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppb})$	55.30 (56.84)	5.27 (4.96)	287(m)		72
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dpph})$	57.46 (58.29)	5.83 (5.91)	290(m)		65
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppph})$	56.23 (57.71)	4.97 (5.24)	290(m)		33
$[\text{Rh}(\text{Cl})(\text{CO})(\mu\text{-dpppen})]_n$	57.89 (59.36)	4.79 (4.49)	305(m)	1950(s)	64
$[\text{Rh}(\text{Cl})(\text{CO})(\mu\text{-dpph})]_n$	59.66 (59.95)	5.11 (5.15)	315(m)	1945(s)	66
$\text{Rh}(\text{SnCl}_3)(\text{COD})(\text{dpph})$	50.52 (50.11)	4.76 (4.64)	300(s),275(s) 260(s)		72

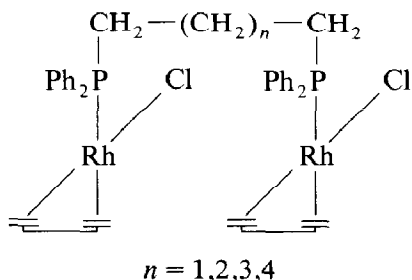
Table 2  
 $^{31}\text{P}$  NMR data for free diphosphine and diphosphine complexes

Complex	$\delta(^{31}\text{P})$ (ppm)	$\delta(^{31}\text{P})$ (ppm)(free)	$\Delta\delta(^{31}\text{P})^a$	$^1J(^{103}\text{Rh}, ^{31}\text{P})$ (Hz)
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dppp})$	11.3	-17.0	28.3	127
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppp})$	17.2	-17.0	34.2	127
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dppb})$	26.2	-15.9	42.1	148
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dppb})$	26.8	-15.9	42.7	169
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dpppen})$ "in situ"	26.8	-15.8	42.6	147
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dpppen})$ "in situ"	27.3	-15.8	43.1	169
$[\text{Rh}(\text{COD})\text{Cl}]_2(\mu\text{-dpph})$	26.7	-15.7	42.4	148
$[\text{Rh}(\text{NBD})\text{Cl}]_2(\mu\text{-dpph})$	27.2	-15.7	42.9	168
$\text{Rh}(\text{Cl})(\text{COD})(\text{PPh}_3)^b$	31.3	-5.4	36.7	149
$\text{Rh}(\text{Cl})(\text{NBD})(\text{PPh}_3)^b$	31.6	-5.4	37.0	171

<sup>a</sup>  $\delta(^{31}\text{P}) - \delta(^{31}\text{P})$  (free) ppm. <sup>b</sup> Ref. 8.

The  $^1J(\text{Rh}-\text{P})$  values are as expected for this type of compound, and are slightly higher for the complexes containing NBD than for those containing COD. The  $^1J(\text{Rh}-\text{P})$  and  $\delta(\text{P})$  values are similar to those for related neutral monophosphine chloro complexes such as  $\text{Rh}(\text{Cl})(\text{COD})(\text{PPh}_3)$  or  $\text{Rh}(\text{Cl})(\text{NBD})(\text{PPh}_3)$  [8] (Table 2) and support a non-chelating diphosphine coordination in our complexes, since chelation should significantly affect the  $\delta(\text{P})$  values [9]. The  $^{31}\text{P}$  NMR spectrum of  $[\text{Rh}(\text{COD})(\text{dpppen})]^+$ , which contains a chelating diphosphine, shows the main signal at much lower frequency (7.3 ppm) and a weak signal at 24.8 ppm that has been suggested to arise from species containing bridging diphosphine groups [10]. Finally, the complexes containing dppp show different  $\delta(\text{P})$  values, but dppp complexes usually do give rather different  $\delta(\text{P})$  values than dppb analogous complexes [5], perhaps owing to lower flexibility in the aliphatic chain of the coordinated dppp.

From these data we conclude that the  $[\{\text{Rh}(\text{diolefin})\text{Cl}\}_2(\mu\text{-LL})]$  must be dimeric, with one diphosphine bridging group and terminal chlorine atoms, as follows:

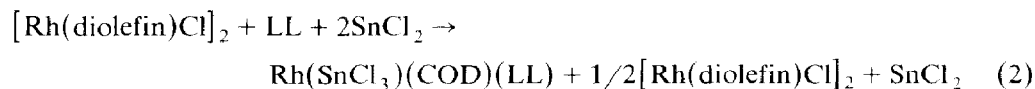


Similar structures have been proposed for other rhodium(I) complexes with 1,5-cyclooctadiene and disilyoxydiphosphine ligands with five or more atoms between the two P-donor atoms [11].

When  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  and the corresponding diphosphine ( $\text{Rh}/\text{LL} = 2/1$ ) react under carbon monoxide, carbonylated species showing two strong absorptions due to  $\nu(\text{C}\equiv\text{O})$  between 2100 and 2000  $\text{cm}^{-1}$  are formed in the solutions. However, the only isolable species were  $[\text{Rh}(\text{Cl})(\text{CO})(\mu\text{-LL})]_2$  complexes containing one

molecule of diphosphine per rhodium atom and showing only one  $\nu(\text{C}\equiv\text{O})$  vibration (see Table 1), which are probably similar to the dimeric complexes described by Sanger [2]. The high insolubility of the complexes with dppen or dppe in common organic solvents has precluded any measurement in solution.

This behaviour indicates that these ligands show a marked tendency to form rhodium compounds containing one molecule of diphosphine per rhodium atom, and this is also the case for the reactions of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  with dppe or dppe and  $\text{SnCl}_2$  in the stoichiometric ratios  $\text{Rh}/\text{LL}/\text{SnCl}_2 = 2/1/2$ , the only isolable species being the previously reported complex  $\text{Rh}(\text{SnCl}_3)(\text{COD})(\text{dppe})$  [12] or the rather insoluble compound  $\text{Rh}(\text{SnCl}_3)(\text{COD})(\text{dppe})$  (Table 1)



A 2/2/2 = Rh/LL/SnCl<sub>2</sub> stoichiometric ratio is required for complete reaction of the starting material.

## Experimental

$[\text{Rh}(\text{COD})\text{Cl}]_2$  [13] and  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  [14] compounds were prepared by published methods. The C and H microanalysis were carried out with a Perkin-Elmer 240C microanalyser. Conductivities were measured for ca.  $2.5 \times 10^{-4}$  M acetone solutions with a Metrohm E 518 conductimeter. IR spectra were recorded with a Perkin-Elmer 598 spectrophotometer in the range 4000–200  $\text{cm}^{-1}$  using Nujol mulls between polyethylene sheets.  $^{31}\text{P}$  NMR spectra were recorded on an XL-300 Varian spectrometer with external  $\text{H}_3\text{PO}_4$  as standard and deuteriochloroform as the solvent. Molecular weights were measured with a Knauer vapor osmometer calibrated with benzil and with benzene or chloroform as solvent.

### *Synthesis of $[\text{Rh}(\text{diolefin})\text{Cl}]_2(\mu\text{-dppp})$*

To a  $\text{CH}_2\text{Cl}_2$  solution of the corresponding  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  dimer (0.06 mmol), cooled to  $-10^\circ\text{C}$ , was added an equimolar amount (0.06 mmol) of 1,3-bis(diphenylphosphino)propane. Addition of cold hexane gave yellow precipitates that were filtered off, washed with cold, hexane and dried. All operations were performed under  $\text{N}_2$ .

### *Synthesis of $[\text{Rh}(\text{diolefin})\text{Cl}]_2(\mu\text{-dppb})$*

To a  $\text{CH}_2\text{Cl}_2$  solution of the corresponding  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  dimer (0.06 mmol) was added an equimolar amount (0.06 mmol) of 1,4-bis(diphenylphosphino)butane in acetone. Evaporation of the  $\text{CH}_2\text{Cl}_2$  gave yellow complexes, which were filtered off, washed with acetone, and air-dried.

### *Synthesis of $[\text{Rh}(\text{diolefin})\text{Cl}]_2(\mu\text{-dpph})$*

Addition of 1,6-bis(diphenylphosphino)hexane (0.06 mmol) to  $\text{CH}_2\text{Cl}_2$  solutions of the corresponding  $[\text{Rh}(\text{diolefin})\text{Cl}]_2$  dimer (0.06 mmol), followed by hexane addition and evaporation of the  $\text{CH}_2\text{Cl}_2$  gave yellow precipitates which were filtered off, washed with hexane, and air-dried.

### *Synthesis of $[Rh(CO)(Cl)(\mu-LL)]_2$*

Carbon monoxide at atmosphere pressure was bubbled for 30 min through  $CH_2Cl_2$  solutions containing  $[Rh(COD)Cl]_2$  (0,06 mmol) and the corresponding diphosphine (0,12 mmol). The complex containing 1,6-bis(diphenylphosphino)hexane separated as it formed, but addition of diethyl ether was required for precipitation of the compound containing 1,5-bis(diphenylphosphino)pentane. The solids obtained were filtered off, washed with diethyl ether, and air-dried.

### *Synthesis of $Rh(SnCl_3)(COD)(dpph)$*

To a  $CH_2Cl_2$  solution of  $[Rh(COD)Cl]_2$  (0.06 mmol) was added 1,6-bis(diphenylphosphino)hexane (0.12 mmol). Upon addition of tin(II) chloride (0.12 mmol) in MeOH a yellow solid separated, and this was filtered off, washed with methanol, and air-dried.

### **Acknowledgment**

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