Rhodium(II) Complexes of Quadridentate Schiff Bases

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Rhodium(I) and rhodium(III) complexes with the quadridentate Schiff base salen (ethylenebis(salycilideneiminato)) are already known and characterized [1–3]. Only a brief report has appeared [1, 2] on the related Rh(II) compounds, namely the diamagnetic dimer $[Rhsalenpy]_2$, although [Co(II)-salen] is a well known and studied compound [4].

In the course of our studies on Schiff base complexes we have found that if $[Rh(CO)_2Cl]_2$ (*1*) and $salenH_2$ are refluxed in methanol, in the presence of bases ($Rh:salenH_2:B$ = 1:1:1, B = Et_3N, $NaHCO_3$) and under argon, the initially formed $[\{Rh(CO)_2\}$-salen] (*2*) [5, 6] in which salen acts as a bridge between two $Rh(CO)_2$ moieties [7, 8], eventually dissolves and a dark green precipitate which analyzes correctly (C, H, N) for Rhsalen (*3*) is obtained after 24 h in about 50% yield. We have prepared by this method the derivatives of salpn (1,2-propylenebis(salycilideneiminato)) (*4*) and of saloph (orthophenylenebis(salycilideneiminato)) (*5*) (**CAUTION**: one sample of this compound ignited spontaneously in air). *3* was also obtained by reaction of *2* with $salenH_2$.

Correct elemental analyses have been obtained for all these compounds. They are fairly stable in the solid state (however see above) and soluble only in donor solvents.

A feature of these complexes, common to most Rh(II) compounds [9], is the possibility of forming dimers with Rh–Rh bonds. It appears that in the present case dimerization can be inhibited to some extent, probably by steric factors. $[Rhsalpn]_2$ and $[Rhsaloph]_2$ are diamagnetic at room temperature, whereas *3* is partially dissociated into monomeric unities: it has μ_{eff} = 0.90 at RT, and an esr spectrum indicative of monomeric Rh(II): g_1 = 2.418, g_2 = 2.230, and g_3 1.99 (powders at 130 K) similar to that reported for another Rh(II) monomeric compound [10]. The reason why steric interactions are less severe in the salpn case, despite the presence of a methyl group, can probably be ascribed to the peculiar conformational behaviour of this ligand [11–13].

The compounds react with atmospheric oxygen in the solid state giving paramagnetic oxygen adducts. The reaction is relatively fast and quantitative for *5*, which, on ageing, becomes a brown paramagnetic material (μ_{eff} = 1.80 at RT) which analyzes for $[Rhsaloph\cdot O_2]$. Its esr spectrum (g_1 = 2.069, g_2 = 2.029, g_3 = 1.978, powders at 130 K) is indicative of a hyperoxo Rh(III) derivative, by comparison with literature data on $[RhPO_2]$ (P = porphirinato ligand) [14, 15], and other Rh(III) hyperoxo complexes [16, 17]. Aged *3* shows the spectra of both the oxygenated species and that of monomeric Rh(II) (see above). Solid *4* is the most stable to oxygenation. The presence of terminal hyperoxo groups in these dioxygen adducts is confirmed by the appearance in the infrared spectra of an ill-defined band at about 1100 cm^{-1} [14, 18].

The pyridine solutions of compounds *3*–*5* are ESR silent, suggesting the presence of dimeric species. These solutions absorb dioxygen at RT in the ratio Rh/O_2 = 1/1 (measured by a gas burette) giving hyperoxo Rh(III) species (g_1 = 2.095, g_2 = 2.010, g_3 = 1.996, for frozen solutions). The appearance of three g values in similar compounds has already been explained as arising from the hyperoxo group being asymmetrically arranged with respect of the plane of the ligand [16, 17]. The oxygenation reaction is very slow (*i.e.* several hours) when compared to the behaviour of the pyridine solutions of [Cosalen] [4, 19], presumably as a consequence of the different species present in this solvent, *i.e.* monomeric for Co(II) [4, 19] and dimeric for Rh(II). The reaction is reversible, since under vacuum the ESR signal disappears. Also this process is very slow at room temperature.

Brown adducts with oxygen can be obtained by precipitation with acetone or by evaporation to dryness of these solutions with a stream of dry oxygen, but the irreproducible elemental analyses and the low magnetic moments show that some decomposition occurs on crystallization.

As for the mechanism of formation of Rh(II) from Rh(I), careful work-up seems to rule out air oxidation. Moreover the analogous reaction *1* + porphyrin yields $[Rh(II)P]_2$ under anaerobic conditions [20], and [Rh(III)PCl] if carried out in the air [21]. $[Rh(II)P]_2$ has also been obtained by oxidation of Rh(I) by H^+ followed by decomposition of the Rh(III) hydride [15, 22]. Such a mechanism could also operate in the present case, the source of hydrogen being $salenH_2$ itself, as the *formal* stoichiometry suggests:

$$[Rh(CO)_2Cl]_2 + 2salenH_2 + 2B \longrightarrow 2[Rh(I)salen]^- + 2BHCl + 2H^+$$

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The finding by gas chromatography that H_2 is evolved during the reaction supports this hypothesis.

Finally a driving force for the formation of Rh(II) derivatives must be the possibility of forming dimers with Rh–Rh bonds, although the presence of some monomeric Rh(II) in *3* remains to be explained. In any case we failed to obtain the Rh(II) derivative of (±)2,3-butanebis(salycilideneiminato), a ligand which is known to exert severe steric repulsions [13, 19].

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