Complexes of Rhodium(III) with 2-pyridinethiol and its Conjugate Anion as the Sole Ligands

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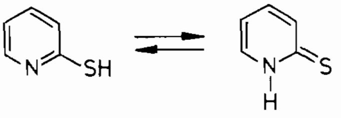
2-Pyridinethiol (**A**) exists in tautomeric equilibrium with the thione form (**B**) [1]. The equilibrium position is sensitive to the solvent polarity [2], and in aqueous solution the thione (**B**) is in overwhelming preponderance. In low polarity solvents the equilibrium is towards the thiol (**A**) and evidence suggests that there is a high degree of H-bonded dimerization [3]. Many important biological molecules (e.g. purines and pyrimidines) exist as tautomers and their coordination chemistry is of considerable interest, not least because the mobile proton permits several modes of coordination.

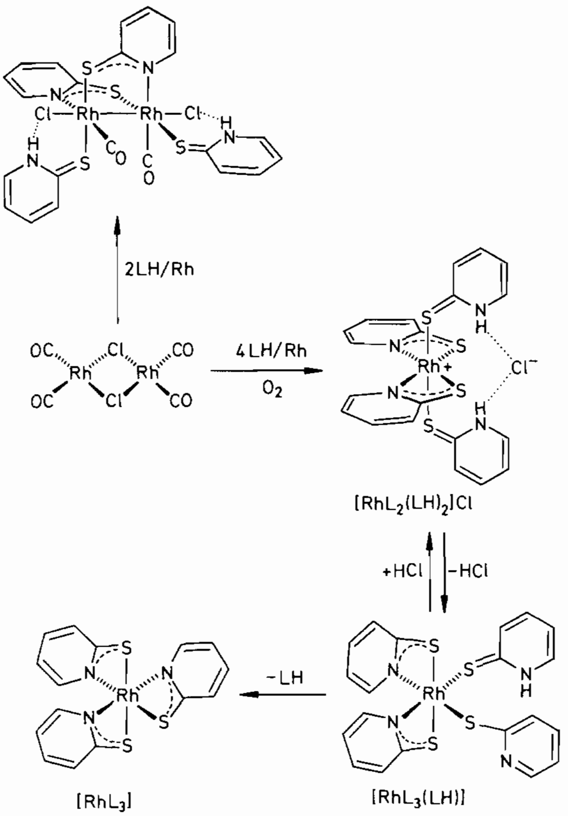


A **B**

Complexes containing 2-pyridinethiol or its conjugate base, 2-pyridinethiolate, have been reported for many transition metals [4]. However, there appears to be little understanding of the factors affecting the coordination adopted. We wish to give here a preliminary account of the reactions of 2-pyridinethiol (LH) with $[RH_2Cl_2(CO)_4]$ and describe four types of coordination: monodentate coordination of LH through sulphur which may involve pseudo-chelation involving H-bonding to a *cis*-ligand, monodentate coordination through sulphur, bridging, and chelation of the conjugate anion, L^-.

Results and Discussion

The addition of 2-pyridinethiol (LH) to $[Rh_2Cl_2(CO)_4]$ in chloroform under nitrogen gives $[RhCl(CO)_2(LH)]$ when 1 mol per mol Rh is added. More LH leads to other rhodium(I) products including a monocarbonyl species which is probably $[RhCl(CO)(LH)_2]$. Leaving such solutions to stand in the absence of oxygen slowly gives a crystalline deposit (75%) of the dinuclear rhodium(II) species, $[Rh_2Cl_2L_2(LH)_2(CO)_2]$, which has the structure shown in Scheme 1 [5]. There seems to be no tendency to form the tetra-bridged rhodium(II) dimer analogous to rhodium(II) acetate [6] and the product contains only two bridging ligands L and two monodentate ligands LH (chelating through H-bonds as shown). Attempts to dehydrochlorinate and decarbonylate to give $[Rh_2L_4]$ were unsuccessful. The subject of this communication is an interesting series of complexes formed by such reaction solutions on exposure to air. Oxidation to rhodium(III) occurs. After several days under air, a solution of $[Rh_2Cl_2(CO)_4]$ and LH (LH/Rh ≥ 4) in chloroform deposits deep orange crystals of $[RhL_2(LH)_2]Cl$ (57%). The ^1H NMR spectrum (Table I) shows the presence of only two ligand environments, one of the deprotonated ligand L and the other of the protonated form LH δ 13.75S, N$\underline{H}$). Proton–proton decoupling experiments have allowed us to assign the two sets of resonances. A single-crystal X-ray study [7] has established the structure in the crystals to be that shown in Scheme 1. H-Bonding between N$\underline{H}$ and chloride links the *trans* monodentate ligands in a pseudo-chelate ring through *trans*-positions. In solution this compound behaves as a 1:1 electrolyte ($\Lambda_M = 57$ ohm^{-1} cm^2 mol^{-1} in $CH_3NO_2/CHCl_3$ mixture, 9:1 by volume).



Scheme 1.

0020-1693/86/$3.50

TABLE I. ^{1}H NMR Data (δ) for Rhodium(III) Complexes of LH and L[a]

Complex	Chelating L		Monodentate LH or L	
$[RhL_2(LH)_2]Cl$	8.17d	H^6	13.75s	$N\underline{H}$
	6.83t	H^5	8.74t	H^6
	7.40m	H^4	6.96t	H^5
	7.51d	H^3	7.40m	H^4
			6.72d	H^3
$[RhL_3(LH)]^b$	8.15d	H^6	7.91d^b	H^6
	6.92t	H^5	6.64t^b	H^5
	7.30m	H^4	7.30m^b	H^4
	7.41d	H^3	6.82d^b	H^3
$[RhL_3]$	8.25m	H^6, H^6		
	7.38m	H^6, H^4, H^4, H^4		
	6.80m	H^5, H^3, H^3, H^3		
	6.65m	H^5, H^5		

[a] In $CDCl_3$ at 200 or 400 MHz at room temperature. Multiplicities (d,t,m) indicate approximate appearance of signals. [b] Time-averaged signals for LH and L are given in monodentate column.

If a chloroform solution of $[RhL_2(LH)_2]Cl$ is stirred with basic alumina or NEt_3, there is a slow formation of the neutral compound $[RhL_3(LH)]$ (95%). In spite of this stoichiometry, the ^{1}H NMR spectrum contains two equal intensity sets of 2-pyridinethiol resonances and the $N\underline{H}$ resonance could not be observed. Our first interpretation was that the compound contained two chelating ligands L and mutually *trans* monodentate ligands L and LH which rapidly exchange by proton transfer leading to their apparent equivalence in NMR spectra even down to −100 °C. However, a single-crystal X-ray structure [8] shows that there has been a major change of coordination geometry; the monodentate ligands L and LH are mutually *cis* as shown in Scheme 1. The appearance of ligand resonances in the intensity ratio 1:1 must nonetheless result from rapid proton-exchange between the monodentate ligands L and LH. This exchange is intermolecular because coupling between the NH and H^6 protons, as observed in $[RhL_2(LH)_2]Cl$, is lost.

The formation of $[RhL_3(LH)]$ from $[RhL_2(LH)_2]Cl$ is slow which could not be explained by a simple deprotonation at nitrogen which would necessarily be fast. Presumably the formation of the observed isomer of $[RhL_3(LH)]$ is slow because a reorganisation of the coordination shell is required which is rate determining. Treatment of $[RhL_3(LH)]$ with HCl regenerates $[RhL_2(LH)_2]Cl$ in its original stereochemistry; again the conversion is slow, taking many hours. It is very likely, in view of this reversibility, that the most stable configurations are adopted in each case but we cannot account for these stereochemical changes.

Electron-impact mass spectra of $[RhL_2(LH)_2]Cl$ and $[RhL_3(LH)]$ do not show parent molecular ions but $[RhL_3]^+$ is the highest mass ion observed. Believing that this was a thermal decomposition product. A sample of $[RhL_3(LH)]$ was heated just above its melting point (melting point (m.p.) 182 °C) for 5 min. The melt was dissolved in dichloromethane and chromatographed on an alumina column to give ruby red crystals of $[RhL_3]$ (70%). The ligand LH was observed to sublime out of the melt when $[RhL_3(LH)]$ was heated in a vacuum. Four ^{1}H NMR multiplets (δ 6.65, 6.80, 7.38, 8.25 in $CDCl_3$) for the ring protons result from overlap of signals of three non-equivalent ligand L in $[RhL_3]$. This is consistent with the *mer* rather than *fac* configuration which was confirmed by an X-ray analysis [9]. Although tris-chelate complexes with four-membered chelate rings are relatively uncommon, the complex $[RhL_3]$ may be compared with the tris-dithiocarbamato-complex $[Rh(Et_2NCS_2)_3]$ which has been characterised structurally [10].

Attempts to react $[RhL_3]$ with LH to regenerate $[RhL_3(LH)]$ gave only decomposition but reactions with tertiary phosphines do lead to chelate ring opening. Attempts to convert *mer*-$[RhL_3]$ to the *fac*-isomer by UV irradiation gave no reaction at all.

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