Schiff-base Complexes of Ruthenium(II) †

By **John R. Thornback** and **Geoffrey Wilkinson**,* Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The interaction of dichlorotris(triphenylphosphine)ruthenium(II) with the sodium salts of various Schiff bases leads to complexes of the type *trans*-$RuL(PPh_3)_2$ for the quadridentate bifunctional ligands and $RuL_2(PPh_3)_2$ for the bifunctional ligands.

Interaction of the chloro-carbonyls, $\{Ru(CO)_2Cl_2\}_n$ or $\{Ru(CO)_3Cl_2\}_3$, with the sodium salt of *NN'*-ethylenebis-(salicylideneimine), (sal_2enH_2), yields the pale yellow complex *cis*-Ru(sal_2en)$(CO)_2$.

Interaction of the bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) complex $\{Ru(nbd)Cl_2\}_n$ with $Na_2(sal_2en)$ yields Ru(sal_2en)(nbd) which has a non-planar ligand structure.

I.r. and ^1H and ^{31}P n.m.r. spectra of the various complexes are given and structures for the compounds proposed.

ALTHOUGH there is extensive knowledge of transition-metal complexes of Schiff bases,[1] it is largely confined to the first row metals, notably iron, cobalt, and nickel; little has been reported for ruthenium. The reaction of $Ru_3(CO)_{12}$ with *NN'*-ethylenebis(salicylideneimine)-(sal_2enH_2) and *N*-phenyl(salicylideneimine)(salphenH) gives a complex of stoicheiometry [Ru(sal_2en)(CO)]$_2$ but of uncertain structure (which we have prepared by other methods) while salphenH gives small yields of Ru(salphen)$_2$(CO)$_2$.[2] The reaction of tris(acetylacetonato)-ruthenium(III) with *N*-α-benzylethylsalicylideneimine in ethyl benzoate[3] gives the chiral tris-complex. Ruthenium Schiff-base complexes are said to act as catalysts although no isolation or characterisation of the complexes was described.[4]

We have prepared ruthenium complexes of various types of Schiff bases which are listed below with their abbreviations.

Ligand	Abbreviation
NN'-Ethylenebis(salicylideneimine)	sal_2enH_2
NN'-Ethylenebis(pyrrole-2-aldimine)	pyr_2enH_2
NN''-*o*-Phenylenebis(pyrrole-2-aldimine)	pyr_2phenH_2
N-2-Pyridyl(salicylideneimine)	salpyH
NN'-*o*-Phenylenebis(salicylideneimine)	sal_2phenH_2
N-Phenyl(salicylideneimine)	salphenH
N-Benzyl(salicylideneimine)	salbenzH
N-β-Hydroxy-α-naphthylmethyl-(salicylideneimine)	$salnapH_2$
NN'-Ethylenebis(penta-2,4-dione monoimine)	$acac_2enH_2$
NN'-Trimethylenebis(salicylideneimine)	sal_2(1,3-tri)H_2
NN'-Hexamethylenebis(salicylideneimine)	sal_2(1,6-hex)-H_2
Bicyclo[2.2.1]hepta-2,5-diene	nbd

RESULTS AND DISCUSSION

(1) *Reaction of Dichlorotris(triphenylphosphine)ruthenium*(II) *with Schiff Bases*.—(a) *Quadridentate bifunctional ligands.* The sodium salts of the Schiff bases were prepared by stirring the latter with an equivalent amount of sodium hydride in diethyl ether.[5] When a suspension of the salt and $RuCl_2(PPh_3)_3$ in tetrahydrofuran (thf) was heated under reflux sodium chloride was precipitated and deep red solutions were formed for ligands derived from salicylaldehyde and orange-red solutions from pyrrole-2-carbaldehyde. The crystalline complexes isolated are listed in Table 1 and ^1H, ^{31}P n.m.r., and i.r. spectra are given in Tables 2 and 3.

The ^{31}P n.m.r. spectra of the triphenylphosphine complexes have only a singlet in the region +25—38 p.p.m. (for $PPhMe_2$ complex at +16.8 p.p.m.) relative to 85% H_3PO_4 external standard which is in the range for *trans*-phosphine complexes.[6] Although isolation of Ru{sal_2(1,3-tri)}$(PPh_3)_2$ and Ru{sal_2(1,6-hex)}$(PPh_3)_2$ proved very difficult as the complexes appear oily, there is no evidence for the formation of *cis*-phosphine complexes with a distorted Schiff base ligand even when the chain length of the methylene bridge is increased to six methylene groups (*cf.* the change in structure of cobalt Schiff base complexes[7]) and the ^{31}P n.m.r. spectra of the two complexes have singlets at +29.81 and +31.58 p.p.m. This is probably because of the tendency for ruthenium(II) to form octahedral complexes and clearly the sterically least hindered arrangement will be with *trans*-phosphines and the ligand planar. The i.r. spectra in the region 1 650—1 500 cm^{-1} are complicated but changing the nature of the phosphine appears to have little effect on the ν(C=N). There is, however, a tendency for ν(C=N) in complexes of Schiff bases from aromatic diamines to shift, on co-ordination, to lower

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† No reprints available.

[1] (*a*) M. D. Hobday and T. D. Smith, *Co-ordination Chem. Rev.*, 1973, **9**, 311; (*b*) M. Calligaris, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[2] F. Calderazzo, C. Floriani, R. Henzi, and F. L'Eplattenier, *J. Chem. Soc.* (*A*), 1969, 1378.

[3] K. S. Finney and G. W. Everett, *Inorg. Chim. Acta*, 1974, **11**, 183.

[4] G. Henrici-Olivé and S. Olivé, *J. Mol. Cat.*, 1976, **1**, 121.

[5] C. Santini-Scampucci and G. Wilkinson, *J.C.S. Dalton*, 1976, 807.

[6] R. G. Caulton and P. R. Hoffman, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

[7] M. Hariharan and F. L. Urbach, *Inorg. Chem.*, 1969, **8**, 556.

TABLE 1

Analytical data for complexes

Compound	Found					Required			
	Colour	C	H	N	P(Ru)	C	H	N	P(Ru)
Ru(sal$_2$en)(PPh$_3$)$_2$	Purple	68.7	5.0	3.1	7.1	70.1	4.9	3.1	6.9
Ru(sal$_2$en)(PPhMe$_2$)$_2$ [a]	Red	59.1	5.7	3.6	9.4	59.7	5.6	4.3	9.6
Ru(pyr$_2$en)(PPh$_3$)$_2$	Orange [b]	68.6	5.7	6.7	7.9	68.8	5.0	6.7	7.4
Ru(pyr$_2$phen)(PPh$_3$)$_2$	Orange	69.9	4.9	6.0	6.8	70.5	4.7	6.3	7.0
Ru(salbenz)$_2$(PPh$_3$)$_2$·2thf	Red	72.7	5.6	2.4	5.2	72.9	5.6	2.4	5.2
{Ru(sal$_2$en)(CO)}$_2$ [c]	Yellow	51.0	4.0	6.4		51.6	3.6	7.1	
cis-Ru(sal$_2$en)(CO)$_2$ [d]	Pale yellow	50.4	4.3	5.7	21.3	51.1	3.3	6.6	23.4
Ru(acac$_2$en)(PPh$_3$)$_2$·2thf	Red	67.6	6.1	3.2	7.1	68.0	5.7	3.3	7.3
Ru(sal$_2$phen)(PPh$_3$)$_2$·2thf	Black	71.9	5.5	2.4	5.5	70.8	5.5	2.6	5.7
[Ru(sal$_2$enH)(PPh$_3$)][BF$_4$] [e]	Red-orange	58.7	4.6	4.1	4.4	57.0	4.2	3.9	4.3
[Ru(sal$_2$enH)(PPh$_3$)][tos] [f]	Red-orange	61.7	5.2	3.5	4.3	61.5	5.1	3.5	3.9
Ru(pyr$_2$en)(CO)(PPh$_3$)	Yellow	61.6	4.8	9.3	5.0	61.7	4.5	9.3	5.1
Ru(salpy)$_2$(PPh$_3$)$_2$·thf	Red	70.3	5.5	4.6	5.8	70.4	5.1	5.1	5.7
Ru(salnap)(CO)(PPh$_3$)·2thf [g]	Yellow	69.2	5.6	1.3	5.6	70.1	5.5	1.3	5.8
Ru(salnap)(PPh$_3$)$_2$·2thf	Green-black	69.8	5.6	1.3	5.9	71.1	5.8	1.3	5.9
Ru(sal$_2$en)(nbd)	Orange-red	58.9	4.9	5.9		60.1	4.8	6.1	

[a] Molecular weight by mass spectrometry $M^+ = 643$ (calc. 644). [b] Orange crystals which gave a yellow powder when washed with light petroleum. [c] Analysis by Calderazzo,[2] C 50.8, 50.9; H, 3.5, 3.4; N, 6.45, 6.75. [d] Molecular weight osmometrically in chloroform 454 (calc. 432). [e] Conductivity in CH$_3$NO$_2$ at 10^{-3} M conc. $\Lambda_M = 49\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. [f] Conductivity in CH$_3NO_2$ at 10^{-3} M concentration $\Lambda_M = 41\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. [g] Molecular wt. osmometrically in chloroform 929 (calc. 928).

TABLE 2

N.m.r. spectra

Compound	^{1}H [a]				^{31}P [b]
	$\tau_{CH=N}$	τ_{phenyl}	τ_{N-CH_2}	Other	
Ru(sal$_2$en)(PPh$_3$)$_2$ [d]	*c*	2.4—4.0(br,m)	6.2—6.2(br,m)		+29.92 [e]
Ru(sal$_2$en)(PPhMe$_2$)$_2$ [h]	1.56(t)	2.1—3.8(br,m)	5.9—6.6(br,m)	τ_{P-Me} 8.38(t), 8.78(t)	+15.41 [f]
Ru(pyr$_2$en)(PPh$_3$)$_2$ [g]	2.75(s)	2.80—3.16(br,s)	6.36(s)	4.17(s)	+38.85 [f]
Ru(pyr$_2$phen)(PPh$_3$)$_2$ [d]	*c*	2.70—3.4(br,m)			+37.76 [f]
Ru(salbenz)$_2$(PPh$_3$)$_2$ [d]	*c*	2.30—3.5(br,m)	5.23(d)		+28.53 [f]
cis-Ru(sal$_2$en)(CO)$_2$ [d]	1.96(s), 2.16(s)	2.87—3.25(m) 3.4—3.6(m)	6.0—6.2(m)		
Ru(acac$_2$en)(PPh$_3$)$_2$ [h]		2.3—3.2(br,s)		6.28(s), 4.12(s), 8.60(s), 8.97(s)	+33.24
Ru(sal$_2$phen)(PPh$_3$)$_2$ [d]	*c*	2.3—3.2(br,s)			+29.04 [f]
[Ru(sal$_2$enH)(PPh$_3$)][BF$_4$] [g]	2.26(s)	2.57—3.6(br,m)	6.6—6.8(br,m)		+64.22 [i]
[Ru(sal$_2$enH)(PPh$_3$)][tos] [g]	*c*	2.40—3.7(br,m)	6.5—6.8(br,m)	7.73(s)	+64.22 [i]
Ru(pyr$_2$en)(CO)(PPh$_3$) [g]	2.54(s)	2.75—3.38(br,m)	6.05(s)	3.78(d), 4.08(d)	+22.78 [f]
Ru(salpy)$_2$(PPh$_3$)$_2$ [d]	*c*	2.1—3.6(br,m)			+30.30 [f]
Ru(salnap)(CO)(PPh$_3$)$_2$ [g]	2.18(s)	2.3—4.0(m)	5.54(s)		+28.51 [f]
Ru(salnap)(PPh$_3$)$_2$ [d]	*c*	2.2—3.4(br,m)	*j*		+23.05 [f]
Ru(sal$_2$en)(nbd) [h]	1.90(s), 2.29(s)	2.80—3.75(br,m)	5.7—6.7(br,m)	5.48(d), 5.63(s) 6.09(d), 6.35(s) 6.65(s), 8.75(s)	

[a] All measurements in p.p.m. relative to SiMe$_4$ = 10 p.p.m. as internal standard or from solvent resonances. [b] All measurements in p.p.m. relative to 85% H$_3$PO$_4$ external standard. All resonances are singlets and resonances to high frequency (low field) are termed positive. [c] Resonance obscured by phenyl protons. [d] Solvent, CDCl$_3$. [e] Solvent, C$_6$D$_6$/C$_6$H$_6$. [f] Solvent, C$_6$D$_6$/thf. [g] Solvent, (CD$_3$)$_2$CO. [h] Solvent, CD$_2$Cl$_2$. [i] Solvent, C$_6$D$_6$/CH$_3$NO$_2$. [j] Not observed due to insolubility of complex.

TABLE 3

I.r. spectra of ruthenium complexes [a,b]

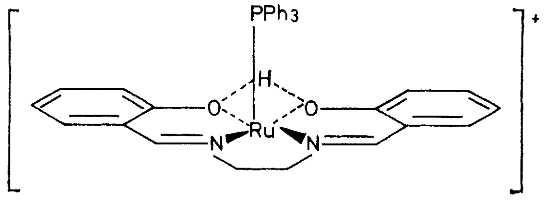
Compound	1 650—1 500 cm^{-1}	Other bands
Ru(sal$_2$en)(PPh$_3$)$_2$	1 595s, 1 525m	
Ru(sal$_2$en)(PPhMe$_2$)$_2$	1 610w, 1 594s, 1 529m	
Ru(pyr$_2$en)(PPh$_3$)$_2$	1 580vs, 1 510w	
Ru(pyr$_2$phen)(PPh$_3$)$_2$	1 573w, 1 540s, 1 510sh	
Ru(salbenz)$_2$(PPh$_3$)$_2$	1 630s, 1 608vs, 1 594s, 1 528m	
Ru(pyr$_2$en)(CO)(PPh$_3$)	1 587s, 1 580sh, 1 510m	ν(CO) 1 940s
Ru(salpy)$_2$(PPh$_3$)$_2$	1 600s, 1 585s, 1 560m, 1 520m	
Ru(acac$_2$en)(PPh$_3$)$_2$	1 573m	
Ru(sal$_2$phen)(PPh$_3$)	1 598s, 1 568s, 1 509m	
{Ru(sal$_2$en)(CO)}$_2$	1 645m, 1 627s, 1 595s, 1 550w, 1 528s	ν(CO) 1 910vs, 1 865vw
cis-Ru(sal$_2$en)(CO)$_2$	1 628s, 1 598s, 1 527s	ν(CO) 2 038s, 1 975sh, 1 965s
[Ru(sal$_2$enH)(PPh$_3$)][BF$_4$]	1 595sh, 1 590s, 1 545m	
[Ru(sal$_2$enH)(PPh$_3$)][tos]	1 590s, 1 548m	
Ru(sal$_2$en)(nbd)	1 611s, 1 590s, 1 525m	1 305m
Ru(salnap)(CO)(PPh$_3$)$_2$	1 623m, 1 610w, 1 598w 1 585m, 1 530m	ν(CO) 1 930vs, 1 887vw
Ru(salnap)(PPh$_3$)$_2$	1 605m, 1 595sh, 1 580sh, 1 530m, 1 500m	

[a] All spectra as Nujol mulls using CsI or KBr plates. [b] All values expressed in cm^{-1}.

frequencies than those with aliphatic diamines. This is probably due to increased metal–ligand π bonding with electron delocalisation over the whole molecule.

The ^1H n.m.r. spectra of these complexes (Table 2) are, in general, difficult to obtain because of low solubility. In the bis-triphenylphosphine complexes the methine resonance is obscured by the phenyl peaks. However, with $(sal_2en)^{2-}$ as the Schiff base and if $PPhMe_2$ is used the methine resonance can be seen at τ 1.96 (compared to τ 1.49 in the free ligand) as a 1 : 2 : 1 triplet due to long range coupling with the two *trans*-phosphorus atoms. The value $J_{P-H} = 5$ Hz; in similar cobalt(III) complexes, $[Co(sal_2en)(PPh_3)_2]^+$, $J_{P-H} = 3.0$—3.5 Hz.[8] The methylene protons in $Ru(sal_2en)(PPh_3)_2$ appear as a broad resonance at τ 6.2—6.4. This broadening is due to the non-equivalence of the four methylene protons on co-ordination. The PMe_2 methyl resonances of $Ru(sal_2en)(PPhMe_2)_2$ occur as two 1 : 2 : 1 triplets ($J_{P-H+P-H'} = 16$ Hz) at τ 8.38 and 8.78 respectively. This indicates non-equivalence of the methyl groups and loss of symmetry in the plane through the P–Ru–P axis.

The complex $Ru(sal_2en)(PPh_3)_2$ reacts with carbon monoxide to give the compound $[Ru(sal_2en)CO]_2$ described by Calderazzo.[2] It also reacts with an excess of aqueous HBF_4 or *p*-toluenesulphonic acid (Htos) in tetrahydrofuran to give a yellow-red solution from which a red solid was isolated; on crystallisation from nitromethane this gave orange crystals with a metallic lustre of stoicheiometry $[Ru(sal_2enH)(PPh_3)]X$ ($X = BF_4$ or tos). The complexes are 1 : 1 electrolytes in CH_3NO_2, although the conductances are somewhat low[9] [$\Lambda(10^{-3}M) = 49$ and 41 Ω^{-1} cm^2 mol^{-1}]. The ^{31}P n.m.r. spectra of the salts show a single resonance at +64.22 p.p.m. which is shifted *ca.* +35 p.p.m. from the value for $Ru(sal_2en)(PPh_3)_2$ suggesting a different structure and probably a five-co-ordinate species. There is no i.r. band in the *ca.* 3 500 cm^{-1} region that would be expected for an OH stretch so that hydrogen bonding O · · · H–O is likely and the protonated species is best formulated as (I). The ^{31}P spectra partially decoupled show no change from the fully decoupled spectrum so there is no Ru–H in the cation. The complexes are also diamagnetic so no oxidation to Ru^{3+} has, apparently, occurred. There is also no co-ordination of the anion in CH_3NO_2 solution as both $[Ru(sal_2enH)(PPh_3)][tos]$ and $[Ru(sal_2enH)(PPh_3)][BF_4]$ have the same ^{31}P resonance frequency and the ^{19}F n.m.r. of the latter shows only a single resonance in the position expected for unco-ordinated $[BF_4]$.



(I)

The reaction of HBF_4 and $Ru(sal_2en)(PPh_3)_2$ is, however, not simple since if the initial reaction solution is warmed other reactions occur. The red solution changes colour and precipitates a red solid which is stable only when it contains solvent, removal of the latter giving rise to a black oil. This process is reversible on addition of solvent. The species isolated is probably co-ordinatively unsaturated, arising by loss of both PPh_3 molecules from the initial $Ru(sal_2en)(PPh_3)_2$. When the red solid is heated further it redissolves to give a green-red solution from which small amounts of an unidentified green solid crystallise. However on adding a large excess of water to the remaining solution $[Ru(sal_2enH)(PPh_3)][BF_4]$ is precipitated.

The ^1H n.m.r. spectrum of the complex *trans*-$Ru(pyr_2en)(PPh_3)_2$ has a broad resonance for the phenyl protons at τ 2.97 with a small shoulder at τ 2.75 due to the reactive protons. There is also a resonance at τ 4.17 due to four protons of the pyrrole groups. The methylene protons remain as a singlet (τ 6.36) in contrast to sal_2enH_2 complexes where the methylene resonances are broadened considerably on co-ordination. On bubbling carbon monoxide through a solution of *trans*-$Ru(pyr_2en)(PPh_3)_2$ the complex $Ru(pyr_2en)(CO)(PPh_3)$ is formed and here the singlet resonance at τ 4.17 splits into a doublet of doublets at τ 3.78 and 4.08. The methylene resonances remain as a singlet but are shifted to τ 6.05; the methine resonance appears as a singlet at τ 2.54. The splitting of the τ 4.17 resonance is due to a change of symmetry in the molecule caused by replacing one PPh_3 by a CO.

The reaction of $Na_2(sal_2en)$ or $Na_2(sal_2phen)$ and $RuCl_2(PPh_3)_3$ in methanol, unlike the reaction in tetrahydrofuran, gives mixtures of the bis-phosphine complex together with a carbonyl-containing species (ν_{CO} 1 900 cm^{-1}) but we have been unable to separate the latter. Using $Na_2(pyr_2en)$ in methanol only the bis-phosphine compound is formed.

(b) *Bidentate monofunctional ligands.* The reaction of Na(salbenz) and $RuCl_2(PPh_3)_2$ in tetrahydrofuran produces red crystals of $Ru(salbenz)_2(PPh_3)_2$ which has equivalent *trans*-PPh_3 groups since the ^{31}P resonance is a singlet in the same region as in *trans*-$Ru(sal_2en)(PPh_3)_2$.

The reaction of Na(salpy), which is potentially tridentate, gives *trans*-$Ru(salpy)_2(PPh_3)_2$ in which the ligand appears to be bidentate. Here the ν(C=N) changes only slightly on co-ordination of the ligands, 1 605 to 1 600 cm^{-1}, whereas in the other phosphine Schiff-base complexes it is shifted by *ca.* 30 cm^{-1}.

(c) *Tridentate bifunctional ligands.* The reaction of the disodium salt of *N*-β-hydroxy-α-naphthylmethyl-(salicylideneimine), ($salnapH_2$, potentially tridentate), with $RuCl_2(PPh_3)_3$ in thf gives a greenish black solution from which no pure compound could be isolated. However, if the reaction is carried out using a large excess of

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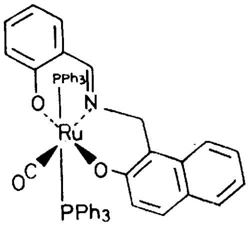
[8] C. W. Smith, G. W. van Loon, and M. C. Baird, *Canad. J. Chem.*, 1976, **54**, 1875.

[9] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

PPh_3 a red solution is formed which on cooling gave a green-black solid, Ru(salnap)$(PPh_3)_2$·2thf, the ^{31}P spectrum of which has a single resonance at +23.05 p.p.m. (*trans*-PPh_3 groups). On bubbling CO through the greenish black solution or through a solution of the complex in thf, a green solution is formed from which a yellow complex Ru(salnap)(CO)$(PPh_3)_2$ (II) can be isolated. The ^{31}P n.m.r. spectrum of the latter has a singlet at +28.51 p.p.m.

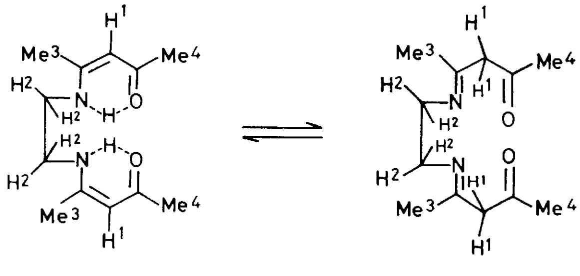
Since the phosphines are equivalent and the resonances in a similar position to those of *trans*-Ru(sal_2en)$(PPh_3)_2$, the complex evidently has mutually *trans* PPh_3 groups with the ligand planar. In solution the complex Ru(salnap)$(PPh_3)_2$ probably has a solvent molecule in the plane of the ligand to give an octahedral structure. This solvent molecule is readily replaced by carbon monoxide to give Ru(salnap)(CO)$(PPh_3)_2$ with the carbonyl *trans* to the nitrogen atom as in (II).



(II)

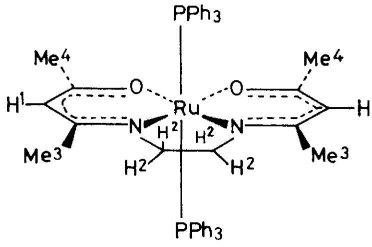
Most of the above PPh_3-containing compounds were found to act as hydroformylation catalysts for hex-1-ene, at 100 °C, although this is merely due to the displacement of Schiff base and the formation of $Ru(CO)_3(PPh_3)_2$ which has been studied before.[10] The complexes do not act as hydrogenation catalysts for hex-1-ene at pressures of H_2 up to 100 atm at 100 °C.

(2) *Reaction of Dichlorotris(triphenylphosphine)ruthenium*(II) *with* NN′-*Ethylenebis(pentane*-2,4-*dione monoimine*) ($acac_2enH_2$).—The ligand $acac_2enH_2$ and sodium hydride in thf on treatment with $RuCl_2(PPh_3)_3$ give an orange-red solution from which the orange crystalline Ru($acac_2$en)$(PPh_3)_2$ can be isolated. The ^{31}P n.m.r. shows again only a singlet at 33.24 p.p.m. The ^{1}H n.m.r. is solvent-dependent. In CD_2Cl_2 there are four resonances ascribable to the ligand at τ 6.28 (2 H), 4.12 (4 H), 8.60 (6 H), and 8.97 (6 H). In C_6D_6 the two high-field resonances coalesce and the values are τ 6.14 (2 H), 7.43 (4 H), and 8.72 (12 H). The free ligand has two main tautomeric forms[11] [(IIIa, b) with hydrogen positions labelled]; in most solvents it exists mainly in form (IIIa) but in $(CD_3)_2CO$ *ca.* 30% of form (IIIb) is present. The shift of H^1 for (IIIa) is *ca.* τ 5, varying τ ±0.2 with solvent, while in (IIIb) H^1 is at τ 7.2. In the complex Ru($acac_2$en)$(PPh_3)_2$, as in other complexes with $acac_2$en as ligand,[11] the (IIIa) form is retained as in (IV). The H^1 proton resonance is shifted considerably because of shielding due to the phenyl ring currents of the PPh_3 in the *trans*-positions. In the presence of an excess of $P(OMe)_3$ the benzene solution becomes yellow-green and the H^1 proton resonance was shifted to τ 5.20 while the methyl resonances split into two at τ 8.09 and 8.39. This change is probably due to displacement of the *trans*-PPh_3 ligands by $P(OMe)_3$ which then reduces the shielding of the H^1 protons.



(a) (III) (b)

In the ^{1}H spectrum of Ru($acac_2$en)$(PPh_3)_2$ the phenyl protons show a broad single peak at τ 2.3—3.2 in CD_2Cl_2 and two broad peaks at τ 2.4 and 2.92 in C_6D_6. The i.r. spectrum has a single band at 1 573 cm^{-1} due to the carbonyl stretching mode which, perturbed by co-ordination, has resulted in a delocalised environment.[12]



(IV)

(3) *Reaction of Dicarbonyldichlororuthenium*, {Ru$(CO)_2Cl_2$}$_n$, *with Schiff Bases*.—On heating a suspension of {$Ru(CO)_2Cl_2$}$_n$ or {$Ru(CO)_3Cl_2$}$_2$ and Na_2(sal_2en) in thf under reflux a red solution and a yellow solid containing {Ru(sal_2en)(CO)}$_2$ [2] are formed. Chromatography of the red solution gave as the major product pale yellow crystals of *cis*-Ru(sal_2en)$(CO)_2$. This probably has a structure with a non-planar Schiff base (V) similar to that proposed for Co(sal_2en)(acac)[13,14] and R_2Sn(sal_2en).[15]

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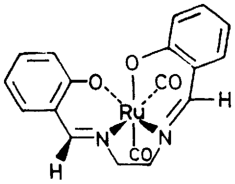
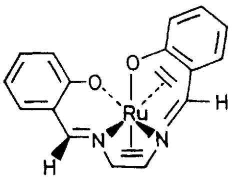
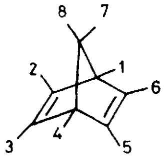
(4) *Reaction of Other Ruthenium Complexes with Schiff Bases*.—On stirring a suspension of the norbornadiene complex $\{Ru(nbd)Cl_2\}_n$ and $Na_2(sal_2en)$ for several days in tetrahydrofuran a deep red solution, and a dark coloured precipitate were formed. Transfer of the mixture to an alumina column followed by chromatography using tetrahydrofuran gave a red eluate from which an orange-red solid was isolated. This has i.r. bands in the 1 650—1 500 cm^{-1} region at 1 640sh, 1 618s, 1 590sh, 1 570sh, and 1 525vs. The ^1H n.m.r. spectrum shows two methine resonances at τ 1.90 and 2.29. The phenyl protons show a complex pattern as expected in the region τ 2.8—3.7. The spectrum in the region for the norbornadiene peaks is complicated by the presence of methylene protons of the ligand. However we may tentatively assign the spectrum to a complex of stoicheiometry Ru(sal$_2$en)(nbd) (VI) with H^2 τ 5.48 (doublet, $J_{H^2-H^3}$ = 4 Hz), H^6 5.63 (broad singlet), H^3 6.09 (doublet, $J_{H^2-H^3}$ = 4 Hz), $H^{1,4}$ 6.35 (broad singlet), H^5 6.65 (broad singlet), $H^{7,8}$ 8.75 (sharp singlet). The norbornadiene is in an asymmetrical environment with a non-planar Schiff-base ligand resulting in a complex of similar structure to *cis*-Ru(sal$_2$en)(CO)$_2$. The complex, dissolved in tetrahydrofuran, reacts with carbon monoxide to yield $\{Ru(sal_2en)(CO)\}_2$ in quantitative yield.



(V)



(VI)



Subsequent elution from the alumina column using methanol gave a very air-sensitive green-red band which we have so far not identified.

A similar reaction with the cyclo-octa-1,5-diene complex $\{Rh(cod)Cl_3\}_2$ has given the complex $\{Rh(cod)\}_2$(sal$_2$en).[16] Attempted preparations of Schiff base complexes from $RuCl_2(MeCN)_4$, $RuCl_2(dmso)_4$, and ' $RuCl_3 \cdot 3H_2O$ ' were unsuccessful.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Ltd. and the Microanalytical Laboratories of Imperial College. I.r. spectra were obtained using a Perkin-Elmer 457 and ^1H n.m.r. spectra using Perkin-Elmer R12 (60 MHz) spectrometers. ^{31}P and ^{19}F n.m.r. spectra were obtained using a Varian Associates XL-100-12 operating in Fourier-transform mode. Conductivities were measured using standard procedures and a Mullard conductivity-bridge type E7566/3 with a matching conductivity cell.[17]

All solvents were thoroughly degassed before use and all operations carried out under an argon atmosphere, using standard suba-seal and thin steel tubing transfer techniques. All light petroleum used had b.p. 40—60 °C.

The Schiff bases were prepared by refluxing equivalent amounts of the amine and aldehyde in methanol for 10 min and were recrystallised from ethanol. The sodium salts were prepared as before,[5] by stirring equivalent amounts of sodium hydride and the Schiff base in diethyl ether until hydrogen gas evolution ceased. The ruthenium complexes $RuCl_2(PPh_3)_3$,[18] $\{Ru(nbd)Cl_2\}_n$,[19] $RuCl_2(PPhMe_2)_4$,[20] $RuCl_2(MeCN)_4$,[21] $RuCl_2(dmso)_4$,[22] and $\{Ru(CO)_2Cl_2\}_n$ [23] were prepared by published procedures.

Microanalytical data for the new complexes are given in Table 1. When heated the compounds all decomposed without melting.

All yields quoted are the average of several preparations.

trans-NN′-*Ethylenebis(salicylideneiminato)bis(triphenylphosphine)ruthenium*(II).—(*a*) The complex $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) was added to a suspension of $Na_2(sal_2en)$ (0.32 g, 1.04 mmol) in tetrahydrofuran (50 cm^3) and the solution was refluxed for 2 h. The deep red solution was then filtered and evaporated to small volume to give purple crystals of the *complex*. These were collected and recrystallised from tetrahydrofuran–light petroleum; yield, *ca*. 60%.

(*b*) The same complex can be prepared using methanol as solvent but refluxing for several days is required.

The preparation of the other *trans* bis-triphenylphosphine complexes was similar to the above, except for Ru(salnap)$(PPh_3)_2$ when a four-fold excess of PPh_3 was added initially.

trans-NN′-*Ethylenebis(pentane-*2,4-*dione monoiminato)-bis(triphenylphosphine)ruthenium*(II).—The complex $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) was added to a suspension of $Na_2(acac_2en)$ (0.27 g, 1.04 mmol) in tetrahydrofuran (50 cm^3) and the solution refluxed for several hours. The resulting red solution was filtered and evaporated to *ca*. 10 cm^3. Light petroleum (50 cm^3) was then added to precipitate the brown *complex*. The complex was recrystallised from acetone and then tetrahydrofuran; yield, *ca*. 30%.

cis-*Dicarbonyl*-NN′-*ethylenebis(salicylideneiminato)-ruthenium*(II).—The complex $Ru(CO)_2Cl_2$ (0.5 g, 2.2 mmol) was added to a suspension of $Na_2(sal_2en)$ (0.68 g, 2.20 mmol) in tetrahydrofuran (50 cm^3) and the suspension refluxed for 1 h to give a red solution and a yellow-white solid [NaCl plus $\{Ru(sal_2en)(CO)\}_2$]. The red solution was passed through an alumina column and the product eluted with tetrahydrofuran. After evaporation to dryness the solid was redissolved in chloroform and cooled to −78 °C

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to give pale yellow, feather-like crystals which were then recrystallised from hot tetrahydrofuran; yield 35%.

Reaction of Ru(sal$_2$en)(PPh$_3$)$_2$ *with Strong Acids.*—(*a*) To Ru(sal$_2$en)(PPh$_3$)$_2$ (0.5 g, 0.6 mmol) in tetrahydrofuran (25 cm^3) was added HBF$_4$ (15 cm^3 of 40% aqueous solution). The yellow-red solution was reduced to 10 cm^3 and water (25 cm^3) was added. The red precipitate was collected, washed with water and ether, and then dried *in vacuo*. Recrystallisation from nitromethane gave orange crystals with a metallic lustre of the salt [Ru(sal$_2$enH)(PPh$_3$)][BF$_4$]; yield 90%.

(*b*) By using *p*-toluenesulphonic acid monohydrate a similar salt [Ru(sal$_2$enH)(PPh$_3$)][tos] was obtained; yield 90%.

Bicyclo[2.2.1]*hepta*-2,5-*diene*-NN′-*ethylenebis*(*salicylideneiminato*)*ruthenium*(II).—The complex {Ru(nbd)Cl$_2$}$_n$ (0.30 g, 1.14 mmol) was added to a suspension of Na$_2$(sal$_2$en) (0.35 g, 1.14 mmol) in tetrahydrofuran (30 cm^3) and the mixture was stirred for three days. The resulting mixture was transferred to an alumina column. Elution with thf gave a red solution which on evaporation gave the red complex which was recrystallised from thf–light petroleum; yield *ca.* 30%.

Reaction of Ru(sal$_2$en)(PPh$_3$)$_2$ *with Carbon Monoxide.*—Through a warm (70 °C) solution of Ru(sal$_2$en)(PPh$_3$)$_2$ (0.2 g, 0.22 mmol) in tetrahydrofuran (20 cm^3) was bubbled carbon monoxide to give an immediate precipitate of the complex {Ru(sal$_2$en)(CO)}$_2$; yield *ca.* 90%.

Reaction of Ru(pyr$_2$en)(PPh$_3$)$_2$ *with Carbon Monoxide.*—Carbon monoxide was bubbled through a solution of Ru(pyr$_2$en)(PPh$_3$)$_2$ (0.2 g, 0.24 mmol) in tetrahydrofuran (20 cm^3) at room temperature to give an immediate colour change of red to yellow.

Evaporation to low volume gave yellow crystals of the complex Ru(pyr$_2$en)(CO)(PPh$_3$) which were recrystallised from thf–light petroleum; yield *ca.* 80%.

Reaction of Ru(salnap)(PPh$_3$)$_2$ *with Carbon Monoxide.*—A solution of Ru(salnap)(PPh$_3$)$_2$ (0.2 g, 0.2 mmol) in tetrahydrofuran (20 cm^3) was refluxed under a carbon monoxide atmosphere for 3 h. On cooling a green solution and some yellow solid were obtained. Evaporation of the green solution to low volume precipitated more of the yellow solid. The combined yellow solid was recrystallised from hot thf (3 times) to give pale yellow crystals of Ru(salnap)(CO)(PPh$_3$)$_2$·2thf; yield *ca.* 60%.

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