The Palladium-catalysed Reaction Between $[Re_2(CO)_{10}]$ and Phosphines and the Crystal and Molecular Structure of Diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$†

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The reaction between $[Re_2(CO)_{10}]$ and PR_3 [PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)_3$, or $P(OMe)_3$] in xylene is catalysed by Pd/C, $Pd/CaCO_3$, and PdO and yields the complexes $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 1 or 2) as the major products (15—80%). Attempts to synthesise $[Re_2(CO)_{10-n}(PR_3)_n]$ from $[Re_2(CO)_{10}]$ and PR_3 in the presence of NMe_3O under milder conditions (*e.g.* refluxing CH_2Cl_2) also gave the above products with n = 1 or 2 as well as high yields of *fac*-$[ReCl(CO)_3(PR_3)_2]$. An *X*-ray crystal structure determination of diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ was carried out: space group $C2/c$, $Z = 4$, $a = 22.779(9)$, $b = 7.166(3)$, $c = 17.249(7)$ Å, $\beta = 95.13(3)°$, $R = 0.0602$. The structure has a staggered geometry with torsion angles deviating by ± 6° from the ideal (45°). The Re–Re bond length was found to be 3.044(1) Å, *cf.*, 3.041(1) Å for $[Re_2(CO)_{10}]$, indicating that this parameter is almost invariant on substitution of CO by PMe_2Ph.

In recent publications[1–3] we have reported on the catalysed reaction between $[M_2(CO)_{10}]$ (M = Mn or Re) and isonitriles which yields $[M_2(CO)_{10-n}(CNR)_n]$ (n = 1—4). In these reactions the stereochemistry of *all* products isolated could be explained in terms of the dominance of electronic over steric factors, which resulted in equatorial isonitrile substitution. In a continuation of this work we now report on the reaction (catalysed and otherwise) between $[Re_2(CO)_{10}]$ and Group 5 donor ligands (PR_3) to give the products $[Re_2(CO)_{10-n}((PR_3)_n]$ (n = 1 or 2) in which steric factors now influence the course of the reaction.

The reaction (both thermal and photochemical) between $[Re_2(CO)_{10}]$ and PR_3 has been investigated by many groups[4] and in most cases the major product(s) obtained are either axial $[Re_2(CO)_9(PR_3)]$ and/or diaxial $[Re_2(CO)_8(PR_3)_2]$ together with minor amounts of products such as $[ReH(CO)_3(PR_3)_2]$.[5] There have also been reports of the synthesis of equatorial $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 1 or 2)[6–8] as well as $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 3 or 4).[9] The use of alternative routes,[10,11] *e.g.* using substituted rhenium dimers, also yields a range of $[Re_2(CO)_8(PR_3)_2]$ complexes of mixed stereochemistry[11] (see below).

Although numerous techniques have been used to establish the stereochemistry of the resulting complexes (*e.g.* ^1H and ^{31}P n.m.r. spectroscopy and mass spectrometry), i.r. spectroscopy is the most ubiquitous means of product identification. However, i.r. spectroscopy is not highly reliable in this regard as the number of ν(CO) bands predicted by group theory does not necessarily correspond with those observed in practice. In this publication we have thus attempted to correlate the observed i.r. spectra (number of bands, intensity) of the complexes $[Re_2(CO)_8L_2]$ (L = substituting ligand) with product stereochemistry using all available reported chemical and physical data on these complexes, with particular emphasis on data obtained from *X*-ray crystallographic studies. The method can be extended to other derivatives of $[Re_2(CO)_{10}]$.[12] As no crystallographic data are available on any $[Re_2(CO)_{10-n}(PR_3)_n]$ ($n > 1$) complexes in the literature, we have also carried out the molecular and crystal structure determination of $[Re_2(CO)_8(PMe_2Ph)_2]$. As this complex was predicted to have a diaxial arrangement of PMe_2Ph ligands (relative to the Re–Re bond) we were also interested in obtaining bond-length and -angle data on the effect of PR_3 substitution on the molecular parameters of the substituted dimer.

Experimental

General.—The complex $[Re_2(CO)_{10}]$ was purchased from Strem Chemicals. The phosphines were obtained from Strem Chemicals [PMe_2Ph, $PMePh_2$, PMe_3, $P(CH_2Ph)_3$, and $AsMe_2Ph$], Merck Chemicals (PPh_3), or British Drug Houses Ltd. [$P(OMe)_3$]. The catalysts Pd/C (10% Pd) and Pd/$CaCO_3$ (10% Pd) were obtained from Merck Chemicals, and PdO from Johnson Matthey Chemicals Ltd. The compound $NMe_3O \cdot 2H_2O$ was purchased from Fluka AG. All chemicals were used as obtained from the manufacturers, without further purification.

Xylene was distilled from sodium under nitrogen prior to use. All reactions were performed under argon. Thin-layer chromatography was carried out on Merck silica gel 60F-254 plates, and preparative layer chromatography was performed using Merck silica gel plates (20 × 20 cm, layer thickness 2 mm). Column chromatography was carried out using Merck 60 (60—200 μm) silica gel.

Infrared spectra were recorded on a JASCO IRA I spectrophotometer. Melting points were determined on a Kofler micro hot-stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories, Council for Scientific and Industrial Research, Pretoria.

Synthesis of $[Re_2(CO)_{10-n}(PR_3)_n]$ [PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2Ph)_3$, *or* $P(OMe)_3$; n = 1 *or* 2] *from the Reaction between* $[Re_2(CO)_{10}]$ *and* PR_3 *in the Presence of Palladium Catalysts.*—The complex $[Re_2(CO)_{10}]$ (163 mg, 0.25 mmol) and catalyst (Pd/C, $Pd/CaCO_3$, or PdO; 15 mg) were stirred in xylene (10 cm^3) and to this solution was added PR_3 (0.75 mmol). The solution was refluxed at *ca.* 140 °C for 1—9 h, depending on PR_3 (see Table 1), and the progress of the reaction monitored by t.l.c. [silica gel; eluant, ethyl acetate–light petroleum (b.p. 80—100 °C) (1:3)]. The products were isolated by preparative layer chromatography (silica, eluant as for t.l.c.), extracted with benzene, and recrystallised from benzene–hexane

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† Bis[tetracarbonyl(dimethylphenylphosphine)rhenium](*Re–Re*).

Supplementary data available (No. SUP 56287, 4 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Details of catalytic syntheses of $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 1 or 2) complexes

PR_3	Catalyst	Reaction time (h)	Product^a	Yield (%)^b
PPh_3	Pd/C (10%)	9	$[Re_2(CO)_9(PPh_3)]$	20
			$[Re_2(CO)_8(PPh_3)_2]$	20
$PMePh_2$	Pd/C (10%)	6	$[Re_2(CO)_9(PMePh_2)]$	20
			$[Re_2(CO)_8(PMePh_2)_2]$	40
	PdO	3	$[Re_2(CO)_8(PMePh_2)_2]$	60
			$[ReH(CO)_3(PMePh_2)_2]$	3
PMe_2Ph	Pd/C or Pd/$CaCO_3$ (10%)	2	$[Re_2(CO)_9(PMe_2Ph)]$	2
			$[Re_2(CO)_8(PMe_2Ph)_2]$	82
			$[ReH(CO)_3(PMe_2Ph)_2]$	3
	PdO	1	$[Re_2(CO)_8(PMe_2Ph)_2]$	84
$P(CH_2Ph)_3$	Pd/C (10%)	8	$[Re_2(CO)_{10}]$	14
			$[Re_2(CO)_9\{P(CH_2Ph)_3\}]$	15
PMe_3	PdO	2	$[Re_2(CO)_9(PMe_3)]$	14
			$[Re_2(CO)_8(PMe_3)_2]$	18
$P(OMe)_3$	Pd/C (10%)	4	$[Re_2(CO)_9\{P(OMe)_3\}]$	55
			$[Re_2(CO)_8\{P(OMe)_3\}_2]$	25

^{a} Traces of other products were also observed but were not isolated. ^{b} Isolated yields.

solutions to yield colourless to yellow solids characterised by i.r. spectroscopy and elemental analyses.

Synthesis of $[Re_2(CO)_{10-n}(PR_3)_n]$ [PR_3 = $PMePh_2$, PMe_3, *or* $P(CH_2Ph)_3$; n = 1 *or* 2] *by the* NMe_3O*-assisted Reaction between* $[Re_2(CO)_{10}]$ *and* PR_3.—The complex $[Re_2(CO)_{10}]$ (163 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (10 cm^3) to which PR_3 (0.75 mmol) had been added, and $NMe_3O{\cdot}2H_2O$ (60 mg, 0.54 mmol) dissolved in degassed MeOH (5 cm^3) was added. The solution was then warmed at 40 °C for 8 h and the progress of the reaction monitored by t.l.c. [silica gel; eluant, ethyl acetate–light petroleum (b.p. 80—100 °C) (1:3)]. The products were isolated by preparative layer chromatography (silica gel, eluant as for t.l.c.), extracted with CH_2Cl_2, and recrystallised from CH_2Cl_2–pentane solutions to yield colourless to yellow solids characterised by i.r. spectroscopy and elemental analyses.

Preparation of $[Re_2(CO)_8(PMe_2Ph)_2]$, *isomer* (**b**).—The complex $[Re_2(CO)_{10}]$ (653 mg, 1 mmol) was dissolved in acetonitrile (10 cm^3) and the solution heated at 80 °C. To this solution was added $NMe_3O{\cdot}2H_2O$ (234 mg, 2.1 mmol) dissolved in degassed methanol (10 cm^3). Reaction to $[Re_2(CO)_8(NCMe)_2]$ was instantaneous as evidenced by the colour change from colourless to pale yellow. The compound PMe_2Ph (2.1 mmol) was added to the pale yellow solution and the mixture heated at 80 °C for 2 h. The product was isolated by column chromatography (2 × 40 cm silica column, gradient elution with hexane–benzene solution starting with hexane and ending with benzene). Recrystallisation from CH_2Cl_2–pentane solution gave a cream solid, m.p. 142—144 °C (Found: C, 33.5; H, 2.7. $C_{24}H_{22}O_8P_2Re_2$ requires C, 33.0; H, 2.6%).

Preparation of $[Re_2(CO)_8(PMePh_2)_2]$, *isomer* (**b**).—The complex $[Re_2(CO)_{10}]$ (667 mg, 1.02 mmol) and $PMePh_2$ (4.0 mmol) were refluxed in xylene (17 cm^3) at *ca.* 140 °C for 15 h. During this time the solution changed from colourless to intense yellow. The xylene and excess of phosphine were removed under vacuum to yield a yellow solid which after chromatographic procedures[7] yielded the required product with spectroscopic and analytical properties similar to those reported previously.[7]

Crystal and Molecular Structure of $[Re_2(CO)_8(PMe_2Ph)_2]$.—*Data collection.* The compound diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ was synthesised *via* the PdO-catalysed reaction between $[Re_2(CO)_{10}]$ and PMe_2Ph. Recrystallisation from diethyl ether–pentane solution under nitrogen at 20 °C yielded fine colourless needle-like crystals. A crystal measuring 0.19 × 0.09 × 0.09 mm was selected for crystallographic analysis.

Preliminary investigation by standard Weissenberg photography established the space group as either *C*2/*c* or *Cc*, from the conditions *hkl*, $h + k = 2n$, *h*0*l*, $l = 2n$ ($h = 2n$), and 0*k*0, $k = 2n$. Refined cell constants were obtained during data collection on a Philips PW1100 four-circle diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å) at room temperature (20 °C).

Crystal data. $C_{24}H_{22}O_8P_2Re_2$, M = 872.76, a = 22.779(9), b = 7.166(3), c = 17.249(7) Å, β = 95.13(3)°, U = 2 804.33 Å^3, $F(000)$ = 1 640, Z = 4, D_c = 2.07 g cm^{-3}, μ(Mo-K_α) = 84.01 cm^{-1}.

Lorentz and polarisation corrections were applied, and the data were empirically corrected for absorption effects using the program DIFABS,[13a] as adapted by Kruger.[13b] Data were collected in ω—2θ scan mode in the region $3 \leqslant \theta \leqslant 23°$. A total of 1 768 reflections as measured at a speed of 0.03° s^{-1} with a scan width of 0.9°ω. After omission of all unobserved reflections with $F < \sigma(F)$ a unique data set of 1 473 observations was retained.

Structure solution and refinement. Structure analysis and refinement were carried out using the program SHELX 82.[14a] Initial co-ordinates for the rhenium atoms were derived from a Patterson synthesis, and the positions of the other non-hydrogen atoms were found by Fourier difference syntheses. The structure was refined in the centrosymmetric space group *C*2/*c* (no. 15), the two halves of the molecule being related by a crystallographic two-fold axis. Positional parameters for all atoms, and anistropic thermal parameters for the rhenium and phosphorus atoms, were refined by full-matrix least-squares analyses. In the initial stages the phenyl rings were treated as rigid hexagons, but all restraints were removed in the later stages of refinement. Least-squares refinement was considered complete when all parameter shifts were less than 0.5σ. At this stage the conventional *R* was 0.0602. Unit weights were used. Scattering factors for Re^0 were taken from ref. 14*b* and anomalous dispersion corrections[14c] were made for rhenium.

Final atomic co-ordinates for all non-hydrogen atoms are given in Table 2, an ORTEP[15] diagram indicating the

Table 2. Final atomic co-ordinates for the non-hydrogen atoms of diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Re	−0.048 0(1)	0.187 9(1)	0.182 7(1)	C(4)	0.008 5(9)	0.295 6(30)	0.119 4(11)
P	−0.124 9(2)	0.196 8(8)	0.082 4(3)	C(5)	−0.147 9(12)	0.429 9(39)	0.047 5(14)
O(1)	−0.125 3(6)	0.001 3(20)	0.301 1(8)	C(6)	−0.111 2(10)	0.081 5(34)	−0.009 3(13)
O(2)	−0.007 8(7)	−0.206 7(24)	0.126 9(9)	C(7)	−0.193 7(9)	0.095 2(30)	0.109 3(11)
O(3)	0.917 4(8)	0.581 1(25)	0.242 3(9)	C(8)	−0.206 7(11)	−0.088 9(35)	0.089 6(13)
O(4)	0.041 2(7)	0.365 9(24)	0.078 9(9)	C(9)	−0.258 0(12)	−0.174 1(41)	0.116 6(15)
C(1)	−0.096 3(9)	0.067 9(29)	0.256 3(11)	C(10)	−0.295 9(12)	−0.078 2(41)	0.156 4(15)
C(2)	−0.021 8(9)	−0.055 1(30)	0.148 6(11)	C(11)	−0.284 3(11)	0.113 1(36)	0.169 7(13)
C(3)	−0.068 5(9)	0.432 5(28)	0.221 5(10)	C(12)	−0.232 0(10)	0.200 1(33)	0.149 0(12)

numbering system used is given in Figure 2, and a packing diagram in Figure 3.

Discussion

The Palladium-catalysed Reaction between $[Re_2(CO)_{10}]$ *and* PR_3.—As part of an extension of the Pd-catalysed reaction of $[Re_2(CO)_{10}]$ with isonitriles[2] to other ligands the reaction of $[Re_2(CO)_{10}]$ with Group 5 donor ligands, PR_3, was investigated.[16] The thermal reaction between $[Re_2(CO)_{10}]$ and PR_3 is extremely sluggish even at elevated temperatures,[7] *e.g.* we have observed that the reaction between $[Re_2(CO)_{10}]$ and PMe_2Ph (140 °C, 10 h) yielded only small amounts of $[Re_2(CO)_9(PMe_2Ph)]$ and $[Re_2(CO)_8(PMe_2Ph)_2]$ (as well as trace amounts of other uncharacterised products) and >80% $[Re_2(CO)_{10}]$ was recovered.

Use of palladium catalysts [*e.g.* Pd/C (10%), Pd/$CaCO_3$ (10%), and PdO] yields mono- and di-substituted derivatives $[Re_2(CO)_{10-n}(PR_3)_n]$ (*n* = 1 or 2) in poor to good yield after moderate reaction times. Examples of this reaction covering a range of PR_3 groups varying in both steric and electronic properties are given in Table 1. In favourable cases the disubstituted complexes can be obtained in good yields as the sole reaction product after relatively short times, *e.g.* 84% $[Re_2(CO)_8(PMe_2Ph)_2]$ after 1 h. Reactions with PR_3 = $PMePh_2$ and PMe_2Ph also yielded trace amounts of products which were isolated, and by comparison with the i.r. spectrum of *fac*-$[ReH(CO)_3(PPh_3)_2]$ [i.r. ($CHCl_3$), ν(CO) 2 009s, 1 960s, and 1 900s cm^{-1}] and elemental analyses were characterised as *fac*-$[ReH(CO)_3(PMePh_2)_2]$ [i.r. ($CHCl_3$), ν(CO) 2 000s,sp, 1 910s, and 1 870s cm^{-1}] and *fac*-$[ReH(CO)_3(PMe_2Ph)_2]$[i.r. ($CHCl_3$), ν(CO) 2 030s,sp, 1 946s, and 1 883s cm^{-1}].[6] Such products were almost certainly formed with other PR_3 ligands but product decomposition on silica plates precluded their isolation.

Comparison of the i.r. data for the $[Re_2(CO)_{10-n}(PR_3)_n]$ (*n* = 1 or 2) products (Table 2) with that of axial $[Mn_2(CO)_9(PMe_2Ph)]$[17] [i.r. (benzene), ν(CO) 2 094w, 2 016s, 1 993vs, 1 969sh, and 1 938m cm^{-1}] and diaxial $[Mn_2(CO)_8(PMePh_2)_2]$ [i.r. (benzene), ν(CO) 1 983w and 1 954vs cm^{-1}],[17] for which axial substitution has been established from *X*-ray crystallographic structure determinations,[18,19] indicates that the products isolated are either axial $[Re_2(CO)_9(PR_3)]$ or diaxial $[Re_2(CO)_8(PR_3)_2]$. An *X*-ray crystal and molecular structure determination of $[Re_2(CO)_8(PMe_2Ph)_2]$ has also confirmed the diaxial substitution geometry (see below).

Alternative Routes to $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 1 *or* 2) *Complexes.*—These complexes can also be synthesised by the NMe_3O-assisted reaction in CH_2Cl_2 between $[Re_2(CO)_{10}]$ and PR_3.[11] Typically, axial $[Re_2(CO)_9(PR_3)]$ (*ca.* 40% yield), diaxial $[Re_2(CO)_8(PR_3)_2]$ (*ca.* 30%), and $[ReCl(CO)_3(PR_3)_2]$ (*ca.* 10%) are the major products obtained after product separation and purification. The last product is almost certainly produced from reaction of initially formed $[ReH(CO)_3(PR_3)_2]$ with the solvent CH_2Cl_2.[20] The i.r. spectra confirm the *fac* stereochemistry,[6] which gives a spectrum quite different from that of *mer-trans*-$[ReX(CO)_3L_2]$ complexes [*e.g.* X = H, L = PPh_3; ν(CO) 1 935s cm^{-1}].[6] The synthesis of the *fac* isomer, the kinetic reaction product, rather than the *mer-trans* product which has been obtained by other workers from the thermal reactions between $[Re_2(CO)_{10}]$ and PR_3, reflects the mild reaction conditions (40 °C) employed in this work as *fac* isomers are known to isomerise readily to the *mer-trans* isomers.[21]

Since the complex $[Mn_2(CO)_8(AsMe_2Ph)_2]$ has been shown by *X*-ray crystallography[19] to have a diequatorial stereochemistry [Figure 1(*c*)], an attempt to prepare arsine derivatives of $[Re_2(CO)_{10}]$ was made. The NMe_3O-assisted reaction between $[Re_2(CO)_{10}]$ and $AsMe_2Ph$ yielded only axial $[Re_2(CO)_9(AsMe_2Ph)]$ (74%) and *fac*-$[ReCl(CO)_3(AsMe_2Ph)_2]$ (15%) characterised by i.r. spectroscopy (Table 3) and elemental analysis. No $[Re_2(CO)_8(AsMe_2Ph)_2]$ was detected.

The reaction of $[Re_2(CO)_{10}]$ and PMe_2Ph in the presence of NMe_3O in CH_3CN rather than CH_2Cl_2 yielded a cream product which analysed for $[Re_2(CO)_8(PMe_2Ph)_2]$ [referred to here as isomer (**b**)] but had an i.r. spectrum different from the thermally synthesised isomer diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ (Table 3). The similarity to the spectrum of axial–equatorial $[Re_2(CO)_8(PPh_3)_2]$[10] suggests that isomer (**b**) is axial–equatorial $[Re_2(CO)_8(PMe_2Ph)_2]$. Attempts to obtain crystals suitable for *X*-ray crystallographic analysis, to confirm this proposal, have so far been unsuccessful. The above reaction almost certainly occurs *via* intermediate formation of diequatorial $[Re_2(CO)_8(NCCH_3)_2]$.[22] Subsequent reaction with PMe_2Ph results in displacement of the CH_3CN ligands, steric considerations determining the axial–equatorial substitution pattern (PMe_2Ph, Tolman cone angle 122°).[23]

Product Characterization.—It is significant to note that sidebands are often observed in the i.r. spectra of diaxial $[Re_2(CO)_8(PR_3)_2]$ complexes. For the related diaxial $[Mn_2(CO)_8(PR_3)_2]$, Lewis *et al.*[24] have ascribed some of the observed minor ν(CO) vibrations to the ^{13}CO isotope absorptions. However, this is unlikely to be the explanation for the $[Re_2(CO)_8(PMe_2Ph)_2]$ complex as the minor ν(CO) bands *disappear* on recrystallisation. The i.r. spectra ($CHCl_3$) recorded for the crystals of $[Re_2(CO)_8(PMe_2Ph)_2]$ used in the *X*-ray study show *no* sidebands. An i.r. spectrum of a crude sample of diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ indicated weak sidebands, and further, when the above complex was heated in toluene (80 °C, 4 h) the sidebands [i.r. (toluene): 2 070w, 2 020m, and 1 930(sh) cm^{-1}] grew in intensity and corresponded to those of another isomer of $[Re_2(CO)_8(PMe_2Ph)_2]$ [isomer (**b**), see above]. Attempts to separate the two isomers by t.l.c. were unsuccessful. A reinvestigation of the reaction between $[Re_2(CO)_{10}]$ and

Table 3. I.r. spectral data for $[Re_2(CO)_{10-n}(PR_3)_n]$ (n = 1 or 2) and $[ReCl(CO)_3(PR_3)_2]$ derivatives

Complex	$\tilde{\nu}(CO)^a$/cm^{-1}
$[Re_2(CO)_9(PPh_3)]$	2 113w,sp, 2 040w,sp, 1 998vs, 1 964(sh), 1 940m
$[Re_2(CO)_9(PMePh_2)]$	2 111w,sp, 2 040w,sp, 1 995vs, 1 962(sh), 1 938m
$[Re_2(CO)_9(PMe_2Ph)]$	2 108w,sp, 2 038m,sp, 1 990vs, 1 960(sh), 1 932m
$[Re_2(CO)_9\{P(CH_2Ph)_3\}]$	2 110w,sp, 2 034w,sp, 1 998vs, 1 962(sh), 1 938m
$[Re_2(CO)_9(PMe_3)]$	2 108w,sp, 2 040m,sp, 1 990vs, 1 956(sh), 1 927m
$[Re_2(CO)_9\{P(OMe)_3\}]$	2 108w,sp, 2 040w,sp, 1 994vs, 1 952(sh), 1 930m
$[Re_2(CO)_9(AsMe_2Ph)]$	2 112w,sp, 2 052m,sp, 1 998vs, 1 964w, 1 930m
$[Re_2(CO)_8(PPh_3)_2]$	2 000(sh), 1 958vs
$[Re_2(CO)_8(PMePh_2)_2]$	2 015w, 1 954vs
$[Re_2(CO)_8(PMe_2Ph)_2]$	2 010w, 1 949vs
$[Re_2(CO)_8\{P(CH_2Ph)_3\}_2]$	2 010(sh), 1 954vs
$[Re_2(CO)_8(PMe_3)_2]$	2 000(sh), 1 943vs
$[Re_2(CO)_8\{P(OMe)_3\}_2]$	2 000(sh), 1 970vs
$[Re_2(CO)_8(PMe_2Ph)_2]^b$	2 078mw,sp, 2 000m,sp, 1 974(sh), 1 964w,br, 1 932ms, 1 916s
$[Re_2(CO)_8(PMePh_2)_2]^c$	2 095w, 2 060m, 2 000s, 1 950s, 1 922m
$[ReCl(CO)_3(PMePh_2)_2]$	2 030s,sp, 1 954s, 1 895s
$[ReCl(CO)_3(PMe_2Ph)_2]$	2 044s,sp, 1 957s, 1 896s
$[ReCl(CO)_3\{P(CH_2Ph)_3\}_2]$	2 024s,sp, 1 940s, 1 900s
$[ReCl(CO)_3(PMe_3)_2]$	2 036s,sp, 1 950s, 1 894s
$[ReCl(CO)_3\{P(OMe)_3\}_2]$	2 040s,sp, 1 970s, 1 910s
$[ReCl(CO)_3(AsMe_2Ph)_2]$	2 050s,sp, 1 960s, 1 914s

[a] Recorded in $CHCl_3$ unless otherwise stated. [b] Recorded in hexane. Isomer (**b**) (see text; corresponds to the axial–equatorial isomer). [c] Recorded in xylene.

Table 4. Correlation between i.r. data and molecular geometry for $[M_2(CO)_8L_2]$ (M = Mn or Re) complexes

Isomer[a]	Number of ν(CO) bands		Intensity pattern	Examples
	Calc.[b]	Obs.[c]		
(**a**) Diaxial	2	2	w, vs	$[Mn_2(CO)_8(PMePh_2)_2]$,[d,17,19] $[Re_2(CO)_8(PMe_2Ph)_2]$[d,e]
(**b**) Axial–equatorial	8	5	w, m, s, s, s	$[Re_2(CO)_8(PR_3)_2]$ (*e.g.* PR_3 = Bu^t or Ph)[9]
(**c**) Equatorial–equatorial (staggered)	8	5(6)	w, m, s,(sh), w, ms	$[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$[d,2,3,f]
(eclipsed)	8	4(5)	w, m, s,(w), m	$[Mn_2(CO)_8(AsMe_2Ph)_2]$[d,17,19]
(**d**) Axial–equatorial	8	5	m, s, vs, s, m	$[Mn_2(CO)_8(C_4H_6)]$[g]
(**e**) *cis*-Diequatorial	8	6	m, vs, vs, w, m, m	$[Mn_2(CO)_8(CNBu^t)_2]$[d,25]
(**f**) *trans*-Diequatorial	8			No examples known

[a] See Figure 1. All complexes have the staggered conformation unless otherwise stated. [b] Calculations were carried out assuming the ligand symmetry is ignored, *i.e.* local symmetry approximation holds. [c] The number of bands may be affected by the solvent medium. [d] Crystal structure determination. [e] This work. [f] K. W. Lee, W. J. Pennington, A. W. Cordes, and T. L. Brown, *Organometallics*, 1984, **3**, 404. [g] M. L. Ziegler, H. Haas, and R. R. Skeline, *Chem. Ber.*, 1965, **98**, 2454.

$PMePh_2$ using published procedures[8] (xylene, 140 °C, 5 h) which was reported to yield the diequatorial isomer yielded a compound analysing as $[Re_2(CO)_8(PMe_2Ph)_2]$ but with i.r. data also characteristic of the (**b**) isomer of $[Re_2(CO)_8(PMePh_2)_2]$, *i.e.* presumably the axial–equatorial isomer. The above data, together with recent studies by Nubel and Brown,[10] allow for a rationalisation of the data that have been published on the synthesis of $[Re_2(CO)_8(PR_3)_2]$ complexes from $[Re_2(CO)_{10}]$ and its derivatives. Electronically, equatorial CO substitution by PR_3 is predicted and provided *low-temperature* ligand-substitution routes are used this is observed {*e.g.* by displacement of bridging ligands from $[Re_2(\mu\text{-}H)(\mu\text{-olefin})(CO)_8]$ by PR_3}.[10] If, in the above reactions, the PR_3 ligands are bulky the diequatorial isomer isomerises to an axial–equatorial isomer and this is observed for PR_3 groups of cone angle *ca.* 110—140°.

However, use of bulky ligands (cone angle *ca.* 140°) or reaction of $[Re_2(CO)_{10}]$ with PR_3 under more forcing conditions yields diaxial $[Re_2(CO)_8(PR_3)_2]$. (This product is also obtained from the NMe_3O-assisted reactions in CH_2Cl_2 or $CHCl_3$[11]). Formation of the axial–equatorial rather than the diaxial isomer when extended reaction times are used[7] can be interpreted in terms of ligand isomerisation. We tentatively propose that this isomerisation occurs *via* metal–metal bond cleavage followed by ligand rearrangement on the radicals followed by radical recombination. Consistent with this proposal is the formation of axial–equatorial $[Re_2(CO)_8(PR_3)_2]$ (PR_3 = $PMePh_2$)[7] obtained by photolysis of $[Re_2(CO)_{10}]$ and PR_3. It thus appears that the size of the ligand as well as the synthetic procedure employed determine the stereochemical outcome of the reaction between $[Re_2(CO)_{10}]$ and PR_3.

Correlation of I.r. Spectral Data with Stereochemistry.—A survey of the literature has suggested that a correlation exists between i.r. spectra (number and intensity of bands) and isomer stereochemistry for $[M_2(CO)_{10-n}L_n]$ (M = Mn or Re, n = 1—4, L = ligand).[12] Herein we comment only on the disubstituted products (n = 2). As shown in Figure 4, six disubstituted isomers are possible (excluding different rotamers) and five of these isomers have been synthesised to date. Table 4 compares the expected number of bands calculated by Group Theory with the number and intensity of the bands actually observed. The

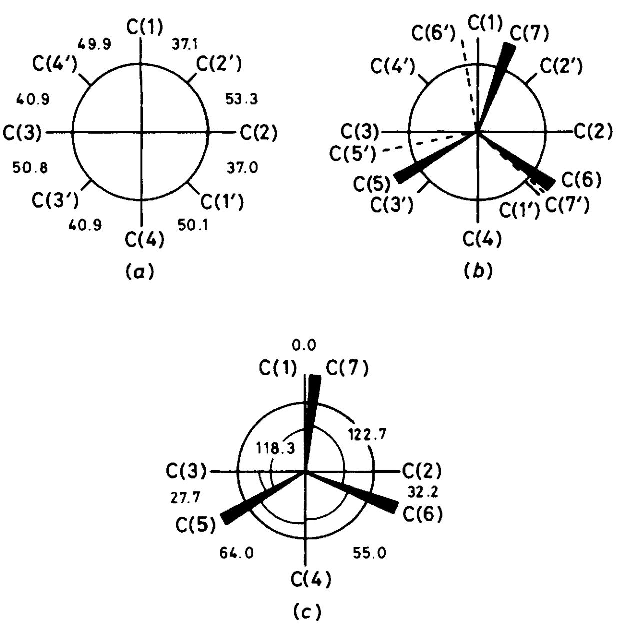

Figure 1. Newman projections of $[Re_2(CO)_8(PMe_2Ph)_2]$. (*a*) View down the Re–Re bond with torsion angles indicated between bonds; (*b*) view down P(1)–Re(1)–Re–(2)–P(2) indicating CO groups, phenyl rings, and methyl groups; (*c*) view down the P–Re bond indicating torsion angles

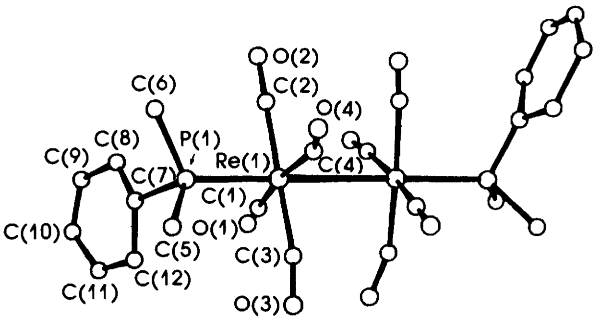

Figure 2. ORTEP[15] diagram of $[Re_2(CO)_8(PMe_2Ph)_2]$

positions of the bands will be dependent on the metal, ligand, solvent, and degree of substitution, and care must thus be excercised in predicting geometry from i.r. data alone. Of interest would be the determination of the structure of the presently unknown $[Re_2(CO)_8(PR_3)_2]$ to establish whether the PR_3 arrangement would be (**d**), (**e**), or (**f**) (Figure 1) and whether the geometry could be predicted from the solution i.r. spectrum.

Structure of Diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$.—The molecular structure of diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ is shown in Figure 2, and an (010) projection of the unit cell is shown in Figure 3. Average bond-length and -angle data are summarised in Table 5. The molecule adopts a staggered conformation, with diaxial phosphine substitution as expected from i.r. data. This is in contrast to the structures of $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$[3] and $[Mn_2(CO)_8(CNBu^t)_2]$[25] where the two isonitrile ligands occupy electronically favoured equatorial sites, and is an example of the dominance of steric factors over electronic site preference in the case of the bulky phosphine ligand. Comparisons of the $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ and $[Re_2(CO)_8(PMe_2Ph)_2]$ structures indicate that the groups on the isonitrile are much further removed from the Re atom than the groups on the P atom: adding average bond lengths for the linear Re–CN (2.05 Å), C≡N (1.15 Å), and N–C(R) (1.43 Å) bonds gives an effective Re ··· C(R) distance of 4.63 Å, compared to the average Re–P distance of 2.349(5) Å. The smaller steric bulk of the isonitrile ligand is also reflected in the 'fan-shaped' angles[26] for $2,6\text{-}Me_2C_6H_3NC$ of 106° (wideness) and 53° (thickness). Axial substitution has also been observed in related $[Mn_2(CO)_{10-n}(PR_3)_n]$ ($n = 1$; $PR_3 = PMe_2Ph$;[18] $n = 2$; $PR_3 = PMePh_2$[19] or PEt_3[27]) structures. In diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$ the Re–Re bond length is 3.044(1) Å, similar to that in $[Re_2(CO)_{10}]$.[28] Comparison with the equatorially substituted $[Re_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)_2]$ [Re–Re 3.047(1) Å] clearly indicates that the bond-length data do not reflect only electronic effects. The substitution of a carbonyl *trans* to the metal–metal bond by a poorer π-accepting[29] phosphine ligand, and the consequent increase in electron density on the metal atoms, perhaps in antibonding orbitals,[30] might have been expected to result in a significant

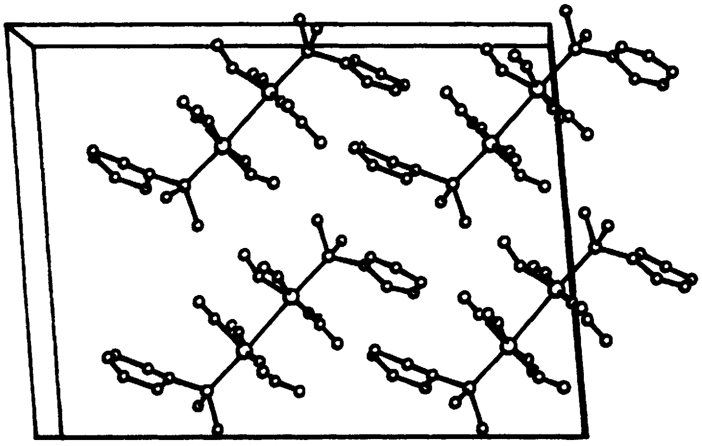

Figure 3. Packing diagram of $[Re_2(CO)_8(PMe_2Ph)_2]$ viewed down the *b* axis

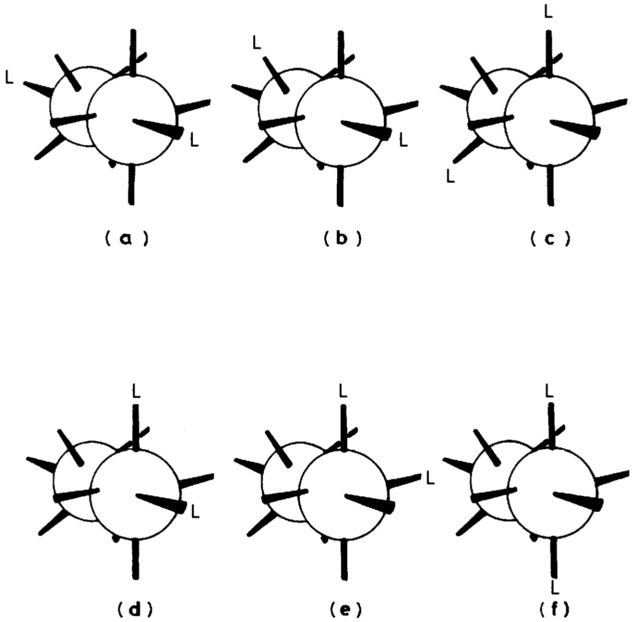

Figure 4. Possible isomers of $[Re_2(CO)_8L_2]$. In all cases a staggered ligand arrangement is indicated

Table 5. Average bond length (Å) and angle (°) data for diaxial $[Re_2(CO)_8(PMe_2Ph)_2]$

Re–Re	3.044(1)	P–Re–C	92.9(6)
Re–P	2.349(5)	C–Re–C(*cis*)	89.9(8)
Re–C	1.94(2)	Re–C–O	177.5(18)
P–C	1.83(2)	Re–P–C	115.5(8)
Re–Re–P	177.2(5)	C–P–C	102.8(11)
Re–Re–C	87.2(5)		

increase in the metal–metal bond length. Such lengthening effects have been suggested for phosphine-substituted metal clusters, *e.g.* $[Fe_3(CO)_{11}(PPh_3)]$,[31] $[Ru_3(CO)_{11}(PPh_3)]$,[32] $[Os_3(CO)_{11}\{P(OMe)\}_3]$,[33] and $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$,[34] but can be ascribed to ligand-packing effects, *i.e.* congestion between phosphine and carbonyl groups causes expansion of the metal core.[33,34] Further, kinetic studies[35] have suggested that the Mn–Mn bond strength in $[Mn_2(CO)_8(PPh_3)_2]$ is less than that in $[Mn_2(CO)_{10}]$.

The average Re–CO bond length is 1.94(2)Å, similar to that [1.976(6) Å] for Re–CO *trans* to CO in $[Re_2(CO)_8(CNC_6H_3\text{-}Me_2\text{-}2,6)_2]$. The Re–P bond length is 2.349(5)Å. Although the two sets of equatorial carbonyl groups are staggered with respect to each other, the C–Re–Re–C torsion angles deviate by an average of 6.0° from the ideal 45° (see Figure 1).

The conformation of the axial PMe_2Ph groups with respect to the equatorial CO groups is interesting in that the phenyl ring of the axial phosphine group *eclipses* a carbonyl ligand [Figure 1(*c*)] with a torsion angle of 0.0° for C(1)–Re–P–C(7). The average Re–P–C and C–P–C bond angles of 115.5(8) and 102.8(11)° and the average P–C bond length of 1.83(2) Å are similar to those for the related $[Mn_2(CO)_{10-n}(PR_3)_n]$ ($n = 1$ or 2) structures.[18,19,27]

The ${}_{ax}P\text{–}Re\text{–}CO_{eq}$ bond angles are obtuse [average 92.9(6)°], ${}_{eq}OC\text{–}Re\text{–}CO_{eq}$ close to 90° [average 89.9(8)°], and the $Re\text{–}Re\text{–}CO_{eq}$ are acute [average 87.2(5)°], *i.e.* the equatorial carbonyls bend in towards the Re–Re bond. This effect of the bending in of the equatorial CO ligands towards the metal–metal bond is observed for related $[Mn_2(CO)_{10-n}(PR_3)_n]$ ($n = 1$ or 2) complexes,[18,19,27] as well as for the series $[M_2(CO)_{10-n}(CNR)_n]$ (M = Re, $n = 1$—4; M = Mn, $n = 2$ or 4)[12] and the parent carbonyls $[M_2(CO)_{10}]$ (M = Re or Mn).[28] Hence this phenomenon would appear to be an electronic effect, unaffected by steric considerations. Various explanations have been proposed to explain it, and Elian and Hoffmann[36] have predicted the effect on the basis of molecular-orbital calculations.

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