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Synthesis and Reactivity Toward Gas Molecules of Chloro 2,6-Di(diphenylphosphinomethyl)pyridine Rhodium(I)

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The synthesis of the title compound and of its adducts with O_2, CO, CO_2, SO_2, tertiary phosphines is described. The reactions of the dioxygen adduct with sulfur dioxide and carbon monoxide are also reported.

Introduction

Although there has been a considerable number of studies on the synthesis, characterization and reactivity of monotertiary and ditertiary phosphine complexes of transition metals, those reported on complexes of multidentate ligands possessing different types of donor atoms are relatively few [1]. In particular, although it is well known that tertiary phosphine complexes of rhodium(I) and iridium(I) easily undergo addition reactions with small molecules such as H_2, O_2, CO, CO_2, SO_2, and catalyze hydrogenation and hydroformilation reactions [2–4], little is known on similar reactions concerning the multidentate ligand complexes of these metals.

The present paper reports the synthesis and the reactivity of the rhodium(I) complexes of the terdentate ligand 2,6-di(diphenylphosphinomethyl)-pyridine (PNP) toward some small molecules.

Experimental

All preparations were carried out in deoxygenated solvents and all operations were routinely performed in an atmosphere of purified nitrogen using standard Schlenk techniques. Infrared spectra were obtained on a Perkin-Elmer 577 instrument. The gaschromatographic determinations were carried out on Porapak Q(0.7mx1/8in) and molecular sieves 13X(3mx1/8in) columns using a Carlo Erba Fractovap C connected to a Hewlett-Packard 3380 A integrator. The gaseous O_2, CO, SO_2, and CO_2 were commercial products of reagent grade and were used without further purification. The terdentate ligand 2,6-bis(diphenylphosphinomethyl)pyridine (PNP) was prepared according to the previously described procedure [5]. Analytical and physical data for complexes are given in Tables I and II.

RhCl(PNP)

A solution of 0.335 g (0.70 mmol) of the ligand in 10 ml of benzene was slowly added with stirring to a solution of 0.250 g (0.70 mmol) of

TABLE I. Analytical and Some Physical Data.

	Complex	Color	M.p., °C	Λ^b (Ω^{-1} cm^2 M^{-1})	Calcd. (Found%)			
					Cl	N	P	S
1	RhCl(PNP)	Red	226–230		5.78(5.67)	2.28(2.1)	10.1(9.9)	
2	$[Rh_2(PNP)_3]Cl_2$	Yellow	195–198	34	4.16(4.1)		10.9(10.6)	
3	$[Rh(PPh_3)(PNP)]Cl$	Yellow	185–188	35	4.05(4.14)		10.6(10.4)	
4	[Rh(CO)(PNP)]Cl	Pale Yellow	192–195	32	5.52(5.40)		9.65(9.50)	
5	$RhCl(O_2)(PNP)$	Orange			5.49(5.50)		9.60(10.1)	
6	$RhCl(SO_2)(PNP)$	Yellow	>300[a]	10	5.23(5.10)		9.14(9.00)	4.73(4.60)
7	$RhCl(CO_2)(PNP)$	Orange	>160[a]		5.30(5.50)		9.42(9.50)	
8	$RhCl(SO_4)(PNP)$	Yellow	>300[a]		4.99(5.00)		8.73(8.84)	4.52(4.40)
9	$RhCl_3(PNP)$	Yellow	>300[a]		14.75(15.5)		8.8(9.05)	

[a] With decomposition. [b] Measured in nitroethane.

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TABLE II. Infrared Frequencies of Complexes (cm^{-1}).[a]

	Compound	ν py ring vibration	Other bands
	PNP	1590, 1585	
1	RhCl(PNP)	1592, 1555	300(m)
2	$[Rh_2(PNP)_3]Cl_2$	1600, 1590, 1562	
3	$[Rh(PPh_3)(PNP)]Cl$	1600, 1562	
4	[Rh(CO)(PNP)]Cl	1600, 1560	1980(vs)
5	$RhCl(O_2)(PNP)$	1602, 1565	880(s)
6	$RhCl(SO_2)(PNP)$	1602, 1565	1155(s), 1030-1020(vs), 325(m)
7	$RhCl(CO_2)(PNP)$	1602, 1565	1660(vs), 1628(s)
8	$RhCl(SO_4)(PNP)$	1605, 1565	1275(vs), 1155(vs), 650(s), 325(s)
9	$RhCl_3(PNP)$	1600, 1569	352(s), 337(m)

[a] Measured in Nujol mull.

$[RhCl(COT)_2]_2$ (COT = cyclooctene) in 10 ml of benzene. The small amount of the yellow solid precipitated was filtered and from the red solution, after reduction of the volume under vacuum to about 5 ml, a red crystalline product was obtained. Yield 60%. The compound, soluble in aromatic solvents, insoluble in ethanol, is air sensitive both in the solid state and in solution.

$Rh_2Cl_2(PNP)_3$

A solution of 0.250 g (0.70 mmol) of $[RhCl(COT)_2]_2$ in 10 ml of benzene was added with stirring to a solution of the ligand (0.700 g, 1.47 mmol) in 10 ml of benzene. The resulting yellow precipitate was filtered off and washed with benzene. Yield 75%. The compound is soluble in ethanol and chloroform.

The same compound identified by its IR spectrum, M.p. and elemental analysis, has been obtained by treating a benzene solution of RhCl(PNP) with the free ligand.

Reactions of RhCl(PNP)

With PPh_3

0.087 g (0.33 mmol) of PPh_3 were added to a solution of 0.200 g (0.33 mmol) of RhCl(PNP) in 6 ml of benzene. The resulting yellow precipitate was filtered off and washed with benzene. Yield 80%. The compound is soluble in ethanol and chloroform. The same compound has been obtained by treating a benzene solution of $RhCl(PPh_3)_3$ with the stoichiometric amount of the PNP ligand.

With CO

Carbon monoxide was bubbled into a benzene solution of RhCl(PNP) for 10 minutes. The light-yellow precipitate formed was filtered off and washed with benzene. The compound is soluble in polar solvents such as EtOH, $CHCl_3$, CH_2Cl_2, Me_2CO, DMF, DMSO and insoluble in non-polar solvents. The same compound, identified by its IR spectrum and M.p., has been obtained by treating a benzene solution of $[RhCl(CO)_2]_2$ with the stoichiometric amount of the PNP ligand.

With O_2

Dioxygen was bubbled through a suspension of 0.300 g (0.50 mmol) of RhCl(PNP) in 20 ml of pentane. After being stirred for 2 h the mixture was filtered and the orange microcrystalline product was air-dried. The compound is soluble with decomposition in benzene and in halogenated solvents. A sample of the product (7.1 mg, 11 μmol), treated with an excess of iodine in a gaschromatographic apparatus as previously described [6], gave off 7.8 μmol of oxygen (71%).

A sample of the product, kept for 2 h at 80 °C *in vacuo,* turned to a red powder, recognised as RhCl(PNP) from its IR spectrum and M.p.

With SO_2

A suspension of RhCl(PNP) in pentane was kept, with stirring, under a sulfur dioxide atmosphere for 30 minutes. The yellow microcrystalline product was filtered off and dried *in vacuo*. The compound is soluble in methylene chloride and in DMF, slightly soluble in ethanol, acetone and THF, insoluble in benzene. A sample of the compound has been recovered unchanged after heating *in vacuo* for 4 h at 135–160 °C.

With CO_2

A benzene solution of RhCl(PNP) was stirred in an atmosphere of carbon dioxide for 12 h to yield an orange microcrystalline precipitate, which was filtered off, washed with benzene and dried *in vacuo.* The compound is slightly soluble in methylene chloride, THF, DMSO.

A sample of the product (0.010 g, 0.015 mmol) was decomposed with sulfuric acid, giving off 0.064 mmol (42%) of carbon dioxide, detected by gaschromatographic way.

With Cl_2

To a solution of 0.200 g (0.33 mmol) of RhCl(PNP) in 8 ml of benzene were added 12 ml of a freshly prepared 0.027 *M* solution of chlorine in benzene. After a few minutes, yellow crystals began to form; the product was filtered off, washed with benzene and dried *in vacuo*. The compound is soluble in dichloromethane, insoluble in chloroform acetone, THF. A mixture of the product and powdered zinc in THF, was kept under stirring for 2 days at room temperature, affording a red solution from which the starting RhCl(PNP) was isolated.

Reactions of $RhCl(O_2)(PNP)$

With SO_2

A suspension of $RhCl(O_2)(PNP)$ in pentane was kept with stirring under a sulfur dioxide atmosphere for 10 minutes; then the yellow product was filtered and dried *in vacuo.*

With CO

A sample of $RhCl(O_2)(PNP)$ (20.1 mg, 31 μmol) was kept at about 60 °C for a few minutes under carbon monoxide atmosphere in a sealed vial. In the gaseous products of the reaction, analysed in a gaschromatographic apparatus as previously described [6], 17.2 μmol of carbon dioxide (55%) were found. The IR spectrum of the solid residue showed strong absorption bands at 1980, 1660, 1610, 1180 and 1110 cm^{-1}.

Results and Discussion

Analytical and physical data for all complexes are presented in Table I, while Table II contains pertinent infrared spectroscopic data. RhCl(PNP) is a diamagnetic, red crystalline compound, soluble in non-polar solvents such as benzene, toluene or THF, insoluble in ethanol and in petroleum ether, very reactive towards a number of small molecules both in the solid state and in solution. It easily activates the dihydrogen molecule, as shown by its ability to catalyze hydrogenation and hydroformilation reactions of olefines [7].

In the solid state it reacts with dioxygen to give an orange adduct formulated as containing 'side-on' bonded O_2 by analogy with previous work [8]. The presence of the bound dioxygen in the complex is confirmed both by the observation of a strong absorption band at 880 cm^{-1} in its infrared spectrum, characteristic of the Rh–O_2 moiety [9], and by the identification of the products of the reactions with carbon monoxide, with sulfur dioxide and with iodine. The dioxygen–complex is fairly stable in the solid state, but decomposes in solution: the infrared spectrum of the product, precipitated by adding pentane to the light-yellow benzene solution of the dioxygen–adduct, does not show any absorption band around 880 cm^{-1}, but shows new absorption bands at 1180 and 1110 cm^{-1}, assignable to the P–O stretching of the oxygenated ligand. The uptake of O_2 by the solid rhodium-complex is reversible, and $RhCl(O_2)(PNP)$ easily deoxygenates under reduced pressure at 60–80 °C, yielding the pure RhCl(PNP), not contaminated by phosphine-oxide byproducts as shown by the lack of bands at 1180 and 1110 cm^{-1} in its infrared spectrum.

The dioxygen–complex reacts quickly and irreversibly at room temperature with gaseous sulfur dioxide to yield a rhodium(III)-sulfato complex. The infrared spectrum (Table II) shows bands consistent with the presence of bidentate sulfate [10, 11], and the electronic spectrum is quite similar to that of the hexacoordinate $RhCl_3(PNP)$ (*vide infra*). The reaction of the solid dioxygen adduct with carbon monoxide at about 60 °C and atmospheric pressure occurs in a less straightforward way. The gaseous products of the reaction contain less than 1 mole of carbon dioxide per mole of rhodium and do not contain free dioxygen. The infrared spectrum of the solid residue shows an absorption band at 1980 cm^{-1}, characteristic of the carbonyl complex RhCl(CO)(PNP) (Table II), besides strong bands at 1180 and 1110 cm^{-1}, characteristic of the P–O stretching, and at 1660 and 1610 cm^{-1}, assignable to the C–O stretchings of a carbonato or a carbon dioxide complex.

These results show that, as in the case of $Ni(O_2)(BuNC)_2$ [11], the carbon monoxide promotes the O–O bond cleavage and that, besides some minor side reactions, the reaction occurs mainly through the

$$RhCl(O_2)(PNP) + 2CO \rightarrow RhCl(CO)(OPNP) + CO_2 \quad (1)$$

transfer, most probably concerted, of the oxygen atoms to both CO and phosphorus atom of the ligand, as shown by eqn. (1).

The attack of a strong electrophile, such as iodine, on the dioxygen adduct yields free dioxygen through the expected oxidative substitution reaction (2):

$$RhCl(O_2)(PNP) + I_2 \rightarrow RhClI_2(PNP) + O_2 \quad (2)$$

The RhCl(PNP) reacts quickly with carbon monoxide, yielding a carbonyl complex that, on the base of its infrared spectrum and its conductance in polar solvents (Table I), we formulate as [Rh(CO)(PNP)]Cl. The infrared spectrum of this compound, like those of the ionic complexes $[Rh(PPh_3)(PNP)]Cl$ and $[Rh_2(PNP)_3]Cl_2$, does not show any absorption in the range 250–380 cm^{-1}, where the absorptions due to the Rh–Cl stretching occur (Table II).

The RhCl(PNP) reacts with sulfur dioxide to give the SO_2 adduct $RhCl(SO_2)(PNP)$. This latter compound is very stable and can be recovered unchanged after heating *in vacuo* at 135–160 °C for 4 h. It reacts very slowly with oxygen at ambient conditions, both in the solid state and in solution, giving the sulfato complex $RhCl(SO_4)(PNP)$. The infrared spectrum of the SO_2 adduct shows strong absorptions at 1155 cm^{-1} and at 1030–1020 cm^{-1}, which are consistent with a bent geometry for the $Rh–SO_2$ moiety [12]. This sulfur dioxide adduct, which shows chemical and physical properties very similar to those of the analogous $RhCl(SO_2)(ttp)$ compound [13] (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$), represents the second exception thus far known to the general correlation that has been found between the reversibility of the SO_2 addition and the coordination geometry of the bound SO_2 [12].

The RhCl(PNP) reacts at ambient conditions also with carbon dioxide yielding the CO_2 adduct $RhCl(CO_2)(PNP)$. The infrared spectrum of this compound shows strong absorptions at 1660 and 1628 cm^{-1}, which are consistent with the presence of the metal–bonded CO_2 [14].

The absence of absorptions in the range 250–380 cm^{-1} would suggest an ionic structure. However, as in the case of the dioxygen adduct, this could not be confirmed by electrolytic conductance measurements.

The reactivity toward carbon dioxide shown by the RhCl(PNP), which represents the first example of a metal complex of multidentate ligands active in the CO_2 fixation, must be correlated with the electronic density increase on the metal made by the coordination of the pyridine nitrogen atom and emphasizes the importance of a careful balance of donor-acceptor properties of the ligand in order to obtain reactive complexes.

The complex RhCl(PNP) reacts easily both with good nucleophiles and electrophiles, such as tertiary phosphines and halogens. With triphenylphosphine it gives the tetracoordinated ionic complex $[Rh(PPh_3)(PNP)]Cl$ and with the PNP ligand it gives the dimeric tetracoordinate ionic complex $[Rh_2(PNP)_3]Cl_2$, in which one of the terdentate ligands PNP is bridging two metal atoms through the phosphorus atoms. The coordination of the pyridine nitrogen atom to the rhodium is indicated for all the complexes in Table II by shifting and splitting of ring vibrations as is usually observed for other metal–pyridine complexes [15]. However, $[Rh_2(PNP)_3]Cl_2$ shows in addition a band at 1590 cm^{-1}, characteristic of the free ligand, and thus in this compound there is evidence for both coordinated and uncoordinated pyridyl groups.

The RhCl(PNP) easily undergoes an oxidative addition reaction with chlorine, affording the hexacoordinate rhodium(III) complex $RhCl_3(PNP)$. Its electronic spectrum in 1,2-dichloethane shows, as does that of the corresponding rhodium(III) complex $RhCl(SO_4)(PNP)$, strong absorptions at 35 kK(ϵ = 20500) and 29.5 kK(ϵ = 12000).

Conclusions

The complex RhCl(PNP) has been shown to be a very versatile substrate for addition reactions and the ability to activate small molecules such as H_2, O_2, CO and CO_2, makes it a potential catalyst for a large number of useful reactions.

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