

77.  $\beta$ -Diketone Complexes of Rhenium.

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We have prepared the series of compounds  $\text{ReOCl}_2(\text{acac})\text{PPh}_3$ ,  $\text{ReCl}_2(\text{acac})(\text{PPh}_3)_2$ ,  $\text{ReCl}(\text{acac})_2\text{PPh}_3$ , and  $\text{Re}_2\text{Cl}_4(\text{acac})_4$  by the interaction of acetylacetonone ( $\text{acacH}$ ) and  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ . The bromides and iodides of some of these are described, together with similar compounds of  $\text{PET}_2\text{Ph}$  and other  $\beta$ -diketones.

The compound  $\text{Re}_2\text{Cl}_4(\text{acac})_4$  is considered to have acetylacetonato-groups bridging the metal atoms.

We have shown that the alkoxy-complexes  $\text{ReOCl}_2(\text{OR})(\text{PPh}_3)_2$  isomerise rapidly in solution in organic solvents.

In previous papers we have described the reactions of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$  and  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  with amines<sup>1,2</sup> and cyanide ion;<sup>3</sup> this work describes the reactions of the tertiary phosphine complexes with  $\beta$ -diketones. The only previously reported  $\beta$ -diketone complex of rhenium is tris(pentane-2,4-dionato)rhenium(III) prepared from rhenium dioxide and acetylacetonone.<sup>4</sup>

*Acetylacetonates.*—The initial product of the interaction of  $\text{ReOX}_2(\text{OEt})(\text{PPh}_3)_2$  ( $X = \text{Cl, Br, or I}$ ) and acetylacetonone is the green acetylacetonato ( $\text{acac}$ ) complex  $\text{ReOX}_2(\text{acac})(\text{PPh}_3)_2$ . These rhenium(v) oxo-compounds all have a strong band in their infrared spectra in the region expected for the  $\nu_{\text{Re=O}}$  vibration<sup>1</sup> (see Table) and all are diamagnetic; this is unexpected for a  $d^2$  complex, but the explanation is probably the same as that for the diamagnetism of *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$  discussed previously.<sup>1</sup> These green complexes are difficult to prepare pure since they rapidly react further with excess of acetylacetonone to give the compounds described below. They are best prepared from the purple isomer of  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ , rather than the green isomer,<sup>1</sup> since the colour change during the reaction may be observed and the reaction halted when the green colour is at a maximum.

When benzene solutions of  $\text{ReOX}_2(\text{OEt})(\text{PPh}_3)_2$  ( $X = \text{Cl, Br or I}$ ) are boiled with acetylacetonone the rhenium(v) complex is reduced to the orange-red rhenium(III) complex  $\text{ReX}_2(\text{acac})(\text{PPh}_3)_2$ . These six-co-ordinate complexes have a  $d^4$  configuration and are expected to be paramagnetic, as is found. The paramagnetism of the complexes  $\text{ReX}_2(\text{acac})(\text{PPh}_3)_2$  ( $X = \text{Cl or Br}$ ) has been investigated in the solid state over a temperature range. The plot of  $\mu_{\text{eff}}$  (B.M.) against  $T^{\frac{1}{2}}$  ( $^{\circ}\text{K}^{\frac{1}{2}}$ ) is linear; this can be compared with the linear variation predicted by the Kotani theory for a regular octahedral  $d^4$  system.<sup>5,6</sup> The values of  $\mu_{\text{eff}}$  at 300°K are 1.4 B.M. for the chloride and 1.6 B.M. for the bromide, compared with previously found values for rhenium(III) compounds of 2.1 B.M. for  $[\text{ReCl}_2(o\text{-phenylenebisdimethylarsine})_2]\text{ClO}_4$ ,<sup>5</sup> 1.65 B.M. for  $\text{ReI}_3[\text{P}(\text{OPh})_3]_3$ ,<sup>7</sup> and 2.3 B.M. for  $\text{Re}(\text{acac})_3$ .<sup>4</sup>

*Other  $\beta$ -Diketones.*—When a benzene solution of  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  was heated with excess of 1,1,1-trifluoropentane-2,4-dione, 1,1,1,5,5,5-hexafluoropentane-2,4-dione or 4,4,4-trifluoro-1,2'-thienyl-1,3-butanedione,  $\beta$ -diketone complexes of rhenium(III) similar to those described above with acetylacetonone, were obtained.

The compound  $\text{ReOCl}_2(\text{OEt})(\text{PET}_2\text{Ph})_2$  reacted with acetylacetonone in the same way as the  $\text{PPh}_3$  compound, described above, to give an oxo complex of rhenium(v) and a complex of rhenium(III).

*The Acetylacetonato-bridged Complex.*—When a solution of  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  in

<sup>1</sup> N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J.*, 1964, 1054.

<sup>2</sup> N. P. Johnson, F. Taha, and G. Wilkinson, *J.*, 1964, 2614.

<sup>3</sup> C. J. L. Lock and G. Wilkinson, *J.*, 1964, 2281.

<sup>4</sup> R. Colton, R. Levitus, and G. Wilkinson, *J.*, 1960, 4121.

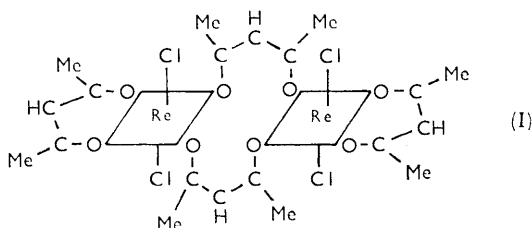
<sup>5</sup> B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," ch. 6, ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.

<sup>6</sup> M. Kotani, *J. Phys. Soc. Japan*, 1949, 4, 293.

<sup>7</sup> M. Freni and V. Valenti, *Gazzetta*, 1960, 90, 1436.

acetylacetonone was refluxed, the reaction proceeded further than in benzene solution. The initial product was  $\text{ReCl}(\text{acac})_2\text{PPh}_3$  and, on prolonged reaction, the product was  $\text{Re}_2\text{Cl}_4(\text{acac})_4$ . The magnetic moment of this dimer, measured in dichloromethane solution, was  $2.9 \pm 0.2$  B.M. per rhenium atom at  $20^\circ$ , in agreement with the value of  $3.2$  B.M. found for  $\text{K}_2[\text{ReCl}_6]$ ,<sup>5</sup> indicating three unpaired electrons per rhenium atom.

The only structure that, in a simple way, satisfies the results is where the octahedral  $\text{Re}(\text{IV}) d\epsilon^3$  configuration is preserved by the formation of acetylacetonato-bridges. There



is no evidence at present to show whether the chlorine atoms in this structure are *cis* or *trans* to each other. All other possible structures involving either metal-metal bonds or bridging halides would involve 7-co-ordinate rhenium(IV), unless one of the acetylacetonato-groups were bound through only one oxygen, and this possibility is excluded by the infrared spectrum, which shows no band in the unco-ordinated keto region. Any such 7-co-ordinate structure that would give three unpaired spins per rhenium atom then must involve utilisation in bonding of outer  $6d$  orbitals, and this would appear to be energetically less favourable than the stereochemistry involved in the structure shown. The complex gave no simple cleavage products when heated with excess of pyridine in chloroform solution, which suggests the absence of chloride bridges.

While we are not aware of any bridging acetylacetonato-groups of this particular type (in  $\text{Ni}_3(\text{acac})_6$  one oxygen is 3-co-ordinate,<sup>8</sup> while in  $[\text{PtMe}_3(\text{acac})_2]$  there is a Pt-C bond to the centre carbon of the acetylacetonate group<sup>9</sup>), there seems no reason why they should not occur; the Re-Re distance with such a structure should be large enough to eliminate any spin-spin interaction.

*Isomerisation of Oxodichloroethoxobis(triphenylphosphine)rhenium(V).*—The visible spectrum of a solution of the green isomer of  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ <sup>1</sup> in dry benzene has been observed to be time-dependent at ordinary temperatures, indicating quite rapid isomerisation, presumably to an equilibrium mixture, over a period of several hours. This was confirmed by the isomerism within 3 hours in refluxing benzene-ethanol<sup>1</sup> of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  to the purple isomer. A further slow reaction, possibly disproportionation, occurs, as is shown by the conversion of a solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  in dry benzene into *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$  when it is shaken for 4 days at  $20^\circ$ . The visible spectrum of a Nujol mull of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  is time-independent, indicating that such changes do not occur in the solid.

Similar rapid spectroscopic changes at room temperature were found in the benzene solution spectra of purple  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ ,<sup>1</sup>  $\text{ReOCl}_2(\text{OEt})(\text{PEt}_2\text{Ph})_2$ ,<sup>10</sup>  $\text{ReOBr}_2(\text{OEt})(\text{PPh}_3)_2$ ,  $\text{ReOI}_2(\text{OEt})(\text{PPh}_3)_2$ ,  $\text{ReOCl}_2(\text{OMe})(\text{PPh}_3)_2$ , and  $\text{ReOI}_2(\text{OMe})(\text{PPh}_3)_2$ .<sup>1</sup> These changes were apparent immediately the compounds had dissolved, and hence dipole-moment measurements of these compounds<sup>10</sup> are probably meaningless.

The spectrum of a fresh benzene solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  showed a maximum at about  $535 \text{ m}\mu$  ( $\epsilon \sim 40$ ) and a minimum at about  $490 \text{ m}\mu$  at room temperature. As time progressed, the absorbance increased and the positions of the maximum and minimum moved. There is a charge-transfer band at about  $450 \text{ m}\mu$ . The spectrum of the purple isomer appeared as a series of shoulders on the charge-transfer band. As expected,

<sup>8</sup> G. J. Bullen, R. Mason, and P. J. Pauling, *Nature*, 1961, **189**, 291.

<sup>9</sup> A. G. Swallow and M. R. Truter, *Proc. Roy. Soc.*, 1960, **A254**, 205.

<sup>10</sup> J. Chatt and G. A. Rowe, *J.*, 1962, 4019.

the spectra were temperature-dependent: if a hot solution was allowed to cool, as time progressed the absorbance decreased. This can be explained by assuming that an equilibrium is set up in solution and is temperature-dependent but kinetically controlled, the high temperature equilibrium being composed of predominantly high absorbing (higher  $\epsilon$ ) compound. Thus on cooling, this equilibrium is quenched and the absorbance decreases as time progresses. We do not intend to study these systems in more detail.

$\beta$ -Diketonato complexes of rhenium.

Compound	Colour	M. p.	Infrared $\nu_{\text{Re=O}}$ (cm. <sup>-1</sup> )	$\mu_{\text{eff}}$ B.M. at 300°K
ReOCl <sub>2</sub> (acac)PPh <sub>3</sub> .....	Green	167—170°	979	Diamag.
ReOBr <sub>2</sub> (acac)PPh <sub>3</sub> .....	Green		976	Diamag.
ReOI <sub>2</sub> (acac)PPh <sub>3</sub> .....	Green		975	
ReOCl <sub>2</sub> (acac)PEt <sub>2</sub> Ph .....	Green		976	
ReCl <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> .....	Orange	182—185		1.4
ReBr <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> .....	Orange	187—193		1.6
ReI <sub>2</sub> (acac)(PPh <sub>3</sub> ) <sub>2</sub> .....	Red	176—177		
ReCl <sub>2</sub> (acac)(PEt <sub>2</sub> Ph) <sub>2</sub> .....	Orange			
ReCl <sub>2</sub> (CF <sub>3</sub> COCHCOCF <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> .....	Deep blue	124—127		
ReCl <sub>2</sub> (CF <sub>3</sub> COCHCOCH <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ...	Purple-red	191—192		
ReCl <sub>2</sub> (T. T. A.)(PPh <sub>3</sub> ) <sub>2</sub> .....	Lilac	188—192		
ReCl(acac) <sub>2</sub> PPh <sub>3</sub> .....	Orange	198—199		
Re <sub>2</sub> Cl <sub>4</sub> (acac) <sub>4</sub> .....	Orange	297—299 (decomp.)		2.9

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratories of Imperial College. Infrared spectra were recorded in Nujol mulls on a Grubb-Parsons Spectromaster. Magnetic measurements of solids were made on a Gouy balance fitted with a temperature control, and in solution by the Evans n.m.r. method. All measurements are corrected for the diamagnetism of the ligands.<sup>11</sup> Melting points were determined on a Kofler hot stage apparatus and are corrected. Molecular weights were determined with a Mechrolab Osmometer operating at 37°, unless otherwise stated. All reactions were carried out under nitrogen, unless otherwise stated.

*Oxodichloro(pentane-2,4-dionato)triphenylphosphinerhenium(v)*.—A solution of purple ReOCl<sub>2</sub>(OEt)(PPh<sub>3</sub>)<sub>2</sub><sup>1</sup> (2 g.) in pentane-2,4-dione (2 ml.) in benzene (50 ml.) was boiled until it turned bright green (about 1 min.) and then poured into light petroleum (b. p. 40—60°; 400 ml.). The mixture was treated in one of two ways:

(a) The mixture was stirred vigorously and the precipitate allowed to settle. If the supernatant liquid was still appreciably green, it was decanted and set aside, green crystals of the compound separating; these were hand-picked from some orange material.

(b) The mixture was stirred vigorously and set aside until the green crystals had settled. The supernatant liquid containing most of the orange material was decanted off. This procedure was repeated with fresh portions of light petroleum (b. p. 40—60°) until practically all the orange material had been removed. The green crystals were hand-picked from any remaining orange material.

The green product from either (a) or (b) was recrystallised by slow evaporation of its benzene solution and washed with diethyl ether to give *prisms* (0.2 g., 10%) [Found: C, 43.0; H, 3.6; Cl, 12.0; O, 7.4; P, 4.7%; *M* (ebullioscopic in benzene), 610. C<sub>23</sub>H<sub>22</sub>Cl<sub>2</sub>O<sub>3</sub>PRe requires C, 43.5; H, 3.5; Cl, 11.2; O, 7.6; P, 4.9%; *M*, 635]. The compound was diamagnetic in benzene solution, soluble in dichloromethane, benzene, chloroform and acetone, sparingly soluble in ethanol and diethyl ether and insoluble in petroleum and carbon tetrachloride.

*Oxodibromo(pentane-2,4-dionato)triphenylphosphinerhenium(v)*.—This was prepared from ReOBr<sub>2</sub>(OEt)(PPh<sub>3</sub>)<sub>2</sub> (2 g.) in a similar manner to the preparation of the chloride, and crystallised in *prisms* (15%) [Found: C, 38.7; H, 3.1; Br, 22.7%; *M* (ebullioscopic in benzene), 660. C<sub>23</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>3</sub>PRe requires C, 38.2; H, 3.1; Br, 22.1%; *M*, 723]. The compound was diamagnetic and similar to the chloro compound.

*Oxodi-iodo(pentane-2,4-dionato)triphenylphosphinerhenium(v)*.—This compound was prepared in a similar manner to that of the above, starting from ReOI<sub>2</sub>(OEt)(PPh<sub>3</sub>)<sub>2</sub>, but has not been prepared pure because of the similar solubility of the red product of the reaction.

*Oxodichloro(pentane-2,4-dionato)diethylphenylphosphinerhenium(v)*.—This was prepared from

<sup>11</sup> P. W. Selwood, "Magnetochemistry," Interscience, New York, 1956.

$\text{ReOCl}_2(\text{OEt})(\text{PET}_2\text{Ph})_2$ <sup>10</sup> in a similar manner to the preparation of the chloro compound of triphenylphosphine and was separated by method (b) as *prisms* (20%) (Found: C, 33.8; H, 4.0.  $\text{C}_{15}\text{H}_{22}\text{Cl}_2\text{O}_3\text{PRe}$  requires C, 33.5; H, 4.1%). The compound was similar to the compound of  $\text{PPh}_3$ , but more soluble in organic solvents.

*Dichloro(pentane-2,4-dionato)bis(triphenylphosphine)rhenium(III)*.—A solution of purple  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (2 g.) and pentane-2,4-dione (2 ml.) in benzene (30 ml.) was boiled under reflux for 6 hr., concentrated to 15 ml., and allowed to cool. The crystals were washed with a little benzene and diethyl ether to give *prisms* (0.5 g., 25%) (Found: C, 55.9; H, 4.3; Cl, 8.0; O, 4.0; P, 6.9%; *M* (ebullioscopic in benzene), 911.  $\text{C}_{41}\text{H}_{37}\text{Cl}_2\text{O}_2\text{P}_2\text{Re}$  requires C, 55.9; H, 4.2; Cl, 8.1; O, 3.6; P, 7.0%; *M*, 881). The compound was soluble in dichloromethane, sparingly soluble in ethanol, benzene, and chloroform, slightly soluble in diethyl ether and insoluble in carbon tetrachloride and petroleum. At the given temperatures ( $^{\circ}\text{K}$ ), the susceptibilities (corrected, in c.g.s. units  $\times 10^6$ ) and values of  $\mu_{\text{eff}}$  are at 293.0 $^{\circ}$ , 797, 1.37; 248.3 $^{\circ}$ , 797, 1.27; 233.0 $^{\circ}$ , 797, 1.22; 223.0 $^{\circ}$ , 797, 1.20; 197.3 $^{\circ}$ , 728, 1.07; 161.2 $^{\circ}$ , 728, 0.97; 142.7 $^{\circ}$ , 694, 0.89; 125.0 $^{\circ}$ , 694, 0.84; 87.0 $^{\circ}$ , 555, 0.63.

*Dibromo(pentane-2,4-dionato)bis(triphenylphosphine)rhenium(III)*.—This was prepared from  $\text{ReOBr}_2(\text{OEt})(\text{PPh}_3)_2$  (4 g.) in a similar manner to the preparation of the chloro complex, and reprecipitated from hot benzene with light petroleum (b. p. 30–40 $^{\circ}$ ) as *prisms* (1.27 g., 30%) (Found: C, 50.5; H, 3.9; Br, 17.0; O, 4.0; P, 6.1.  $\text{C}_{41}\text{H}_{37}\text{Br}_2\text{O}_2\text{P}_2\text{Re}$  requires C, 50.8; H, 3.9; Br, 16.5; O, 3.3; P, 6.4%). At the given temperatures ( $^{\circ}\text{K}$ ), the susceptibilities (corrected, in c.g.s. units  $\times 10^6$ ) and values of  $\mu_{\text{eff}}$  are at 295.3 $^{\circ}$ , 1016, 1.55; 194.0 $^{\circ}$ , 1016, 1.26; 157.7 $^{\circ}$ , 965, 1.11; 180.8 $^{\circ}$ , 1033, 1.23; 167.8 $^{\circ}$ , 999, 1.16; 143.3 $^{\circ}$ , 1033, 1.09; 131.3 $^{\circ}$ , 982, 1.02; 126.3 $^{\circ}$ , 932, 0.98; 220.0 $^{\circ}$ , 1033, 1.35.

*Di-iodo(pentane-2,4-dionato)bis(triphenylphosphine)rhenium(III)*.—This was prepared from  $\text{ReOI}_2(\text{OEt})(\text{PPh}_3)_2$  (1.24 g.) in a similar manner to the preparation of the chloro complex as *needles* (0.4 g., 31%) (Found: C, 45.9; H, 3.7.  $\text{C}_{41}\text{H}_{37}\text{I}_2\text{O}_2\text{P}_2\text{Re}$  requires C, 46.3; H, 3.5%).

*Dichloro(pentane-2,4-dionato)bis(diethylphenylphosphine)rhenium(III)*.—This was prepared in the same way as the above compounds, starting from *trans*- $\text{ReOCl}_3(\text{PET}_2\text{Ph})_2$ <sup>10</sup> as *prisms* (25%) (Found: C, 43.8; H, 5.4.  $\text{C}_{25}\text{H}_{37}\text{Cl}_2\text{O}_2\text{P}_2\text{Re}$  requires C, 43.6; H, 5.4%). The compound was more soluble in organic solvents than  $\text{ReCl}_2(\text{acac})(\text{PPh}_3)_2$ .

*Dichloro-(1,1,1-trifluoropentane-2,4-dionato)bis(triphenylphosphine)rhenium(III)*.—A solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (1 g.) and 1,1,1-trifluoropentane-2,4-dione (2 ml.) in benzene (40 ml.) was heated under reflux for 15 min., cooled and light petroleum (b. p. 30–40 $^{\circ}$ ) added. The product was collected and reprecipitated from benzene with light petroleum (b. p. 30–40 $^{\circ}$ ) as *needles* (0.68 g., 61%) [Found: C, 53.2; H, 4.0%; *M*, 838 (chloroform), 941 (benzene).  $\text{C}_{41}\text{H}_{34}\text{Cl}_2\text{F}_3\text{O}_2\text{P}_2\text{Re}$  requires C, 52.7; H, 3.7%; *M*, 934].

*Dichloro-(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis(triphenylphosphine)rhenium(III)*.—This was prepared and purified in the same way as the above from green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (0.95 g.) and 1,1,1,5,5,5-hexafluoropentane-2,4-dione (2 ml.) in benzene (40 ml.); *microcrystals* (0.79 g., 71%) [Found: C, 49.3; H, 3.2; F, 11.5%; *M*, 986 (benzene).  $\text{C}_{41}\text{H}_{31}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_2\text{Re}$  requires C, 49.8; H, 3.1; F, 11.5%; *M*, 989].

*Dichloro-[4,4,4-trifluoro-1-2'-thienylbutane-1,3-dionato]bis(triphenylphosphine)rhenium(III)*.—This compound was prepared and purified in the same way as the compound above from green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (0.5 g.) and thenoyltrifluoroacetone (0.25 g.) in benzene (30 ml.); *needles* (0.26 g., 44%) [Found: C, 52.6; H, 3.6; S, 3.5%; *M*, 1059 (chloroform).  $\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{F}_3\text{O}_2\text{P}_2\text{ReS}$  requires C, 52.7; H, 3.4; S, 3.2%; *M*, 1002].

*Chlorobis(pentane-2,4-dionato)triphenylphosphinerhenium(III)*.—A solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (3.33 g.) in pentane-2,4-dione (30 ml.) was heated under reflux for 16 hr. and cooled. The product was collected, refluxed in benzene for 16 hr., exposed to the atmosphere, and cooled, and the product precipitated with diethyl ether as *prisms* (0.60 g., 22%) [Found: C, 49.0; H, 4.1; O, 9.3%; *M*, 683 (chloroform).  $\text{C}_{28}\text{H}_{29}\text{ClO}_4\text{PRe}$  requires C, 49.3; H, 4.3; O, 9.4%; *M*, 682].

*Tetrachlorobis(pentane-2,4-dionato)- $\mu_2$ -(pentane-2,4-dionato)-dirhenium(IV)*.—A solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (4.28 g.) in pentane-2,4-dione (40 ml.) was refluxed for 50 hr. and cooled. The product was collected and reprecipitated from chloroform with light petroleum (b. p. 30–40 $^{\circ}$ ) as *microcrystals* (1.15 g., 25%) [Found: C, 26.5; H, 2.7; Cl, 15.4; O, 14.4%; *M*, 939 (chloroform); 909 (ebullioscopic in chlorobenzene).  $\text{C}_{20}\text{H}_{28}\text{Cl}_4\text{O}_3\text{Re}_2$  requires C, 26.4; H, 3.1; Cl, 15.6; O, 14.1%; *M*, 911].

*Decomposition of Green*  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$ .—A solution of green  $\text{ReOCl}_2(\text{OEt})(\text{PPh}_3)_2$  (1 g.) in benzene (60 ml.) was shaken at  $20^\circ$  for 4 days. The insoluble product was collected and washed with diethyl ether to give *trans*- $\text{ReOCl}_3(\text{PPh}_3)_2$  as *prisms* (0.3 g., 30%) (Found: C, 51.7; H, 3.8. Calculated for  $\text{C}_{36}\text{H}_{30}\text{Cl}_3\text{OP}_2\text{Re}$ : C, 51.9; H, 3.6%). The infrared spectrum has a strong band at  $967\text{ cm}^{-1}$  ( $\text{Re}=\text{O}$ ) and no band at  $910\text{ cm}^{-1}$  ( $\text{OEt}$ ),<sup>1</sup> and was identical with that of the authentic specimen.

We thank Albright and Wilson (Mfg.) Ltd. for gifts of triphenylphosphine and the Hercules Powder Company for financial support.

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[Received May 26th, 1964.]

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