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STUDIES ON FORMATION OF FIRST NEUTRAL MONONUCLEAR Rh (II) COMPLEX OF 1, 10-PHENANTHROLINE, CATALYTIC HYDROFORMYLATION AND ANTIMICROBIAL ACTIVITY

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ABSTRACT

A study of rhodium (II) catalyzed hydroformylation of olefins and also formation of mononuclear complexes with 1,10-phenonthraline with polar phosphines to form unexpectedly neutral mononuclear Rh(II) complexes was carried out. The synthesized compounds [$RhCl_3$(1,10-phenonthralone(II)] and [Rh(II)Cl_2(1,10-phen)$_2$] tested for their antimicrobial activity.

Key words: Hydroformylation, 1, 10-phenonthraline, Phosphines, Olefins.

INTRODUCTION

Rhodium can access a variety of oxidation states as a coordination compound. The significance of these rhodium compounds as catalysts in several organic transformations such as hydroformylation, carbonylation, and hydrogenation is well documented in literature[1]. A large variety of monodentate and bidentate ligands N, O, S and P donor ligands have been explored to design these rhodium compounds[2]. Among the rhodium catalyzed organic transformations, hydoformylation of olefins has got tremendous reputation and industrial demand[3].

The synthesis of oxygenated organic products by reaction of an olefinic substrate with CO and H_2 in the presence of transition metal complexes is known as *oxo* reaction[4,5]. This reaction, which was accidentally discovered by Otto Roelen in 1938, has received considerable attention[6,7]. Although much progress has been made since then through the development of more efficient metal catalysts, hydroformylation continues to be the subject

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of innumerable studies, motivated by the need to increase the selectivity to linear or branched aldehydes, to reduce by-product formation, and to achieve milder and more environmentally friendly reaction conditions[8]. The homogeneous hydroformylation reaction is one of the oldest processes making use of soluble transition metal catalysts and it is one of the largest volumes of industrial applications of these catalysts[9]. Mononuclear rhodium complexes are the most efficient catalysts for this reaction and, consequently, a great deal of work has been devoted to the improvement of rates and selectivities by ligand design[10]. Recently, chelating bisphosphine rhodium catalysts were developed that show remarkably high product regioselectivity[11]. In addition to the Rhodium chemistry, we were interested to develop the Rh(II) chemistry with the polar phosphines.

RESULTS AND DISCUSSION

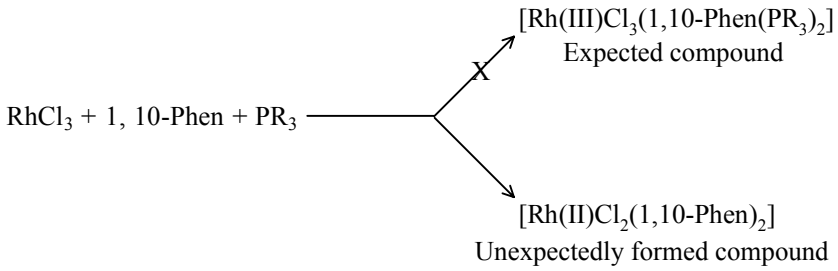
The aim of this work was to incorporate a variety polar-group functionalized phosphines viz., carboxyl, into the $[Rh(III)Cl_2(1,10\text{-}Phen)]^+$ core to afford new water soluble cationic $[Rh(III)Cl_2,(1,10\text{-}Phen)(PR_3)_2]^+$ complexes **(Scheme 1)**. However, when the rhodium precursor $[Rh(III)Cl_2$ was treated with 1,10-phenanthroline followed by a carboxyl group functionalized phosphine in refluxing ethanol, unexpectedly formed the first neutral mononuclear Rh(II) complex of 1,10-phenenathrline as $[Rh\ Cl_2(1,10\text{-}phen)_2]$ was identified, which was confirmed by the data obtained from elemental analysis, IR, Mass and ESR spectroscopic techniques. A premilnary result on the antibacterial studies using this compound is also presented.

Generally, the Rh(II) compounds can be generated as short lived intermediates by the one available on the isolation of stable mononuclear Rh(II)compounds[12]. It is known that the stability of mononuclear compounds can be improved by sterically bulky ligands such as crown ethers, porphyrins, Schiff's bases and pyridines. In this case, the mononuclear Rh(III) compounds with 1,10-phenanthroline[13] and the Rh(II) metal center, only the formation of dinuclear compound containing 1,10-phenanthroline were reported[14]. We postulate that the formation of neutral mononuclear $[Rh(II)Cl_2(1,10\text{-}phen)_2$ is to proceed through the reduction of Rh(III) by polar–phosphine added in the reaction. The reduction of metal ions by phosphine ligands is a known phenomenon in cross-coupling reactions.

To provide evidence for the existence of +2 oxidation state of rhodium, EPR spectroscopic experiments were monitored. The EPR spectrum recorded at 273 K in acetone showed only very broad signals. However, the EPR spectrum recorded at 77 K showed fine spectrum signals of $g_1 = 2.286 + 0.001$ and $g_{11} = 2.198 + 0.001$ (g values are normal). The trivalent rhodium has an outer electronic configuration of 4 d^6 and is known to exist in its low spin diamagnetic form when it traps one electron from polar-phosphine successively, it

goes into lower valence states Rh^{+2} ($4d^7$). The $[Rh(II)Cl_2(1,10\text{-phen})_2]$ complex is paramagnetic and can satisfactorily explain the observed EPR parameters for Rh center[15]. The g-values of the Rh^{+2} center with g1 > g11 > 2.0 suggest that the unpaired electron is in a metal orbital having predominant (dx^2-dy^2) character. This suggests Rh^{+2} at an axial site with compressed to an octahedral coordination[16,17].

The molecular ion peak and isotopic pattern of $[Rh(II)Cl_2(1,10\text{-phen})_2]$ complex shows different intensities as 376 (100%), 377 (19.5%) and 378 (6.6%). These values are good arrangement with the proposed molecular formula.



Scheme 1

1, 10-Phen = 1, 10-Phenanthroline

PR_3 = Polar Phoshphine (3-carboxyphenyl)diphenyl phosphine)

EXPERIMENTAL

Elemental analysis data was collected from a Perkin-Elmer 2400 CHN analyzer. EPR Spectrum was recorded on ESR spectra were recorded on JEOL-JES-FE-3X spectrometer. Mass spectrum was recorded on a MICROMASS-7070 spectrometer.

Experimental procedure for the synthesis of Rh (II) complex

In a Schlenk flask, an ethanolic solution (30 mL) of $RhCl_3H_2O$ (1 mmol) was allowed to react with 1,10-phenanthroline (1.0 mmol) followed by (3-carboxyphenyl) diphenyl phosphine (2 m mol). The reaction mixture was refluxed for 4 h; during the reaction color was changed from orange to yellow. While the reaction solution was left over night for slow cooling, a yellow colored semi crystalline solid was separated in the solution. Recrystallization of this solid material in dichoromethane/hexane produced yellow colored crystals.

Experimental procedure for the catalytic hydrofomylation of olefins (a-g)

A mixture of olefin (2 mmol) and catalyst Rh (II) complex (5 x 10^{-3} mmol) with or without adding polar phospine were mixed with the alcohols like ter-butanol or iso-propanol or ethanol or methanol and taken in to a glass lined mini autoclave and purged with argon. Later, the reaction mixture was with CO + H_2 at 25 atmospheres pressure and then placed in oil bath thermostatted at the desired temperature (50°C and 80°C). The hydroformylation of all olefins **(a-g)** conducted at the temperature of 50°C in any one of the above mentioned solvent systems has shown limited conversions of 20% only even after the prolonged reaction periods (> 24 h). However, when the temperature was raised to 80°C, the rate of hydroformylation i.e. conversion of olefins **(a-g)** to hydroformylated products was increased dramatically except cyclohexene and the data is presented in Tables 1-4. The rate of hydroformylation of the olefins in terms of conversions and yields was found in the order of 1-hexene > 1-octence >1-dodecene > 2,3-diemethylbutane > allyl benzene > styrene > cyclohexene. The lowest hydroformylation rates of styrene and cyclohexene could be due to the electron withdrawing nature and structure unstabilities.

Table 1: Hydroformylation of 1-alkenes in tertiary butanol by use of Rh (II) Complex

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yield (%)	n/i	Yield (%)	n/i
1	1-Hexene	96	62	2.5	34	7.7
2	1-Octene	92	60	2.8	32	7.4
3	1-Dodecene	89	57	3.2	32	6.8
4	2,3-Dimethyl-1-butene	87	57	3.1	30	6.2
5	Allyl benzene	84	55	3.5	29	5.8
6	Styrene	80	54	3.8	26	4.9
7	Cyclohexene	75	51	-	24	-

Table 2: Hydrofomylation of 1-alkenes in isopropanol using Rh (II) complex

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yields (%)	n/i	Yields (%)	n/i
1	1-Hexene	94	70	2.4	24	7.2
2	1-Octene	89	67	2.6	22	7.6

Cont…

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yields (%)	n/i	Yields (%)	n/i
3	1-Dodecene	86	65	3.3	21	6.6
4	2,3-Dimethyl-1-butene	82	60	3.0	22	6.0
5	Allybenzene	80	59	3.4	21	5.5
6	Styrene	77	57	3.8	20	4.8
7	Cyclohexene	72	51	-	21	-

Table 3: Hydroformylation of 1-alkenes in ethanol using Rh (II) Complex

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yields (%)	n/i	Yields (%)	n/i
1	1-Hexene	91	74	2.0	17	7.5
2	1-Octene	86	70	2.5	16	7.0
3	1-Dodecene	82	67	3.3	15	6.5
4	2,3-Dimethyl-1-butene	78	65	3.4	13	5.7
5	Allybenzene	75	60	4.2	15	6.4
6	Styrene	72	60	4.1	12	5.2
7	Cyclohexene	67	55	-	12	-

Table 4: Hydroformylation of 1-alkenes in methanol using Rh (II) Complex

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yields (%)	n/i	Yields (%)	n/i
1	1-Hexene	88	77	1.8	11	5.2
2	1-Octene	85	75	2.5	10	4.2
3	1-Dodecene	81	72	2.8	9	3.5
4	2,3-Dimethyl-1-butene	76	67	3.4	9	3.5
5	Allybenzene	73	63	3.5	10	4.0
6	Styrene	69	60	3.6	9	3.7
7	Cyclohexene	64	56	-	8	-

Finally, we have also investigated the catalytic efficiency of [Rh(II)Cl_2(1,10-phen)$_2$] complex in combination with polar (2-carboxyphenyl)diphenylphosphine ligand (1 : 1 ratio) in hydroformylation. Indeed, it was our main aim to develop water–soluble rhodium catalytic systems with reference to green chemistry protocols. Since the phospine ligand used in our containing polar carboxyl functional group, the hydroformylation reaction was investigated in water + methanol (1 : 1 ratio) solvent systems. The mixture of [Rh(II)Cl_2(1,10-Phen)$_2$] and the polar phosphine was found to be miscible and stable in water in the presence of BF_4^-counter ion. This feature indicates the role of BF_4^- ion in the stabilization of Rh(II) oxidation state. It is very interesting to note that the combination of [Rh(II)Cl_2(1,10-Phen)$_2$] and polar phosphine worked out well and provided appreciable conversion of olefins especially the less reactive allyl benzene, styrene and cyclohexene during the hydroformylation reaction (Table 5). Nevertheless, the formation both higher aldehydes and alcohols has been revealing the potential of phosphine ligands in the rhodium catalyzed hydroformylations.

Table 5: Hydroformylation of 1-alkenes in aqueous methanol using Rh (II) complex

S. No.	Substrate	Conversion (%)	Aldehydes		Alcohols (%)	
			Yields (%)	n/i	Yields (%)	n/i
1	1-Hexene	95	60	1.5	35	8.4
2	1-Octene	94	62	1.9	32	7.9
3	1-Dodecene	92	65	2.1	27	7.5
4	2,3-Dimethyl-1-butene	88	59	2.9	29	6.8
5	Allybenzene	86	60	3.6	26	6.3
6	Styrene	85	60	3.9	25	6.0
7	Cyclohexene	85	65	-	20	-

Antimicrobial activity

The antibacterial activity of the synthesized compounds was screened against the Gram positive bacteria such as *S. aureus, B. substilis S. pyogenes*, and the Gram negative bacteria such as *S. typhimurium, E. coli* and *K. pneumonia* using nutrient agar medium. The antifungal activity of the compounds was tested against *A. niger*, *C. albicans* and *T. viridae* using Potato dextrose agar medium (PDA). The minimum inhibitory concentration (MIC) was carried out using micro dilution susceptibility method. Ampicillin was used as a standard antibacterial drug and Ketoconazole was used as standard antifungal drug[18]. Stock

solutions of test samples with 2.5, 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 µg/mL concentrations were prepared with appropriate solvent. The solutions of standard drugs, Ampicillin and ketoconazole were prepared in the same concentrations. Inoculums of the bacterial and fungal culture were also prepared. To a series of tubes containing 1 mL each of compound ($RhCl_3$)/1,10-phananthroline/[Rh(II)Cl_2(1,10-Phen)$_2$] solution with different concentrations and 0.2 mL of the inoculum was added. Further 4.0 mL of the sterile water was added to each of test tubes. These test tubes were incubated for 24 h and observed for the presence of turbidity. This method was repeated by changing compounds with standard drug Ampicillin (in case of bacteria) and with ketoconazole (in case of fungi) for comparison. The minimum inhibitory concentration at which no growth was observed was taken as the MIC values.

Comparison of MIC values (in µg/mL) $RhCl_2$, 1,10-phenanthroline and [Rh(II)Cl_2)(1,10-Phen)$_2$] and standard drugs against different bacteria and fungi are presented in Tables 6 and 7. From these results, it is evident that [Rh(II)Cl_2)(1,10-Phen)$_2$] compound is showing superior activity when compared to Ampicillin and towards inhibiting all tested bacterial strains. Though there is sufficient increase in the fungicidal activity of [Rh(II)Cl_2)(1,10-Phen)$_2$] complex as compared to the free ligand, it could not reach the effectiveness of the conventional fungicide Ketoconazole. The results showed that the [Rh(II)Cl_2)(1,10-Phen)$_2$] chelate are more toxic as compared with their parent ligand against the same microorganism under identical experimental conditions. The increase in the antimicrobial activity of Rh(II) chelate may be due to the effect of the metal ion on the normal cell process. A possible mode of toxicity increase may be considered in the light of Tweedy's chelation theory[19,20].

Table 6: MIC values of $RhCl_3$ (I), 1,10-phenanthroline (II), [Rh(II)Cl_2)(1,10-Phen)$_2$] (III) and Ampicillin (A) towards bacteria

Compd.	Range of concentration (µg/mL)					
	Gram-positive bacteria			Gram-negative bacteria		
	S. aureus	***B. subtilis***	***S. pyogenes***	***S. yphimurium***	***E. coli***	***K-pneumonia***
I	25	35	40	25	45	35
II	15	30	30	20	25	25
III	5	5	10	2.5	10	5
A	10	20	25	10	15	10

Table 7: MIC values of $RhCl_3$ (I), 1,10-phenanthroline (II), $[Rh(II)Cl_2)(1,10\text{-}Phen)_2]$ (III) and Ketacanozole (K) towards fungi

Compd.	Range of concentration (µg/mL)		
	A. niger	***C. Albicans***	***T. viridae***
I	45	40	50
II	30	35	35
III	20	30	30
K	15	25	20

Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible π-electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophillic character of the central metal atom, which subsequently favors its permeation through the lipid layers of cell membrane. The general trend of growth of inhibition against the bacteria/fungi was found to lie in the order, for bacteria $RhCl_3$ < 1,10-phenanthroline < Ampicillin < $[Rh(II)Cl_2)(1,10\text{-}Phen)_2]$ for fungi: $RhCl_3$ < 1,10-phenanthroline < $[Rh(II)Cl_2)$ $(1,10\text{-}Phen)_2]$ < Ketoconazole.

CONCLUSION

A special emphasis has been given on the usefulness of rhodium complexes in industrial catalysis, specifically hydroformylation, and also in biology. The serendipitous formation of neutral mononuclear complex of $[Rh(II)Cl_2(1,10\text{-}Phen)_2]$ was demonstrated on the basis of spectroscopic evidences. To our knowledge this the first neutral mononuclear Rh (II) complex with 1,10-phenanthroline. According to our observation, a polar-phosphine can reduce the Rh (III) to Rh (II) depending on the synthetic reaction conditions. Regarding the application part results reported here in, this work suggests that these compounds possess good antimicrobial activity. Specifically, when combined with polar phosphines, water soluble catalytic system has been developed and shown appreciable conversions of olefins in hydroformylation reaction.

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