Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND REDUCTION OF RHODIUM(III) COMPLEXES OF A QUADRIDENTATE SCHIFF-BASE LIGAND, AND SYNTHESIS OF ORGANO–RHODIUM(III) DERIVATIVES

R. J. COZENS, K. S. MURRAY and B. O. WEST
Department of Chemistry, Monash University, Clayton, Victoria, 3168 (*Australia*).

(Received December 13th, 1971)

SUMMARY

The Rh^{III} Schiff-base complexes RhSalenClPy and (PyH)(RhSalenCl_2), and the Rh^{II}–Rh^{II} bonded dimer (RhSalenPy)$_2$ have been prepared, and their probable structures and reactivities are discussed.

RhSalenClPy has been reduced using both 0.2% sodium amalgam and $NaBH_4/PdCl_2$ to produce solutions containing mono- and di-sodium derivatives, and the di-sodium derivative has been treated with a number of organic halides to yield a series of derivatives of the general formula R–RhSalenPy (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, CH_3CO, CH_2=$CHCH_2$ and $C_6H_5CH_2$). Spectral evidence confirms that these derivatives are Rh–C bonded.

INTRODUCTION

The Rh^{III}–carbon σ-bond has been found to be stabilized, in complexes of the general formula RhXYR(CO)L_2 (R = alkyl, perfluoroalkyl, acyl, aryl; X,Y = halides), by ligands such as L = tertiary phosphine or arsine[1–4], amine[5,6] or thioether[7,8].

Recently it was shown that the planar ligand, $(DmgH)_2$, the dianion of bis-(dimethylglyoxime), produced a series of "rhodoximes" of general formula R–Rh-$(DmgH)_2$B (R = alkyl; B = base such as pyridine), containing stable Rh^{III}–carbon σ-bonds[9], and analogous to the well-known cobaloximes[10].

Quadridentate Schiff-base complexes of cobalt are well-known, and have been used to stabilize a number of σ-bonded organo–Co^{III} derivatives[11–15]. However, only one Rh^{III} complex containing the Schiff-base ligand, (Salen), the dianion of *N*,*N*′-ethylenebis(salicylaldimine), reported to have the formula RhSalenHCl_2[16], has previously been described.

We now report the preparation of the Rh^{III} Schiff-base complex RhSalenClPy and related compounds, and the synthesis of organo–Rh^{III} derivatives of general formulae R–RhSalenPy (R = alkyl or acyl).

Preliminary results have been reported[17].

RESULTS AND DISCUSSION

(1). *Synthesis of RhSalenClPy and related complexes*

Substitution reactions involving Rh^{III} compounds are generally extremely slow, but it has been found that for the synthesis of Rh^{III} complex compounds, the addition of suitable 2-electron reducing agents allows a considerable increase in the rate of substitution[18]. Such reactions have been shown to be catalysed by a Rh^{I} complex[19]. Thus the reaction of *N*-substituted salicylaldimines with $RhCl_3 \cdot 3\,H_2O$, $Na_3RhCl_6 \cdot 12H_2O$ and $RhCl_3$, which does not normally take place readily, can be achieved in the presence of various reducing agents.

When a solution of $RhCl_3 \cdot 3H_2O$ or $Na_3RhCl_6 \cdot 12H_2O$ in methanolic pyridine is treated with a solution of $SalenH_2$ in methanol, in the presence of excess 5% zinc amalgam, careful evaporation of the resultant pale yellow solution produces a fine, cream-yellow insoluble powder of analytical composition RhSalenPy. A similar treatment of a methanolic solution of $(RhPy_4Cl_2)Cl \cdot 5H_2O$ produces the same product. This reaction sequence does not produce a Schiff-base chelate when either of the related ligands, *N*,*N*'-ethylenebis(acetylacetoneimine), ($AcacenH_2$), or *N*,*N*'-*o*-phenylenebis(salicylaldimine), ($SalophenH_2$), is used, the major product of both reactions being 1,2,6-$RhPy_3Cl_3$. $SalophenH_2$ can be recovered unreacted, but $AcacenH_2$ appears to undergo dissociation.

When a solution of $SalenH_2$ in hot pyridine is treated with a trace of Zn metal powder, followed by the addition of a stoichiometric amount of either $RhCl_3 \cdot 3H_2O$, $Na_3RhCl_6 \cdot 12H_2O$ or anhydrous $RhCl_3$, a sparingly soluble, bright-yellow powder is rapidly produced, and it can be recrystallized from pyridine. This compound has the formulation RhSalenClPy. The yield of the product varies with the choice of the starting material, being highest (75–85%) when anhydrous $RhCl_3$ is used, and lowest (35–55%) when $RhCl_3 \cdot 3H_2O$ is used. The active catalyst in this reaction sequence is presumably a chloro–Rh^{I}–pyridine species, which reacts with $SalenH_2$, and can in turn reduce more Rh^{III} in the course of its re-oxidation. The presence of strongly bonded aquo-groups about Rh^{III} in such a reaction would be expected to hinder formation of the active catalyst, and may even promote side-reaction leading to less reactive species highly substituted by pyridine, thus explaining the consistently lower yields observed when hydrated $RhCl_3 \cdot 3H_2O$ is used.

The major by-products of the synthesis of RhSalenClPy are 1,2,6-$RhPy_3Cl_3$ and $(PyH)(RhSalenCl_2)$. This latter complex is also obtained when a solution of $SalenH_2$ in pyridine, under strong reflux, is treated with hydrated $RhCl_3 \cdot 3H_2O$, followed by a large quantity of Zn metal powder. After removal of the Zn by filtration of the hot solution, $(PyH)(RhSalenCl_2)$ can be crystallized by the addition of a large volume of methanol, and it can be re-crystallized from methanol. The complex is reasonably soluble in alcohol, and quite soluble in water. We have been unable to repeat the synthesis of $RhSalenHCl_2$, according to the method of Dwyer and Nyholm[16], from the reaction of RhDmgH $DmgH_2Cl_2$ with $SalenH_2$. While we have obtained the red solution from which the desired complex is reported to crystallize, subsequent crystallization has produced only unreacted ligand and dimethylglyoxime compound. Unlike $RhSalenHCl_2$, which is reported to give rise to a violet-blue coloration in alkaline solution, $(PyH)(RhSalenCl_2)$ dissolves to give a pale yellow solution. Again, the ligands $SalophenH_2$ and $AcacenH_2$ have failed to produce Schiff-base chelates

by the above reaction sequence, while *N,N'*-ethylenebis(5-ClSalicylaldimine), (5-ClSalenH_2), has produced Rh(5-ClSalen)ClPy. RhSalenBrPy and RhSalenIPy have not been successfully synthesised directly, but have been indirectly obtained as a result of attempts to prepare perfluoroalkyl derivatives using perfluoroalkyl bromides and iodides, as described later.

(2). *Structures of RhSalenClPy and related complexes*

The infrared spectra of RhSalenClPy, RhSalenPy and (PyH)(RhSalenCl_2) are all typical of chelated Schiff-base complexes, but show sufficient variations to enable a rapid and accurate identification. The spectra in the range 1800–450 cm^{-1} are shown in Fig. 1.

By analogy with the complex $[Rh(DmgH)_2PPh_3]_2$[20], which has recently been shown to contain an Rh–Rh bond[21], the compound RhSalenPy is also considered

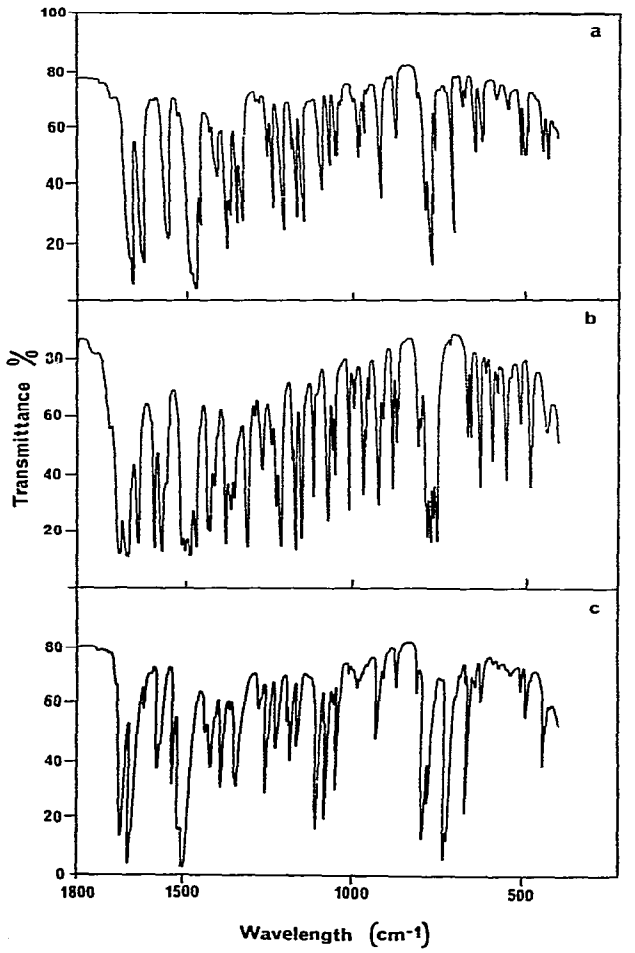
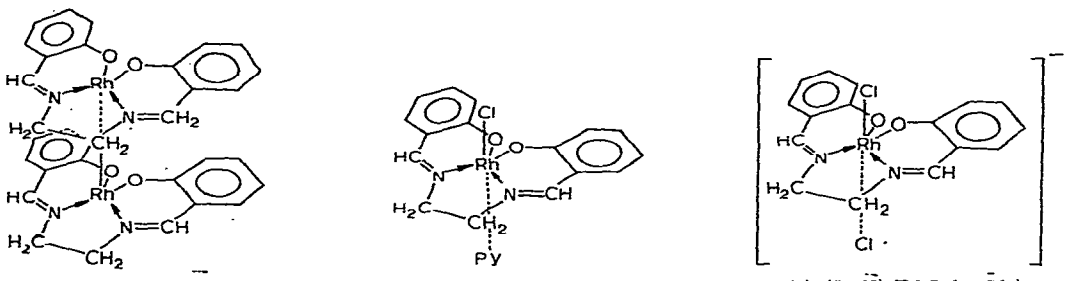


Fig. 1. Infrared spectra of: (a)RhSalenClPy; (b)(RhSalenPy)$_2$; and (c)(PyH)(RhSalenCl_2) in the range 1800–450 cm^{-1}.



(a). $(RhSalenPy)_2$ (b). RhSalenClPy (c). $(PyH)(RhSalenCl_2)$

Fig. 2. Suggested structures of (a) $(RhSalenPy)_2$, (b) RhSalenClPy and (c) $(PyH)(RhSalenCl_2)$.

to be a dimer, Fig. 2(a). The solid is diamagnetic, consistent with an Rh–Rh bond involving the interaction of two d^7 electron configurations, each possessing one unpaired electron. Furthermore, the alternative possibility of a complex of the type H–RhSalenPy is ruled out by the absence of an Rh–H absorption in the spectral range 2200–1800 cm^{-1}. The insolubility of both $(RhSalenPy)_2$ and RhSalenClPy prevented the measurement of NMR spectra.

The most probable structure for RhSalenClPy, which is also diamagnetic in the solid state, would be a six-coordinate monomeric unit involving a square-planar Schiff-base ligand, with Cl and Py occupying the axial ligand positions, Fig. 2(b). This is the structure determined for a number of related $R-Co^{III}SalenB$ complexes[22]. $(PyH)(RhSalenCl_2)$ would presumably contain an octahedral anionic unit, with square-planar Salen, and the halides in axial ligand sites, Fig. 2.(c), similar to the structure determined for the complex $[CrSalen(H_2O)_2]Cl$[23].

Both $(RhSalenPy)_2$ and RhSalenClPy are relatively inert complexes. $(RhSalenPy)_2$ will not react with methyl iodide at 120° in a sealed tube, which is in complete contrast to the related dimethylglyoxime dimer, $[Rh(DmgH)_2PPh_3]_2$, which reacts readily with RCl (R=alkyl) to give $Rh(DmgH)_2Cl(PPh_3)$[20]. The chloride group of RhSalenClPy is very resistant to substitution by either bromide or iodide. For example, treatment of the complex in saturated aqueous alcoholic solution of KI or KBr under reflux, regardless of the duration of the reaction led, at most, to 30–40% substitution. Both $(RhSalenPy)_2$ and RhSalenClPy are unaffected by Grignard and organolithium reagents, even under conditions of prolonged reflux, unlike related Co^{III} Schiff-base complexes which readily react with Grignard reagents, providing a source of aryl–Co^{III} Schiff-base complexes[12,13].

(3). *Reduction of RhSalenClPy*

When either RhSalenClPy or $(PyH)(RhSalenCl_2)$ is suspended in dry, degassed tetrahydrofuran under nitrogen, in the presence of excess 0.2% sodium amalgam, and the mixture is shaken mechanically, a deep blue-green color rapidly develops, which gradually changes to a deep brown. When sodium sand is used in place of amalgam a similar sequence is observed, although the reduction time is somewhat longer. While a thorough study of these reduction reactions and the nature of the species involved is currently in progress, it appears that the 0.2% sodium amalgam reductions proceed to the formation of a species believed to have the formulation "$Na_2RhSalen$" (deep brown in color), and that the intermediate blue-green stage

corresponds to the formulation "NaRhSalen"[24]. In fact, solutions of "Na_2RhSalen" have been found to react with 0.5 molar equivalents of unreduced complex to produce the blue-green mono-sodium species, according to the equation:

$$2\ Na_2RhSalen + RhSalenClPy \rightarrow NaCl + 3\ NaRhSalen + Py$$

and a solid of analytical composition NaRhSalenTHF has been isolated from the mono-sodium solutions by crystallization from THF/heptane. The reduction with sodium sand proceeds even beyond the "Na_2RhSalen" stage[24] since solutions of RhSalenClPy reduced by sodium sand for a similar time to that employed in the amalgam reductions have been found to react with up to three equivalents of RhSalenClPy before the "NaRhSalen" stage is reached. In the present work, we will be concerned only with the "Na_2RhSalen" solutions, obtained from prolonged reduction reactions with 0.2% sodium amalgam. Preparations of these reduced solutions are quite reproducible, there being no evidence so far that reduction beyond "Na_2RhSalen" can be achieved regardless of the reduction time and the quantity of amalgam employed, and the solutions react successfully with a range of organic halides.

When RhSalenClPy is suspended in aqueous methanol containing 15% (w/v) of sodium hydroxide, and treated with excess $NaBH_4$ in the presence of $PdCl_2$ catalyst, a deep red-brown air-sensitive solution was formed from which alkyl derivatives were isolated after reaction with alkyl halides. The reduced solution formed by this procedure presumably contains species of the general formulation "Na_2RhSalen", analogous to the Co^I nucleophiles postulated to be the reactive species in reductive alkylations of the complex Co^{II}Salen under similar conditions[14]. The applications of this synthetic procedure are limited, due to the strongly alkaline reaction conditions required for reduction.

(4). *Syntheses of organo–Rh^{III} Schiff-base chelates*

In the reaction of any organic halide R–X with a solution of reduced RhSalenClPy, both the polarity of the molecule and the strength of the R–X bond appear to compete in determining the reactivity of the organic halide, the desired products R–RhSalenPy often being contaminated by the corresponding halo-complex RhSalenXPy, so that for specific R groups one particular halide is found to react more successfully than another. Both CH_3I and C_2H_5Cl produce the compounds R–RhSalenPy (R=CH_3, C_2H_5) when reacted with reduced solutions prepared by $NaBH_4$/$PdCl_2$ reduction reactions. n-C_3H_7Br and n-C_4H_9Br react similarly with analogous reduced solutions, but the alkyl derivatives are contaminated by traces of the corresponding halo complexes. CH_3Cl, C_2H_5Cl, n-C_3H_7Br, n-C_3H_7Cl, i-C_3H_7Br, i-C_3H_7Cl and n-C_4H_9Br react with amalgam-reduced solutions to yield R–RhSalenPy (R=CH_3, C_2H_5, n-C_3H_7, i-C_3C_7, n-C_4H_9). CH_3I and C_2H_5Br react with analogous reduced solutions to produce alkyl derivatives contaminated by the corresponding halo complexes, which are difficult to remove by recrystallization, and n-C_4H_9Cl produced almost entirely RhSalenClPy.

The major products of the reactions of amalgam-reduced solutions with the fluorocarbon halides CF_3I, C_2F_5I, C_3F_7I and C_6F_5Br were the halo complexes. The organo derivatives (CH_3CO)RhSalenPy, ($C_6H_5CH_2$)RhSalenPy and (CH_2=$CHCH_2$)RhSalenPy were obtained from the reaction of amalgam-reduced solutions with CH_3COCl, $C_6H_5CH_2Br$ and CH_2=$CHCH_2Cl$ respectively. In the present series of complexes there is clearly a delicate balance between the stabilization achieved by the

formation of an Rh–C bond and the ionic nature, $Rh^{\delta+}-C^{\delta-}$, of the resultant bond which, when too great, would lead to heterolysis of the bond. The latter factor is presumably responsible for the failure to synthesize complexes containing the highly

TABLE 1

^1H NMR SPECTRA OF ORGANO-Rh^{III} SCHIFF-BASE CHELATES

Compound	*Chemical shift*[a] *δ (ppm)*	*Multiplicity*	*Integrated area*	*Assignment*
CH_3RhSalenPy	8.44	Doublet (*J* 3Hz)	2	N=CH
	8.25–6.28	Complex pattern	13	Aromatic
	3.68	Singlet	4	CH_2CH_2
	0.95	Doublet (*J* 3Hz)	3	CH_3
C_2H_5RhSalenPy	8.45	Doublet (*J* 3Hz)	2	N=CH
	8.22–6.26	Complex pattern	13	Aromatic
	3.69	Singlet	4	CH_2CH_2
	2.15–1.62	~ Octet	2	CH_2 of C_2H_5
	0.48	Triplet (*J* 7Hz)	3	CH_3 of C_2H_5
n-C_3H_7RhSalenPy	8.42	Doublet (*J* 3Hz)	2	N=CH
	8.22–6.26	Complex pattern	13	Aromatic
	3.70	Singlet	4	CH_2CH_2
	2.04–1.65	Complex pattern	2	CH_2 of C_3H_7
	1.20–0.80	Complex pattern	2	CH_2 of C_3H_7
	0.68	Triplet (*J* 7Hz)	3	CH_3 of C_3H_7
i-C_3H_7RhSalenPy	8.42	Doublet (*J* 3Hz)	2	N=CH
	8.23–6.26	Complex pattern	13	Aromatic
	3.75	Singlet	4	CH_2CH_2
	0.55	Singlet	3	CH_3 of C_3H_7
	0.51	Singlet	3	CH_3 of C_3H_7
n-C_4H_9RhSalenPy	8.45	Doublet (*J* 3Hz)	2	N=CH
	8.22–6.26	Complex pattern	13	Aromatic
	3.69	Singlet	4	CH_2CH_2
	2.07–0.73	Complex pattern	6	$3 \times CH_2$ of C_4H_9
	0.62	Triplet (*J* 7Hz)	3	CH_3 of C_4H_9
(CH_2=$CHCH_2$)RhSalenPy[b]	8.38	Doublet (*J* 3Hz)	2	N=CH
	8.25–6.31	Complex pattern	13	Aromatic
	5.84–5.42	~ Sextet	1	CH of alkyl group
	4.83–4.42	~ Octet	2	Terminal=CH_2
	3.68	Singlet	4	CH_2CH_2
	2.72–2.60	~ Quartet	2	CH_2 of alkyl group
($C_6H_5CH_2$)RhSalenPy[b]	8.34	Doublet (*J* 3Hz)	2	N=CH
	8.12–6.31	Complex pattern	18	Aromatic
	3.53–3.02	Complex pattern	6	CH_2 groups of Salen and benzyl group
(CH_3CO)RhSalenPy[b]	8.48	Doublet (*J* 3Hz)	2	N=CH
	8.36–6.14	Complex pattern	13	Aromatic
	4.04–3.80	Complex pattern	4	CH_2CH_2
	1.10	Singlet	3	CH_3

[a] Spectra recorded in DMSO-d_6, with TMS(δ 0 ppm) as internal reference. [b] Due to the low solubility of these derivatives, the spectra were recorded on slurries of the solids in DMSO-d_6.

electronegative perfluoroalkyl and perfluoroaryl groups.

When $CH_3RhSalenPy$ was heated in vacuo at 100° for 24 h the pyridine was removed, and on air exposure, the solid rapidly absorbed water vapor to produce $CH_3RhSalenH_2O$. This sequence is a general feature of most of the organo derivatives. All of the derivatives R–RhSalenPy and R–RhSalenH_2O are yellow to orange crystalline solids, stable in air, and notably less sensitive to light than their cobalt analogues. They are all soluble or sparingly soluble in organic solvents such as alcohol, acetone, chloroform, dimethylsulfoxide, and are insoluble in water and ether.

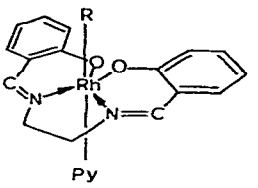


Fig. 3. Proposed structure for the organo–Rh^{III} Schiff-base chelates R–RhSalenPy.

(5). *Spectra and structure of organo–Rh^{III} Schiff-base chelates*

The infrared spectra of all the derivatives are typical of chelated Schiff-base complexes. The spectra of the alkyl derivatives are very similar to that of RhSalenClPy. An additional strong absorption band at 1656 cm^{-1} is observed in the spectrum of $(CH_3CO)RhSalenPy$, and is assigned to the ν(C=O) of the acyl group.

The ^1H NMR spectra of all the organo derivatives in $(CD_3)_2SO$ (Table 1) exhibit a characteristic splitting of the resonance of the organo group, or the part of the organo group directly bonded to Rh, as a result of ^{103}Rh–^1H coupling. This confirms that the derivatives are Rh–C bonded complexes. The CH=N resonance in the spectra of the complexes is symmetrically split by about 3 Hz, presumably due to ^{103}Rh–^1H coupling. It is apparent, as a result of the significant shifts of the organo group proton resonances compared to the related RCoSalen derivatives, *e.g.* $CH_3CoSalenPy$, $\delta(CH_3)$ 2.22 ppm[13]; $C_2H_5CoSalenPy$, $\delta(CH_3)$ 0.06 and $\delta(CH_2)$ 3.34 ppm[25], that the overall shielding effect of the RhSalen moiety on the organo group is greater than that of CoSalen. However, the shielding effect of RhSalen has a lesser effective range than that of CoSalen, since the extent of shielding on protons removed from Rh along the organo group, in all derivatives, is considerably less than that observed for the corresponding cobalt complexes. The pattern of allyl group proton resonances of $(CH_2{=}CHCH_2)RhSalenPy$ is similar to those reported for other σ-allyl transition metal complexes[26–29], ruling out the possibility of a π-allyl structure.

In view of the proven Rh–C bonded nature of the organo derivatives, and the similarity of their infrared and NMR spectra to related RCoSalen compounds, the majority of which have been shown to exist in the *trans* form[22], the present complexes can be postulated as octahedral monomers, with a square-planar Schiff-base ligand, as shown in Fig. 3.

EXPERIMENTAL

$RhCl_3 \cdot xH_2O$ and $Na_3RhCl_6 \cdot 12H_2O$ (Alfa Inorganics Inc.) were used with-

TABLE 2

ANALYTICAL DATA ON SODIUM AND ORGANO DERIVATIVES OF RhSalenClPy

Compound	*Formula*	*Analysis, found (calcd.) (%)*				*Method of preparation**
		C	*H*	*N*	*X*	
RhSalenClPy	$C_{21}H_{19}N_3O_2ClRh$	52.43 (52.14)	4.11 (3.96)	8.81 (8.69)	7.63 (7.33)	
$(RhSalenPy)_2$	$[C_{21}H_{19}N_3O_2Rh]_2$	56.20 (56.25)	4.44 (4.27)	9.28 (9.37)		
(PyH)($RhSalenCl_2$)	$C_{21}H_{20}N_3O_2Cl_2Rh$	48.35 (48.48)	3.81 (3.88)	8.46 (8.08)	14.40 (13.63)	
Rh(5-ClSalen)ClPy	$C_{21}H_{17}N_3O_2Cl_3Rh$	46.54 (46.79)	2.87 (3.03)	7.63 (7.44)	19.60 (18.84)	
NaRhSalenTHF	$C_{20}H_{22}N_2O_3NaRh$	51.76 (51.73)	4.69 (4.78)	6.33 (6.03)		
CH_3RhSalenPy	$C_{22}H_{22}N_3O_2Rh$	57.20	5.02	8.72		a
		57.25	5.02	8.95		b
		(57.03)	(4.79)	(9.07)		
$CH_3RhSalenH_2O$	$C_{17}H_{19}N_2O_3Rh$	51.13 (50.76)	4.40 (4.76)	7.24 (6.97)		d
C_2H_5RhSalenPy	$C_{23}H_{24}N_3O_2Rh$	58.31	5.48	8.69		a
		58.12	5.35	8.47		b
		(57.87)	(5.07)	(8.81)		
n-C_3H_7RhSalenPy	$C_{24}H_{26}N_3O_2Rh$	57.88	5.11	7.81		a
		58.82	5.84	8.79		b
		(58.66)	(5.33)	(8.55)		
i-C_3H_7RhSalenPy	$C_{24}H_{26}N_3O_2Rh$	58.79 (58.66)	5.72 (5.33)	8.45 (8.55)		b
n-C_4H_9RhSalenPy	$C_{25}H_{28}N_3O_2Rh$	58.50	5.66	7.84		a
		58.87	5.71	7.93		b
		(59.41)	(5.58)	(8.32)		
(CH_3CO)RhSalenPy	$C_{23}H_{22}N_3O_3Rh$	55.73 (56.19)	4.85 (4.51)	8.98 (8.55)		b
(CH_3CO)$RhSalenH_2O$	$C_{18}H_{19}N_2O_4Rh$	50.42 (50.24)	4.63 (4.45)	6.68 (6.51)		
(CH_2=$CHCH_2$)RhSalenPy	$C_{24}H_{24}N_3O_2Rh$	58.85 (58.90)	5.37 (4.94)	7.90 (8.59)		b
($C_6H_5CH_2$)RhSalenPy	$C_{28}H_{26}N_3O_2Rh$	61.51 (62.34)	5.02 (4.86)	7.21 (7.79)		b
RhSalenBrPy	$C_{21}H_{19}N_3O_2BrRh$	46.69 (47.75)	4.10 (3.63)	7.30 (7.96)	14.86 (15.13)	c
RhSalenIPy	$C_{21}H_{19}N_3O_2IRh$	44.47 (43.87)	3.37 (3.33)	7.47 (7.31)	21.72 (22.06)	c

* a, RhSalenClPy $\xrightarrow[(ii)\ RX]{(i)\ PdCl_2/NaBH_4}$ R–RhSalenPy;

b, RhSalenClPy $\xrightarrow[(ii)\ RX]{(i)\ 0.2\%Na(Hg)}$ R–RhSalenPy;

c, RhSalenClPy $\xrightarrow[(ii)\ C_3F_7]{(i)\ 0.2\%Na(Hg)}$ RhSalenXPy;

d, R–RhSalenPy $\xrightarrow[(ii)\ H_2O]{(i)\ 100°/Vacuo}$ R–$RhSalenH_2O$.

out further purification. Anhydrous $RhCl_3$ was prepared by electrolysis of rhodium metal in conc. hydrochloric acid[30,31], followed by dehydration of the hydrated rhodium chloride in a stream of HCl vapour at 235°. Pyridine was B.D.H. laboratory reagent grade, used without further purification.

All reactions were carried out in the air unless otherwise stated. Analytical results are given in Table 2.

RhSalenClPy

N,N'-ethylenebis(salicylaldimine), ($SalenH_2$) (1.4 g, 5.3 mmole) was dissolved in pyridine (75 ml) and heated to 80–90° with stirring. Zinc metal powder (0.03 g) was added, followed by anhydrous $RhCl_3$ (1.0 g, 4.8 mmole), or the equivalent amount of $RhCl_3 \cdot 3H_2O$ or $Na_3RhCl_6 \cdot 12H_2O$, added as solid. The reaction mixture became a deep orange colour as the rhodium compound dissolved, and a light yellow sparingly soluble powder began to form. When no further solid appeared to precipitate, the mixture was allowed to cool to 40–50°, while being continually stirred. It was then filtered. The solid was washed with hot methanol to remove unreacted $SalenH_2$. It was then recrystallized from the minimum volume of pyridine, filtered, washed with methanol and dried *in vacuo*. Yield of RhSalenClPy: (anhydrous $RhCl_3$), 75–85; ($Na_3RhCl_6 \cdot 12H_2O$), 45–65; ($RhCl_3 \cdot 3H_2O$), 35–55%. This yield has been found to be slightly improved by the addition of 3–4 ml of triethylamine immediately after the Zn powder, and before the addition of rhodium halide, with the apparatus fitted with a reflux condenser.

Evaporation of the filtrates to dryness, followed by recrystallization of the solid from methanol produced the by-products $(PyH)(RhSalenCl_2)$ (sparingly soluble in alcohol) and 1,2,6-$RhPy_3Cl_3$ (soluble in alcohol).

The above reaction sequence is also observed for the ligand 5-$ClSalenH_2$, but purification of the extremely insoluble solid is difficult.

IR spectrum of RhSalenClPy (nujol mull): 3108 vw, 3078 vw, 3039 vw, 1632 s, 1600 s, 1527 s, 1462 (sh), 1449 s, br, 1430 (sh), 1378 w, 1355 m, 1341 w, 1321 m, 1308 m, 1230 w, 1218 m, 1189 m, 1148 m, 1128 m, 1074 m, 1048 w, 1032 w, 1027 w, 965 w, 958 w, 947 w, 901 m, 853 w, 773 m, 760 s, 751 m, 740 w, 692 s, 655 vw, 648 vw, 621 w, 602 w, 555 vw, 522 vw, 489 w, 480 w, 476 (sh), 423 w, 410 w.

$(RhSalenPy)_2$

The following preparation proceeds by a synthesis *in situ* of the $(RhPy_4Cl_2)^+$ species[18], but the reaction can also be carried out using a methanol solution of preformed $(RhPy_4Cl_2)Cl \cdot 5H_2O$.

Anhydrous $RhCl_3$ (0.50 g, 2.4 mmole), or the equivalent amount of $RhCl_3 \cdot 3H_2O$ or $Na_3RhCl_6 \cdot 12H_2O$, was dissolved in a warm (40–50°) solution of pyridine (5 ml) in methanol (30 ml), in the presence of 5% zinc amalgam (ca. 150 g). When hydrated rhodium halides were used, heating was not necessary. A pale yellow solution resulted which contained the ionic species $(RhPy_4Cl_2)^+$. $SalenH_2$ (0.66 g, 2.5 mmole) dissolved in methanol (40–50 ml) was added, and the mixture stirred at room temperature for an hour. After this time a thick cream-yellow precipitate was present in the solution. The slurry was decanted away from the amalgam, the complex filtered, washed thoroughly with hot methanol, and dried *in vacuo*. If the solid fails to appear after one hour of stirring, removal of the amalgam and careful evaporation

of the solution should cause the solid to precipitate. (Yield 80–90%.)

IR spectrum of $(RhSalenPy)_2$ (nujol mull): 3068 (sh), 3050 w, 3020 w, 1657s, 1635 s, 1602 s, 1552 s, 1532 s, 1475 (sh), 1465 (sh), 1450 s, br, 1432 s, 1398 (sh), 1392 m, 1380 (sh), 1346 s, 1331 (sh), 1320 (sh), 1285 s, 1240 w, 1212 vw, 1200 (sh), 1188, s, 1142 s, 1128 s, 1091 m, 1051 s, 1038 (sh), 1030 w, 989 m, 975 vw, 949 m, 904 m, 890 (sh), 862 m, 851 w, 790 w, 762 s, 752 s, 746 (sh), 737 s, 648 w, 639 w, 611 m, 576 m, 560 vw, 535 m, 493 w, 466 m, 415 w.

(PyH)(RhSalenCl$_2$)

$SalenH_2$ (0.40 g, 1.5 mmole) was dissolved in pyridine (75 ml) under reflux, and $Na_3RhCl_6 \cdot 12H_2O$ (0.90 g, 1.5 mmole), or the equivalent amount of $RhCl_3 \cdot 3H_2O$, was added as a solid, producing a deep orange solution. Zinc metal powder (200 mg) was added and the mixture refluxed with stirring for 10 min. The solution was allowed to cool to 50–60°, then filtered away from the Zn powder. The filtrate was then concentrated on a rotary evaporator to about 20 ml, and hot methanol (100 ml) added. On standing overnight, a yellow precipitate appeared which was filtered and washed with cold methanol. The solid was dried *in vacuo*. (Yield 60–70%). A further crop of less pure material could be isolated by further addition of methanol, and cooling the solution in ice.

IR spectrum of (PyH)(RhSalenCl$_2$) (nujol mull): 3110 w, 1630 s, 1607 s, 1571 w, 1530 m, 1485 m, 1462 (sh), 1447 s, 1393 (sh), 1375 m, 1345 m, 1299 m, 1245 w, 1215 m, 1188 w, 1159 (sh), 1147 w–m, 1130 w, 1068 m, 1042 m, 1012 m, 960 w, 900 w–m, 848 w, 788 w, 760 s, 749 (sh), 697 s, 688 (sh), 638 s, 604 w, 490 w, 472 w, 420 m.

Reduction of RhSalenClPy

(1). *Using 0.2% sodium amalgam.* Tetrahydrofuran, THF, was purified by initially drying it over calcium chloride, twice refluxing the solvent for 3–4 h over sodium wire and finally distilling it under nitrogen into a flask in which was placed $LiAlH_4$. The solvent was then distilled under nitrogen from this flask directly into the reduction vessel.

RhSalenClPy (100 mg) was suspended in dry, degassed THF (60 ml) under nitrogen, in a flask containing 0.2% sodium amalgam (40–50 g). The flask was shaken at moderate speed on a mechanical shaker for 12 h, after which time a deep brown solution, believed to contain the species "Na_2RhSalen" was obtained.

When the amalgam was removed, and RhSalenClPy (100 mg) added to the solution of "Na_2RhSalen", a deep blue-green solution resulted after shaking for a further 12 h. This solution was filtered under nitrogen to remove unreduced RhSalenClPy (ca. 50 mg, after drying in an oven at 100°) and the reduced solution was then carefully treated dropwise with dry, degassed heptane until a dark green solid began to crystallize. This solid was filtered under nitrogen and dried *in vacuo*. It was extremely air sensitive, oxidizing to a bright orange powder. The solid had the analytical composition NaRhSalenTHF. (Yield 40–60%.)

(2). *Using $NaBH_4/PdCl_2$.* RhSalenClPy (100 mg) was suspended in a mixture of methanol (60–70 ml) and 50% sodium hydroxide solution (10 ml), degassed by bubbling nitrogen through it for 10 min. Then, with the reaction mixture under nitrogen and stirring, in succession were added 50% sodium hydroxide solution (10 ml), sodium borohydride (0.50 g) and 5% $PdCl_2$ solution (2 ml). After 3–5 min, a deep red-brown solution, believed to contain the species "Na_2RhSalen", resulted.

Synthesis of organo derivatives

(1). *From 0.2% Na amalgam reductions.* To a solution of "Na_2RhSalen" prepared as described, about 1 ml of an organic halide was added, after removal of the amalgam, causing an immediate colour change to bright orange. The solution was filtered, treated with pyridine (20 ml), methanol (50 ml) and water (30 ml), and the mixture was concentrated on a rotary evaporator at room temperature until orange crystals began to appear, after which the flask was removed. The solution was filtered after standing overnight, and the crystals washed with water and dried *in vacuo* over P_2O_5. The organo derivatives could be recrystallized from the mixture of pyridine, methanol and water described above. (Yields of organo derivatives 55–80%.)

(2). *From $NaBH_4/PdCl_2$ reductions.* To a solution of "Na_2RhSalen" prepared as described was added 2–3 ml of alkyl halide, resulting in a colour change to bright orange. Pyridine (10 ml) was added to the mixture and the solution was warmed and stirred for several minutes. The solution was then filtered and concentrated on a rotary evaporator at room temperature until orange crystals began to appear, when the flask was removed. Isolation and recrystallization of the alkyl derivatives was as described for the 0.2% sodium amalgam system. (Yields of the alkyl derivatives 40–60%.)

Attempted Synthesis of RhSalenHCl$_2$

The preparation was carried out as outlined[16] using analytically pure dimethylglyoxime complex RhDmgHDmgH_2Cl_2 prepared as described previously[32].

RhDmgHDmgH_2Cl_2 (0.15 g) was dissolved in water (10 ml) containing sodium acetate (2 g), and treated with a solution of SalenH_2 (0.1 g) in warm ethanol. The mixture was boiled for 2–10 min, cooled to 0°, filtered, and the filtrate treated with cold concentrated hydrochloric acid, whereupon the Schiff-base complex should have crystallized. Although an orange-red solution always appeared on boiling, as described, virtually all the SalenH_2 crystallized out on cooling, and only RhDmgHDmgH_2Cl_2, characterized by infra-red spectral and micro-analysis, could be isolated after treatment of the filtrate with hydrochloric acid.

Instrumentation

Infra-red spectra were obtained on Perkin–Elmer 257 and 251 instruments. ^{1}H NMR spectra were recorded on Varian A 60 or HA 100 spectrometers. Magnetic measurements were made using the Gouy method.

REFERENCES

1 J. P. Collman and W. R. Roper, *Adv. Organometal. Chem.*, 7 (1968) 53.
2 J. P. Collman, *Accounts Chem. Res.*, 1 (1968) 136.
3 A. J. Mukhedkar, V. A. Mukhedkar, M. Green and F. G. A. Stone, *J. Chem. Soc. A*, (1970) 3166.
4 A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 9 (1970) 2658 and references therein.
5 K. Thomas, J. A. Osborn, A. R. Powell and G. Wilkinson, *J. Chem. Soc. A*, (1968) 1801.
6 A. C. Skapsi and P. G. H. Troughton, *Chem. Commun.*, (1969) 666.
7 F. Faraone, R. Pietropaolo and S. Sergi, *J. Organometal. Chem.*, 24 (1970) 797.
8 E. F. Paulus, H. P. Fritz and K. E. Schwartzhans, *J. Organometal. Chem.*, 11 (1968) 647.
9 J. H. Weber and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 92 (1970) 726.
10 G. N. Schrauzer, *Accounts Chem. Res.*, 1 (1968) 97.

11 G. Costa, G. Mestroni, G. Tauzher and L. Stefani, *J. Organometal. Chem.*, 6 (1966) 181.
12 G. Costa, G. Mestroni and L. Stefani, *J. Organometal. Chem.*, 7 (1967) 493.
13 C. Floriani, M. Puppis and F. Calderazzo, *J. Organometal. Chem.*, 12 (1968) 209.
14 G. N. Schrauzer, J. W. Sibert and R. J. Windgassen, *J. Amer. Chem., Soc.*, 90 (1968) 6681.
15 R. J. Cozens, G. B. Deacon, P. W. Felder, K. S. Murray and B. O. West, *Aust. J. Chem.*, 23 (1970) 481.
16 F. P. Dwyer and R. S. Nyholm, *Proc. Roy. Soc., N.S.W.*, 79 (1945) 126.
17 R. J. Cozens, K. S. Murray and B. O. West, *Chem. Commun.*, (1970) 1262.
18 R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.*, (1965) 1951.
19 R. D. Gillard, B. T. Heaton and D. H. Vaughan, *J. Chem. Soc. A*, (1971) 1840.
20 S. A. Schepinov, E. N. Salnikova and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 2128.
21 K. G. Caulton and F. A. Cotton, *J. Amer. Chem. Soc.*, 91 (1969) 6517.
22 M. Cesari, C. Neri, G. Perero, E. Perotti and A. Zazzatta, *Chem. Commun.*, (1970) 276 and references therein.
23 P. Coggon, A. T. McPhail, P. M. Cross, F. E. Mabbs, A. Richards and A. S. Thornley, *J. Chem. Soc. A*, (1970) 3296.
24 R. J. Cozens, K. S. Murray and B. O. West, unpublished results.
25 H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni and G. Costa, *J. Organometal. Chem.*, 11 (1968) 167.
26 M. Cousins and M. L. H. Green, *J. Chem. Soc.*, (1963) 889.
27 M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, (1963) 189.
28 M. L. H. Green and A. N. Stear, *J. Organometal. Chem.*, 1 (1963) 230.
29 H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch. B*, 15 (1960) 763.
30 A. I. Ryazanov and G. D. Petrenko, *Tr. Vses. Nauch. Issled. Inst. Khim. Reactivov. Osobo. Chist. Khim. Veshchestv.*, 28 (1966) 327.
31 V. V. Krokhv, A. I. Vol'fson and N. R. Zakharova, *Zh. Prikl. Khim. (Leningrad)*, 35 (1962) 2566.
32 F. P. Dwyer and R. S. Nyholm, *Proc. Roy. Soc.*, N.S.W., 77 (1944) 266.