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CATIONIC COMPLEXES OF RHODIUM(I) WITH NITROGEN DONOR LIGANDS

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Summary

Five-coordinate cationic complexes of rhodium(I) of the type [Rh$(CO)_2L_3$]ClO_4 where L is a tertiary phosphine or arsine react with a number of (more basic) monodentate nitrogen donor ligands (Y) to give four-coordinate complexes of the type [Rh(CO)YL_2]ClO_4. *p*-Tolyl isocyanide however gives five-coordinate complexes of the type [Rh(*p*-tolyl-NC)$_2L_3$] ClO_4. The bidentate ligand 4,4'-bipyridyl(Y—Y) gives four-coordinate bridged complexes of the type [(CO)L_2Rh(Y—Y)RhL_2(CO)]$(ClO_4)_2$. Structures have been assigned to all the complexes.

Introduction

In recent years a number of cationic complexes of rhodium(I) have been reported [1-7]. In several of these complexes rhodium has a coordination number five, in others it takes up a coordination number four. It is generally believed that in such complexes, in which the metal has a d^8 electron configuration, an increase in the electron density at the central metal atom will favour the formation of a five-coordinate rather than a four-coordinate complex [8]. However, Mays and coworkers [9] while preparing a series of cationic complexes of iridium(I) found that use of the most basic phosphines, which would increase the electron density at the metal atom, produced only four-coordinate complexes. They suggested that factors other than the electron density at the metal atom, for example, steric effects, may determine the relative stability of five- in comparison with four-coordinate complexes.

We have reported [7] recently the isolation of several five-coordinate cationic complexes of rhodium(I) of the type [Rh$(CO)_2L_3$]ClO_4, where L is a tertiary phosphine or arsine or triphenyl stibine. When these complexes are treated with the bidentate nitrogen donor ligands 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen), which are more basic than either carbon monoxide or a tertiary phosphine (or arsine), the bidentate ligand replaces a molecule of carbon monoxide and a phosphine (or arsine) to give complexes of the type $[Rh(CO)(Y{-}Y)L_2]ClO_4$, (Y—Y is bipy or phen), where the metal continues to have a coordination number five. It was therefore of interest to find what coordination the metal would take if in these reactions the bidentate nitrogen ligands are replaced by monodentate ligands of a similar type. The results of these investigations are reported here.

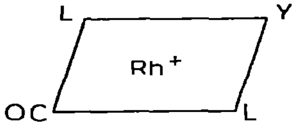
Results and discussions

The cationic complexes $[Rh(CO)_2L_3]ClO_4$ in alcoholic medium react with the monodentate nitrogen donor ligands (Y) pyridine (py), α-, β-, γ-picolines (pic), quinoline (qn), isoquinoline (iqn) and benzo[*f*] quinoline (bfqn) in the mole ratio 1/2 to 1/3 to give four-coordinate complexes of the type $[Rh(CO)YL_2]ClO_4$. These are 1/1 electrolytes in nitrobenzene and show a ν(CO) band ca. 2010 cm^{-1} in the infrared. At least in the case of pyridine use of even a twentyfold excess of the ligand did not yield a five-coordinate complex. Similar four-coordinate complexes of rhodium(I) containing pyridine and its derivatives have been synthesised by other workers [4, 10]. Due to steric reasons it is likely that the new cations would have a *trans* configuration (I). This is supported by the fact that the cations $[Rh(CO)(py)\{(p\text{-}CH_3C_6H_4)_3P\}_2]^+$ and $[Rh(CO)(py)\{(o\text{-}CH_3C_6H_4)_3P\}_2]^+$ show a single methyl resonance in their NMR spectra (Table 1). In a *cis* configuration each of the two phosphines would have a different ligand *trans* to it and so it is likely that their methyl resonances do not overlap.

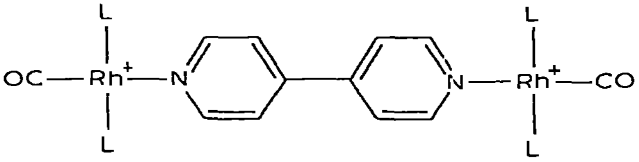
It is seen that introduction of a monodentate nitrogen donor ligand which has a greater σ-donor but a poorer π-acceptor capacity than either carbon monoxide or a tertiary phosphine (or arsine) favours coordination number four rather than five for the rhodium atom. We believe that bipy and phen favour five-coordination for the metal because of their chelating ability and not due to their better σ-donor capacity.

These results suggest that at least in cationic complexes of rhodium(I) (and other similar complexes) the moderately basic tertiary phosphines and arsines generally favour a coordination number five. If, however, the phosphines are bulky, the metal may have a coordination number four, as in some of the compounds of iridium reported by Mays et al. [9]. If one or more nitrogen donor ligands, which are more basic than the phosphine or arsine ligands, are also present in the complex, then the metal appears to prefer a coordination number four [4, 10].

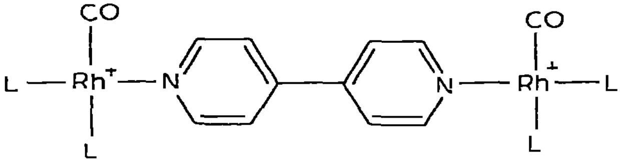
The bidentate but non-chelating ligand, 4,4'-bipyridyl (4,4'-bipy = Y—Y) gives binuclear complexes of the type $[(CO)L_2Rh(Y{-}Y)RhL_2(CO)](ClO_4)_2$ where the metal again has a coordination number four. These complexes behave as 1/2 electrolytes in nitrobenzene and show a single ν(CO) band ca. 2000 cm^{-1} in the infrared, and hence should have configuration II or III. Pyrazine (pyz), which also could act as a bridging bidentate ligand [11], however, gives only mononuclear four-coordinate complexes and the cations of these compounds should have configuration I. *p*-Tolyl isocyanide (RNC), which is a poorer σ-donor but a better π-acceptor than pyridine and similar nitrogen donor ligands, replaces both the carbon monoxide molecules and gives five-coordinate complexes of the type $[Rh(RNC)_2L_3]ClO_4$. These cations show a single ν(NC) peak in the infrared at ca. 2130 cm $^{-1}$ and hence should have configuration IV. The NMR spectra of these isocyanide complexes show a single methyl resonance (Table 1). This result, though not conclusive, is consistent with configuration IV for these cations.



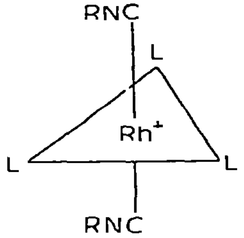
(I)



(II)



(III)



(IV)

Experimental

The infrared (Nujol mulls) and NMR (in $CDCl_3$, using TMS as internal reference) measurements were carried out with Carl Zeiss UR 10 spectrophotometer and Varian T-60 instruments respectively. Conductivity measurements were made using Toshniwal Instruments Conductivity bridge type CLO1.02.

The complexes of the type $[Rh(CO)_2L_3]ClO_4$ were made as reported earlier [7]. Microanalyses were carried out at the University of Surrey and University of Manchester, England.

Carbonylpyridinebis(tertiary phosphine or arsine)rhodium(I) perchlorate, $[Rh(CO)(py)L_2]ClO_4$

To an ethanolic suspension of the complex $[Rh(CO)_2L_3]ClO_4$, ($[Rh(CO)_2L_2]ClO_4$ in the case of L = *o*-tolyl$_3$P), pyridine, dissolved in ethanol, was added in the mole ratio 1/2. The mixture was refluxed on a water bath for about ½h. The resulting yellow solution on evaporation under reduced pressure deposited the required compound as shining yellow crystals.

The corresponding compounds containing α-, β-, γ-picolines, quinoline, isoquinoline, benzo[*f*]quinoline and pyrazine were prepared in the same way.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR CATIONIC COMPLEXES OF RHODIUM(I)

Compound[a]	M.p. or dec. p (°C)	Λ^b	ν(CO) (cm^{-1})	Analysis found (calcd.) (%)		
				C	H	N
$[Rh(CO)(py)(Ph_3P)_2]ClO_4$[c]	185-187	21.0	2007	60.3(60.4)	4.3(4.2)	1.8(1.7)
$[Rh(CO)(py)(Ph_3As)_2]ClO_4$	201-203	27.6	2007	55.1(54.7)	3.9(3.8)	1.7(1.5)
$[Rh(CO)(py)(p\text{-tolyl}_3P)_2]ClO_4$[d]	191-194	23.1	2000	62.0(62.8)	5.3(5.2)	1.7(1.5)
$[Rh(CO)(py)(o\text{-tolyl}_3P)_2]ClO_4$[e]	215-219	24.7	2013	61.8(62.8)	5.2(5.2)	1.5(1.5)
$[Rh(CO)(\alpha\text{-pic})(Ph_3P)_2]ClO_4$	185-186	23.2	2008	61.1(60.9)	4.3(4.4)	1.7(1.7)
$[Rh(CO)(\beta\text{-pic})(Ph_3P)_2]ClO_4$	185-188	25.6	2017	61.1(60.9)	4.4(4.4)	1.7(1.7)
$[Rh(CO)(\gamma\text{-pic})(Ph_3P)_2]ClO_4$	179-180	23.4	2020	60.8(60.9)	4.4(4.4)	1.8(1.7)
$[Rh(CO)(qn)(Ph_3P)_2]ClO_4$	147-150	22.9	2010	62.3(62.5)	4.2(4.2)	1.5(1.6)
$[Rh(CO)(qn)(p\text{-tolyl}_3P)_2]ClO_4$	222-225	22.2	2003	64.5(64.5)	5.0(5.1)	1.5(1.6)
$[Rh(CO)(qn)(Ph_3As)_2]ClO_4$	127-130	21.4	2000	56.4(56.8)	4.4(3.7)	1.1(1.4)
$[Rh(CO)(iqn)(Ph_3P)_2]ClO_4$	194-195	21.2	2000	62.1(62.5)	4.6(4.2)	1.6(1.6)
$[Rh(CO)(iqn)(p\text{-tolyl}_3P)_2]ClO_4$	205-207	22.6	2013	63.6(64.5)	5.0(5.1)	1.4(1.5)
$[Rh(CO)(iqn)(Ph_3As)_2]ClO_4$	213-215	22.2	2020	56.8(56.8)	3.9(3.7)	1.2(1.4)
$[Rh(CO)(bfqn)(Ph_3P)_2]ClO_4$	207-208	21.9	2007	64.2(64.3)	4.1(4.2)	1.5(1.5)
$[Rh(CO)(bfqn)(Ph_3As)_2]ClO_4$	243-244	22.8	2003	58.6(58.8)	4.1(3.9)	1.5(1.4)
$[Rh(CO)(pyz)(Ph_3P)_2]ClO_4$	215-219	23.0	2015	59.0(59.0)	4.0(4.1)	3.4(3.4)
$[Rh(CO)(pyz)(Ph_3As)_2]ClO_4$	217-220	22.7	2013	53.3(53.4)	3.6(3.7)	3.1(3.0)
$[Rh_2(CO)_2(4,4'\text{-bipy})(Ph_3P)_4](ClO_4)_2$	183-186	41.2	2000	59.9(60.5)	4.0(4.1)	1.7(1.7)
$[Rh_2(CO)_2(4,4'\text{-bipy})(Ph_3As)_4](ClO_4)_2$	182-184	42.8	1995	54.4(54.8)	4.0(3.7)	1.9(1.5)
$[Rh(RNC)_2(Ph_3P)_3]ClO_4$[f]	176-180	24.1	2136	68.2(68.7)	4.8(4.9)	2.1(2.3)
$[Rh(RNC)_2(Ph_3As)_3]ClO_4$[g]	200-201	20.1	2133	62.4(62.0)	4.7(4.4)	2.0(2.1)
$[Rh(RNC)_2(Ph_3Sb)_3]ClO_4$	198-200	22.3	2123	55.4(56.0)	3.8(4.0)	1.8(1.9)

[a] Compounds are yellow or orange-yellow in colour. [b] Molar conductance (ohm^{-1}cm^{2}mol^{-1}) of ca 10^{-3} M solutions in nitrobenzene (ca. 25°). [c] Reported earlier and made by a different route [10]. [d] τ (Me) 7.58. [e] τ (Me) 7.70. [f] τ (Me) 7.68 [g] τ (Me) 7.67.

Dicarbonyl-μ-4,4'-bipyridyltetrakis(tertiary phosphine or arsine)dirhodium(I) perchlorate, $[Rh_2(CO)_2(Y{-}Y)L_4](ClO_4)_2$

To an ethanolic suspension of $[Rh(CO)_2L_3]ClO_4$, was added 4,4'-bipyridyl, in ethanol, in the mole ratio 1/2. The mixture was refluxed on a waterbath for 2h. The resulting yellow solution on cooling deposited the yellow crystals of the required compound.

Bis(p-tolyl isocyanide)tris(tertiary phosphine or arsine or stibine)rhodium(I) perchlorate, $[Rh(RNC)_2L_3]ClO_4$

p-Tolyl isocyanide in ethanol was added to an ethanolic suspension of $[Rh(CO)_2L_3]ClO_4$ in the mole ratio 2/1. The mixture was refluxed for an hour on a water-bath. The resulting orange-yellow solution was concentrated under reduced pressure and cooled when the required compound separated as shining crystals.

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