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Schiff-base Complexes of Ruthenium(11) †

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The interaction of dichlorotris(triphenylphosphine)ruthenium(II) with the sodium salts of various Schiff bases leads to complexes of the type *trans*-RuL(PPh₃)₂ for the quadridentate bifunctional ligands and RuL₂(PPh₃)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 ³P n.m.r. spectra of the various complexes are given and structures for the compounds proposed.

ALTHOUGH there is extensive knowledge of transitionmetal 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 with NN'-ethylenebis(salicylideneimine)- $\operatorname{Ru}_{3}(\operatorname{CO})_{12}$ $(sal_{2}enH_{2})$ and N-phenyl(salicylideneimine)(salphenH) gives a complex of stoicheiometry [Ru(sal₂en)(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 $N-\alpha$ -benzylethylsalicylideneimine in ethyl benzoate³ 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 ₂ enH ₂
NN'-Ethylenebis(pyrrole-2-aldimine)	pyr,enH,
NN"-o-Phenylenebis(pyrrole-2-aldimine)	pyr,phenH ₂
N-2-Pyridyl(salicylideneimine)	salpyH
NN'-o-Phenylenebis(salicylideneimine)	sal_phenH_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, enH,
NN'-Trimethylenebis(salicylideneimine)	sal ₂ (1,3-tri)H ₂
NN'-Hexamethylenebis(salicylideneimine)	$\operatorname{sal}_2(1, 6-\operatorname{hex})$ -
	H_2
Bicyclo[2.2.1]hepta-2,5-diene	nbđ

RESULTS AND DISCUSSION

(1) Reaction of Dichlorotris(triphenylphosphine)ruthenium(11) with Schiff Bases.—(a) Quadridentate bifunctional

† 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. *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 $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$ 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, ³¹P n.m.r., and i.r. spectra are given in Tables 2 and 3.

The ³¹P n.m.r. spectra of the triphenylphosphine complexes have only a singlet in the region +25-38p.p.m. (for PPhMe₂ complex at +16.8 p.p.m.) relative to 85% H₃PO₄ external standard which is in the range for trans-phosphine complexes.⁶ Although isolation of $\operatorname{Ru}\{\operatorname{sal}_2(1,3-\operatorname{tri})\}(\operatorname{PPh}_3)_2$ and $\operatorname{Ru}\{\operatorname{sal}_2(1,6-\operatorname{hex})\}(\operatorname{PPh}_3)_2$ 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 ³¹P n.m.r. spectra of the two complexes have singlets at +29.81 and +31.58p.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 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									
	Found				Required				
Compound	Colour	С	H	N	P(Ru)	C	H	N	P(Ru)
$Ru(sal_2en)(PPh_3)_2$	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
$Ru(pyr_2en)(PPh_3)_2$	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), (PPh ₃), 2thf	Red	72.7	5.6	2.4	5.2	72.9	5.6	2.4	5.2
$\{\operatorname{Ru}(\operatorname{sal}_{2}\operatorname{en})(\operatorname{CO})\}_{2}^{c}$	Yellow	51.0	4.0	6.4		51.6	3.6	7.1	
cis-Ru(sal,en)(CO), 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, phen) (PPh_), 2thf	Black	71.9	5.5	2.4	5.5	70.8	5.5	2.6	5.7
[Ru(sal,enH)(PPh)][BF]	Red-orange	58.7	4.6	4.1	4.4	57.0	4.2	3.9	4.3
[Ru(sal,enH)(PPh,)][tos] f	Red-orange	61.7	5.2	3.5	4.3	61.5	5.1	3.5	3.9
Ru(pyr,en)(CO)(PPh_)	Yellow	61.6	4.8	9.3	5.0	61.7	4.5	9.3	5.1
Ru(salpy), (PPh,), thf	Red	70.3	5.5	4.6	5.8	70.4	5.1	5.1	5.7
Ru(salnap)(CO)(PPh ₃)·2thf "	Yellow	69.2	5.6	1.3	5.6	70.1	5.5	1.3	5.8
Ru(salnap)(PPh), v2thf	Green-black	69.8	5.6	1.3	5.9	71.1	5.8	1.3	5.9
Ru(sal,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 CH₃NO₂ at 10⁻³ M conc. $\Lambda_{\rm M} = 49 \ \Omega^{-1} \ {\rm cm^2 \ mol^{-1}}$. ^f Conductivity in CH₃NO₂ at 10⁻³ M concentration $\Lambda_{\rm M} = 41 \ \Omega^{-1} \ {\rm cm^2 \ mol^{-1}}$. ^g Molecular wt. osmometrically in chloroform 929 (calc. 928).

TABLE 2

N.m.r. spectra

Compound	τ _{CH=N}	$\tau_{\rm phenyl}$	$\tau_{ m N-CH_2}$	Other	31P b
$Ru(sal_{2}en)(PPh_{3})_{2}$ ^d	С	2.4 - 4.0(br,m)	6.2 - 6.2(br,m)		+29.92 °
Ru(sal en) (PPhMe), h	1.56(t)	2.1 - 3.8(br,m)	5.9 - 6.6(br,m)	$\tau_{\rm P-Me}$ 8.38(t), 8.78(t)	$+15.41^{f}$
$Ru(pyr_2en)(PPh_3)_2^{g}$	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)			$+37.76^{f}$
$\operatorname{Ru}(\operatorname{salbenz})_2(\operatorname{PPh}_3)_2^d$	с	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)	6.0 - 6.2(m)		
		3.4 - 3.6(m)			
$\operatorname{Ru}(\operatorname{acac}_2\operatorname{en})(\operatorname{PPh}_3)_2$ ^h		2.3 - 3.2 (br,s)		6.28(s), 4.12(s),	
				8.60(s), 8.97(s)	
$\operatorname{Ru}(\operatorname{sal}_2\operatorname{phen})(\operatorname{PPh}_3)_2^d$	С	2.3 - 3.2(br,s)			+ 29.04 ^f
$[\operatorname{Ru}(\operatorname{sal}_2\operatorname{enH})(\operatorname{PPh}_3)][\operatorname{BF}_4]^g$	2.26(s)	2.573.6(br,m)	6.6—6.8(br,m)		+64.22 i
$[\operatorname{Ru}(\operatorname{sal}_2\operatorname{en}H)(\operatorname{PPh}_3)][\operatorname{tos}]^g$	С	2.40-3.7(br,m)	6.56.8(br,m)	7.73(s)	+64.22 i
$\operatorname{Ru}(\operatorname{pyr}_2\operatorname{en})(\operatorname{CO})(\operatorname{PPh}_3)$ ^g	2.54(s)	2.753.38(br,m)	6.05(s)	3.78(d), 4.08(d)	+22.78 f
$\operatorname{Ru}(\operatorname{salpy})_2(\operatorname{PPh}_3)_2 d$	С	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
$\operatorname{Ru}(\operatorname{salnap})(\operatorname{PPh}_3)_2 d$	С	2.2 - 3.4(br,m)	j		$+23.05$ f
$\operatorname{Ru}(\operatorname{sal}_2\operatorname{en})(\operatorname{nbd})^h$	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% H₃PO₄ external standard. All resonances are singlets and resonances to high frequency (low field) are termed positive. ^c Resonance obscured by phenyl protons. ^d Solvent, CDCl₃. ^e Solvent, C₆D₆/C₆H₆. ^f Solvent, C₆D₆/c₆H₆. ^f Solvent, C₆D₆/c₆H₆. ^f Solvent, C₆D₆/c₆H₆.

	TABLE 3	
	I.r. spectra of ruthenium comple	$xes^{a,b}$
Compound	1 650—1 500 cm ⁻¹	Other bands
$Ru(sal_2en)(PPh_3)_2$	1 595s, 1 525m	
Ru(sal ₂ en)(PPhMe ₂) ₂	1 610w, 1 594s, 1 529m	
$Ru(pyr_2en)(PPh_3)_2$	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	
$Ru(pyr_2en)(CO)(PPh_3)$	1 587s, 1 580sh, 1 510m	v(CO) 1 940s
$Ru(salpy)_2(PPh_3)_2$	1 600s, 1 585s, 1 560m, 1 520m	
$Ru(acac_2en)(PPh_3)_2$	1 573m	
Ru(sal ₂ phen)(PPh ₃)	1 598s, 1 568s, 1 509m	
$\{\operatorname{Ru}(\operatorname{sal}_2\operatorname{en})(\operatorname{CO})\}_2$	1 645m, 1 627s, 1 595s, 1 550w,	v(CO) 1 910vs, 1 865vw
	1 528s	
cis-Ru(sal ₂ en)(CO) ₂	1 628s, 1 598s, 1 527s	$-\nu$ (CO) 2 038s, 1 975sh, 1 965s
$[Ru(sal_2enH)(PPh_3)][BF_4]$	1 595sh, 1 590s, 1 545m	
$[Ru(sal_2enH)(PPh_3)][tos]$	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	v(CO) 1 930vs, 1 887vw
	1 585m, 1 530m	
$Ru(salnap)(PPh_3)_2$	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.

111

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 (sal₂en)²⁻ as the Schiff base and if PPhMe₂ 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 transphosphorus atoms. The value $J_{P-H} = 5$ Hz; in similar cobalt(III) complexes, $[Co(sal_2en)(PPh_3)_2]^+,$ $J_{\rm P-H} = 3.0-3.5$ 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 $(J_{P-H+P-H'} = 16 \text{ Hz})$ at $\tau 8.38$ 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(sal₂en)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 low⁹ $[\Lambda(10^{-3}M) = 49 \text{ and } 41 \ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}].$ The ³¹P n.m.r. spectra of the salts show a single resonance at +64.22p.p.m. which is shifted ca. +35 p.p.m. from the value for $Ru(sal_{2}en)(PPh_{3})_{2}$ suggesting a different structure and probably a five-co-ordinate species. There is no i.r. band in the ca. 3500 cm^{-1} region that would be expected for an OH stretch so that hydrogen bonding $O \cdots H$ -O is likely and the protonated species is best formulated as (I). The ³¹P 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 Ru³⁺ has, apparently, occurred. There is also no co-ordination of the anion in CH₃NO₂ solution as both [Ru(sal₂enH)(PPh₃)][tos]

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.

J.C.S. Dalton

and [Ru(sal₂enH)(PPh₃)][BF₄] have the same ³¹P resonance frequency and the ¹⁹F n.m.r. of the latter shows only a single resonance in the position expected for unco-ordinated $[BF_4]$.

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 PPh₃ molecules from the initial Ru(sal₂en)(PPh₃)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 sal₂enH₂ complexes where the methylene resonances are broadened considerably on co-ordination. On bubbling carbon monoxide through a solution of trans-Ru(pyr_en)(PPh_3), the complex Ru(pyr_en)(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 PPh₃ by a CO.

The reaction of Na₂(sal₂en) or Na₂(sal₂phen) 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 ($\nu_{\rm CO}$ 1 900 cm⁻¹) but we have been unable to separate the latter. Using Na₂(pyr₂en) in methanol only the bisphosphine compound is formed.

(b) Bidentate monofunctional ligands. The reaction of Na(salbenz) and RuCl₂(PPh₃)₂ in tetrahydrofuran produces red crystals of Ru(salbenz)₂(PPh₃)₂ which has equivalent trans-PPh₃ groups since the ³¹P resonance is a singlet in the same region as in trans-Ru(sal₂en)(PPh₃)₂.

The reaction of Na(salpy), which is potentially tridentate, gives trans-Ru(salpy)₂(PPh₃)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 $N-\beta-hydroxy-\alpha-naphthylmethyl-$ (salicylideneimine), (salnapH₂, potentially tridentate), with RuCl₂(PPh₃)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

PPh₃ a red solution is formed which on cooling gave a green-black solid, Ru(salnap)(PPh₃)₂·2thf, the ³¹P spectrum of which has a single resonance at +23.05 p.p.m. (*trans*-PPh₃ 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)(PPh₃)₂ (II) can be isolated. The ³¹P 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(sal₂en)-(PPh₃)₂, the complex evidently has mutually trans PPh₃ groups with the ligand planar. In solution the complex Ru(salnap)(PPh₃)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)(PPh₃)₂ with the carbonyl *trans* to the nitrogen atom as in (II).



Most of the above PPh₃-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 $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ which has been studied before.¹⁰ The complexes do not act as hydrogenation catalysts for hex-1-ene at pressures of H₂ up to 100 atm at 100 °C.

(2) Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) with NN'-Ethylenebis(pentane-2,4-dione mono*imine*) (acac₂enH₂).—The ligand acac₂enH₂ and sodium hydride in thf on treatment with $RuCl_2(PPh_3)_3$ give an orange-red solution from which the orange crystalline Ru(acac₂en)(PPh₃)₂ can be isolated. The ³¹P n.m.r. shows again only a singlet at 33.24 p.p.m. The ¹H n.m.r. is solvent-dependent. In CD₂Cl₂ 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 C₆D₆ 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 (CD₃)₂CO ca. 30% of form (IIIb) is present. The shift of H¹ for (IIIa) is ca. τ 5, varying $\tau \pm 0.2$ with solvent, while in (IIIb) H¹ is at τ 7.2. In

the complex $\operatorname{Ru}(\operatorname{acac_2en})(\operatorname{PPh_3})_2$, as in other complexes with $\operatorname{acac_2en}$ as ligand,¹¹ the (IIIa) form is retained as in (IV). The H¹ proton resonance is shifted considerably



because of shielding due to the phenyl ring currents of the PPh₃ in the *trans*-positions. In the presence of an excess of P(OMe)₃ the benzene solution becomes yellow-green and the H¹ 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*-PPh₃ ligands by P(OMe)₃ which then reduces the shielding of the H¹ protons.

In the ¹H spectrum of Ru(acac₂en)(PPh₃)₂ the phenyl protons show a broad single peak at τ 2.3—3.2 in CD₂Cl₂ and two broad peaks at τ 2.4 and 2.92 in C₆D₆. 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

(3) Reaction of Dicarbonyldichlororuthenium, {Ru-(CO)₂Cl₂)_n, with Schiff Bases.—On heating a suspension of {Ru(CO)₂Cl₂}_n or {Ru(CO)₃Cl₂}₂ and Na₂(sal₂en) in thf under reflux a red solution and a yellow solid containing {Ru(sal₂en)(CO)}₂² are formed. Chromatography of the red solution gave as the major product pale yellow crystals of *cis*-Ru(sal₂en)(CO)₂. This probably has a structure with a non-planar Schiff base (V) similar to that proposed for Co(sal₂en)(acac)^{13,14} and R₂Sn-(sal₂en).¹⁵

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¹⁴ M. Callizario, G. Mangini, G. Nardin, and L. Randaccio, J.C.S. Dalton, 1972, 543.

¹⁵ A. van der Bergen, R. J. Cozens, and K. S. Murray, *J. Chem. Soc.* (A), 1970, 3060.

J.C.S. Dalton

(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(sal₂en)(nbd) (VI) with H² τ 5.48





(doublet, $J_{\text{H}^2-\text{H}^3} = 4$ Hz), H⁶ 5.63 (broad singlet), H³ 6.09 (doublet, $J_{\text{H}^2-\text{H}^3} = 4$ Hz), H^{1.4} 6.35 (broad singlet), H⁵ 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(sal₂en)(CO)₂. The complex, dissolved in tetrahydrofuran, reacts with carbon monoxide to yield {Ru(sal₂en)(CO)₂ in quantitative yield.

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)Cl₃}₂ has given the complex {Rh(cod)}₂-(sal₂en).¹⁶ Attempted preparations of Schiff base complexes from RuCl₂(MeCN)₄, RuCl₂(dmso)₄, and 'RuCl₃·3H₂O' were unsuccessful.

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¹⁹ E. W. Abel and G. Wilkinson, J. Chem. Soc., 1959, 3178.

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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. ³¹P and ¹⁹F 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 conductivitybridge 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 $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$,¹⁸ { $\operatorname{Ru}(\operatorname{nbd})\operatorname{Cl}_2$ },¹⁹ RuCl_2 -(PPhMe₂)₄,²⁰ $\operatorname{RuCl}_2(\operatorname{MeCN})_4$,²¹ $\operatorname{RuCl}_2(\operatorname{dmso})_4$,²² and { Ru -(CO)₂Cl₂},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(triphenyl-

phosphine)ruthenium(II).—(a) The complex $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$ (1.0 g, 1.04 mmol) was added to a suspension of $\operatorname{Na}_2(\operatorname{sal}_2\operatorname{en})$ (0.32 g, 1.04 mmol) in tetrahydrofuran (50 cm³) 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)- $(PPh_a)_2$ when a four-fold excess of PPh_a was added initially.

trans-NN'-Ethylenebis(pentane-2,4-dione monoiminato)bis(triphenylphosphine)ruthenium(II).—The complex RuCl₂-(PPh₃)₃ (1.0 g, 1.04 mmol) was added to a suspension of Na₂(acac₂en) (0.27 g, 1.04 mmol) in tetrahydrofuran (50 cm³) and the solution refluxed for several hours. The resulting red solution was filtered and evaporated to ca. 10 cm³. Light petroleum (50 cm³) 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 $\operatorname{Ru}(\operatorname{CO})_2\operatorname{Cl}_2$ (0.5 g, 2.2 mmol) was added to a suspension of $\operatorname{Na}_2(\operatorname{sal}_2\operatorname{en})$ (0.68 g, 2.20 mmol) in tetrahydrofuran (50 cm³) and the suspension refluxed for 1 h to give a red solution and a yellow-white solid [NaCl plus { $\operatorname{Ru}(\operatorname{sal}_2\operatorname{en})(\operatorname{CO})$ }]. 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

²¹ D. Rose, J. G. Gilbert, and G. Wilkinson, J. Chem. Soc. (A), 1970, 2765.

²² I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.

²³ M. J. Cleare and W. P. Griffith, J. Chem. Soc. (A), 1969, 372.

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

Reaction of $\operatorname{Ru}(\operatorname{sal}_2\operatorname{en})(\operatorname{PPh}_3)_2$ with Strong Acids.—(a) To $\operatorname{Ru}(\operatorname{sal}_2\operatorname{en})(\operatorname{PPh}_3)_2$ (0.5 g, 0.6 mmol) in tetrahydrofuran (25 cm³) was added HBF₄ (15 cm³ of 40% aqueous solution). The yellow-red solution was reduced to 10 cm³ and water (25 cm³) 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_2enH)(PPh_3)][BF_4]; yield 90%.

(b) By using p-toluenesulphonic acid monohydrate a similar salt $[Ru(sal_2enH)(PPh_3)][tos]$ was obtained; yield 90%.

Bicyclo[2.2.1]hepta-2,5-diene-NN'-ethylenebis(salicylidene $iminato)ruthenium(II).—The complex {Ru(nbd)Cl₂}_n (0.30 g,$ 1.14 mmol) was added to a suspension of Na₂(sal₂en) (0.35 g,1.14 mmol) in tetrahydrofuran (30 cm³) and the mixturewas stirred for three days. The resulting mixture wastransferred to an alumina column. Elution with thf gavea red solution which on evaporation gave the red complexwhich was recrystallised from thf-light petroleum; yieldca. 30%.

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

Reaction of $\operatorname{Ru}(\operatorname{pyr_2en})(\operatorname{PPh_3})_2$ with Carbon Monoxide.— Carbon monoxide was bubbled through a solution of $\operatorname{Ru}(\operatorname{pyr_2en})(\operatorname{PPh_3})_2$ (0.2 g, 0.24 mmol) in tetrahydrofuran (20 cm³) at room temperature to give an immediate colour change of red to yellow.

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

Reaction of Ru(salnap)(PPh₃)₂ with Carbon Monoxide.—A solution of Ru(salnap)(PPh₃)₂ (0.2 g, 0.2 mmol) in tetrahydrofuran (20 cm³) 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)-(PPh₃)₂·2thf; yield ca. 60%.

We thank the S.R.C. for a studentship (J. R. T.), Johnson Matthey Limited for the loan of ruthenium, and Albright and Wilson Limited for gifts of triphenylphosphine.

[7/607 Received, 6th April, 1977]