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THE REACTION OF RHENIUM CARBONYL WITH METHYLDIPHENYLPHOSPHINE

J. T. MOELWYN-HUGHES, A. W. B. GARNER AND N. GORDON

Department of Chemistry Including Biochemistry, University of the Witwatersrand, Johannesburg (South Africa)

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SUMMARY

Dirhenium decacarbonyl reacts photochemically with 1 mole of methyldiphenylphosphine to give the compounds, $[Re_2(CO)_9(PMePh_2)]$, $[Re(CO)_4(PMePh_2)]_2$, two isomers of formula $[Re_2(CO)_7(PMePh_2)_3]$, and the new cluster compound, $[Re_4(CO)_{10}(PMePh_2)_6]$. Dirhenium decacarbonyl reacts photochemically with 2 moles of methyldiphenylphosphine to give the same two isomers of $[Re_2(CO)_7(PMePh_2)_3]$, in greater yield, and $[Re(CO)_3(PMePh_2)_2]$. In contrast to these reactions the thermal reaction of dirhenium decacarbonyl with dimethylphenylphosphine (1 mole) results in the isolation of $[Re_2(CO)_8(PMePh_2)_2]$ as the sole reaction product. Reactions of $[Re_2(CO)_4(PMePh_2)]_2$, $[Re_2(CO)_7(PMePh_2)_3]$, $[Re_4(CO)_{10}(PMePh_2)_6]$ and $[Re(CO)_3(PMePh_2)_2]$ with dry HCl gas results in the formation of the chloro compounds, *cis-* and *trans-*$[Re(CO)_4(PMePh_2)Cl]$, and *trans-*$[Re(CO)_3(PMePh_2)_2Cl]$.

Reaction of *mer-*$[ReCl_3(PMePh_2)_3]$ with CO in ethanol yields *trans-*$[Re(CO)_3(PMePh_2)_2Cl]$ and *mer-*$[Re(CO)_2(PMePh_2)_3Cl]$; whereas reduction of *mer-*$[ReCl_3(PMePh_2)_3]$ with Na/Hg and reaction with CO yields *trans-*$[Re(CO)_3(PMePh_2)Cl]$. $[ReCl_4(PMePh_2)_2]$ reacts with CO in 2-methoxyethanol to yield *trans-*$[Re(CO)_3(PMePh_2)Cl]$.

The stereochemistries of these new compounds are deduced from a study of their proton NMR and IR spectra, and, in some cases, their reactions.

INTRODUCTION

The basic dimethylphenylphosphine reacts with rhenium carbonyl[1] substituting carbonyls *cis* to the Re–Re bond. This is in contrast to reaction of rhenium carbonyl with triphenylphosphine in which substitution of the carbonyls *trans* to the metal–metal bond is reported[2-6].

By varying the reaction times, the solvent, the ratio of phosphine to rhenium, the reaction of PMe_2Ph with $Re_2(CO)_{10}$ yielded a greater variety of products than reported for PPh_3 as ligand. We therefore decided to study the reaction of the intermediate phosphine, $PMePh_2$, with rhenium carbonyl.

Rhenium carbonyl reacted photochemically with methyldiphenylphosphine to yield a variety of products which were separated and purified by chromatography.

One, two or three carbonyls of rhenium carbonyl could be substituted by methyldiphenylphosphine, but when two phosphines were substituted per rhenium atom, the paramagnetic $[Re(CO)_3(PMePh_2)_2]$ was isolated.

Phosphine substituted halocarbonyl complexes of rhenium have been prepared by the reaction of halogens on compounds such as $[Re(CO)_4PR_3]_2$, ($PR_3 = PPh_3$[5], $PR_3 = PMe_2Ph$[1]) and by the action of phosphines on halocarbonyl complexes[7,8]. Reaction of the binuclear species $[Re_2(CO)_{10-n}(PMePh_2)_n]$ ($n = 1$, 2 or 3) with dry HCl gas resulted in splitting the Re–Re bond and the formation of the chloro derivatives, *cis*- and *trans*-$[Re(CO)_4(PMePh_2)Cl]$ and *trans*-$[Re(CO)_3(PMePh_2)Cl]$. Douglas and Shaw[9] have prepared a variety of carbonyl complexes of rhenium(I) and rhenium(III) containing PMe_2Ph as ligand by reaction of *mer*-$[ReCl_3(PMe_2Ph)_3]$ with CO in a number of solvents and sometimes in the presence of a reducing agent. Shaw *et al.*[9] also reported the reaction of *mer*-$[ReCl_3(PMePh_2)_3]$ with CO in ethanol to yield *trans*-$[Re(CO)_3(PMePh_2)_2Cl]$, but this was the only case in which they used $PMePh_2$ as a ligand. On repeating this reaction we isolated *mer*-$[Re(CO)_2(PMePh_2)_3Cl]$ in addition to the *trans*-$[Re(CO)_3(PMePh_2)_2Cl]$ reported by Shaw *et al.*[9] *trans*-$[ReCl_4(PMePh_2)]_2$ also reacted with CO in 2-methoxyethanol resulting in the isolation of *trans*-$[Re(CO)_3(PMePh_2)_2Cl]$.

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[10], which is based on the formation of a red coloured rhenium α-furildioxine complex.

Rhenium carbonyl (Strem Chemicals and Alfa Inorganic Chemicals) was used as obtained from commercial sources. Methyldiphenylphosphine was prepared according to the method of Davis *et al.*[11].

Molecular weights were determined using a Mechrolab Model 301A osmometer in benzene solution at 37°. Melting points were determined on a Kofler hot stage melting point apparatus and are corrected. The NMR spectra were recorded on a Hitachi-Perkin–Elmer R20 spectrometer and the IR spectra were recorded on a Perkin–Elmer 521 spectrometer.

All reactions were carried out under nitrogen.

Thermal reaction of $Re_2(CO)_{10}$ with methyldiphenylphosphine. Preparation of $[Re(CO)_4(PMePh_2)]_2$

$Re_2(CO)_{10}$ (2.0 g, 3.07 mmoles) and methyldiphenylphosphine (2.4 g, 12.0 mmoles) were refluxed in xylene (50 ml) under nitrogen for 15 h. The xylene was evaporated off and the oily residue pumped on (20°/0.1 mm) for 12 h to remove excess $PMePh_2$. The residue was then chromatographed on alumina using ethyl acetate/petroleum ether (1/10) as eluant.

The initial fractions on evaporation yielded unreacted $Re_2(CO)_{10}$ (815 mg) while later fractions yielded pale yellow crystals (933 mg), which were recrystallized from hot methanol to yield pale yellow needles of $[Re(CO)_4(PMePh_2)]_2$, m.p. 156–160°. Yield 30%. (Found: C, 40.87; H, 2.62. $C_{34}H_{26}O_8P_2Re_2$ calcd.: C, 40.96; H, 2.63%.)

Photochemical reaction of $Re_2(CO)_{10}$ with methyldiphenylphosphine

Reaction with 1 mole of $PMePh_2$ per Re atom. Preparation of $[Re_2(CO)_9(PMePh_2)]$, $[Re(CO)_4(PMePh_2)]_2$, two isomers of $[Re_2(CO)_7(PMePh_2)_3]$ and $[Re_4(CO)_{10}(PMePh_2)_6]$. $Re_2(CO)_{10}$ (3.58 g) and $PMePh_2$(2.2 g) were irradiated with UV light in cyclohexane (80 ml) for 12 h under nitrogen. The solution slowly assumed a dark orange colour. The cyclohexane was evaporated off and the viscous residue pumped on (20°/0.1 mm) for 12 h to remove excess phosphine and leave a pale yellow crystalline material (5.4 g). The crude material was chromatographed on Al_2O_3 using ethyl acetate/petroleum ether (2/10). 50 fractions of approximately 15 ml each were collected after "washing" the column with 50 ml of petroleum ether. The initial fractions contained unreacted $Re_2(CO)_{10}$ and methyldiphenylphosphine.

Evaporation of the fractions 5–10 yielded a yellow oil. Crystallization from hot methanol yielded white crystals of $[Re_2(CO)_9(PMePh_2)]$ (214 mg), m.p. 135° Yield 4%. (Found: C, 32.01; H, 1.56. $C_{22}H_{13}O_9Re_2$ calcd.: C, 32.04; H, 1.59%.)

Evaporation of fractions 16–21 yielded pale yellow needle-like crystals in an oily residue. The crystals were washed in cold methanol, and filtered to yield yellow needles of $[Re(CO)_4(PMePh_2)]_2$ (362 mg), m.p. 154°. Yield 7%. (Found: C, 41.11; H, 2.60; Re, 37.01; mol.wt. osmometric in benzene, 1004. $C_{34}H_{26}O_8P_2Re_2$ calcd.: C, 40.96; H, 2.63; Re, 37.36%; mol.wt., 997.)

Evaporation of fractions 24–30 yielded an oily residue. The residue was washed with petroleum ether and white prisms of $[Re_2(CO)_7(PMePh_2)_3]$ (432 mg) crystallized from ethyl acetate/petroleum ether at −20°. M.p. 175°. Yield 7%. (Found: C, 47.32; H, 3.58; Re, 32.21; mol.wt. osmometric in benzene, 1142. $C_{46}H_{39}O_7P_3Re_2$ calcd.: C, 47.30; H, 3.36; Re, 31.88%; mol.wt., 1168.)

Evaporation of fractions 32–38 yielded a pale yellow residue which was crystallized from ethyl acetate/petroleum ether and then recrystallized from ethyl acetate/methanol on standing at −20° to yield white prisms of $[Re_2(CO)_7(PMePh_2)_3]$ (185 mg), m.p. 156–158°. Yield 3%. (Found: C, 47.22; H, 3.33; Re, 31.06; mol.wt. osmometric in benzene, 1148. $C_{46}H_{39}O_7P_3Re_2$ calcd.: C, 47.30; H, 3.36; Re, 31.88% mol.wt., 1168.)

Evaporation of fractions 43–49 yielded a brownish residue containing a crystalline product. The brownish residue was removed by washing with petroleum ether to leave white prisms of $[Re_4(CO)_{10}(PMePh_2)_6]$ (89 mg). The crystals were recrystallized from ethyl acetate/petroleum ether on standing at −20°; m.p. 156–158°. Yield < 1%. (Found: C, 47.00; H, 3.20; Re, 33.40; mol.wt. osmometric in benzene, 2282. $C_{90}H_{78}O_{12}P_6Re_4$ calcd.: C, 47.50; H, 3.53; Re, 33.47%; mol.wt., 2225.)

Reaction with 2 moles of $PMePh_2$ per Re atom. Preparation of $[Re(CO)_3(PMePh_2]$ and two isomers of $[Re_2(CO)_7(PMePh_2)_3]$. $Re_2(CO)_{10}$ (2.18 g) and $PMePh_2$ (2.73 g) were irradiated in cyclohexane (80 ml) for 12 h under nitrogen. Cyclohexane was evaporated off and the yellow oily residue pumped on (25°/0.1 mm) for 12 h to leave a crystalline product (4.30 g).

The crude product was chromatographed using silica gel and ethyl acetate/petroleum ether (1/9) as eluant. Approximately 50 fractions (15–20 ml) were collected. The initial fractions contained unreacted $Re_2(CO)_{10}$ and methyldiphenylphosphine. Fractions 10–21 yielded an oily yellow residue. The residue was dissolved in methanol, filtered and on slow evaporation of the methanol bright yellow crystals of $[Re(CO)_3(PMePh_2)_2]$ (56 mg) formed, m.p. 145–150°. Yield 2%. (Found: C, 52.00; H, 4.02;

Re, 27.00; mol.wt. osmometric in benzene, 659. $C_{29}H_{26}O_3P_2Re$ calcd.: C, 51.98; H, 3.91; Re, 27.78%; mol.wt., 670.)

Evaporation of fractions 25–36 yielded a pale yellow oily residue. The residue was washed with petroleum ether and crystallized from ethyl acetate/petroleum ether to yield white prisms of $[Re_2(CO)_7(PMePh_2)_3]$ (386 mg), m.p. 174°. Yield 10%.

Evaporation of fractions 38 to 45 yielded a pale yellow residue. Extraction with hot petroleum ether, followed by cooling to −20° yielded white prisms of $[Re_2(CO)_7(PMePh_2)_3]$, (460 mg), m.p. 154°. Yield 12%.

Reaction of $[Re(CO)_4(PMePh_2)]_2$ *with HCl gas. Preparation of cis-*$[ReCl(CO)_4(PMePh_2)]$

$[Re(CO)_4(PMePh_2)_2]$ (50 mg) was suspended in dry CCl_4 at 0° and dry HCl gas slowly passed into the solution for 5 min. The solvent was removed and the residue crystallized from benzene/petroleum ether to yield white crystals of $[ReCl(CO)_4(PMePh_2)]$ (42 mg), m.p. 124°. Yield 75%. (Found: C, 38.36; H, 2.48. $C_{17}H_{13}ClO_4PRe$ calcd.: C, 38.28; H, 2.44%.)

Reaction of $[Re_2(CO)_7(PMePh_2)_3]$ *(IV) with HCl gas. Preparation of trans-*$[ReCl(CO)_3(PMePh_2)_2]$ *and cis-*$[ReCl(CO)_4(PMePh_2)]$

$[Re_2(CO)_7(PMePh_2)_3]$ (150 mg) was dissolved in $CHCl_3$ (25 ml) and HCl gas slowly passed through the solution. Thin layer chromatography showed that two products had been formed. The solvent was removed and the residue taken up in hot methanol. On cooling to 0° for 6 h white prisms of $[ReCl(CO)_3(PMePh_2)_2]$ (43 mg) separated out; m.p. 145°. Yield 47%. (Found: C, 49.17; H, 3.76. $C_{19}H_{22}ClO_3P_2Re$ calcd.: C, 49.35; H, 3.70%.)

The methanol filtrate was evaporated to dryness and the residue of $[ReCl(CO)_4(PMePh_2)]$ crystallized (22 mg) from benzene/hexane on standing at −20° for 24 h; m.p. 124°. Yield 31%. (Found: C, 38.89; H, 2.60. $C_{17}H_{13}ClO_4PRe$ calcd.: C, 38.28; H, 2.44%.)

Reaction of $[Re_2(CO)_7(PMePh_2)_3]$ *(V) with HCl gas. Preparation of trans-*$[ReCl(CO)_3(PMePh_2)_2$ *and cis-*$[ReCl(CO)_4(PMePh_2)]$

$[Re_2(CO)_7(PMePh_2)_3]$ (150 mg) was dissolved in $CHCl_3$ (20 ml) and HCl gas passed into the solution for 5 min at 20°. The reaction was followed by chromatography which indicated that three products had been formed. Evaporation of the solvent and crystallization of the residue from methanol yielded $[ReCl(CO)_3(PMePh_2)_2]$ (52 mg); m.p. 145°. The methanol filtrate was evaporated to dryness and chromatographed on silica gel and ethyl acetate/petroleum as eluant to yield *cis*-$[ReCl(CO)_4(PMePh_2)]$; m.p. 124° (16 mg) and *trans*-$[ReCl(CO)_4(PMePh_2)]$; m.p. 140°.

Reaction of $[Re_4(CO)_{10}(PMePh_2)_6]$ *with HCl gas*

$[Re_4(CO)_{12}(PMePh_2)_6]$ (50 mg) was dissolved in dry $CHCl_3$ (25 ml) and dry HCl gas was slowly passed into the solution. Thin layer chromatography indicated that three products were formed. $[ReCl(CO)_3(PMePh_2)_2]$ (40 mg) could be isolated from a methanol extract. Evaporation of the methanol produced an oily residue which failed to produce any significant amount of product. Thin layer chromatography indicated that both *cis*- and *trans*-$[ReCl(CO)_4(PMePh_2)]$ were formed in small yield, which were insufficient to allow crystallization.

Reaction of $[Re(CO)_3(PMePh_2)_2]$ *with HCl gas*

The bright yellow oily material from which $[Re(CO)_3(PMePh_2)_2]$ could be crystallized was dissolved in CCl_4 at 0° and HCl gas passed slowly into the solution. The bright yellow solution assumed an opaque pale yellow color. The solvent was evaporated off and the residue crystallized from methanol to yield *trans*-$[ReCl(CO)_3(PMePh_2)]$; m.p. 145°.

Reaction of $[Re_2(CO)_9(PMePh_2)]$ *with HCl gas*

$[Re_2(CO)_9(PMePh_2)]$ (100 mg) was dissolved in $CHCl_3$ (20 ml) and HCl gas passed slowly into the solution for 5 min at 20°. The reaction was followed by TLC, which indicated the formation *trans*-$[ReCl(CO)_4(PMePh_2)]$.

The solvent was evaporated off and the residue taken up in methanol which on evaporation yielded pale yellow crystals of *trans*-$[ReCl(CO)_4(PMePh_2)]$, m.p. 140°.

Preparation of $[ReCl(CO)_3(PMePh_2)_2]$ *and* $[ReCl(CO)_2(PMePh_2)_3]$ *from mer*-$[ReCl_3(PMePh_2)_3]$

Carbon monoxide was passed for 24 h through a boiling solution of *mer*-$[ReCl_3(PMePh_2)_3]^9$ (2.00 g) in ethanol (100 ml). The solvent was evaporated down (20 ml) whereupon pale yellow prisms of $[ReCl(CO)_2(PMePh_2)_3]$ (76 mg) separated out; m.p. 162–165°. (Found: C, 55.73; H, 4.43. $C_{26}H_{33}ClO_2P_3Re$ calcd.: C, 56.00; H, 4.44%.)

The ethanol was cooled to −20° for 6 h to yield white prisms of $[ReCl(CO)_3(PMePh_2)_2]$ (399 mg); m.p. 144–146°. Yield 26%. (Found: C, 49.57; H, 3.72. $C_{19}H_{22}ClO_3P_2Re$ calcd.: C, 49.35, H, 3.70%.)

Preparation of $[ReCl(CO)_3(PMePh_2)_2]$ *by reduction of mer*-$[ReCl_3(PMePh_2)_3]$ *with CO and Na/Hg*

Sodium amalgam from sodium (0.43 g) and Hg (10 ml) was added to a solution of *mer*-$[ReCl_3(PMePh_2)_3]$ (1.00 g) in dry THF (40 ml) and CO was then passed through for 30 min. The product $[ReCl(CO)_3(PMePh_2)_2]$ was then isolated by evaporation of the organic layer and recrystallization of the residue from methanol (87 mg). Yield 11%; m.p. 145°. (Found: C, 49.06; H, 3.68. $C_{19}H_{22}ClO_3P_2Re$ calcd.: C, 49.35; H, 3.70%.)

Preparation of trans-$[ReCl_4(PMePh_2)_2]$

A mixture of $KReO_4$ (2.0 g), methyldiphenylphosphine (4.85 g), concentrated HCl (4 ml) and ethanol (150 ml) was refluxed for 18 h. The solution gradually assumed a purple colour. Isolation gave the required product as dark red needles from $CHCl_3$/methanol, m.p. 199–202°. Yield 62%. (Found: C, 42.76; H, 3.64. $C_{26}H_{26}Cl_4P_2Re$ calcd.: C, 42.78; H, 3.57%.)

Preparation of $[ReCl(CO)_3(PMePh_2)_2]$ *from trans*-$[ReCl_4(PMePh_2)_2]$

trans-$[ReCl_4(PMePh_2)_2]$ (1 g) was dissolved in 2-methoxyethanol and CO passed through the boiling solution for 24 h. The purple coloured solution gradually faded. The solvent was removed and the required product (428 mg) isolated from methanol; m.p. 146–148°. Yield 44%. (Found: C, 49.09; H, 3.83. $C_{19}H_{22}ClO_3P_2Re$ calcd.: C, 49.35; H, 3.70%.)

Reaction of $Re_2(CO)_{10}$ with 2 moles of PMe_2Ph. Preparation of $Re_2(CO)_9(PMe_2Ph)$

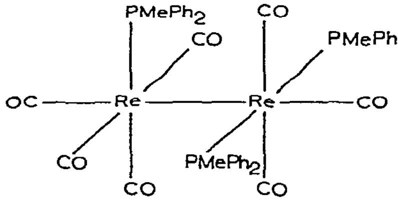
The reaction between $Re_2(CO)_{10}$ (3.10 g, 4.24 mmoles) and dimethylphenylphosphine (1.30 g, 9.4 mmoles), described in our earlier paper[1] was repeated using n-hexane as the solvent and using a shorter reaction time of 5 h. The crude product was worked up as before, and the products separated by chromatography on alumina using ethyl acetate/petroleum ether (2/10) as the eluant. A pale yellow crystalline compound $[Re_2(CO)_9(PMe_2Ph)]$, m.p. 109°, (138 mg) was isolated from the second and third aliquots (12 ml) collected. Recrystallized from hot methanol. (Found: C, 26.82; H, 1.49; Re, 48.64. $C_{17}H_{11}O_9PRe_2$ calcd.: C, 26.82; H, 1.49; Re, 49.2%.)

Preparation of $Re(CO)_5(PMe_2Ph)$

The reaction between $Re_2(CO)_{10}$ (3.10 g, 4.24 mmoles) and dimethylphenylphosphine (1.30 g, 9.4 mmoles) was repeated exactly as described in the literature[1]. Evaporation of fractions 5–8 from the chromatographic separation yielded a pale yellow residue which was crystallized from methanol/petroleum ether to yield pale yellow crystals of $[Re(CO)_5(PMe_2Ph)]$ (63 mg), m.p. 136°. (Found: C, 33.81; H, 2.39; Re, 39.80. $C_{13}H_{11}O_5PRe$ calcd.: C, 33.64; H, 2.38; Re, 40.01%.) The other products described earlier[1] were isolated from the subsequent fractions collected.

DISCUSSION

Dirhenium decacarbonyl reacted with methyldiphenylphosphine on refluxing for 15 h in xylene to produce the disubstituted dirhenium compound $[Re(CO)_4(PMePh_2)]_2$ (II) in only moderate yield. This compound was isolated and purified chromatographically using alumina but no other products were separated in any significant amount.



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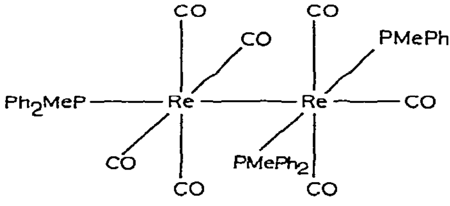

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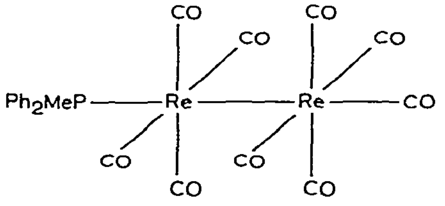

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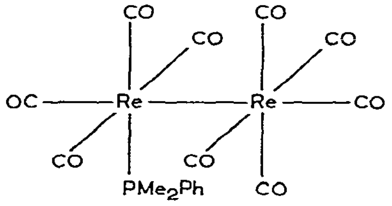

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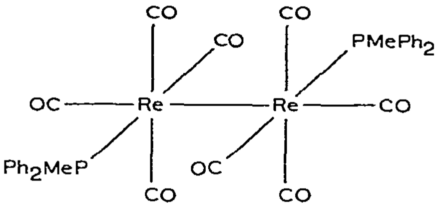

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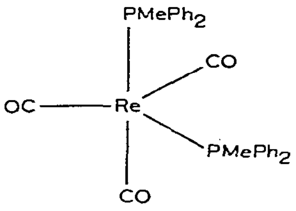

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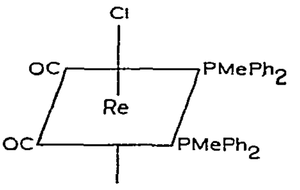

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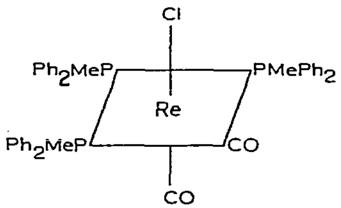

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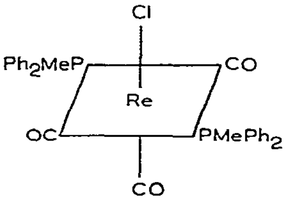

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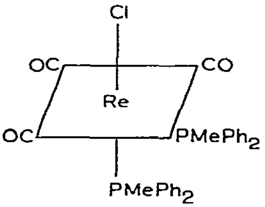

(10)

$Re_2(CO)_{10}$ also reacted photochemically with 1 mole of $PMePh_2$ per rhenium atom in cyclohexane to yield five main products which were readily separated from unreacted $Re_2(CO)_{10}$ and isolated by chromatography. The monosubstituted dirhenium complex $Re_2(CO)_9(PMePh_2)$ (I) was isolated in low yield. The disubstituted dirhenium complex $[Re(CO)_4(PMePh_2)]_2$ identical to the product formed in the thermal reaction, *i.e.* (II), was also isolated, but in lower yield.

The molecular weight of (II) (1004 in benzene, calcd. 997) proves that it is dimeric in solution, agreeing with the dimeric formulation for $[Re(CO)_4(PR_3)]_2$ ($PR_3 = PPh_3$[3,4], or PMe_2Ph[1]). The NMR spectrum of (II) in $CDCl_3$ broadened with time, indicating that (II) is oxidized by $CDCl_3$ forming a paramagnetic species.

Two isomeric trisubstituted dirhenium complexes (IV) and (V) were also isolated. Analyses and molecular weights are consistent with the formulation, $[Re_2(CO)_7(PMePh_2)_3]$. The isomers have distinctive melting points [compound (IV), 175° and compound (V), 154°]. Reaction of both compounds (IV) and (V) with HCl gas at 20° produced *trans*-$[ReCl(CO)_3(PMePh_2)_2]$ in good yield. A small yield of the monophosphine complex, *cis*-$[ReCl(CO)_4(PMePh_2)]$ (IX) was also isolated from that of (IV) with HCl gas reaction, while compound (V) produced both *cis*- and *trans*-$[ReCl(CO)_4(PMePh_2)]$ in low yield. This evidence indicates that compound (IV) contains two *trans*-substituted phosphine ligands on one rhenium atom, while the other rhenium atom has a carbonyl group substituted by a phosphine which is situated *cis* to the metal–metal bond (Fig. 1). Compound (IV) is thus analogous to $Re_2(CO)_7(PMe_2Ph)_3$ reported earlier[1].

Compound (V) also has two *trans*-phosphines on one rhenium atom and the third phosphine on the second rhenium atom. As reaction of (V) with HCl gas yielded both *cis*- and *trans*-$[ReCl(CO)_4(PMePh_2)]$, we are less certain of the configuration around the monosubstituted rhenium atom. *trans*-$ReBr(CO)_4PPh_3$[3] and *trans*-$ReBr(CO)_4(PMe_2Ph)$[1] both rapidly isomerize to the *cis*-isomer on refluxing in chloroform. Thus, we presume that *trans*-$ReCl(CO)_4(PMePh_2)$, the isomer isolated in the smaller amount, was formed initially in the reaction of (V) with HCl gas and that this subsequently partially isomerized to the *cis*-isomer.

We propose that (V) has the configuration (2), in which the monosubstituted rhenium atom is substituted *trans* to the metal–metal bond. The IR spectra of (IV) and (V) show no bands in the bridging carbonyl region, and so the two rhenium atoms must be linked only by a metal–metal bond.

Compound (VI) was also isolated in low yield in the photochemical reaction of $Re_2(CO)_{10}$ with 1 mole of $PMePh_2$ per rhenium atom. The molecular weight of this compound (2282, determined in benzene) indicates that this is a new cluster compound, and we tentatively formulate it as $Re_4(CO)_{10}(PMePh_2)_6$. The number of carbonyl ligands in the cluster cannot be determined accurately from the carbon analyses as an increase in two carbonyls in the cluster as formulated decreases the percentage carbon in the compound from 47.50 to 47.40. Further work will be undertaken to characterize this compound.

The monosubstituted dirhenium compound (I) reacted with HCl gas at 20° to form *trans*-$[ReCl(CO)_4(PMePh_2)]$ and $Re(CO)_5Cl$. Assuming no rearrangement took place in the isolation of products then compound (I) contains a phosphine ligand which has substituted a carbonyl *trans* to the metal–metal bond. In this case substitution of $Re_2(CO)_{10}$ by $PMePh_2$ parallels that of PPh_3[6].

The reaction of HCl gas at 20° with $[Re(CO)_4(PMePh_2)]_2$ resulted only in the isolation of *cis*-$[ReCl(CO)_4(PMePh_2)]$ indicating that the phosphine ligands are situated *cis* to the metal–metal bond, and that $Re_2(CO)_{10}$ is symmetrically substituted.

When compound (VI) reacted with HCl gas at 20° only *trans*-$[ReCl(CO)_3(PMePh_2)_2]$ (VIII) could be isolated from the reaction mixture, although thin layer chromatography showed that both *cis*- and *trans*-$[ReCl(CO)_4(PMePh_2)]$ were also formed in the reaction.

In none of these reactions of dimeric rhenium(0) compounds with HCl did we observe any sign of a hydride species, although complexes of the type *cis*-$Re(CO)_4(L)H$ and *trans*-$Re(CO)_3(L)_2H$ ($L = PPh_3$, PEt_3) are known to exist[12,13].

Freni *et al.*[13] have reported that the hydrogen in $ReH(CO)_3(PPh_3)_2$ is readily replaced by a chlorine when the complex reacts with hydrogen chloride. Thus, the hydride species could have been produced on fission of rhenium–rhenium and subsequently been converted into a chloride by reaction with further HCl (gas).

When $Re_2(CO)_{10}$ was reacted photochemically with two moles of $PMePh_2$ per rhenium atom, the two unsymmetrically substituted dirhenium complexes (IV) and (V) were obtained in only slightly increased yields when compared to the reaction using only 1 mole of $PMePh_2$. The products (IV) and (V) are identical in both reactions.

In addition to these products a paramagnetic complex $[Re(CO)_3(PMePh_2)_2]$ (III) was isolated in poor yield. (III) is extremely soluble in all organic solvents, even petroleum ether, and was difficult to purify. The bright yellow oily residue from which $[Re(CO)_3(PMePh_2)_2]$ could be isolated, reacted with HCl gas at 0° to yield *trans*-$[ReCl(CO)_3(PMePh_2)_2]$ (VIII). The monomeric formulation of (III) agrees with its PMe_2Ph analogue[1], and supports Nyman's[4] monomeric formulation for $Re(CO)_3(PPh_3)_2$. We found no evidence for a dimeric species similar to $[Re(CO)_3(PPh_3)_2]_2$ reported by Freni and co-workers[5].

The complex (VIII) could also be prepared directly from the Re^{III} (d^4) complex *mer*-$ReCl_3(PMePh_2)_3$ and the Re^{IV} (d^3) complex *trans*-$ReCl_4(PMePh_2)_2$. Chatt *et al.*[14,15] prepared these complexes from $ReCl_3OL_2$ ($L = PMePh_2$) by treatment with additional phosphine. Shaw *et al.*[9] reacted potassium perrhenate with HCl in the presence of a 5.3 molar excess of PMe_2Ph and isolated *mer*-$[ReCl_3(PMePh_2)_3]$ in good yield. In contrast to Shaw's work, reaction of $KReO_4$ with a 3.4 molar excess of $PMePh_2$ and HCl resulted in the isolation of the Re^{IV} complex $[ReCl_4(PMePh_2)_2]$ in good yield. This Re^{IV} compound reacted readily with CO in boiling 2-methoxyethanol resulting in the facile introduction of CO to form *trans*-$[ReCl(CO)_3(PMePh_2)_2]$ in a 44% yield.

Carbon monoxide also reacted with *mer*-$[ReCl_3(PMePh_2)_3]$ in boiling ethanol to produce not only (VIII) as reported by Shaw[9], but also $[ReCl(CO)_2(PMePh_2)_3]$ (VII). The complex *mer*-$[ReCl_3(PMePh_2)_3]$ could also be reduced by Na/Hg in the presence of CO to form $[ReCl(CO)_3(PMePh_2)_2]$ (VIII) but only in an 11% yield. In no case could the *fac*-isomer of $[ReCl(CO)_3(PMePh_2)_2]$ be isolated.

The isolation of $Re_2(CO)_9(PMePh_2)$ (I) prompted us to repeat the reaction between $Re_2(CO)_{10}$ and PMe_2Ph to determine whether we could isolate the PMe_2Ph analogue of (I). The repeat of our reaction in petroleum ether[1] resulted in the isolation of $Re(CO)_5(PMe_2Ph)$ (XI) as a new product. (XI) is unusual in that it violates the noble gas rule, there being six donor ligands surrounding a rhenium(0) d^7 atom. However, when $Re_2(CO)_5$ was reacted with 2 moles of PMe_2Ph in n-hexane and for a shorter reaction time of 5 h, $Re_2(CO)_9(PMe_2Ph)$ was isolated.

Infrared spectra

The $\nu(C{\equiv}O)$ frequencies in the IR spectra of the compounds described in this paper are given in Table 1. The monosubstituted dirhenium compound (I), exhibits five bands in this region. Based on chemical evidence we have assumed that (I) has a structure (3) in which the phosphine ligand is *trans* to the rhenium–rhenium bond. The axially substituted $Mn_2(CO)_9PPh_3$ has been studied by a number of workers[16-19], who have shown that five IR bands are expected for this molecule, which is assumed to have an overall C_{4v} symmetry. The intensities of the carbonyl bands of $Mn_2(CO)_9PPh_3$[17] (strong, strong, very strong, weak and strong) differ from those of (I). Alternatively, we can consider the symmetry of each half of the molecule in turn. The rhenium atom surrounded by five carbonyls will have C_{4v} symmetry, for which three IR active absorptions are expected ($2A_1 + E$). This environment is essentially the same as that of $LW(CO)_5$ (L = amine, pyridine or phosphine)[20]. The second rhenium atom has four carbonyls in the equatorial plane and this half of the molecule will also have C_{4v} symmetry. This corresponds to *trans*-$Re(CO)_4(PMe_2Ph)X$ (X = Br or I)[1] for which two bands were observed ($A_1 + E$). The weak intensity A_1 band is rendered IR active

TABLE 1

INFRARED ABSORPTIONS OF METHYL DIPHENYLPHOSPHINE SUBSTITUTED RHENIUM CARBONYL COMPLEXES

Compound	M.p. (°C)	Point group	Carbonyl modes predicted	Carbonyl stretching frequency (cm^{-1})
$[Re_2CO_9(PMePh_2)]$ (I)	135	C_{4v} C_{4v}	$2\ (A_1+E)^d$ $3\ (2\ A_1+E)$	2060 w, 2000 m, 1972 (sh)[a], 1945 s(br), 1910 m
$[Re(CO)_4(PMePh_2)]_2$ (II)	156–160	C_{2h}	$4\ (3\ B_u+A_u)^c$	2090 w, 2058 m, 2000 s[b], 1955 s(br), 1925 s
$[Re(CO)_3(PMePh_2)_2]$ (III)	145–150	C_s	$3\ (2A'+A'')$	2005 m, 1928 s, 1912 s[a]
$[Re_2(CO)_7(PMePh_2)_3]$ (IV)	175	C_s C_{2v}	$4\ (3\ A'+A'')^d$ $3\ (2\ A_1+B_1)$	1990 s, 1910 s, 1885 m[b] 2021 w, 1995 ms, 1938 s
$[Re_2(CO)_7(PMePh_2)_3]$ (V)	154	C_{4v} C_{2v}	$2\ (A_1+E)^d$ $3\ (2\ A_1+B)$	2043 w, 1994 s 1930 w, 1907 s, 1877 m
$[Re_4(CO)_{10}(PMePh_2)_6]$ (VI)	156–158			2075 w, 2040 w, 2019 m[b] 1992 s, 1975 (sh), 1908 s, 1875 m, 1790 mw
$[ReCl(CO)_2(PMePh_2)_3]$ (VII)	162–165	C_s	$2\ (2\ A')$	1938 s, 1833 s[a]
$[ReCl(CO)_3(PMePh_2)]$ (VIII)	144–146	C_{2v}	$3\ (2\ A_1+B_1)$	2050 w, 1954 s, 1898 m[a]
cis-$[ReCl(CO)_4(PMePh_2)]$ (IX)	124	C_s	$4\ (3\ A'+A'')$	2110 m, 2015 (sh), 2005 s, 1950 s[a]
trans-$[ReCl(CO)_4(PMePh_2)]$ (X)	140	C_{4v}	$2\ (A_1+E)$	2108 w, 1994 s[a]
$[Re(CO)_5PMe_2Ph]$ (XI)	136	C_{4v}	$3\ (2\ A_1+E)$	2030 w, 2005 w, 1950 s, 1905 w
$[Re_2(CO)_9PMe_2Ph]$ (XII)	109	C_s C_{4v}	$4\ (3\ A'+A'')^d$ $3\ (2\ A_1+E)$	2090 w, 2020 m, 2010 (sh), 1995 (sh), 1975 s, 1940 s, 1915 (sh)

[a] $CHCl_3$ as solvent. [b] C_6H_6 as solvent. [c] See discussion. [d] Symmetry of each half of the molecule considered independently.

by the axially unsymmetrical phosphine ligand. Thus, we would predict five IR absorptions for structure (3) which agrees with the observed spectrum.

The PMe_2Ph analogue of (I), $Re_2(CO)_9(PMe_2Ph)$ (XII) has a total of seven carbonyl bands, showing that (XII) has a lower symmetry than (I). Based on the reactions of (XII) with HCl (gas) we have proposed structure (4) for this compound. To determine the number of IR active modes for (XII), we will consider each half of the molecule separately. The unsubstituted Re atom will have C_{4v} symmetry, for which three IR active absorptions are expected ($2\ A_1+E$). The phosphine substituted Re atom will have C_s symmetry and approximates to *cis*-$Re(CO)_4(PR_3)Br$ ($PR_3=PMe_2Ph^1$ or $PPh_3{}^3$). In this case, four IR active carbonyl bands are expected and we predict a total of seven IR active bands for structure (4) which agrees with the observed spectrum. The only other reported case of equatorial substitution of the dimeric carbonyls, $M_2(CO)_{10}$, is *eq*-$Mn_2(CO)_9L^{19}$ (L = pyridine or nitrile). These compounds exhibit six bands in the $\nu(C{\equiv}O)$ region, in contrast to the nine bands predicted.

The unusual paramagnetic compound $Re(CO)_5(PMe_2Ph)$ (XI) shows two weak bands at high frequency, a strong band at 1950 cm^{-1}, and a third weak band at 1905 cm^{-1}. This compound corresponds to $-Re(CO)_5$ described above; the molecule has C_{4v} symmetry and three IR active absorptions are expected. According to Adams[21] when L is not a monoatomic ligand in the complex $M(CO)_5L$, the formally IR inactive B_1 mode often appears as a weak feature due to lifting of the selection rules if L is not axially symmetric. Thus, four bands were observed in the IR spectra of $Mo(CO)_5Py$[22] although $W(CO)_5(PPh_3)$[20] shows only two $\nu(C{\equiv}O)$ bands as the A_1 and E modes are accidentally degenerate[20]. The weak band at 2030 cm^{-1} is assigned to an A_1 mode and the intense band at 1950 cm^{-1} to the E mode.

$[Re(CO)_4(PMePh_2)]_2$ (II) exhibits no absorptions in the bridging carbonyl region and thus the two halves of the molecule are joined solely by a rhenium–rhenium bond. The reaction of (II) with HCl (gas) led us to postulate structure (5) for this compound. The five carbonyl stretching frequencies observed indicate that (II) has a lower symmetry than the axially substituted $Ph_3P(CO)_4Re{-}Re(CO)_4PPh_3$[3-5], which has either D_{4d} or D_{4h} symmetry and exhibits two carbonyl bands. The manganese analogue, $Ph_3P(CO)_4Mn{-}Mn(CO)_4PPh_3$[16,23,24] is also axially substituted. Haines and Poe[16], and Osborne and Stiddard[23] report only two carbonyl bands, but Lewis *et al.*[24] have studied the $\nu(C{=}O)$'s in detail of a large number of complexes *ax*-$[Mn(CO)_4PR_3]_2$ and reported that although only two bands are IR allowed, the Raman active bands can appear as weak absorptions in the IR. Thus, in the spectrum of $[Ph_2EtPMn(CO)_4]_2$, for example, five bands were observed. Structure (5) has C_{2h} symmetry and four modes of vibration ($3\,B_u + A_u$) which are infrared active and four modes ($3\,A_g + B_g$) which are Raman active. The three strong absorptions are assigned the B_u modes and the medium intensity band to the A_u mode. The additional weak band observed at 2090 cm^{-1} is probably one of the Raman active modes made weakly IR active by the asymmetry of the ligand.

The paramagnetic compound $Re(CO)_3(PMePh_2)_2$ (III) has a spectrum–two strong bands and a medium band at high frequency–consistent with the trigonal bipyramidal structure (6), which has C_s symmetry. The medium intensity band is assigned to the A'' mode, and the two strong bands at lower frequency to the A' modes. This assignment is very similar to that proposed for $Re(CO)_3(PMe_2Ph)_2$[1].

$Fe(CO)_3[(C_6H_5)_2P(C_6H_5)_2]$[25] in which the phosphorus donor atoms must be *cis* has a very similar IR spectrum.

Both isomers of $Re_2(CO)_7(PMePh_2)_3$ (IV) and (V) have complex spectra. Structures (1) and (2) have been proposed for isomers (IV) and (V), respectively, on chemical evidence. The local symmetry of each half of the molecule is considered independently in order to explain the observed IR spectra. In both (IV) and (V), the disubstituted half of the molecules will have C_{2v} symmetry, for which three IR bands would be expected ($2\,A_1 + B_1$). The monosubstituted Re atom in (IV) would have C_s symmetry, thus giving rise to four IR bands ($3\,A' + A''$) while the monosubstituted Re atom in (V) would have C_{4v} symmetry for which only two bands are expected, ($A_1 + E$). Thus, we would predict seven bands in the IR of (IV), and five in the case of (V). Combination and overlap of the two sets of vibrations expected for (IV) could give rise to the observed six line spectrum. The spectrum of (V) shows one weak and one strong band at high frequency which are assigned to the C_{4v} half of the molecule ($A_1 + E$). The bands at lower frequencies, which exhibit the intensity pattern weak, strong and medium, are assigned to the C_{2v} half of the molecule.

The spectrum of (VI) is too complex to permit deduction of the structure of this compound. We assign the band at 1790 cm^{-1} to bridging carbonyl groups.

The trisubstituted complex $ReCl(CO)_2(PMePh_2)_3$ (VII) has two intense carbonyl bands, which indicates that the carbonyls must be *cis* to each other. Two structures (7) and (8) are possible for (VII), both of which would give rise to two strong carbonyl bands. Compound (VII) has been assigned structure (8) from a study of its ^1H NMR spectrum.

The disubstituted complex $[ReCl(CO)_3(PMePh_2)_2]$ (VIII) exhibits three carbonyl absorptions with the intensity distribution, weak, strong, and medium. This intensity pattern eliminates the *fac*-isomer, for which three strong absorptions are expected[1]. Structures (9) (C_{2v} symmetry) and structure (10) (C_s symmetry) could both theoretically give rise to the observed spectrum. Structure (9) is chosen on ^1H NMR evidence. The band at highest frequency is assigned to the A_1^b mode and that at lowest frequency to the A_1^a mode. The strong absorption is assigned to the B_1 mode. Abel and Tyfield[26] have isolated the Ph_3P analogue of (VIII) in an unusual reaction in which the chlorine atom bound to Re is abstracted from the perchlorate ion

$$PPh_3 + [Re(CO)_6]^+ClO_4^- \rightarrow (Ph_3P)_2Re(CO)_3Cl$$

They used IR to postulate the structure of this compound. The very close similarity of the $\nu(C{\equiv}O)$ region of this compound to (VIII) adds support to their suggestion that $Re(CO)_3(PPh_3)_2Cl$ has a structure analogous to (9).

$ReCl(CO)_4(PMePh_2)$ has been isolated in two isomeric forms, (IX) and (X). (IX) has four carbonyl bands ($3\,A'+A''$), which is consistent with C_s symmetry. Thus, (IX) is the *cis* isomer. Compound (X) shows only two bands (A_1+E) in the carbonyl region, one weak and one strong absorption. This intensity pattern is indicative of C_{4v} symmetry of the *trans*-isomer. The weak intensity band is assigned to the A_1 mode and the strong absorption at lower frequency to the E mode. These assignments agree with those made for *cis*- and *trans*-$Re(CO)_4(PPh_3)X$ ($X=Cl$, Br[3] orI[5]).

Nuclear magnetic resonance spectra

^1H NMR has been successively used to determine the stereochemistry of PMe_2Ph complexes of the platinum metals[27] and rhenium complexes of formula $Re(CO)_{5-n}(PMe_2Ph)_nX$ ($n=2, 3, 4$; $X=Cl$, Br or I)[1,9]. The characteristic 1/2/1 triplet for two *trans*-phosphines is only observed if $J(P-P)$ is large compared to the sum of the $J(P-H)$ coupling constants[28]. In complexes of the type $[M(CO)_{6-x}L_x]$ ($M=Co$, Mo or W; $L=PMe_2Ph$, PMe_3 or $P(OMe)_3$[28]), $J(P-P)$ is not large enough for the distinctive triplet to be observed and thus, the phosphines cannot be used to determine the stereochemistry. The use of $PMePh_2$ has received much less attention, but as the diagnostic feature of the NMR spectra depends on $J(P-P)$ rather than the number of methyl groups, it should be as useful as PMe_2Ph for determining stereochemistry. Ruddick and Shaw have reported ^1H NMR spectra for *cis* and *trans* $PtClMe(PMePh_2)_2$[29]. The *trans*-isomer exhibits a 1/2/1 triplet at τ 7.79 [$J(P-H)$ 7.2 Hz], whereas the *cis*-isomer exhibits two doublets at τ 8.44 and 8.35 [$J(P-H)$ 10.4 and 9.0 Hz, respectively]. Two doublets are observed in the *cis*-isomer as the methyl groups have different chemical environments.

The methyl resonances of compounds (I) and (II) show well-defined 1/1 doublets at τ 7.53 and 7.50, respectively. The $J(P-H)$ values agree with those reported by Shaw[29]. The doublet in the case of (II) becomes less well-defined with time, indicating that (II) reacts with the solvent forming a paramagnetic species.

The methyl resonances of the isomeric compounds $Re_2(CO)_7(PMePh_2)$, (IV) and (V), both exhibit five line multiplets at approximately τ 8.20 equivalent to six protons, and a doublet at lower field ($\tau \sim 7.75$) equivalent to three protons. The five-line multiplets are assigned to the two *trans*-phosphines on the one rhenium atom, which lacks a plane of symmetry through the two phosphorus nuclei. In this case the methyl groups of the two ligands occupy unique environments, and the five-line multiplet arises from overlap of two 1/2/1 triplets[30]. The doublets are assigned to the phosphine attached to the monosubstituted rhenium atom in (IV) and (V).

The cluster compound $[Re_4(CO)_{10}(PMePh_2)_6]$ (VI) shows a broad multiplet between τ 7.5 and 8.0 equivalent to six protons and a doublet at higher field which is equivalent to three protons. We tentatively interpret this spectrum to mean that two rhenium atoms have one phosphine (the doublet resonance at high yield) and the remaining two rhenium atoms each have two *trans*-phosphines (the multiplet resonance centered at τ 7.85). In the latter case asymmetry through the P–Re–P plane would account, in part, for the complexity of the resonance.

It was not possible to assign the configuration of $ReCl(CO)_2(PMePh_2)_3$, (VII), by a study of $\nu(C{=}O)$ in the IR spectrum. Structures (7) and (8) both could account for the IR spectrum. The methyl resonances of (VII) are a four-line multiplet at τ 8.08, J(P–H) 3.5 Hz, corresponding to six protons and a singlet at τ 8.25, corresponding to three protons. The four line multiplet is assigned to two *trans*-phosphines, which thus eliminates structure (7). Structure (8) lacks a plane of symmetry through P–Re–P, and this asymmetry results in the methyl groups of the *trans*-phosphine occupying unique chemical environments. Overlap of two 1/2/1 triplets accounts for the observed spectrum. The singlet at τ 8.25 is assigned to the third phosphine ligand which is *cis* to both the *trans*-phosphines.

$ReCl(CO)_3(PMePh_2)_2$ (VIII) has either structure (9) or (10) based on IR evidence. The methyl resonance of (VIII) is a single 1/2/1 triplet, J(P–H) 5.0 Hz, equivalent to six protons. This is only consistent with structure (9), in which the two phosphines are *trans* to each other.

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)
$Re_2(CO)_9(PMePh_2)$ (I)	7.53	8.5		
$[Re(CO)_4(PMePh_2)]_2$ (II)	7.50	8.0		
$Re_2(CO)_7(PMePh_2)_3$ (IV)	7.74	7.0	8.18	5 line multiplet
$Re_2(CO)_7(PMePh_2)_3$ (V)	7.80	5.0	8.22	5 line multiplet
$Re_4(CO)_{10}(PMePh_2)_6$ (VI)	8.50	7.0	7.5–8.2	multiplet
$ReCl(CO)_2(PMePh_2)_3$ (VII)	8.25	singlet	8.08	3.5 (4-line multiplet)
$ReCl(CO)_3(PMePh_2)_2$ (VIII)			7.78	5.0
$Re(CO)_5(PMe_2Ph)$ (XI)	8.0[a]	multiplet		
$Re_2(CO)_9(PMe_2Ph)$ (XII)	7.95	9.0		

[a] This resonance is a diffuse and ill-defined multiplet, indicating that the sample is paramagnetic.

The ^1H NMR spectrum of (XI) is poorly defined, indicating that the compound is paramagnetic. $Re_2(CO)_9(PMe_2Ph))$ (XII) exhibits a doublet at τ 7.95 [$J(P-H)$ 9.0 Hz]. The difference in τ values of (I) and (XII) is most likely related to the difference in basicity of the phosphines rather than the different structures (3). In general, the methyl resonances of the $PMePh_2$ complexes described here have lower τ values than their PMe_2Ph analogues[1].

CONCLUSION

The reaction of $PMePh_2$ and $Re_2(CO)_{10}$ has resulted in the isolation of a number of new phosphine carbonyl complexes of rhenium, in which initial substitution of a carbonyl appears to have been either *cis* or *trans* to the metal–metal bond. (I) has the $PMePh_2$ ligand *trans* to the rhenium–rhenium bond, whereas in (II) substitution is *cis* to the rhenium–rhenium bond. Thus, $PMePh_2$ is intermediate between PPh_3, in which case *trans*-substitution occurs[3-6] and PMe_2Ph, when *cis*-substitution occurs[1]. Thus, the basicity of the phosphine seems to play an important part in determining the course of the reaction. Basolo and Wawersik's mechanism for the reaction of $Mn_2(CO)_{10}$ with PPh_3[19] is a dissociative one and might be expected to apply in the photochemical reaction used in this work. However, Basolo's arguments are based on the formation of *ax*-$Mn_2(CO)_9PPh_2$ as the initial product. Further substitution by PPh_3 to form *ax*-$Mn_2(CO)_8(PPh_3)_2$ is independent of the concentration of PPh_3 and Basolo and Wawersik suggested that the axial phosphine in $Mn_2(CO)_9PPh_3$ labilizes the CO *trans* to it, even though the two groups are separated by two atoms of Mn. An alternative mechanism has been postulated for $Mn_2(CO)_{10}$[16] and $Re_2(CO)_{10}$[6] reacting with PPh_3, which involves the migration of a carbonyl into the metal–metal bond to form $(CO)_5MCOM(CO)_4$ as an intermediate. In the case of $Mn_2(CO)_{10}$ Basolo and Wawersik argue convincingly in favour of their dissociative mechanism.

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