Dithiocarbamate Complexes of Rhenium(V) and (III) †

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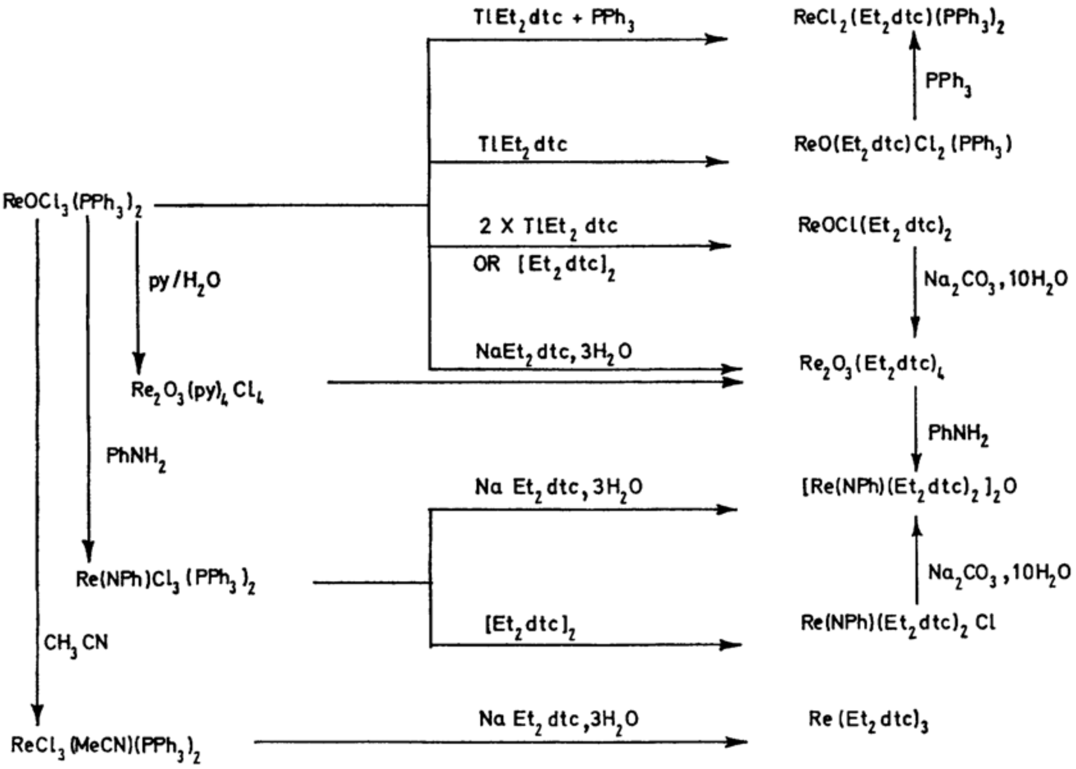
Dithiocarbamate complexes of oxorhenium(V) such as $ReOCl_2(S_2CNEt_2)(PPh_3)$, $ReOCl(S_2CNR_2)_2$, and $Re_2O_3(S_2CNR_2)_4$ have been prepared from $ReOCl_3(PPh_3)_2$.

The interaction of a variety of chloro-complexes of rhenium with dithiocarbamates leads to the compounds $[Re(NPh)(S_2CNEt_2)_2]_2O$, $Re(NPh)Cl(S_2CNEt_2)_2$, $ReN(S_2CNEt_2)_2$, $Re(S_2CNEt_2)_3$, and $ReCl_2(S_2CNEt_2)(PPh_3)_2$. The properties and infrared spectra are reported.

THE rhenium dithiocarbamate complexes previously reported[1] are $ReCl_2(R_2dtc)$ (R = Me or Et; dtc = $>NCS_2$) whose structures are unknown but which are possibly related to the Re_3Cl_{12} cluster. Following our preliminary note[2] on the preparation of oxo and other rhenium dithiocarbamates now reported in detail and their structure, other workers[3] have confirmed the structure of $Re_2O_3(Et_2dtc)_4$.

A number of rhenium(V) complexes and three rhenium(III) complexes, have been characterised. Typical syntheses and reactions are given in the Scheme.



ised from acetone. Similar compounds are obtained using sodium dimethyl- and diphenyl-dithiocarbamates. All three compounds analyse as $Re_2O_3(R_2dtc)_4$ (R = Me, Et, or Ph); their infrared spectra (Table 1) show the presence of Re=O, and Re–O–Re groups, as discussed later. The *X*-ray crystal structure of the diethyl complex[2] confirms the structure with a linear O=Re–O–Re=O grouping and chelate dithiocarbamate groups so that the rhenium(V) atom is octahedral. Molybdenum dithiocarbamates of the same stoicheiometry have been reported[4] but these are thought to have *cis* Mo(O)–O–Mo(O) groups;[5] such a grouping has been confirmed by the *X*-ray crystal structure determination for the xanthate $Mo_2O_3(EtOCS_2)_4$.[6]

Oxorhenium(V) *Dithiocarbamates*

(1) *μ-Oxo-bis*[*oxobis*(*dithiocarbamato*)*rhenium*(V)] *Complexes*.—A suspension of oxotrichlorobistriphenylphosphinerhenium(V), $ReOCl_3(PPh_3)_2$ reacts rapidly when refluxed with an acetone solution of sodium diethyldithiocarbamate trihydrate, to form sodium chloride and shiny, dark brown crystals which can be recrystallised from acetone.

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† No reprints available.

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It is possible that in the reaction of sodium dithiocarbamate with $ReOCl_3(PPh_3)_2$, unstable hydroxo-species, which condense to form the bridged oxo-complex, are formed similar to the reaction of the halide with moist pyridine[7] in the preparation of $Re_2O_3(py)_4Cl_4$.

The complex $Re_2O_3(Et_2dtc)_4$ is readily available from the reactions between sodium dithiocarbamate and either $ReOBr(PPh_3)_2$ or $Re_2O_3(py)_4Cl_4$ and by the action of water on $ReOCl(Et_2dtc)_2$ in benzene containing triethylamine. It is also produced in good yield by the action of sodium dithiocarbamate on $ReCl_4(MeCN)_2$ and $ReCl_4(PPh_3)_2$ and in poor yield from $ReO(OEt)Cl_2(PPh_3)_2$ and $Re_2Cl_8^{2-}$.

(2) *Oxohalogenodithiocarbamatorhenium*(V) *Complexes*.—The oxohalogeno-compounds $ReOCl(R_2dtc)_2$ ($R = Me$, Et, or $R_2 = [CH_2]_5$) and $ReOBr(R_2dtc)_2$ ($R = Me$ or Et), are very readily obtained by the reaction of $ReOX_3(PPh_3)_2$ ($X = Cl$ or Br) with the appropriate thiuram disulphide. The ethyl derivative can also be prepared using thallium diethyldithiocarbamate and, in poor yield, by an *in situ* reaction using carbon disulphide and diethylamine.

The reaction of $ReOCl(Et_2dtc)_2$ with water in acetone in the presence of sodium carbonate (to remove HCl) gives the oxo-bridged complex quantitatively.

The oxodichloro-complex, $ReOCl_2(Et_2dtc)(PPh_3)$, is obtained as blue crystals on treatment of $ReOCl_3(PPh_3)_2$ in dry acetone with one equivalent of thallium diethyldithiocarbamate. When the blue crystals are treated with sodium carbonate decahydrate in acetone a brown solution is formed but the only isolable crystalline product is the oxo-bridged complex, $Re_2O_3(Et_2dtc)_4$.

Imido and Nitrido Derivatives

The action of aniline on $Re_2O_3(Et_2dtc)_4$ in refluxing benzene solution leads to the formation of red-brown crystals of an imido-derivative, $[Re(NPh)(Et_2dtc)_2]_2O$, which probably has the PhN=Re–O=Re=NPh grouping. The same compound can also be made by the reaction of an acetone solution of sodium dithiocarbamate trihydrate with the imido chloro complex $Re(NPh)Cl_3(PPh_3)_2$.

An acetone solution of tetraethylthiuram disulphide reacts very readily with $Re(NPh)Cl_3(PPh_3)_2$ producing dark green crystals of $Re(NPh)Cl(Et_2dtc)_2$ in high yield. The interaction of aniline with oxohalogenodithiocarbamate $ReOCl(Et_2dtc)_2$ gave only a dark solution and small amounts of the oxo-bridged, imido-derivative, $[Re(NPh)(Et_2dtc)_2]_2O$, and despite the reaction[8] between phenyl isocyanate and $ReOCl_3(PPh_3)_2$, $ReOCl(Et_2dtc)_2$ did not behave similarly. The imidochlorodithiocarbamate, $Re(NPh)Cl(Et_2dtc)_2$, in wet acetone in the presence of sodium carbonate gives the oxo-bridged imido-derivative $[Re(NPh)(S_2CNEt_2)_2]_2O$.

The interaction of $ReNCl_2(PPh_3)_2$ with $NaEt_2NCS_2{,}3H_2O$ in acetone leads to the formation of bright, lemon-yellow crystals of $ReN(Et_2dtc)_2$, whose crystal structure has already been determined.[2]

Dithiocarbamate Complexes of Rhenium(III)

The reaction of trichloro(acetonitrile)bis(triphenylphosphine)rhenium(III) with sodium diethyldithiocarbamate in acetone leads to the formation of red-brown needles of the tris-complex $Re(Et_2dtc)_3$. A similar reaction using sodium diphenyldithiocarbamate produces a deep purple crystalline derivative, the infrared spectrum and analysis of which is in accord with the formulation $Re(Ph_2dtc)_3(PPh_3)$.

Attempts to isolate an ethoxy-derivative $ReO(OEt)(Et_2dtc)_2$ were unsuccessful but an attempted synthesis, namely the reaction of $ReOCl_3(PPh_3)_2$ with carbon disulphide and diethylamine in anhydrous ethanol, gave $Re(Et_2dtc)_3$.

The compound $ReCl_2(Et_2dtc)(PPh_3)_2$ is produced by the reaction between $ReOCl_2(Et_2dtc)(PPh_3)_2$ and triphenylphosphine by prolonged refluxing in alcohol. It is also produced in small amounts as a by-product of the reaction between equivalent quantities of $ReOCl_3(PPh_3)_2$ and thallium diethyldithiocarbamate which produces the rhenium(V) complex, $ReOCl_2(Et_2dtc)(PPh_3)$.

TABLE 1

I.r. spectra (cm^{-1}) of rhenium dithiocarbamate complexes in Nujol and hexachlorobutadiene mulls[a]

	ν(CN)	ν(CS)	ν(Re=O)	ν(Re–O–Re)
$Re_2O_3(S_2CNEt_2)_4$	1515s	995m	955m	670s
$Re_2O_3(S_2CNMe_2)_4$	1535s		970s[b]	660s
$Re_2O_3(S_2CNPh_2)_4$	1495s	1000m	955m	670s
$Re_2O_3(S_2CN(CH_2)_5)_4$	1500s	1000s 980m	950m	660s
$(Re(NPh)(S_2CNEt_2)_2)_2O$	1505s	995m		660s
$ReOCl(S_2CNEt_2)_2$	1515s		980s[b]	
$ReOBr(S_2CNEt_2)_2$	1525s		985s[b]	
$ReOCl(S_2CNMe_2)_2$	1570s		970s[b]	
$ReOCl(S_2CN(CH_2)_5)_2$	1535s	1000m 970s	965s	
$ReOBr(S_2CNMe_2)_2$	1560s		965s[b]	
$ReOCl_2(S_2CNEt_2)PPh_3$	1540s		980s[b]	
$ReCl_2(S_2CNEt_2)_2(PPh_3)_2$	1515s	1000w		
$Re(S_2CNEt_2)_3$	1505s	1000m		
$Re(S_2CNPh_2)_3PPh_3$	1495m 1460w	1005w 980w		
$Re(NPh)Cl(S_2CNEt_2)_2$	1525s	995m		
$ReN(S_2CNEt_2)_2$	1525m	1075s	(1005m 990m)	

[a] Range of absorption bands for ν(CN) 1480—1550 cm^{-1},[10] ν(CS) 989—1006 cm^{-1},[11] ν(Re=O) (1100—900). [b] Re=O and CS bands overlap substantially.

Infrared Spectra of the Complexes.—Significant bands in the spectra taken between 2000 and 650 cm^{-1} are listed in Table 1. All the complexes show absorption bands in the regions expected for dithiocarbamates.[9-11]

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In the complexes for which the Re–O–Re grouping is known to be present there is a strong broad band between 660 and 670 cm^{-1}. This band does not appear in the spectra of the free ligands or in the other complexes. However, a similar strong broad band occurs in the spectrum of $Re_2O_3(py)_4Cl_4$ compared with a medium sharp band at 690 cm^{-1} in the spectrum of $ReO(OEt)(py)_2Cl_2$. Consequently we conclude that this strong band is associated with vibrations involving the bridging oxygen.

The assignment of ν(Re=O) is complicated by the presence of C–S bands in the same region (1000—900 cm^{-1}). However, comparison with the spectra of the free ligand, and with the complexes in which Re=O is replaced by R=NPh, leads to the assignment of ν(Re=O) in $Re_2O_3(Et_2dtc)_4$ and $Re_2O_3(Ph_2dtc)_4$ at 955 cm^{-1}. The oxohalogeno-complexes, $ReOX(R_2dtc)_2$, show one strong band in the 900—1000 cm^{-1} region which is probably due to overlap of ν(CS) and ν(Re=O) bands.

For the complex $Re(Ph_2dtc)_3(PPh_3)$ one of the dithiocarbamate groups is evidently unidentate [*cf.* $Rh(Me_2dtc)_3PPh_3$][9] and the complex is octahedral and not seven-co-ordinated. There are two bands in the spectrum assignable to ν(CN) and two assignable to ν(CS). The splitting of the ν(CN)[9] band and ν(CS) band[11] for unidentate dithiocarbamate has been noted previously.

TABLE 2

Analytical data for the new rhenium compounds

Compound	Found (%)								Required (%)								M.p. (°C)
	C	H	Hal	N	O	P	S	M	C	H	Hal	N	O	P	S	M	
$Re_2O_3(Et_2dtc)_4$	23·9	4·0		5·5	5·0		25·2	900	23·7	4·0		5·5	4·8		25·3	1012	215
$Re_2O_3(Me_2dtc)_4$	16·3	2·7		6·4			27·3		16·0	2·7		6·2			28·4	900	
$Re_2O_3(Ph_2dtc)_4$	44·8	2·9		4·1			16·2		44·7	2·9		4·0			18·4	1396	228
$Re_2O_3([CH_2]_5dtc)_4$	27·9	3·8		5·3	6·2				27·2	3·8		5·3	4·5				
$[Re(NPh)(Et_2dtc)_2]_2O$	33·2	4·3		7·3	1·9		21·3	1140	33·2	4·3		7·2	1·4		22·0	1162	230
$ReOCl(Et_2dtc)_2$	22·9	3·7	6·8	4·9	3·1		24·0	650	22·5	3·7	6·7	5·3	3·0		24·0	534	225
$ReOBr(Et_2dtc)_2$	21·4	3·5	12·1	4·7					20·8	3·5	13·8	4·8					195
$ReOCl(Me_2dtc)_2$	15·7	2·8	8·0	5·8					15·1	2·5	7·4	5·9					
$ReOCl([CH_2]_5dtc)_2$	25·7	3·4	6·2	5·2					25·8	3·6	6·4	5·0					250
$ReOBr(Me_2dtc)_2$	14·1	2·8	15·2	5·3					13·8	2·3	15·3	5·4					252
$ReOCl_2(Et_2dtc)PPh_3$	40·2	3·9	10·0	2·1		4·4			40·4	3·7	10·4	2·1		4·5			170
$ReCl_2(Et_2dtc)(PPh_3)_2$	52·8	4·4	7·7	1·2					53·0	4·3	7·7	1·5					160
$Re(Et_2dtc)_3$	28·6	4·6		6·7			30·6	600	28·5	4·7		6·7			30·4	630	230
$Re(Ph_2dtc)_3PPh_3$	58·2	4·0		3·1		2·6	15·1	900	57·9	3·8		3·6		2·6	16·3	1180	150
$Re(NPh)Cl(Et_2dtc)_2$	31·9	4·0	6·0	6·6					31·6	4·1	5·8	6·9					255
$ReN(Et_2dtc)_2$	24·3	4·0		8·7			25·6		24·2	4·0		8·5			25·8		230

EXPERIMENTAL

Analyses were by the Microanalytical Laboratory, Imperial College. Molecular weights were measured on a Perkin-Elmer–Hitachi model 115 osmometer. Analytical data are collected in Table 2. Acetone was dried over molecular sieves type 4A, XW.

μ-*Oxo-bis[oxobis(diethyldithiocarbamato)rhenium*(V)].—*Method A*. A suspension of oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3(PPh_3)_2$ (10 g), and $NaEt_2dtc,3H_2O$ (10 g) in acetone (250 ml), was refluxed for 45 min. A stream of nitrogen was passed through the reaction mixture to prevent bumping. The product was precipitated as dark brown crystals together with sodium chloride. The reaction mixture was cooled, filtered, and the solid washed with ether, water, and again with ether leaving the *complex* (3·8 g). The filtrate deposited a further crop of well formed crystals (1·4 g) when set aside for two days. Total yield 5·2 g (85%). The product was recrystallised from benzene, washed with ether, and dried *in vacuo*. This compound was shown to be diamagnetic by direct measurement of the bulk susceptibility and by the n.m.r. method, and was nonconducting in solution in nitrobenzene.

Method B. Oxochlorobis(diethyldithiocarbamato)rhenium(V), $ReOCl(Et_2dtc)_2$ (0·2 g), water (1 ml), triethylamine (1 ml), and benzene (80 ml) were refluxed for 1 h. The collected precipitate was washed with acetone and ether leaving the *complex* as brown crystals (0·14 g, 73%).

μ-*Oxo-bis[oxobis(dimethyldithiocarbamato)rhenium*(V)].—The reaction was carried out as above (Method A) using $NaMe_2dtc,2H_2O$; it produced the *complex* as a light brown powder (74%). The product was too insoluble for recrystallisation and for molecular-weight determination.

μ-*Oxo-bis[oxobis(diphenyldithiocarbamato)rhenium*(V)].—The reaction was carried out as above (Method A) using $NaPh_2dtc,2H_2O$; it produced the *complex* as dark brown crystals (63%). The compound was recrystallised from dichloromethane–acetone.

μ-*Oxo-bis[oxobis(cyclopentamethylenedithiocarbamato)-rhenium*(V)].—The reaction was carried out as above (Method B) using $ReOCl([CH_2]_5dtc)_2$ (0·23 g), water (0·5 ml), triethylamine (0·5 ml), and benzene (40 ml); it produced the *complex* as a light brown powder (0·21 g, 96%). The complex was virtually insoluble in acetone or benzene but slightly soluble in dichloromethane from which a sample was recrystallised for analysis.

Oxohalogenobis(dialkyldithiocarbamato)rhenium(V) *Complexes*.—Three methods were used for the preparation of these complexes from the oxotrihalogenobistriphenylphosphine compound, $ReOX_3(PPh_3)_2$ (R = Cl or Br).

Method A. Using the appropriate thiuram disulphide is the most convenient method and gives the best yields.

$ReOX_3(PPh_3)_2$ (X = Cl or Br) (2 mmol) and tetra-alkylthiuram disulphide, $(R_2NCS_2)_2$ (R = Me, Et, or $R_2 = [CH_2]_5$)

(4 mmol), were refluxed in dry acetone (40 ml), with stirring for 30 min and allowed to cool. The complexes were collected, washed with ether, and dried *in vacuo*.

ReOCl(Et_2dtc)$_2$, olive green crystals, 70% recrystallised from dry acetone.

ReOBr(Et_2dtc)$_2$, dark brown crystals, 64% recrystallised from dry acetone.

ReOCl(Me_2dtc)$_2$, light brown crystals, 85%, washed with acetone and ether; too insoluble for recrystallisation.

ReOBr(Me_2dtc)$_2$, light brown crystals, 70%, washed with acetone and ether, too insoluble for recrystallisation.

ReOCl([CH_2]$_5$dtc)$_2$, light brown crystals 90%, washed with acetone and ether, too insoluble for recrystallisation.

Method B. Oxochlorobis(diethyldithiocarbamato)rhenium-v). $ReOCl_3(PPh_3)_2$ (0·4 g) and thallium diethyldithiocarbamate (0·34 g) were dried *in vacuo*, over P_2O_5, at 57 °C, before being added to dry acetone (40 ml), and refluxed for 30 min, under nitrogen, with stirring. The solution which turned pale brown and produced a white precipitate of thallium(I) chloride, was filtered hot and evaporated to half its volume under nitrogen; it was then set aside overnight (over silica gel). Olive-green crystals of the *complex* were deposited (0·13 g, 50%).

Method C. Using carbon disulphide and diethylamine is unreliable, gives poor yields, and was only used to prepare the diethyl derivative.

Diethylamine (0·5 ml), carbon disulphide (0·25 ml), 2,2-dimethoxypropane (10 ml), and acetone (previously dried over K_2CO_3) (30 ml) were refluxed under nitrogen for 20 min. $ReOCl_3(PPh_3)_2$ (0·4 g) was added and the reaction mixture was refluxed, with stirring, for 1 h. A brown solution was formed which was evaporated to half its volume under nitrogen and then set aside; it deposited olive-green crystals of the complex ReOCl(Et_2dtc)$_2$ (0·04 g, 16%).

Oxodichloro(diethyldithiocarbamato)(triphenylphosphine)-rhenium(V).—$ReOCl_3(PPh_3)_2$ (0·8 g) and thallium diethyldithiocarbamate (0·34 g) were dried over P_2O_5 at 57 °C *in vacuo*; they were then added to dry acetone (60 ml) and refluxed under nitrogen for 5 h. The suspension first turned brown, then green-blue and deposited a white residue of thallium(I) chloride. The solution was filtered whilst hot and was then set aside over silica gel overnight. Blue crystals were deposited, which were collected, washed with ether, and dried *in vacuo* (0·38 g, 67%). The compound was recrystallised from dry acetone.

μ-Oxo-bis[phenylimidobis(diethyldithiocarbamato)rhenium-(V)].—*Method A.* Oxobis[oxobis(diethyldithiocarbamato)-rhenium(V)], $Re_2O_3(Et_2NCS_2)_4$ (0·1 g), aniline (2 ml), and benzene (20 ml) were refluxed under nitrogen for 5 h. The dark brown solution was evaporated to dryness by a stream of nitrogen, redissolved in acetone, filtered, and then set aside. Evaporation of this solution produced brown needles of the complex which were collected and washed with ether (0·03 g, 25%).

Method B. Trichloro(phenylimido)bis(triphenylphosphine)rhenium(V) (0·1 g) and $NaEt_2$dtc,$3H_2O$ (0·3 g), in acetone (25 ml), were refluxed for 30 min. The dark brown solution was filtered free from the precipitated sodium chloride and then evaporated to 5 ml and cooled. The precipitated brown powder was collected, washed with ether, water, and again with ether, and then recrystallised from acetone to give the *complex* as brown needles (0·35 g, 55%).

Method C. Chloro(phenylimido)bis(dithiocarbamato)-rhenium(V) (0·1 g) and sodium carbonate decahydrate (0·5 g) in acetone (20 ml), were refluxed for 30 min and then filtered whilst hot; the brown solution was evaporated to 5 ml. Brown needles of the *complex* (0·06 g, 63%) separated when the solution was set aside.

Chloro(phenylimido)bis(diethyldithiocarbamato)rhenium(V).—Trichloro(phenylimido)bis(triphenylphosphine)rhenium-(V), Re(NPh)$Cl_3(PPh_3)_2$ (1·25 g), tetraethylthiuram disulphide, $(Et_2NCS_2)_2$ (0·88 g), and dry acetone (30 ml) were refluxed under nitrogen, with stirring, for 3½ h. A green solid was present throughout. The reaction mixture was left to cool (3 h) and was then filtered. The dark green crystals of the *complex* were washed with ether and dried *in vacuo* (0·8 g, 96%). The complex was recrystallised from benzene.

Nitridobis(diethyldithiocarbamato)rhenium(V).—A suspension of $ReNCl_2(PPh_3)_2$ (0·5 g) in a saturated solution of $NaEt_2$dtc,$3H_2O$ in acetone (50 ml) was refluxed for 4 h under a stream of nitrogen. The solution gradually became yellow-brown and deposited a mixture of sodium chloride and a yellow solid. The solid residue was extracted with hot acetone giving a yellow solution which when set aside deposited yellow crystals of the *complex*. These crystals were recrystallised from acetone, washed with ether, and dried *in vacuo* (0·14 g, 45%).

Tris(diethyldithiocarbamato)rhenium(III).— $ReCl_3$(MeCN)-$(PPh_3)_2$ (0·5 g) and a saturated acetone solution of $NaEt_2$-dtc,$3H_2O$ (50 ml) were refluxed under a stream of nitrogen for 1 h. The reaction mixture turned to a deep red-brown colour and deposited sodium chloride which was filtered off. The remaining solution was evaporated to near dryness leaving a viscous brown liquid which was dissolved in ethanol, filtered, and then set aside. In time a brown powder was deposited which was contaminated with a little white solid. This solid residue was washed with ether, water, and then more ether. The remaining brown powder was recrystallised from ethanol to give the *complex* as red-brown needles (0·04 g, 11%).

Tris(diphenyldithiocarbamato)triphenylphosphinerhenium-(III).—$ReCl_3$(MeCN)$(PPh_3)_2$ (0·5 g), $NaPh_2$dtc,$2H_2O$ (1·2 g), and acetone (50 ml) were refluxed for 30 min to produce a dark purple solution and an off-white residue of sodium chloride. The reaction mixture was filtered whilst hot and was then left to cool; it deposited dark purple crystals of the *complex* (0·26 g, 49%) which were washed with ether and dried *in vacuo*.

Dichloro(diethyldithiocarbamato)bis(triphenylphosphine)-rhenium(III).—*Method A.* The complex was first prepared as a by-product of the reaction between equimolar quantities of $ReOCl_3(PPh_3)_2$ and thallium dithiocarbamate. The filtrate remaining after the blue complex ReOCl-(Et_2dtc)(PPh_3) had crystallised out was treated with ether to produce yellow needles of the complex (0·02 g, 2%).

Method B. Equimolar proportions of $ReOCl_3(PPh_3)_2$ (2·73 g) and thallium diethyldithiocarbamate (1·16 g) and three molar proportions of triphenylphosphine (2·58 g) were refluxed in dry acetone, under nitrogen, with stirring for 20 h; the mixture was cooled and filtered. The yellow residue was extracted with hot benzene (100 ml) to form a yellow solution which was filtered free from the thallium(I) chloride, and then cooled and treated with ether to yield the *complex* as a yellow powder (1·81 g, 60%).

Method C. $ReOCl_2$(Etdtc)(PPh_3) (0·32 g), triphenylphosphine (0·37 g), and dry acetone (30 ml) were refluxed under nitrogen with stirring for 20 h; the mixture was then cooled and filtered. The yellow *complex* was washed with ether and dried (0·32 g, 74%). The filtrate was evaporated to dryness and the residue obtained showed a strong band in the i.r. region at 1190 cm^{-1} (Nujol mull) indicating the formation of Ph_3PO.

We thank the Royal Society, Government Grant Board C, for the purchase of the osmometer (J. F. R.), Albright and Wilson Limited for the gifts of triphenylphosphine, and Esso Research S.A. for some research expenses.

[1/1941 *Received, 22nd October*, 1971]