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THE REACTION OF RHENIUM CARBONYL WITH DIMETHYLPHENYLPHOSPHINE AND DIMETHYLPHENYLARSINE

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SUMMARY

Dirhenium decacarbonyl reacts with dimethylphenylphosphine and arsine to give compounds $[Re(CO)_4(XMe_2Ph)]_2$ $Re(CO)_3(XMe_2Ph)_2$ and $Re_2(CO)_7(XMe_2Ph)_3$ ($X = P$ or As). Addition of chlorinated solvents to the crude reaction product results in the isolation of additional compounds such as *fac*-$Re(CO)_3(AsMe_2Ph)_2Cl$, *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$, *fac*-$Re(CO)_3(PMe_2Ph)_2Cl$ and $Re(CO)_2(PMe_2Ph)_3Cl$. Reactions of $[Re(CO)_4(PMe_2Ph)]_2$ and $[Re(CO)_4(AsMe_2Ph)]_2$ with hydrochloric acid gas and halogens results in the formation of halogeno compounds *cis*-$Re(CO)_4(PMe_2Ph)Cl$, *cis*- and *trans*-$Re(CO)_4(PMe_2Ph)Br$, *cis*- and *trans*-$Re(CO)_4(PMe_2Ph)I$, *cis*-$Re(CO)_4(AsMe_2Ph)Cl$ and *cis*-$Re(CO)_4(AsMe_2Ph)Br$. The compound $Re_2(CO)_7(PMe_2Ph)_3$ reacts with dry HCl gas, molar quantities of bromine and iodine to give the compounds, *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$, *trans*-$Re(CO)_3(PMe_2Ph)_2Br$, *trans*-$Re(CO)_3(PMe_2Ph)_2I$, *cis*-$Re(CO)_4(PMe_2Ph)Cl$, *cis*-$Re(CO)_4(PMe_2Ph)Br$ and *trans*-$Re(CO)_4(PMe_2Ph)I$. When $Re_2(CO)_7(PMe_2Ph)_3$ was reacted with an excess of bromine at 0° the compounds $Re(CO)(PMe_2Ph)_2Br_3$ and $Re(PMe_2Ph)_2Br_4$ were isolated.

The IR and proton NMR spectra of these new compounds are discussed. The mass spectra of a number of these compounds have been recorded and are also discussed.

INTRODUCTION

Rhenium carbonyl is a rather inert molecule. Reaction of rhenium carbonyl with π-ligands such as R_3P ($R = Ph$), $(C_2H_5)_2Ph$[1,2] and phosphites $[(PhO)_3P]$[3] under moderate conditions have resulted only in the replacement of two of the carbonyl groups with the formation of compounds such as $[Re(CO)_4PR_3]_2$, $[Re(CO)_3(PR_3)_2]_2$ and $Re(CO)_3(PR_3)_2$. Nyman[4] reported that increased yields were obtained when the reactions were carried out by irradiation with UV light. He reported the

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formation of one main product when $Re_2(CO)_{10}$ was reacted with triphenylphosphine for 10 h, namely $[Re(CO)_4PPh_3]_2$ to which he assigned a D_{4h} or D_{4d} symmetry due to the presence of two carbonyl stretching bands in the IR spectrum, analogous to the manganese compound $[Mn(CO)_4PPh_3]_2$ reported by Nyholm[5] *et al.* This has been confirmed by later workers such as Stone[2] and Freni[6]. Freni also achieved further substitution in the case of rhenium carbonyl by using drastic conditions with 1,2-bis(diphenylphosphino)ethane as the ligand to yield compounds such as $Re(CO)(DFE)_2$. $[DFE = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$.

We have reacted the basic phosphines dimethylphenylphosphine and dimethylphenylarsine under both thermal and UV conditions for different time periods and find that up to three ligands can be added to a rhenium atom, *viz.* the formation of $Re(CO)_2(PMe_2Ph)_3Cl$ and that unsymmetrically substituted products can be isolated *e.g.* $Re_2(CO)_7(PMe_2Ph)_3$.

When these reactions are activated by irradiation a number of different products are formed and these have been readily separated and purified by chromatography; as many as five products being isolated from one reaction.

Both $[Re(CO)_4(PMe_2Ph)]_2$ and $[Re(CO)_4(AsMe_2Ph)]_2$, analogous to the triphenylphosphine compound reported by Nyman[4] have been isolated but the IR spectra shows five bands in the carbonyl stretching region of the IR spectrum and so cannot have D_{4h} or D_{4d} symmetry.

Substituted halocarbonyl complexes of rhenium have been prepared by the reaction of halogens on compounds such as $Re(CO)_3(PR_3)_2$ and by the action of π-ligands on halocarbonyl complexes[7,8]. We have found that similar chloro compounds may be prepared by the addition of a chlorinated solvent such as dichloromethane to the products formed by the reaction of $Re_2(CO)_{10}$ and dimethylphenylphosphine and dimethylphenylarsine.

The IR spectra, NMR spectra and the mass spectra of some compounds have been recorded and are discussed in respect to the structure of these compounds.

EXPERIMENTAL

Microanalysis of the compounds for C, H and O were performed by the Microanalytical Laboratory at this University using a Perkin–Elmer Elemental Analyzer model 240. The rhenium metal analyses were performed using a colorimetric method described by Meloche, Martin and Webb[9], which is based on the formation of a red coloured rhenium α-furildioxime complex.

Molecular weights were determined using a Mechrolab Model 301A osmometer in chloroform solution at 37°.

Melting points were determined on a Kofler hot stage melting point apparatus and are corrected.

Dimethylphenylphosphine and dimethylphenylarsine were prepared in this laboratory.

All reactions were carried out under nitrogen and the rhenium carbonyl was purchased from Alfa Inorganic Chemicals Inc.

The NMR spectra were recorded on a Hitachi–Perkin–Elmer R20 spectrometer and the IR spectra were recorded on a Perkin–Elmer 521 spectrometer.

The mass spectra were recorded by Varian M.A.T. of Bremen, Germany, using a Varian CH7 mass spectrometer. The operating conditions were 70 eV electron energy and a source temperature of 200°.

Irradiation of $Re_2(CO)_{10}$ and dimethylphenylphosphine with UV light

Preparation of $[Re(CO)_4(PMe_2Ph)]_2$, $Re(CO)_3(PMe_2Ph)_2$, $Re_2(CO)_7(PMe_2Ph)_3$ and cis- and trans-$Re(CO)_3(PMe_2Ph)_2Cl$

$Re_2(CO)_{10}$ (3.10 g, 4.24 mmoles) and dimethylphenylphosphine (1.30 g, 9.4 mmoles) were dissolved in 80 ml of petroleum ether (60°–80°) and the solution irradiated for 6 h. The solution assumed a yellow colour with the formation of an oily residue. 10 ml of dichloromethane used to dissolve the residue, and this added to main solution and all evaporated to dryness to yield 4.2 g of crude material. Crude material then chromatographed using alumina and dichloromethane/petroleum ether (4/10) as eluant and three products were separated. 30 fractions of 12 ml each were collected. Fraction 1–3 contained unused $Re_2(CO)_{10}$ and dimethylphenylphosphine.

Evaporation of fractions 4–6 yielded pale yellow plates. Crystallized from ethyl acetate/petroleum ether or ethyl acetate/methanol to yield 123 mg. M.p. 158°. Yield: 4.36%. {Found: C, 32.99; H, 2.50; O, 14.01; Re, 41.08. $C_{24}H_{22}O_8P_2Re_2$, $[Re(CO)_4(PMe_2Ph)]_2$, calcd.: C, 33.00; H, 2.53; O, 14.64; Re, 42.50%.}

Evaporation of fractions 8–12 yielded 66 mg of pale yellow material. Crystallized from methanol to yield 60 mg of pale yellow needle like crystals. M.p. 101°. Yield; 1.6%. [Found: C, 41.87; H, 4.27; O, 7.81; Re, 34.50; mol.wt., 546. $C_{19}H_{22}O_3P_2Re$, $Re(CO)_3(PMe_2Ph)_2$, calcd.: C, 41.60; H, 4.05; O, 7.90; Re, 34.10%; mol.wt., 546.]

Evaporation of fractions 14–20 yielded a brownish white residue. Crystallization from ethyl acetate by the addition of methanol yielded 420 mg of white prisms, m.p. 148°. Yield: 13.4%. [Found: C, 37.51; H, 3.43; O, 11.57; Re, 37.90; mol.wt. (Osmometer), 990. $C_{31}H_{33}O_7P_3Re_2$, $Re_2(CO)_7(PhMe_2Ph)_3$, calcd.: C, 37.80; H, 3.35; O, 11.40; Re, 37.52%; mol.wt., 982.89.]

A brown material was left on the top of the alumina column. This was eluted with ethanol; evaporation of the ethanol left a dark brown oil. This oil was pumped on for 12 h (25°/0.5 mm), dissolved in hot methanol and set aside at −20° for 12 h, whereupon 590 mg of yellow needle like crystals and pearly white prisms crystallized out. Crystals filtered off, dried (50°/1 mm) and dissolved in a minimum of ethyl acetate and separated chromatographically using alumina and ethyl acetate/petroleum ether as eluant. A good separation of isomers was achieved to yield 226 mg of *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$, yellow needles, m.p. 132° and 359 mg of *fac*-$Re(CO)_3(PMe_2Ph)_2Cl$, white blades, m.p. 134°. Both isomers may be readily crystallized from methanol. [Found: C, 39.08; H, 3.82; O, 8.57; Re, 31.5; mol.wt. osmometer, 581. $C_{19}H_{22}ClO_3P_2Re$ (*trans*-isomer) calcd.: C, 39.18; H, 3.79; O, 8.26; Re, 31.8%; mol.wt., 582.02.] [Found: C, 38.95; H, 3.79; O, 8.60; Re, 31.5; mol.wt. osmometric, 581. $C_{19}H_{22}ClO_3P_2Re$ (*fac*-isomer) calcd.: C, 39.18; H, 3.79; O, 8.26; Re, 31.8%; mol.wt., 582.02.]

Reaction of dimethylphenylphosphine with $Re_2(CO)_{10}$ in cyclohexane

Preparation of $Re_2(CO)_7(PMe_2Ph)_3$ and trans-$Re(CO)_3(PMe_2Ph)_2Cl$

$Re_2(CO)_{10}$ (3.10 g) and dimethylphenylphosphine (1.30 g) dissolved in cyclohexane and irradiated with UV light for 3 h. Evaporated to dryness to yield 4.3 g of orange crude material. Dissolved in dichloromethane and separated chromatographically on alumina using ethanol/petroleum ether (1/10) to yield two products.

400 mg of $Re(CO)_7(PMe_2Ph)_3$ obtained, m.p. 148°. Crystallized from ethyl acetate/petroleum ether to yield white prisms.

45 mg of *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$ was obtained; m.p. 132°. Crystallized from methanol to yield yellow needles.

Thermal reaction of dimethylphenylphosphine and $Re_2(CO)_{10}$

Preparation of $Re(CO)_2(PMe_2Ph)_3Cl$, $[Re(CO)_4(PMe_2Ph)]_2$ and $Re(CO)_3(PMe_2Ph)_2$

(*a*). $Re_2(CO)_{10}$ (3.1 g, 4.22 mmoles) and dimethylphenylphosphine (1.30 g, 9.4 mmoles) were dissolved in 150 ml of petroleum ether (100–120°) and refluxed under nitrogen for 60 h. The colourless solution gradually assumed a pale yellow colour. The petroleum ether removed under vacuum (20°/1 mm) to leave 3.8 g of crude material. Crude material was chromatographed on alumina with ethyl acetate/petroleum ether (2/10) to yield three products. 30 fractions of 12 ml each were collected after "washing" the crude material on the column with 50 ml of petroleum ether to remove any dimethylphenylphosphine.

Fractions 1–4 contained 0.82 g of unreacted rhenium carbonyl.

Fractions 6–10 contained 150 mg of pale yellow material, crystallized from methanol at −20° to yield pale yellow radiating crystals of $[Re(CO)_4(PMe_2Ph)]_2$ (115 mg), m.p. 156°. Yield: 4.08%.

Fractions 13–16 yielded light yellow material which was crystallized from methanol to yield 37 mg of yellow crystals of $Re(CO)_3(PMe_2Ph)_2$ m.p. 100°. Yield: 1.0%.

Fractions 18–20 yielded a pale brown residue on evaporation. Crystallization from ethyl acetate/petroleum ether yielded 26 mg of shiny white prisms of $Re_2(CO)_7(PMe_2Ph)_3$, m.p. 147°. Yield: 0.8%.

(*b*). $Re_2(CO)_{10}$ (3.1 g, 4.24 mmoles) and dimethylphenylphosphine (1.30 g, 9.4 mmoles) were dissolved in 150 ml of petroleum ether (80–100°) and refluxed under nitrogen. The course of reaction followed chromatographically and after 48 h no phosphine ligand remained but $Re_2(CO)_{10}$ was still present and so another 1.1 g of PMe_2Ph was added. This was repeated after 72 h when an additional 0.5 g of phosphine was added and the reaction was stopped after refluxing for 96 h. The solution was evaporated to dryness to yield 6 g of yellow oil. Crude material dissolved in dichloromethane and chromatographed on alumina using ethyl acetate/petroleum ether (2/10) as eluant to yield three distinct products. 30 fractions of 12 ml each collected.

Evaporation of fractions 3–4 yielded 160 mg of white pentagonal plates m.p. 152°. [Found: C, 44.98; H, 4.81; mol.wt. mass spec., 692. $C_{26}H_{33}ClO_2P_2Re$, $Re(CO)_2(PMe_2Ph)_3Cl$, calcd.: C, 45.00; H, 4.80%; mol.wt., 692.17.]

Evaporation of fractions 6–12 yielded 1.52 g of pale yellow material which was rechromatographed to yield 1.31 g of pale yellow crystals. M.p. 158°, *i.e.* $[Re(CO)_4(PMe_2Ph)]_2$. Yield: 46%.

Evaporation of fractions 14–20 yielded light yellow material which was crystallized from methanol to yield 195 mg of pale yellow crystals. M.p. 101°, *i.e.* $Re(CO)_3(PMe_2Ph)_2$. Yield: 5.5%.

Preparation of cis-$Re(CO)_4(PMe_2Ph)Cl$

Tetracarbonyl(dimethylphenylphosphine)rhenium dimer (100 mg) was suspended in 10 ml of CCl_4 at 0°, and dry HCl gas was slowly bubbled through the solution. The solution gradually changed from a pale yellow to a colourless solution. Solution was evaporated (20°/1 mm) to dryness to yield 106 mg of crude material. Crude material dissolved in ether and crystallized by the addition of petroleum ether to yield white crystals, m.p. 95°. (Found: C, 30.64; H, 2.39. $C_{12}H_{11}ClO_4PRe$ calcd.: C, 30.58; H, 2.33%.)

Preparation of cis-$Re(CO)_4(PMe_2Ph)Br$

Tetracarbonyl(dimethylphenylphosphine)rhenium dimer (100 mg, 0.1146 mmole) was suspended in CCl_4 at 0°. To this bromine (18.7 mg, 0.1170 mmole) dissolved in 5 ml of CCl_4 was added dropwise with shaking and then allowed to stand for 1 h. Solution evaporated to dryness and then pumped on (0°/0.5 mm) for 2 h to remove any unreacted bromine. Residue dissolved in ether and crystallized by the addition of petroleum to yield 115 mg of white needle like crystals, m.p. 89°. (Found: C, 27.50; H, 2.09. $C_{12}H_{11}BrO_4PRe$ calcd.: C, 27.38; H, 2.09%.)

Preparation of trans-$Re(CO)_4(PMe_2Ph)Br$

$[Re(CO)_4(PMe_2Ph)]_2$ (100 mg, 0.1146 mmole) was suspended in CCl_4 at 20°. To this bromine (18.7 mg, 0.1170 mmole) dissolved in 5 ml of CCl_4 was added dropwise with shaking and allowed to stand for $\frac{1}{2}$ h. Solution evaporated to dryness and then pumped on (20°/0.5 mm) for 2 h. Residue dissolved in methanol and crystallized by the addition of petroleum ether to yield pale brown prisms, m.p. 121°. About 20 mg of *cis*-isomer may be crystallized out by cooling the solution to −20° for several hours, m.p. 89°. (Found: C, 27.46; H, 2.31. $C_{12}H_{11}BrO_4PRe$ calcd.: C, 27.38; H, 2.09%.)

trans-Bromotetracarbonyl(dimethylphenylphosphine)rhenium (50 mg) was heated under reflux in chloroform (10 ml) for 2 h when isomerization to the *cis*-isomer took place. This reaction was followed spectroscopically.

Preparation of trans-$Re(CO)_4(PMe_2Ph)I$

$[Re(CO)_4(PMe_2Ph)]_2$ (100 mg, 0.1146 mmole) was suspended in CCl_4 at 20°. To this iodine (30 mg, 0.118 mmole) in 5 ml of CCl_4 was added dropwise with shaking and allowed to stand for $\frac{1}{2}$ h. Solution evaporated to dryness. The residue was dissolved in methanol and crystallized by the addition of petroleum ether to yield 142 mg of pale yellow crystals, m.p. = 122°. (Found: C, 25.85; H, 1.94. $C_{12}H_{11}IO_4PRe$ calcd.: C, 25.60; H, 1.94%.)

trans-Iodotetracarbonyl(dimethylphenylphosphine)rhenium (50 mg) was heated under reflux in chloroform (10 ml) for 2 h, when isomerization to the *cis*-isomer took place. The reaction was followed spectroscopically. M.p. 78°.

Reaction of $Re(CO)_7(PMe_2Ph)_3$ with HCl gas

Preparation of $Re(CO)_3(PMe_2Ph)_2Cl$ and $Re(CO)_4PMe_2PhCl$

$Re(CO)_7(PMe_2Ph)_3$ (100 mg, 0.102 mmole) was suspended in 10 ml of CCl_4 at 0° and dry HCl gas was bubbled through the solution for 30 min. Solution evaporated to dryness (0°/0.5 mm). The crude material was then eluted on an alumina column using ethyl acetate/petroleum ether (2/10) to yield 35 mg of pale yellow needle like crystals, which were recrystallized from methanol, m.p. 132°. Spectroscopically identical to (III). (Found: C, 39.98; H, 3.83. $C_{19}H_{22}ClO_3P_2Re$ calcd.: C, 39.18; H, 3.79%.)

A second product was also isolated in low yield (6 mg), which was recrystallized from methanol/petroleum ether on cooling at −20° for 12 h. M.p. 95°. Spectroscopically identical to (IX). (Found: C, 30.64; H, 2.39. $C_{12}H_{11}ClO_4PRe$ calcd.: C, 30.58; H, 2.33%.)

Reaction of [$Re(CO)_7(PMe_2Ph)_3$] *with bromine*

Preparation of $Re(CO)_3(PMe_2Ph)_2Br$ *and* $Re(CO)_4(PMe_2Ph)Br$

$Re(CO)_7(PMe_2Ph)_3$ (100 mg, 0.102 mmole) was suspended in 10 ml of dry CCl_4 at 0°. Bromine (20 mg, 0.125 mmole) in 5 ml of CCl_4 was added dropwise and the brown solution allowed to stand for 30 min. Solution evaporated to dryness and then pumped on (0°/0.5 mm) for 2 h to remove any excess bromine. The crude material was chromatographed on alumina using ethyl acetate/petroleum ether (2/10) to yield two products. The yellow product was crystallized from methanol to yield 42 mg of pale yellow needles, shown spectroscopically to be compound (IV), m.p. 132°. (Found: C, 36.41; H, 3.56. $C_{19}H_{22}BrO_3P_2Re$ calcd.: C, 36.39; H, 3.51%.)

The second product which was pale brown (12 mg) was crystallized from ether by the addition of petroleum ether to yield white crystals, m.p. 89°. Spectroscopically these crystals were identical to (X). (Found: C, 27.69; H, 2.08. $C_{12}H_{11}BrO_4PRe$ calcd.: C, 27.40; H, 2.09%.)

Reaction of $Re(CO)_7(PMe_2Ph)_3$ *with iodine*

Preparation of $Re(CO)_3(PMe_2Ph)_2I$ *and* $Re(CO)_4(PMe_2Ph)I$

$Re(CO)_7(PMe_2Ph)_3$ (100 mg, 0.102 mmole) was suspended in 10 ml of dry CCl_4 at 20°. Iodine (26 mg, 0.11 mmole) dissolved in 5 ml of CCl_4 was added dropwise and then allowed to stand for 30 min. Solution evaporated to dryness (20°/1 mm) to yield 115 mg of crude material. Crude material spotted on an alumina thin layer plate and eluted with a solution of ethyl acetate/petroleum ether to yield two main product spots. Crude material dissolved in warm methanol and cooled at −20° for 4 h to yield 32 mg of white needle like crystals, m.p. 115°. [Found: C, 33.73; H, 3.17. $C_{19}H_{22}IO_3P_2Re$, $Re(CO)_3(PMe_2Ph)_2I$, calcd.: C, 33.90; H, 3.26%.]

Petroleum ether was then added to the methanol and set aside at −20° for 24 h to yield 30 mg of pale yellow crystals, m.p. 122°. Separation of the compounds by chromatography using alumina and ethyl acetate/petroleum ether (2/10) as eluant produced 2.5 mg of pale yellow crystals m.p. 78°. [Found: C, 25.60; H, 1.94. $C_{12}H_{11}IO_4PRe$, $Re(CO)_4(PMe_2Ph)I$, calcd.: C, 25.62; H, 1.94%.]

Reaction of $Re(CO)_7(PMe_2Ph)_3$ *with excess bromine*

Preparation of $Re(CO)_7(PMe_2Ph)_2Br_3$ *and* $Re(PMe_2Ph)_2Br_4$

$Re(CO)_7(PMe_2Ph)_3$ (0.500 g, 0.510 mmole) was suspended in 50 ml of dry CCl_4 at 0°. Bromine (800 mg, 5.05 mmoles) dissolved in 5 ml of CCl_4 at −10° was added dropwise to yield a brown solution. The reaction was allowed to stand at 0° for 2 h. Solution evaporated to dryness (0°/10 mm) and then pumped on (10°/0.5 mm) for 12 h, to remove any excess bromine. The crude material partially dissolved in dry ether to yield a dark red solution, containing a yellow residue. The ether extract evaporated to dryness to leave a dark red material which was recrystallized from benzene/petroleum ether to yield 100 mg of dark red needles, m.p. 168°. [Found: C, 27.62; H, 3.02; Re, 27.10. $C_{17}H_{22}Br_3OP_2Re$, $Re(CO)(PMe_2Ph)_2Br_3$, calcd.: C, 27.96; H, 3.02; Re, 25.48%.]

The ether insoluble residue was dissolved in methanol to leave a residue of pale yellow material. This residue was recrystallized from benzene/petroleum ether to yield 25 mg of light yellow crystals m.p. 154°. [Found: C, 24.66; H, 2.80; Re, 24.8. $C_{16}H_{22}Br_4P_2Re$, $Re(PMe_2Ph)_2Br_4$, calcd.: C, 24.56; H, 2.83; Re, 23.8%.]

Preparation of $[Re(CO)_4(AsMe_2Ph)]_2$

$Re_2(CO)_{10}$ (1.0 g, 0.8 mmole) and dimethylphenylarsine (0.555 g, 1.60 mmoles) were dissolved in 80 ml of petroleum ether (40–60°) and irradiated for 6 h. The yellow solution was evaporated to dryness (40°/1 mm) to yield 1.430 g of crude material consisting of a brownish oil. The crude material was purified by chromatography using silica gel with ethanol/petroleum ether (1/10) as eluant to yield 200 mg of pale yellow material. This was crystallized from methanol to yield 80 mg of pure $[Re(CO)_4(AsMe_2Ph)]_2$. Yield 9%. M.p. 128°. (Found: C, 30.18; H, 2.30; O, 13.50. $C_{24}H_{22}As_2O_8Re_2$: C, 30.00; H, 2.29; O, 13.33%.)

Preparation of $Re(CO)_4(AsMe_2Ph)Br$

$[Re(CO)_4(AsMe_2Ph)]_2$ (120 mg, 0.125 mmole) suspended in 5 ml of carbon tetrachloride at 0°. Bromine (0.02 g, 0.125 mmole) dissolved in 5 ml of CCl_4 was added dropwise with stirring. Reaction was allowed to stand at 0° for 1 h and then evaporated to dryness to yield 0.146 g of crude material. Crude material purified chromatographically using silica gel and ether/petroleum ether (3/1) as eluant to yield 120 mg of white needle like crystals. Recrystallized from petroleum ether. M.p. 83°. Yield, 90%. (Found: C, 25.80; H, 2.04; mol.wt. mass spec., 561. $C_{12}H_{11}AsBrO_4Re$ calcd.: C, 25.62; H, 1.96%; mol.wt., 561.29.)

Preparation of $Re(CO)_4(AsMe_2Ph)Cl$

$[Re(CO)_4(AsMe_2Ph)]_2$ (20 mg) was suspended in dry petroleum ether (5 ml, 80–100°) and dry HCl gas passed through solution for 30 min. Yellow solution gradually changed to colourless solution. Solution evaporated (50°/1 mm) to dryness to yield white crystals which were recrystallized from petroleum ether. M.p. 77°. Yield quantitative. (Found: C, 28.24; H, 2.23. $C_{12}H_{11}AsClO_4Re$ calcd.: C, 28.00; H, 2.13%.)

$Re(CO)_4(AsMe_2Ph)Cl$ may also be prepared by addition of $CDCl_3$ to $[Re(CO)_4AsMe_2Ph]_2$. The solution was evaporated to dryness after allowing to stand for 12 h to yield white needle crystals. M.p. 77°. (Found: C, 28.19; H, 2.21%.)

Preparation of $Re(CO)_3(AsMe_2Ph)_2Cl$

$Re_2(CO)_{10}$ (2.10 g, 3.2 mmoles) and dimethylphenylarsine (2.3 g, 13.6 mmoles) dissolved in high boiling petroleum ether (80–100°) and irradiated for 6 h. Solution evaporated (50°/1 mm) to dryness to leave a brown oil. Oil dissolved in dichloromethane and refluxed for 10 min, and then evaporated to dryness to yield 4.2 g of crude material. Crude material was purified by chromatography using silica gel and ethanol/petroleum ether (1/10) as eluant to yield 0.623 g of light brownish yellow crystalline compound. Recrystallized from n-hexane on cooling to −20° to yield 0.561 g of white needle like crystals. M.p. 116°. Yield, 26%. (Found: C, 34.17; H, 3.34; mol.wt. mass spec., 670. $C_{19}H_{22}ClO_3Re$ calcd.: C, 34.20; H, 3.29%; mol.wt., 669.86.)

Preparation of $Re(CO)_3(AsMe_2Ph)_2Br$

$Re_2(CO)_{10}$ (2.10 g, 3.2 mmoles) and dimethylphenylarsine (2.3 g, 13.6 mmoles) dissolved in high boiling petroleum ether (80–100°) and irradiated for 6 h. Solution assumed a yellow colour. Evaporated to dryness (50°/1 mm) to yield 4.35 g of material. Material dissolved in methanol and 0.300 g of bromine in $CHCl_3$ added slowly and allowed to stand for 1 h. Solution evaporated to dryness and purified by chromatography using silica gel and ether/petroleum ether (1/10) as eluant, to yield 0.83 g of product. Material crystallized from n-hexane on standing at −20° to yield white blade like crystals. M.p. 129°. Yield 52%. (Found: C, 32.07; H, 3.12; mol.wt., mass spec., 712. $C_{19}H_{22}BrO_3Re$ calcd.: C, 32.10; H, 3.10%; mol.wt., 712.)

Preparation of $Re(CO)_3(AsMe_2Ph)_2$ *and* $Re_2(CO)_7(AsMe_2Ph)_3$

$Re_2(CO)_{10}$ (2.10 g, 3.12 mmoles) dissolved in petroleum ether (80 ml) and 2.3 g (13.6 mmoles) of dimethylphenylarsine added. The mixture was irradiated for 6 h, and then evaporated to dryness to yield 4.34 g of crude material. Crude material separated by means of chromatography using silica gel and ethanol/petroleum ether (1/10). Fractions collected and evaporated to dryness to yield two main products of light yellow crystals of $Re(CO)_3(AsMe_2Ph)_2$ (250 mg) and white crystals of $Re_2(CO)_7(AsMe_2Ph)_3$ (321 mg). The latter may be crystallized from ethyl acetate/petroleum ether and the former from methanol. [Found: C, 36.06; H, 3.51; O, 7.86. $C_{19}H_{22}AsO_3Re$, $Re(CO)_3(AsMe_2Ph)_2$ calcd.: C, 36.00; H, 3.50; O, 7.57%.) [Found: C, 33.15; H, 3.35. $C_{31}H_{33}AsO_7Re$, $Re(CO)_7(AsMe_2Ph)_3$ calcd.: C, 33.40; H, 3.05%.]

DISCUSSION

Dirhenium decacarbonyl reacts with 1 equivalent per rhenium atom of dimethylphenylphosphine on being irradiated with UV light to yield products such as $Re(CO)_4(PMe_2Ph)$, $Re(CO)_3(PMe_2Ph)_2$ and $Re_2(CO)_7PMe_2Ph_3$. Intermediate products, presumably $Re(CO)_3(PMe_2Ph)_2$ and $[Re(CO)_3(PMe_2Ph)_2]_2$ reacted with chlorinated solvents such as dichloromethane and chloroform in which the crude material was dissolved and gently warmed to form halocarbonyl–phosphine complexes such as *cis*- and *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$. These compounds were, however, formed only in very low yields of normally less than 10%. Thermal reactions although producing some different products tended to give similar products in higher yields but the reaction time was considerably longer. The disubstituted compound $[Re(CO)_4(PMe_2Ph)]_2$ obtained both by a thermal and UV reaction was obtained in a 46% yield by thermal means as compared to 4.3%, obtained from the UV reaction. The time of irradiation and the solvent used also affected the nature of the products and the percentage yields. When petroleum ether was used as the solvent compounds (I), (II), (III), (VI) and (VIII) were obtained on irradiation for 6 h but when cyclohexane was used and irradiated for 3 h only compounds (II) and (VIII) could be isolated.

$Re_2(CO)_{10}$ also reacted with dimethylphenylarsine under irradiation to yield analogous compounds such as $[Re(CO)_4(AsMe_2Ph)]_2$ and $Re(CO)_3(AsMe_2Ph)_2$.

Intermediates such as $Re(CO)_3(AsMe_2Ph)_2$ were also presumably formed and reacted with chlorinated solvents to form compounds such as $Re(CO)_3(AsMe_2Ph)_2Cl$.

Thermal reaction of $Re_2(CO)_{10}$ and dimethylphenylarsine failed to produce any significant products even after refluxing in high boiling petroleum ether for 24 h.

The products from these reactions were readily separated and purified by column chromatography, the value of which appears to be not fully appreciated by workers in this field. It was found that the viscous ligands such as dimethylphenylphosphine and dimethylphenylarsine were extremely difficult to remove from the products using normal means, but could be readily removed by chromatographic means.

The disubstituted products $[Re(CO)_4(PMe_2Ph)]_2$ and $[Re(CO)_4(AsMe_2Ph)]_2$ appeared to be dimeric both in solid and in solvent. There is some anomalous behaviour of the analogous manganese compounds, $[Mn(CO)_4(PR_3)]_2$ and confusion exists as to whether these are monomeric $[(R_3P)Mn(CO)_4]$ or dimeric. The most recent studies[10,11] fail to confirm the original[12] postulations of monomeric $(R_3P)Mn(CO)_4$ compounds. For these rhenium compounds sharp NMR spectra are obtained indicating that no paramagnetic species such as $Re(CO)_4(PMe_2Ph)$ exists in solution. The IR spectra of these compounds (I) and (XVI) show four bands in the carbonyl stretching region (see Table 1). Analogous triphenylphosphine complexes show only two such bands; which indicates D_{4h} or D_{4d} symmetry. This symmetry results from substitution of carbonyls which are *trans* to the metal–metal bond by the triphenylphosphine. In the case of the dimethylphenylphosphine and -arsine analogues substitution of at least one ligand which is *cis* to the metal–metal bond must take place to give the lower symmetry. In fact the IR data obtained indicates that both substituted carbonyls must be *cis* to the metal–metal bond, in order to give a symmetry condition which corresponds to the number of $\nu(C{\equiv}O)$ active modes observed.

Compounds (I) and (XVI) react readily with halogens at 0° to give almost exclusively *cis*-isomers, structure assignments being made on the basis of their IR spectra. The *trans*-isomer may be obtained when the reaction is carried out at room temperature (20°). Although stable in solution at room temperature, it is isomerised to the *cis* form in refluxing chloroform.

The formation of compounds (II) and (XVIII) where analysis indicate that $1\frac{1}{2}$ carbonyl groups on each rhenium atom have been substituted are of interest structurally. Reaction of compound (II) with dry HCl gas and equimolar quantities of bromine and iodine at 0° results in the formation of *trans* substituted phosphine compounds (III), (IV) and (V) and the compounds (IX), (X) and (XI). The latter monosubstituted compounds only being obtained in very low yields, the reason for this being uncertain. From these reactions we deduced that two carbonyl groups on one rhenium atom have been substituted, *trans* to one another and thus *cis* to the metal–metal bond; while only one carbonyl group on the other rhenium atom has been substituted by a ligand. The molecular weight of this compound, determined in chloroform was shown to be 990, indicating that at least two rhenium atoms existed in the compound. The IR spectrum shows no bands in the bridging carbonyl region and so the two rhenium atoms must be linked only by a metal–metal bond.

The compound (II) was also reacted with an excess of bromine at 0° to yield products (XIV) and (XV) where replacement of three and four carbonyls have been achieved by the halogen. Both (XIV) and (XV) contain two dimethylphenylphosphine

TABLE 1

INFRARED ABSORPTIONS OF RHENIUM CARBONYL COMPLEXES

Compound	M.p. (°C)	Point group	Carbonyl modes predicted[a]	Carbonyl stretching frequency (cm^{-1})[b]	Assigned metal-halogen stretch (cm^{-1})[f]
$[Re(CO)_4(PMe_2Ph)]_2$ (I)	158	C_{2h}	$4(3B_u+A_u)^a$	2100 w, 2060 mw, 2000 s, 1955 s (br), 1905 s^d	
$Re_2(CO)_7(PMe_2Ph)_3$ (II)	148 (dec.)	C_{2v} C_s	$3(2A_1+B_1)$ $4(3A'+A'')^e$	2018 w, 1995 ms, 1940 s, 1918 (sh), 1910 s, 1885 s^d	
trans-$Re(CO)_3(PMe_2Ph)_2Cl$ (III)	130–132	C_{2v}	$3(2A_1+B_1)^f$	2022 w, 1950 s, 1895 m^d	372
trans-$Re(CO)_3(PMe_2Ph)_2Br$ (IV)	132	C_{2v}	$3(2A_1+B_1)$	2005 w, 1960 s, 1900 m^g	368
trans-$Re(CO)_3(PMe_2Ph)_2I$ (V)	115	C_{2v}	$3(2A_1+B_1)$	2000 w, 1945 s, 1895 m^g	360
fac-$Re(CO)_3(PMe_2Ph)_2Cl$ (VI)	134	C_s	$3(2A'+A'')^f$	2012 s, 1955 s, 1895 s^d	345
$Re(CO)_2(PMe_2Ph)_3Cl$ (VII)	152–155	C_s	$2(2A')$	1940 s, 1840 s^g	360
cis-$Re(CO)_3(PMe_2Ph)_2$ (VIII)	101	C_s	$3(2A'+A'')^h$	2000 m, 1925 s, 1910 s^d	
cis-$Re(CO)_4(PMe_2Ph)Cl$ (IX)	95	C_s	$4(3A'+A'')^i$	2105 ms, 2010 (sh), 2000 s, 1942 s^g	365
cis-$Re(CO)_4(PMe_2Ph)Br$ (X)	91	C_s	$4(3A'+A'')$	2100 ms, 2000 (sh), 1990 s, 1945 s^g	368
cis-$Re(CO)_4(PMe_2Ph)I$ (XI)	90	C_s	$4(3A'+A'')$	2100 ms, 2005 (sh), 1990 s, 1940 s^g	372
trans-$Re(CO)_4(PMe_2Ph)Br$ (XII)	121	C_{4v}	$2(A_1+E)$	2105 w, 1990 s^g	368
trans-$Re(CO)_4(PMe_2Ph)I$ (XIII)	122	C_{4v}	$2(A_1+E)$	2100 w, 1985 s^g	372
$Re(PMe_2Ph)_2Br_4$ (XIV)	169 (dec.)	D_{4h}			340
$Re(PMe_2Ph)_2(CO)Br_3$ (XV)	168	C_{2v}	$1(A_1)$	1988 m^g	335
$[Re(CO)_4(AsMe_2Ph)]_2$ (XVI)	128	C_{2h}	$4(3B_u+A_u)^a$	2105 w, 2060 mw, 2005 s, 1945 s (br), 1905 s^d	
$Re_2(CO)_7(AsMe_2Ph)_3$ (XVII)	150–154	C_{2v}	$3(2A_1+B_1)$ $4(3A'+A'')^e$	2030 w, 1990 ms, 1945 s, 1920 (sh), 1900 s, 1840 s^g	
fac-$Re(CO)_3(AsMe_2Ph)_2Br$ (XVIII)	129	C_s	$3(2A'+A'')$	2014 s, 1952 s, 1900 s^d	370
fac-$Re(CO)_3(AsMe_2Ph)_2Cl$ (XIX)	116	C_s	$3(2A'+A'')$	2012 s, 1948 s, 1898 s^d	368
cis-$Re(CO)_4(AsMe_2Ph)Br$ (XX)	83	C_s	$4(3A'+A'')$	2095 w, 2040 (sh), 1995 vs, 1940 s^d	370
cis-$Re(CO)_4(AsMe_2Ph)Cl$ (XXI)	77	C_s	$4(3A'+A'')$	2095 w, 2020 (sh), 1995 vs, 1938 s^d	365
cis-$Re(CO)_3(AsMe_2Ph)_2$ (XXII)	89–92	C_s	$3(2A'+A'')^h$	2002 m, 1930 s, 1912 s^g	

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[a] See discussion. [b] (sh): shoulder; (br): broad. [c] KBr disc. [d] CCl_4 as solvent. [e] Symmetry of each half of the molecule considered independently. [f] See ref. 31. [g] $CHCl_3$ as solvent. [h] See ref. 22. [i] See refs. 13 and 20.

groups. No monophosphine substituted compounds could be isolated from the reaction mixture.

Reaction of dirhenium decacarbonyl with dimethylphenylphosphine in petroleum ether for 90 h resulted in the isolation of the trisubstituted monomeric compound(VII). Presumably some intermediate such as $[Re(CO)_2(PMe_2Ph)_3]_2$ or paramagnetic $Re(CO)_2(PMe_2Ph)_3$ were formed as intermediates which readily reacted with a chlorinated solvent to form the halogenated complex (VII).

Infrared spectra

The $\nu(C\equiv O)$ and ν(Re–halogen) frequencies in the IR spectra of the compounds described in this paper are given in Table 1. The $\nu(C\equiv O)$ region of the monosubstituted dimeric compounds $[Re(CO)_4(PMe_2Ph)]_2$ (I), and $[Re(CO)_4(AsMe_2Ph)]_2$ (XVI), are not consistent with those obtained by other workers for similar compounds[13-15]. The IR spectra exhibit no bands in the bridging carbonyl region indicating that the halves of the two molecules are joined solely by a rhenium–rhenium bond. Three strong, one weak and one medium $\nu(C\equiv O)$ frequencies are obtained in both cases. This appears to eliminate D_{4d} or D_{4h} symmetry, *i.e.* ligands substituted *trans* to the metal–metal bonds, as reported for the analogous triphenylphosphine compound[13,16]. As a carbonyl on each of the rhenium atoms of $Re_2(CO)_{10}$ has been substituted (see reactions) and substitution *trans* to the Re–Re bond is unlikely, we conclude that CO groups have been substituted *cis* to the metal–metal bond. If we consider the local symmetry of the two halves of the molecules as indicated by Freni[14] each half would have C_s symmetry, and the number of IR modes predicted would be four $(3A'+A'')$. These modes are both IR and Raman active so any lowering of the symmetry by the asymmetry of the ligands could not give rise to any additional weakly IR active bands. In view of this we consider the IR absorptions of the molecules are related to the total symmetry. Steric factors would favour *trans* substitution on the different rhenium atoms in the *cis* position to the metal–metal bond leading to C_{2h} symmetry and four modes $(3B_u+A_u)$ of vibration which are infrared active and four $(3A_g+B_g)$ modes which are Raman active. The three strong absorptions are assigned to the B_u mode and the medium absorption assigned to A_u mode. The additional weak band observed in the infrared spectra at high frequency is probably one of the Raman active modes made weakly IR active by the asymmetry of the ligand.

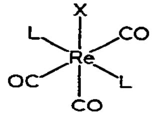
The monomeric complexes $Re(CO)_4(PMe_2Ph)Cl$ (IX), $Re(CO)_4(PMe_2Ph)Br$ (X) and $Re(CO)_4(PMe_2Ph)I$ (XI) show four bands $(3A'+A'')$ in the carbonyl stretching region, consistent with these compounds having C_s symmetry, with the ligand and the halogen in mutually *cis* positions. This pattern has been previously observed in other compounds of the type *cis*-$XRe(CO)_4L$ (X=Cl, Br[13] or I[14]; L=Ph_3P) and *cis*-$XMn(CO)_4L$ (X=Cl, Br or I[17]; L=Ph_3P). The appearance of medium bands in the far IR spectra of (IX), (X) and (XI) at 365, 368 and 372 cm^{-1} respectively, which are absent in the precursors (I) and (XVI) are assigned tentatively to the metal–halogen stretch[18].

The compounds *trans*-$Re(CO)_4(PMe_2Ph)Br$ (XII) and $Re(CO)_4(PMe_2Ph)I$ (XIII) show the two terminal carbonyl stretching absorptions (A_1+E) expected for C_{4v} symmetry. The weak intensity absorption at 2100–2105 cm^{-1} can be assigned to the A_1 mode and the strong absorption at 1985–1990 cm^{-1} to the E mode; no splitting of the E mode was observed but the spectra were recorded in chloroform owing to insolubility in hydrocarbon solvents and this would lead to band broadening and loss of resolution.

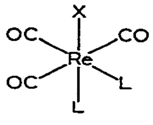
The arsine compounds *cis*-$Re(CO)_4(AsMe_2Ph)Br$ (XX) and *cis*-$Re(CO)_4(AsMe_2Ph)Cl$ (XXI) show four terminal carbonyl stretching absorptions ($3A'+A''$) as expected for C_s symmetry. Two strong bands (A'_a and A'_b modes) occur at high frequency, a very strong band (A″ mode) at medium frequency and a strong band (A'_c mode) at low frequency. These spectra are similar to the analogous phosphine complexes (IX), (X) and (XI). Medium bands also occur in the far IR at 370 for (XX) and at 365 cm^{-1} for (XXI) assigned to the rhenium–halogen stretch.

The disubstituted complexes *fac*-$Re(CO)_3(PMe_2Ph)_2Cl$ (VI), *fac*-$Re(CO)_3(AsMe_2Ph)_2Br$ (XVIII) and *fac*-$Re(CO)_3(AsMe_2Ph)_2Cl$ (XIX) show three strong bands ($2A'+A''$) of approximately the same intensity in the carbonyl stretching frequency region. This is consistent with a stereochemistry of C_s symmetry in which the two phosphine or arsine ligands are *cis* to each other and *cis* to the halogen atom[19,20] (3).

The disubstituted compounds *trans*-$Re(CO)_3(PMe_2Ph)_2Cl$ (III), $Re(CO)_3(PMe_2Ph)_2Br$ (IV) and $Re(CO)_3(PMe_2Ph)_2I$ (V) also show three $\nu(C{\equiv}O)$ bands but the band at highest frequency is of weak intensity, a very strong band at lower frequency and a medium band. Three possible structures for these complexes are (1), (2) and (3).



(1)



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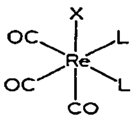
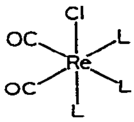


(3)

Structure (3) (C_s symmetry) is eliminated as a possibility, since by analogy with other known compounds it would be expected to have three bands of approximately equal intensity in the $\nu(C{\equiv}O)$ region such as those of compounds (VI), (XVIII) and (XIX). Structure (1) (C_{2v} symmetry) and structure (2) (C_s symmetry) could both theoretically give rise to a pattern in the carbonyl stretching region similar to the one actually observed. The complex $PhMn(CO)_3(Diphos)$[21] in which the two P atoms must have a *cis* configuration, shows only two strong carbonyl stretching frequencies in its IR spectrum, consistent therefore only with structure (2). This suggests that in compounds of type (2), the A' mode arising from the *trans*-CO groups does not couple with the A' mode arising from the CO *trans* to the ligands, and is not IR-active.

On this basis the complexes (III), (IV) and (V) are assigned the *trans* structure (1), having C_{2v} symmetry and 3 expected bands ($2A_1+B_1$). The band at highest frequency is assigned to the A_1^b mode and that at lowest frequency to the A_1^a mode, since the CO *trans* to the halogen group is expected to have the greatest degree of metal–CO π bonding. This assigned structure is confirmed by the ^1H NMR spectra obtained for these compounds (see later).

The trisubstituted compound $Re(CO)_2(PMe_2Ph)_3Cl$ (VII), shows two strong bands in the carbonyl stretching region. There are three possible structures for this compound. Structure (5) (C_{2v} symmetry) can be eliminated as it should show only one strong band (B_1) in the carbonyl region. Structure (4) might be expected to show two strong bands of approximately equal intensity in the carbonyl region, while structure (6) might also be expected to have two strong carbonyl bands, although prediction of



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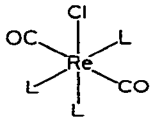
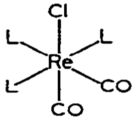


(5)

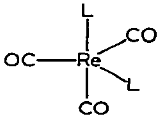


(6)

the ratio of their intensities is less certain. It is therefore not possible to choose between structures (4) and (6) solely on IR evidence. The compounds have been assigned structure (6) from supplementary ^{1}H NMR data.

The paramagnetic compounds $Re(CO)_3(PMe_2Ph)_2$ (VIII) and $Re(CO)_3(AsMe_2Ph)_2$ (XXII) ($2A'+A''$) show two strong bands and one medium band in the IR spectrum. This is consistent with C_s symmetry, the medium band at high frequency assigned to the A'' mode and the two strong bands at lower frequency to the two A' modes. This assignment is contrary to that reported for the analogous triphenylphosphine compound $[Re(CO)_3(PPh_3)_2]$[14,16] which has a trigonal bipyramid structure, with the three carbon monoxide molecules at the equatorial positions and the two phosphines at the apices (symmetry D_{3h}) giving one strong band in the $\nu(C{\equiv}O)$ region assigned by the rigid selection rules to the E'mode. A weak satellite is generally found at higher frequency[22], and this is probably the A'_a mode made weakly IR-active by asymmetry of the ligands. However, compounds with bidentate ligands never give spectra of this simple sort, but always yield a three-band spectrum such as that for $Fe(CO)_3(Ph_2P{-}C_2H_4{-}PPh_2)$[23] which is similar to that obtained for compounds (VIII) and (XXII).

Two possible structures exist having *cis* configuration for compounds (VIII)



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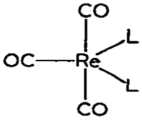


(8)

and (XXII). Structure (7) has C_s symmetry with 3 IR active modes ($2A'+A''$) and (8) had C_{2v} symmetry also giving rise to 3 IR active modes ($2A_1+B_2$), but it is doubtful whether the formal difference between (7) and (8) has any meaning. From the spectra there must be substantial mixing of the two A' (or A_1) modes; the most symmetrical mode must be assigned to the highest frequency band but the order of the lower pair is not known. Reckziegel and Bigorgne[23] have tried to relate $\nu(C{\equiv}O)$ intensities to bond angles in substituted iron carbonyls. Experimentally, the intensities of the CO bands of $Fe(CO)_3(C_7H_8)$ and $Fe(CO)_3(Ph_2P{-}C_2H_4{-}PPh_2)$ are similar and this may indicate that the disposition of the CO groups in space is much the same for both possible *cis* substituted structures, analogous to (7) and (8).

The compounds $Re_2(CO)_7(PMe_2Ph)_3$ (II) and $Re_2(CO)_7(AsMe_2Ph)_3$ (XVII) show six $\nu(C{\equiv}O)$ bands; four strong (one being a shoulder), one medium to strong and one weak. Reactions carried out on these compounds indicate that two carbonyls *trans* to one another on one rhenium atom have been substituted by ligands while only one carbonyl on the other rhenium atom has been substituted. The local symmetry of each half of the molecule is considered independently in order to explain the observed IR spectrum. The disubstituted half of the molecule would have C_{2v} symmetry giving rise to 3 bands ($2A_1+B_1$) in the IR, while the monosubstituted half (considered to be substituted in the *cis* position to the metal–metal bond) would have C_s symmetry giving rise to 4 bands ($3A'+A''$) in the IR. These symmetry conditions give rise, in the case of the C_{2v} half of the molecule, to three bands, a weak band (A_1^a mode) at high frequency, a medium band (A_1^b mode) at low frequency and a strong band (B_1 mode) at intermediate frequency while the C_s half of the molecule would give rise to four bands, two at high frequency (A'_a and A'_b modes) of medium to strong and strong intensity, one band of very strong intensity at intermediate frequency (A'' mode) and the fourth band (A'_c mode) of strong intensity at low frequency. Combination and overlap of these two sets of vibrations could give rise to the observed spectra. The weak (A_1^a mode) band of the C_{2v} half of the molecule appearing at high frequency, a medium to strong band (A'_a) from the C_s half at lower frequency and four strong bands at lower frequency resulting from overlap of the A_1^b and B_1 modes of the C_{2v} half of the molecule with the very strong A'' and strong A'_b and A'_c modes of the half of the molecule having C_s symmetry.

The IR spectrum of the disubstituted phosphine complex (XV) containing only one carbonyl group shows the expected one band (A_1 mode) of medium intensity in the $\nu(C{\equiv}O)$ region.

Nuclear magnetic resonance spectra

Tertiary phosphines are not only important ligands for stabilising a wide variety of transition metal complexes but also in certain cases such as dimethylphenylphosphine the stereochemistry of complexes may be determined from their NMR spectra[24]. The resonance of the methyl protons in free dimethylphenylphosphine is a symmetrical doublet due to spin–spin interaction with the phosphorus nucleus (^{31}P, spin $\frac{1}{2}$, 100% abundance), but when two dimethylphenylphosphine ligands are mutually *trans* the methyl resonance is a 1/2/1 triplet, usually well defined and narrow. The methyl protons couple equally with both phosphorus nuclei with $J(P\text{–}H) \simeq 4$ Hz. This is an example of "virtual coupling"[25]. When the two phosphines ligands are in the *cis*-position the resonance of the methyl protons is split into a 1/1 doublet by the phosphorus, showing that the two phosphorus nuclei do not couple strongly, as there is no evidence for this coupling in the NMR spectra of compounds described by Shaw[28] or in this work. Shaw examined complexes of some ten transition metals, and found 1/1 doublets with $J(P\text{–}H) = 7\text{–}13$ Hz provided that two dimethylphenylphosphine ligands were not present in mutually *trans*-positions.

The methyl resonances of a number of the compounds prepared are shown in Tables 2–4. The methyl resonance of the diamagnetic compound (I) gave an ill defined doublet, $J(P\text{–}H) = 6.0$ Hz. The nature of the spectrum would indicate that there is an equilibrium between a paramagnetic species $Re(CO)_4(PMe_2Ph)$ and a diamagnetic species $[Re(CO)_4(PMe_2Ph)]_2$ in carbon tetrachloride solution. The ^1H NMR spectrum of the arsine analogue (XVI) also indicates the presence of a paramagnetic species $[Re(CO)_4(AsMe_2Ph)]$ in carbon tetrachloride solution as an ill defined broad singlet is observed at τ 8.2.

The methyl resonances of the yellow complexes (III), (IV) and (V) show well defined 1/2/1 triplets, $J(P\text{–}H) = 3.4\text{–}4.0$ Hz. Such spectra are consistent with cases where the phosphine ligands are *trans* to one another (1). The isomer (VI) shows two

TABLE 2

METHYL RESONANCES OF SOME RHENIUM DIMETHYLPHENYLPHOSPHINE CARBONYL COMPLEXES

In deuteriochloroform unless otherwise stated, τ values ± 0.01 J values ± 0.1 Hz.

Compound	Doublet		Triplet (or multiplet)	
	τ	$J(P–H)$ (Hz)	τ	$J(P–H)$ (Hz)
$[Re(CO)_4(PMe_2Ph)]_2$ (I)	8.35	6.0[a]		
$Re_2(CO)_7(PMe_2Ph)_3$ (II)	8.72	8.5[a]	8–8.5	Multiplet
trans-$Re(CO)_3(PMe_2Ph)_2Cl$ (III)			7.98	4.0
trans-$Re(CO)_3(PMe_2Ph)_2Br$ (IV)			7.92	3.5
trans-$Re(CO)_3(PMe_2Ph)_2I$ (V)			7.83	3.5
fac-$Re(CO)_3(PMe_2Ph)_2Cl$ (VI)	8.22, 8.36	8.0		
$Re(CO)_2(PMe_2Ph)_3Cl$ (VII)	8.74	8.0	8.61	5 line multiplet 3.5

[a] In carbon tetrachloride.

TABLE 3

METHYL RESONANCES OF RHENIUM DIMETHYLPHENYLARSINE CARBONYL COMPLEXES

In deuteriochloroform unless otherwise stated.

Compound	Singlet(s) τ	Multiplet τ
$[Re(CO)_4(AsMe_2Ph)]_2$ (XVI)	8.2[a]	
$Re_2(CO)_7(AsMe_2Ph)_3$ (XVII)	8.76	8.36
fac-$Re(CO)_3(AsMe_2Ph)_2Br$ (XVIII)	8.31, 8.41	
fac-$Re(CO)_3(AsMe_2Ph)_2Cl$ (XIX)	8.35, 8.48	
trans-$Re(CO)_4(AsMe_2Ph)Br$ (XX)	8.08	

[a] In carbon tetrachloride.

TABLE 4

METHYL RESONANCES OF DIMETHYLPHENYLPHOSPHINE AND DIMETHYLPHENYLARSINE

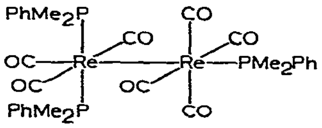
Compound	τ	$J(P–H)$ (Hz)
PMe_2Ph	8.86	4.0
$AsMe_2Ph$	9.31	

well defined 1/1 doublets, $J(P–H) = 8.0$ Hz in the methyl resonance region. Such a spectrum indicates that the two phosphine ligands are *cis* to one another and the halogen atom is *cis* to these two phosphines (3), *i.e.* it is the *fac*-isomer. This isomer would give rise to two doublets, as there is no plane of symmetry through the two phosphorus atoms so that the shielding experienced by the two methyl groups on the same phosphine ligand may differ significantly[28], even without any effects due to restricted rotation about the phosphorus–rhenium bond. The analogous arsine complexes (XVIII), (XIX) show two well defined singlets in the methyl resonance region.

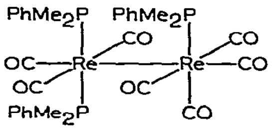
The trisubstituted phosphine complex (VII) could be one of three possible isomers (4), (5) or (6). (5) has been eliminated on the basis of its IR spectrum but it was shown that it is not possible to distinguish between structures (4) and (6) by IR means. For structure (4) the ^{1}H NMR spectrum would be expected to give methyl resonances consisting of doublets only since the three phosphine ligands are *cis* to each other. The methyl resonances expected for (6), where two phosphines are *trans* to one another and the third is *cis* to the other two would theoretically give a 1/2/1 triplet due to "virtual coupling" with both phosphorus nuclei, with total relative intensity two and a doublet at higher field of total intensity one due to a phosphine in a mutually *cis*-position. The actual spectrum obtained shows a well defined 1/1 doublet at τ 8.74 of relative intensity one J(P–H) = 8.0 Hz and a five line multiplet at τ 8.16 of relative intensity two. The five line multiplet appears to be the partial overlap of two triplets giving a 1/2/2/2/1 multiplet, J(P–H) = 3.5 Hz. The five line multiplet results owing to the fact that there is no plane of symmetry through the two *trans*-phosphorus atoms so that the shielding experienced by the two methyl groups on the same phosphine ligand may differ significantly, even without any effects due to restricted rotation about the phosphorus–rhenium bond. Thus the ^{1}H NMR methyl resonance spectrum observed corresponds well with that expected for structure (6).

The methyl proton resonance for the unsymmetrically substituted phosphine complex (II) consists of a well defined 1/1 doublet at τ 8.72, J(P–H) = 8.5 Hz of the total relative intensity one and a seven line multiplet at τ 8–8.5 of total intensity two. The analogous arsine complex (XVII) gives a methyl resonance spectrum consisting of a singlet at τ 8.76 and a four line multiplet centred at τ 8.36 ppm. Chemical evidence indicates that two *trans*-carbonyls on the one rhenium atom have been substituted by the ligands which necessitates substitution *cis* to the metal–metal bond. One carbonyl group has been substituted on the other rhenium atom and this is also believed to be situated *cis* to the metal–metal bond from chemical evidence. The doublet J(P–H) = 8.5 Hz, at high field of relative intensity one is assigned to the single ligand on the one rhenium atom. The seven line multiplet, τ 8–8.5 must be assigned to the two phosphine ligands *trans* to each other on the other rhenium atom. Owing to the fact that the other ligands are carbonyls there is a plane of symmetry through the phosphorus atoms in this half of the molecule, so one would expect a well defined 1/2/1 triplet at lower field.

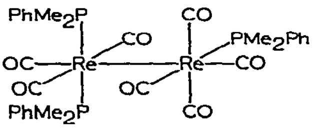
Construction of models of the various possible isomers of this complex indicate that for configuration (9 *i*) the lone dimethylphenylphosphine ligand is distant from the two which are *trans* and there is no possibility of "through space coupling" of the hydrogen atoms of the methyl groups on different ligands. The configuration (9 *ii*) is not possible owing to steric effects but if the lone phosphine is substituted *cis* to the metal–metal bond as in configuration (9 *iii*), then steric requirements show the hydrogen of the methyl groups of the lone phosphine can approach those of the two *trans*-phosphines on the other rhenium atom as closely as 0.6 Å but are never further



(9i)



(9ii)



(9iii)

apart than ≃ 1.4 Å. This configuration could give rise to "through space coupling" leading to the observed multiplet. Surprisingly, there is no evidence for additional coupling in the doublet at τ 8.72, which is attributed to the lone phosphine.

For the series of complexes of the type $Re(CO)_3(PMe_2Ph)_2X$ (X = Cl, Br and I) (III), (IV) and (V). The τ values of the triplet resonance decreases in the order Cl > Br > I (see Table 2). It has tentatively been suggested that the dominant factor causing such a decrease is the removal of electron density from the methyl groups, thus lowering the τ values, by the halogen which has the ability to accept back-donation of electrons from the metal. This ability is believed to increase in the order Cl < Br < I[29].

Mass spectra

The mass spectra of some of the monomeric compounds reported, (III), (VI), (VII), (VIII), (XVIII), (XIX) and (XX), have been recorded. The mass spectra of the remaining compounds reported are being recorded at present and will be reported later in detail elsewhere.

In the cases where mass spectra have been recorded the carbonyl groups break away in a stepwise fashion, but the remaining carbonyls become progressively more strongly bonded as would be expected from the bonding theory of carbonyls. This observation agrees with that of Lewis *et al.*[30] who studied the mass spectra of substituted polynuclear metal carbonyl derivatives. This is shown by the appearance of the carbide ion only after two or more carbonyls have been lost, and the observation that, in general, the loss of phosphine and halogen ligands occurs only after some carbonyl ligands have been lost. The breakdown pattern of compounds (III), (VI), (VII), (VIII), (XVIII), (XIX) and (XX) confirm the number of carbonyl groups in each of these compounds.

The loss of carbonyl groups prior to the loss of phosphine or arsine groups is in marked contrast to the thermal behaviour of these complexes, where the phosphine or arsine may be lost to give a metal carbonyl residue.

The mass spectra of the two isomers (III) and (VI) have the same fragmentation pattern, although the relative abundances of the ions produced differ. The molecular weight obtained in both cases is 582.

The mass spectra of the compound $Re(CO)_3(PMe_2Ph)_2$ (VIII), shows a strong intensity molecular ion at *m/e* of 546, indicating that this compound is monomeric in the solid state.

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