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Five-coordinated Rhodium(I) Carbonyl Compounds[+]

K. JOSEPH, S. A. PARDHY, S. K. PANDIT, S. GOPINATHAN and C. GOPINATHAN

Inorganic Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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The title compounds were synthesised by the replacement of chlorine in $Rh(CO)(PPh_3)_2Cl$ *with monobasic bidentate chelating ligands such as salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane, 8-hydroxyquinoline, benzoylphenyl hydroxylamine, 2-hydroxyacetophenone and 2-hydroxybenzophenone. IR spectral evidence points out that these compounds have a trigonal bipyramidal geometry around rhodium in the solid state. However, in benzene solutions, except for the 8-hydroxyquinoline and 2-hydroxybenzophenone derivatives they all take a square planar structure, as seen from their electronic spectra.*

Introduction

There are very few reports on pentacoordinated rhodium(I) compounds in the literature. Complexes of the type $Rh(CO)(PPh_3)_2(OOCR)$, where R = Me, Et, having square planar structures are reported to be useful as hydroformulating catalysts [1–5]. By proper adjustment of reaction conditions, we have prepared stable rhodium(I) complexes of the type $Rh(CO)(Chelate)(PPh_3)_2$ using monobasic bidentate chelating ligands.

Rhodium(I) complexes are obtained by the chlorine substitution reaction of $Rh(CO)(PPh_3)_2Cl$ using sodio derivatives of bidentate chelating ligands such as salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane, 8-hydroxyquinoline, benzoylphenyl hydroxylamine, 2-hydroxyacetophenone and 2-hydroxybenzophenone. These reactions have been conducted in benzene and the chlorine-free chelated compounds separated as yellowish microcrystalline products from benzene–hexane solutions in good yields.

Experimental

Reactions were carried out in dry, oxygen-free nitrogen atmosphere using freshly dried, distilled and degassed solvents. The starting material $Rh(CO)(PPh_3)_2Cl$ was prepared by a reported method [6]. The sodio derivative of the bidentate ligand was prepared by reacting it with stoichiometric quantity of sodium hydride in ether. After the reaction, the solvent was pumped off in vacuum. The sodio derivative was then suspended in benzene, the calculated amount of $Rh(CO)(PPh_3)_2Cl$ was added and the mixture allowed to react under reflux for 3 h. The contents were then allowed to cool, the insoluble separated by centrifugation, the benzene solution concentrated and allowed to crystallise by the addition of a small quantity of hexane. The yellow solid separated was extracted with hot hexane and processed to get the required product. Yield 80–85% in all cases. The compounds are listed in the Table I.

Results and Discussion

IR Spectra

The IR spectra of the compounds (Table II) were taken in Nujol. The spectrum of $Rh(CO)(PPh_3)_2Cl$ showed a strong band at 1965 cm^{-1} due to $\nu(C\equiv O)$. All the chelated complexes of rhodium showed $\nu(C\equiv O)$ as a sharp band around 1965 cm^{-1} or below, suggesting rhodium in its +1 oxidation state [7]. The chelated nature of the β-diketonates in the solid complexes was ascertained from the appearance of a new band at 1520 cm^{-1}, due to $\nu(C=O)$. In the spectrum of the benzoylphenyl hydroxylamine complex, the coordinated $\nu(C=O)$ was seen at 1535 cm^{-1}. The appearance of two medium-intensity bands at 915 and 940 cm^{-1} was due to metal bonded $\nu(N-O)$ [8]. In the 8-hydroxyquinoline derivative, the $\nu(C=O)$ at 1945 cm^{-1} suggested an increased Rh–C bond order which could be attributed to the increased σ donating strength of the oxyanion (of the oxine residue) in comparison with the more electronegative chlorine atom having considerable π acceptor strength. The presence of two sharp bands at 1575 and 1605 cm^{-1} [ν(C=N, C=C)] indicated strong coordination. This spectral evidence suggests the rhodium atom to have a trigonal bipyramidal geometry with the organic ligands acting as monobasic bidentate moieties.

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TABLE I. Rhodium(I) Carbonyl Compounds.

No.	Compound*	M.p. (°C)	% Analysis found (calc.)		
			C	H	P
1	$Rh(CO)L_2Cl$	198	64.01 (64.31)	4.13 (4.34)	8.72 (8.98)
2	$Rh(CO)L_2(Sal)$	140	68.23 (68.05)	4.17 (4.51)	7.77 (7.99)
3	$Rh(CO)L_2(Acac)$	146	66.80 (66.85)	4.61 (4.90)	8.01 (8.22)
4	$Rh(CO)L_2(Ba)$	180	68.90 (69.10)	4.52 (4.77)	7.13 (7.59)
5	$Rh(CO)L_2(Dbm)$	140	71.30 (71.05)	4.44 (4.66)	7.23 (7.05)
6	$Rh(CO)L_2(8\text{-}Hq)$	140	69.13 (69.09)	4.13 (4.50)	7.42 (7.76)
7	$Rh(CO)L_2(Bpha)$	155	69.03 (69.21)	4.43 (4.61)	7.03 (7.15)
8	$Rh(CO)L_2(Acph)$	175	68.07 (68.34)	4.34 (4.68)	7.52 (7.84)
9	$Rh(CO)L_2(Benph)$	122	70.27 (70.41)	4.24 (4.57)	7.15 (7.27)

L = triphenylphosphine, SalH = salicylaldehyde, AcacH = acetylacetone, BaH = benzoylacetone, DbmH = dibenzoylmethane, 8-HqH = 8-hydroxyquinoline, BphaH = benzoylphenyl hydroxylamine, AcphH = 2-hydroxyacetophenone, BenphH = 2-hydroxybenzophenone.

*Colours of the compounds were shades of yellow.

TABLE II. IR and Electronic Spectra of Rhodium(I) Carbonyl Compounds.[a]

S. No.	in cm^{-1}		λ, nm	(ϵ_{max})
	ν(C≡O)	ν(C=O)		
1	1965	–	366 br	(4550)
2	1960	1950	330	(4000)
3	1960	1515	332	(6200)
4	1960	1520	332	(6200)
5	1965	1525	332	(11800)
6	1945	1575[b]	338	(8400)
			428	(5400)
7	1965	1530	332	(7000)
8	1960	1550	332	(4400)
9	1960	1550	332	(6700)
			425	(2600)

[a] Serial numbers same as in Table I. [b] ν(CN).

NMR Spectra

^{31}P NMR spectra were recorded on a Bruker WH 90 spectrometer as $CDCl_3$ solutions using phosphoric acid (85%) as external standard, with a positive sign indicating shift to lower field. The proton noise decoupled spectrum of $Rh(CO)(PPh_3)_2Cl$ showed a simple doublet split by J(Rh–P) ~ 127 Hz with a chemical shift δ 29 assignable to equivalent ^{31}P nuclei as reported by Brown *et al.* [9]. The 8-hydroxyquinoline complex $Rh(CO)(PPh_3)_2(8\text{-}Hq)$ showed a doublet, J(Rh–P) ~ 164 Hz, suggesting the phosphorus atoms to be *trans* to each other; the chemical shift δ 41 was higher than that of the chloro compound by 12 units. This shift to the higher frequency side was indicative of diminished electron density around the phosphorus nuclei, possibly due to a change in the geometry of the molecule from square planar in the chloro compound to trigonal bipyramidal in the oxinate complex with axial phosphorus atoms.

The large value for J(Rh–P) could possibly be due to the combined effect of several factors, including the change in the π acceptor property of phosphorus in the chlorine-free complex. The assumption is that the greater the Rh–P interaction, the greater will be the coupling constant. Another possibility could be the pseudo rotation of the phosphine groups around rhodium, as a result of which phosphorus atoms move to equatorial sites thereby increasing the *s* character of the Rh–P bond.

Electronic Spectra

The spectra were measured at ambient temperature in benzene. The large intensity of the absorption bands (Table II) in the spectra of the complexes established that the responsible transitions were fully allowed. The relatively high energy of the oxo-complexes compared to the chloro-compounds can be explained by increased σ donating power of the oxyanions. Absence of absorption bands in the visible region rules out the bidentate nature of the ligand. Hence the geometry around rhodium could be square planar with non-coordinating ligand groups, especially in solution. However, the spectra of 8-hydroxyquinoline and 2-hydroxybenzophenone complexes furnished an additional band around 428 nm (ϵ = 5400) which might be attributed to ligand–metal charge transfer transition, as the complexes still existed as five coordinated in solution [10].

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