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Synthesis Rh(III) Mononuclear Complexes of Polar Tertiaryphosphines for Aqueous Biphasic Catalysis

**Srinivas Kunta[1], Ramesh Balaboina[1], Narasimha Swamy Thirukovela[1],
Manda Srinivas,[1] Ravinder Vadde[1] Satyanarayana Mavurapu[2],
P. Muralidhar Reddy[3] and Chandra Sekhar Vasam[2]***

1. Department of Chemistry, Kakatiya University, Warangal, (T.S.), **INDIA**
2. Department of Pharmaceutical Chemistry, Telangana University, Nizamabad, (T.S.), **INDIA**
3. Department of Chemistry, Nizam College, Osmania University, Hyderabad, (T.S.), **INDIA**
Email: ravichemkuc@gmail.com, csvasam@telanganauniversity.ac.in

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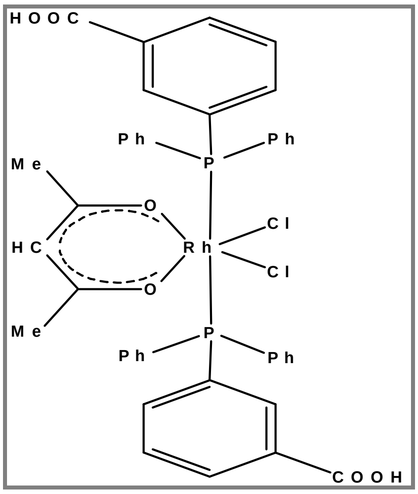
ABSTRACT

A series of new Rh(III) complexes $[RhCl_2(acac)(PR_3)_2]$ *with polar tertiaryphosphines viz., (2, formyl phenyl) diphenylphosphine, (2-carboxy)phenyldiphenylphosphine, (3-carboxy) phenyldiphenyl phosphine, (4-carboxy) phenyldiphenylphosphine, (4-pyridyl) diphenylphosphine, bis (carboxymethyl) phenyl phosphine, tris (carboxymethyl)phosphine have been synthesized and characterized by elemental analysis, IR,* ^{1}H, ^{13}C, ^{31}P *and electronic spectral data. The spectral data revealed that co-ordination chemistry about Rh(III) metal center is octahedral with two phosphine ligands in the trans positions. Preliminary results indicate that these water-soluble complexes are efficient in benzyl alcohol oxidation in toluene/water biphasic media.*

Graphical Abstract



Proposed geometry of Rh(III)-phosphines.

Keywords: Polar phosphines, Rh(III)-phosphine catalysts, Aqueous biphasic catalysis, Alcohol oxidation.

INTRODUCTION

Recently much attention has been devoted to the synthesis of water-soluble transition metal complexes **[1-4]**, because of their great application in homogeneous catalysis in terms of recovery and recycling. This is particularly effective when expensive transition metal complexes [**5, 6**] like the members of platinum group metals were used. Generally the water-solubility of the metal complexes can be achieved via the coordination of water-soluble or polar group appended ligands (Figure 1). It is well known and extremely common for the transition metal complexes to contain organo-phosphorous ligands those used for homogeneous catalysis. Much emphasis has been put on hydrophilic i.e. polar group functionalized phosphines in organometallic chemistry [**1**] because these ligands can accord water solubility to their coordination compounds. Besides, among the metal complexes of phosphines, a special attention has been focused on phosphine complexes with rhodium metal center in terms of synthesis, characterization, reactivity and application.

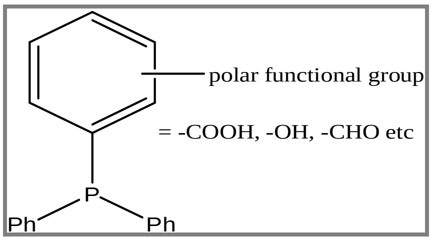


Figure 1. Polar group appended tertiaryphosphines.

Previously we have reported the synthesis, characterization and catalytic performance of water-soluble Rh(I) complexes of hydrophilic tertiaryphosphines containing polar functional groups such as carboxyl and formyl [**6**]. Depending on the steric environments around the metal center, these functionalized tertiary phosphines can behave as either monodentate or bidentate. We now consider to investigate the accessibility of water-soluble Rh(III) complexes with hydrophilic tertiary phosphines (Scheme 1) and their coordination behavior. The possible reversibility associated with (+3) and (+1) oxidation states of rhodium is much useful in catalysis and other application **[7]**. This manuscript describe the synthesis, spectral characterization and catalytic behavior of new Rh(III) mononuclear complexes with the general formula $[RhCl_2(acac)(PR_3)_2]$, using $[RhCl_2(acac)(acaH)]$as a precursor (Where PR_3 = tertiary phosphines shown in scheme-1 and acac = acetylacetonate).The precursor complex, $[RhCl_2(acac)(acaH)]$, containing a neutral acacH, which was substituted by the tertiary phosphine ligands during the reaction course as follows.

MATERIALS AND METHODS

All the solvents, organic reagents and $RhCl_3$ used were AR grade. $RhCl_3$, acac were obtained from Aldrich chemical company, Inc., USA. The deutirated solvents were procured from the same. The functionalized tertiaryphosphines were prepared according to the literature methods [**8, 9**].

The precursor $[RhCl_2(acac)(acacH)]$ was also synthesized according to the literature method. All the synthetic reactions have been carried out in the inert atmosphere using shlenk technique. The IR spectra of the metal complexes were recorded in KBr pellets on Nicolet-740 spectrophotometer and Perkin-Elmer 580B spectrophotometer. The scanning time was 6 min in the range of 4000-200 cm^{-1}. Jeol 100 MHz FT NMR spectrophotometer and Brucker WH 270 (270 MHz) NMR spectrophoto-meter were used for recording ^{1}H,^{13}C ^{31}P NMR available at technical university Berlin were used to record the corresponding spectra. The C, H, and N analysis of metal complexes were carried using a Perkin Elmer CHN analyzer 240C. The electronic spectra of metal complexes in solutions of methanol were recorded on Schimadzu MPS-5000 spectrophotometer

Synthesis of Rh(III) Complexes:

$[RhCl_2(acac)(Ph_2P\text{-}2\text{-}C_6H_4CHO)_2]$: The ligand (2-formylphenyl)diphenylphosphine (0.290 g 1 mmol) was dissolved in 15 mL of methanol and was added drop wise to a methanolic solution of $[RhCl_2(acac)(acacH)]$(0.185g 0.5mmol). The above reaction mixture was heated under refluxing condition for 2 h. During the reaction period a change in the colour of the solution from yellow brown to orange red was observed. The solvent volume was reduced to 10 mL under vacuum. Addition of diethyl ether resulted in the formation of orange crystalline precipitate. It was filtered and washed with ether and dried in vacuo: Yield 0.29g (62%): Anal. Calc. For $C_{43}H_{37}O_4P_2Cl_2Rh$: C, 60.49;H, 4.33;Cl, 8.32. Found: C, 59.13;H, 4.56;Cl, 8.57%. IR (v cm-1): 1680(CHO), 1590 and 1545(ms C=C+C=O and C=O+C=C), 370(ws Rh-Cl). ^{1}H-NMR (δ ppm): 2.40(CH_3), 5.20(CH), 10.80(CHO), 7.20-8.50(H aryl). ^{13}C-NMR (δ ppm): 193.34(C=O), 108.46(-CH), 185.01 (CHO), 27.61(-CH_3) 128.52-138.41(arylC): ^{31}P-NMR in CD_3OD; 26.75(d):

$[RhCl_2(acac)(Ph_2P\text{-}2\text{-}C_6H_4COOH)_2]$: A mixture of (2-carboxyphenyl)diphenylphosphine (0.306 g 1 mmol) and Rh(acac)(acacH) (0.185 0.5 mmol) in acetone (10 mL) was refluxed on a water bath for 1.5 h. The yellow solution was evaporated to dryness and the yellow compound was recrystallized from methanol. The product was washed with cold methanol and dried in vacuo: Yield 0.32g(65%): Anal. Calc. For $C_{43}H_{37}O_6P_2Cl_2Rh$: C, 58.31;H, 4.18;Cl, 8.02. Found: C, 58.14;H, 4.26;Cl, 7.84%. IR (vcm-1): 1695(COOH), 1570 and1530 (C=C+C=O and C=O+ C=C), 360(Rh-Cl).^{1}H-NMR (δ ppm): 2.25(CH_3), 5.30(CH), 10.95(COOH), 7.20-8.40(H-aryl).^{13}C-NMR(δppm): 193.58(C=O), 107.52(CH), 171.35 (COOH), 24.85(CH_3) 125.73-138.65 (aryl C): ^{31}P-NMR in CD_3OD 31.14(d):

$[RhCl_2(acac)(Ph_2P\text{-}3\text{-}C_6H_4COOH)_2]$: To a hot [Rh(acac)(acacH)] (0.185g 0.5mmol) solution in hexane (10 mL) (3-carboxyphenyl)diphenylphosphine (0.306g 1mmol) was added. The mixture was refluxed for ca. 3h. The dark yellow product was filtered off, washed with hexane and dried in vacuo. Yield 0.30g (62%): Anal. Calc. For $C_{43}H_{37}O_6P_2Cl_2Rh$: C, 58.31;H,4.18;Cl,8.02. Found: C, 58.43;H, 4.16;Cl, 8.13%. IR (v cm-1): 1710(COOH), 1560 and 1515(ms C=C+C=O and C=O+C=C), 355 (ws Rh-Cl). ^{1}H-NMR (d ppm): 2.20(CH_3), 5.30(CH), 11.3(COOH), (7.15-8.30)(H aryl). ^{13}C-NMR (d ppm): 195.12(C=O), 108.07(CH), 171.65(COOH), 29.98(CH_3) 125.36-139.82(aryl C): ^{31}P-NMR in CD_3OD 34.83(d).

$[RhCl_2(acac)(Ph_2P\text{-}4\text{-}C_6H_4COOH)_2]$: A mixture of (4-carboxyphenyl)diphenylphosphine (0.306g 1mmol) and [Rh(acac)(acacH)] (0.185g 0.5mmol) in ethanol (10 mL) was refluxed for ca. 2h. The light yellow product was filtered off, washed with cold ethanol and dried in vacuo: Yield 0.30 g (62%): Anal. Calc. For $C_{43}H_{37}O_6P_2Cl_2Rh$: C, 58.31;H, 4.18;Cl, 8.02. Found: C, 59.05; H, 4.25; Cl, 7.91%. IR (ν cm-1): 1720(COOH), 1580 and 1535(ms C=C+C=O and C=O+C=C), 375(Rh-Cl).^{1}H-NMR (δ ppm): 2.25(CH_3), 5.25(CH), 11.40(COOH),7.20-8.35(H aryl). ^{13}C-NMR (δ ppm): 194.31(C=O), 108.35(CH), 168.45(COOH), 28.60(CH_3) 126.49-138-85(aryl C): ^{31}P-NMR in CD_3OD 36.05(d).

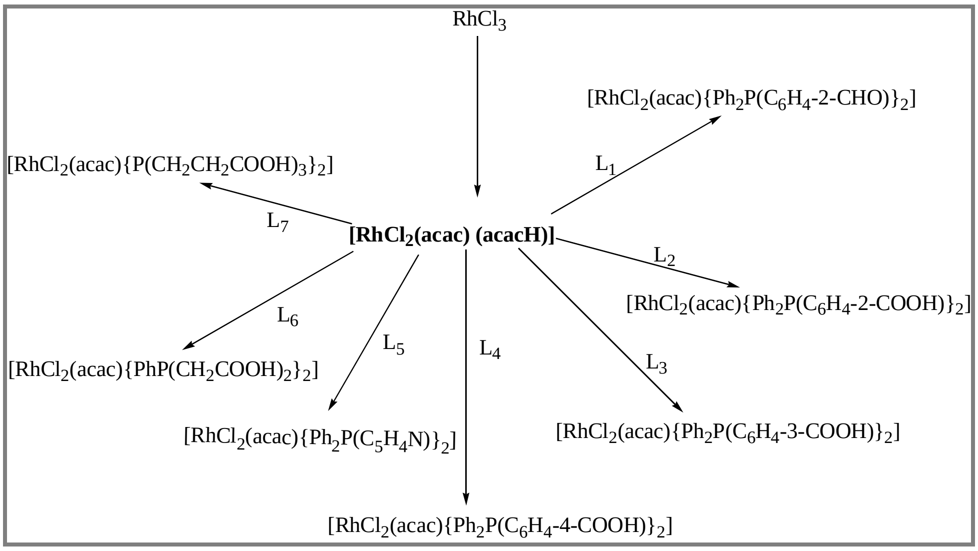
$[RhCl_2(acac)(Ph_2P\text{-}2\text{-}C_5H_4N)_2]$: A mixture of (2-pyridyl)diphenylphosphine (0.263 g 1 mmol) and [RhCl2(acac)(acacH)] (0.185g 0.5mmol) in methanol (8 mL) was stirred at room temperature for ca. 1 h and then concentrated to ca 4 mL. After addition of diethyl ether, the yellow product was filtered off, washed with cold methanol and diethyl ether and dried in vacuo: Yield 0.295g(66%): Anal. Calc. For $C_{39}H_{35}N_2O_2P_2Cl_2Rh$: C, 58.58;H, 4.38;N, 3.50;Cl, 8.88. Found: C, 58.34;H, 4.26;N, 3.65;Cl, 8.57%. IR (ν cm-1): 1630(C=N), 1575 and1520(ms C=C+C=O and C=O+C=C), 365(Rh-Cl).^{1}H-NMR (δ ppm): 2.25(CH_3), 5.10(CH), 7.10-8.25(H aryl). ^{13}C-NMR (δ ppm): 189.35(C=O), 108.60(CH), 140.25(C=N), 25.30(CH_3) 127.51-139.24(aryl C): ^{31}P-NMR in CD_3OD 32.97(d).

$[RhCl_2(acac)\{PhP(CH_2COOH)_2\}]$: To a hot [$RhCl_2$ (acac)(acacH)](0.185 g 0.5 mmol) in dichloromethane (10 mL), the ligand $P(CH2CH_2COOH)_2$ (0.226g 1 mmol) in dichloromethane (10 mL) was added. The resulting solution was refluxed for 2 h on a water-bath. During that time the solution colour was gradually changed from red to lemon yellow. Later the solution was concentrated to one third of its volume and added chilled hexane. The lemon yellow crystalline precipitate separated was filtered off, washed with hexane and dried in vacuo. Yield 0.292g (62%): Anal. Calc. For $C_{25}H_{29}O_{10}P_2Cl_2Rh$: C, 41.38; H, 4.00;Cl, 9.79. Found: C, 40.72; H, 4.16;Cl, 9.62%. IR (ν cm-1): 1715(COOH), 1585 and 1530(ms C=C+C=O and C=O+C=C), 360(ws Rh-Cl).^{1}H-NMR (δ ppm): 2.26(CH_3), 5.28(CH), 11.90(COOH), 7.25-8.05(H aryl). ^{13}C-NMR (δ ppm): 192.80(C=O), 109.25 (CH), 169.40(COOH), 128.30-132.55 (C-aryl), 28.45(CH_3) 129.94-138.56(aryl C): ^{31}P-NMR in CD_3OD 75.37(d).

[$RhCl_2$(acac){P(CH_2CH_2COOH)$_2$}$_2$]: A hot solution of [$RhCl_2$ (acac)(acacH)](0.185g 0.5 m mol) in hexane (10cm3) was added dropwise to a suspension of tris(carboxyethyl)phosphine (0.286g 1mmol) in hexane (8 mL). The mixture was refluxed for ca. 3h. The orange product was filtered off, washed with hexane and dried in vacuo: Yield 0.263 g (64%): Anal. Calc. For $C_{23}H_{37}O_{14}P_2Cl_2Rh$: C, 35.70;H, 4.78;Cl, 9.18. Found: C, 34.95; H,4.56; Cl,9.29%. IR(ν cm-1): 1705(COOH), 1575 and 1525(ms C=C+C=O and C=O+C=C), 375(Rh-Cl).^{1}H-NMR (δ ppm): 2.15(CH_3), 5.20(CH), 11.45(COOH). ^{13}C-NMR (δ ppm): 193.25(C=O), 109.30(CH), 172.05(COOH), 27.85(CH_3) 139.24 (-C-P): ^{31}P-NMR in CD_3OD 24.16(d).

RESULTS AND DISCUSSION

Reaction of [$RhCl_2$(acac)(acaH)] with polar tertiaryphosphines ligands: The precursor, [$RhCl_2$ (acac) (acaH)], was obtained by the reaction of $RhCl_3$ in acetyl acetone medium [10]. As [$RhCl_2$ (acac) (acaH)], containing a neutral acetyl acetone, is soluble in many organic solvents viz., acetonitrile, chloroform, methanol, ethanol, allowing a wide range of its reactivity studies. The IR spectrum of this compound in CH_2Cl_2 has shown a new band at 1730cm^{-1}, which can be attributed to νCO of the free acetyl acetone and indicates the possible generation of [$RhCl_2$(acac)(solvent)$_2$]. A reaction of which with P donor tertiary phosphines is resulted in the formation of [$RhCl_2$(acac)(L)$_2$] type complexes [where L=(2, formylphenyl) diphenylphosphine, (2-carboxy) phenyldiphenyl phosphine, (3-carboxy) phenyl diphenyl phosphine, (4-carboxy) phenyldiphenylphosphine, (4pyridyl) diphenylphosphine, bis (carboxy ethyl) phenylphosphine, tris(carboxymethyl)phosphine (Scheme 1). All the Rh(III) complexes (1-7, Scheme 1) are diamagnetic, confirming no change in the (+3) oxidation state of metal during the substitution with tertiaryphosphine. The molecular formulae and geometry for all the Rh(III) complexes is proposed by based on the data obtained from elemental



Scheme 1. The formation of the Rh(III)-phosphine complexes.

analysis, IR, ^{1}H, ^{13}C, ^{31}P and electronic spectral data. The formation of the Rh(III) complexes is shown in the scheme 1.

Elemental analysis: The percentage of C, H and N of complexes and their decompositions are given in materials and method section. The calculated values of percentage content are found to be in agreement with the experimental value. It is observed that metal reacts with the phosphine ligands in 1:2 ratios.

IR and NMR Spectral data: In the characterization part, first we discuss the electronic changes that associates with acac moiety and then the tertiary phosphines in the Rh(III) coordination sphere. The IR spectra of all the Rh(III) complexes (1-7) show the two characteristic absorption bands at 1500-1600cm^{-1}are assignable to only νC-C+νC-O and νC-O+νC-C of chelated O-bonded acetylacetonate [10-11].The band corresponds to neutral acac at 1630 cm^{-1}, which appeared in the precursor spectrum, is disappeared in the spectra complexes **1-7** suggests that the neutral acetylacetone moiety was displaced from the coordination sphere by the tertiaryphosphines.^{1}H and ^{13}C-NMR data also did not show the signals correspond to neutral acac-H. The ν(Rh-P) assignations for the new bands found at 550-570 cm^{-1} are consistent with previous reports. In presence of the tertiaryphosphines, the symmetrical coordination of acetylacetonate to the Rh(III) metal center is supported by ^{1}H-NMR and ^{13}C-NMR spectra, where two methyl groups appeared as only one intense singlet signal in the region of 2.1-2.4ppm of ^{1}H and 27-30ppm of ^{13}C-NMR shifts [12]. Furthermore, the ν(Rh-Cl) assignments found at ~ 370-390 cm^{-1} possesses a split band, suggests that the two chlorides are in *cis* position. Based on this result we propose that the tertiaryphosphine ligands are *trans* to each other and in *cis*-positions to the two carbonyls groups of acac ligand and show equal electronic effect on methyl groups. The trans-position of phosphines is clearly evidenced from the ^{31}P-NMR spectra, which discussion will fall soon.

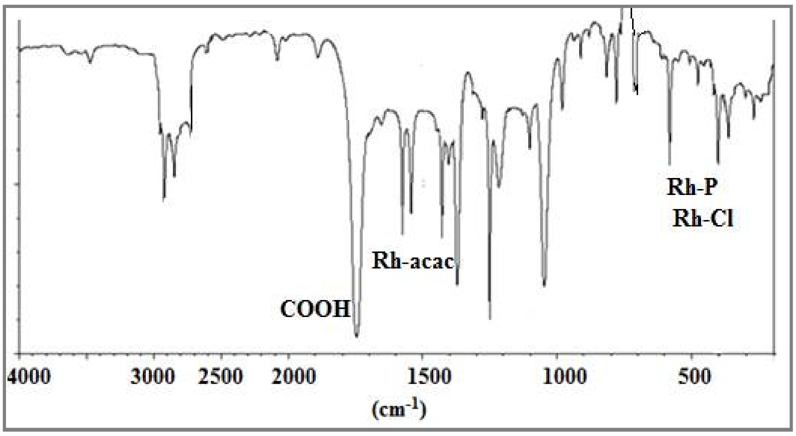


Figure 2. IR spectrum of $[RhCl_2(acac)(Ph_2P\text{-}2\text{-}C_6H_4COOH)_2]$

Regarding the study of electronic changes associates with the functionalized tertiaryphosphines; both IR and NMR (1^H, ^{13}C and ^{31}P) spectral data evident that the functionalized tertiaryphosphines coordinates to the Rh(III) metal center only through the phosphorous atom and the polar functional groups on phosphine did not participate in the chelation. However, the prominent Rh-P vibrations are observed at ~570-540 cm^{-1}, which are consistent with the previous reports. For example, a representative IR spectrum of Rh(III) complex (**2**) (Figure 2), which is formed with (2-carboxyphenyl) diphenylphosphine displayed a band at ~1730cm^{-1} corresponds to free ν(COOH). This band is exactly similar to the free ligand absorption [12]. The same phenomenon is observed with tertiaryphoshines of formyl, other carboxyl and pyridyl functional groups, where complexes1, 3,4,6 show the bands at 1690-1720 for free ν(COOH) and ν(CHO), and complex **5** at 1630 cm^{-1} for free pyridyl nitrogen.

Analysis of the ^{1}H and ^{13}C NMR spectra also reflected the non-involvement of functional groups of phosphines in the chelation. For example, the Rh(III) complex **3**formed with (3-carboxyphenyl) diphenylphosphine exhibit one characteristic ^{1}H-NMR signal at 11.30 ppm and ^{13}C-NMR signal at 171.65 ppm corresponds to the uncoordinated carboxyl group. Similar pattern is observed in the rest of the Rh(III) complexes. Further, the aryl protons of the complexes are displayed the signals as a multiplet towards down field in the range of ~6.5-8.50 ppm and the aryl carbon signals in the range of ~127-140 ppm respectively. The data is given in the experimental part. It is suggested that the monodentate behavior possessed by tertiaryphosphine ligands are likely to be controlled by the acidic nature of substituent [13].

The coordination of phosphorous atom of tertiary phosphine can be explained better in terms of ^{31}P-NMR spectral evidence than IR and other NMR spectra. It has long been proposed that phosphines can act as sigma donors and as well as pi acceptors. The ^{31}P-NMR chemical shifts in the coordination compounds are usually observed in down field as compared to that of free ligand mainly due to the strong σ donor bond from phosphorous to metal with small dπ-dπ back donation from the metal ion to phosphorous. The ^{31}P-NMR spectra of all the complexes exhibited only one doublet signal. The appearance of only doublet signal for each complex strongly suggests that the two phosphines are mutually *trans* to each other in the coordination sphere as shown in the figure 3. The extent of chemical shift of phosphine ligand in the complex depends on its sigma donation (^{31}P-NMR δ difference correlation) capacity as shown in table 1.

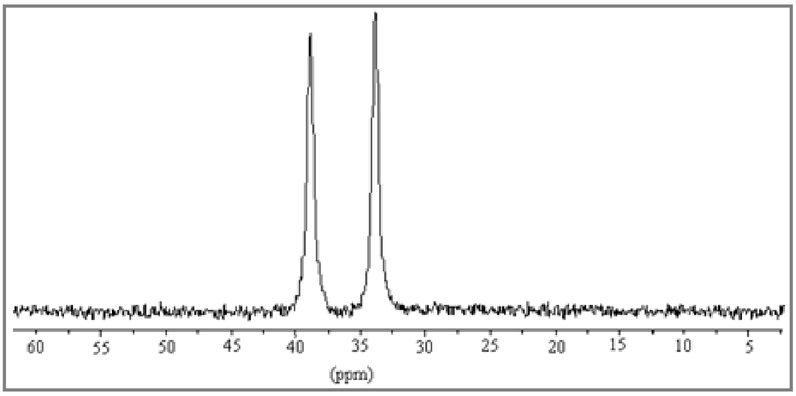


Figure 3. ^{31}P-NMR spectrum of $[RhCl_2(acac)(Ph_2P\text{-}3\text{-}C_6H_4COOH)_2]$.

Table 1. Correlation between Δ δ^{31}P-NMR of complex and free ligand

S.No.	Complex ^{31}P-NMR δ (ppm)	Free ligand ^{31}P-NMR δ (ppm)	Δ δ^{31}P-NMR δ (ppm)
1	26.75	11.44	-38.19
2	31.14	-4.7	35.84
3	36.72	-6.4	43.12
4	36.03	--5.1	41.13
5	29.74	5-3.2	32.94
6	75.37	29.00	46.37
7	24.16	7-26.3	50.4

Electronic spectra: The electronic spectra of all the complexes in room temperature in acetone exhibited two or three bands of comparable intensity in the range of 340-270 nm. The Rh(III) species is a strongly reducing in character that their d-d transitions are usually obscured by intense charge transfer transitions. The band at 340-310 nm may be assigned to metal-ligand charge-transfer transaction. Whereas the bands at 265-270 nm may be assigned to intra-ligand pi-pi transitions of acetyl acetonate or phenyl rings. However the selected complexes 2, 3 and 7 in methanol, exhibited an additional band in the region of 450-470 (ε=400-450), which may be assigned to the d-d transition $^{1}A_{1g}$—$^{1}E_{1g}$ or $^{1}A_{2g}$ [**14-17**].

Based on IR, ^{1}H, ^{13}C,^{31} P-NMR and electronic spectral data of the present series Rh(III) Complexes, it is confirmed that among the six bonding sites on rhodium metal center in which two are occupied by O-O donor *acac*, two are occupied by two chlorides (*cis*) and the remained two bonding sites are occupied by two tertiaryphosphine ligands coordinating through phosphorous atoms. In view of the above discussions, the structures proposed tentatively as octahedral for the above complexes. A representative complex structure is shown in the following way (Figure 4).

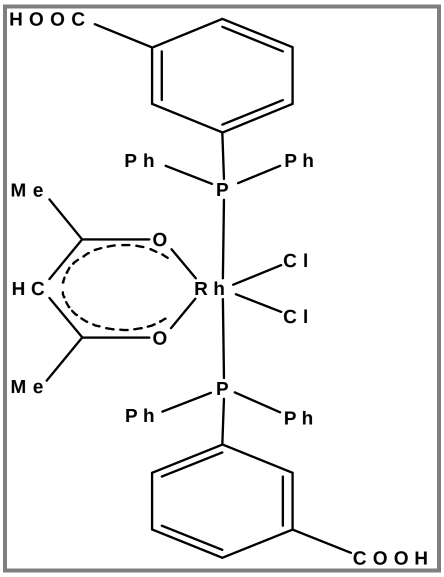


Figure 4. Proposed geometry of Rh(III)-phosphines.

APPLICATION

Catalytic oxidation of alcohols is one of the important topics in both homogeneous and heterogeneous catalysis [1+ R]. The catalytic oxidation reactions carried out with Rh(III) water-soluble catalysts on benzyl alcohol in toulene/water biphasic media at 90°C in the presence of tetrabutyl hydroperoxide (TBHP) as oxidant and tetrabutylammonium bromide (TBABr) as PTC has produced the benzaldehyde as the major product and benzoic acid and benzyl benzoate as minor products. Addition of excess tertiaryphosphine does not greatly affect the reaction. At this stage we have been trying to optimize the over oxidation of benzyl alcohol to benzoic acid and as well as the ester condensed product. It is our aim to limit the oxidation of benzyl alcohol selectively to benzaldehyde only. Full details of the selective oxidation and catalyst recycling work will be communicated soon.

CONCLUSION

A series of water-soluble Rh(III) complexes with functionalized tertiaryphosphines have been synthesized simply by using $[RhCl_2(acac)(acac-H)]$ as a precursor. The data obtained from IR, ^{1}H, ^{13}C,^{31} P-NMR techniques suggests that the tertiary phosphines coordinates to the Rh(III) only through the phosphorous atom and the functional groups did not take part in the chelation. The appearance only one doublet ^{31}P-NMR signal suggests that the two phosphines are mutually *trans* to each other and *cis* to the carbonyl groups of *acac* and chlorides. These water-soluble complexes are efficient for alcohol oxidation in toluene/water biphasic media.

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REFERENCES

[1]. K. H. Shaughnessy, Hydrophilic Ligands and Their Application in Aqueous-Phase Metal-Catalyzed Reactions, *Chem. Rev.*, **2009**, 109, 643-710.

[2]. P. H. Dixneuf, V. Cadierno, *Metal-Catalyzed Reactions in Water*; Wiley-VCH: Weinheim, Germany, **2013**.

[3]. A. K. Singh, R. K. Singh, J. Srivastava, R. Patel and S. Rahmani,Kinetics Of Oxidation Of Trehalose By Protonated N-Bromosuccinimide Using Rh (III) Chloride As Homogeneous Catalyst, *J. Applicable Chem.*, **2016**, 5, 204-218.

[4]. M. Ferreira, H. Bricout, S. Tilloy, E. Monflier, Transition Metal Complexes Coordinated by Water Soluble Phosphane Ligands: How Cyclodextrins Can Alter the Coordination Sphere?, *Molecules*, **2017**, 22, 140.

[5]. O. Bistri and O. Reinaud, Supramolecular control of transition metal complexes in water by a hydrophobic cavity: a bio-inspired strategy, *Org. Biomol. Chem.*, **2015**, 13, 2849.

[6]. M. Sarangapani, K. Shravankumar, B. Ramesh, T. N. Swamy, J. B. Sreekantha, V. Ravinder, V. C. Sekhar., Decarbonylation of Salicylaldehyde Activated by *p*-Cymene Ruthenium(II) Dimer: Implication for Catalytic Alkyne Hydrothiolation, *Eur. J. Org.Chem.* **2016**, 27, 4635-4642

[7]. K. G. M. Kou, D. N.Le, V. M. Dong, Rh(I)-Catalyzed Intermolecular Hydroacylation: Enantioselective Cross-Coupling of Aldehydes and Ketoamides, *J. Am. Chem. Soc.*, **2014**, 136, 9471.

[8]. M. A. Kakli, E. G. Delmar, R. C. Tailor, The Preparation and Characterization of Some Phosphinoacetic Acids, Salts, and Esters, *Synt.React.Inorg.Metal-Org.Chem.*, **1975**, 5, 357.

[9]. D. Noskova, J. Padlahova, Ethylphosphinediacetic acid: synthesis, characterization and coordinating behaviour towards Ca(II), Ni(II) and Hg(II) ions in solution, *Polyhedron*, **1983**, 2, 349.

[10]. P. Sarkel, B. C. Paul, R. K. Poddar, Rhodium(III) complexes containing acetylacetonate and mono- or bidentate ligands, *Ind. J. Chem.*, **1999**, 38A, 150.

[11]. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination compounds* (John Wiely, N.Y.) 4 th edn., **1986**.

[12]. R. E. Crammer, M. A. Chudyk, Nuclear magnetic resonance contact shifts and spin delocalization mechanisms in *tris*(acetylacetone) nickel(II) perchlorate, *J. Magn. Reson.*, **1973**, 12, 168-181.

[13]. H. Schumann, H. Hemling, V. Ravinder, Effects of changes in the ligands on the skeleton and the catalytic activity of some new rhodium complexes with pyrazolato moieties, *J. Organomet. Chem.*, **1994**, 469, 213.

[14]. T. Kenji, I. Kiyoshi, N. Yukio, K. Shinichi, Some Mixed-Ligand Iron (III) Complexes Produced by Reactions of Tris (acetylacetonato) iron (III) with Hydrogen Halides in Organic Solvents; *Bull. Chem. Soc. Jpn.*, **1976**, 49, 1010.

[15]. A. B. P. Lever, *Inorganic Spectroscopy* (Elsievier Amsterdam) 2nd. edn, **1984**, 334, 468.

[16]. J. H. Tocher, J. P. Fackler, Electrochemical investigations of several transition metal tris (acetylacetonate) complexes, *Inorg.Chim.Acta.*,**1985**, 102, 211.

[17]. A. Changotra, R. Gupta, S. Paul, Selective Oxidation of Benzyl Alcohol over Hydroxyapatite-Supported Au-Pd Nanoparticles, *J. Applicable Chem.*, **2014**, 3, 653-662.