806. *Some Complex Compounds of Rhenium.**

By R. Colton, R. Levitus, and G. Wilkinson.

Complexes have been obtained from rhenium trichloride and rhenium tetraiodide with a variety of phosphorus, nitrogen, sulphur, and oxygen ligands.

Comparatively few complexes of rhenium in the IV, III, and I oxidation states have been prepared. The halide complexes of the types $[ReCl_4]^-$ and $[ReCl_6]^{2-}$ are well known.[1,2] When rhenium trichloride and tribromide dissolved in liquid ammonia they formed compounds which were thought [3] to be ammoniates, *e.g.*, $ReCl_2,6NH_3$. Nyholm and his colleagues [4] have prepared diarsine derivatives of Re(III) of the type $[Re(Diarsine)_2Cl_3]ClO_4$, and a 5-co-ordinate compound, $Re(Diarsine)Cl_3$, has also been mentioned.[5] A complex hexacyanide of Re(III) is also known.[6] Since our work began the preparation of triphenylphosphinerhenium trichloride and bis(triphenylphosphine)rhenium trichloride reported here was briefly reported by others.[2] The only complexes of Re(I) known are the two series of carbonyl halides of the types $Re(CO)_5Cl$ [8] and $[Re(CO)_4Cl]_2$,[9] other substituted carbonyl compounds,[10,11] and the complex cyanide $K_5Re(CN)_6$.[12]

This paper is the first of a series to be concerned with complexes of rhenium in various oxidation states, and here we describe the preparation of a range of different types of compound by reaction of the trichloride and tetraiodide with various donor ligands. Compounds have been obtained with phosphorus, nitrogen, sulphur, and oxygen ligands. In many cases starting from rhenium trichloride the compounds appear to be polymeric, presumably with chlorine bridges, but a series of 5-co-ordinate Re(III) complexes has been prepared which are monomeric and soluble in most organic solvents.

Phosphorus Ligands.—Rhenium trichloride and triphenylphosphine yield two products. When acetone solutions are mixed, reddish-purple crystals of triphenylphosphinerhenium trichloride, $(PPh_3)ReCl_3$, are quickly deposited, since the complex is only sparingly soluble in organic solvents. The residual red solution contains bis(triphenylphosphine)rhenium trichloride $(PPh_3)_2ReCl_3$, which is soluble in many organic solvents. It is rather difficult to obtain good yields of the latter compound by this reaction and it is best made by treating a suspension of triphenylphosphinerhenium(III) trichloride in acetone with chlorine in the presence of excess of triphenylphosphine. The solution rapidly reddened and bis(triphenylphosphine)rhenium(III) trichloride was obtained almost quantitatively. It is surprising that a reaction involving chlorine yields a new complex with rhenium in the same valency state, but this can be explained by assuming that the chlorine oxidises the PPh_3ReCl_3 to an unstable Re(IV) diphosphine complex which then spontaneously loses chlorine to give the observed product.

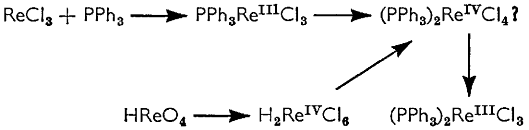
This behaviour is in agreement with the observations of Freni *et al.*[7] who prepared $(PPh_3)_2ReCl_3$ by the action of the phosphine and hydrogen chloride on per-rhenic acid in alcohol. It is known that halogen acids normally reduce Re^{VII} only to Re^{IV} (owing to the

---

* Cf. Colton and Wilkinson, *Chem. and Ind.*, 1959, 1314; Colton, Levitus, and Wilkinson, *Nature*, 1960, **186**, 233.

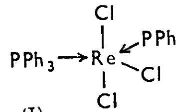
[1] Geilmann and Wrigge, *Z. anorg. Chem.*, 1935, **223**, 144.
[2] Enk, *Ber.*, 1931, **64**, 791.
[3] Klemm and Frischmuth, *Z. anorg. Chem.*, 1937, **230**, 209.
[4] Curtiss, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625.
[5] Nyholm, 10th Solvay Conference, 1956, p. 225.
[6] Colton, Peacock, and Wilkinson, *J.*, 1960, 1374.
[7] Freni and Valenti, XVIIth Internat. Congr. Pure Appl. Chem., Munich, 1959, Abs. A 1057.
[8] Schulten, *Z. anorg. Chem.*, 1939, **243**, 145.
[9] Abel, Hargreaves, and Wilkinson, *J.*, 1958, 3149.
[10] Hieber and Fuchs, *Z. anorg. Chem.*, 1942, **248**, 269.
[11] Abel and Wilkinson, *J.*, 1959, 1506.
[12] Clauss and Lissner, *Z. anorg. Chem.*, 1958, **297**, 300.

formation of ReX_6^{2-} ions)[13] but in this case some unstable Re^{IV}–phosphine complex must be formed which decomposes to a Re^{III} complex. Possible reaction schemes are:



Triphenylphosphinerhenium trichloride forms purple-reddish crystals which dissolve slightly in acetone, alcohol, and nitrobenzene; it is monomeric and is a non-electrolyte in nitrobenzene. The complex is diamagnetic and may thus be regarded as showing the rather unusual d^3s tetrahedral hybridisation, as was suggested for the $[ReCl_4]^-$ ion.[5] It reacts easily with pyridine at room temperature to give the corresponding green pyridine complex, $pyReCl_3$ (see below).

Bis(triphenylphosphine)rhenium trichloride is a red solid very soluble in alcohol and fairly soluble in acetone and nitrobenzene, in which it is a non-electrolyte. It is diamagnetic, monomeric, and appears to contain 5-co-ordinate rhenium. The fact that it is diamagnetic implies that the structure is trigonal bipyramidal (d^3sp) (I) rather than square pyramidal, since ligand-field considerations[14] for the two cases indicate that only the bipyramidal form (level order $d_{xy} = d_{yz}$; $d_{x^2-y^2} = d_{xy}$; d_{z^2}) would lead to a diamagnetic complex with Re^{III} (d^4). Although we cannot be specific concerning the relative positions of the groups in (I), it seems likely, in view of the orbitals available for multiple bonding, that the phosphine groups are in the equatorial plane of the molecule.



(I)

Polarographic reduction of bis(triphenylphosphine)rhenium trichloride in absolute ethanol has been studied with 0·3M-tetramethylammonium chloride as the supporting electrolyte (Table 1). The polarogram showed two waves of relative heights 1 : 3. The first wave, with a half-wave potential of —0·46 v, probably corresponds to reduction to bis(triphenylphosphine)rhenium dichloride $(PPh_3)_2ReCl_2$, as has been demonstrated chemically by Freni *et al.*[7] using hydrazine hydrochloride as the reductant. If this is so the second wave ($E_{\frac{1}{2}}$ *ca.* —1·45 v) must correspond to a three-electron reduction to Re(—1). It is noteworthy that the high reduction potential of this second wave corresponds very closely to that observed when other rhenium compounds are reduced polarographically to Re(—1) (*e.g.*, $KReO_4$ in KCl, $E_{\frac{1}{2}} = -1{\cdot}55$ v; $K_3[Re(CN)_8]$ in KCl, $E_{\frac{1}{2}} = -1{\cdot}52$ v).[13] The ratio of the heights of the waves is constant at different concentrations, virtually ruling out the possibility that the second wave is a catalytic one.

The visible absorption spectrum of $(PPh_3)_2ReCl_3$ shows a peak at 750 mμ (ε *ca.* 2000) which was observed in all the 5-co-ordinate complexes where the spectrum could be studied (see below); this band appears to be characteristic of 5-co-ordinate Re(III).

TABLE 1. *Polarographic reduction of* $(PPh_3)_2ReCl_3$ *in absolute alcohol* (0·3M-Me_4NCl *as supporting electrolyte*).

	First wave		Second wave			First wave		Second wave			First wave		Second wave	
Concn. (mM)	i_d (μA)	i_d/c	i_d (μA)	i_d/c	Concn. (mM)	i_d (μA)	i_d/c	i_d (μA)	i_d/c	Concn. (mM)	i_d (μA)	i_d/c	i_d (μA)	i_d/c
7·07	6	0·85	—	—	3·90	3·2	0·82	9·3	2·4	3·04	2·6	0·85	7·4	2·45
	5·8	0·82	—	—		3·1	0·80				2·6	0·85		

Although we have been unable to isolate $(PPh_3)_2ReCl_4$, yet with rhenium tetraiodide triphenylphosphine gives purple crystals of bis(triphenylphosphine)rhenium tetraiodide. The compound is paramagnetic and only very slightly soluble in solvents such as acetone and alcohol.

---

[13] Briscoe, Robinson, and Rudge, *J.*, 1936, 3218.

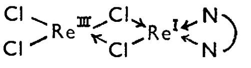
[14] Figgis and Lewis, " Modern Co-ordination Chemistry," Lewis and Wilkins, Editors (Interscience Publishers, London and New York, 1960), p. 422.

We have also studied the reaction between rhenium trichloride and tri-n-butylphosphine and phosphorus trichloride. Products similar to bis(triphenylphosphine)rhenium trichloride are obtained, being red, organic-soluble substances, but we have been unable to purify them adequately by crystallisation and analyses were unsatisfactory.

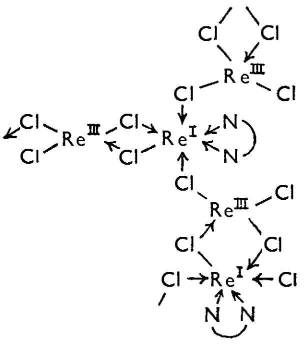
Nitrogen Ligands.—The complexes appear to be of several types: (*a*) The highly insoluble and presumably polymeric products of stoicheiometry Re_2Cl_4L obtained by direct reaction of rhenium trichloride with 1,10-phenanthroline and 2,2′-bipyridyl are diamagnetic. The simplest unit structure (since the two nitrogen atoms must occupy *cis*-positions) is (II), but polymeric structures, perhaps of the type (III), [where Re(I) is octahedrally co-ordinated, since octahedral Re(III) would lead to paramagnetism] are possible in view of the insoluble nature of the complexes. In any formulation rhenium atoms in both I and III oxidation states must be present. It is well known that complexes containing mixed valency states are highly coloured, and these rhenium complexes are deep purple.

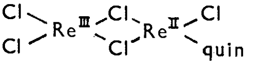
The Re(III) atom presumably has d^3s hybridisation as is found in other tetrahedral Re(III) complexes. The Re(I) atom (d^6) cannot be d^3s, and sp^3 hybridisation would lead to paramagnetism. The other likely possibilities are (i) that for the single unit (II) it is square planar [the only reported square planar complex is for Re(II) in $Re(py)_2Cl_2$],[16] or (ii) that, in view of the polymeric structure, it is octahedral owing to further donation from chlorine atoms attached to Re(III) atoms in other units of the complex; the Re(III) atom cannot be octahedral as this would lead to paramagnetism.

There is further indirect evidence that a lower oxidation state of rhenium is present in the above compounds since when suspended in acetone at room temperature they are smoothly oxidised by chlorine to 5-co-ordinate Re(III) complexes such as $phenReCl_3$, of the same type as (I). These complexes show a visible absorption band at 750 mμ, very similar to that shown by bis(triphenylphosphine)rhenium(III) trichloride.



(II)





(IV)

denotes 1,10-phenanthroline or 2,2′-bipyridyl.

Similarly, the complexes are red, very soluble in alcohol, and moderately soluble in acetone, chloroform, and nitrobenzene. They are diamagnetic, non-conductors in nitrobenzene, and appear to be true 5-co-ordinate complexes. The arguments cited above for the bipyramidal rather than the square pyramidal structure apply equally in this case.

(*b*) With quinaldine a purple complex is obtained with stoicheiometry Re_2Cl_5(quin). It is insoluble in water and contains no ionic chlorine. It is paramagnetic with a room-temperature susceptibility approximating to one unpaired electron. Again, the complex is insoluble in organic solvents, and no conductometric measurements of molecular weights in solution could be effected. The structure may be of the type (IV), but there is no way of distinguishing between sp^3 or dsp^2 hybridisation for the Re(II) atom. In addition there

---

[15] Colton, Dalziel, Griffith, and Wilkinson, *J.*, 1960, 71.

[16] Tronev and Bandin, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 87.

is also the possibility of a polymeric structure (cf. III); in any case one unpaired electron would be expected.

(*c*) With other amines, complexes of the types $Re_2Cl_6L_2$ (α-picoline) and Re_2Cl_6L (2,6-lutidine, 2-vinylpyridine, and triethylenetetramine) were obtained. These were very slightly soluble in water and contained ionic chlorine, but the fraction of ionisable chlorine is not easy to determine since the cation is quite rapidly hydrolysed by water to hydrated rhenium(III) oxide and chlorine ions, as is well known for the trichloride itself. As a result only total chlorine was determined.

(*d*) Pyridine seems to be the only amine so far studied which gives mononuclear species from the trichloride. The reaction is similar to that described for triphenylphosphine. The red solution obtained by allowing a solution of rhenium trichloride in acetone to stand with pyridine contains some dipyridinerhenium trichloride, $(py)_2ReCl_3$. Precipitation with ether, however, always gives some unchanged rhenium trichloride mixed with the product. When warmed, the solution becomes green and a pale green, sparingly soluble pyridinerhenium trichloride can be precipitated with ether. As mentioned above, this compound can also be prepared by treating triphenylphosphinerhenium trichloride with pyridine.

Pyridine reacts with an acetone solution of rhenium tetraiodide to give brown paramagnetic crystals of dipyridinerhenium tetraiodide, $(py)_2ReI_4$. Like the corresponding triphenylphosphine complex it is only slightly soluble in organic solvents.

Sulphur Ligands.—With 3,4-dimethylthiotoluene an insoluble complex of the same type as those obtained from 1,10-phenanthroline and 2,2′-bipyridyl was readily obtained.

Reaction of 1,2-dimethylthioethane with rhenium trichloride, on the other hand, gave an organic-soluble, red, diamagnetic complex $LReCl_3$, which again is clearly 5-co-ordinate (cf. I).

Oxygen Ligands.—Rhenium trisacetylacetonate was prepared by refluxing either the hydrated Re(III) or Re(IV) oxide, or several of the halide complexes mentioned above, *e.g.*, $pyReCl_3$, with acetylacetone. The compound forms dark brown crystals soluble in alcohol, acetone, and chloroform and slightly soluble in carbon tetrachloride. It is paramagnetic and no nuclear magnetic proton resonance lines could be obtained owing to excessive broadening. Between room temperature and 130° K the effective magnetic moment varies linearly with temperature from 2·33 to 1·90 B.M., probably on account of ferromagnetic interactions. The low moment for octahedral d^4 complexes (spin-only value 2·83 B.M.) has been explained by Kotani [17] in terms of spin-orbit coupling, and his theory has been applied to other octahedral Re(III) complexes.[4]

The infrared spectrum of rhenium trisacetylacetonate is similar to the spectra of other metal trisacetylacetonates,[13] the strong band at about 1550 cm.$^{-1}$ being attributable to the chelated carbonyl group.

EXPERIMENTAL

Microanalyses and molecular-weight determinations were made by the Microanalytical Laboratory, Imperial College.

Rhenium trichloride was prepared by the usual method of chlorinating metallic rhenium and thermally decomposing the resulting pentachloride in a stream of nitrogen.[19] Rhenium tetraiodide was made by evaporating a solution of per-rhenic acid and hydriodic acid.[20]

None of the compounds described below has a sharp m. p. and they all decompose above *ca.* 150°.

Phosphorus Ligands.—(a) *Triphenylphosphinerhenium trichloride.* An acetone solution of triphenylphosphine (0·6 g. in 25 ml.) was slowly added to one of rhenium trichloride in acetone (0·3 g. in 25 ml.). After a few minutes the red solution [which contains some bis(triphenylphosphine)rhenium trichloride] was decanted and the remaining reddish-purple crystals were

---

[17] Kotani, *J. Phys. Soc. Japan,* 1949, **4**, 293.

[18] Cotton, in ref. 14, p. 382.

[19] Geilmann and Wrigge, *Z. anorg. Chem.*, 1933, **214**, 244.

[20] Peacock, Welch, and Wilson, *J.*, 1958, 2901.

washed with acetone and ether and finally dried (yield 0·35 g., *ca.* 60%, based on rhenium trichloride) (Found: C, 40·5; H, 3·2; P, 5·3; Cl, 19·4. $C_{18}H_{15}Cl_3PRe$ requires C, 39·7; H, 2·8; P, 5·7; Cl, 19·5%).

(b) *Bis(triphenylphosphine)rhenium trichloride.* Chlorine was passed into a suspension of PPh_3ReCl_3 (0·2 g.) in acetone for about ½ hr., in the presence of excess of triphenylphosphine (*ca.* 0·3 g.). The red *compound* was precipitated with ether and recrystallised from acetone (yield 0·24 g., *ca.* 85%) [Found: C, 52·5; H, 4·1; Cl, 13·1%; *M* (ebullioscopic in chlorobenzene), 780. $C_{36}H_{30}Cl_3P_2Re$ requires C, 52·8; H, 3·6; Cl, 13·0%; *M*, 817].

(c) *Bis(triphenylphosphine)rhenium tetraiodide.* An acetone solution of triphenylphosphine (0·2 g. in 20 ml.) was added to one of rhenium tetraiodide in acetone (0·1 g. in 10 ml.). The purple crystals were washed with acetone, then ether, and dried in a nitrogen stream; yield 0·2 g., *ca.* 95% (Found: Re, 15·1. $C_{36}H_{30}I_4P_2Re$ requires Re, 15·3%).

Nitrogen Ligands.—(a) 1,10-*Phenanthrolinedirhenium tetrachloride and* 1,10-*phenanthrolinerhenium trichloride.* Excess of 1,10-phenanthroline (*ca.* 0·15 g.) in acetone (10 c.c.) was slowly added to rhenium trichloride (0·1 g.) in hot acetone (25 ml.). The purple precipitate (phen)Re_2Cl_4 was centrifuged off, washed with acetone and ether, and dried in a nitrogen stream (yield *ca.* 0·1 g., 95%) (Found: C, 20·1; H, 1·7; N, 4·1; Cl, 19·8. $C_{12}H_8Cl_4N_2Re$ requires C, 20·7; H, 1·1; H, 4·0; Cl, 20·4%).

A suspension of (phen)Re_2Cl_4 (0·1 g.) in acetone (10 ml.) was oxidised with chlorine for about ½ hr. in the presence of excess of 1,10-phenanthroline (*ca.* 0·15 g.). The resulting red, soluble *complex*, (phen)$ReCl_3$, was precipitated with ether and recrystallised from acetone (yield 0·11 g., *ca.* 85%) [Found: C, 30·4; H, 1·7; N, 5·9; Cl, 22·5%; *M* (ebullioscopic in chlorobenzene), 445. $C_{12}H_8Cl_3N_2Re$ requires C, 30·3; H, 1·7; N, 5·9; Cl, 22·4%; *M*, 472].

(b) 2,2′-*Bipyridyldirhenium tetrachloride and* 2,2′-*bipyridylrhenium trichloride.* The preparations with 2,2′-bipyridyl were (*mutatis mutandis*) identical with those described for 1,10-phenanthroline.

(c) With quinaldine, α-picoline, 2-vinylpyridine, triethylenetetramine and 2,6-lutidine the techniques were identical. The amine in acetone was added to an acetone solution of rhenium trichloride. The insoluble purple precipitates were washed with acetone and ether and dried in a stream of nitrogen. The yields in all cases were 85—90%. Analogues of the *products* are tabulated.

	Found (%)				Required (%)			
	C	H	N	Cl	C	H	N	Cl
$ReCl_5$(quin).........	17·4	2·0	2·2	25·1	17·3	1·3	2·0	25·6
Re_2Cl_6(α-pic)	18·7	2·5	3·5	27·2	18·7	1·8	3·6	27·6
Re_2Cl_6(2,6-lut) ...	12·7	2·0	2·1	30·5	12·1	1·4	2·0	30·8
Re_2Cl_6(trien)	9·4	2·9	7·1	28·1	9·8	2·5	7·6	28·7
Re_2Cl_6(2-vinyl-py)	12·0	1·5	2·0	—	12·2	1·1	2·0	—

The susceptibility of the quinaldine complex is 600 × 10^{-6} c.g.s.u. at 293° K; $\mu_{\text{eff.}} = 1{\cdot}2$ B.M.

(d) *Pyridinerhenium trichloride.* Pyridine (*ca.* 2 ml.) was added to rhenium trichloride (0·2 g.) in hot acetone (25 ml.). After a few minutes ether was added to the red solution and a precipitate containing dipyridinerhenium trichloride was obtained. If the red solution was gently warmed it became green and on addition of ether the light green *pyridinerhenium trichloride* was precipitated (yield 0·2 g., *ca.* 65%) (Found: C, 16·1; H, 1·5; N, 3·8. $C_5H_5Cl_3NRe$ requires C, 16·1; H, 1·3; N, 3·8%).

(e) *Dipyridinerhenium tetraiodide.* Pyridine (*ca.* 2 ml.) was added to rhenium tetraiodide (0·1 g.) in acetone (10 ml.). The small amount of precipitate was filtered off and after a few minutes brown paramagnetic crystals were deposited. The supernatant liquid was decanted and the crystals of *complex* were washed with acetone and ether and dried in a nitrogen stream (yield 0·11 g., *ca.* 85%) (Found: Re, 21·8; C, 14·6; N, 3·4; H, 1·0. $C_{12}H_{10}I_4N_2Re$ requires Re, 21·9; C, 14·2; N, 3·3; H, 1·2%); χ_M (corr.) = 5600 × 10^{-6} c.g.s.u. at 293° K; $\mu_{\text{eff.}} = 3{\cdot}7$ B.M.

Sulphur Ligands.—(a) 3,4-*Dimethylthiotoluene.* The sulphide (0·2 g.) in acetone (10 ml.) was added to rhenium trichloride (0·2 g.) in hot acetone (25 ml.). The purple precipitate of a *complex* LRe_2Cl_4 was centrifuged off, washed with acetone and ether, and dried in a stream of nitrogen (yield 0·23 g., *ca.* 90%) (Found: C, 15·3; H, 2·0; S, 9·7. $C_9H_{12}Cl_4Re_2S_2$ requires C, 15·4; H, 1·3; S, 9·4%).

(b) 1,2-*Dimethylthioethane*. Addition of an excess of 1,2-dimethylthioethane (5 c.c.) to rhenium trichloride (0·2 g.) in acetone (20 ml.) gave, after 1 hour's refluxing, a light red solution. Addition of ether gave a red precipitate of the *complex* which was recrystallised from acetone (yield 0·2 g., *ca.* 65%) (Found: C, 11·5; H, 2·3. $C_4H_{10}Cl_3ReS_2$ requires C, 11·6; H, 2·4%).

Rhenium Trisacetylacetonate.—Rhenium dioxide or sesquioxide (*ca.* 0·4 g.) was refluxed with acetylacetone (*ca.* 50—60 ml.) for 48 hr. The brown solution was filtered to remove remaining oxide, then evaporated to dryness at 0·1 mm. The brown solid was dissolved in the minimum amount of acetone and reprecipitated by adding a large amount of ether (50 ml.). The flocculent brown *complex* was centrifuged off and recrystallised from acetone (yield 0·5 g., *ca.* 60%) [Found: C, 36·7; H, 3·7; O, 20·1; Re, 38·9%; *M* (ebullioscopic in chlorobenzene), 471. $C_{15}H_{21}O_6Re$ requires C, 36·0; H, 4·3; O, 19·7; Re, 38·3%; *M*, 484]. At the given temperatures, the susceptibilities (corrected, in c.g.s.u. × 10^6) and values of $\mu_{eff.}$ are, respectively: 293·8°, 2220, 2·33; 267·4°, 2290, 2·26; 233·0°, 2530, 2·24; 207·3°, 2660, 2·14; 169·0°, 2970, 2·03; 130·5°, 3370, 1·90.

Physical Measurements.—The infrared spectrum of rhenium trisacetylacetonate was recorded in a Perkin–Elmer model 21 double-beam infrared spectrophotometer with sodium chloride optics for a Nujol mull. Magnetic measurements were made by the Gouy method; susceptibilities are corrected for diamagnetism of ligands.[21] Conductivity measurements were made in anhydrous nitrobenzene with a type E7566 Mullard bridge; visible spectra were recorded by using a Unicam S.P. 500 spectrophotometer.

The polarographic reduction of bis(triphenylphosphine)rhenium trichloride was made by using a Tinsley 19/2 recording polarograph.

Rhenium Analyses.—The complexes were oxidised by fusing them with sodium hydroxide and peroxide and extracting the melt with water. The rhenium content was then determined spectrophotometrically by the furil α-dioxime method.[22]

The authors thank Johnson, Matthey and Co. Ltd. for the loan of rhenium metal, the Atomic Energy Authority, Harwell (R. C.), and the Consejo Nacional de Investigaciones Científicas y Técnicas of the Argentine Republic (R. L.) for financial support.

INORGANIC CHEMISTRY LABORATORIES, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.
[*Received, April 6th,* 1960.]

---

[21] Selwood, "Magnetochemistry," Interscience Publ. Inc., New York 1956.
[22] Meloche, Martin, and Webb, *Analyt. Chem.*, 1957, **29**, 527.