Schiff Base Complexes of Rhenium(IV) and Rhenium(V) [†]

By **A. Robert Middleton, Anthony F. Masters,** and **Geoffrey Wilkinson,*** Chemistry Department, Imperial College of Science and Technology, London SW7 2AY

The interaction of various Schiff bases, LH_2, with trichloro-oxobis(triphenylphosphine)rhenium(V), tetrachlorobis(triphenylphosphine)ruthenium(IV), and other rhenium complexes has given rise to complexes of the following types: (a) $Re^{V}_{2}O_3L_2$ that have a linear O=Re–O–Re=O system with quadridentate ligands on each rhenium; (b) $Re^{V}OClL$ that appear to be octahedral with *trans* O=Re–Cl groups; (c) $Re^{IV}Cl_2L$ that are octahedral with *trans* chlorines; (d) complexes that have neutral Schiff bases, LH_2 bound to the metal.

We have recently described Schiff base complexes of ruthenium.[1] Another element for which such complexes were not known is rhenium and we now describe complexes in the IV and V oxidation states. The abbreviations used have been listed.[1] Analytical and spectroscopic data for the new compounds are collected in the Table.

TABLE

Analytical and spectroscopic data for Schiff base complexes of rhenium

		Analysis (%)						I.r. and Raman data			
Compound *	Colour	C	H	N	Cl	M [a]		C=N	Re=O	M–Cl	Other
$Re_2O_3(sal_2en)_2$	Green	40.4	2.9	6.0	0	949	IR	1 633, 1 595	965		690 [b]
		(40.2)	(2.9)	(5.9)	(0)	(949)	R	1 646, 1 599	931		197 [c]
$Re_2O_3(sal_2prop)_2$	Green	40.3	3.2	5.7	0	977	IR	1 628, 1 596	970		700 [b]
		(41.5)	(3.2)	(5.7)	(0)	(977)	R	1 632, 1 606	936		186 [c]
$Re_2O_3(sal_2phen)_2$	Brown	45.6	2.8	5.4	0	1 045	IR	1 609, 1 597	962		700 [b]
		(45.7)	(2.7)	(5.3)	(0)	(1 045)	R	1 608, 1 580	930		198 [c]
$Re_2O_3(acac_2en)_2$	Green	33.4	4.1	6.3	0	860	IR	1 575	975		720 [b]
		(33.3)	(4.2)	(6.5)	(0)	(860)	R	1 580	927		
$ReOCl(sal_2en)$	Green	37.8	3.0	5.6	7.2		IR	1 598	955	300	
		(38.0)	(2.8)	(5.6)	(7.0)	(504)	R	1 598	958	324	
$ReOCl(sal_2prop)$	Green	38.6	3.2	4.5	7.5	517	IR	1 598	960	300	
		(39.3)	(3.1)	(5.4)	(6.8)	(517)	R	1 600	960	320	
$ReOCl(sal_2phen)$	Brown	43.0	3.2	5.1	7.1	550	IR	1 596	948	290	
		(43.4)	(2.5)	(5.1)	(6.4)	(550)	R	1 590	950	318	
$ReOCl(acac_2en)$	Brown	31.0	4.3	5.7	6.7		IR	1 545	973	302	
		(31.3)	(3.9)	(6.1)	(7.7)	(459)					
$ReOCl_3(acac_2enH_2)$	Mustard	26.2	3.9	5.4	27.0		IR	1 618	960	300s	3 250s,br [d]
		(27.1)	(3.8)	(5.3)	(26.7)						
$Re_2O_2Cl_4(PPh_3)_2(sal_2en)$	Lime-green	46.8	3.4	2.2	10.3	3.5 [e]	IR	1 600	962, 955	318s, 280	3 632sh [d]
		(46.7)	(3.2)	(2.1)	(10.6)	(4.6)					
$Re_2O_2Cl_6(PPh_3)_2(acac_2enH_2)$	Lime-green	42.3	3.9	2.0	14.2	4.6 [e]	IR	1 610	945	304s, 289	3 220sh
		(41.5)	(3.5)	(2.0)	(15.6)	(4.6)					
$ReCl_2(sal_2en)$	Red-brown	36.2	3.2	4.7	13.1	521	IR	1 585		308s	
		(36.6)	(2.7)	(5.3)	(13.5)	(521)					
$ReCl_2(sal_2prop)$	Red-brown	37.8	3.4	4.9	13.0	535	IR	1 598		307s	
		(37.9)	(3.0)	(5.2)	(13.2)	(535)					
$ReCl_2(sal_2phen)$	Brown	41.5	2.6	4.6	12.7	569	IR	1 590		305s	
		(41.9)	(2.5)	(4.9)	(12.4)	(569)					
$ReCl_2(acac_2en)$	Red-brown	30.2	3.8	5.8	14.6	477	IR	1 562		302s	
		(30.0)	(3.8)	(5.8)	(14.8)	(477)					
$ReCl_4(sal_2enH_2)$	Orange	31.9	2.9	4.5	25.0		IR	1 655		302s	3 100s,br
		(32.2)	(2.7)	(4.7)	(23.8)						
$ReCl_4(sal_2propH_2)$	Orange-brown	34.8	3.0	4.4	21.3		IR	1 655		308s	3 100s,br [d]
		(33.4)	(3.0)	(4.6)	(23.3)						

* Sal_2enH_2 = *NN′*-ethylenebis(salicylideneimine), sal_2propH_2 = *NN′*-trimethylenebis(salicylideneimine), sal_2phenH_2 = *NN′*-*o*-phenylenebis(salicylideneimine), and $acac_2enH_2$ = *NN′*-ethylenebis(acetylacetimine).

[a] Molecular ion based on ^{185}Re and ^{35}Cl. [b] ν_{as}(Re–O–Re). [c] ν_s(Re–O–Re). [d] ν(O–H). [e] P analysis. [f] ν(N–H).

μ-Oxo-bis[oxo (Schiff base)rhenium(V)] Complexes.—The interaction of trichloro-oxobis(triphenylphosphine)rhenium(V), $ReOCl_3(PPh_3)_2$, with the Schiff bases, LH_2 (sal_2enH_2, sal_2propH_2, sal_2phenH_2, and $acac_2enH_2$ [‡]) in the presence of two equivalents of triethylamine in air and without special drying of materials so that some water is always present, leads to the formation of complexes of stoicheiometry $Re_2O_3L_2$.

This formulation is established by analysis, osmometric and mass spectrometric molecular-weight determinations, and by spectroscopic measurements. The compounds are sparingly soluble in organic solvents (the $acac_2en$ derivative is most soluble), air stable, and thermally robust with melting points above 300 °C although decomposition may occur above 250 °C.

Spectroscopic evidence noted below indicates that there is a linear O=Re–O–Re=O grouping as in several other complexes containing the Re_2O_3 unit, *e.g.* the octaethylporphyrin [2] and dithiocarbamate [3] complexes.

[†] No reprints available.

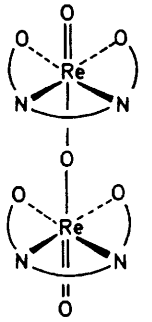
[‡] Definitions given in Table footnote.

A molybdenum(v) complex of similar stoicheiometry $Mo_2O_3(sal_2en)_2$, is also known.[4] The formation of $Re_2O_3L_2$ from $ReOCl_3(PPh_3)_2$ doubtless involves water and the formation of intermediate hydroxo-species, as in the reaction of $ReOCl_3(PPh_3)_2$ with moist pyridine to give $Re_2O_3Cl_4(py)_4$ and $[ReO_2(py)_4]Cl$,[5] but in the present case no intermediates could be isolated. However $Re_2O_3(sal_2en)_2$ could be obtained also from $Re_2O_3(py)_4Cl_4$ and from $ReCl_3(MeCN)(PPh_3)_2$, and $ReCl_4(PPh_3)_2$ where oxidation by air and/or water doubtless occurs.

The vibrational spectra of the complexes $Re_2O_3L_2$ show typical Schiff base ligand bands together with strong Re=O and Re–O–Re absorptions as found in other Re_2O_3 species.[3,6] The band at *ca.* 690 cm^{-1} in the i.r. region can be assigned to ν_{as}(Re–O–Re) while the band at *ca.* 200 cm^{-1} in the Raman spectra corresponds with those reported for ν_s(Re–O–Re) of other linear μ-oxo-rhenium complexes. The strong Raman active band at *ca.* 930 cm^{-1} can be assigned as ν(Re=O). The compounds are too insoluble for n.m.r. study except for $Re_2O_3(acac_2en)_2$ which in deuteriochloroform has peaks at δ 2.11 (3 H, s), 2.15 (3 H, s), 3.70 (2 H, m), and 4.91 (1 H, s) indicative of the quadridentate ligand.

In the mass spectra, the parent molecular ions were observed as well as more intense peaks due to $Re_2O_2L^+$, $ReOL^+$, and ReL^+; in $Mo_2O_3(sal_2en)_2$ the molecular ion was not observed.[4]

The data are thus consistent with the structure (1), though the relative orientation of the two planar Schiff base ligands cannot be specified.



(1)

Chloro-oxo(Schiff base)rhenium(v) *Complexes*.—These compounds are readily obtained when $ReOCl_3(PPh_3)_2$, the Schiff base LH_2, and two equivalents of triethylamine are refluxed in dry toluene under nitrogen. If air and moisture are not excluded the $Re_2O_3L_2$ compounds are obtained.

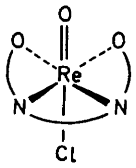
The stoicheiometries ReOClL are confirmed by analyses, molecular weight, and mass spectral data.

The compounds show slight decomposition above 250 °C and melt above 300 °C. They are stable in air in the solid state and are but sparingly soluble in common organic solvents with the exception of $ReOCl(acac_2en)$ which is soluble in toluene, dichloromethane, and tetrahydrofuran. The analogous molybdenum compounds[7] also have limited solubility.

The vibrational spectra are similar to those of the $Re_2O_3L_2$ compounds except that only Re=O (*ca.* 955 cm^{-1}) bands are present. These bands are strong in the i.r. region and of medium intensity in the Raman, whereas in the $Re_2O_3L_2$ compounds the Re=O was weak in the i.r. region and very strong in the Raman. Although the Re–Cl absorptions are difficult to locate due to ligand absorptions in the same region a band at *ca.* 300 cm^{-1} would seem to be ν(Re–Cl).

The n.m.r. spectrum of $ReOCl(acac_2en)$ was similar to that of $Re_2O_3(acac_2en)$ with bands at δ 2.18 (3 H, s), 2.22 (3 H, s), 3.75 (2 H, m), and 4.94 (1 H, s). The mass spectra of the sal_2prop and sal_2phen compounds alone showed the molecular ions; all had fragments due to $ReOL^+$ and either $ReLCl^+$ or ReL^+.

The compounds are diamagnetic and $ReOCl(acac_2en)$ is monomeric in solution. Although isomers are conceivable, the ligands are probably planar and the chlorine is *trans* to oxygen as in (2); this can then account for the hydrolytic reaction giving $Re_2O_3L_2$. The structure (2) with a planar ligand is also consistent with the n.m.r. spectrum of the acac$_2$en complex, where only two singlets are observed for the four methyl groups, and only a singlet for the two methine hydrogens which indicates that the end methyls and central methyls are equivalent as are the two C–H groups. Further, unlike the molybdenum analogues[7] all four compounds have but one Re=O and one Re–Cl stretching frequency.



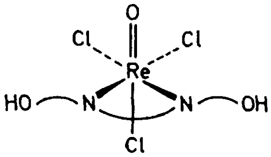
(2)

For the aromatic Schiff bases the complexes ReOClL are also formed in the absence of triethylamine if tetrahydrofuran is used as solvent. Prolonged reaction of the Schiff bases with $ReOCl_3(PPh_3)_2$ in toluene led to reduction and the formation of rhenium(IV) complexes, discussed below, probably *via* the loss of the terminal oxide ligand, to form a rhenium(III) species, which is then oxidised to rhenium(IV).[8]

It may be noted that interaction of $ReCl_3(PPh_3)_2(MeCN)$ with the Schiff bases in the presence of triethylamine gives $ReCl_2L$. $ReCl_3(PMe_2Ph)_3$, however, did not appear to react.

Other Schiff Base Complexes Derived from $ReOCl_3(PPh_3)_2$.—The ligand $acac_2enH_2$ in refluxing tetrahydrofuran gave a mustard-yellow complex of stoicheiometry $ReOCl_3LH_2$. This decomposed at 198 °C and was only sparingly soluble in most organic solvents except dichloromethane and chloroform in which it is air sensitive. The i.r. spectrum contains a peak at 960 cm^{-1} (Re=O), and a strong, broad unresolved peak at 300 cm^{-1} which can be assigned to Re–Cl vibrations. The Schiff base C=N band at 1 600 cm^{-1} has been shifted up to 1 618 cm^{-1} and a strong broad band is present at 3 250 cm^{-1}. These bands suggest the binding of a neutral Schiff base *via* nitrogen atoms only, as in some other known compounds.[9-11] This mode of bonding is supported by the n.m.r. spectrum in deuteriochloroform which is consistent with the $acac_2enH_2$ ligand in the enolised form [δ 2.38 (3 H, s), 2.44 (3 H, s), 4.05 (2 H, m), 5.47 (1 H, s), and 10.95br (1 H)].

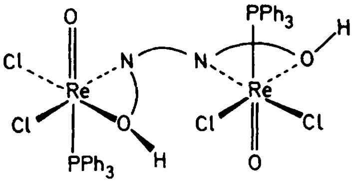
The complex showed weak paramagnetism; its mass spectrum failed to show the molecular ion but only decomposition species $ReCl_2L^+$ and ReL^+.



(3)

The complex could have a structure of the type (3). The Schiff bases (except sal_2phenH_2) when stirred with $ReOCl_3(PPh_3)_2$ in tetrahydrofuran gave lime-green phosphine-containing complexes; satisfactory analyses were obtained only for the sal_2enH_2 and $acac_2enH_2$ complexes. The reaction with sal_2enH_2 gave a complex of stoicheiometry $Re_2O_2Cl_4(PPh_3)_2(sal_2en)$. This complex was virtually insoluble in organic solvents, but sparingly soluble in dichloromethane. It was thermally and air stable. The mass spectrum gave no molecular ion but only fragments corresponding to $ReCl_2L^+$, $ReOL^+$, and ReL^+.

The i.r. spectrum had bands at 318 and 280 cm^{-1} due to Re–Cl modes and a doublet at 960 cm^{-1} (Re=O). The splitting of this band may be due to the two oxygens being inequivalent. The C=N band moved from 1 635 cm^{-1} in the free ligand to 1 600 cm^{-1} similar to the complexes of the charged ligand above. These data are best explained by a bridging ligand co-ordinated to two $ReOCl_2(PPh_3)$ units where the Schiff base is bidentate in each case co-ordinated *via* both oxygen and nitrogen atoms, as in (4).

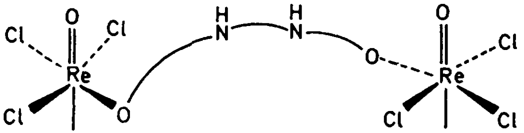


(4)

The room temperature reaction with $acac_2enH_2$ also gives a lime-green product but this has a different stoicheiometry $Re_2O_2Cl_6(PPh_3)_2(acac_2enH_2)$, according to analysis. The solid complex appeared to be air stable and decomposed at 142 °C.

The complex was feebly paramagnetic, consistent with rhenium(V), and the mass spectra gave only fragmentation products $ReCl_2L^+$, $ReOL^+$, and ReL^+. The i.r. spectrum had a band at 945 cm^{-1} (Re=O) and two peaks in the far-i.r. region at 304 and 289 cm^{-1} (Re–Cl) together with bands due to PPh_3. The bands attributable to the Schiff base included one at 3 220 cm^{-1} which was sharp and of medium intensity; the C=N band moved to higher frequency, 1 610 cm^{-1}, indicative of a neutral Schiff base but, unlike the above complexes, the acidic hydrogen does not appear to be H-bonded. Further, the band at 3 220 cm^{-1} seems more consistent with an N–H mode rather than O–H which would be expected at higher frequency. This keto-imine form has been well established [12,13] especially in bridging systems. The most likely structure for the complex has two $ReOCl_3(PPh_3)$ units linked by a bridging Schiff base co-ordinated through the oxygen atoms of the type (5).

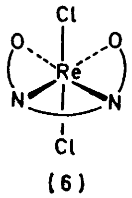
Dichloro(*Schiff base*)*rhenium*(IV) *Complexes.*—These complexes of stoicheiometry $ReCl_2L$ are readily obtained by refluxing $ReCl_4(PPh_3)_2$ with one equivalent of the appropriate base LH_2 and two equivalents of triethylamine in dry toluene under nitrogen. Air and moisture must be excluded or the compounds $Re_2O_3L_2$ are formed, whilst absence of triethylamine leads to mixtures of complexes including $ReCl_4LH_2$ reported below.



(5)

These complexes have limited solubility with the $acac_2en$ derivative being the most soluble particularly in toluene, tetrahydrofuran, and dichloromethane. They are air stable in the solid state and begin to decompose above 250 °C. The i.r. spectra are dominated by Schiff base bands but contain no O–H or N–H modes and the C=N band at *ca.* 1 590 cm^{-1} is indicative of a quadridentate ligand. The spectra also show a strong band at *ca.* 305 cm^{-1} (ν_{as} Re–Cl) but no bands assignable to Re=O.

The Raman spectra obtained were poor due to the nature and colour of these compounds. The n.m.r. spectra of the $acac_2en$ derivative had broad ill-defined peaks as expected from its paramagnetic properties (μ_{eff} *ca.* 2). The mass spectra showed molecular ions for all four complexes as well as fragments due to ReL^+. The more-soluble $acac_2en$ derivative gave an osmometric molecular weight of 464 (479) in dichloromethane indicating a monomeric structure. The presence of only one strong band in the Re–Cl region of the i.r. and the similarity of spectra with the sal_2phen derivative suggests that the chlorines are probably *trans* as in (6).



(6)

Tetrachloro(*neutral Schiff base*)*rhenium*(IV) *Complexes.*—In the absence of triethylamine, the reaction of sal_2enH_2 and sal_2propH_2 with $ReCl_4(PPh_3)_2$ in dry refluxing tetrahydrofuran under nitrogen yields the microcrystalline complexes $ReCl_4LH_2$.

The solids are quite stable under nitrogen though in solution, especially in the presence of base, conversion into $ReCl_2L$ occurs. In fact the $ReCl_2L$ complexes can also be isolated in small yield from the same reaction mixture, whilst refluxing in toluene gives $ReCl_2L$ as the major product.

The $ReCl_4LH_2$ complexes are insoluble in most organic solvents but sparingly soluble in dichloromethane and tetrahydrofuran, and soluble in dimethyl sulphoxide. They are thermally quite stable, decomposing at *ca.* 200 °C.

The i.r. spectra show a strong incompletely resolved band just above 300 cm^{-1} (Re–Cl). The C=N vibration is shifted to higher frequency by *ca.* 20 cm^{-1} to *ca.* 1 655 cm^{-1}. This together with the presence of a strong broad band ν(OH) at *ca.* 3 100 cm^{-1} is indicative of a neutral Schiff base bound *via* its nitrogen atoms only.[9-11] The mass spectra show peaks corresponding to $ReCl_2L^+$ and ReL^+ but no molecular ions. Similar behaviour is observed for the rhenium(V) neutral Schiff base complex. The compounds are paramagnetic (μ_{eff} *ca.* 2) which is typical of most rhenium(IV) complexes.

EXPERIMENTAL

Analyses were by the Imperial College and Butterworth microanalytical laboratories.

Physical Measurements.—The following spectrometers were used: infrared, Perkin-Elmer 457 calibrated with polystyrene peaks to ± 5 cm^{-1}; Raman, Spex Ramalog V with laser excitation at 647.1 or 568.2 nm on rotating samples; nuclear magnetic resonance, Perkin-Elmer R12A (60 MHz); mass, Vacuum Generators Limited Model 7070. Molecular weights were determined osmometrically using a Perkin-Elmer–Hitachi osmometer in benzene or CH_2Cl_2. Magnetic susceptibilities were measured on solid samples at room temperature on an Evans' balance.

Materials.—$ReOCl_3(PPh_3)_2$, $Re_2O_3(py)_4Cl_4$, $[ReO_2(py)_4]Cl\cdot 2H_2O$, $ReCl_4(PPh_3)_2$, and $ReCl_3(PPh_3)_2(MeCN)$ were made by standard methods,[8] and the Schiff bases prepared by condensation of two equivalents of the appropriate carbonyl compound with one equivalent of the amine in methanol, followed by recrystallisation from hot ethanol.

(1) *μ-Oxo-bis*{[NN'*-ethylenebis*(*salicylideneiminato*)]*oxorhenium*(V)}, $Re_2O_3(sal_2en)_2$.—The following syntheses were carried out in air and without specially dried solvents.

(a) Powdered $ReOCl_3(PPh_3)_2$ (1.02 g, 1.22 mmol) was added to a stirred acetonitrile solution (50 ml) of sal_2enH_2 (0.33 g, 1.23 mmol), and triethylamine (0.34 ml, 2.45 mmol). The suspension was stirred at *ca.* 45 °C, and two further amounts of triethylamine (0.2 ml aliquots) were added at 2 h intervals. The solution was then stirred at room temperature for 12 h.

The green crystals of the product were collected, washed with methanol, hot toluene, and ether and dried *in vacuo*; yield 51% based on $ReOCl_3(PPh_3)_2$.

(b) $Re_2O_3(py)_4Cl_4$ (0.5 g, 0.6 mmol), sal_2enH_2 (0.31 g, 1.2 mmol), and triethylamine (0.32 ml, 2.3 mmol) in acetonitrile as in method (a) yielded the green product; yield 26% based on $Re_2O_3(py)_4Cl_4$.

(c) A solution of sal_2enH_2 (0.11 g, 0.4 mmol) and triethylamine (0.11 ml, 0.8 mmol) in methanol (75 ml) was added to a solution of $[ReO_2(py)_4]Cl\cdot 2H_2O$ (0.25 g, 0.4 mmol) in methanol (25 ml) and the stirred solution refluxed for 45 min. The solution was cooled, and the green microcrystals were collected, washed with methanol and ether, and dried *in vacuo*; yield 51% based on $[ReO_2(py)_4]Cl\cdot 2H_2O$.

(d) One equivalent of each of the complexes $ReOCl_3(PPh_3)_2$, $ReCl_3(PPh_3)_2(MeCN)$, or $ReCl_4(PPh_3)_2$ was added separately to a solution of sal_2enH_2 (1 mol equiv.) and triethylamine (2 mol equiv.) in toluene and the suspension stirred and refluxed in air for 3 h. The resulting mixture was cooled and the resulting green complex washed with water, methanol, and ether and dried *in vacuo*; yield 50—60%.

(2) *μ-Oxo-bis*{*oxo*[NN'*-trimethylenebis*(*salicylideneiminato*)]*rhenium*(V)}, $Re_2O_3(sal_2prop)_2$.—$ReOCl_3(PPh_3)_2$ (1 g, 1.2 mmol), sal_2propH_2 (0.34 g, 1.2 mmol), and triethylamine (0.33 ml, 2.4 mmol) were refluxed in acetonitrile (100 ml) for 36 h after which the reaction mixture was treated as in method (1d) to give green crystals; yield 24% based on $ReOCl_3(PPh_3)_2$.

(3) *μ-Oxo-bis*{*oxo*[NN'-o-*phenylenebis*(*salicylideneiminato*)]*rhenium*(V), $Re_2O_3(sal_2phen)_2$.—$ReOCl_3(PPh_3)_2$ (1 g, 1.2 mmol), sal_2phenH_2 (0.38 g, 1.2 mmol), and triethylamine (0.33 ml, 2.4 mmol) were refluxed in toluene for 2 h. The solution was cooled and the brown complex washed with toluene, water, methanol, and ether; yield of product, 79% based on $ReOCl_3(PPh_3)_2$.

(4) *μ-Oxo-bis*{[NN'*-ethylenebis*(*acetylacetiminato*)]*oxorhenium*(V)}, $Re_2O_3(acac_2en)_2$.—$ReOCl_3(PPh_3)_2$ (1 g, 1.2 mmol), $acac_2enH_2$ (0.27 g, 1.2 mmol), and triethylamine (0.33 ml, 2.4 mmol) were refluxed in toluene (50 ml) for 3 h. The resulting solution was filtered and evaporated to small volume (10 ml). Light petroleum (b.p. 40—60 °C, 50 ml) was added to it and the precipitated product was collected, washed with water, methanol, and diethyl ether and dried *in vacuo*. Upon recrystallisation from dichloromethane–light petroleum (b.p. 80—100 °C) it gave green crystals; yield 40% based on $ReOCl_3(PPh_3)_2$.

(5) *Chloro*[NN'*-ethylenebis*(*salicylideneiminato*)](*oxo*)*rhenium*(V), $ReOCl(sal_2en)$.—A stirred suspension of $ReOCl_3(PPh_3)_2$ (1.5 g, 1.8 mmol), sal_2enH_2 (0.48 g, 1.8 mmol), and triethylamine (0.5 ml, 3.6 mmol) was refluxed in dry, degassed toluene (100 ml) for 1 h under nitrogen. The suspension was filtered hot, and the residual green powder washed with toluene, methanol, and ether and dried *in vacuo*; yield 68% based on $ReOCl_3(PPh_3)_2$.

(6) *Chloro*(*oxo*)[*trimethylenebis*(*salicylideneiminato*)]*rhenium*(V), $ReOCl(sal_2prop)$.—$ReOCl_3(PPh_3)_2$ (1.5 g, 1.8 mmol), sal_2propH_2 (0.51 g, 1.8 mmol), and triethylamine (0.5 ml, 3.6 mmol) were allowed to react under the conditions described in (5) to give a green powder; yield 77% based on $ReOCl_3(PPh_3)_2$.

(7) *Chloro*(*oxo*){NN'-[o-*phenylenebis*(*salicylideneiminato*)]}*rhenium*(V), $ReOCl(sal_2phen)$.—$ReOCl_3(PPh_2)_2$ (1 g, 1.2 mmol), sal_2phenH_2 (0.38 g, 1.2 mmol), and triethylamine (0.33 ml, 2.4 mmol) were allowed to react under the conditions described in (5) to give a brown powder; yield 91% based on $ReOCl_3(PPh_3)_2$.

(8) *Chloro*[NN'*-ethylenebis*(*acetylacetiminato*)](*oxo*)*rhenium*(V), $ReOCl(acac_2en)$.—$ReOCl_3(PPh_3)_2$ (1 g, 1.2 mmol), $H_2(acac_2en)$ (0.27 g, 1.2 mmol), and triethylamine (0.33 ml, 2.4 mmol) were refluxed in dry degassed toluene (100 ml). The resultant solution was filtered and evaporated to small volume (10 ml). Light petroleum was added

to precipitate the brown product which was collected, washed with water, methanol, and ether, and recrystallised from dichloromethane–light petroleum (b.p. 80—100 °C) to give brown crystals; yield 55% based on $ReOCl_3(PPh_3)_2$.

(9) *Trichloro*[NN′-*ethylenebis*(*acetylacetimine*)](*oxo*)*rhenium*(V), $ReOCl_3(acac_2enH_2)$.—$ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) and $acac_2enH_2$ (0.3 g, 1.3 mmol) were refluxed in dry degassed tetrahydrofuran (thf) for 16 h in an inert atmosphere of N_2. The suspension was cooled and the mustard-yellow product collected and washed with water, methanol, thf, and diethyl ether; yield 39% based on $ReOCl_3(PPh_3)_2$.

(10) NN′-*Ethylenebis*(*salicylideneiminato*)*bis*[*dichloro*(*oxo*)(*triphenylphosphine*)*rhenium*(V)], $[ReOCl_2(PPh_3)]_2(sal_2en)$.—$ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) and sal_2enH_2 (0.32 g, 1.2 mmol) were stirred in dry, degassed thf for 16 h in an inert atmosphere of N_2. The lime-green product was collected, washed with water, methanol, acetone, and diethyl ether; yield 60% based on $ReOCl_3(PPh_3)_2$.

(11) NN′-*Ethylenebis*(*acetylacetimine*)*bis*[*trichloro*(*oxo*)(*triphenylphosphine*)*rhenium*(V)], $[ReOCl_3(PPh_3)]_2(acac_2enH_2)$.—$ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) and $acac_2enH_2$ (0.27 g, 1.2 mmol) were stirred in dry degassed thf as described in (10) to yield the lime-green product; yield 68% based on $ReOCl_3(PPh_3)_2$.

(12) *Dichloro*[NN′-*ethylenebis*(*salicylideneiminato*)]*rhenium*(IV), $ReCl_2(sal_2en)$.—$ReCl_4(PPh_3)_2$ (0.5 g, 0.59 mmol), sal_2enH_2 (0.157 g, 0.59 mmol), and triethylamine (0.16 ml, 1.6 mmol) were refluxed in dry, degassed toluene (50 ml) for 3 h in an inert atmosphere of N_2. The suspension was cooled and the red-brown solid collected and washed with water, methanol, and ether. The solid, although only sparingly soluble in organic solvents, can be recrystallised from hot toluene; yield 46% based on $ReCl_4(PPh_3)_2$.

(13) *Dichloro*[NN′-*trimethylenebis*(*salicylideneiminato*)]*rhenium*(IV), $ReCl_2(sal_2prop)$.—The reaction was carried out as described in (12) with $ReCl_4(PPh_3)_2$ (0.5 g, 0.59 mmol), sal_2propH_2 (0.165 g, 0.59 mmol), and triethylamine (0.16 ml, 1.6 mmol) to yield a red-brown powder; yield 57% based on $ReCl_4(PPh_3)_2$.

(14) *Dichloro*{NN′-[o-*phenylenebis*(*salicylideneiminato*)]}*rhenium*(IV), $ReCl_2(sal_2phen)$.—The reaction was carried out as described in (12) with $ReCl_4(PPh_3)_2$ (0.5 g, 0.59 mmol), sal_2phenH_2 (0.185 g, 0.59 mmol), and triethylamine (0.16 ml, 1.6 mmol) to yield a brown powder; yield 57% based on $ReCl_4(PPh_3)_2$.

(15) *Dichloro*[NN′-*ethylenebis*(*acetylacetiminato*)]*rhenium*(IV), $ReCl_2(acac_2en)$.—$ReCl_4(PPh_3)_2$ (0.5 g, 0.59 mmol), $acac_2enH_2$ (0.132 g, 0.59 mmol), and triethylamine (0.16 ml, 1.6 mmol) were refluxed in dry, degassed toluene (50 ml) under N_2 for 3 h. The resultant solution was filtered whilst hot and evaporated to small volume (10 ml). Light petroleum (b.p. 40—60 °C, 50 ml) was added and the precipitated red-brown powder collected and washed with water, methanol, and ether. Recrystallisation from CH_2Cl_2–light petroleum (80—100 °C) gave dark red-brown crystals; yield 64% based on $ReCl_4(PPh_3)_2$.

(16) *Tetrachloro*[NN′-*ethylenebis*(*salicylideneimine*)]*rhenium*(IV), $ReCl_4(sal_2enH_2)$.—$ReCl_4(PPh_3)_2$ (1.0 g, 1.18 mmol) and sal_2enH_2 (0.31 g, 1.18 mmol), were refluxed in dry degassed thf for 16 h in an inert atmosphere of N_2. The suspension was cooled and the orange product collected and washed with water, methanol, acetone, and diethyl ether; yield 47% based on $ReCl_4(PPh_3)_2$.

(17) *Tetrachloro*[NN′-*trimethylenebis*(*salicylideneimine*)]*rhenium*(IV), $ReCl_4(sal_2propH_2)$.—This reaction was carried out as described in (13) from $ReCl_4(PPh_3)_2$ (1.0 g, 1.18 mmol) and sal_2propH_2 (0.33 g, 1.18 mmol) to yield an orange-brown powder; yield 90% based on $ReCl_4(PPh_3)_2$.

We thank the S.R.C. for a studentship (to A. R. M.).

[8/1169 *Received*, *23rd June*, 1978]

REFERENCES

[1] J. R. Thornback and G. Wilkinson, *J.C.S. Dalton*, 1978, 110.

[2] J. W. Buckler and K. Rohbock, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1073.

[3] J. F. Rowbotton and G. Wilkinson, *J.C.S. Dalton*, 1972, 826.

[4] A. van der Bergen, K. S. Murray, and B. O. West, *Austral. J Chem.*, 1972, **25**, 705.

[5] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, 1972, 3rd edn., p. 985; C. J. L. Lock and G. Turner, *Canad. J. Chem.*, 1977, **55**, 333.

[6] J. San Filippo, jun., R. L. Grayson, and H. J. Sniadoch, *Inorg. Chem.*, 1976, **5**, 269; J. San Filippo, jun., R. J. Fagan, and F. J. Di Salvo, *Inorg. Chem.*, 1977, **16**, 1016; K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.

[7] J. R. Dilworth, C. A. McAuliffe, and B. J. Sayle, *J.C.S. Dalton*, 1977, 849.

[8] G. Rouschias, *Chem. Rev.*, 1974, **74**, 531.

[9] C. A. McAuliffe, F. P. McCullough, M. J. Parrott, C. A. Rice, B. J. Sayle, and W. Levason, *J.C.S. Dalton*, 1977, 1762.

[10] F. L. Bowden and D. Ferguson, *J.C.S. Dalton*, 1974, 46.

[11] V. A. Kogan, O. A. Dripov, V. I. Minken, and V. P. Sodolov, *Russ. J. Inorg. Chem.*, 1965, **10**, 45.

[12] K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta*, 1974, **11**, 223.

[13] L. Rondaccio, *J. Organometallic Chem.*, 1973, **55**, C58.